Viraht Sahni

Quantal Density Functional Theory

Second Edition

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'Tis not nobler in the mind to suffer
The slings and arrows of outrageous fortune,
'Tis nobler, and ennobling,
To get off the ground and fight like hell.

In Memoriam
My beloved mother and father,
Hema and Harbans Lal

Preface to the Second Edition

The idea of writing a second edition within slightly more than a decade of the publication of the first is a consequence of the considerable new understandings of Quantal Density Functional Theory (Q–DFT) achieved over this period. But there have also been further insights into Schrödinger theory, and to the significance of the first theorems of Hohenberg-Kohn and Runge-Gross density functional theory (DFT). The book is still comprised of the three principal components: a description of Schrödinger theory from the new perspective of the 'Quantal Newtonian' second and first laws for the individual electron; traditional Hohenberg-Kohn, Runge-Gross, and Kohn-Sham density functional theory; and Q–DFT together with applications to explicate the theory, and the physical insights it provides into traditional DFT, Slater theory, and local effective potential energy theory in general. However, each component has been revised to incorporate the new understandings. Then there is the new material on the extension of Q–DFT to the added presence of an external magnetostatic field. It was the attempt to extend the theory to the presence of magnetic fields that forced the reexamination of both traditional DFT and Q–DFT, thereby leading to many of the new insights. The extension to external magnetic fields required a critical reevaluation of the existing literature. This in turn led to the proof of the corresponding Hohenberg-Kohn theorems for uniform magnetostatic fields, one that is distinct from but in the rigorous sense of the original. The Q–DFT in a magnetic field is then explicated by an example in two-dimensional space. Working on the second edition has been akin to writing a new book.

The pedagogical nature of the book has been maintained. Most of the new derivations are once again given in detail. And as a result of the new understandings, it has been possible to present Q–DFT for arbitrary external electromagnetic fields whether they be time-dependent or time-independent in a most general and comprehensive manner. The common thread of the 'Quantal Newtonian' laws for the individual electron is now weaved throughout the book.

Xioayin Pan has been a principal contributor to the new developments. Our collaboration has been productive, and working with Xiaoyin has been a pleasure.

Together with Doug Achan, a former graduate student, and Lou Massa, a friend and colleague, new physics of the Wigner low-density high-electron correlation regime of a nonuniform density system has been discovered. Thus, an additional characterization of the Wigner regime is proposed. The example studied also provides a contrast to the high-density low-electron correlation regime of atoms and molecules.

Thanks are also due to Xiaoyin and Lou for their critical comments on various chapters.

Once again I wish to acknowledge Brooklyn College for the support and freedom afforded to me to pursue the research of my interest.

Finally, with much gratitude, I wish to thank my wife Catherine for typing the book despite the travails of life.

Brooklyn, NY, USA Viraht Sahni

Preface to the First Edition

The idea underlying this book is to introduce the reader to a new local effective potential energy theory of electronic structure that I refer to as Quantal Density Functional Theory (Q–DFT). It is addressed to graduate students who have had a one year course on Quantum Mechanics, and to researchers in the field of electronic structure. It is pedagogical, with detailed proofs, and many figures to explain the physics. The theory is based on the first Hohenberg–Kohn theorem, and is distinct from Kohn–Sham density functional theory. No prior understanding of traditional density functional theory is required as the theorems of Hohenberg and Kohn, and Kohn–Sham theory, and their extension to time-dependent phenomenon are described. There are other excellent texts on traditional density functional theory, and as such I have kept the overlap with the material in these texts to a minimum. It is also possible via Q–DFT to provide a rigorous physical interpretation of Kohn–Sham theory and other local effective potential energy theories such as Slater theory and the Optimized Potential Method. A second component to the book is therefore the description and the explanation of the physics of these theories.

My interest in density functional theory began in the early 1970s simultaneously with my work on metal surface physics. The origins of Q–DFT thus lie in my attempts to understand the physics underlying the formal framework of Kohn–Sham density functional theory and of various approximations within it in the context of the nonuniform electron gas at a metal surface. My work with Manoj Harbola [1, 2] constitutes the ideas seminal to Q–DFT. The history of how these ideas developed, and of their evolution to Q–DFT, is a classic example of how science works. This is not the place to describe the many twists and turns in the path to the final version of the theory. However, together with a further understanding [3] noted, credit must also be afforded Andrew Holas and Norman March whose work [4] helped congeal and close the circle of ideas.

I wish to gratefully acknowledge my graduate students Cheng Quinn Ma, Abdel Mohammed, Manoj Harbola, Marlina Slamet, Alexander Solomatin, Zhixin Qian, and Xiaoyin Pan whose creative work has contributed both directly and indirectly to the writing of this book.

Then there is my friend and colleague Lou Massa whose enthusiasm for the subject matter of the book and whose consistent support and critique during its writing have proved invaluable.

Brooklyn College has been home, and I thank the College for its support of my research.

The book was typed by Suzanne Whiter, throughout with a smile. To her my heartfelt thanks.

To my wife, Catherine, I owe an immense debt of gratitude. She has suffered happily over the years through the many referee reports of my papers. I thank her for being there with me every step of the way.

Brooklyn, NY, USA Viraht Sahni
October 2003

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Contents

Chapter 1
Introduction

Abstract The introductory chapter provides a brief description of Quantal density functional theory (Q–DFT), a physical local effective potential energy theory of the electronic structure of matter. The theory is based on a more recent perspective of the Schrödinger theory of electrons. This is a perspective of the individual electron in a sea of electrons in the presence of external fields. The corresponding equation of motion is described by the 'Quantal Newtonian' second law for each electron, the first law being a special case for the description of stationary state systems. Q–DFT is also based on a further understanding of the first Hohenberg-Kohn theorem of density functional theory, and the concept derived therefrom of the properties that constitute the basic variables of quantum mechanics. The Introduction is a description of the forthcoming chapters in the context of their relationship to Q–DFT and to each other: Schrödinger theory from the new perspective; Q–DFT, the corresponding 'Quantal Newtonian' laws, and its application to model and realistic systems; the rigorous generalization of the Hohenberg-Kohn theorems to the added presence of an external uniform magnetostatic field; the subsequent generalization of Q–DFT to such an external field; the Hohenberg-Kohn, Runge-Gross and Kohn-Sham density functional theories; the further insights into the fundamental theorems of density functional theory via density preserving unitary transformations and corollaries; the physical interpretation via Q–DFT of the energy and action functionals and corresponding functional derivatives of Kohn-Sham theory, and of other aspects of traditional density functional and other local effective potential theories.

Introduction

Since the publication in 2004 of the original edition of *Quantal Density Functional Theory* [1] (referred to now as ***QDFT1***), there has been a significant evolution in the understanding and development of the theory (Q–DFT). This in turn has arisen from a deeper understanding of the Schrödinger theory of electrons in external fields from the perspective of the properties of the individual electron in the sea of electrons. This perspective, based on the 'Quantal Newtonian' second and first laws for each electron, differs from that of traditional treatises on quantum mechanics. It is one that is both more tangible and insightful. Thus, it is my sense that Schrödinger theory taught from this perspective would be more efficacious in explaining the subject matter. There has also been a further appreciation of the proof and implications of the first

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Hohenberg-Kohn [2] theorem. These insights too are not part of the literature on traditional density functional theory (DFT). A significant consequence of these new understandings has been the generalization [3], in the rigorous sense of the original proofs, of the Hohenberg-Kohn theorems to the added presence of an external uniform magnetostatic field. All the new understandings within Schrödinger and Hohenberg-Kohn theories have contributed to the further development of Q–DFT. The focus of ***QDFT1*** was the theoretical framework of Q–DFT. Additionally, the rigorous physical interpretation of Kohn-Sham [4] and Slater [5] theories, as well as physical insights into local effective potential energy theory in general, as arrived at via Q–DFT were described. Approximation methods within Q–DFT and various applications are described in *Quantal Density Functional Theory II: Approximation Methods and Applications* [6] (referred to now as ***QDFT2***). The focus on the theoretical underpinnings of Q-DFT and the overall structure of ***QDFT1*** is maintained in this second edition. However, although there is revision in each chapter, the foundational chapters on Schrödinger theory, and the traditional DFT of Hohenberg-Kohn and Runge-Gross [7] have been revised to a considerable degree. Then there are the new chapters and affiliated appendices on the generalization [3, 8] of the Hohenberg-Kohn theorems and Q-DFT to the presence of both external electrostatic and magnetostatic fields.

Quantal density functional theory (Q–DFT) is a *local effective potential energy* theory of electronic structure of both ground and excited states. It is based on the new description of Schrödinger theory, and on the concept of a *basic variable* of quantum mechanics, one that originates from the first Hohenberg-Kohn theorem. The definition of a local effective potential energy theory is the following. Consider a system of N electrons in an arbitrary time-dependent external electromagnetic field $\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}t) : \boldsymbol{\mathcal{E}}(\mathbf{r}t) = -\boldsymbol{\nabla} v(\mathbf{r}t) + \partial[\mathbf{A}(\mathbf{r}t)/c]\partial t, \mathbf{B}(\mathbf{r}t) = \boldsymbol{\nabla} \times \mathbf{A}(\mathbf{r}t)$, where $v(\mathbf{r}t)$ and $\mathbf{A}(\mathbf{r}t)$ are the scalar and vector potentials. This system of interacting particles and its evolution in time is described by the non-relativistic time-dependent Schrödinger equation. As noted above, there is a new description [9] of Schrödinger theory based on the 'Quantal Newtonian' second law for *each* electron [10–12], one that is in terms of 'classical' fields, and their quantal sources which are expectations of Hermitian operators. The fields are termed 'classical' because as in classical physics they pervade all space. *A basic variable is defined as a gauge invariant quantum-mechanical property, knowledge of which determines the wave function of the system.* The identification of a property as a basic variable is achieved via the proof of the one-to-one relationship or bijectivity between the property and the external potential experienced by the electrons. Q–DFT is a mapping from the interacting system of electrons described via Schrödinger theory in terms of fields and quantal sources to one of *noninteracting* fermions possessing the same basic variable or variables. The Q–DFT description of the model fermions is thus also in terms of 'classical' fields and quantal sources. The model system is referred to as the S system. For the external field considered, the basic variables are [13] the electronic density $\rho(\mathbf{r}t)$ and the current density $\mathbf{j}(\mathbf{r}t)$: there is a one-to-one relationship between $\{\rho(\mathbf{r}t), \mathbf{j}(\mathbf{r}t)\}$ and the external potentials $\{v(\mathbf{r}t), \mathbf{A}(\mathbf{r}t)\}$ (to within a time-dependent function and the gradient of a time-dependent scalar function). Within Q–DFT, it is possible to map [14] to a model system of noninteracting fermions possessing the same basic variable properties of $\{\rho(\mathbf{r}t), \mathbf{j}(\mathbf{r}t)\}$.

For the description of time-dependent Q–DFT [10–12] in Chap. 3, we will consider as in the first edition, the example of the external time-dependent electric field $\mathcal{F}^{\text{ext}}(\mathbf{r}t) = \mathcal{E}(\mathbf{r}t) = -\nabla v(\mathbf{r}t)$. In this case, in spite of there being no magnetic component to the external field, the basic variables are [7] the density $\rho(\mathbf{r}t)$ and the current density $\mathbf{j}(\mathbf{r}t)$: there is a one-to-one relationship between both $\rho(\mathbf{r}t)$ and $\mathbf{j}(\mathbf{r}t)$, and the external potential $v(\mathbf{r}t)$ (to within a time-dependent function $C(t)$). Within Q–DFT, it is possible to map to a model system possessing either the same density $\rho(\mathbf{r}t)$, or one with the same density $\rho(\mathbf{r}t)$ *and* current density $\mathbf{j}(\mathbf{r}t)$. The latter mapping, such that the model system possesses both the basic variable properties, turns out to be more advantageous. The equivalent non-conserved total energy $E(t)$ of the interacting system is also thereby obtained in each mapping. As the model fermions are noninteracting, the effective potential energy of each such model fermion is the *same* at each instant of time, and can therefore be represented by a *local* or multiplicative potential energy operator $v_s(\mathbf{r}t)$. With the assumption that the model fermions are subject to the same external field $\mathcal{F}^{\text{ext}}(\mathbf{r}t)$ as that of the interacting electrons, the operator $v_s(\mathbf{r}t)$ is the sum of the external potential energy operator $v(\mathbf{r}t)$, and an effective *local* electron-interaction potential energy operator $v_{\text{ee}}(\mathbf{r}t)$ that accounts for all the quantum many-body correlations. The corresponding S system wave function is a single Slater determinant of the noninteracting fermion spin orbitals. The mapping to such a model system is what is meant by a local effective potential energy theory. Thus, Q–DFT is a theory that describes the physics of mapping from the Schrödinger description of electrons in an external field to one of noninteracting fermions possessing the same basic variables.

For the mapping from the Schrödinger description of the interacting electrons to the model system of noninteracting fermions possessing the same basic variable properties, one must understand how all the many-body correlations of the former are incorporated into the local electron-interaction potential energy operator $v_{\text{ee}}(\mathbf{r}t)$ of the latter. Further, one must understand how the energy $E(t)$ may be expressed in terms of the model S system properties. The many-body correlations that must be accounted for by the S system are the following: (a) Electron correlations due to the Pauli exclusion principle, or equivalently the requirement of antisymmetry of the wave function (referred to as Pauli correlations), and (b) Electron correlations due to Coulomb repulsion (referred to as Coulomb correlations). Furthermore, the kinetic energy and current density of the interacting and model systems differ. These differences constitute the correlation contributions to these properties, and must also be accounted for by the model system. We refer to these correlations as (c) Correlation-Kinetic, and (d) Correlation-Current-Density effects. If, for the example of the external field $\mathcal{F}^{\text{ext}}(\mathbf{r}t) = \mathcal{E}(\mathbf{r}t) = -\nabla v(\mathbf{r}t)$ considered, the mapping is to a model system such that only the density $\rho(\mathbf{r}t)$ of the interacting and S systems are the same, then the corresponding Q–DFT equations indicate that all the above correlations must be accounted for. However, if the mapping is to a model system with the same density $\rho(\mathbf{r}t)$ *and* current density $\mathbf{j}(\mathbf{r}t)$, then within Q–DFT, only those correlations due to the Pauli exclusion principle, Coulomb repulsion, and Correlation-Kinetic effects must be accounted for. The more general statement [14] with regard to Q-DFT is the following. Irrespective of the type of external field $\mathcal{F}^{\mathrm{ext}}(\mathbf{r}t)$ to which the electrons are subjected, whether it be a time-dependent or time-independent electromagnetic field, if (a) the model fermions are subject to the same external field, and (b) the mapping is to a model system which possesses *all* the basic variable properties, then in each case the electron correlations that must be accounted for by the model S system are always only those due to the Pauli principle, Coulomb repulsion, and Correlation-Kinetic effects. If the mapping to the model system is such that only the density $\rho(\mathbf{r}t)$ is reproduced, then additional correlations such as the Correlation-Current-Density and Correlation-Magnetic effects must also be accounted for.

As the Q–DFT description of the mapping to the S system is in terms of fields and quantal sources, the local electron-interaction potential energy operator $v_{\mathrm{ee}}(\mathbf{r}t)$ of the model fermions is provided a rigorously derived *physical* definition [10–12]. *The potential energy* $v_{\mathrm{ee}}(\mathbf{r}t)$ *is the work required at each instant of time to move the model fermion in the force of a conservative effective field* $\mathcal{F}^{\mathrm{eff}}(\mathbf{r}t)$. As the effective field $\mathcal{F}^{\mathrm{eff}}(\mathbf{r}t)$ is conservative, the work done is *path-independent*. The field $\mathcal{F}^{\mathrm{eff}}(\mathbf{r}t)$ is a sum of component fields. These components of $\mathcal{F}^{\mathrm{eff}}(\mathbf{r}t)$, through the quantal sources that give rise to them, are *separately* representative of the Pauli and Coulomb correlations, and of the Correlation-Kinetic and Correlation-Current-Density effects. The sources of the component fields are quantum-mechanical expectations of Hermitian operators taken with respect to the Schrödinger and S system wave functions. *The non-conserved total energy* $E(t)$, *and its components are also expressed in integral virial form in terms of these component fields*. In particular, its *separate* Hartree, Pauli, Coulomb, and Correlation-Kinetic contributions can be so expressed. Thus, unlike Schrödinger theory in which the contributions to the energy $E(t)$ of correlations due to the Pauli principle and Coulomb repulsion cannot be separated, within Q–DFT it is possible to determine the contribution of each type of correlation. Furthermore, via Q–DFT, it is possible to determine the contribution of electron correlations to the kinetic energy, viz. the Correlation-Kinetic contribution. Note that all these properties are determined from the *same* model S system, and one for which the basic variables are those of the interacting system.

As in Schrödinger theory, stationary state Q–DFT constitutes a special case of the time-dependent theory discussed above. For a system of N electrons in an external electrostatic field $\mathcal{F}^{\mathrm{ext}}(\mathbf{r}) = \boldsymbol{\mathcal{E}}(\mathbf{r}) = -\boldsymbol{\nabla} v(\mathbf{r})$, it is proved via the first Hohenberg-Kohn theorem [2] that the single basic variable is the nondegenerate ground state density $\rho(\mathbf{r})$. The identification of this property as the basic variable is via the proof of bijectivity between the density $\rho(\mathbf{r})$ and the external potential $v(\mathbf{r})$ (to within a constant C). The proof is for *arbitrary* external potential $v(\mathbf{r})$ but for *fixed* electron number N. The equations governing the Q–DFT mapping to an S system with the equivalent density $\rho(\mathbf{r})$ are thus the same [15, 16], but with the time parameter and Correlation-Current Density field absent. The equations are based on the 'Quantal Newtonian' first law [17] which is the stationary state version of the 'Quantal Newtonian' second law [10–12]. Again, with the assumption that the model fermions are subject to the same external electrostatic field, a mathematically rigorous *physical* definition of the corresponding local electron-interaction potential energy $v_{\mathrm{ee}}(\mathbf{r})$ in which all the many-body effects are incorporated follows. *The potential energy* $v_{\mathrm{ee}}(\mathbf{r})$ *is the work done to move a model fermion in the force of a conservative effective field* $\boldsymbol{\mathcal{F}}^{\mathrm{eff}}(\mathbf{r})$. As this field is conservative, the work done is *path-independent*. The components of the effective field $\boldsymbol{\mathcal{F}}^{\mathrm{eff}}(\mathbf{r})$ are *separately* representative of the Pauli and Coulomb correlations, and Correlation-Kinetic effects. *The total energy E, and in particular its Hartree, Pauli, Coulomb, and Correlation-Kinetic components can be expressed in integral virial form in terms of these fields*. It is reiterated, that the separate Pauli and Coulomb correlation contributions to the total energy E are for the same density $\rho(\mathbf{r})$. (In contrast, in traditional quantum chemistry, a separate Hartree-Fock theory calculation must be performed. The Hartree-Fock theory density differs from that of the fully interacting system. Hence, the quantum chemistry definition of the Coulomb correlation energy as the difference between the total energy E and the Hartree-Fock theory value, is based on two different densities, and is thereby different from that of Q–DFT.) When the interacting system of electrons is described within the Hartree-Fock and Hartree theory approximations, the corresponding Q–DFT mapping [15, 16] to model systems having the same density $\rho(\mathbf{r})$ is similar, leading thereby to the Q–DFT of Hartree-Fock and Hartree theory.

There is a further generality to the Q-DFT description of local effective potential energy theory, or equivalently the mapping from the interacting system of electrons to one of noninteracting fermions with the same basic variables. Consider a stationary state of electrons in a *nondegenerate ground state* with density $\rho(\mathbf{r})$, total energy E, and ionization potential I. It is possible via Q–DFT to map this interacting system of electrons to one of noninteracting fermions in their *ground* state with the same basic variable of the density $\rho(\mathbf{r})$. However, it is also possible to map the interacting system to a model system of noninteracting fermions in an *excited state* with a *different* electronic configuration but again possessing the same density $\rho(\mathbf{r})$. In each case, the same total energy E is obtained, and in each case, the highest occupied eigenvalue is the negative of the ionization potential I. What this means, in other words, is that there exist an *infinite* number of *local* effective potentials $v_s(\mathbf{r})$ that can generate the nondegenerate *ground* state density $\rho(\mathbf{r})$. Consider next, a system of electrons in a *nondegenerate excited* state with density $\rho^e(\mathbf{r})$. Via Q–DFT, it is possible to map this interacting system of electrons to a system of noninteracting model fermions in an *excited* state having the *same* electronic configuration and density $\rho^e(\mathbf{r})$. It is, however, also possible to map the *excited* state of the interacting electrons to model fermions in a *ground* state with density $\rho^e(\mathbf{r})$. It is furthermore also possible to map to a system of model fermions in other *excited* states with *different* electronic configurations but with the same density $\rho^e(\mathbf{r})$. Once again the total energy E is obtained, and in each case, the highest occupied eigenvalue corresponds to the negative of the ionization potential I. Hence, once again, there exist an *infinite* number of local effective potentials $v_s(\mathbf{r})$ that can generate an excited state density $\rho^e(\mathbf{r})$. Note that the density $\rho^e(\mathbf{r})$ of the lowest excited state of a given symmetry different from that of the ground state is also a basic variable [18, 19]. However, the densities $\rho^e(\mathbf{r})$ of other excited states are not. There is therefore yet a further generality to Q–DFT with regard to these excited states. It is possible to map to model fermion systems possessing the same excited state density $\rho^e(\mathbf{r})$ even though for these states the density is not a basic variable. In the Q–DFT mapping, the state of the S system is thus *arbitrary*. It is proved that irrespective of the state of the S system fermions, the contributions due to Pauli and Coulomb correlations to each local effective potential $v_{ee}(\mathbf{r})$ and to the total energy E remains the same. It is the Correlation-Kinetic contributions that differ.

The mapping via Q–DFT and the arbitrariness of the state and electronic configuration of the model system, are explicated for the example of the analytically solvable Hooke's atom [20]. This is a two-electron atom in which the electrons interact Coulombically, but are confined by an external potential $v(\mathbf{r})$ that is harmonic. As such this model atom is particularly useful for the study of electron correlations. A nondegenerate *ground* state [21] and a first *excited* singlet state [22, 23] of the atom are both mapped to model S systems in a *ground* state having the requisite densities. (For the mapping from the ground state to an S system in an excited singlet state, and for a discussion of the arbitrariness of the S system wave function, see ***QDFT2*** and references to the original literature therein.) These applications of Q–DFT correspond to the high-density *low-electron-correlation* regime in which the electron-interaction energy is less than the kinetic energy. An additional application [24, 25] to the Wigner low-electron-density *high-electron-correlation* regime in which the electron-interaction energy is greater than the kinetic energy is also provided. A key conclusion of this work is that in addition to a low density and a high value of the electron-interaction energy, the Wigner high-electron-correlation regime must now be also characterized by a high Correlation-Kinetic energy value. The new concepts of 'quantal compression' and 'quantal decompression' of the kinetic energy density are then introduced to explain the difference in results between the low- and high-electron-correlation regimes.

Within time-independent Q–DFT, it is also possible (see Chap. 6) to map a *ground* or *excited* state of a system of electrons in an external field $\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}) = \boldsymbol{\mathcal{E}}(\mathbf{r}) = -\boldsymbol{\nabla} v(\mathbf{r})$, to one of *noninteracting bosons* in their *ground* state such that the equivalent density, energy, and ionization potential are obtained. We refer to the model of noninteracting bosons as the B system. The wave function of the B system is the density amplitude $\sqrt{\rho(\mathbf{r})}$. The eigenvalue of the B system differential equation is the negative of the ionization potential I. Once again, the Q–DFT description of the local effective potential energy $v_B(\mathbf{r})$ of the bosons as well as the system total energy E is in terms of 'classical' fields and quantal sources. For any two-electron system, the mapping to a B system is the same as the mapping to an S system in its ground state. Hence, the examples of the mapping from the Hooke's atom in a ground and excited state to one of noninteracting fermions as discussed above also constitute examples of the mappings to the B system. For further examples of the mappings to a B system, see [26] and ***QDFT2***. The Q–DFT mapping also makes evident that the B system is a special case of the model S system. Finally, the S and B systems are related by what is referred to in the literature as the Pauli kinetic energy and the Pauli potential. The equations of Q–DFT clearly show that these properties are solely due to kinetic effects.

In this edition, Q-DFT has been extended [8, 14] in Chap. 9 to the added presence of an external magnetostatic field $\mathbf{B}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r})$, with $\mathbf{A}(\mathbf{r})$ the vector potential. This first requires knowledge of which gauge invariant properties constitute the basic variables in this case. Hence, prior to discussing the Q–DFT, the first Hohenberg-Kohn theorem is generalized [3] in Chap. 8 to the presence of a *uniform* magnetostatic field $\mathbf{B}(\mathbf{r}) = B\mathbf{i}_z$. Proofs for spinless electrons for the corresponding Schrödinger Hamiltonian, and one for electrons with spin for the Schrödinger-Pauli Hamiltonian, are provided. The proofs of the generalized theorems differ in significant ways from that of the proof of the original Hohenberg-Kohn theorem. This is because in the presence of a magnetostatic field, there is a fundamental change in the physics relating the external potentials and the nondegenerate ground state wave function, and this difference must be accounted for in the proof. It is proved that there is a bijective relationship between the external potentials $\{v(\mathbf{r}), \mathbf{A}(\mathbf{r})\}$ and the nondegenerate ground state density $\rho(\mathbf{r})$ and the current density $\mathbf{j}(\mathbf{r})$, so that the basic variables in this case are $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$. (In the presence of a magnetostatic field, the current density $\mathbf{j}(\mathbf{r})$ is a sum of its paramagnetic and diamagnetic components.) The constraints in this case, in addition to that of fixed electron number N, are those of either fixed canonical orbital angular momentum $\mathbf{L}$ (corresponding to the Schrödinger Hamiltonian for spinless electrons) or of both fixed canonical orbital $\mathbf{L}$ and spin $\mathbf{S}$ angular momentum (for the Schrödinger-Pauli Hamiltonian for electrons with spin). The Q–DFT mapping from a system of electrons in both an external electrostatic $\boldsymbol{\mathcal{E}}(\mathbf{r}) = -\boldsymbol{\nabla} v(\mathbf{r})$ and magnetostatic $\mathbf{B}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r})$ field to one of noninteracting fermions with the same $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ is then described [8, 14]. The equations of the mapping are based on the corresponding 'Quantal Newtonian' first law [8, 27]. The Q-DFT mapping is then explicated for a quantum dot as represented by the analytically solvable Hooke's atom in a magnetic field [28, 29]. The mapping in this two-dimensional example is from a ground state of the interacting system to a model fermionic system with the same $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ also in its ground state. As this is a two-electron system, the mapping may also be considered as one to noninteracting bosons in their ground state.

As Q–DFT is a description of the mapping from an interacting system of electrons as defined by Schrödinger theory to one of noninteracting fermions or bosons with the same basic variables, it is necessary to first describe [9] Schrödinger theory as in Chap. 2 from the perspective of 'classical' fields and quantal sources. This is a 'Newtonian' description of the electronic system from the perspective of the *individual electron* in the sea of electrons subject to an external field. In addition to the external field, the 'Quantal Newtonian' second and first laws describe the *internal* field experienced by *each electron*, and in the time-dependent case, its response. The internal field is a sum of fields that are separately representative of electron correlations due to the Pauli exclusion principle and Coulomb repulsion, the kinetic effects, and the density. In the added presence of a magnetostatic field, there is yet another contribution to the internal field arising from the magnetic field. As in classical physics, the internal field summed over all the electrons vanishes, thus leading to a more insightful derivation [30] of Ehrenfest's theorem, the quantal equivalent of Newton's second law. Examples of Schrödinger theory from the 'Newtonian' perspective are provided via the Hooke's atom for both a ground and excited state. There are other facets of Schrödinger theory not described in the literature that emanate from the

'Quantal Newtonian' laws. The external scalar potential is shown to arise from a curl-free field, and hence its *path-independence* demonstrated. The laws also show that the external scalar potential is a known functional of the system wave function via the quantal sources of the fields. Thus, by replacing the external scalar potential in the Schrödinger equation by this functional, the *intrinsic self-consistent* nature of the Schrödinger equation is exhibited. A new expression for the Schrödinger equation is obtained in the presence of a magnetic field $\mathbf{B}(\mathbf{r})$. When written in self-consistent form, the magnetic field $\mathbf{B}(\mathbf{r})$ now appears explicitly in the Schrödinger equation in addition to the vector potential $\mathbf{A}(\mathbf{r})$ which appears in traditional form. The 'Quantal Newtonian' laws also help explain [31] the relationship between Schrödinger theory and quantum fluid dynamics.

The concept of a basic variable which is fundamental to all local effective potential energy theories such as Q-DFT, and Kohn-Sham and Runge-Gross theories, stems from the first Hohenberg-Kohn theorem. Accordingly, a basic variable is a *gauge invariant* property, knowledge to which determines the external potential, hence the Hamiltonian, and therefore via solution of the Schrödinger equation, the wave functions of the system. The theorem proves that the nondegenerate ground state density $\rho(\mathbf{r})$ is a basic variable. The proof of bijectivity between the density $\rho(\mathbf{r})$ and the external scalar potential $v(\mathbf{r})$ is for v-representable densities, i.e. for densities obtained from wave functions of interacting particle Hamiltonians, and for fixed electron number N. The theorem thus proves that the wave functions are functionals of the basic variable: $\psi = \psi[\rho(\mathbf{r})]$. *This is the Hohenberg-Kohn path from the basic variable $\rho(\mathbf{r})$ to the wave function ψ.* Chapter 4 on the Hohenberg-Kohn (HK) and Runge-Gross (RG) density functional theories has been revised with a greater focus on the first theorem of each theory. The first HK theorem is *generalized* [32] via a *density preserving* unitary transformation to show that the wave function ψ must also be a functional of a gauge function $\alpha(\mathbf{R}), \mathbf{R} = \mathbf{r}_1, \ldots, \mathbf{r}_N$, i.e. $\psi = \psi[\rho(\mathbf{r}), \alpha(\mathbf{R})]$. In this manner, the wave function ψ when written as a functional is *gauge variant* as it must be. Further, the theorem is valid for each choice of gauge function $\alpha(\mathbf{R})$. Similarly [32], in the RG time-dependent case, for which a basic variable is shown to be the density $\rho(\mathbf{r}t)$, the wave function $\psi(t)$ is a functional of a gauge function $\alpha(\mathbf{R}t) : \psi(t) = \psi[\rho(\mathbf{r}t), \alpha(\mathbf{R}t)]$. (The other basic variable is the current density $\mathbf{j}(\mathbf{r}t)$). This then leads to a hierarchy in the theorems in terms of the gauge functions. For example, when $\alpha(\mathbf{R}t) = \alpha$, a constant, one obtains the original HK theorem. When $\alpha(\mathbf{R}t) = \alpha(t)$, one obtains the RG theorem. In the presence of a magnetic field $\mathbf{B}(\mathbf{r})$, it is proved [3] for v-representable densities, and for fixed electron number N and canonical orbital angular momentum $\mathbf{L}$ and spin angular momentum $\mathbf{S}$, that the basic variables are the nondegenerate ground state density $\rho(\mathbf{r})$ and the *physical* current density $\mathbf{j}(\mathbf{r})$. Via a *density and current density preserving* unitary transformation, it is shown that the wave function ψ is the functional $\psi = \psi[\rho(\mathbf{r}), \mathbf{j}(\mathbf{r}), \alpha(\mathbf{R})]$. As each physical system is independent of the gauge, the choice of the gauge function is arbitrary, and can be chosen so as to vanish.

The first HK theorem is also fundamental in a different context. As noted above, the proof of bijectivity between the density $\rho(\mathbf{r})$ and the external scalar potential $v(\mathbf{r})$

is for v-representable densities and for a nondegenerate ground state. The variational constrained-search generalization of the theorem by Percus-Levy-Lieb [33] (PLL) to N-representable densities and to degenerate states—*the PLL path from* $\rho(\mathbf{r})$ *to* ψ—is only possible [34] provided one knows *a priori* that it is the ground state density $\rho(\mathbf{r})$ which is the basic variable. That knowledge is gleaned from the first HK theorem. Without this knowledge, one would not know to constrain the search to functions that reproduce the density $\rho(\mathbf{r})$ and not some other property. In a similar vein, when a magnetostatic field $\mathbf{B}(\mathbf{r})$ is present, a PLL constrained-search path and the generalization to N-representable densities and degenerate states is possible only following the proof that the basic variables in this case are $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$.

A corollary to both the first HK and RG theorems is also provided [35]. These corollaries show that it is possible to construct degenerate Hamiltonians $[\hat{H}; \hat{H}(t)]$ that correspond to *different* physical systems but yet possess the same density $[\rho(\mathbf{r}); \rho(\mathbf{r}t)]$. The physical systems differ by $[C; C(t)]$, where C is an intrinsic constant and $C(t)$ an intrinsic temporal function. By intrinsic is meant as being part of the Hamiltonian. Thus, in such examples, knowledge of the density $[\rho(\mathbf{r}); \rho(\mathbf{r}t)]$ cannot uniquely determine the physical system. These examples, however, do not violate the HK and RG theorems because the degenerate Hamiltonians constructed still differ by a constant C or function $C(t)$. The proofs of the HK and RG theorems are independent of whether $[C; C(t)]$ are extrinsically additive or intrinsic to the Hamiltonian.

The final component on traditional density functional theory (DFT) is a description in Chap. 4 of Kohn-Sham (KS) theory. KS–DFT, the precursor to Q–DFT, is based on the two Hohenberg-Kohn theorems. The theory is another but different description of the mapping from an interacting system of electrons in an external electrostatic field $\boldsymbol{\mathcal{E}}(\mathbf{r}) = -\boldsymbol{\nabla} v(\mathbf{r})$ to one of noninteracting fermions possessing the same basic variable property of the nondegenerate ground state density $\rho(\mathbf{r})$. With the wave function a functional of the density, the energy E—the expectation value of the Hamiltonian—is a unique functional of the density: $E = E[\rho(\mathbf{r})]$. The theory further employs the second Hohenberg-Kohn theorem according to which the energy variational principle is valid for arbitrary variations of the density. Each density variation is for fixed electron number N. The ground state energy E can then be obtained via the functional $E[\rho(\mathbf{r})]$ from the corresponding variational Euler-Lagrange equation for the density $\rho(\mathbf{r})$. The energy E is a minimum for the true density $\rho(\mathbf{r})$. However, instead of solving the Euler-Lagrange equation, it is *assumed* that there exists a model system of noninteracting fermions that possesses the same density $\rho(\mathbf{r})$. As the model fermions are noninteracting, their kinetic energy can be determined exactly. With the assumption that the model fermions are subject to the same external field $\boldsymbol{\mathcal{E}}(\mathbf{r})$, the many-body correlations due to the Pauli exclusion principle, Coulomb repulsion, and the correlation contributions to the kinetic energy—the Correlation-Kinetic effects—are all subsumed into the KS electron-interaction energy functional $E_{ee}^{KS}[\rho(\mathbf{r})]$ component of the total energy E. The corresponding local electron-interaction potential energy $v_{ee}(\mathbf{r})$ of the model fermions is then *defined* (via the Euler-Lagrange equation) as the *functional derivative* $\delta E_{ee}^{KS}[\rho(\mathbf{r})]/\delta\rho(\mathbf{r})$. Thus, the KS description of the mapping to the noninteracting system is strictly *mathematical* in that it is in terms of functionals of the density and functional derivatives. KS–DFT does not describe how the various many-body correlations are incorporated into the functional $E_{ee}^{KS}[\rho(\mathbf{r})]$ or its derivative $v_{ee}(\mathbf{r})$. Furthermore, KS–DFT is a ground state theory. As such the KS mapping can only be from the ground state of the interacting system to the model system also in its ground state. This is why in the DFT literature it is stated that the local potential $v_{ee}(\mathbf{r})$ which generates the ground state density $\rho(\mathbf{r})$ is *unique*. (Of course, we now know via Q–DFT that there exist an infinite number of potentials that can generate the density $\rho(\mathbf{r})$. In this context, KS–DFT constitutes a special case of Q–DFT.)

For excited states, the HK theorems can be proved [18, 19] only for the lowest excited state of a given symmetry different from that of the ground state. The proof is for v-representable densities derived from wave functions that have the excited state symmetry. Thus, there exists a one-to-one relationship between the density $\rho^e(\mathbf{r})$ of such an excited state and the external potential $v(\mathbf{r})$ (to within a constant), and hence $\rho^e(\mathbf{r})$ is a basic variable. Thus, the excited state wave function ψ^e is a functional of the density $\rho^e(\mathbf{r})$. The corresponding energy variational principle for arbitrary variations of the density $\rho^e(\mathbf{r})$ for fixed electron number N follows. This is referred to as the Gunnarsson-Lundqvist theorem [19] as these authors originally proved this theorem for the special case of spin-density functional theory. The reason why the HK theorems can be extended to these excited states is that within Schrödinger theory, the variational principle is also applicable to the lowest excited state of a given symmetry. In the variational procedure, one restricts the approximate wave functions to have the given excited-state symmetry, and the lowest state of that symmetry is achieved by energy minimization. For the other excited states, it is known [18, 36, 37] that there is no equivalent of the HK theorem. As knowledge of the density $\rho^e(\mathbf{r})$ of these excited states does not uniquely determine the external potential $v(\mathbf{r})$, the implication is that there could exist several potentials $v(\mathbf{r})$ for which the corresponding Schrödinger equations all generate the same excited state density $\rho^e(\mathbf{r})$. For a demonstration of the satisfaction of the Gunnarsson-Lundqvist theorem, i.e. the *uniqueness* of the external potential $v(\mathbf{r})$ for a lowest excited state of density $\rho^e(\mathbf{r})$, and the multiplicity of the potentials for other excited states, the reader is referred to [19]. It is reiterated that within Q–DFT, an *infinite* number of local potentials that can generate the density $\rho^e(\mathbf{r})$ of *any* excited state may be constructed.

The final component of the book is a description of physical insights arrived at via Q–DFT of Kohn-Sham DFT and Slater theory, and of local effective potential energy theory in general.

As noted above, the KS–DFT mapping to the S system is intrinsically *mathematical* in that it is a description in terms of energy functionals of the density and of their functional derivatives. How the electron correlations due to the Pauli exclusion principle, Coulomb repulsion, and Correlation-Kinetic effects are incorporated in the KS electron-interaction energy functional $E_{ee}^{KS}[\rho(\mathbf{r})]$ or its functional derivative $v_{ee}(\mathbf{r})$ is not described by the theory. As the Q–DFT mapping is *physical*, and in terms of quantal sources and fields representative of the various electron correlations, it is possible to provide as in Chap. 5 a rigorous physical interpretation of the functional derivative $v_{ee}(\mathbf{r})$ and to explain how the various electron correlations are incorporated into the functional $E_{ee}^{KS}[\rho(\mathbf{r})]$. For the noninteracting fermions (or bosons) to have a component of the total energy and a corresponding local potential energy in which all the many-body effects are incorporated, there must exist a *force* field. That field is *identified* and *defined* by Q–DFT. The potential energy is the work done in this conservative field. The total energy component in turn is defined in integral virial form in terms of the components of the conservative field or in terms of their quantal sources. It is further shown [38] via adiabatic coupling-constant perturbation theory, that what is referred to as KS 'exchange' is not solely due to Pauli correlations, but in fact due to Pauli correlations and lowest-order Correlation-Kinetic effects. Similarly, KS 'correlation' is comprised of Coulomb correlations and second- and higher-order Correlation-Kinetic effects. In a similar manner, Runge-Gross DFT and its action functionals and functional derivatives can be provided [12] a rigorous physical interpretation via Q-DFT. The Optimized Potential Method [39], yet another mathematically based local effective potential theory, is also provided [40] a physical interpretation. Slater theory [5], the original local effective potential energy theory, is explained in Chap. 10. As a consequence of the quantal-source and field perspective, it is shown [41, 42] that the Slater 'potential' does not represent the potential energy of an electron.

A consequence of the mapping from the interacting system of electrons to one of noninteracting fermions or bosons is that the potential energy of these model fermions exhibits a discontinuity as the electron number passes through an integer value. In Chap. 7 the origin of the discontinuity is explained. It is proved [43] both analytically and by example via Q–DFT that correlations due to the Pauli exclusion principle and Coulomb repulsion do not contribute to the discontinuity, and that it is *solely* a consequence of Correlation-Kinetic effects.

In Kohn-Sham DFT, the ground state energy functional $E[\rho(\mathbf{r})]$ is not known because the component involving the many-body effects $E_{ee}^{KS}[\rho(\mathbf{r})]$ is unknown. Hence, this functional is approximated in application of the theory. (The variational rigor of the second Hohenberg-Kohn theorem is thus lost because this is akin to approximating the Hamiltonian.) The most extensively employed approximation within KS–DFT, and one that constitutes the leading order term in most other approximations, is the local density approximation (LDA). The understanding of the electron correlations in this approximation according to KS–DFT is as follows. At each point of the nonuniform density system, the electron correlations are those of the *uniform* electron gas, but for a density corresponding to the local value at that point. In Chap. 10 it is proved [44–47] via Q–DFT that at each point, in addition to the uniform electron gas correlations, the approximation explicitly accounts for the nonuniformity of the electron density via a term proportional to the gradient of the density at that point. Thus, the representation of electron correlations in the LDA is in fact far more accurate than previously understood to be the case. This constitutes the principal reason for the accuracy of the approximation.

The Epilogue is Chap. 11. In the previous edition, the epilogue was concluded with the results of application of Q–DFT to the determination of the asymptotic structure of the electron-interaction potential energy $v_{ee}(\mathbf{r})$ and of its Pauli, Coulomb, and Correlation-Kinetic contributions in the classically forbidden region of atoms and metal surfaces. This material with detailed derivations is now given in ***QDFT2***, and is thus not repeated in this edition. More recent work [48] on the metal-vacuum inhomogeneity reaffirms and furthers the original analytical work presented there.

Finally, the choice of nomenclature of Quantal Density Functional Theory based on prior understandings is as follows. The word *'quantal'* is employed because the sources of the fields are expectations taken with respect to the Schrödinger and noninteracting model system wave functions. It is a *density functional theory* because these wave functions are functionals of the nondegenerate ground state density, and the interacting Schrödinger system is being mapped to one of noninteracting fermions with the same density. The present understanding is more general. The fundamental property of interest is no longer solely the density but rather the basic variables of quantum mechanics. It is the fact that the wave functions are functionals of the basic variables that is now employed. As such it is efficacious to map to model systems with the same basic variables as that of the interacting system. The original terminology of Quantal Density Functional Theory is, however, still maintained.

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Chapter 2
Schrödinger Theory from the 'Newtonian' Perspective of 'Classical' Fields Derived from Quantal Sources

Abstract Schrödinger theory of the electronic structure of matter—N electrons in the presence of an external time-dependent field—is described from the perspective of the *individual* electron. The corresponding equation of motion is expressed via the 'Quantal Newtonian' second law, the first law being a description of the stationary state case. This description of Schrödinger theory is 'Newtonian' in that it is in terms of 'classical' fields which pervade space, and whose sources are quantum-mechanical expectations of Hermitian operators taken with respect to the system wave function. In addition to the external field, each electron experiences an internal field, the components of which are representative of correlations due to the Pauli Exclusion Principle and Coulomb repulsion, the kinetic effects, and the density. The resulting motion of the electron is described by a response field. Ehrenfest's theorem is derived by showing the internal field vanishes on summing over all the electrons. The 'Newtonian' perspective is then explicated for both a ground and excited state of an exactly solvable model. Various facets of quantum mechanics such as the Integral Virial Theorem, the Harmonic Potential Theorem, the quantum-mechanical 'hydrodynamical' equations in terms of fields, coalescence constraints, and the asymptotic structure of the wave function and density are derived. The equivalence of the 'Quantal Newtonian' second law and the Euler equation of Quantum Fluid Dynamics is proved.

Introduction

In order to understand quantal density functional theory (Q-DFT), it is necessary to first understand Schrödinger theory [1] from the new perspective of the 'Quantal Newtonian' second and first laws, the latter being the time-independent version of the former. These laws represent the equations of motion of the *individual* electrons. The description of these laws is in terms of 'classical' fields and their quantal sources [2]. The terminology 'classical' is employed in the original sense of fields as pervading all space, and not necessarily as solutions of Maxwell's equations. The description of a quantum system, and of its energy and energy components in terms of fields, provides a new perspective on Schrödinger theory, one that is physically tangible. This different perspective, however, still lies within the rubric of the theory's probabilistic description of a quantum system in that the sources of the fields are quantum mechanical expectations of Hermitian operators or of complex sums of Hermitian

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operators taken with respect to the system wavefunction. Thus, these fields may be thought of as being inherent to the quantal system, (just as the solution to Maxwell's equations are inherent to an electromagnetic system), with each field, or sum of fields, contributing to a specific energy component. Another important facet of this new perspective is that it reveals the intrinsic self-consistent nature of the Schrödinger equation. This chapter is a description of Schrödinger theory from this 'Newtonian' perspective of fields and quantal sources. The equivalence of Schrödinger theory as described by its field perspective to the corresponding Euler equation of Quantum Fluid Dynamics (QFD) is also derived.

2.1 Time-Dependent Schrödinger Theory

Consider a system of N electrons in the presence of a time-dependent (TD) external field $\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}t)$ such that $\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}t) = -\boldsymbol{\nabla} v(\mathbf{r}t)$, where $v(\mathbf{r}t)$ is the scalar potential energy of an electron. The TD Schrödinger equation in the Born–Oppenheimer approximation [3] is (in atomic units: $e = \hbar = m = 1$)

$$\hat{H}(t)\Psi(\mathbf{X}t) = i\frac{\partial\Psi(\mathbf{X}t)}{\partial t}, \tag{2.1}$$

where $\Psi(\mathbf{X}t)$ is the wavefunction, $\mathbf{X} = \mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N$, $\mathbf{x} = \mathbf{r}\sigma$, $\mathbf{r}$ and σ are the spatial and spin coordinates. The Hamiltonian operator $\hat{H}(t)$ is a sum of the kinetic energy $\hat{T}$, external potential energy $\hat{V}(t)$, and electron–interaction potential energy $\hat{U}$ operators:

$$\hat{H}(t) = \hat{T} + \hat{V}(t) + \hat{U}, \tag{2.2}$$

where

$$\hat{T} = -\frac{1}{2}\sum_i \nabla_i^2, \tag{2.3}$$

$$\hat{V}(t) = \sum_i v(\mathbf{r}_i t), \tag{2.4}$$

and

$$\hat{U} = \frac{1}{2}\sum_{i,j}{}' \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \tag{2.5}$$

As electrons are fermions, the wave function $\Psi(\mathbf{X}t)$ is antisymmetric in an interchange of the coordinates of the particles including spin, and thus accounts for electron correlations due to the Pauli exclusion principle. Due to the electron-interaction term in the Hamiltonian, the wave function also accounts for correlations due to Coulomb repulsion. Also *implicit* in the writing of the Hamiltonian is the fact that the external potential energy function $v(\mathbf{r}t)$ is *path-independent* at each instant of time. By providing a rigorous physical interpretation for $v(\mathbf{r}t)$ in terms of the system wave function $\Psi(\mathbf{X}t)$, this will be shown to be the case.

In quantum mechanics, properties of a system are determined in terms of the position probability density, or equivalently as expectation values of the corresponding operators taken with respect to the wavefunction. These expectations are functions of time since the wavefunction depends upon time, and the spatial and spin coordinates are integrated out. Thus, with $\Psi(\mathbf{X}t) = \Psi(t)$, the (non conserved) energy $E(t)$ is the expectation

$$E(t) = \langle \Psi(t) \mid i\frac{\partial}{\partial t} \mid \Psi(t)\rangle = \langle \Psi(t) \mid \hat{H}(t) \mid \Psi(t)\rangle. \tag{2.6}$$

The energy in turn may be written in terms of its kinetic $T(t)$, external potential $E_{\mathrm{ext}}(t)$, and electron–interaction potential $E_{\mathrm{ee}}(t)$ energy components:

$$E(t) = T(t) + E_{\mathrm{ext}}(t) + E_{\mathrm{ee}}(t), \tag{2.7}$$

where

$$T(t) = \langle \Psi(t) \mid \hat{T} \mid \Psi(t)\rangle, \tag{2.8}$$

$$E_{\mathrm{ext}}(t) = \langle \Psi(t) \mid \hat{V}(t) \mid \Psi(t)\rangle, \tag{2.9}$$

and

$$E_{\mathrm{ee}}(t) = \langle \Psi(t) \mid \hat{U} \mid \Psi(t)\rangle. \tag{2.10}$$

The quantum-mechanical system described by the time-dependent Schrödinger equation (2.1) can alternately be described from a 'Newtonian' perspective. Thus, there exists a 'Quantal Newtonian' second law. A special case is the 'Quantal Newtonian' first law, which in turn is an equivalent description of the time-independent Schrödinger equation. These 'Newtonian' laws are in terms of 'classical' fields derived from quantal sources that are quantum-mechanical expectations of Hermitian operators or of the complex sum of Hermitian operators taken with respect to the system wave function. The fields obtained from these sources are *separately* representative of the kinetic, external, and electron-interaction components of the physical system. Thus, with each property is associated a 'classical' field.

We next describe the quantal sources.

2.2 Definitions of Quantal Sources

In this section we define the quantum–mechanical sources of the fields intrinsic to the system. These sources are the electronic density $\rho(\mathbf{r}t)$, the spinless single–particle density matrix $\gamma(\mathbf{r}\mathbf{r}'t)$, the pair–correlation density $g(\mathbf{r}\mathbf{r}'t)$ and from it the Fermi–Coulomb hole charge distribution $\rho_{\mathrm{xc}}(\mathbf{r}\mathbf{r}'t)$, and the current density $\mathbf{j}(\mathbf{r}t)$. The current density may also be expressed in terms of the density matrix. The sources are written both in terms of their probabilistic definitions and as expectations of Hermitian operators.

2.2.1 Electron Density $\rho(\mathbf{r}t)$

The electron density $\rho(\mathbf{r}t)$ is N times the probability of an electron being at $\mathbf{r}$ at time t:

$$\rho(\mathbf{r}t) = N \sum_{\sigma} \int \Psi^* \left(\mathbf{r}\sigma, \mathbf{X}^{N-1}, t\right) \Psi \left(\mathbf{r}\sigma, \mathbf{X}^{N-1}, t\right) d\mathbf{X}^{N-1}, \tag{2.11}$$

where $\mathbf{X}^{N-1} = \mathbf{x}_2, \mathbf{x}_3, \ldots, \mathbf{x}_N, d\mathbf{X}^{N-1} = d\mathbf{x}_2, \ldots, d\mathbf{x}_N,$ and $\int d\mathbf{x} = \sum_{\sigma} \int d\mathbf{r}$. The density is also the expectation of the Hermitian density operator

$$\hat{\rho}(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i), \tag{2.12}$$

so that

$$\rho(\mathbf{r}t) = \langle \Psi(t) \mid \hat{\rho}(\mathbf{r}) \mid \Psi(t) \rangle. \tag{2.13}$$

The total electronic charge is

$$\int \rho(\mathbf{r}t) d\mathbf{r} = N. \tag{2.14}$$

The electron density is a *static* or *local* charge distribution in that its structure remains unchanged as a function of electron position for each instant of time.

2.2.2 Spinless Single–Particle Density Matrix $\gamma(\mathbf{R}\mathbf{r}'t)$

The spinless single–particle density matrix $\gamma(\mathbf{r}\mathbf{r}'t)$ is defined as

$$\gamma(\mathbf{r}\mathbf{r}'t) = N \sum_{\sigma} \int \Psi^* \left(\mathbf{r}\sigma, \mathbf{X}^{N-1}, t\right) \Psi \left(\mathbf{r}'\sigma, \mathbf{X}^{N-1}, t\right) d\mathbf{X}^{N-1}, \tag{2.15}$$

and it may also be expressed as the expectation of the density matrix operator $\hat{\gamma}(\mathbf{r}\mathbf{r}')$ [4, 5]:

$$\gamma \left(\mathbf{r}\mathbf{r}'t\right) = \langle \Psi(t) \mid \hat{\gamma} \left(\mathbf{r}\mathbf{r}'\right) \mid \Psi(t) \rangle, \tag{2.16}$$

where

$$\hat{\gamma} \left(\mathbf{r}\mathbf{r}'\right) = \hat{A} + \mathrm{i}\hat{B}, \tag{2.17}$$

$$\hat{A} = \frac{1}{2} \sum_j \left[\delta \left(\mathbf{r}_j - \mathbf{r} \right) T_j(\mathbf{a}) + \delta \left(\mathbf{r}_j - \mathbf{r}' \right) T_j(-\mathbf{a}) \right], \tag{2.18}$$

$$\hat{B} = -\frac{i}{2} \sum_j \left[\delta \left(\mathbf{r}_j - \mathbf{r} \right) T_j(\mathbf{a}) - \delta \left(\mathbf{r}_j - \mathbf{r}' \right) T_j(-\mathbf{a}) \right], \tag{2.19}$$

$T_j(\mathbf{a})$ is a translation operator such that $T_j(\mathbf{a})\Psi(\ldots, \mathbf{r}_j, \ldots, t) = \Psi(\ldots, \mathbf{r}_j + \mathbf{a}, \ldots, t)$, and $\mathbf{a} = \mathbf{r}' - \mathbf{r}$. The operators $\hat{A}$ and $\hat{B}$ are each Hermitian.

To prove (2.16) we note that

$$\langle \hat{A} \rangle = \langle \Psi(t) | \hat{A} | \Psi(t) \rangle = \frac{1}{2} \left[\gamma(\mathbf{r}\mathbf{r}'t) + \gamma(\mathbf{r}'\mathbf{r}t) \right] \tag{2.20}$$

and since

$$\gamma(\mathbf{r}'\mathbf{r}t) = \gamma^\star(\mathbf{r}\mathbf{r}'t) \tag{2.21}$$

we have

$$\langle \hat{A} \rangle = \Re \gamma(\mathbf{r}\mathbf{r}'t). \tag{2.22}$$

Similarly

$$\langle \hat{B} \rangle = -\frac{i}{2} \left[\gamma(\mathbf{r}\mathbf{r}'t) - \gamma(\mathbf{r}'\mathbf{r}t) \right] \tag{2.23}$$

$$= \Im \gamma(\mathbf{r}\mathbf{r}'t). \tag{2.24}$$

Thus, the single-particle density matrix is the expectation of the complex sum of Hermitian operators. It is a *nonlocal* source since it depends on both $\mathbf{r}$ and $\mathbf{r}'$.

Another property of the single particle density matrix, which distinguishes it from the Dirac density matrix to be defined later, is that it is not idempotent and satisfies instead the inequality

$$\int \gamma \left(\mathbf{r}\mathbf{r}''t \right) \gamma \left(\mathbf{r}''\mathbf{r}'t \right) d\mathbf{r}'' \ < \ \gamma \left(\mathbf{r}\mathbf{r}'t \right). \tag{2.25}$$

The diagonal matrix element of the density matrix is the density: $\gamma(\mathbf{r}\mathbf{r}t) = \rho(\mathbf{r}t)$.

2.2.3 Pair–Correlation Density $g(\mathbf{r}\mathbf{r}'t)$, and Fermi–Coulomb Hole $\rho_{\mathrm{xc}}(\mathbf{r}\mathbf{r}'t)$

The pair–correlation density $g(\mathbf{r}\mathbf{r}'t)$ is a property representative of electron correlations due to the Pauli exclusion principle and Coulomb repulsion. At each instant of time, it is the conditional density at $\mathbf{r}'$ of all the other electrons, given that one electron is at $\mathbf{r}$. It is defined as the ratio of the expectations of two Hermitian operators:

$$g(\mathbf{r}\mathbf{r}'t) = \frac{P(\mathbf{r}\mathbf{r}'t)}{\rho(\mathbf{r}t)}, \tag{2.26}$$

with the pair function $P(\mathbf{r}\mathbf{r}'t)$ being the expectation

$$P(\mathbf{r}\mathbf{r}'t) = \langle \Psi(t)|\hat{P}(\mathbf{r}\mathbf{r}')|\Psi(t)\rangle, \tag{2.27}$$

where $\hat{P}(\mathbf{r}\mathbf{r}')$ is the Hermitian pair-correlation operator

$$\hat{P}(\mathbf{r}\mathbf{r}') = \sum_{i,j}{}' \delta(\mathbf{r}_i - \mathbf{r})\delta(\mathbf{r}_j - \mathbf{r}'). \tag{2.28}$$

The pair function $P(\mathbf{r}\mathbf{r}'t)$ is the probability of simultaneously finding electrons at $\mathbf{r}$ and $\mathbf{r}'$ at time t.

The total charge of the pair-correlation density for each electron position $\mathbf{r}$ at time t is

$$\int g(\mathbf{r}\mathbf{r}'t)d\mathbf{r}' = N - 1. \tag{2.29}$$

To prove the sum rule of (2.29) we rewrite the pair function $P(\mathbf{r}\mathbf{r}'t)$ as

$$\begin{aligned} P(\mathbf{r}\mathbf{r}'t) = \langle \Psi(t)| \sum_{i,j} \delta(\mathbf{r}_i - \mathbf{r})\delta(\mathbf{r}_j - \mathbf{r}')|\Psi(t)\rangle \\ -\langle \Psi(t)| \sum_{i} \delta(\mathbf{r}_i - \mathbf{r})\delta(\mathbf{r}_i - \mathbf{r}')|\Psi(t)\rangle \qquad (2.30) \\ = \langle \Psi(t)| \sum_{i} \delta(\mathbf{r}_i - \mathbf{r}) \sum_{j} \delta(\mathbf{r}_j - \mathbf{r}')|\Psi(t)\rangle - \delta(\mathbf{r} - \mathbf{r}')\rho(\mathbf{r}). \qquad (2.31) \end{aligned}$$

On integrating:

$$\begin{aligned} \int P(\mathbf{r}\mathbf{r}'t)d\mathbf{r}' = \langle \Psi(t)| \sum_{i} \delta(\mathbf{r}_i - \mathbf{r}) \sum_{j} \int \delta(\mathbf{r}_j - \mathbf{r}')d\mathbf{r}'|\Psi(t)\rangle \\ -\rho(\mathbf{r}t) \int \delta(\mathbf{r} - \mathbf{r}')d\mathbf{r}' \qquad (2.32) \\ = N\rho(\mathbf{r}t) - \rho(\mathbf{r}t), \qquad (2.33) \end{aligned}$$

so that

$$\frac{1}{\rho(\mathbf{r}t)} \int \hat{P}(\mathbf{r}\mathbf{r}'t)d\mathbf{r}' = N - 1. \tag{2.34}$$

The pair-correlation density is a *dynamic* or *nonlocal* charge distribution in that its structure changes as a function of electron position for nonuniform density systems. If there were no electron correlations, the density at $\mathbf{r}'$ would simply be $\rho(\mathbf{r}'t)$. However, due to electron correlations—the keeping apart of electrons—there is a reduction in the density at $\mathbf{r}'$. Hence, the pair-correlation density is the density $\rho(\mathbf{r}'t)$ at $\mathbf{r}'$ plus the reduction in this density at $\mathbf{r}'$ due to the electron correlations. The reduction in density about an electron which occurs as a result of the Pauli exclusion principle and Coulomb repulsion is the Fermi–Coulomb hole charge distribution $\rho_{\mathrm{xc}}(\mathbf{r}\mathbf{r}'t)$. Thus, we may write the pair-correlation density as

$$g(\mathbf{r}\mathbf{r}'t) = \rho(\mathbf{r}'t) + \rho_{\mathrm{xc}}(\mathbf{r}\mathbf{r}'t). \tag{2.35}$$

In this manner, the pair density is separated into its *local* and *nonlocal* components. Further, as a consequence, the total charge of the Fermi–Coulomb hole, for arbitrary electron position at $\mathbf{r}$, is

$$\int \rho_{\mathrm{xc}}(\mathbf{r}\mathbf{r}'t)d\mathbf{r}' = -1. \tag{2.36}$$

Note that there is no self–interaction in the pair-correlation density. This is evident from its definition (2.26). In its definition of (2.35), the self–interaction contribution to the Fermi–Coulomb hole charge is cancelled by the corresponding term of the density.

An associated property is the pair–correlation function $h(\mathbf{r}\mathbf{r}'t)$ defined as

$$h(\mathbf{r}\mathbf{r}'t) = \frac{g(\mathbf{r}\mathbf{r}'t)}{\rho(\mathbf{r}'t)}, \tag{2.37}$$

which is symmetrical in an interchange of $\mathbf{r}$ and $\mathbf{r}'$:

$$h(\mathbf{r}\mathbf{r}'t) = h(\mathbf{r}'\mathbf{r}t). \tag{2.38}$$

This property of symmetry of the pair function is of value in various proofs to follow.

2.2.4 Current Density $\mathbf{j}(\mathbf{r}t)$

The current density $\mathbf{j}(\mathbf{r}t)$ at point $\mathbf{r}$ and at time t is defined as

$$\mathbf{j}(\mathbf{r}t) = \mathrm{Re}N \sum_{\sigma} \int \Psi^{*}\left(\mathbf{r}\sigma, \mathbf{X}^{N-1}, t\right) \frac{1}{i} \nabla \Psi\left(\mathbf{r}\sigma, \mathbf{X}^{N-1}, t\right) d\mathbf{X}^{N-1}. \tag{2.39}$$

It may also be expressed in terms of the single–particle density matrix $\gamma(\mathbf{r}\mathbf{r}'t)$ non-local source as

$$\mathbf{j}(\mathbf{r}t) = \frac{i}{2}\left[\boldsymbol{\nabla}' - \boldsymbol{\nabla}''\right] \gamma\left(\mathbf{r}'\mathbf{r}''t\right) |_{\mathbf{r}'=\mathbf{r}''=\mathbf{r}}, \tag{2.40}$$

or as the expectation value

$$\mathbf{j}(\mathbf{r}t) = \langle \Psi(t) \mid \hat{j}(\mathbf{r}) \mid \Psi(t) \rangle, \tag{2.41}$$

where $\hat{j}(\mathbf{r})$ is the Hermitian current density operator:

$$\hat{\mathbf{j}}(\mathbf{r}) = \frac{1}{2i} \sum_j \left[\nabla_{\mathbf{r}_j} \delta\left(\mathbf{r}_j - \mathbf{r}\right) + \delta(\mathbf{r}_j - \mathbf{r}) \nabla_{\mathbf{r}_j} \right]. \tag{2.42}$$

The quantal sources defined above then give rise to 'classical' fields that pervade all space. These fields are defined below.

2.3 Definitions of 'Classical' Fields

The different fields associated with the quantum system defined by (2.1) are the electron–interaction $\boldsymbol{\mathcal{E}}_{\mathrm{ee}}(\mathbf{r}t)$ field which is a sum of the Hartree $\boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r}t)$ and Pauli–Coulomb $\boldsymbol{\mathcal{E}}_{\mathrm{xc}}(\mathbf{r}t)$ fields, the differential density $\boldsymbol{\mathcal{D}}(\mathbf{r}t)$, kinetic $\boldsymbol{\mathcal{Z}}(\mathbf{r}t)$, and current–density $\boldsymbol{\mathcal{J}}(\mathbf{r}t)$ fields.

2.3.1 Electron–Interaction Field $\boldsymbol{\mathcal{E}}_{\mathbf{ee}}(\mathbf{r}t)$

The electron–interaction field $\boldsymbol{\mathcal{E}}_{\mathrm{ee}}(\mathbf{r}t)$ is representative of electron correlations due to the Pauli exclusion principle and Coulomb repulsion. The quantal source of this field is the pair-correlation density $g(\mathbf{r}\mathbf{r}'t)$. It is obtained from this charge distribution via Coulomb's law as

$$\boldsymbol{\mathcal{E}}_{\mathrm{ee}}(\mathbf{r}t) = \int \frac{g(\mathbf{r}\mathbf{r}'t)(\mathbf{r} - \mathbf{r}')}{\mid \mathbf{r} - \mathbf{r}' \mid^3} d\mathbf{r}'. \tag{2.43}$$

The field $\boldsymbol{\mathcal{E}}_{\mathrm{ee}}(\mathbf{r})$ may be rewritten in terms of an electron-interaction 'force' $\mathbf{e}_{ee}(\mathbf{r})$ and the density $\rho(\mathbf{r}t)$ as

$$\boldsymbol{\mathcal{E}}_{\mathrm{ee}}(\mathbf{r}t) = \frac{\mathbf{e}_{ee}(\mathbf{r}t)}{\rho(\mathbf{r}t)}, \tag{2.44}$$

where $\mathbf{e}_{ee}(\mathbf{r}t)$ is obtained via Coulomb's law from the pair function $P(\mathbf{r}\mathbf{r}'t)$:

$$\mathbf{e}_{ee}(\mathbf{r}t) = \int \frac{P(\mathbf{r}\mathbf{r}'t)(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} d\mathbf{r}'. \tag{2.45}$$

(The quantal source of the field $\boldsymbol{\mathcal{E}}_{\mathrm{ee}}(\mathbf{r}t)$ can thus also be thought of as being the pair function $P(\mathbf{r}\mathbf{r}'t)$.) With the pair-correlation density expressed as in (2.35), the field

$\mathcal{E}_{\mathrm{ee}}(\mathbf{r}t)$ may be written as a sum of its Hartree $\mathcal{E}_{\mathrm{H}}(\mathbf{r}t)$ and Pauli–Coulomb $\mathcal{E}_{\mathrm{xc}}(\mathbf{r}t)$ components as

$$\mathcal{E}_{\mathrm{ee}}(\mathbf{r}t) = \mathcal{E}_{\mathrm{H}}(\mathbf{r}t) + \mathcal{E}_{\mathrm{xc}}(\mathbf{r}t), \tag{2.46}$$

where

$$\mathcal{E}_{\mathrm{H}}(\mathbf{r}t) = \int \frac{\rho(\mathbf{r}'t)(\mathbf{r}-\mathbf{r}')}{\mid \mathbf{r}-\mathbf{r}' \mid^3} d\mathbf{r}', \tag{2.47}$$

and

$$\mathcal{E}_{\mathrm{xc}}(\mathbf{r}t) = \int \frac{\rho_{\mathrm{xc}}(\mathbf{r}\mathbf{r}'t)(\mathbf{r}-\mathbf{r}')}{\mid \mathbf{r}-\mathbf{r}' \mid^3} d\mathbf{r}'. \tag{2.48}$$

The Hartree field $\mathcal{E}_{\mathrm{H}}(\mathbf{r}t)$ is conservative as its source is a local charge distribution $\rho(\mathbf{r}t)$, so that $\nabla \times \mathcal{E}_{\mathrm{H}}(\mathbf{r}t) = 0$. In general, nonlocal sources such as the pair-correlation density and Fermi–Coulomb hole charge do not lead to conservative fields. Thus, the fields $\mathcal{E}_{\mathrm{ee}}(\mathbf{r}t)$ and $\mathcal{E}_{\mathrm{xc}}(\mathbf{r}t)$ are in general not conservative, i.e. $\nabla \times \mathcal{E}_{\mathrm{ee}}(\mathbf{r}t) \neq 0$ and $\nabla \times \mathcal{E}_{\mathrm{xc}}(\mathbf{r}t) \neq 0$.

2.3.2 Differential Density Field $\mathcal{D}(\mathbf{r}t)$

The differential density field $\mathcal{D}(\mathbf{r}t)$ is defined as

$$\mathcal{D}(\mathbf{r}t) = \frac{\mathbf{d}(\mathbf{r}t)}{\rho(\mathbf{r}t)}, \tag{2.49}$$

where the differential density ‘force’

$$\mathbf{d}(\mathbf{r}t) = -\frac{1}{4}\nabla\nabla^2\rho(\mathbf{r}t). \tag{2.50}$$

This field also arises from a local source, the electronic density $\rho(\mathbf{r}t)$, so that it too is conservative, and $\nabla \times \mathcal{D}(\mathbf{r}t) = 0$. The vanishing of the curl of the ‘force’ $\mathbf{d}(\mathbf{r}t)$ is evident since the curl of the gradient of a scalar function vanishes. (Although the field $\mathcal{D}(\mathbf{r}t)$ is intrinsic to Schrödinger theory, it plays no role within Q-DFT as will become clear in the following chapter.)

2.3.3 Kinetic Field $\mathcal{Z}(\mathbf{r}t)$

The kinetic field $\mathcal{Z}(\mathbf{r}t)$ is so named because the kinetic energy density, and hence, the kinetic energy may be obtained from it. The field, whose source is the nonlocal single–particle density matrix $\gamma(\mathbf{r}\mathbf{r}'t)$, is defined as

$$\mathcal{Z}(\mathbf{r}t) = \frac{z(\mathbf{r}t; [\gamma])}{\rho(\mathbf{r}t)}, \tag{2.51}$$

where the kinetic 'force' $z(\mathbf{r}t)$ is defined by its component $z_\alpha(\mathbf{r}t)$ as

$$z_\alpha(\mathbf{r}t) = 2\sum_\beta \frac{\partial}{\partial r_\beta} t_{\alpha\beta}(\mathbf{r}t), \tag{2.52}$$

and where $t_{\alpha\beta}(\mathbf{r}t)$ is the second-rank kinetic-energy-density tensor defined in turn as

$$t_{\alpha\beta}(\mathbf{r}t) = \frac{1}{4}\left[\frac{\partial^2}{\partial r'_\alpha \partial r''_\beta} + \frac{\partial^2}{\partial r'_\beta \partial r''_\alpha}\right]\gamma(\mathbf{r}'\mathbf{r}''t)|_{\mathbf{r}'=\mathbf{r}''=\mathbf{r}}. \tag{2.53}$$

The field $\mathcal{Z}(\mathbf{r}t)$ is 'classical' in the sense that it is derived as the derivative of a tensor. Its source $\gamma(\mathbf{r}\mathbf{r}'t)$, however, is quantum mechanical. As the source is nonlocal, in general the field $\mathcal{Z}(\mathbf{r}t)$ is not conservative and $\nabla \times \mathcal{Z}(\mathbf{r}t) \neq 0$.

2.3.4 Current Density Field $\mathcal{J}(\mathbf{r}t)$

The current density field $\mathcal{J}(\mathbf{r}t)$, whose source is the nonlocal single particle density matrix $\gamma(\mathbf{r}\mathbf{r}'t)$, is defined as

$$\mathcal{J}(\mathbf{r}t) = \frac{1}{\rho(\mathbf{r}t)}\frac{\partial}{\partial t}\mathbf{j}(\mathbf{r}t), \tag{2.54}$$

where $\mathbf{j}(\mathbf{r}t)$ is the current density. This field too may be thought of as being 'classical' from the perspective of the hydrodynamic continuity and force equations to be discussed later in this chapter. In general, this field too is nonconservative so that $\nabla \times \mathcal{J}(\mathbf{r}t) \neq 0$.

The fields $\mathcal{E}_{\mathrm{ee}}(\mathbf{r}t)$, $\mathcal{E}_{\mathrm{xc}}(\mathbf{r}t)$, $\mathcal{Z}(\mathbf{r}t)$, and $\mathcal{J}(\mathbf{r}t)$ are in general not conservative. However, their sum always is, so that

$$\nabla \times [\mathcal{E}_{\mathrm{ee}}(\mathbf{r}t) + \mathcal{Z}(\mathbf{r}t) + \mathcal{J}(\mathbf{r}t)] = 0. \tag{2.55}$$

If the system in the presence of the time-dependent external field $\mathcal{F}^{\mathrm{ext}}(\mathbf{r}t)$ has a symmetry which reduces these fields to being one dimensional, or when such a symmetry is imposed as by application of the central field approximation, the individual fields are then separately conservative. In such cases

$$\nabla \times \mathcal{E}_{\mathrm{ee}}(\mathbf{r}t) = 0, \tag{2.56}$$

$$\nabla \times \mathcal{Z}(\mathbf{r}t) = 0, \tag{2.57}$$

$$\nabla \times \mathcal{J}(\mathbf{r}t) = 0. \tag{2.58}$$

The central field approximation can be achieved by spherically averaging the fields.

2.4 Energy Components in Terms of Quantal Sources and Fields

The kinetic $T(t)$, external $E_{\rm ext}(t)$, and electron–interaction $E_{\rm ee}(t)$ energies as defined by the expectations of (2.8)–(2.10), may be expressed directly in terms of the quantal sources, and also in integral virial form in terms of the respective fields described above.

2.4.1 Electron–Interaction Potential Energy $E_{\rm ee}(t)$

The electron–interaction energy $E_{\rm ee}(t)$ may be interpreted as the energy of interaction between the density $\rho(\mathbf{r}t)$ and the pair-correlation density $g(\mathbf{rr}'t)$:

$$E_{\rm ee}(t) = \frac{1}{2}\iint \frac{\rho(\mathbf{r}t)g(\mathbf{rr}'t)}{\mid \mathbf{r}-\mathbf{r}' \mid} d\mathbf{r}d\mathbf{r}'. \tag{2.59}$$

Employing the decomposition of $g(\mathbf{rr}'t)$ as in (2.35), we may write

$$E_{\rm ee}(t) = E_{\rm H}(t) + E_{\rm xc}(t), \tag{2.60}$$

where $E_{\rm H}(t)$ is the Hartree or Coulomb self–energy:

$$E_H(t) = \frac{1}{2}\iint \frac{\rho(\mathbf{r}t)\rho(\mathbf{r}'t)}{\mid \mathbf{r}-\mathbf{r}' \mid} d\mathbf{r}d\mathbf{r}', \tag{2.61}$$

and $E_{\rm xc}(t)$ the *quantum–mechanical* exchange–correlation—Pauli–Coulomb—energy

$$E_{\rm xc}(t) = \frac{1}{2}\iint \frac{\rho(\mathbf{r}t)\rho_{\rm xc}(\mathbf{rr}'t)}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}'. \tag{2.62}$$

The energy $E_{\rm xc}(t)$ may in turn be interpreted as the energy of interaction between the density $\rho(\mathbf{r}t)$ and the Fermi–Coulomb hole charge distribution $\rho_{\rm xc}(\mathbf{rr}'t)$.

These energy components may also be expressed in terms of the fields as follows. Since

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} = \frac{(\mathbf{r}-\mathbf{r}')\cdot(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} = \frac{\mathbf{r}\cdot(\mathbf{r}-\mathbf{r}') - \mathbf{r}'\cdot(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}, \tag{2.63}$$

we may write $E_{\rm ee}(t)$ in terms of the pair-correlation function $h(\mathbf{rr}'t)$ of (2.37) as

$$E_{\rm ee}(t) = \frac{1}{2}\iint \frac{[\mathbf{r}\cdot(\mathbf{r}-\mathbf{r}') - \mathbf{r}'\cdot(\mathbf{r}-\mathbf{r}')]}{|\mathbf{r}-\mathbf{r}'|^3} \rho(\mathbf{r}t)\rho(\mathbf{r}'t)h(\mathbf{rr}'t). \tag{2.64}$$

On interchanging $\mathbf{r}$ and $\mathbf{r}'$ in the second term of (2.64) and employing the symmetry property of $h(\mathbf{rr}'t)$, we see that it is the same as the first, so that

$$\begin{aligned} E_{\mathrm{ee}}(t) &= \iint \frac{\mathbf{r}\cdot(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}t)g(\mathbf{rr}'t)}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}d\mathbf{r}' \\ &= \int \rho(\mathbf{r}t)\mathbf{r}\cdot \int \frac{g(\mathbf{rr}'t)(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}' \\ &= \int \rho(\mathbf{r}t)\mathbf{r}\cdot \boldsymbol{\mathcal{E}}_{\mathrm{ee}}(\mathbf{r}t)d\mathbf{r}. \end{aligned} \tag{2.65}$$

Employing the decomposition of $\boldsymbol{\mathcal{E}}_{\mathrm{ee}}(\mathbf{r}t)$ of (2.46), we then have

$$E_{\mathrm{H}}(t) = \int \rho(\mathbf{r}t)\mathbf{r}\cdot \boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r}t)d\mathbf{r}, \tag{2.66}$$

and

$$E_{\mathrm{xc}}(t) = \int \rho(\mathbf{r}t)\mathbf{r}\cdot \boldsymbol{\mathcal{E}}_{\mathrm{xc}}(\mathbf{r}t)d\mathbf{r}. \tag{2.67}$$

Note that the expressions for the energy components in terms of the fields is *independent* of whether or not the fields are conservative.

2.4.2 Kinetic Energy $T(t)$

The kinetic energy $T(t)$ may be written in terms of its quantal source, the single–particle density matrix $\gamma(\mathbf{rr}'t)$ as

$$T(t) = \int t(\mathbf{r}t)d\mathbf{r}, \tag{2.68}$$

where the kinetic energy density $t(\mathbf{r}t)$ is the trace of the kinetic energy density tensor $t_{\alpha\beta}(\mathbf{r}t)$:

$$t(\mathbf{r}t) = \sum_{\alpha} t_{\alpha\alpha}(\mathbf{r}t) = \frac{1}{2}\boldsymbol{\nabla}_{\mathbf{r}'}\cdot\boldsymbol{\nabla}_{\mathbf{r}''}\gamma(\mathbf{r}'\mathbf{r}''t)\,|_{\mathbf{r}'=\mathbf{r}''=\mathbf{r}}\ . \tag{2.69}$$

The kinetic energy $T(t)$ may also be expressed in terms of the kinetic field $\boldsymbol{\mathcal{Z}}(\mathbf{r}t)$ as

$$T(t) = -\frac{1}{2}\int \rho(\mathbf{r}t)\mathbf{r}\cdot \boldsymbol{\mathcal{Z}}(\mathbf{r}t)d\mathbf{r}, \tag{2.70}$$

or in terms of the kinetic ‘force’ $\mathbf{z}(\mathbf{r}t)$ as

$$T(t) = -\frac{1}{2}\int \mathbf{r}\cdot \mathbf{z}(\mathbf{r}t)d\mathbf{r}. \tag{2.71}$$

Equation (2.70) can be shown to be equivalent to (2.68) by partial integration and by employing the fact that the wavefunction and hence the single–particle density matrix vanishes as $\mathbf{r}$, $\mathbf{r}'$ tend towards infinity. Once again, the expression for $T(t)$ in terms of the kinetic field $\mathcal{Z}(\mathbf{r}t)$ is *independent* of whether or not the field is conservative.

2.4.3 External Potential Energy $E_{\mathbf{ext}}(t)$

The external potential energy $E_{\text{ext}}(t)$ may be expressed in terms of the electronic density $\rho(\mathbf{r}t)$ and the potential energy $v(\mathbf{r}t)$ of an electron in the external field $\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}t)$ as

$$E_{\text{ext}}(t) = \int \rho(\mathbf{r}t)v(\mathbf{r}t)d\mathbf{r}. \tag{2.72}$$

Through the external potential energy $v(\mathbf{r}t)$, this component of the total energy depends on *all* the fields present in the quantal system. As the quantal sources of these fields are expectations taken with respect to the wave function $\Psi(t)$, the potential energy $v(\mathbf{r}t)$ is a functional of $\Psi(t)$, i.e. $v(\mathbf{r}t) = v[\Psi(t)]$. The explanation of this is arrived at via the ‘Quantal Newtonian’ second law to be discussed next.

2.5 Schrödinger Theory and the ‘Quantal Newtonian’ Second Law

The Schrödinger theory description of a quantum system can alternatively be interpreted in terms of fields representative of the various electron correlations and properties. This description is based on the *pure* state ‘Quantal Newtonian’ second law or time-dependent differential virial theorem [6–8]. (A state is said to be *pure* if it is described by a wavefunction i.e. by the solution of (2.1). It is said to be *mixed* if it cannot be so described. A system in a mixed state can be characterized by a probability distribution over all accessible pure states).

As a prelude to the description of this quantal law, let us review the classical mechanics of a system of N particles that obey Newton’s third law of action and reaction, and exert forces on each other that are equal and opposite, and lie along the line joining them. Then Newton’s second law for the ith particle is

$$\mathbf{F}_i^{\text{ext}} + \sum_j \mathbf{F}_{ji} = \frac{d}{dt}\mathbf{p}_i, \tag{2.73}$$

where $\mathbf{F}_i^{\text{ext}}$ is the external force, $\mathbf{F}_{ji}$ the internal force on the ith particle due to the jth particle, and $\mathbf{p}_i$ is the linear momentum. Summing over all particles, (2.73) reduces to Newton’s second law for the system of particles:

$$\mathbf{F}^{\text{ext}} = \frac{d^2}{dt^2}\sum_i \mathbf{r}_i, \tag{2.74}$$

where $\mathbf{F}^{\mathrm{ext}} = \sum_i \mathbf{F}_i^{\mathrm{ext}}$ is the total external force. The internal forces corresponding to the term $\sum'_{i,j} \mathbf{F}_{ji}$ vanish as a consequence of Newton's third law.

The 'Quantal Newtonian' second law is the quantum-mechanical counterpart of the classical equation of motion (2.73) for the individual particles. Its statement is

$$\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}t) + \boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r}t) = \boldsymbol{\mathcal{J}}(\mathbf{r}t), \tag{2.75}$$

where *each* electron experiences the *external* field $\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}t)$:

$$\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}t) = -\boldsymbol{\nabla} v(\mathbf{r}t), \tag{2.76}$$

and a field *internal* to the system $\boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r}t)$ that is representative of the correlations between the electrons, the density, and the kinetic effects:

$$\boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r}t) = \boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}t) - \boldsymbol{\mathcal{D}}(\mathbf{r}t) - \boldsymbol{\mathcal{Z}}(\mathbf{r}t), \tag{2.77}$$

where the component fields $\boldsymbol{\mathcal{E}}_{\mathrm{ee}}(\mathbf{r}t)$, $\boldsymbol{\mathcal{D}}(\mathbf{r}t)$, $\boldsymbol{\mathcal{Z}}(\mathbf{r}t)$ are defined by (2.43), (2.44), (2.49), and (2.51). The response of each electron to the external and internal fields is the current density field $\boldsymbol{\mathcal{J}}(\mathbf{r}t)$ defined by (2.54) which is the quantum analog of the time derivative of $\mathbf{p}_i$ of (2.73). The internal field $\boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r}t)$ is discussed more fully in Sect. 2.8.

From the 'Quantal Newtonian' second law of (2.75) a rigorous physical interpretation of the external potential energy $v(\mathbf{r}t)$ follows: It is the work done, at each instant of time, to move an electron from some reference point, say at infinity, to its position at $\mathbf{r}$ in the force of a *conservative* field $\boldsymbol{\mathcal{F}}(\mathbf{r}t)$:

$$v(\mathbf{r}t) = \int_\infty^{\mathbf{r}} \boldsymbol{\nabla} v(\mathbf{r}'t) \cdot d\boldsymbol{\ell}' = \int_\infty^{\mathbf{r}} \boldsymbol{\mathcal{F}}(\mathbf{r}'t) \cdot d\boldsymbol{\ell}' \tag{2.78}$$

where

$$\boldsymbol{\mathcal{F}}(\mathbf{r}t) = \boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r}t) - \boldsymbol{\mathcal{J}}(\mathbf{r}t). \tag{2.79}$$

The work done is *path-independent* since $\boldsymbol{\nabla} \times \boldsymbol{\mathcal{F}}(\mathbf{r}t) = 0$. The fact that the field $\boldsymbol{\mathcal{F}}(\mathbf{r}t)$ is conservative is consistent with the assumption in the construction of the Hamiltonian of (2.2) that the potential energy $v(\mathbf{r}t)$ at each instant of time is path-independent.

As the external potential energy $v(\mathbf{r}t)$ depends upon the internal $\boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r}t)$ and the response $\boldsymbol{\mathcal{J}}(\mathbf{r}t)$ fields, and these fields in turn are obtained from quantal sources that are expectations taken with respect to the wave function $\Psi(t)$, the potential energy $v(\mathbf{r}t)$ is a functional of the wave function: $v(\mathbf{r}t) = v[\Psi(t)]$. The time-dependent Schrödinger equation (2.1) may then be written as

$$\Big\{ -\frac{1}{2}\sum_i \nabla_i^2 + \frac{1}{2}\sum_{i,j}{}' \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i v_i[\Psi(t)] \Big\} \Psi(t) = i\frac{\partial \Psi(t)}{\partial t}, \tag{2.80}$$

where $v_i = v(\mathbf{r}_i t)$. More explicitly it may be written in terms of the conservative field $\boldsymbol{\mathcal{F}}(\mathbf{r}t)$ of (2.79) as

$$\left[-\frac{1}{2}\sum_i \nabla_i^2 + \frac{1}{2}\sum_{i,j}{}' \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i \left\{\int_\infty^{\mathbf{r}_i} \boldsymbol{\mathcal{F}}(\mathbf{r}t)\cdot d\boldsymbol{\ell}\right\}\right]\Psi(t) = i\frac{\partial\Psi(t)}{\partial t}. \quad (2.81)$$

The purpose of rewriting the Schrödinger equation as in (2.80) or (2.81) is to emphasize the *self-consistent* nature of its solution $\Psi(t)$. One begins with an approximate wave function $\Psi(t)$. With this wave function one determines the quantal sources and thereby the field $\boldsymbol{\mathcal{F}}(\mathbf{r}t)$ and the corresponding work done at each instant of time. The differential equation is then solved to obtain a new solution $\Psi(t)$. The true wave function is obtained when the solution of the differential equation $\Psi(t)$ is the same as that employed for the determination of the field $\boldsymbol{\mathcal{F}}(\mathbf{r}t)$. This understanding of the self-consistent nature of the Schrödinger equation is a consequence of the 'Quantal Newtonian' second law. The derivation of the second law is given in Appendix A. The proof is for arbitrary $\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}t)$, and hence valid for both adiabatic and sudden switching on of the field.

An equation of motion similar [9] to the pure state expression (2.75) can be derived for nonequilibrium phenomena described by systems in a time-dependent external field $\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}t)$ and finite temperature T. Such systems are described in terms of a mixed state, the expectation value of operators being *defined* in terms of the grand canonical ensemble of statistical mechanics. This grand canonical ensemble in turn is defined *at the initial time* in terms of the eigenfunctions and eigenvalues of the time-independent Hamiltonian. The physics underlying this similar equation of motion is intrinsically different since properties such as the density and current density are in terms of statistical averages. Furthermore, the expression in terms of the grand canonical ensemble is valid for sudden switching on of the external field at some initial time.

2.6 Integral Virial Theorem

The time-dependent integral virial theorem can be obtained from the 'Quantal Newtonian' second law (2.75) by operating on it with $\int d\mathbf{r}\rho(\mathbf{r}t)\mathbf{r}\cdot$ to obtain

$$\int \rho(\mathbf{r}t)\mathbf{r}\cdot\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}t)d\mathbf{r} + E_{\text{ee}}(t) + 2T(t) = \int \rho(\mathbf{r}t)\mathbf{r}\cdot\boldsymbol{\mathcal{J}}(\mathbf{r}t)d\mathbf{r}. \quad (2.82)$$

The last term on the right hand side of (2.82) may be expressed entirely in terms of the density $\rho(\mathbf{r}t)$ as follows. The integral

$$\int \rho(\mathbf{r}t)\mathbf{r}\cdot\boldsymbol{\mathcal{J}}(\mathbf{r}t)d\mathbf{r} = \frac{\partial}{\partial t}\int \mathbf{r}\cdot\mathbf{j}(\mathbf{r}t)d\mathbf{r}. \quad (2.83)$$

Thus, consider the integral

$$\begin{aligned}\int x j_{\mathrm{x}}(\mathbf{r}t) d\mathbf{r} &= \frac{1}{2}\int j_{\mathrm{x}}(\mathbf{r}t) dx^2 dy dz \\ &= -\frac{1}{2}\int x^2 dj_{\mathrm{x}}(\mathbf{r}t) dy dz \\ &= -\frac{1}{2}\int x^2 \frac{\partial j_{\mathrm{x}}(\mathbf{r}t)}{\partial x} d\mathbf{r},\end{aligned} \tag{2.84}$$

where we employ the vanishing of the current density $j_x(\mathbf{r}t)$ at the boundaries at $x = +\infty, -\infty$. Now, since for the same reason

$$\int x^2 \frac{\partial j_{\mathrm{y}}(\mathbf{r}t)}{\partial y} d\mathbf{r} = 0 \;\; \text{and} \int x^2 \frac{\partial j_{\mathrm{z}}(\mathbf{r}t)}{\partial z} d\mathbf{r} = 0, \tag{2.85}$$

we have

$$\int x j_{\mathrm{x}}(\mathbf{r}t) d\mathbf{r} = -\frac{1}{2}\int x^2 \boldsymbol{\nabla}\cdot\mathbf{j}(\mathbf{r}t) d\mathbf{r}. \tag{2.86}$$

Therefore

$$\begin{aligned}\int \mathbf{r}\cdot\mathbf{j}(\mathbf{r}t) d\mathbf{r} &= -\frac{1}{2}\int r^2 \boldsymbol{\nabla}\cdot\mathbf{j}(\mathbf{r}t) d\mathbf{r} \\ &= \frac{1}{2}\int r^2 \frac{\partial \rho(\mathbf{r}t)}{\partial t} d\mathbf{r},\end{aligned} \tag{2.87}$$

where in the last step we have employed the continuity equation $\boldsymbol{\nabla}\cdot\mathbf{j}(\mathbf{r}t) = -\partial\rho(\mathbf{r}t)/\partial t$ (see Sect. 2.7). Thus,

$$\int \rho(\mathbf{r}t)\mathbf{r}\cdot\boldsymbol{\mathcal{J}}(\mathbf{r}t) d\mathbf{r} = \frac{1}{2}\frac{\partial^2}{\partial t^2}\int r^2 \rho(\mathbf{r}t) d\mathbf{r}, \tag{2.88}$$

and the integral virial theorem may alternatively be written as

$$\int \rho(\mathbf{r}t)\mathbf{r}\cdot\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}t) d\mathbf{r} + E_{ee}(t) + 2T(t) = \frac{1}{2}\frac{\partial^2}{\partial t^2}\int r^2 \rho(\mathbf{r}t) d\mathbf{r}. \tag{2.89}$$

The reason for writing the current density field term of (2.82) in terms of the density is to later draw an equivalence to the corresponding equation of the S system of noninteracting fermions for which the density, and hence the corresponding term is the same.

2.7 The Quantum–Mechanical 'Hydrodynamical' Equations

The electron density $\rho(\mathbf{r}t)$ and current density $\mathbf{j}(\mathbf{r}t)$ may also be determined by solution of the quantum–mechanical 'hydrodynamical' equations. The first of these, the continuity equation, is derived [10] from the Schrödinger equation and is

$$\frac{\partial \rho(\mathbf{r}t)}{\partial t} = -\boldsymbol{\nabla} \cdot \mathbf{j}(\mathbf{r}t). \tag{2.90}$$

The second, the force equation, describes the evolution of the quantum system. The field perspective of Schrödinger theory allows for the force equation to be written explicitly in terms of the fields inherent to the quantum system. Thus, we have from the 'Quantal Newtonian' second law (2.75) which is also derived from the Schrödinger equation, that

$$\frac{\partial \mathbf{j}(\mathbf{r}t)}{\partial t} = \mathbf{P}(\mathbf{r}t), \tag{2.91}$$

where the force $\mathbf{P}(\mathbf{r}t)$ is

$$\mathbf{P}(\mathbf{r}t) = \rho(\mathbf{r}t)\left[\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}t) + \boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r}t)\right] = \rho(\mathbf{r}t)\left[\boldsymbol{\mathcal{F}}^{\mathrm{ext}} + \boldsymbol{\mathcal{E}}_{\mathrm{ee}}(\mathbf{r}t) - \boldsymbol{\mathcal{D}}(\mathbf{r}t) - \boldsymbol{\mathcal{Z}}(\mathbf{r}t)\right]. \tag{2.92}$$

In this manner the force $\mathbf{P}(\mathbf{r}t)$ is described in terms of the different electron correlations. The internal field is discussed in the next section. The force $\mathbf{P}(\mathbf{r}t)$ may also be expressed [11] as the expectation value of the commutator of the current density operator and the Hamiltonian. This follows from the quantum mechanical equation of motion for the expectation value of an operator $\hat{A}(t)$ which is [10]

$$\frac{d\langle \hat{A}(t)\rangle}{dt} = -i\langle[\hat{A}(t), \hat{H}(t)]\rangle + \left\langle \frac{\partial \hat{A}(t)}{\partial t} \right\rangle. \tag{2.93}$$

Substitution of the current density operator $\hat{\mathbf{j}}(\mathbf{r})$ into (2.93) leads to (2.91) with

$$\mathbf{P}(\mathbf{r}t) = -i\langle \Psi(t) \mid \left[\hat{\mathbf{j}}(\mathbf{r}), \hat{H}(t)\right] \mid \Psi(t)\rangle. \tag{2.94}$$

The continuity equation may also be derived from the equation of motion (2.93) for the density operator $\hat{\rho}(\mathbf{r})$.

The continuity and force equations have a counterpart in Quantum Fluid Dynamics in which the electron gas is treated as a classical fluid. The equivalence of the Schrödinger theory equations to those of quantum fluid dynamics is proved in Sect. 2.12.

2.8 The Internal Field of the Electrons and Ehrenfest's Theorem

The Schrödinger theory analogue of Newton's second law of motion is Ehrenhest's theorem [10, 12]. For a system of electrons in some arbitrary time-dependent external field $\mathcal{F}^{\mathrm{ext}}(\mathbf{r}t)$, Ehrenhest's theorem states that the mean value of the field $\langle\mathcal{F}^{\mathrm{ext}}(\mathbf{r})\rangle(t)$ is equal to the second temporal derivative of the average position $\langle\mathbf{r}\rangle(t)$ of the electrons. In order that the average position $\langle\mathbf{r}\rangle(t)$ actually follow Newton's classical equation, one must be able to replace the mean value of the external field $\langle\mathcal{F}^{\mathrm{ext}}(\mathbf{r})\rangle(t)$ by its value $\mathcal{F}^{\mathrm{ext}}(\langle\mathbf{r}\rangle)(t)$. This is the case when either the force vanishes or when it depends linearly on $\mathbf{r}$. The substitution is also justified if the wavefunction remains localized in a small region of space so that the force has a constant value over that region. Thus, Ehrenfest's theorem describes the evolution of the system in terms of its average position as governed by the averaged external field. What Ehrenfest's theorem does not describe is the evolution in time of *each* individual electron as the entire system evolves. As described by the 'Quantal Newtonian' second law (see Sect. 2.5 and (2.75)), in addition to the external force field, *each* electron also experiences an *internal* field $\mathcal{F}^{\mathrm{int}}(\mathbf{r}t)$. It is the sum of these fields that then describes the behavior of the electron and its evolution with time. Furthermore, for Ehrenfest's theorem to be satisfied, the averaged internal field $\langle\mathcal{F}^{\mathrm{int}}(\mathbf{r})\rangle(t)$ must vanish. Similarly, the average torque of the internal field $\langle\mathbf{r}\times\mathcal{F}^{\mathrm{int}}(\mathbf{r})\rangle(t)$ too must vanish. In this section, we draw a rigorous parallel with the equations of classical mechanics by proving that on summing over all electrons, the contribution of the internal field vanishes, thereby leading to Ehrenfest's theorem.

We first derive Ehrenfest's theorem in the traditional manner. Substituting the operator

$$\hat{\mathbf{r}} = \int \mathbf{r}\hat{\rho}(\mathbf{r})d\mathbf{r}, \tag{2.95}$$

into the equation of motion (2.93) leads to

$$\frac{d}{dt}\langle\hat{\mathbf{r}}\rangle = \frac{d}{dt}\int \mathbf{r}\rho(\mathbf{r}t)d\mathbf{r} = -i\langle[\hat{\mathbf{r}}, \hat{H}(t)]\rangle. \tag{2.96}$$

On differentiating (2.96) again with respect to time and applying the equation of motion to the resulting right hand side, one obtains

$$\frac{d^2}{dt^2}\int \mathbf{r}\rho(\mathbf{r}t)d\mathbf{r} = -\langle[[\hat{\mathbf{r}}, \hat{H}(t)], \hat{H}(t)]\rangle, \tag{2.97}$$

since $\partial[\hat{H}(t), \hat{\mathbf{r}}]/\partial t = 0$. Evaluating the double commutator leads to Ehrenfest's theorem:

$$\int \rho(\mathbf{r}t)\mathcal{F}^{\mathrm{ext}}(\mathbf{r}t)d\mathbf{r} = \frac{\partial^2}{\partial t^2}\int \mathbf{r}\rho(\mathbf{r}t)d\mathbf{r}. \tag{2.98}$$

This equation is the quantal analogue of Newton's second law of motion (2.74).

The quantal analog of Newton's equation of motion for the ith particle is the 'Quantal Newtonian' second law of (2.75). When summed over all the electrons, it must lead to Ehrenfest's theorem (2.98), with the contributions of the internal fields vanishing. Thus on operating with $\int d\mathbf{r}\rho(\mathbf{r}t)$ on (2.75) we have

$$\int \rho(\mathbf{r}t)\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}t)d\mathbf{r} + \int \rho(\mathbf{r}t)\boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r}t)d\mathbf{r} = \int \rho(\mathbf{r}t)\boldsymbol{\mathcal{J}}(\mathbf{r}t)d\mathbf{r}. \tag{2.99}$$

To simplify the right hand side of (2.99), consider the integral

$$\int j_{\mathrm{x}}(\mathbf{r}t)d\mathbf{r} = -\int x\, dj_{\mathrm{x}}\, dy\, dz = -\int x\frac{\partial j_{\mathrm{x}}}{\partial x}dx\, dy\, dz, \tag{2.100}$$

where the second step is a consequence of the vanishing of the current density at the boundaries $x = +\infty, -\infty$. Now, for the same reason

$$\int x\frac{\partial j_{\mathrm{y}}}{\partial y}dx\, dy\, dz = 0 \quad \text{and} \int x\frac{\partial j_{\mathrm{z}}}{\partial z}dxdydz = 0, \tag{2.101}$$

so that

$$\int j_{\mathrm{x}}(\mathbf{r}t)d\mathbf{r} = -\int x\boldsymbol{\nabla}\cdot\mathbf{j}(\mathbf{r}t)d\mathbf{r}. \tag{2.102}$$

Thus,

$$\int \mathbf{j}(\mathbf{r}t)d\mathbf{r} = -\int \mathbf{r}\boldsymbol{\nabla}\cdot\mathbf{j}(\mathbf{r}t)d\mathbf{r}, \tag{2.103}$$

and on employing the continuity equation (2.90) we have the right hand side of (2.99) to be

$$\begin{aligned}\int \rho(\mathbf{r}t)\boldsymbol{\mathcal{J}}(\mathbf{r}t)d\mathbf{r} &= -\frac{\partial}{\partial t}\int \mathbf{r}\boldsymbol{\nabla}\cdot\mathbf{j}(\mathbf{r}t)d\mathbf{r} \\ &= \frac{\partial^2}{\partial t^2}\int \mathbf{r}\rho(\mathbf{r}t)d\mathbf{r}.\end{aligned} \tag{2.104}$$

In order for Ehrenfest's theorem to be satisfied, what remains to be proved is that the average value of each component of $\boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r}t)$ of (2.77) vanish:

$$\int \rho(\mathbf{r}t)\boldsymbol{\mathcal{E}}_{\mathrm{ee}}(\mathbf{r}t)d\mathbf{r} = 0, \tag{2.105}$$

$$\int \rho(\mathbf{r}t)\boldsymbol{\mathcal{D}}(\mathbf{r}t)d\mathbf{r} = 0, \tag{2.106}$$

and

$$\int \rho(\mathbf{r}t)\boldsymbol{\mathcal{Z}}(\mathbf{r}t)d\mathbf{r} = 0. \tag{2.107}$$

In order to prove (2.105) we rewrite the left hand side in terms of the pair-correlation function $h(\mathbf{r}\mathbf{r}'t)$ of (2.37):

$$\int \rho(\mathbf{r}t)\boldsymbol{\mathcal{E}}_{\mathrm{ee}}(\mathbf{r}t)d\mathbf{r} = \int \rho(\mathbf{r}t)\rho(\mathbf{r}'t)h(\mathbf{r}\mathbf{r}'t)\frac{(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}\, d\mathbf{r}d\mathbf{r}'. \tag{2.108}$$

On interchanging $\mathbf{r}$ and $\mathbf{r}'$, the right hand side of (2.108) is

$$\int \rho(\mathbf{r}t)\rho(\mathbf{r}'t)h(\mathbf{r}'\mathbf{r}t)\frac{(\mathbf{r}'-\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|^3}\, d\mathbf{r}d\mathbf{r}'. \tag{2.109}$$

As $h(\mathbf{r}\mathbf{r}'t)$ is symmetric in an interchange of $\mathbf{r}$ and $\mathbf{r}'$ (see (2.38)), (2.108) is

$$\int \rho(\mathbf{r}t)\rho(\mathbf{r}'t)h(\mathbf{r}\mathbf{r}'t)\frac{(\mathbf{r}'-\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|^3}\, d\mathbf{r}d\mathbf{r}' = -\int \rho(\mathbf{r}t)\boldsymbol{\mathcal{E}}_{\mathrm{ee}}(\mathbf{r}t)d\mathbf{r}, \tag{2.110}$$

which proves (2.105). Equation (2.106) follows from partial integration and the vanishing of the density at the boundary at infinity. To prove (2.107) we show that [8]

$$\int z(\mathbf{r}t)d\mathbf{r} = 0. \tag{2.111}$$

Consider the integral for the component

$$\int z_\alpha(\mathbf{r}t)d\mathbf{r} = 2\sum_\beta \int \frac{\partial}{\partial r_\beta} t_{\alpha\beta}(\mathbf{r}t)d\mathbf{r}. \tag{2.112}$$

The integral

$$\int \frac{\partial}{\partial x} t_{\alpha x}(\mathbf{r}t)dx \int dy\, dz = 0, \tag{2.113}$$

etc., since the tensor vanishes at the boundary $x = +\infty, -\infty$. Thus, (2.111) and hence (2.107) is proved.

As a consequence, the averaged internal force vanishes:

$$\int \rho(\mathbf{r}t)\boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r}t)d\mathbf{r} = 0, \tag{2.114}$$

and Ehrenfest's theorem is recovered. An alternate way of expressing Ehrenfest's theorem in terms of the response of the system to the external field as represented by the current density field $\boldsymbol{\mathcal{J}}(\mathbf{r}t)$ is

$$\int \rho(\mathbf{r}t)\left[\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}t) - \boldsymbol{\mathcal{J}}(\mathbf{r}t)\right] = 0. \tag{2.115}$$

The vanishing of the average of the internal field $\langle \boldsymbol{\mathcal{F}}^{\text{int}} \rangle$ may then be thought of as being a consequence of the quantal analog to Newton's third law. Note that although Coulomb's law, and hence the electron interaction field obeys Newton's third law, the vanishing of the averaged differential density and kinetic fields is not a direct consequence of the third law.

Returning to Newton's second law for the ith particle (2.73), one obtains the total angular momentum $\mathbf{L}$ of the system by performing the cross product $\mathbf{r}_i\times$ on it and summing over all particles to obtain

$$\frac{d\mathbf{L}}{dt} = \mathbf{N}^{\text{ext}}, \tag{2.116}$$

where $\mathbf{L} = \sum_i (\mathbf{r} \times \mathbf{p}_i)$, and $\mathbf{N}^{\text{ext}} = \sum_i (\mathbf{r}_i \times \mathbf{F}_i^{\text{ext}})$ is the torque of the external force about a given point. The torque of the internal forces $\sum_{ij}' \mathbf{r}_i \times \mathbf{F}_{ji}$ once again vanishes as a consequence of Newton's third law.

For the quantal equivalent of (2.116), operate by $\int d\mathbf{r}\rho(\mathbf{r}t)\times$ on (2.75) to obtain

$$\int \rho(\mathbf{r}t)\mathbf{r} \times \boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}t)d\mathbf{r} = \frac{\partial}{\partial t}\int \mathbf{r} \times \mathbf{j}(\mathbf{r}t)d\mathbf{r}, \tag{2.117}$$

where once again it can be proved [8] along the lines described above, that the averaged torques of the individual components of the internal field vanish: $\langle \mathbf{r} \times \boldsymbol{\mathcal{F}}^{\text{int}}(\mathbf{r}t)\rangle = 0$. *Defining* a velocity field $\boldsymbol{\nu}(\mathbf{r}t)$ of the electrons by the equation

$$\mathbf{j}(\mathbf{r}t) = \rho(\mathbf{r}t)\boldsymbol{\nu}(\mathbf{r}t), \tag{2.118}$$

and a momentum field $\mathbf{p}(\mathbf{r}t) = m\boldsymbol{\nu}(\mathbf{r}t)$, we have (with $m = 1$) the quantum analogue of the classical torque equation

$$\int \rho(\mathbf{r}t)\boldsymbol{\mathcal{N}}^{\text{ext}}(\mathbf{r}t)d\mathbf{r} = \frac{\partial}{\partial t}\int \rho(\mathbf{r}t)\boldsymbol{\mathcal{L}}(\mathbf{r}t)d\mathbf{r}, \tag{2.119}$$

where $\boldsymbol{\mathcal{L}}(\mathbf{r}t) = \mathbf{r} \times \mathbf{p}(\mathbf{r}t)$ is the angular momentum field at each instant of time.

Thus, each electron in a sea of electrons, experiences in addition to the external field, an internal field. This internal field defined by (2.77) is representative of the motion of the electrons, and the fact that they are kept apart as a result of the Pauli exclusion principle and Coulomb repulsion. As in classical physics, the average of this field and its averaged torque vanish at each instant of time. The structure of the components of the internal field is exhibited for both a ground and excited state of an exactly solvable model in Sect. 2.11.

2.9 The Harmonic Potential Theorem

A theorem that can be employed to demonstrate the field perspective of Schrödinger theory as well as the corresponding perspective within Q-DFT is the Harmonic Potential Theorem (HPT) [13]. The HPT is concerned with the system of N electrons for the case when the potential energy $v(\mathbf{r}t)$ of (2.4) is of the form

$$v(\mathbf{r}t) = \frac{1}{2}\mathbf{r} \cdot \mathbf{K} \cdot \mathbf{r} - \mathbf{F}(t) \cdot \mathbf{r}, \tag{2.120}$$

where $\mathbf{K}$ is a symmetric spring constant matrix, and $\mathbf{F}(t)$ a spatially uniform time-dependent external force. For example, $\mathbf{F}(t)$ could correspond to the electric field of a high intensity laser pulse employed in the study of atoms and molecules. The Hamiltonian for the system is then

$$\hat{H} = \hat{H}_0 - \mathbf{F}(t) \cdot \sum_i \mathbf{r}_i, \tag{2.121}$$

$$\hat{H}_0 = \sum_i H_{0i}, \tag{2.122}$$

$$H_{0i} = -\frac{1}{2}\nabla_i^2 + \frac{1}{2}\mathbf{r}_i \cdot \mathbf{K} \cdot \mathbf{r}_i + \frac{1}{2}\sum_j{}' \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\,, \tag{2.123}$$

and the Schrödinger equation is

$$\hat{H}(t)\Psi_{\mathrm{HPT}}(t) = i\frac{\partial \Psi_{\mathrm{HPT}}(t)}{\partial t}, \tag{2.124}$$

with Ψ_{HPT} the corresponding solution. Let $\psi_n(\mathbf{r}_1, \ldots, \mathbf{r}_{\mathrm{N}})$ be *any* (ground or excited) many–body eigenstate of the Hamiltonian $\hat{H}_0$ so that

$$\hat{H}_0\psi_n = E_n\psi_n. \tag{2.125}$$

Next apply a position–independent, time-dependent shift $\mathbf{y}(t)$ to the coordinates $\mathbf{r}_1, \ldots, \mathbf{r}_{\mathrm{N}}$ in ψ_n, and write the solution of the time-dependent Schrödinger equation as

$$\Psi_{\mathrm{HPT}}(t) = \mathrm{e}^{-\mathrm{i}(E_n t + NS(t) - N\frac{d\mathbf{y}}{dt}\cdot\mathbf{R})}\psi_n(\bar{\mathbf{r}}_1, \bar{\mathbf{r}}_2, \ldots, \bar{\mathbf{r}}_{\mathrm{N}}), \tag{2.126}$$

where $\bar{\mathbf{r}}_i = \mathbf{r}_i - \mathbf{y}(t)$ is the shifted coordinate operator, $\mathbf{R} = \sum_i \mathbf{r}_i/N$ the center of mass operator, and the phase angle

$$S(t) = \int_{\mathrm{t}_0}^{t}\left[\frac{1}{2}\dot{\mathbf{y}}(t')^2 - \frac{1}{2}\mathbf{y}(t') \cdot \mathbf{K} \cdot \mathbf{y}(t')\right]dt'. \tag{2.127}$$

Substitution of $\Psi_{\mathrm{HPT}}(t)$ of (2.126) into the Schrödinger equation leads to

$$\left(\hat{H}(t) - i\frac{\partial}{\partial t}\right)\Psi_{\mathrm{HPT}}(t) = [\ddot{\mathbf{y}}(t) + \mathbf{K}\cdot\mathbf{y}(t) - \mathbf{F}(t)]\cdot\left[\sum_i \mathbf{r}_i\right]\Psi_{\mathrm{HPT}}(t). \quad (2.128)$$

Thus, $\Psi_{\mathrm{HPT}}(t)$ is a solution of the Schrödinger equation provided that $\mathbf{y}(t)$ satisfies the classical driven harmonic oscillator equation

$$\ddot{\mathbf{y}}(t) + \mathbf{K}\cdot\mathbf{y}(t) - \mathbf{F}(t) = 0. \quad (2.129)$$

The wavefunction $\Psi_{\mathrm{HPT}}(t)$ is then the solution ψ_{n} to the time-independent Schrödinger equation (2.125) shifted by $\mathbf{y}(t)$ and multiplied by a phase factor. Hence, if the solution to (2.125) is known, then the time-evolution of all properties,—quantal sources and fields—is known. In particular, observables represented by non-differential operators such as the density $\rho(\mathbf{r}t)$ possess the translational property $\rho(\mathbf{r}t) = \rho_0(\mathbf{r} - \mathbf{y}(t))$, where $\rho_0(\mathbf{r})$ is the density corresponding to the time-independent system of (2.125). This is because the phase factor cancels out, However, because of the phase factor, such a translational property is not obeyed for observables involving differential operators such as the current density $\mathbf{j}(\mathbf{r}t)$.

By a suitable choice of $\mathbf{K}$, the time-independent model describes a wide range of physical situations such as Hooke's atom [14–16], Hooke's species ([17] and Sect. 4.8), and spherical nuclear models [18]. The Hooke's atom is comprised of two electrons harmonically confined to a nucleus, whereas the species is comprised of two electrons harmonically confined to an arbitrary number of nuclei. The significance of these models lies in the fact that the interaction between the electrons is Coulombic. For these models systems, *closed-form analytical* solutions of the time-independent Schrödinger equation exist for both the ground and excited states for a denumerably infinite set of force constants. These solutions may then be employed to determine the structure of the various fields, and their evolution with time via the Harmonic Potential Theorem.

The proof of the HPT given above due to Dobson [13] assumes the structure of the wave function as the starting point. With the same ansatz, the HPT can also be proved via the 'operator' method as given in Appendix B. However, in Appendix B, the HPT wave function is derived [19] from *first principles* via the Feynman Path Integral method [20, 21]. In this manner, the wave function is revealed as a result of the derivation. For completeness, the HPT wave function has also been derived [22] via the 'interaction' representation of quantum mechanics.

2.10 Time-Independent Schrödinger Theory: Ground and Bound Excited States

For a system of N electrons in a time-independent external field $\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r})$ such that $\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}) = -\boldsymbol{\nabla} v(\mathbf{r})$, the Schrödinger equation (2.1) is

$$\hat{H}\Psi_{\mathrm{n}}(\mathbf{X}t) = E_{\mathrm{n}}\Psi_{\mathrm{n}}(\mathbf{X}t) = i\frac{\partial \Psi_n(\mathbf{X}t)}{\partial t}, \tag{2.130}$$

where now the Hamiltonian operator $\hat{H}$ is

$$\hat{H} = -\frac{1}{2}\sum_i \nabla_i^2 + \sum_i v(\mathbf{r}_i) + \frac{1}{2}\sum_{i,j}{}' \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \tag{2.131}$$

and where the wavefunction $\Psi_{\mathrm{n}}(\mathbf{X}t)$ are eigenfunctions of $\hat{H}$, and E_{n} the eigenvalues of the energy. The solutions of the (2.131) are of the form

$$\Psi_{\mathrm{n}}(\mathbf{X}t) = \psi_{\mathrm{n}}(\mathbf{X})e^{-iE_{\mathrm{n}}t}, \tag{2.132}$$

where the functions $\psi_{\mathrm{n}}(\mathbf{X})$ and eigenvalues E_{n} of the energy are determined by the time-independent Schrödinger equation

$$\hat{H}\psi_{\mathrm{n}}(\mathbf{X}) = E_{\mathrm{n}}\psi_{\mathrm{n}}(\mathbf{X}). \tag{2.133}$$

2.10.1 The 'Quantal Newtonian' First Law

Time-independent Schrödinger theory can also be described in terms of 'classical' fields and quantal sources via the 'Quantal Newtonian' first law. The description of the time-independent Schrödinger system for both the ground and bound excited states in terms of fields [23–25] is the same as for the time-dependent case, but with the time-independent quantal sources and fields now determined by the functions $\psi_{\mathrm{n}}(\mathbf{X})$. The phase factor of (2.132) vanishes in the determination of the source expectation values. Further, the current density field $\boldsymbol{\mathcal{J}}(\mathbf{r}t) = 0$, so that the total energy components $E_{\mathrm{ee}}, E_{\mathrm{H}}, E_{\mathrm{xc}}, T$ and the potential energy $v(\mathbf{r})$ are defined as before but by the time-independent fields $\boldsymbol{\mathcal{E}}_{\mathrm{ee}}(\mathbf{r})$, $\boldsymbol{\mathcal{D}}(\mathbf{r})$, and $\boldsymbol{\mathcal{Z}}(\mathbf{r})$.

The 'Quantal Newtonian' first law is the time-independent version of the second law of (2.75) [23–26]:

$$\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}) + \boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r}) = 0, \tag{2.134}$$

where

$$\boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r}) = \boldsymbol{\mathcal{E}}_{\mathrm{ee}}(\mathbf{r}) - \boldsymbol{\mathcal{D}}(\mathbf{r}) - \boldsymbol{\mathcal{Z}}(\mathbf{r}). \tag{2.135}$$

The fields $\boldsymbol{\mathcal{E}}_{\mathrm{ee}}(\mathbf{r})$, $\boldsymbol{\mathcal{D}}(\mathbf{r})$, and $\boldsymbol{\mathcal{Z}}(\mathbf{r})$ are representative of correlations between the electrons due to the Pauli exclusion principle and Coulomb repulsion, the density, and kinetic effects, respectively. Since, by assumption, the external field $\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r})$ is conservative ($\boldsymbol{\nabla} \times \boldsymbol{\nabla} v(\mathbf{r}) = 0$), so is the internal field $\boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r})$.

Again, the external potential energy $v(\mathbf{r})$ can be afforded a rigorous physical interpretation via the 'Quantal Newtonian' first law: It is work done to move an electron from some reference point at infinity to its position at $\mathbf{r}$ in the force of the *conservative* internal field $\boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r})$:

$$v(\mathbf{r}) = \int_{\infty}^{\mathbf{r}} \boldsymbol{\nabla} v(\mathbf{r}') \cdot d\boldsymbol{\ell}' = \int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r}') \cdot d\boldsymbol{\ell}'. \tag{2.136}$$

The work done is *path-independent*.

Since the internal field $\boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r})$ is obtained from quantal sources that are expectations of Hermitian operators taken with respect to the eigenfunctions $\psi_n(\mathbf{X})$, the potential energy $v(\mathbf{r})$ is a functional of these eigenfunctions: $v(\mathbf{r}) = v[\psi_n]$. Thus, the time-independent Schrödinger equation (2.133) may be written as

$$\left\{ -\frac{1}{2}\sum_i \nabla_i^2 + \frac{1}{2}{\sum_{i,j}}' \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i v_i[\psi_n] \right\} \psi_n = E_n \psi_n, \tag{2.137}$$

where $v_i = v(\mathbf{r}_i)$. This demonstrates the *self-consistent* nature of the Schrödinger equation. Written more explicitly in terms of the internal field $\boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r})$ we have (2.137) to be

$$\left[-\frac{1}{2}\sum_i \nabla_i^2 + \frac{1}{2}{\sum_{i,j}}' \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i \left\{ \int_{\infty}^{\mathbf{r}_i} \boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r}) \cdot d\boldsymbol{\ell} \right\} \right] \psi_n = E_n \psi_n. \tag{2.138}$$

In order to solve the Schrödinger equation, one begins with an approximation to ψ_n. With this wave function one obtains the quantal sources and thereby the internal field $\boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r})$, and solves the integro-differential equation (2.138) to obtain the new solution ψ_n and eigenvalue E_n. This process is continued till self-consistency is achieved, and the exact ψ_n, E_n obtained.

The integral virial theorem is the time-independent version of (2.82):

$$\int \rho(\mathbf{r})\mathbf{r} \cdot \boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}) d\mathbf{r} + E_{ee} + 2T = 0. \tag{2.139}$$

Finally, the average and averaged torque of the internal field $\boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r})$ vanishes:

$$\int \rho(\mathbf{r}) \boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r}) d\mathbf{r} = 0, \tag{2.140}$$

$$\int \rho(\mathbf{r})\mathbf{r} \times \boldsymbol{\mathcal{F}}^{\text{int}}(\mathbf{r})d\mathbf{r} = 0, \tag{2.141}$$

since the contribution of each component vanishes.

To reiterate, the perspective of time-independent Schrödinger theory in terms of fields and quantal sources representative of the different electron correlations, is valid for both ground and bound excited pure states whether non-degenerate or degenerate. In Sect. 2.11 this perspective is described for a ground and excited state of the Hooke's atom. In addition, the perspective brings out the intrinsic self-consistent nature of the Schrödinger equation. The self-consistent form of the Schrödinger equation (2.138) also makes clear that for different self-consistently obtained solutions ψ_n, there exist different external potentials $v(\mathbf{r})$.

2.10.2 Coalescence Constraints

As a consequence of the Coulomb interaction, the Hamiltonian (2.131) is singular when two electrons coalesce. It is also singular for the case where the potential energy $v(\mathbf{r})$ is Coulombic as when an electron coalesces with the nucleus of charge Z. In order for the wavefunction $\psi(\mathbf{X})$ to satisfy the Schrödinger equation (2.133) and remain bounded, it must satisfy a coalescence condition at each singularity. These coalescence constraints play a significant role in Q-DFT and other local effective potential energy theories as discussed later in the section. There are two forms of these coalescence constraints: the integral and differential forms. The integral form is more general in that it retains the angular dependence of the wave function at coalescence, and the differential form can be readily derived from it. Historically, it was the differential form that was originally derived [27], and we follow that path of description in this section.

With $\mathbf{s} = \mathbf{r} - \mathbf{r}'$, and $\mathbf{r}, \mathbf{r}'$ the positions of the two particles, the differential form of the coalescence condition on the wavefunction is

$$\frac{d\psi_{\text{sp.av}}}{ds}\,|_{s=0} = \zeta\psi|_{s=0}\,, \tag{2.142}$$

where $\psi_{\text{sp.av}}$ is the spherical average of the wavefunction about the singularity:

$$\psi_{\text{sp.av}}(s) = \frac{1}{4\pi}\int \psi d\Omega_{\mathbf{s}}. \tag{2.143}$$

For the electron–electron cusp condition, the coeffiecient $\zeta = \frac{1}{2}$; for the electron–nucleus cusp condition $\zeta = -Z$.

The electron–nucleus coalescence condition may also be expressed [28] in terms of the derivative of the density and density at the nucleus. Thus, with the time-independent density defined as (see (2.11))

$$\rho(\mathbf{r}) = N \sum_{\sigma} \int \psi^* \left(\mathbf{r}\sigma, \mathbf{X}^{N-1}\right) \psi \left(\mathbf{r}\sigma, \mathbf{X}^{N-1}\right) d\mathbf{X}^{N-1}, \tag{2.144}$$

we have on taking the derivative in the limit of the electron–nucleus coalescence

$$\begin{aligned} \lim_{r\to 0} \frac{d\rho(\mathbf{r})}{dr} =& N \sum_{\sigma} \int \left\{ \frac{d\psi^*(\mathbf{r}\sigma, \mathbf{X}^{N-1})}{dr} |_{r\to 0} \psi\left(\mathbf{r} = 0, \sigma; \mathbf{X}^{N-1}\right) \right. \\ & \left. + \psi^*(\mathbf{r} = 0, \sigma; \mathbf{X}^{N-1}) \; \frac{d\psi(\mathbf{r}\sigma, \mathbf{X}^{N-1})}{dr} |_{r\to 0} \right\} d\mathbf{X}^{N-1}. \end{aligned} \tag{2.145}$$

Integrating the previous equation over the angular variables of the coalescing electron we obtain

$$\begin{aligned} \lim_{r\to 0} \frac{d\rho(r)}{dr} =& N \sum_{\sigma} \int \left\{ \frac{d\psi^*_{sp.av}(r\sigma, \mathbf{X}^{N-1})}{dr} |_{r\to 0} \psi\left(r = 0, \sigma; \mathbf{X}^{N-1}\right) \right. \\ & \left. + \psi^*(r = 0, \sigma; \mathbf{X}^{N-1} \frac{d\psi_{\text{sp.av}}(r\sigma, \mathbf{X}^{N-1})}{dr} |_{r\to 0} \right\} d\mathbf{X}^{N-1}, \end{aligned} \tag{2.146}$$

which on substituting the cusp condition on the right hand side leads to

$$= -2ZN \sum_{\sigma} \int \psi^*(r = 0, \sigma; \mathbf{X}^{N-1}) \psi(r = 0, \sigma; \mathbf{X}^{N-1}) d\mathbf{X}^{N-1}. \tag{2.147}$$

The electron-nucleus coalescence or cusp condition in terms of the density is then

$$\lim_{r\to 0} \frac{d\rho(r)}{dr} = -2Z\rho(r = 0). \tag{2.148}$$

Thus, the densities in atoms, molecules, and solids exhibit a cusp at the nuclei. The cusp for electron–electron coalescence is exhibited in the structure of the Fermi–Coulomb hole charge distribution.

The integral form of the *cusp coalescence constraint* for an arbitrary state of a system of N charged particles as particles 1 and 2 coalesce is

$$\begin{aligned} \psi(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N) =& \; \psi(\mathbf{r}_2, \mathbf{r}_2, \mathbf{r}_3, \ldots \mathbf{r}_N)(1 + \zeta r_{12}) \\ & + \mathbf{r}_{12} \cdot \mathbf{C}(\mathbf{r}_2, \mathbf{r}_3, \ldots \mathbf{r}_N) + O(r_{12}^2). \end{aligned} \tag{2.149}$$

Here $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$, $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$, and $\mathbf{C}(\mathbf{r}_2, \mathbf{r}_3, \ldots \mathbf{r}_N)$ an undetermined vector. The spin index is suppressed. The integral form of the coalescence condition was originally [29] a conjecture. It can, however be derived [30, 31] directly from the Schrödinger equation. The integral form of the coalescence condition retains the angular dependence of the wave function at coalescence, and is thus more general and useful. The differential form of the coalescence condition (2.142) is readily obtained by taking the spherical average and differentiating about the point of coalescence. It is evident from the integral cusp coalescence condition (2.149) and the definition of the density (2.144), that *there can be no differential form similar to* (2.148) *in terms of the density of the cusp condition for electron-electron coalescence*. However, it is possible to derive the integral and differential forms of the coalescence constraints for the time-independent pair function $P(\mathbf{r}\mathbf{r}')$ of (2.27) (see [32] and Chap. 2 of ***QDFT2***). Note that the integral coalescence expression is equally valid even if the wave function vanishes at the point of coalescence, i.e. if $\psi(\mathbf{r}_2, \mathbf{r}_2, \ldots, \mathbf{r}_N) = 0$. This is referred to as a *node coalescence condition* as opposed to the *cusp coalescence condition*.

Employing the integral form of the electron-nucleus coalescence constraint, it can be proved [33] (see also Chap. 8 of ***QDFT2***) that the local effective potential energy function within Q-DFT which incorporates all the many-body effects is *finite* at the nucleus. This is also the case for all other local effective potential theories. (Prior to [33–35], there was controversy in the literature with regard to the structure of the potential at and near the nucleus. For a brief historical description of this controversy, and for the derivation of this structure, see Chap. 8 of ***QDFT2***.)

For the generalization of the derivation of the integral coalescence condition to dimensions $D \geq 2$ see [32] and Chap. 2 of ***QDFT2***

2.10.3 Asymptotic Structure of Wavefunction and Density

Another important property of the wavefunction and density is their asymptotic structure in the classically forbidden region because this structure is related to the first ionization potential. (This fact is significant in providing a rigorous physical interpretation of the highest occupied eigenvalue within Q-DFT (see Sect. 3.4.8) and other local effective potential energy theories.) To show this [36, 37] we rewrite the N–electron Hamiltonian of (2.131) as

$$\hat{H} = -\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \sum_{i=2}^{N} \frac{1}{|\mathbf{r} - \mathbf{r}_i|} + \hat{H}^{N-1}, \tag{2.150}$$

where the $(N-1)$ electron Hamiltonian $\hat{H}^{N-1}$ is

$$\hat{H}^{(N-1)} = -\frac{1}{2}\sum_{i=2}^{N} \nabla_i^2 + \sum_{i=2}^{N} v(\mathbf{r}_i) + \frac{1}{2}\sum_{i \neq j \neq 1}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \tag{2.151}$$

Now the complete set of eigenfunctions and eigenenergies of the $(N-1)$–electron system are defined by the equation

$$\hat{H}^{N-1}\psi_s^{(N-1)}(\mathbf{X}^{N-1}) = E_s^{(N-1)}\psi_s^{(N-1)}(\mathbf{X}^{N-1}). \tag{2.152}$$

Next expand the N–electron wavefunction $\psi_n(\mathbf{X})$ (see 2.133) in terms of the eigenfunctions $\psi_s^{(N-1)}$:

$$\psi_n(\mathbf{r}\sigma, \mathbf{X}^{N-1}) = \sum_s C_{s\sigma}(\mathbf{r})\psi_s^{(N-1)}(\mathbf{X}^{N-1}), \tag{2.153}$$

and rewrite the Schrödinger equation (2.133) as

$$\left(-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \sum_{i=2}^{N}\frac{1}{|\mathbf{r}-\mathbf{r}_i|} + \hat{H}^{(N-1)}\right)\sum_s C_{s\sigma}(\mathbf{r})\psi_s^{(N-1)}(\mathbf{X}^{N-1})$$
$$= E_n \sum_s C_{s\sigma}(\mathbf{r})\psi_s^{(N-1)}(\mathbf{X}^{N-1}). \tag{2.154}$$

For asymptotic positions of the electron we have by Taylor expansion

$$\frac{1}{|\mathbf{r}-\mathbf{r}_i|} = \frac{1}{r} + \frac{\mathbf{r}_i\cdot\mathbf{r}}{r^3} + \frac{1}{2}\sum_{\alpha,\beta} r_{i\alpha}r_{i\beta}\frac{\partial^2}{\partial r_\alpha \partial r_\beta}\frac{1}{r} + \ldots, \tag{2.155}$$

so that on retaining just the leading term, (2.154) becomes

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \frac{N-1}{r}\right]\sum_s C_{s\sigma}(\mathbf{r})\psi_s^{(N-1)}(\mathbf{X}^{N-1})$$
$$= \sum_s \left[E_n - E_s^{(N-1)}\right] C_{s\sigma}(\mathbf{r})\psi_s^{(N-1)}(\mathbf{X}^{N-1}). \tag{2.156}$$

Multiplying (2.156) by $\psi_s^{(N-1)*}(\mathbf{X}^{N-1})$ from the left, integrating over $\int d\mathbf{X}^{N-1}$, and employing the orthonormality condition

$$\left\langle \psi_{s'}^{(N-1)} | \psi_s^{(N-1)} \right\rangle = \delta_{ss'}, \tag{2.157}$$

we have

$$\left(-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \frac{N-1}{r} + I_{s,n}\right) C_{s\sigma}(\mathbf{r}) = 0, \tag{2.158}$$

where the ionization potential $I_{s,n}$ is

$$I_{s,n} = E_s^{(N-1)} - E_n. \tag{2.159}$$

The $I_{s,n}$ are the ionization potentials from the N–electron state with energy E_n into various states of the $(N-1)$–electron ion. It is assumed that $I_{s,n} < I_{s+1,n}$ etc.

For atomic systems, $v(\mathbf{r}) = -Z/r$. For molecules in the far asymptotic region, $v(\mathbf{r}) = -Q/r$, where Q is the total nuclear charge. Thus, the Schrödinger equation in the asymptotic region is of the form

$$\left[-\frac{1}{2}\nabla^2 - \frac{(Z-N+1)}{r} + I_{s,n}\right] C_{s\sigma}(\mathbf{r}) = 0, \tag{2.160}$$

and the asymptotic solution is

$$C_{s\sigma}(\mathbf{r})_{r \rightrightarrows \infty}\ r^{\beta_s} e^{-\alpha_s r} \chi(\sigma), \tag{2.161}$$

where $(1+\beta_s) = (Z-N+1)/\alpha_s$, and $\alpha_s = \sqrt{2I_{s,n}}$. The satisfaction of the differential equation (2.160) with this solution occurs on neglecting the $0(1/r^2)$ term of $\nabla^2 C_{s\sigma}(\mathbf{r})$.

The density $\rho(\mathbf{r})$ defined by (2.144) employing (2.153) is then

$$\rho(\mathbf{r}) = N \sum_{\sigma} \sum_{s} |C_{s\sigma}(\mathbf{r})|^2\,, \tag{2.162}$$

so that asymptotically

$$\rho(\mathbf{r})_{r \rightrightarrows \infty}\ \exp\,(-2\alpha_s r) =\ \exp\,\left(-2\sqrt{2I_{s,n}}r\right). \tag{2.163}$$

Thus, the asymptotic structure of the density is related to the first ionization potential $I_{s,n}$. This is the case whether the system is in a ground or excited state. For asymptotic positions of the electron in finite systems, it has been shown [38] that if the $(N-1)$–electron ion ground state is degenerate, then the eigenfunctions $\psi_s^{(N-1)}$ and hence the ground–state wavefunction ψ_0, depend parametrically on the direction of electron removal. This then translates to a parametric dependence on this direction for the asymptotic structure of the single particle density matrix $\gamma(\mathbf{r}\mathbf{r}')$ and the pair-correlation density $g(\mathbf{r}\mathbf{r}')$ [38].

For the derivation of the asymptotic structure to higher order of the wave function $\psi_n(\mathbf{X})$, density $\rho(\mathbf{r})$, single-particle density matrix $\gamma(\mathbf{r}\mathbf{r}')$, and pair-correlation density $g(\mathbf{r}\mathbf{r}')$, see Chap. 7 of ***QDFT2***

2.11 Examples of the ‘Newtonian’ Perspective: The Ground and First Excited Singlet State of the Hooke’s Atom

2.11.1 The Hooke’s Atom

The physics underlying the ‘Newtonian’ perspective of Schrödinger theory is demonstrated in this section by application to the analytically solvable Hooke’s atom [14] in both its ground and first excited singlet state. This atom comprises of two electrons in an external field such that the potential energy $v(\mathbf{r}t)$ due to the field is of the form

$$\begin{aligned} v(\mathbf{r}t) &= v_0(\mathbf{r}) \quad \text{for} \;\; t \leq t_0 \\ &= v_0(\mathbf{r}) \;+\; v_1(\mathbf{r}t) \;\; \text{for} \;\; t > t_0, \end{aligned} \tag{2.164}$$

where $v_0(\mathbf{r}) = \frac{1}{2}kr^2$, k is the spring constant, $v_1(\mathbf{r}t) = -\mathbf{F}(t) \cdot \mathbf{r}$, with the force $\mathbf{F}(t)$ arbitrary. The Coulomb interaction between the electrons is treated *exactly* in this model atom. Based on the Harmonic Potential Theorem of Sect. 2.9, the wavefunction for $t > t_0$ is the time-independent solution for $t \leq t_0$, multiplied by a phase factor, and shifted by the function $\mathbf{y}(t)$ satisfying (2.129). Thus, the time evolution of *all* observables is known *exactly* for $t > t_0$. However, for properties that are the expectation value of Hermitian operators such as the density, the time evolution is the same as that of the property derived for $t \leq t_0$ but translated by a finite time-dependent value. Hence, we describe here a study via the ‘Newtonian’ perspective of the system in its stationary state.

The time-independent Hamiltonian for the Hooke’s atom is

$$\hat{H} = -\frac{1}{2}\nabla^2_{\mathbf{r}_1} - \frac{1}{2}\nabla^2_{\mathbf{r}_2} + \frac{1}{2}kr_1^2 + \frac{1}{2}kr_2^2 + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}, \tag{2.165}$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the coordinates of the electrons. This Hamiltonian is separable by transforming to the relative and center of mass coordinates:

$$\mathbf{s} = \mathbf{r}_1 - \mathbf{r}_2; \qquad \mathbf{R} = \frac{\mathbf{r}_1 + \mathbf{r}_2}{2} \tag{2.166}$$

so that

$$\mathbf{r}_1 = \mathbf{R} + \frac{\mathbf{s}}{2}; \qquad \mathbf{r}_2 = \mathbf{R} - \frac{\mathbf{s}}{2}; \tag{2.167}$$

and

$$\nabla^2_{\mathbf{r}_1} = \frac{1}{4}\nabla^2_{\mathbf{R}} + \nabla^2_{\mathbf{s}} + \nabla_{\mathbf{R}} \cdot \nabla_{\mathbf{s}}; \;\; \nabla^2_{\mathbf{r}_2} = \frac{1}{4}\nabla^2_{\mathbf{R}} + \nabla^2_{\mathbf{s}} - \nabla_{\mathbf{R}} \cdot \nabla_{\mathbf{s}}. \tag{2.168}$$

The Hamiltonian is then

$$\hat{H} = \hat{H}_{\mathbf{s}} + \hat{H}_{\mathbf{R}} \tag{2.169}$$

where

$$\hat{H}_{\mathbf{s}} = -\nabla^2_{\mathbf{s}} + \frac{1}{4}ks^2 + \frac{1}{s}, \tag{2.170}$$

$$\hat{H}_{\mathbf{R}} = -\frac{1}{4}\nabla^2_{\mathbf{R}} + kR^2. \tag{2.171}$$

As the Hamiltonian is both separable and independent of spin, the wavefunction $\psi(\mathbf{x}_1\mathbf{x}_2)$ may be written as

$$\psi(\mathbf{x}_1\mathbf{x}_2) = \psi(\mathbf{r}_1\mathbf{r}_2)\chi(\sigma_1\sigma_2) = \phi(\mathbf{s})\xi(\mathbf{R})\chi(\sigma_1\sigma_2), \tag{2.172}$$

where $\psi(\mathbf{r}_1\mathbf{r}_2)$ is the spatial part of the wave function, $\chi(\sigma_1\sigma_2)$ the spin component, and where $\phi(\mathbf{s})$, $\zeta(\mathbf{R})$ are orbital functions. Since $\mathbf{R}$ is symmetric in an interchange of the spatial electronic coordinates, the function $\xi(\mathbf{R})$ is symmetric. According to the Pauli exclusion principle then, if the spin function $\chi(\sigma_1\sigma_2)$ is symmetric (triplet state) in an interchange of the electrons, then the orbital function $\phi(\mathbf{s})$ must be antisymmetric $[\phi(-\mathbf{s}) = -\phi(\mathbf{s})]$, and if $\chi(\sigma_1\sigma_2)$ is antisymmetric (singlet state), then $\phi(\mathbf{s})$ must be symmetric $[\phi(-\mathbf{s}) = \phi(\mathbf{s})]$. There are no constraints on the orbital function $\xi(\mathbf{R})$ due to its symmetry.

The Schrödinger equation $H\psi = E\psi$ then separates into the equations

$$\hat{H}_{\mathbf{s}}\phi(\mathbf{s}) = \epsilon\phi(\mathbf{s}), \tag{2.173}$$

$$\hat{H}_{\mathbf{R}}\xi(\mathbf{R}) = \eta\xi(\mathbf{R}), \tag{2.174}$$

with the total energy

$$E = \epsilon + \eta. \tag{2.175}$$

The normalization condition on ψ also separates into

$$\int |\phi(\mathbf{s})|^2 d\mathbf{s} = 1 \quad \text{and} \quad \int |\xi(\mathbf{R})|^2 d\mathbf{R} = 1. \tag{2.176}$$

The equation for $\xi(\mathbf{R})$, (2.174), is the harmonic oscillator equation whose solutions are analytical. The reader is referred to the original literature [14] for the solution of (2.173) for the orbital $\phi(\mathbf{s})$. It turns out that closed form analytical solutions exist only for certain discreet values of the spring constant k. Further, excited states of the Hooke's atom are defined in terms of the number of nodes of $\phi(\mathbf{s})$. Those solutions with zero nodes are ground states, those with one node correspond to the first excited state, and so on. However, the analytical solutions for the ground and excited states correspond to *different* values of the spring constant k. The properties of the Hooke's atom in a ground and first excited singlet state, and the fields representative of the different electron correlations, are described in the following subsections [39, 40]. The analytical expressions for these properties are given in Appendix C.

2.11.2 Wavefunction, Orbital Function, and Density

The ground $\psi_{00}(\mathbf{r}_1\mathbf{r}_2)$ and first excited singlet $\psi_{01}(\mathbf{r}_1\mathbf{r}_2)$ state wavefunctions we consider are

$$\psi_{00}(\mathbf{r}_1\mathbf{r}_2) = \xi_0(\mathbf{R})\phi_0(\mathbf{s}), \tag{2.177}$$

$$\xi_0(\mathbf{R}) = \left(\frac{2\omega}{\pi}\right)^{3/4} e^{-\omega R^2}, \tag{2.178}$$

$$\phi_0(\mathbf{s}) = a_{00}e^{-\omega s^2/4}(1+\omega s), \tag{2.179}$$

where $a_{00} = \omega^{5/4}(3\pi\sqrt{\pi/2} + 8\pi\sqrt{\omega} + 2\pi\sqrt{2\pi}\omega)^{-1/2} = 1/14.55670, k = 1/4,$ $\omega = \sqrt{k} = 1/2$;

$$\psi_{01}(\mathbf{r}_1\mathbf{r}_2) = \xi_0(\mathbf{R})\phi_1(\mathbf{s}) \tag{2.180}$$

$$\phi_1(\mathbf{s}) = a_{01}e^{-\omega s^2/4}\left[1 + C_1\sqrt{\frac{\omega}{2}}s + C_2\frac{\omega}{2}s^2 + C_3\left(\frac{\omega}{2}\right)^{3/2}s^3\right], \tag{2.181}$$

where $a_{01} = \omega^{3/4}[8\sqrt{2}\pi(C_1 + 2C_1C_2 + 2C_3 + 6C_2C_3) + \pi\sqrt{2\pi}(\frac{15}{2}C_2^2 + \frac{105}{4}C_3^2 + 3C_1^2 + 6C_2 + 15C_1C_3 + 2)]^{-1/2} = 1/13.21931$, $C_1 = 1.146884$, $C_2 = -0.561569$, $C_3 = -0.489647$, $k = 0.144498$, $\omega = \sqrt{k} = 0.380129$.

In order to provide a pictorial representation [41] of the wave function and to exhibit the electron-electron coalescence in its structure, we plot in Fig. 2.1 the ground state wave function $\psi_{00}(\mathbf{r}_1\mathbf{r}_2)$ of (2.177) for $\theta_{\mathbf{r}_1,\mathbf{r}_2} = 0°$, where $\theta_{\mathbf{r}_1,\mathbf{r}_2}$ is the angle

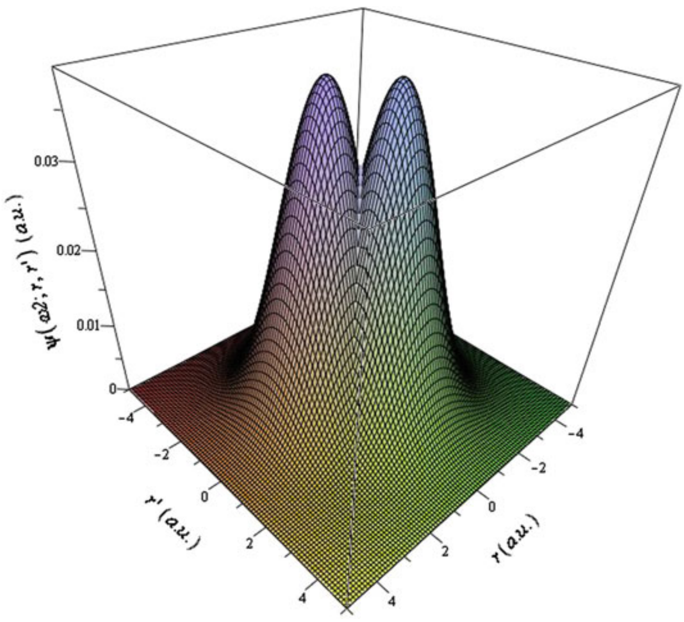

Fig. 2.1 Structure of the ground state wave function $\psi_{00}(\mathbf{r}_1\mathbf{r}_2)$ for $\theta_{\mathbf{r}_1,\mathbf{r}_2} = 0°$, where $\theta_{\mathbf{r}_1,\mathbf{r}_2}$ is the angle between vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ which are oriented along both the positive and negative z-axis

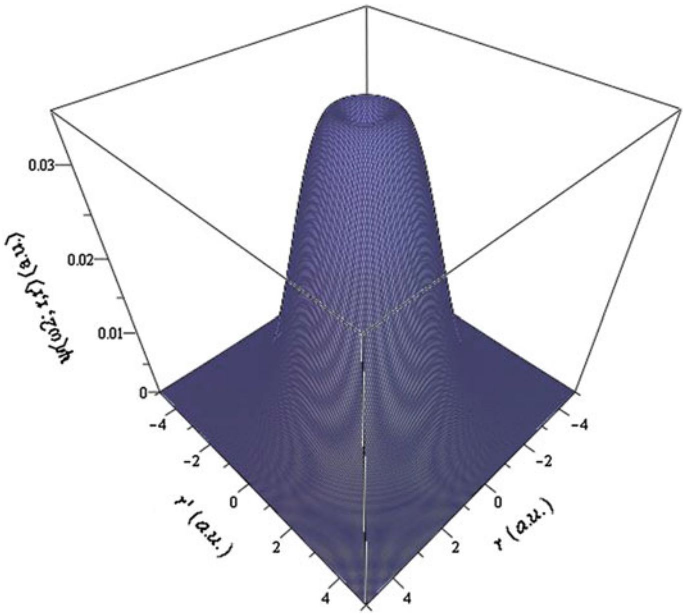

Fig. 2.2 Same as in Fig. 2.1 but for $\theta_{\mathbf{r}_1,\mathbf{r}_2} = 90°$. The vector $\mathbf{r}_1$ is along the z-axis, and the vector $\mathbf{r}_2$ in the xy-plane

between the vectors $\mathbf{r}_1$ and $\mathbf{r}_2$. Figure 2.2 is a plot for $\theta_{\mathbf{r}_1,\mathbf{r}_2} = 90°$. Figure 2.3 is the same as Fig. 2.2 except that the $\mathbf{r}_2$ vector has been confined to the positive quadrant of the xy-plane. Observe that the electron-electron coalescence cusp is clearly visible along the diagonal defined by $r_1 = r_2$ in Fig. 2.1, and at $r_1 = r_2 = 0$ at the nucleus in Fig. 2.3.

In both the ground and first excited singlet state, the atom is spherically symmetric. The orbital functions $\phi_0(s)$ and $\phi_1(s)$ are plotted in Fig. 2.4. Note that there are no nodes in $\phi_0(s)$, and one node in $\phi_1(s)$ corresponding to a first excited state. Also observe the electron-electron coalescence cusp at the coalescence of the two electrons for $s = 0$. In Fig. 2.5 the ground $\rho_{00}(\mathbf{r})$ and excited $\rho_{01}(\mathbf{r})$ state densities are plotted. Recall that this source is static in that its structure is independent of and remains unchanged as a function of electron position. Since the potential energy $v(\mathbf{r})$ is not Coulombic, these densitites do not exhibit a cusp at the nucleus. The corresponding radial probability densities $r^2\rho_{00}(\mathbf{r})$ and $r^2\rho_{01}(\mathbf{r})$ are plotted in Fig. 2.6. Observe the distinct shoulder in $r^2\rho_{01}(\mathbf{r})$ prior to the maximum indicative of a ‘shell’ type structure with each electron being in a different shell.

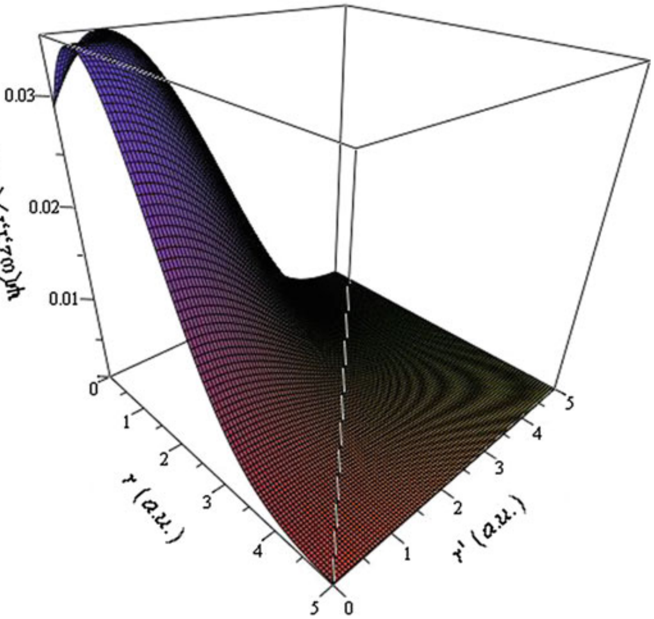

Fig. 2.3 Same as in Fig. 2.2 except that the $\mathbf{r}_2$ vector has been confined to the positive quadrant of the xy-plane

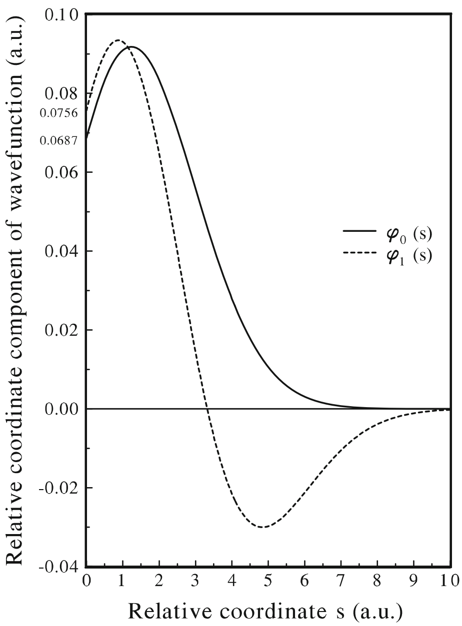

Fig. 2.4 The relative coordinate component of the wavefunction for the ground $\phi_0(s)$ and the first excited singlet $\phi_1(s)$ states

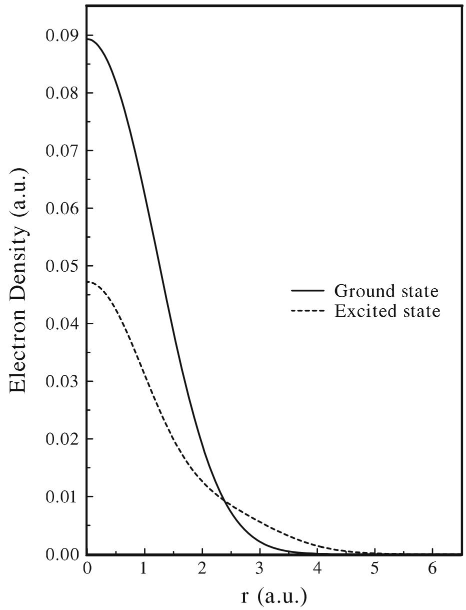

Fig. 2.5 The electron density $\rho(r)$ of the ground and first excited singlet states

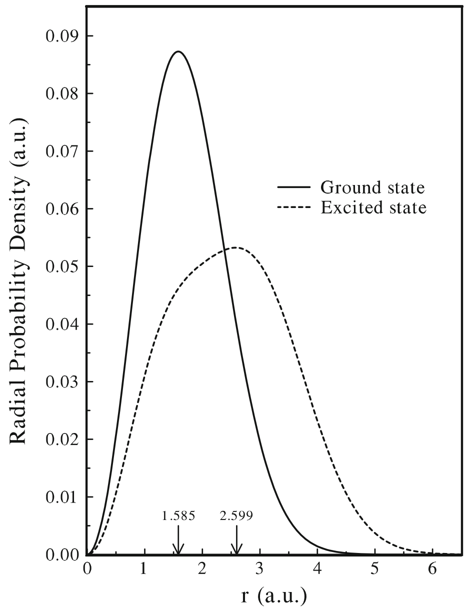

Fig. 2.6 The radial probability density $r^2\rho(r)$ of the ground and first excited singlet states. The *arrows* indicate the position of the maxima

2.11.3 Fermi–Coulomb Hole Charge Distribution $\rho_{xc}(\mathbf{rr}')$

In Figs. 2.7, 2.8, 2.9 and 2.10, the Fermi–Coulomb hole charge distribution $\rho_{xc}(\mathbf{rr}')$ for both the ground and excited states is plotted for electron positions at the nucleus $r = 0$, and at $r = 0.5$, 1, 2, 10, 20, 50, and 200 a.u. The electron position is indicated by an arrow. For the electron at the nucleus Fig. 2.7a, the hole is spherically symmetric about the electron. Further, at the electron position, the hole exhibits a cusp representative of the electron–electron coalescence condition of (2.149). In Figs. 2.7b, 2.8, 2.9 and 2.10, the electron is along the z-axis corresponding to $\theta = 0°$. The cross sections plotted correspond to $\theta' = 0°$ with respect to the electron–nucleus direction. The graph for $r' < 0$ is the structure for $\theta = \pi$ and $r' > 0$.

The dynamic or nonlocal nature of the Fermi–Coulomb hole as a function of electron position is clearly evident in these figures, as is the cusp at the electron position in Figs. 2.7b, 2.8a, 2.9b, and the fact that these holes are not spherically symmetric about the electron. For asymptotic positions of the electron, these charge distributions become essentially spherically symmetric about the nucleus as well as static (Fig. 2.10b). In other words, the change in the structure for these asymptotic positions is minimal. Finally, observe that the structure of the holes for the ground and excited states is distinctly different, although their broad features are similar.

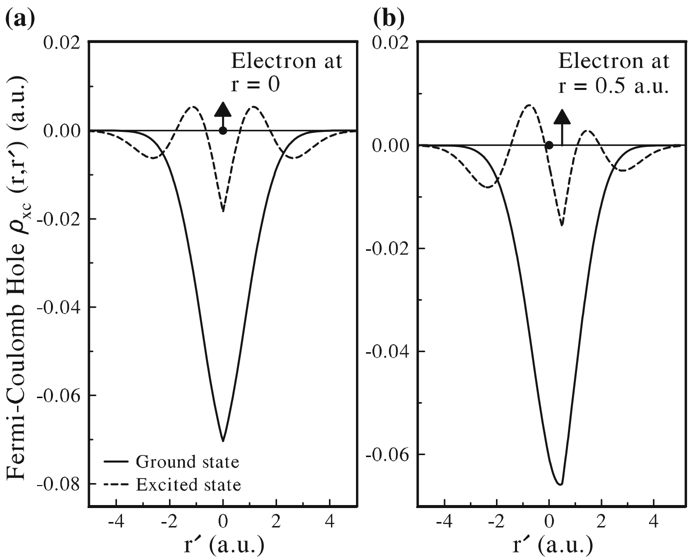

Fig. 2.7 Cross–section through the Fermi–Coulomb hole charge $\rho_{xc}(\mathbf{rr}')$ for the ground and first excited singlet states. In (**a**) the electron is at the nucleus $r = 0$, and in (**b**) at $r = 0.5$ a.u. The electron is on the z-axis corresponding to $\theta = 0$. The graphs for $r' < 0$ correspond to the structure for $\theta = \pi$, $r' > 0$

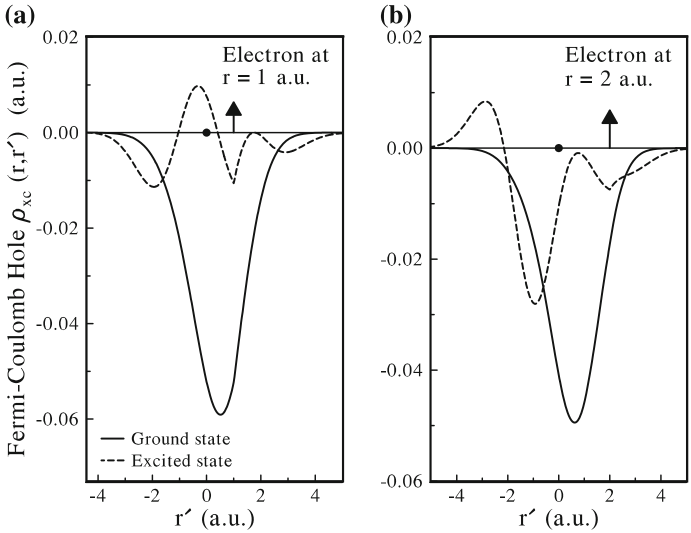

Fig. 2.8 Same as in Fig. 2.7 but for the electron at (**a**) $r = 1$ a.u. and (**b**) $r = 2$ a.u

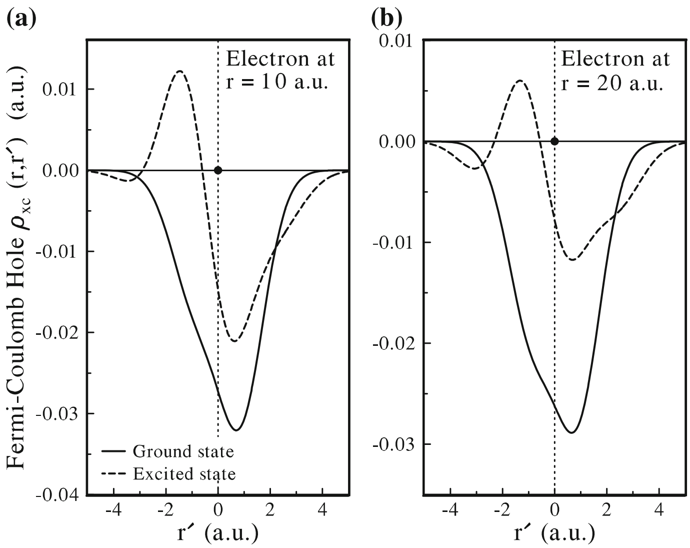

Fig. 2.9 Same as in Fig. 2.7 but for the electron at (**a**) $r = 10$ a.u. and (**b**) $r = 20$ a.u

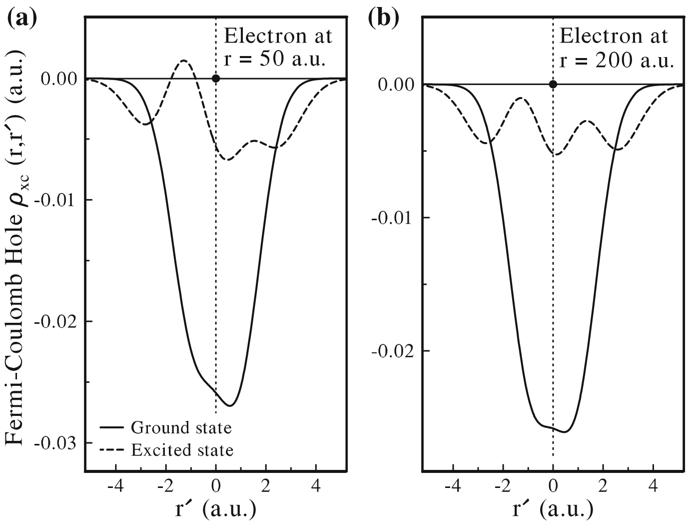

Fig. 2.10 Same as in Fig. 2.7 but for the electron at **(a)** $r = 50$ a.u. and (**b**) $r = 200$ a.u

2.11.4 Hartree, Pauli–Coulomb, and Electron–Interaction Fields $\mathcal{E}_{\mathbf{H}}(\mathbf{r})$, $\mathcal{E}_{\mathbf{xc}}(\mathbf{r})$, $\mathcal{E}_{\mathbf{ee}}(\mathbf{r})$ and Energies $E_{\mathbf{H}}, E_{\mathbf{xc}}, E_{\mathbf{ee}}$

The Hartree field $\mathcal{E}_{\mathrm{H}}(\mathbf{r})$ whose source is the density $\rho(\mathbf{r})$ (see (2.47)) is plotted in Fig. 2.11 for the ground and excited states. Since for each state, the density is spherically symmetric, the field vanishes at the nucleus. The fact that there is a single 'shell' is evident from the ground state plot. A careful examination of the field for the excited state shows a slight shoulder between $r = 2$ and 4 a.u. indicating the existence of the second 'shell'. As the density is static, localized about the nucleus, and of total charge 2 a.u., the structure of the Hartree field $\mathcal{E}_{\mathrm{H}}(\mathbf{r})$ for asymptotic positions of the electron is

$$\mathcal{E}_{\mathrm{H}}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}' \underset{r \to \infty}{\approx} \frac{1}{r^2} \int \rho(\mathbf{r}') d\mathbf{r}' = \frac{2}{r^2}. \tag{2.182}$$

The fields $\mathcal{E}_{\mathrm{H}}(\mathbf{r})$ for both the ground and excited state are observed to merge asymptotically with the function $2/r^2$ also plotted in Fig. 2.11.

The Pauli–Coulomb field $\mathcal{E}_{\mathrm{xc}}(\mathbf{r})$ for both states is plotted in Fig. 2.12. Since for the electron position at the nucleus, the Fermi–Coulomb hole charge $\rho_{\mathrm{xc}}(\mathbf{r}\mathbf{r}')$ is spherically symmetric about the electron (see Fig. 2.7a), the fields $\mathcal{E}_{\mathrm{xc}}(\mathbf{r})$ vanish there. Further, as the atom is spherically symmetric, the field $\mathcal{E}_{\mathrm{xc}}(\mathbf{r})$ has only a radial component and is dependent only on the radial coordinate. This is the case in spite of the fact that the Fermi–Coulomb hole is not spherically symmetric about the nucleus

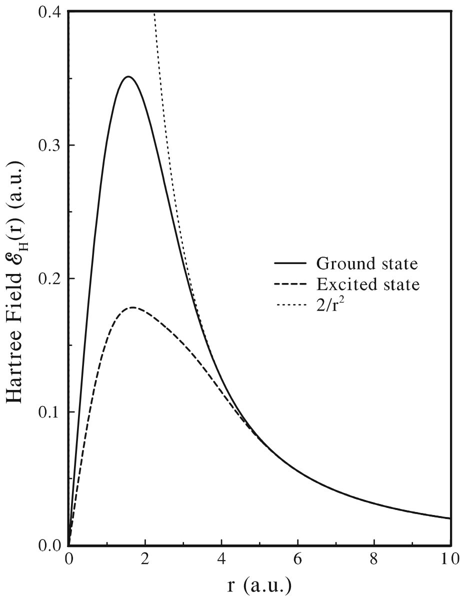

Fig. 2.11 The Hartree field $\boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r})$ for the ground and excited states

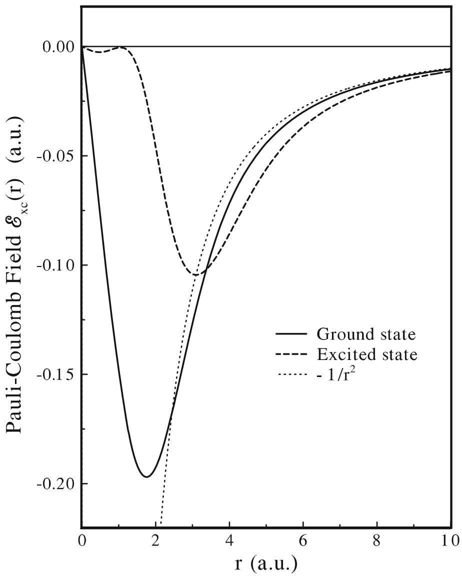

Fig. 2.12 The Pauli-Coulomb field $\boldsymbol{\mathcal{E}}_{\mathrm{xc}}(\mathbf{r})$ for the ground and excited states

for other electron positions. The fields are negative because the Fermi–Coulomb hole charge is negative. The two 'shells' are clearly evident in the field $\boldsymbol{\mathcal{E}}_{xc}(\mathbf{r})$ for the excited state, and the single shell for the ground state. As noted previously, for asymptotic positions of the electron, the Fermi–Coulomb hole is essentially a static charge and spherically symmetric, and localized about the nucleus. Since the total charge of the hole is negative unity, the asymptotic structure of the Pauli–Coulomb field is

$$\boldsymbol{\mathcal{E}}_{xc}(\mathbf{r}) \underset{r\to\infty}{\sim} -\frac{1}{r^2}. \tag{2.183}$$

Once again, the field $\boldsymbol{\mathcal{E}}_{xc}(\mathbf{r})$ for both the ground and excited state merge asymptotically with the function $-1/r^2$ also plotted in Fig. 2.12. This result is general and valid for any finite system.

The electron–interaction field $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$ which is the sum of the Hartree $\boldsymbol{\mathcal{E}}_{H}(\mathbf{r})$ and Pauli–Coulomb $\boldsymbol{\mathcal{E}}_{xc}(\mathbf{r})$ fields is plotted in Fig. 2.13 for both states. Since the total charge of its source, the pair-correlation density, is unity, the fields decays as $1/r^2$ asymptotically. For purposes of comparison with the other components of the internal field $\boldsymbol{\mathcal{F}}^{int}(\mathbf{r})$ experienced by the electrons, $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$ is also plotted in Fig. 2.16 for the ground state and in Fig. 2.17 for the excited state.

The Hartree E_H, Pauli–Coulomb E_{xc}, and electron–interaction E_{ee} energies as determined from the corresponding fields are given in Table 2.1. A comparison of the fields for the ground and excited states makes clear why the Hartree and Pauli–Coulomb energies for the former are greater in magnitude. The graphs of the fields also show the region of space from which the principal contribution to the energy arises.

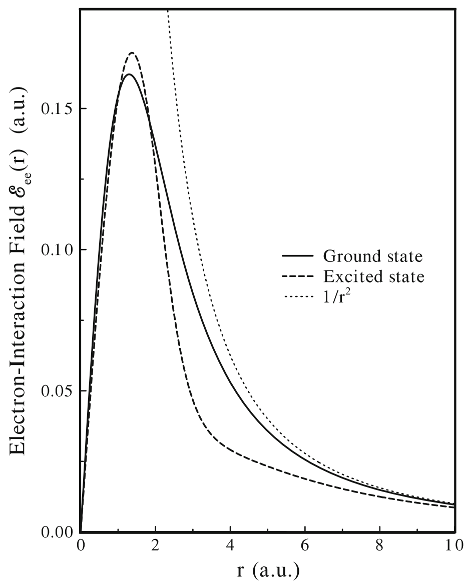

Fig. 2.13 The electron–interaction field $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$ for the ground and excited states

Table 2.1 Properties of the Hooke's atom in its ground ($k = 0.25$) and first excited singlet ($k = 0.144498$) states in atomic units

Property	Ground state[a]	Excited state[b]
E	2.000000	2.280775
η	0.750000	1.710581
ϵ	1.250000	0.570194
$E^{N=1}$	0.750000	0.570194
I	−1.250000	−1.710581
T	0.664418	0.876262
E_{ee}	0.447448	0.352142
E_{H}	1.030250	0.722217
E_{xc}	−0.582807	−0.370075
E_{ext}	0.888141	1.052372
$\langle r \rangle$	3.489025	4.971112
$\langle r^2 \rangle$	7.105114	14.565898
$\langle r^{-1} \rangle$	1.442940	1.053870
$\langle r^{-2} \rangle$	1.926359	0.936753
$\langle \delta(\mathbf{r}) \rangle$	0.089319	0.047243

[a] From [39]
[b] From [40]

2.11.5 *Kinetic Field $\mathcal{Z}(\mathbf{r})$ and Kinetic Energy T*

As the Hooke's atom is spherically symmetric in both its ground and first excited singlet states, the kinetic-energy-density tensor $t_{\alpha\beta}(\mathbf{r}; [\gamma])$ is of the form

$$t_{\alpha\beta}(\mathbf{r}; [\gamma]) = \frac{r_\alpha r_\beta}{r^2} f(r) + \delta_{\alpha\beta} k(r), \tag{2.184}$$

where the functions $f(r)$ and $k(r)$ for the ground state are given in Appendix C. (The detailed derivation of (2.184) for the ground state is given in Appendix D.) The second term contributes only to the diagonal elements of the tensor.

The kinetic 'force' $\mathbf{z}(\mathbf{r})$ for the ground and excited states is plotted in Fig. 2.14. The kinetic field $\mathcal{Z}(\mathbf{r})$ for the ground state is plotted in Fig. 2.16 and for the excited state in Fig. 2.17. The kinetic 'force' vanishes at the nucleus, and asymptotically as a power series times a Gaussian function (see Appendix C). The fields too vanish at the nucleus, but diverge asymptotically in the classically forbidden region. Observe the greater structure in the kinetic 'force' and field for the excited state representative of 'shell' structure. The corresponding values for the kinetic energy for the two states are given in Table 2.1.

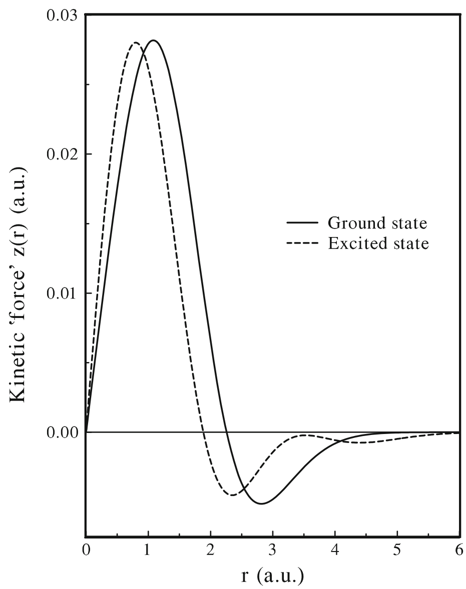

Fig. 2.14 The kinetic 'force' $\mathbf{z}(\mathbf{r})$ for the ground and excited states

2.11.6 *Differential Density Field* $\mathcal{D}(\mathbf{r})$

The differential density 'force' $\mathbf{d}(\mathbf{r})$ is plotted in Fig. 2.15 for the ground and excited states, and the corresponding fields $\mathcal{D}(\mathbf{r})$ in Figs. 2.16 and 2.17, respectively. Again, 'shell' structure is clearly evident. The 'force' vanishes at the nucleus, and asymptotically in the classically forbidden region. The fields thus vanish at the nucleus, but are divergent asymptotically.

For comparison, the components $\mathcal{E}_{\mathrm{ee}}(\mathbf{r})$, $\mathcal{D}(\mathbf{r})$, and $\mathcal{Z}(\mathbf{r})$ of the internal field $\mathcal{F}^{\mathrm{int}}(\mathbf{r})$ are plotted together in Figs. 2.16 and 2.17 for the ground and excited state, respectively. Observe that although both $\mathcal{D}(\mathbf{r})$ and $\mathcal{Z}(\mathbf{r})$ diverge asymptotically, their sum $\sim -kr$ in this region as $\mathcal{E}_{\mathrm{ee}}(\mathbf{r})$ vanishes there. Further, the sum $-\mathcal{E}_{\mathrm{ee}}(\mathbf{r}) + \mathcal{D}(\mathbf{r}) + \mathcal{Z}(\mathbf{r}) = -\mathcal{F}^{\mathrm{int}}(\mathbf{r}) = -kr$ throughout space, as must be the case because it is the statement of the 'Quantal Newtonian' first law for this model problem.

2.11.7 *Total Energy E and Ionization Potential I*

The total energy E for the ground $E_0^{N=2}$ and first excited singlet $E_1^{N=2}$ states, and their eigenvalue components ϵ and η (see (2.175)) are quoted in Table 2.1. The energy of the ions $E^{N=1} = \omega(n + \frac{3}{2})$, $n = 0$, and the corresponding ionization potentials I for the ground state $I_{00} = E_0^{N=1} - E_0^{N=2}$ and excited state $I_{01} = E_0^{N=1} - E_1^{N=2}$ are also quoted in the table.

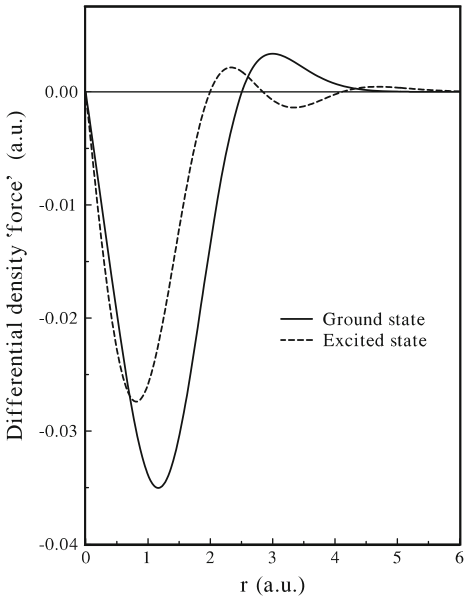

Fig. 2.15 The differential density 'force' $\mathbf{d}(\mathbf{r})$ for the ground and excited state

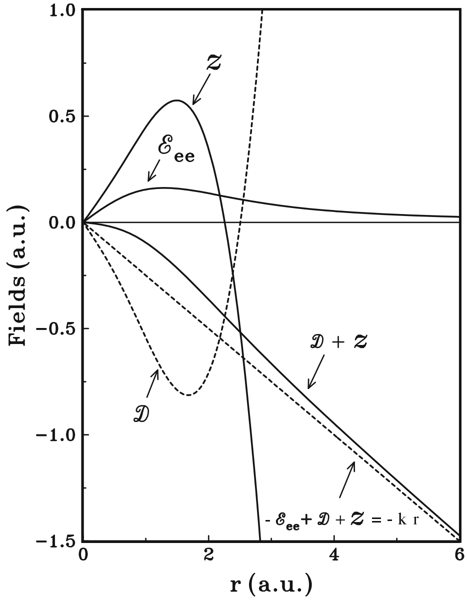

Fig. 2.16 The electron interaction $\boldsymbol{\mathcal{E}}_{\mathrm{ee}}(\mathbf{r})$, differential density $\boldsymbol{\mathcal{D}}(\mathbf{r})$, and kinetic $\boldsymbol{\mathcal{Z}}(\mathbf{r})$ field components of the internal field $\boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r})$ for the ground state. The sum $\boldsymbol{\mathcal{D}}(\mathbf{r}) + \boldsymbol{\mathcal{Z}}(\mathbf{r})$, and $-\boldsymbol{\mathcal{E}}_{\mathrm{ee}}(\mathbf{r}) + \boldsymbol{\mathcal{D}}(\mathbf{r}) + \boldsymbol{\mathcal{Z}}(\mathbf{r})$ are also plotted

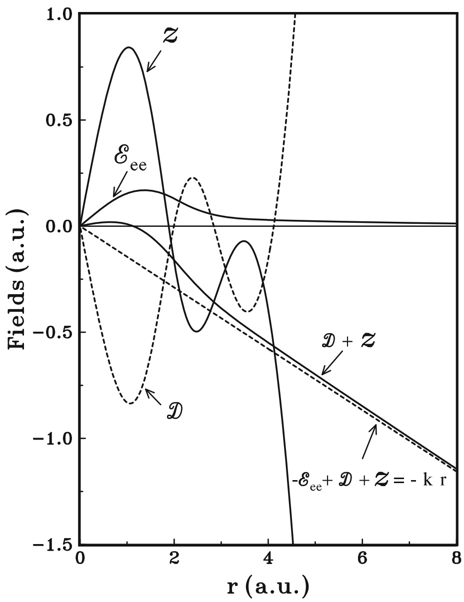

Fig. 2.17 Same as in Fig. 2.16 but for the first excited singlet state

2.11.8 Expectations of Other Single–Particle Operators

In Table 2.1 the expectations $\langle \sum_i r_i^n \rangle$, $n = -2, -1, 1, 2$ and $\langle \delta(\mathbf{r}) \rangle$ are also quoted for the ground and first excited state. In terms of the density $\rho(\mathbf{r})$, the expectation

$$\left\langle \sum_i r_i^n \right\rangle = \langle \psi | \sum_i r_i^n | \psi \rangle = \int r^n \rho(\mathbf{r}) d\mathbf{r}. \tag{2.185}$$

These expectations emphasize different regions of the electronic density distribution. They are also related to various properties of atoms [42]: $\langle r \rangle$ is the average size of the atom; the diamagnetic susceptiblity is proportional to $\langle r^2 \rangle$; the expectation $\langle 1/r \rangle$ is required for the determination of the nuclear magnetic shielding constant; the electric field gradient, the magnetic dipole interaction, and spin–orbit coupling depends on $\langle 1/r^3 \rangle$; the electron density at the nucleus $\rho(0) = \langle \delta(\mathbf{r}) \rangle$ is required for the Fermi contact term when electron spin–nuclear spin interactions are considered.

2.12 Schrödinger Theory and Quantum Fluid Dynamics

In quantum fluid dynamics (QFD) [43–45] the electron gas of a many–electron system is treated as a classical fluid moving under the action of the external field $\mathcal{F}^{\text{ext}}(\mathbf{r}t)$ as well as of the quantal internal field $\mathcal{F}^{\text{int}}(\mathbf{r}t)$ described in Sect. 2.8. As with the quantum mechanical hydrodynamical equations of Sect. 2.7—the continuity and force equations—, the equations of QFD—the continuity and Euler equations—are also derived from the Schrödinger equation, and hence the two theories are intrinsically equivalent. Thus, whereas in deriving (See Appendix A) the 'Quantal Newtonian' second law of (2.75), the wavefunction $\Psi(\mathbf{X}t)$ is explicitly written in terms of its real and imaginary parts, the QFD equations are obtained by expressing the wavefunction or spinless single particle density matrix $\gamma(\mathbf{r}\mathbf{r}'t)$ in polar form. Here we show [46] the equivalence of the 'Quantal Newtonian' second law to the Euler equation for both the single–electron and many–electron cases.

2.12.1 Single–Electron Case

For a single electron in an external field $\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}t) = -\boldsymbol{\nabla} v(\mathbf{r}t)$, the Schrödinger equation (2.1) is

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}t)\right]\Psi(\mathbf{r}t) = i\frac{\partial\Psi(\mathbf{r}t)}{\partial t}. \tag{2.186}$$

Substitution of the polar form of the wavefunction:

$$\Psi(\mathbf{r}t) = R(\mathbf{r}t)\exp\left[iS(\mathbf{r}t)\right], \tag{2.187}$$

where $R(\mathbf{r}t)$, $S(\mathbf{r}t)$ are real, into (2.186) leads to the QFD continuity and Euler equations, respectively:

$$\frac{\partial\rho(\mathbf{r}t)}{\partial t} = -\boldsymbol{\nabla}\cdot\mathbf{j}(\mathbf{r}t), \tag{2.188}$$

$$\frac{D\boldsymbol{\nu}(\mathbf{r}t)}{Dt} = \boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}t) - \boldsymbol{\nabla} f(\mathbf{r}t), \tag{2.189}$$

where the density $\rho(\mathbf{r}t) = R^2(\mathbf{r}t)$, the current density $\mathbf{j}(\mathbf{r}t) = \rho(\mathbf{r}t)\boldsymbol{\nabla}S(\mathbf{r}t)$, the velocity field $\boldsymbol{\nu}(\mathbf{r}t) = \mathbf{j}(\mathbf{r}t)/\rho(\mathbf{r}t) = \boldsymbol{\nabla}S(\mathbf{r}t)$, the scalar function $f(\mathbf{r}t) = -\frac{1}{2}(\nabla^2 R/R)$, and the total time derivative

$$\frac{D\boldsymbol{\nu}(\mathbf{r}t)}{Dt} = \frac{\partial\boldsymbol{\nu}(\mathbf{r}t)}{\partial t} + [\boldsymbol{\nu}(\mathbf{r}t)\cdot\boldsymbol{\nabla}]\boldsymbol{\nu}(\mathbf{r}t). \tag{2.190}$$

The Euler and continuity equations lead to an expression for the current density field $\boldsymbol{\mathcal{J}}(\mathbf{r}t)$ of (2.54) as follows. Multiplying (2.189) by $\rho(\mathbf{r}t)$ leads to

$$\rho\frac{\partial\boldsymbol{\nu}}{\partial t} + \mathbf{j}\cdot\boldsymbol{\nabla}\boldsymbol{\nu} = \rho\boldsymbol{\mathcal{F}}^{\text{ext}} - \rho\boldsymbol{\nabla} f. \tag{2.191}$$

From the definition of the current density $\mathbf{j}(\mathbf{r}t)$ and the continuity equation we have

$$\rho \frac{\partial \boldsymbol{\nu}}{\partial t} = \frac{\partial \mathbf{j}}{\partial t} + \boldsymbol{\nu} \nabla \cdot \mathbf{j}. \tag{2.192}$$

Thus,

$$\boldsymbol{\mathcal{J}}(\mathbf{r}t) = \frac{1}{\rho(\mathbf{r}t)} \frac{\partial \mathbf{j}(\mathbf{r}t)}{\partial t} = \boldsymbol{\mathcal{F}}^{\text{ext}} - \nabla f - \frac{1}{R^2}[\boldsymbol{\nu}\nabla \cdot \mathbf{j} + \mathbf{j} \cdot \nabla \boldsymbol{\nu}]. \tag{2.193}$$

The differential density field (2.49) is

$$\boldsymbol{\mathcal{D}}(\mathbf{r}t) = \frac{\mathbf{d}(\mathbf{r}t)}{\rho(\mathbf{r}t)} = -\frac{1}{R^2}\left(\frac{1}{2}\nabla|\nabla R|^2 + \nabla R \nabla^2 R\right) + \nabla f. \tag{2.194}$$

The kinetic–energy–density tensor of (2.53) is

$$\begin{aligned} t_{\alpha\beta}(\mathbf{r}) &= \frac{1}{4}\left(\frac{\partial \Psi^*}{\partial r_\alpha}\frac{\partial \Psi}{\partial r_\beta} + \frac{\partial \Psi^*}{\partial r_\beta}\frac{\partial \Psi}{\partial r_\alpha}\right) \\ &= \frac{1}{2}\left(\frac{\partial R}{\partial r_\alpha}\frac{\partial R}{\partial r_\beta} + R^2 \frac{\partial S}{\partial r_\beta}\frac{\partial S}{\partial r_\alpha}\right). \end{aligned} \tag{2.195}$$

Thus, the kinetic field (2.51) is

$$\boldsymbol{\mathcal{Z}}(\mathbf{r}t) = \frac{\mathbf{z}(\mathbf{r}t)}{\rho(\mathbf{r}t)} = \frac{1}{R^2}\left(\frac{1}{2}\nabla|\nabla R|^2 + \nabla R \nabla^2 R\right) + \frac{1}{R^2}(\boldsymbol{\nu}\nabla \cdot \mathbf{j} + \mathbf{j} \cdot \nabla \boldsymbol{\nu}). \tag{2.196}$$

On adding the fields $\boldsymbol{\mathcal{J}}(\mathbf{r}t)$, $\boldsymbol{\mathcal{D}}(\mathbf{r}t)$, and $\boldsymbol{\mathcal{Z}}(\mathbf{r}t)$, one recovers the 'Quantal Newtonian' second law for the single electron:

$$\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}t) + \boldsymbol{\mathcal{F}}^{\text{int}}(\mathbf{r}t) = \boldsymbol{\mathcal{J}}(\mathbf{r}t), \tag{2.197}$$

where the internal field $\boldsymbol{\mathcal{F}}^{\text{int}}(\mathbf{r}t) = -\boldsymbol{\mathcal{D}}(\mathbf{r}t) - \boldsymbol{\mathcal{Z}}(\mathbf{r}t)$.

2.12.2 Many–Electron Case

For the many–electron case with the Hamiltonian of (2.2), the continuity and Euler equations of QFD are derived from the equation of motion for the spinless single particle density matrix $\gamma(\mathbf{r}\mathbf{r}'t)$ defined by (2.15). The equation of motion, which may be derived directly from the Schrödinger equation or from the quantum mechanical equation of motion (2.93) for the expectation value of the density matrix operator $\hat{\gamma}(\mathbf{r}\mathbf{r}')$ of (2.17), is

$$
\begin{aligned}
i\frac{\partial \gamma(\mathbf{r}'\mathbf{r}''t)}{\partial t} &= -\frac{1}{2}\left(\nabla'^2 - \nabla''^2\right)\gamma(\mathbf{r}'\mathbf{r}''t) \\
&+ 2\int \left[U\left(\mathbf{r}'-\mathbf{r}\right) - U\left(\mathbf{r}''-\mathbf{r}\right)\right]\Gamma_2\left(\mathbf{r}'\mathbf{r},\mathbf{r}''\mathbf{r};t\right)d\mathbf{r} \\
&+ \left[v\left(\mathbf{r}'t\right) - v\left(\mathbf{r}''t\right)\right]\gamma\left(\mathbf{r}'\mathbf{r}''t\right),
\end{aligned}
\tag{2.198}
$$

where $U(\mathbf{r}-\mathbf{r}') = |\mathbf{r}-\mathbf{r}'|^{-1}$ is the electron–interaction term, and Γ_2 the two–particle density matrix defined in Appendix A.

The QFD equations are obtained by first expressing the density matrix $\gamma(\mathbf{r}'\mathbf{r}''t)$ in polar form:

$$
\gamma(\mathbf{r}'\mathbf{r}''t) = R(\mathbf{r}'\mathbf{r}''t)\exp\left[iS\left(\mathbf{r}'\mathbf{r}''t\right)\right], \tag{2.199}
$$

where the amplitude is symmetric: $R(\mathbf{r}'\mathbf{r}''t) = R(\mathbf{r}''\mathbf{r}'t)$, the phase antisymmetric: $S(\mathbf{r}'\mathbf{r}''t) = -S(\mathbf{r}''\mathbf{r}'t)$, and $S(\mathbf{r}\mathbf{r}t) = 0$. The next step is to transform to the center of mass and relative coordinates:

$$
\mathbf{r} = \frac{1}{2}(\mathbf{r}' + \mathbf{r}'')\ ; \qquad \mathbf{s} = \mathbf{r}' - \mathbf{r}'', \tag{2.200}
$$

$$
\mathbf{r}' = \mathbf{r} + \frac{\mathbf{s}}{2}\ ; \qquad \mathbf{r}'' = \mathbf{r} - \frac{\mathbf{s}}{2}, \tag{2.201}
$$

so that

$$
\nabla_{\mathbf{r}} = \nabla' + \nabla''\ ; \qquad \nabla_{\mathbf{s}} = \frac{1}{2}(\nabla' - \nabla'') \tag{2.202}
$$

and

$$
\nabla' = \frac{1}{2}\nabla_{\mathbf{r}} + \nabla_{\mathbf{s}}\ ; \qquad \nabla'' = \frac{1}{2}\nabla_{\mathbf{r}} - \nabla_{\mathbf{s}}. \tag{2.203}
$$

The density $\rho(\mathbf{r}t)$ and current density $\mathbf{j}(\mathbf{r}t)$ are then obtained as (dropping the explicit time dependence in the following equations)

$$
\rho(\mathbf{r}) = \gamma(\mathbf{r}'\mathbf{r}'')|_{\mathbf{r}'=\mathbf{r}''=\mathbf{r}} = \lim_{\mathbf{s}\to 0}\gamma\left(\mathbf{r}+\frac{\mathbf{s}}{2},\mathbf{r}-\frac{\mathbf{s}}{2}\right), \tag{2.204}
$$

$$
\mathbf{j}(\mathbf{r}) = \frac{i}{2}[\nabla' - \nabla'']\gamma(\mathbf{r}'\mathbf{r}'')|_{\mathbf{r}'=\mathbf{r}''=\mathbf{r}} = i\lim_{\mathbf{s}\to 0}\nabla_{\mathbf{s}}\gamma\left(\mathbf{r}+\frac{\mathbf{s}}{2},\mathbf{r}-\frac{\mathbf{s}}{2}\right). \tag{2.205}
$$

Further, employing the polar form (2.199), the current density may be written as

$$
\mathbf{j}(\mathbf{r}) = \rho(\mathbf{r})\boldsymbol{\nu}(\mathbf{r}), \tag{2.206}
$$

where the velocity field $\boldsymbol{\nu}(\mathbf{r})$ is

$$
\boldsymbol{\nu}(\mathbf{r}) = \lim_{\mathbf{s}\to 0}\nabla_{\mathbf{s}}S\left(\mathbf{r}+\frac{\mathbf{s}}{2},\mathbf{r}-\frac{\mathbf{s}}{2}\right). \tag{2.207}
$$

The equation of motion in the transformed coordinates is then

$$i\frac{\partial}{\partial t}\gamma\left(\mathbf{r}+\frac{\mathbf{s}}{2},\mathbf{r}-\frac{\mathbf{s}}{2}\right)=-\boldsymbol{\nabla}_{\mathbf{r}}\cdot\boldsymbol{\nabla}_{\mathbf{s}}\gamma\left(\mathbf{r}+\frac{\mathbf{s}}{2},\mathbf{r}-\frac{\mathbf{s}}{2}\right)$$
$$+Q\left(\mathbf{r}+\frac{\mathbf{s}}{2},\mathbf{r}-\frac{\mathbf{s}}{2}\right), \tag{2.208}$$

where

$$Q\left(\mathbf{r}'\mathbf{r}''\right)=2\int\left[\mathrm{U}\left(\mathbf{r}'-\mathbf{r}\right)-\mathrm{U}\left(\mathbf{r}''-\mathbf{r}\right)\right]\Gamma_2(\mathbf{r}'\mathbf{r};\mathbf{r}''\mathbf{r})d\mathbf{r}$$
$$+\left[v(\mathbf{r}')-v(\mathbf{r}'')\right]\gamma\left(\mathbf{r}'\mathbf{r}''\right). \tag{2.209}$$

The continuity equation

$$\frac{\partial\rho(\mathbf{r}t)}{\partial t}=-\boldsymbol{\nabla}\cdot\mathbf{j}(\mathbf{r}t), \tag{2.210}$$

is obtained from the equation of motion (2.208) on employing the definitions of the density and current density, and on taking the limit $\mathbf{s}\to 0$. The term $Q(\mathbf{rr})=0$.

The Euler equation is derived by taking the derivative of the equation of motion (2.208) with respect to the relative coordinate $\mathbf{s}$ and then taking the limit as $\mathbf{s}\to 0$. The last term on the right hand side of the equation thus yields

$$\lim_{\mathbf{s}\to 0}\boldsymbol{\nabla}_{\mathbf{s}}Q\left(\mathbf{r}+\frac{\mathbf{s}}{2},\mathbf{r}-\frac{\mathbf{s}}{2}\right)=-2\int\boldsymbol{\nabla}_{\mathbf{r}}U(\mathbf{r}-\mathbf{r}')\Gamma_2(\mathbf{rr}';\mathbf{rr}')d\mathbf{r}'$$
$$-\rho(\mathbf{r})\boldsymbol{\nabla}v(\mathbf{r}). \tag{2.211}$$

The diagonal matrix element of the two particle density matrix is related to the pair-correlation density by $\Gamma_2(\mathbf{rr}';\mathbf{rr}')=\rho(\mathbf{r})g(\mathbf{rr}')/2$. Thus, the previous equation may be expressed in terms of fields as

$$\lim_{\mathbf{s}\to 0}\boldsymbol{\nabla}_{\mathbf{s}}Q\left(\mathbf{r}+\frac{\mathbf{s}}{2},\mathbf{r}-\frac{\mathbf{s}}{2}\right)=\rho(\mathbf{r})\boldsymbol{\mathcal{E}}_{\mathrm{ee}}(\mathbf{r})+\rho(\mathbf{r})\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}). \tag{2.212}$$

The contribution of the first term on the right hand side of (2.208) is obtained by first showing that

$$-\lim_{\mathbf{s}\to 0}\frac{\partial}{\partial s_k}\frac{\partial}{\partial s_\ell}\gamma\left(\mathbf{r}+\frac{\mathbf{s}}{2},\mathbf{r}-\frac{\mathbf{s}}{2}\right)=2T^0_{k\ell}(\mathbf{r})+\rho(\mathbf{r})\nu_k(\mathbf{r})\nu_\ell(\mathbf{r}), \tag{2.213}$$

where $T^0_{k\ell}$ is the $k\ell$th element of a tensor $\mathbf{T}^0$ defined as

$$T^0_{k\ell}(\mathbf{r})=-\frac{1}{2}\lim_{\mathbf{s}\to 0}\frac{\partial^2 R}{\partial s_k\partial s_\ell}, \tag{2.214}$$

and

$$\rho(\mathbf{r})\nu_k(\mathbf{r})\nu_\ell(\mathbf{r}) = \lim_{\mathbf{s}\to 0} R\frac{\partial S}{\partial s_k}\frac{\partial S}{\partial s_\ell}. \tag{2.215}$$

In deriving (2.213), the symmetry properties of the amplitude R, and phase S together with $S(\mathbf{rr}) = 0$ have been employed. The left hand side of (2.208) is

$$i\frac{\partial}{\partial t}\lim_{\mathbf{s}\to 0}\nabla_{\mathbf{s}}\gamma\left(\mathbf{r}+\frac{\mathbf{s}}{2},\mathbf{r}-\frac{\mathbf{s}}{2}\right) = \frac{\partial \mathbf{j}(\mathbf{r})}{\partial t}. \tag{2.216}$$

The Euler equation of QFD is then

$$\boldsymbol{\mathcal{J}}(\mathbf{r}t) = \boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}t) + \boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}t) - \frac{1}{\rho(\mathbf{r}t)}\boldsymbol{\nabla}\cdot\left[2\mathbf{T}^0(\mathbf{r}t) + \rho(\mathbf{r}t)\boldsymbol{\nu}(\mathbf{r}t)\boldsymbol{\nu}(\mathbf{r}t)\right]. \tag{2.217}$$

All that is required to prove the equivalence of the Euler equation to the 'Quantal Newtonian' second law is to show that the sum of the other components of the internal field $\boldsymbol{\mathcal{F}}^{\text{int}}(\mathbf{r}t)$ satisfy

$$\boldsymbol{\mathcal{D}}(\mathbf{r}t) + \boldsymbol{\mathcal{Z}}(\mathbf{r}t) = \frac{1}{\rho(\mathbf{r}t)}\boldsymbol{\nabla}\cdot\left[2\mathbf{T}^0(\mathbf{r}t) + \rho(\mathbf{r}t)\boldsymbol{\nu}(\mathbf{r}t)\boldsymbol{\nu}(\mathbf{r}t)\right], \tag{2.218}$$

where $\boldsymbol{\mathcal{D}}(\mathbf{r}t) = -\frac{1}{4}\boldsymbol{\nabla}\nabla^2\rho(\mathbf{r}t)/\rho(\mathbf{r}t)$ and $\boldsymbol{\mathcal{Z}}(\mathbf{r}t) = \mathbf{z}(\mathbf{r}t)/\rho(\mathbf{r}t)$. This is readily seen to be the case by writing the kinetic 'force' $\mathbf{z}(\mathbf{r})$ in terms of the transformed coordinates to obtain

$$\begin{aligned} z_\alpha(\mathbf{r}) = \sum_\beta \frac{\partial}{\partial r_\beta}\lim_{\mathbf{s}\to 0}&\left\{\frac{1}{4}\frac{\partial}{\partial r_\alpha}\frac{\partial}{\partial r_\beta} - \frac{\partial}{\partial s_\alpha}\frac{\partial}{\partial s_\beta}\right\} \\ &\gamma\left(\mathbf{r}+\frac{\mathbf{s}}{2},\mathbf{r}-\frac{\mathbf{s}}{2}\right), \end{aligned} \tag{2.219}$$

so that

$$\begin{aligned} -\frac{1}{4}\sum_\beta \frac{\partial}{\partial r_\beta}\lim_{\mathbf{s}\to 0}&\left(\frac{\partial}{\partial r_\alpha}\frac{\partial}{\partial r_\beta}\right)\gamma\left(\mathbf{r}+\frac{\mathbf{s}}{2},\mathbf{r}-\frac{\mathbf{s}}{2}\right) + z_\alpha(\mathbf{r}) \\ &= -\sum_\beta \frac{\partial}{\partial r_\beta}\lim_{\mathbf{s}\to 0}\left(\frac{\partial}{\partial s_\alpha}\frac{\partial}{\partial s_\beta}\right)\gamma\left(\mathbf{r}+\frac{\mathbf{s}}{2},\mathbf{r}-\frac{\mathbf{s}}{2}\right), \end{aligned} \tag{2.220}$$

which proves (2.218). The 'Quantal Newtonian' second law of (2.75) is therefore recovered, which proves that for the many–electron system, Schrödinger theory as described in terms of 'classical' fields and quantal sources, and the Euler equation of quantum fluid dynamics are equivalent.

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Chapter 3
Quantal Density Functional Theory

Abstract Quantal density functional theory (Q–DFT) is a physical local effective potential theory of electronic structure of both ground and excited states. It constitutes the mapping from any state of an interacting system of N electrons in a time-dependent external field as described by Schrödinger theory to one of noninteracting fermions in the same external field and possessing the same quantum-mechanical properties of the basic variables. Time-independent Q–DFT constitutes a special case. The Q–DFT mapping can be to any arbitrary state of the model system. Q–DFT is based on the 'Quantal Newtonian' second and first laws of both the interacting and noninteracting systems. As such it is a description in terms of 'classical' fields derived from quantal sources as experienced by each model fermion. The internal field components are separately representative of electron correlations due to the Pauli Exclusion Principle, Coulomb repulsion, kinetic effects and the density. Thus, as opposed to Schrödinger theory, within Q–DFT, the *separate* contributions to the total energy and local potential due to the Pauli principle, Coulomb repulsion, and the correlation contribution to the kinetic energy—the Correlation-Kinetic effects—are explicitly defined in terms of fields representative of these correlations. The local potential incorporating all the many-body effects is the work done in the force of a conservative effective field which is the sum of these fields. The many-body components of the energy are expressed in integral virial form in terms of the individual fields representative of the different electron correlations. Various sum rules for the model system such as the Integral Virial Theorem, Ehrenfest's Theorem, the Zero Force and the Torque Sum Rule are derived. Q–DFT is explicated by application to both a ground and excited state of a model system in the low electron-correlation regime, and to a ground state in the Wigner high-electron correlation regime. A new characterization of the Wigner regime based on the newly discovered significance of Correlation-Kinetic effects is proposed. The multiplicity of potentials as obtained via Q–DFT which can generate the same basic variables, and the significance of Correlation-Kinetic effects in such mappings, is discussed. The Q–DFT of degenerate states is described, as is the Q–DFT of Hartree and Hartree-Fock theories.

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Introduction

Quantal density functional theory (Q–DFT) is a local effective potential energy theory [1–21] along the lines of Slater theory [22, 23] and traditional Hohenberg-Kohn-Sham [24–26] (KS) and Runge-Gross (RG) [27–29] density functional theories (DFT). It is based on the 'Quantal Newtonian' first and second laws discussed in the previous chapter, and is thus a description in terms of 'classical' fields and quantal sources. As is the case in Schrödinger theory, time-independent Q-DFT constitutes a special case of the time-dependent theory. The basic idea underlying the theory, one in common with traditional DFT, is the mapping from the Schrödinger theory of interacting electrons in an external field $\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}t)/\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}) = -\boldsymbol{\nabla}[v(\mathbf{r}t)/v(\mathbf{r})]$ to one of *noninteracting fermions* with the *same* density $\rho(\mathbf{r}t)/\rho(\mathbf{r})$ as that of the interacting system. (The notation $f(\mathbf{r}t)/f(\mathbf{r})$ refers to the time-dependent/time-independent property as the case may be.) A more recent understanding of time-dependent Q-DFT is that it is efficacious to map to a model system with the same *basic variables* as that of the interacting system. In the time-dependent case the basic variables are the density $\rho(\mathbf{r}t)$ and the current density $\mathbf{j}(\mathbf{r}t)$. (A property that constitutes a basic variable of quantum mechanics is defined below.) In the time-independent case the basic variable is the nondegenerate ground state density $\rho(\mathbf{r})$. However, the mapping in time-independent Q-DFT is not restricted solely to this density but is more general in that it is applicable to all *nondegenerate* and *degenerate ground* and *excited* state densities. From these model systems the corresponding total energy (non-conserved) $E(t)/E$, the ionization potential I or electron affinity A, equivalent to that of the interacting system can be obtained. There are two additional attributes of Q-DFT that distinguish it from Schrödinger theory. For one, it allows for the separation of the contributions to the energy $E(t)/E$ (and local effective potential) of correlations due to the Pauli exclusion principle and Coulomb repulsion. Second, the contribution to the kinetic energy and current density due to the electron correlations—the Correlation-Kinetic and Correlation-Current-Density components—is determinable. There is also a Q-DFT of the Hartree and Hartree-Fock theory approximations to the interacting system whereby the corresponding densities and energies are determined. (The Q-DFT mapping from the interacting system of electrons to one of *noninteracting bosons* such that the same density and energy are obtained will be described in Chap. 6.)

As the model fermions are noninteracting, the effective potential energy $v_s(\mathbf{r}t)/v_s(\mathbf{r})$ of each fermion is the same. The corresponding quantum mechanical operator representative of this potential energy is *multiplicative*, and it is said to be a *local* operator. We refer to this model as the S system, S being a mnemonic for 'single Slater' determinant. Within Q-DFT the potential energy of the noninteracting fermions is defined (at each instant of time) as *the work done in a conservative effective field*. The effective field, in turn, can be expressed as a sum of fields each representative of the different electron correlations that must be accounted for by the S system in order to ensure it possesses the same basic variable properties as that of the interacting system. These correlations are comprised of those due to the Pauli exclusion principle and Coulomb repulsion. But in addition the S system must also account for the difference in the kinetic energy and physical current density between the interacting and noninteracting systems, i.e. the correlation contributions to these properties. These are the Correlation-Kinetic and Correlation-Current-Density contributions. The total energy, equivalent to that of the interacting system, as obtained from the model system, can also be expressed in terms of these individual fields in integral virial form.

Q-DFT *generalizes* and thereby provides a broader perspective to local effective potential theory. For example, in time-independent Q-DFT, a nondegenerate *ground* state of the interacting system with density $\rho(\mathbf{r})$ can be mapped to an S system in a *ground* state with the same density. (This mapping is akin to that in KS-DFT). But the *ground* state of the interacting system can also be mapped via Q-DFT to an S system in *any arbitrary excited* state with a *different* local effective potential which also generates the same density $\rho(\mathbf{r})$. In other words, there exist an *infinite* number of local effective potentials that can generate the ground state density $\rho(\mathbf{r})$. Similarly, an interacting system in an *excited* state with density $\rho^{e}(\mathbf{r})$ can be mapped to an S system which is either in a *ground* state; or in an *excited* state having the *same* configuration as that of the interacting system (as in excited-state KS-DFT); or in *any* other *arbitrary excited* state, each with a *different* local effective potential. Each such potential, however, generates the same excited state density $\rho^{e}(\mathbf{r})$. Once again, we learn that there exist an *infinite* number of local effective potentials that can generate the density $\rho^{e}(\mathbf{r})$ of an excited state of the interacting system. In this context, it is evident that KS-DFT constitutes a special case of Q-DFT.

In RG and KS-DFT, the description of the mapping to the S system is in terms of action/energy functionals of the density $\rho(\mathbf{r}t)/\rho(\mathbf{r})$, and of their functional derivatives. In that regard, these theories are strictly *mathematical*. As the Q-DFT description of the mapping is in terms of fields and quantal sources representative of the different electron correlations, it therefore provides a *rigorous physical* interpretation of the RG and KS-DFT functionals and functional derivatives. The physical interpretation of RG and KS-DFT via Q-DFT in terms of electron correlations is described in Chap. 5.

The justification for the construction of the model S system stems from the first of the two Hohenberg-Kohn theorems [24] to be discussed more fully in a following chapter. The theorem was originally derived for a *nondegenerate* ground state of electrons in the presence of an external electrostatic field $\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}) = -\boldsymbol{\nabla} v(\mathbf{r})$, where the external potential $v(\mathbf{r})$ is arbitrary. The theorem is derived for *fixed* electron number N. It was extended [26] later to degenerate states. In the theorem, it is first proved that there is a one-to-one relationship between the external potential $v(\mathbf{r})$ (to within an additive constant) and the nondegenerate ground state wave function $\psi_0(\mathbf{X})$. *Employing this bijectivity*, it is then proved that there is a one-to-one relationship between $\psi_0(\mathbf{X})$ and the nondegenerate ground state density $\rho(\mathbf{r})$. Thus, knowledge of the nondegenerate ground state density $\rho(\mathbf{r})$ *uniquely* determines the external potential $v(\mathbf{r})$ to within an additive constant. Hence, since the kinetic $\hat{T}$ and electron-interaction $\hat{U}$ operators of the electrons is *assumed* known, so is the Hamiltonian. The solution of the corresponding Schrödinger equation then leads to the nondegenerate ground state wave function $\psi_0(\mathbf{X})$. (Note that the Schrödinger equation can also be solved for the wave function of an excited state.) The wave function $\psi_0(\mathbf{X})$ is thus a functional of the nondegenerate ground state density $\rho(\mathbf{r})$ i.e. $\psi_0(\mathbf{X}) = \psi_0[\rho]$. As such the expectation value of any operator is a unique functional of this density. The theorem, however, does not describe the explicit dependence of the wave function on the density, and hence the unique functionals of the various expectations are unknown. The profundity of the theorem lies in the fact that all the information about the electronic system as determined from its wave functions is contained in the ground state density $\rho(\mathbf{r})$, and it is for this reason that a model system of noninteracting fermions with equivalent density $\rho(\mathbf{r})$ is constructed. However, in contrast to KS–DFT, the fact that the wave function is a functional of the density is not explicitly employed in the Q-DFT mapping to the S system.

The concept of a *basic variable* of quantum mechanics of electrons in an external field also stems from the first Hohenberg-Kohn theorem [24]. A basic variable is a gauge invariant property of the system of electrons that has a *unique* one-to-one relationship with the external potential. Thus, knowledge of this property determines the Hamiltonian of the system uniquely, and thereby via solution of the Schrödinger equation, the wave functions of the system. The nondegenerate ground state density $\rho(\mathbf{r})$ is thus a basic variable. So is the density $\rho^e(\mathbf{r})$ of the lowest excited state of a given symmetry [30] that differs from that of the ground state. This is the Gunnarsson-Lundqvist theorem [31]. That knowledge of such an excited state density leads to a unique external potential has been shown by example [31].

The extension of the first Hohenberg-Kohn theorem to time-dependent external electric fields $\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}t) = -\boldsymbol{\nabla} v(\mathbf{r}t)$ is the Runge-Gross (RG) theorem [27–29] which then provides the justification for time-dependent Q-DFT. The RG theorem is proved for external potential energies $v(\mathbf{r}t)$ that are Taylor expandable about some initial time. It is first proved that there is a one-to-one relationship between the external potential $v(\mathbf{r}t)$ (to within an additive function of time) and the current density $\mathbf{j}(\mathbf{r}t)$. *Employing this fact*, it is then proved that there is a one-to-one relationship between the external potential $v(\mathbf{r}t)$ (to within an additive function of time) and the density $\rho(\mathbf{r}t)$. Thus, in the time-dependent case, both $\rho(\mathbf{r}t)$ and $\mathbf{j}(\mathbf{r}t)$ are basic variables since the relationship of each with the external potential is one-to-one. With the kinetic $\hat{T}$ and electron-interaction $\hat{U}$ operators of the electrons *assumed* known, the Hamiltonian is known, and solution of the time-dependent Schrödinger equation then leads to the wave function $\Psi(\mathbf{X}t)$ of the system. The wave function $\Psi(\mathbf{X}t)$ is thus a functional of either $\rho(\mathbf{r}t)$ or $\mathbf{j}(\mathbf{r}t)$ i.e. $\Psi(\mathbf{X}t) = \Psi[\rho(\mathbf{r}t)]$ or $\Psi[\mathbf{j}(\mathbf{r}t)]$ to within a purely time-dependent phase. In the calculation of expectation values, the phase factor cancels out, and once again the expectations are a unique functional of either $\rho(\mathbf{r}t)$ or $\mathbf{j}(\mathbf{r}t)$. But as in the HK case, the RG theorem does not define the explicit dependence of the wave function on $\rho(\mathbf{r}t)$ or $\mathbf{j}(\mathbf{r}t)$. The fact that the wave function is a functional of either $\rho(\mathbf{r}t)$ or $\mathbf{j}(\mathbf{r}t)$ is not employed in the Q-DFT mapping to the S system. It simply constitutes the justification for the mapping.

In time-independent Q-DFT, as in KS-DFT, the existence of the S system is an *assumption*. In time-dependent RG-DFT, the existence of the S system for Taylor expandable external potentials is predicated [32] on the constraints that the corresponding wave function yield the correct density and its time derivative at the initial time. (There has been a critique [33] of this proof, and responses [34, 35]. See also [36] for the response to a different aspect of the critique, and to other critiques [37, 38] of time-dependent DFT.) Time-dependent Q-DFT *assumes* the existence of the S system. The Q-DFT mapping to the S-system is accomplished via the 'Quantal Newtonian' second laws for the interacting and noninteracting fermion systems. In this manner, the equivalence of the density $\rho(\mathbf{r}t)$ (or of the density $\rho(\mathbf{r}t)$ and the current density $\mathbf{j}(\mathbf{r}t)$) of the two systems is ensured at the outset.

In the next section the Q-DFT mapping (Part I) from an interacting system with density $\rho(\mathbf{r}t)$ to one of noninteracting fermions possessing the same density $\rho(\mathbf{r}t)$ is described. This description is in terms of 'classical' fields and quantal sources representative of the different electron correlations. Various sum rules such as the Integral Virial Theorem, Ehrenfest's Theorem, the Zero Force Sum Rule, and the Torque Sum Rule, are then derived. In the section that follows, the Q-DFT mapping (Part II) to an S system with the same density $\rho(\mathbf{r}t)$ *and* current density $\mathbf{j}(\mathbf{r}t)$ is described. The equations governing the latter mapping constitute a special case of the former, and are therefore simpler. Further, the mapping such that *both* the basic variables $\rho(\mathbf{r}t)$ and $\mathbf{j}(\mathbf{r}t)$ are reproduced leads to a consistency [39] within Q-DFT with regard to the electron correlations that must be accounted for by the model S system. If the Q-DFT mapping is such that *all* the basic variables are reproduced, then the only correlations that must be accounted for are those of the Pauli exclusion principle, Coulomb repulsion and Correlation–Kinetic effects. This is the case irrespective of whether the external field additionally includes a time-dependent electromagnetic field, or whether it is comprised of an electrostatic and magnetostatic field, or solely an electrostatic field. In this chapter, the description is restricted to an external field of the form $\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}t) = -\boldsymbol{\nabla} v(\mathbf{r}t)$. As the scalar external potential $v(\mathbf{r}t)$ is arbitrary, the Q-DFT equations are valid for both adiabatic and sudden switching on of the field. To explicate the theory, the application to both a ground and an excited state of the exactly solvable Hooke's atom is provided.

As the 'Quantal Newtonian' first law is a special case of the second law, time-independent Q-DFT, as noted previously, constitutes a special case of time-dependent Q-DFT. Time-independent nondegenerate and degenerate Q-DFT are subsequently described. Nondegenerate Q-DFT is then applied to the Wigner low-density high-electron-correlation regime of a nonuniform density system as represented by the weakly confined Hooke's atom. Finally, the Q–DFT of the Hartree-Fock and Hartree theory approximations are described. Once again, these Q-DFT's are based on the corresponding 'Quantal Newtonian' first law for each approximation.

3.1 Time-Dependent Quantal Density Functional Theory: Part I

In this section we describe the Q-DFT mapping from a system of N electrons in an external field $\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}t) = -\boldsymbol{\nabla} v(\mathbf{r}t)$ to an S system with the same density $\rho(\mathbf{r}t)$. The

Hamiltonian for the corresponding N model noninteracting fermions is

$$\hat{H}_{\mathrm{s}}(t) = \sum_i \hat{h}_{\mathrm{s}}(\mathbf{r}_i t), \tag{3.1}$$

where the Hamiltonian for each fermion is

$$\hat{h}_s(\mathbf{r}t) = -\frac{1}{2}\nabla^2 + v_s(\mathbf{r}t), \tag{3.2}$$

with $v_s(\mathbf{r}t)$ their *effective* potential energy. The time-dependent Schrödinger equation for these fermions is

$$\hat{h}_s(\mathbf{r}t)\phi_i(\mathbf{x}t) = i\frac{\partial \phi_i(\mathbf{x}t)}{\partial t}, \tag{3.3}$$

We assume that the model fermions are subjected to the same external field as that of the interacting system of electrons. Thus, the potential energy $v_{\mathrm{s}}(\mathbf{r}t)$ is the sum of the potential energy $v(\mathbf{r}t)$ of these model fermions in the external field, and an effective 'electron-interaction' potential energy $v_{\mathrm{ee}}(\mathbf{r}t)$ representative of *all* the electron correlations that the S system must account for in order that its density $\rho(\mathbf{r}t)$ be the same as that of the interacting system:

$$v_{\mathrm{s}}(\mathbf{r}t) = v(\mathbf{r}t) + v_{\mathrm{ee}}(\mathbf{r}t). \tag{3.4}$$

The fundamental correlations that must be accounted for by $v_{\mathrm{ee}}(\mathbf{r})$ are those due to the Pauli exclusion principle and Coulomb repulsion. But in addition to these correlations, the S system must also account for Correlation–Kinetic and Correlation–Current–Density effects. These latter correlations arise as a consequence of the differences in kinetic energy and current density between the interacting and noninteracting systems. Thus, for the model system to reproduce the true TD density $\rho(\mathbf{r}t)$, the potential energy $v_{\mathrm{ee}}(\mathbf{r}t)$ must incorporate the effects of four distinct electron correlations. These correlations are then intrinsically incorporated in the wavefunction of the S system which is a Slater determinant $\Phi\{\phi_i\}$ of the orbitals $\phi_i(\mathbf{x}t)$. The assumption of existence of the effective potential energy $v_{\mathrm{ee}}(\mathbf{r}t)$ of the model fermions in which all the many-body effects are incorporated implies that there exists a corresponding *conservative* effective field $\boldsymbol{\mathcal{F}}^{\mathrm{eff}}(\mathbf{r}t)$ such that $\boldsymbol{\mathcal{F}}^{\mathrm{eff}}(\mathbf{r}t) = -\boldsymbol{\nabla} v_{\mathrm{ee}}(\mathbf{r}t)$. The S system is therefore fully defined by this effective field.

3.1.1 Quantal Sources

Here we define quantal sources within the framework of the S system paralleling those of the interacting case discussed in the previous chapter. These sources are the density $\rho(\mathbf{r}t)$, the Dirac spinless single-particle density matrix $\gamma_{\mathrm{s}}(\mathbf{r}\mathbf{r}'t)$, the pair–correlation density $g_s(\mathbf{r}\mathbf{r}'t)$ and from it the *nonlocal Fermi* hole charge distribution $\rho_x(\mathbf{r}\mathbf{r}'t)$, and the current density $\mathbf{j}_s(\mathbf{r}t)$. Since the wavefunction of the S system is a Slater determinant, the definition of the Fermi hole representation of Pauli correlations follows naturally. This then permits a definition of the *nonlocal Coulomb* hole distribution $\rho_c(\mathbf{r}\mathbf{r}'t)$ within the S system framework. The definitions of the sources as expectations of Hermitian operators taken with respect to the Slater determinant results in their being expressed explicitly in terms of the orbitals $\phi_i(\mathbf{x}t)$ of the S system.

A. Electron Density $\rho(\mathbf{r}t)$

The electronic density $\rho(\mathbf{r}t)$ is the expectation of the density operator $\hat{\rho}(\mathbf{r})$ of (2.12):

$$\rho(\mathbf{r}t) = \langle \Phi\{\phi_i\}|\hat{\rho}(\mathbf{r})|\Phi\{\phi_i\}\rangle = \sum_\sigma \sum_i |\phi_i(\mathbf{x}t)|^2, \tag{3.5}$$

and satisfies the normalization condition

$$\int \rho(\mathbf{r}t)d\mathbf{r} = N. \tag{3.6}$$

Note that the density is the same as for the interacting system.

B. Dirac Spinless Single–Particle Density Matrix $\gamma_s(\mathbf{r}\mathbf{r}'t)$

The Dirac spinless single-particle density matrix $\gamma_s(\mathbf{r}\mathbf{r}'t)$ is the expectation of the density matrix operator $\hat{\gamma}(\mathbf{r}\mathbf{r}')$ of (2.17):

$$\gamma_s(\mathbf{r}\mathbf{r}'t) = \langle \Phi\{\phi_i\}|\hat{\gamma}(\mathbf{r}\mathbf{r}')|\Phi\{\phi_i\}\rangle = \sum_\sigma \sum_i \phi_i^*(\mathbf{r}\sigma, t)\phi_i(\mathbf{r}'\sigma, t). \tag{3.7}$$

The properties of the Dirac density matrix are that

$$\gamma_s(\mathbf{r}\mathbf{r}t) = \rho(\mathbf{r}t), \tag{3.8}$$

$$\gamma_s(\mathbf{r}'\mathbf{r}t) = \gamma_s^*(\mathbf{r}\mathbf{r}'t), \tag{3.9}$$

and that it is idempotent:

$$\int \gamma_s(\mathbf{r}\mathbf{r}''t)\gamma_s(\mathbf{r}''\mathbf{r}'t)d\mathbf{r}'' = \gamma_s(\mathbf{r}\mathbf{r}'t). \tag{3.10}$$

The interacting system density matrix of (2.15, 2.16) and the Dirac density matrix are inequivalent. It is only their diagonal matrix elements that are equal.

C. Pair–Correlation Density $g_s(\mathbf{r}\mathbf{r}'t)$; Fermi $\rho_x(\mathbf{r}\mathbf{r}'t)$ and Coulomb $\rho_c(\mathbf{r}\mathbf{r}'t)$ Holes

The pair–correlation density $g_s(\mathbf{r}\mathbf{r}'t)$ is the ratio of the expectations of the pair-correlation and density operators of (2.28) and (2.12), respectively,

$$g_s(\mathbf{r}\mathbf{r}'t) = \frac{\langle \Phi\{\phi_i\}|\hat{P}(\mathbf{r}\mathbf{r}')|\Phi\{\phi_i\}\rangle}{\rho(\mathbf{r}t)}, \tag{3.11}$$

and satisfies the condition

$$\int g_s(\mathbf{r}\mathbf{r}'t)d\mathbf{r}' = N - 1 \tag{3.12}$$

for arbitrary electron positron $\mathbf{r}$ at each instant of time.

As was the case for the interacting system, the pair–correlation density $g_s(\mathbf{r}\mathbf{r}'t)$ may also be separated into its local and nonlocal components as

$$g_s(\mathbf{r}\mathbf{r}'t) = \rho(\mathbf{r}'t) + \rho_x(\mathbf{r}\mathbf{r}'t), \tag{3.13}$$

where $\rho_x(\mathbf{r}\mathbf{r}'t)$ is the *Fermi* hole charge distribution. The Fermi hole [40] is the reduction in density at $\mathbf{r}'$ due to the presence of an electron of parallel spin at $\mathbf{r}$ for each instant of time. It represents the reduction in probability of two electrons of *parallel* spin approaching each other. The Fermi hole is derived in terms of the S system orbitals to be

$$\begin{aligned}\rho_x(\mathbf{r}\mathbf{r}'t) &= -\frac{\displaystyle\sum_{i,j(\text{spin } j\|\text{spin } i)} \phi_i^*(\mathbf{r}t)\phi_j^*(\mathbf{r}'t)\phi_i(\mathbf{r}'t)\phi_j(\mathbf{r}t)}{\displaystyle\sum_\sigma \sum_k \phi_k^*(\mathbf{x}t)\phi_k(\mathbf{x}t)} \\ &= -\frac{|\gamma_s(\mathbf{r}\mathbf{r}'t)|^2}{2\rho(\mathbf{r}t)},\end{aligned} \tag{3.14}$$

and satisfies the following sum rules for arbitrary electron position $\mathbf{r}$ at each instant of time:

$$\int \rho_x(\mathbf{r}\mathbf{r}'t)d\mathbf{r}' = -1 \tag{3.15}$$

$$\rho_x(\mathbf{r}\mathbf{r}t) = -\rho(\mathbf{r}t)/2, \tag{3.16}$$

$$\rho_x(\mathbf{r}\mathbf{r}'t) \leq 0. \tag{3.17}$$

Note that the self-interaction term in the Fermi hole is cancelled by a similar term in the density, and as such there is no self-interaction in the pair–correlation density. The S system pair–correlation function $h_s(\mathbf{r}\mathbf{r}'t)$ is defined as

$$h_s(\mathbf{r}\mathbf{r}'t) = \frac{g_s(\mathbf{r}\mathbf{r}'t)}{\rho(\mathbf{r}'t)}, \tag{3.18}$$

and it is symmetrical in a interchange of $\mathbf{r}$ and $\mathbf{r}'$:

$$h_s(\mathbf{r}\mathbf{r}'t) = h_s(\mathbf{r}'\mathbf{r}t). \tag{3.19}$$

This property of symmetry is employed in various proofs.

Since in the S system, the effects of Pauli correlation can be explicitly accounted for via the Fermi hole, it is possible to define a *Coulomb* hole $\rho_c(\mathbf{r}\mathbf{r}'t)$ which is a nonlocal charge distribution representative of Coulomb correlations. The Coulomb hole at $\mathbf{r}'$ for an electron at $\mathbf{r}$ at each instant of time is defined as

$$\rho_c(\mathbf{r}\mathbf{r}'t) = g(\mathbf{r}\mathbf{r}'t) - g_s(\mathbf{r}\mathbf{r}'t) \tag{3.20}$$

$$= \rho_{xc}(\mathbf{r}\mathbf{r}'t) - \rho_x(\mathbf{r}\mathbf{r}'t), \tag{3.21}$$

where $g(\mathbf{r}\mathbf{r}'t)$ and $\rho_{xc}(\mathbf{r}\mathbf{r}'t)$ are the interacting system pair–correlation density and Fermi–Coulomb hole charge, respectively. As the total charge of the Fermi–Coulomb and Fermi holes is the same (see (2.36) and (3.15)), the charge sum rule satisfied by the Coulomb hole for each electron position $\mathbf{r}$ at each instant of time is

$$\int \rho_c(\mathbf{r}\mathbf{r}'t)d\mathbf{r}' = 0. \tag{3.22}$$

D. Current Density $\mathbf{j}_s(\mathbf{r}t)$

The current density $\mathbf{j}_s(\mathbf{r}t)$ which is the expectation of the current density operator $\hat{\mathbf{j}}(\mathbf{r})$ of (2.42) is

$$\begin{aligned}\mathbf{j}_s(\mathbf{r}t) &= \langle\Phi\{\phi_i\}|\hat{\mathbf{j}}(\mathbf{r})|\Phi\{\phi_i\}\rangle \\ &= \frac{1}{2i}\sum_\sigma\sum_k\left[\phi_k^*(\mathbf{x}t)\nabla\phi_k(\mathbf{x}t) - \phi_k(\mathbf{x}t)\nabla\phi_k^*(\mathbf{x}t)\right],\end{aligned} \tag{3.23}$$

or it may be expressed in terms of the Dirac density matrix as

$$\mathbf{j}_s(\mathbf{r}t) = \frac{i}{2}[\nabla' - \nabla'']\gamma_s(\mathbf{r}'\mathbf{r}''t)|_{\mathbf{r}'=\mathbf{r}''=\mathbf{r}}. \tag{3.24}$$

The quantal sources defined above then give rise to 'classical' fields corresponding to the S system

3.1.2 Fields

The fields required for the description of the potential energy $v_{ee}(\mathbf{r}t)$ of the S system and total (nonconserved) energy $E(t)$ are the electron-interaction field $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}t)$ of (2.43), or its Hartree $\boldsymbol{\mathcal{E}}_H(\mathbf{r}t)$, *Pauli* $\boldsymbol{\mathcal{E}}_x(\mathbf{r}t)$ and *Coulomb* $\boldsymbol{\mathcal{E}}_c(\mathbf{r}t)$ components, the

Correlation–Kinetic $\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r}t)$, and *Correlation–Currrent–Density* $\boldsymbol{\mathcal{J}}_c(\mathbf{r}t)$ fields. To ensure that the model S system density $\rho(\mathbf{r}t)$ is the same as that of the interacting case, the difference in kinetic energy and current density between the interacting and noninteracting systems must be accounted for. Thus, the fields describing the S system are in terms of the properties of both systems. As noted previously there must therefore exist an effective field $\boldsymbol{\mathcal{F}}^{\mathrm{eff}}(\mathbf{r}t)$ in which the potential energy of the model fermions is $v_{\mathrm{ee}}(\mathbf{r}t)$.

A. Electron-Interaction Field $\boldsymbol{\mathcal{E}}_{\mathrm{ee}}(\mathbf{r}t)$, and Its Hartree $\boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r}t)$, Pauli $\boldsymbol{\mathcal{E}}_{\mathrm{x}}(\mathbf{r}t)$, and Coulomb $\boldsymbol{\mathcal{E}}_{\mathrm{c}}(\mathbf{r}t)$ Components

We begin by further subdividing the electron–interaction field $\boldsymbol{\mathcal{E}}_{\mathrm{ee}}(\mathbf{r}t)$ (see (2.43)–(2.48)) of the interacting system. The S system electron–interaction field $\boldsymbol{\mathcal{E}}_{\mathrm{ee,s}}(\mathbf{r}t)$ is obtained from its quantal source, the pair–correlation density $g_{\mathrm{s}}(\mathbf{r}\mathbf{r}'t)$ via Coulomb's law as

$$\boldsymbol{\mathcal{E}}_{\mathrm{ee,s}}(\mathbf{r}t) = \int \frac{g_{\mathrm{s}}(\mathbf{r}\mathbf{r}'t)(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}'. \tag{3.25}$$

This field may be rewritten in terms of a corresponding electron-interaction 'force' and the density $\rho(\mathbf{r}t)$ as

$$\boldsymbol{\mathcal{E}}_{ee,s}(\mathbf{r}t) = \frac{\mathbf{e}_{ee,s}(\mathbf{r}t)}{\rho(\mathbf{r}t)}, \tag{3.26}$$

where $\mathbf{e}_{ee,s}(\mathbf{r}t)$ is determined via Coulomb's law from the pair function $P_s(\mathbf{r}\mathbf{r}'t) = \langle\Phi\{\phi_i\}|\hat{P}(\mathbf{r}\mathbf{r}')|\Phi\{\phi_i\}\rangle$ obtained from the Slater determinant $\Phi\{\phi_i\}$ with $\hat{P}(\mathbf{r}\mathbf{r}')$ the pair–correlation operator of (2.28). Thus, the 'force' is

$$\mathbf{e}_{ee,s}(\mathbf{r}t) = \int \frac{P_s(\mathbf{r}\mathbf{r}'t)(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}'. \tag{3.27}$$

(The quantal source of the field $\boldsymbol{\mathcal{E}}_{ee,s}(\mathbf{r}t)$ can thus also be thought of as being the pair function $P_s(\mathbf{r}\mathbf{r}'t)$.)

On employing the decomposition (3.13), the field $\boldsymbol{\mathcal{E}}_{ee,s}(\mathbf{r}t)$ may then be written as the sum

$$\boldsymbol{\mathcal{E}}_{ee,s}(\mathbf{r}t) = \boldsymbol{\mathcal{E}}_H(\mathbf{r}t) + \boldsymbol{\mathcal{E}}_x(\mathbf{r}t), \tag{3.28}$$

where the Hartree field $\boldsymbol{\mathcal{E}}_H(\mathbf{r}t)$ is defined by (2.47), and the Pauli field $\boldsymbol{\mathcal{E}}_x(\mathbf{r}t)$ due to the Fermi hole charge $\rho_x(\mathbf{r}\mathbf{r}'t)$ is

$$\boldsymbol{\mathcal{E}}_x(\mathbf{r}t) = \int \frac{\rho_x(\mathbf{r}\mathbf{r}'t)(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}', \tag{3.29}$$

The interacting system electron-interaction field $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}t)$ can on employing the definition of the Coulomb hole $\rho_c(\mathbf{r}\mathbf{r}'t)$ of (3.21) be then written as

$$\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}t) = \boldsymbol{\mathcal{E}}_{ee,s}(\mathbf{r}t) + \boldsymbol{\mathcal{E}}_c(\mathbf{r}t), \tag{3.30}$$

so that with (3.28) we have

$$\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}t) = \boldsymbol{\mathcal{E}}_H(\mathbf{r}t) + \boldsymbol{\mathcal{E}}_x(\mathbf{r}t) + \boldsymbol{\mathcal{E}}_c(\mathbf{r}t), \tag{3.31}$$

where the Coulomb field $\boldsymbol{\mathcal{E}}_{\mathrm{c}}(\mathbf{r}t)$ due to the Coulomb hole charge $\rho_{\mathrm{c}}(\mathbf{r}\mathbf{r}'t)$ is

$$\boldsymbol{\mathcal{E}}_{\mathrm{c}}(\mathbf{r}t) = \int \frac{\rho_{\mathrm{c}}(\mathbf{r}\mathbf{r}'t)(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}'. \tag{3.32}$$

In this manner, Pauli correlations are represented by the Pauli field $\boldsymbol{\mathcal{E}}_{\mathrm{x}}(\mathbf{r}t)$, and Coulomb correlations beyond those incorporated in the Hartree field $\boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r}t)$ by the Coulomb field $\boldsymbol{\mathcal{E}}_{\mathrm{c}}(\mathbf{r}t)$. Since both the Fermi and Coulomb holes are nonlocal sources, the fields $\boldsymbol{\mathcal{E}}_{\mathrm{x}}(\mathbf{r}t)$ and $\boldsymbol{\mathcal{E}}_{\mathrm{c}}(\mathbf{r}t)$ are in general not conservative.

B. Kinetic $\boldsymbol{\mathcal{Z}}_{\mathrm{s}}(\mathbf{r}t)$ and Correlation–Kinetic $\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r}t)$ Fields

The S system kinetic field $\boldsymbol{\mathcal{Z}}_{\mathrm{s}}(\mathbf{r}t)$ is defined in a manner similar to the kinetic field $\boldsymbol{\mathcal{Z}}(\mathbf{r}t)$ (2.51) of the interacting system, but its quantal source is the Dirac density matrix $\gamma_{\mathrm{s}}(\mathbf{r}\mathbf{r}'t)$. Thus

$$\boldsymbol{\mathcal{Z}}_{\mathrm{s}}(\mathbf{r}t) = \frac{\mathbf{z}_{\mathrm{s}}(\mathbf{r}t; [\gamma_{\mathrm{s}}])}{\rho(\mathbf{r}t)}, \tag{3.33}$$

where the S system kinetic 'force' is defined by its component $z_{\mathrm{s},\alpha}(\mathbf{r}t)$ as

$$z_{\mathrm{s},\alpha}(\mathbf{r}t) = 2\sum_{\beta} \frac{\partial}{\partial r_\beta} t_{\mathrm{s},\alpha\beta}(\mathbf{r}t), \tag{3.34}$$

and where $t_{\mathrm{s},\alpha\beta}(\mathbf{r}t)$ is the S system kinetic-energy-density tensor defined in turn as

$$t_{s,\alpha\beta}(\mathbf{r}t) = \frac{1}{4}\left[\frac{\partial^2}{\partial r'_\alpha \partial r''_\beta} + \frac{\partial^2}{\partial r'_\beta \partial r''_\alpha}\right] \gamma_{\mathrm{s}}(\mathbf{r}'\mathbf{r}''t)|_{\mathbf{r}'=\mathbf{r}''=\mathbf{r}}. \tag{3.35}$$

The kinetic field $\boldsymbol{\mathcal{Z}}_{\mathrm{s}}(\mathbf{r}t)$ leads to the S system kinetic energy density and hence to the kinetic energy of the noninteracting fermions (see Sect. 3.1.3).

The *Correlation–Kinetic* field $\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r}t)$ is defined as the difference between the interacting and noninteracting system kinetic fields:

$$\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r}t) = \boldsymbol{\mathcal{Z}}_{\mathrm{s}}(\mathbf{r}t) - \boldsymbol{\mathcal{Z}}(\mathbf{r}t). \tag{3.36}$$

Thus, $\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r})$ is the correlation component of the interacting system kinetic field $\boldsymbol{\mathcal{Z}}(\mathbf{r}t)$.

C. Current Density $\mathcal{J}_s(\mathbf{r}t)$ and Correlation–Current–Density $\mathcal{J}_c(\mathbf{r}t)$ Fields

The S system current density field $\mathcal{J}_s(\mathbf{r}t)$ is defined in a manner similar to that of the interacting system field $\mathcal{J}(\mathbf{r}t)$ of (2.54) as

$$\mathcal{J}_s(\mathbf{r}t) = \frac{1}{\rho(\mathbf{r}t)}\frac{\partial}{\partial t}\mathbf{j}_s(\mathbf{r}t), \tag{3.37}$$

where $\mathbf{j}_s(\mathbf{r}t)$ is the corresponding current density. The Correlation–Current–Density field $\mathcal{J}_c(\mathbf{r}t)$ which represents the difference in current densities of the interacting and noninteracting systems is then

$$\mathcal{J}_c(\mathbf{r}t) = \mathcal{J}_s(\mathbf{r}t) - \mathcal{J}(\mathbf{r}t), \tag{3.38}$$

where $\mathcal{J}(\mathbf{r}t)$ is the interacting system current density field.

D. Differential Density Field $\mathcal{D}(\mathbf{r}t)$

In the S system there also exists a differential density field $\mathcal{D}(\mathbf{r}t)$. The definition of this field is the same as for the interacting case (2.49), and since the densities of the two systems are the same, the fields are equivalent.

The fields $\mathcal{E}_{ee}(\mathbf{r}t)$, $\mathcal{E}_x(\mathbf{r}t)$, $\mathcal{E}_c(\mathbf{r}t)$, $\mathcal{Z}_s(\mathbf{r}t)$, $\mathcal{Z}_{t_c}(\mathbf{r}t)$, and $\mathcal{J}_c(\mathbf{r}t)$ are in general not conservative. However, the sums $[\mathcal{Z}_s(\mathbf{r}t) + \mathcal{J}_s(\mathbf{r}t)]$ and $[\mathcal{E}_{ee}(\mathbf{r}t) + \mathcal{Z}_{t_c}(\mathbf{r}t) + \mathcal{J}_c(\mathbf{r}t)]$ are conservative so that

$$\nabla \times [\mathcal{Z}_s(\mathbf{r}t) + \mathcal{J}_s(\mathbf{r}t)] = 0, \tag{3.39}$$

and

$$\nabla \times \left[\mathcal{E}_{ee}(\mathbf{r}t) + \mathcal{Z}_{t_c}(\mathbf{r}t) + \mathcal{J}_c(\mathbf{r}t)\right] = 0. \tag{3.40}$$

The condition of (3.39) follows from the S system 'Quantal Newtonian' second law proved in Appendix E. The proof of (3.40) is given in Sect. 3.1.4 For certain symmetries, or when such symmetry is imposed, the individual fields may separately be conservative so that then $\nabla \times \mathcal{E}_x(\mathbf{r}t) = 0$, $\nabla \times \mathcal{E}_c(\mathbf{r}t) = 0$, $\nabla \times \mathcal{Z}_s(\mathbf{r}t) = 0$, $\nabla \times \mathcal{J}_s(\mathbf{r}t) = 0$, $\nabla \times \mathcal{Z}_{t_c}(\mathbf{r}t) = 0$, $\nabla \times \mathcal{J}_c(\mathbf{r}t) = 0$.

3.1.3 *Total Energy and Components in Terms of Quantal Sources and Fields*

As was the case for the interacting system, the energy components in the S system framework may be expressed directly in terms of the quantal sources, or in integral virial form in terms of the respective fields. The latter expressions are independent of whether or not the fields are conservative.

A. Electron-Interaction Potential Energy $E_{\mathrm{ee}}(t)$, and Its Hartree $E_{\mathrm{H}}(t)$, Pauli $E_{\mathrm{x}}(t)$, and Coulomb $E_{\mathrm{c}}(t)$ Energy Components

We first write the electron-interaction energy $E_{\mathrm{ee}}(t)$ of the interacting system in terms of its components. The S system electron-interaction potential energy $E_{\mathrm{ee,s}}(t)$ is the energy of interaction between the density $\rho(\mathbf{r}t)$ and the pair–correlation density $g_{\mathrm{s}}(\mathbf{r}\mathbf{r}'t)$:

$$E_{\mathrm{ee,s}}(t) = \frac{1}{2}\iint \frac{\rho(\mathbf{r}t)g_{\mathrm{s}}(\mathbf{r}\mathbf{r}'t)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}', \tag{3.41}$$

which on employing the decomposition (3.13) may be written as the sum

$$E_{\mathrm{ee,s}}(t) = E_{\mathrm{H}}(t) + E_{\mathrm{x}}(t), \tag{3.42}$$

where the Hartree energy $E_{\mathrm{H}}(t)$ is defined by (2.61), and the exchange or Pauli energy $E_{\mathrm{x}}(t)$ is the energy of interaction between the density $\rho(\mathbf{r}t)$ and the Fermi hole charge $\rho_{\mathrm{x}}(\mathbf{r}\mathbf{r}'t)$:

$$E_{\mathrm{x}}(t) = \frac{1}{2}\iint \frac{\rho(\mathbf{r}t)\rho_{\mathrm{x}}(\mathbf{r}\mathbf{r}'t)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'. \tag{3.43}$$

These energies may be expressed in terms of fields by following the procedure of Sect. 2.4 and employing the symmetry property of the S system pair–correlation function $h_{\mathrm{s}}(\mathbf{r}\mathbf{r}'t)$. Thus, we obtain

$$E_{\mathrm{ee,s}}(t) = \int \rho(\mathbf{r}t)\mathbf{r}\cdot\boldsymbol{\mathcal{E}}_{ee,s}(\mathbf{r}t)d\mathbf{r}, \tag{3.44}$$

$$E_{\mathrm{x}}(t) = \int \rho(\mathbf{r}t)\mathbf{r}\cdot\boldsymbol{\mathcal{E}}_{\mathrm{x}}(\mathbf{r}t)d\mathbf{r}, \tag{3.45}$$

and $E_{\mathrm{H}}(t)$ is defined in terms of $\boldsymbol{\mathcal{E}}_{\mathrm{H}}(t)$ as in (2.66). Next, by employing the definition of the Coulomb hole $\rho_{\mathrm{c}}(\mathbf{r}\mathbf{r}'t)$ of (3.21), the interacting system electron-interaction energy $E_{\mathrm{ee}}(t)$ of (2.59) may be written in terms of its Hartree, Pauli, and Coulomb components as

$$E_{\mathrm{ee}}(t) = E_{\mathrm{H}}(t) + E_{\mathrm{x}}(t) + E_{\mathrm{c}}(t), \tag{3.46}$$

where the Coulomb energy $E_{\mathrm{c}}(t)$ is the energy of interaction between the density $\rho(\mathbf{r}t)$ and the Coulomb hole charge $\rho_{\mathrm{c}}(\mathbf{r}\mathbf{r}'t)$:

$$E_{\mathrm{c}} = \frac{1}{2}\iint \frac{\rho(\mathbf{r}t)\rho_{\mathrm{c}}(\mathbf{r}\mathbf{r}'t)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}', \tag{3.47}$$

or equivalently in terms of the Coulomb field $\boldsymbol{\mathcal{E}}_{\mathrm{c}}(\mathbf{r}t)$ as

$$E_{\mathrm{c}}(t) = \int \rho(\mathbf{r}t)\mathbf{r}\cdot\boldsymbol{\mathcal{E}}_{\mathrm{c}}(\mathbf{r}t)d\mathbf{r}. \tag{3.48}$$

B. Kinetic $T_s(t)$ and Correlation–Kinetic $T_c(t)$ Energies

The S system kinetic energy $T_s(t)$ may be expressed in terms of its quantal source, the Dirac density matrix $\gamma_s(\mathbf{r}\mathbf{r}'t)$, as

$$T_s(t) = \int t_s(\mathbf{r}t) d\mathbf{r}, \tag{3.49}$$

where the kinetic energy density $t_s(\mathbf{r}t)$ is the trace of the kinetic-energy-density tensor $t_{s,\alpha\beta}(\mathbf{r}t)$:

$$t_s(\mathbf{r}t) = \sum_{\alpha} t_{s,\alpha\alpha}(\mathbf{r}t) = \frac{1}{2} \nabla_{\mathbf{r}'} \cdot \nabla_{\mathbf{r}''} \gamma_s(\mathbf{r}'\mathbf{r}''t)|_{\mathbf{r}'=\mathbf{r}''=\mathbf{r}}. \tag{3.50}$$

It may also be expressed in terms of the kinetic field $\mathcal{Z}_s(\mathbf{r}t)$ and 'force' $z_s(\mathbf{r}t)$ as

$$T_s(t) = -\frac{1}{2} \int \rho(\mathbf{r}t) \mathbf{r} \cdot \mathcal{Z}_s(\mathbf{r}t) d\mathbf{r} \tag{3.51}$$

$$= -\frac{1}{2} \int \mathbf{r} \cdot z_s(\mathbf{r}t) d\mathbf{r}. \tag{3.52}$$

The proof of the equivalence of (3.49) and (3.51) is again based on the vanishing of the Dirac density matrix on the boundaries at infinity. The energy $T_s(t)$ may also be obtained directly in terms of the S system orbitals $\phi_i(\mathbf{x}t)$ as the expectation

$$T_s(t) = \langle \Phi\{\phi_i\} | \hat{T} | \Phi\{\phi_i\} \rangle = \sum_i \sum_{\sigma} \langle \phi_i(\mathbf{r}\sigma, t)| - \frac{1}{2} \nabla^2 | \phi_i(\mathbf{r}\sigma, t) \rangle. \tag{3.53}$$

The Correlation–Kinetic energy $T_c(t)$ is the correlation contribution to the kinetic energy:

$$T_c(t) = T(t) - T_s(t), \tag{3.54}$$

and may be expressed in terms of the Correlation–Kinetic field $\mathcal{Z}_{t_c}(\mathbf{r}t)$ as

$$T_c(t) = \frac{1}{2} \int \rho(\mathbf{r}t) \mathbf{r} \cdot \mathcal{Z}_{t_c}(\mathbf{r}t) d\mathbf{r}. \tag{3.55}$$

C. External Potential Energy $E_{\text{ext}}(t)$

Since the electrons in the interacting case, and the noninteracting fermions of the S system experience the same external field $\mathcal{F}^{\text{ext}}(\mathbf{r}t)$, and are constrained to have the same density $\rho(\mathbf{r}t)$, the expression for the external potential energy $E_{\text{ext}}(t)$ for both systems is the same:

$$E_{\text{ext}}(t) = \int \rho(\mathbf{r}t) v(\mathbf{r}t) d\mathbf{r}. \tag{3.56}$$

In a manner similar to that of the interacting system of electrons (see Sect. 2.5), the external potential $v(\mathbf{r})$, and hence the energy component $E_{\text{ext}}(t)$, can be expressed in terms of all the fields present within the S system. This follows from the 'Quantal Newtonian' second law for the S system described in the next section.

As noted previously in Sect. 3.1.2, the S system must account for correlations due to the Pauli exclusion principle, Coulomb repulsion, Correlation-Kinetic, and Correlation-Current-Density effects. The fields $\boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}t)$ and $\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r}t)$ give rise to the electron-interaction $E_{\text{ee}}(t)$ and Correlation-Kinetic $T_{\text{c}}(t)$ energy, respectively. The field $\boldsymbol{\mathcal{J}}_{\text{c}}(\mathbf{r}t)$ does not contribute to the total energy directly. However, it does so indirectly because it contributes to the potential $v_{\text{ee}}(\mathbf{r}t)$ as shown in the next section. The proof that there is no direct contribution to the total energy follows readily.

As in Sect. 2.6, it can be shown that

$$\int \rho(\mathbf{r}t)\mathbf{r} \cdot \boldsymbol{\mathcal{J}}_{\text{s}}(\mathbf{r}t)d\mathbf{r} = \frac{1}{2}\frac{\partial^2}{\partial t^2}\int r^2 \rho(\mathbf{r}t)d\mathbf{r}, \tag{3.57}$$

where the continuity equation $\boldsymbol{\nabla} \cdot \mathbf{j}_s(\mathbf{r}t) = -\partial\rho(\mathbf{r}t)/\partial t$ is employed.

Therefore, together with (2.88) we have

$$\int \rho(\mathbf{r}t)\mathbf{r} \cdot \boldsymbol{\mathcal{J}}_{\text{c}}(\mathbf{r}t)d\mathbf{r} = 0. \tag{3.58}$$

Thus, the total energy $E(t)$ may be expressed as

$$E(t) = T_{\text{s}}(t) + \int \rho(\mathbf{r}t)v(\mathbf{r}t)d\mathbf{r} + E_{\text{ee}}(t) + T_{\text{c}}(t), \tag{3.59}$$

or by employing the decomposition of $E_{\text{ee}}(t)$ as

$$E(t) = T_{\text{s}}(t) + \int \rho(\mathbf{r}t)v(\mathbf{r}t)d\mathbf{r} + E_{\text{H}}(t) + E_{\text{x}}(t) + E_{\text{c}}(t) + T_{\text{c}}(t). \tag{3.60}$$

In this manner, the *separate* contributions of the various electron correlations to the total energy are clearly delineated.

3.1.4 The S System 'Quantal Newtonian' Second Law

The 'Quantal Newtonian' second law for the S system of noninteracting fermions derived in Appendix E is

$$\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}t) + \boldsymbol{\mathcal{F}}_s^{\text{int}}(\mathbf{r}t) = \boldsymbol{\mathcal{J}}_s(\mathbf{r}t) = \frac{1}{\rho(\mathbf{r}t)}\frac{\partial \mathbf{j}_s(\mathbf{r}t)}{\partial t}, \tag{3.61}$$

where *each* model fermion experiences the *external* field $\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}t)$:

$$\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}t) = -\boldsymbol{\nabla} v(\mathbf{r}t), \tag{3.62}$$

and an *internal* field $\boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r}t)$:

$$\boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r}t) = -\boldsymbol{\nabla} v_{\mathrm{ee}}(\mathbf{r}t) - \boldsymbol{\mathcal{D}}(\mathbf{r}t) - \boldsymbol{\mathcal{Z}}_s(\mathbf{r}t), \tag{3.63}$$

with the component fields $\boldsymbol{\mathcal{D}}(\mathbf{r}t)$, $\boldsymbol{\mathcal{Z}}_s(\mathbf{r}t)$, and $\boldsymbol{\mathcal{J}}_s(\mathbf{r}t)$ being defined previously. The response of the model fermion to the external and internal fields is the S system current density field $\boldsymbol{\mathcal{J}}_s(\mathbf{r}t)$.

From the 'Quantal Newtonian' second law of (3.61), the external potential $v(\mathbf{r}t)$ can be expressed in terms of the various S system fields as

$$v(\mathbf{r}t) = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{F}}_s(\mathbf{r}'t) \cdot d\boldsymbol{\ell}', \tag{3.64}$$

where

$$\boldsymbol{\mathcal{F}}_s(\mathbf{r}t) = \boldsymbol{\mathcal{J}}_s(\mathbf{r}t) - \boldsymbol{\mathcal{F}}_s^{\mathrm{int}}(\mathbf{r}t) \tag{3.65}$$

$$= \boldsymbol{\mathcal{J}}_s(\mathbf{r}t) + \boldsymbol{\nabla} v_{\mathrm{ee}}(\mathbf{r}t) + \boldsymbol{\mathcal{D}}(\mathbf{r}t) + \boldsymbol{\mathcal{Z}}_s(\mathbf{r}t). \tag{3.66}$$

Thus, the external potential $v(\mathbf{r}t)$ can be interpreted solely in terms of S system properties as the work done in the conservative field $\boldsymbol{\mathcal{F}}_s(\mathbf{r}t)$. This work done is path-independent since $\boldsymbol{\nabla} \times \boldsymbol{\mathcal{F}}_s(\mathbf{r}t) = 0$. The expression for $v(\mathbf{r}t)$ of (3.64) can be employed to determine the external energy $E_{\mathrm{ext}}(t)$. Of course, with an assumed external field $\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}t)$, the energy $E_{\mathrm{ext}}(t)$ can be obtained directly from (3.56).

In Q-DFT, one assumes the external field $\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}t)$ of the interacting and model fermions to be the same. In order to fully define the S system Hamiltonian $\hat{h}_s(\mathbf{r}t)$ of (3.2), what remains then is the determination of the electron-interaction potential energy $v_{\mathrm{ee}}(\mathbf{r}t)$. This is accomplished by further ensuring that the density $\rho(\mathbf{r}t)$, the basic variable, is the same for the interacting and model systems. *For there to be such a local potential energy function $v_{\mathrm{ee}}(\mathbf{r}t)$, there must exist an effective field $\boldsymbol{\mathcal{F}}^{\mathrm{eff}}(\mathbf{r}t)$ which encompasses all the many-body effects the S system must account for*. Hence, in the 'Quantal Newtonian' second law (3.61) we associate the term $-\boldsymbol{\nabla} v_{\mathrm{ee}}(\mathbf{r}t)$ with this effective field:

$$\boldsymbol{\mathcal{F}}^{\mathrm{eff}}(\mathbf{r}t) = -\boldsymbol{\nabla} v_{\mathrm{ee}}(\mathbf{r}t). \tag{3.67}$$

As the curl of the gradient of a scalar function vanishes, the effective field $\boldsymbol{\mathcal{F}}^{\mathrm{eff}}(\mathbf{r}t)$ is conservative.

In the following section we determine $\boldsymbol{\mathcal{F}}^{\mathrm{eff}}(\mathbf{r}t)$ via the 'Quantal Newtonian' second law for the interacting and model fermions.

3.1.5 *Effective Field* $\boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r}t)$ *and Electron-Interaction Potential Energy* $v_{\text{ee}}(\mathbf{r}t)$

The electron-interaction potential energy $v_{\text{ee}}(\mathbf{r}t)$ of the model fermions, whose density $\rho(\mathbf{r}t)$ is the same as of the interacting system is defined as follows. *It is the work done at each instant of time to move a model fermion from some reference point at infinity to its position at* $\mathbf{r}$ *in the force of the conservative effective field* $\boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r}t)$:

$$v_{\text{ee}}(\mathbf{r}t) = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r}'t) \cdot d\boldsymbol{\ell}', \tag{3.68}$$

where

$$\boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r}t) = \boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}t) + \boldsymbol{\mathcal{Z}}_{\text{t}_\text{c}}(\mathbf{r}t) + \boldsymbol{\mathcal{J}}_{\text{c}}(\mathbf{r}t). \tag{3.69}$$

This work done is *path–independent* since $\nabla \times \boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r}t) = 0$. The vanishing of the curl implies (3.68) provided $\boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r}t)$ is smooth in a simply connected region. (A function is smooth if it is continuous, differentiable, and has continuous first derivatives. By definition, a region is simply connected if any closed curve lying entirely within this region can shrink down to a point without leaving the region.) The component fields $\boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}t)$, $\boldsymbol{\mathcal{Z}}_{\text{t}_\text{c}}(\mathbf{r}t)$, and $\boldsymbol{\mathcal{J}}_{\text{c}}(\mathbf{r}t)$ are in general not conservative. Their sum always is.

The proof of the above description of the potential energy $v_{\text{ee}}(\mathbf{r}t)$ is as follows. The 'Quantal Newtonian' second law for the interacting system of electrons is (2.75) (see Appendix A)

$$\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}t) + \boldsymbol{\mathcal{F}}^{\text{int}}(\mathbf{r}t) = \boldsymbol{\mathcal{J}}(\mathbf{r}t), \tag{3.70}$$

where the internal field $\boldsymbol{\mathcal{F}}^{\text{int}}(\mathbf{r}t)$ is

$$\boldsymbol{\mathcal{F}}^{\text{int}}(\mathbf{r}t) = \boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}t) - \boldsymbol{\mathcal{D}}(\mathbf{r}t) - \boldsymbol{\mathcal{Z}}(\mathbf{r}t). \tag{3.71}$$

The 'Quantal Newtonian' second law for the S system is (3.61) (see Appendix E)

$$\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}t) + \boldsymbol{\mathcal{F}}_s^{\text{int}}(\mathbf{r}t) = \boldsymbol{\mathcal{J}}_s(\mathbf{r}t), \tag{3.72}$$

where the corresponding internal field is

$$\boldsymbol{\mathcal{F}}_s^{\text{int}}(\mathbf{r}t) = -\nabla v_{\text{ee}}(\mathbf{r}t) - \boldsymbol{\mathcal{D}}(\mathbf{r}t) - \boldsymbol{\mathcal{Z}}_s(\mathbf{r}t). \tag{3.73}$$

Employing the constraints that the external field $\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}t)$ and the density $\rho(\mathbf{r}t)$ are the same for the interacting and model systems in (3.70) and (3.72) one obtains

$$-\nabla v_{\text{ee}}(\mathbf{r}t) = \boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}t) + [\boldsymbol{\mathcal{Z}}_s(\mathbf{r}t) - \boldsymbol{\mathcal{Z}}(\mathbf{r}t)] + [\boldsymbol{\mathcal{J}}_s(\mathbf{r}t) - \boldsymbol{\mathcal{J}}(\mathbf{r}t)] \tag{3.74}$$

$$= \boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}t) + \boldsymbol{\mathcal{Z}}_{\text{t}_\text{c}}(\mathbf{r}t) + \boldsymbol{\mathcal{J}}_{\text{c}}(\mathbf{r}t) = \boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r}t), \tag{3.75}$$

from which the definition for $v_{ee}(\mathbf{r}t)$ of (3.68) and (3.69) follows.

In addition to providing a rigorous physical interpretation for the potential energy $v_{ee}(\mathbf{r}t)$, the above derivation leads to insights, and relates the interacting and model systems in a rigorous quantum-mechanical sense. It shows that the electron correlations due to the Pauli exclusion principle and Coulomb repulsion are accounted for in the mapping to the S system via the electron-interaction field $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}t)$. Further, what emerges from the derivation is that in this mapping to the model system, one must additionally account for the difference in kinetic energy and current density between the interacting and model systems. This in turn is accomplished via the Correlation-Kinetic $\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r}t)$ and Correlation-Current-Density $\boldsymbol{\mathcal{J}}_c(\mathbf{r}t)$ fields.

For systems of symmetry such that each component of $\boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r}t)$ is irrotational (conservative):

$$\nabla \times \boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}t) = 0, \tag{3.76}$$

$$\nabla \times \boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r}t) = 0, \tag{3.77}$$

$$\nabla \times \boldsymbol{\mathcal{J}}_c(\mathbf{r}t) = 0, \tag{3.78}$$

the potential energy $v_{ee}(\mathbf{r}t)$ may be expressed as the sum

$$v_{ee}(\mathbf{r}t) = W_{ee}(\mathbf{r}t) + W_{t_c}(\mathbf{r}t), \tag{3.79}$$

where $W_{ee}(\mathbf{r}t)$ and $W_{t_c}(\mathbf{r}t)$ are respectively the work done in the fields $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}t)$ and $\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r}t)$:

$$W_{ee}(\mathbf{r}t) = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}'t) \cdot d\boldsymbol{\ell}', \tag{3.80}$$

$$W_{t_c}(\mathbf{r}t) = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r}'t) \cdot d\boldsymbol{\ell}'. \tag{3.81}$$

For systems of such symmetry, the field $\boldsymbol{\mathcal{J}}_c(\mathbf{r}t) = 0$, and does not contribute to the potential energy. The field $\boldsymbol{\mathcal{J}}_c(\mathbf{r}t)$ vanishes because both $\nabla \times \boldsymbol{\mathcal{J}}_c(\mathbf{r}t) = 0$ and $\nabla \cdot \boldsymbol{\mathcal{J}}_c(\mathbf{r}t) = 0$, the latter following from the continuity equations $\nabla \cdot \mathbf{j}(\mathbf{r}t) = -\partial\rho(\mathbf{r}t)/\partial t$ and $\nabla \cdot \mathbf{j}_s(\mathbf{r}t) = -\partial\rho(\mathbf{r}t)/\partial t$.

Employing the decomposition of the electron–interaction field $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}t)$ into its Hartree $\boldsymbol{\mathcal{E}}_H(\mathbf{r}t)$, Pauli $\boldsymbol{\mathcal{E}}_x(\mathbf{r}t)$, and Coulomb $\boldsymbol{\mathcal{E}}_c(\mathbf{r}t)$ components, the effective field $\boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r}t)$ may be written as

$$\boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r}t) = \boldsymbol{\mathcal{E}}_H(\mathbf{r}t) + \boldsymbol{\mathcal{E}}_x(\mathbf{r}t) + \boldsymbol{\mathcal{E}}_c(\mathbf{r}t) + \boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r}t) + \boldsymbol{\mathcal{J}}_c(\mathbf{r}t). \tag{3.82}$$

Thus, as for the total energy, the *separate* contributions of the different electron correlations to the potential energy $v_{ee}(\mathbf{r}t)$ are delineated.

Since the source $\rho(\mathbf{r}t)$ of the Hartree field $\boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r}t)$ is a local charge distribution, for each instant of time, the field may be written as

$$\boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r}t) = -\boldsymbol{\nabla} W_{\mathrm{H}}(\mathbf{r}t), \tag{3.83}$$

where $W_{\mathrm{H}}(\mathbf{r}t)$ is a scalar function. This shows that the field $\boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r}t)$ is irrotational (conservative): $\boldsymbol{\nabla} \times \boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r}t) = 0$. Thus, the scalar function $W_{\mathrm{H}}(\mathbf{r}t)$, which equivalently is the work done in the field $\boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r}t)$, may be expressed as

$$W_{\mathrm{H}}(\mathbf{r}t) = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r}'t) \cdot d\boldsymbol{\ell}' \tag{3.84}$$

$$= \int \frac{\rho(\mathbf{r}'t)}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'. \tag{3.85}$$

Hence, the potential energy $v_{\mathrm{ee}}(\mathbf{r}t)$ for arbitrary symmetry may be written as

$$v_{\mathrm{ee}}(\mathbf{r}t) = W_{\mathrm{H}}(\mathbf{r}t) + \left(-\int_{\infty}^{\mathbf{r}} [\boldsymbol{\mathcal{E}}_{\mathrm{x}}(\mathbf{r}'t) + \boldsymbol{\mathcal{E}}_{\mathrm{c}}(\mathbf{r}'t) + \boldsymbol{\mathcal{Z}}_{t_{\mathrm{c}}}(\mathbf{r}'t) + \boldsymbol{\mathcal{J}}_{\mathrm{c}}(\mathbf{r}'t)] \cdot d\boldsymbol{\ell}' \right). \tag{3.86}$$

For systems with symmetry such that (3.76)–(3.78) are satisfied, $v_{\mathrm{ee}}(\mathbf{r}t)$ is the sum of the work done in the individual fields:

$$v_{\mathrm{ee}}(\mathbf{r}t) = W_{\mathrm{H}}(\mathbf{r}t) + W_{\mathrm{x}}(\mathbf{r}t) + W_{\mathrm{c}}(\mathbf{r}t) + W_{t_{\mathrm{c}}}(\mathbf{r}t), \tag{3.87}$$

where

$$W_{\mathrm{x}}(\mathbf{r}t) = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{E}}_{\mathrm{x}}(\mathbf{r}'t) \cdot d\boldsymbol{\ell}', \tag{3.88}$$

$$W_{\mathrm{c}}(\mathbf{r}t) = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{E}}_{\mathrm{c}}(\mathbf{r}'t) \cdot d\boldsymbol{\ell}', \tag{3.89}$$

$$W_{t_{\mathrm{c}}}(\mathbf{r}t) = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{Z}}_{t_{\mathrm{c}}}(\mathbf{r}'t) \cdot d\boldsymbol{\ell}'. \tag{3.90}$$

Each work done, at each instant of time, is separately path–independent.

The S system of noninteracting fermions whereby the density $\rho(\mathbf{r}t)$ and total energy $E(t)$ equivalent to that of electrons in the same time-dependent external field $\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}t)$ is thus fully defined. The total energy $E(t)$ and the effective potential energy $v_{\mathrm{s}}(\mathbf{r}t)$ are described in terms of component fields representative of the properties and different electron correlations present within the model system. The delineation in terms of the various fields then allows for an understanding of the contribution of each type of electron correlation to a property. Further, it is the *same* source, and hence field, representative of a specific electron correlation that contributes to the corresponding component of both the total energy $E(t)$ *and* potential energy

$v_{\mathrm{ee}}(\mathbf{r}t)$. The delineation thus also allows for the construction of approximations whereby each type of electron correlation—Pauli, Coulomb, Correlation–Kinetic, Correlation–Current–Density—is systematically introduced.

3.2 Sum Rules

In this section we derive sum rules satisfied by the effective field $\mathcal{F}^{\mathrm{eff}}(\mathbf{r}t)$ and the resulting S system integral virial theorem, Ehrenfest's theorem, and the zero force and torque sum rules.

3.2.1 Integral Virial Theorem

Operating by $\int d\mathbf{r}\rho(\mathbf{r}t)\mathbf{r}\cdot$ on (3.67) and (3.69) leads on using (2.65) and (3.55) to

$$-\int \rho(\mathbf{r}t)\mathbf{r}\cdot\boldsymbol{\nabla} v_{\mathrm{ee}}(\mathbf{r}t)d\mathbf{r} = E_{\mathrm{ee}}(t) + 2T_{\mathrm{c}}(t) + \int \rho(\mathbf{r}t)\mathbf{r}\cdot\mathcal{J}_{\mathrm{c}}(\mathbf{r}t)d\mathbf{r}. \tag{3.91}$$

Since the last term vanishes (see (3.58)), we have

$$E_{\mathrm{ee}}(t) + 2T_{\mathrm{c}}(t) = \int \rho(\mathbf{r}t)\mathbf{r}\cdot\mathcal{F}^{\mathrm{eff}}(\mathbf{r}t)d\mathbf{r}. \tag{3.92}$$

This is the S system integral virial theorem.

3.2.2 Ehrenfest's Theorem and the Zero Force Sum Rule

The model fermions of the S system too must satisfy Ehrenfest's Theorem (2.98). This requirement then leads to the zero force sum rule for the effective field $\mathcal{F}^{\mathrm{eff}}(\mathbf{r}t)$.

Operating with $\int d\mathbf{r}\rho(\mathbf{r}t)$ on the S system 'Quantal Newtonian' second law (3.72) and employing (3.67) we have

$$\int \rho(\mathbf{r}t)\mathcal{F}^{\mathrm{ext}}(\mathbf{r}t)d\mathbf{r} + \int \rho(\mathbf{r}t)\mathcal{F}^{\mathrm{int}}_{s}(\mathbf{r}t)d\mathbf{r} = \int \rho(\mathbf{r}t)\mathcal{J}_{\mathrm{s}}(\mathbf{r}t)d\mathbf{r}. \tag{3.93}$$

Employing the continuity equation $\boldsymbol{\nabla}\cdot\mathbf{j}_{\mathrm{s}}(\mathbf{r}t) = -\partial\rho(\mathbf{r}t)/\partial t$, it can be shown by following the procedure of Sect. 2.8 that

$$\int \rho(\mathbf{r}t)\mathcal{J}_{\mathrm{s}}(\mathbf{r}t)d\mathbf{r} = \frac{\partial^2}{\partial t^2}\int \mathbf{r}\rho(\mathbf{r}t)d\mathbf{r}. \tag{3.94}$$

As was the case for the interacting system, $\int \rho(\mathbf{r}t)\boldsymbol{\mathcal{D}}(\mathbf{r}t)d\mathbf{r} = 0$ and $\int \rho(\mathbf{r}t)\boldsymbol{\mathcal{Z}}_{\mathrm{s}}(\mathbf{r}t)d\mathbf{r} = 0$. Hence, for Ehrenfest's theorem (2.98) to be satisfied requires that the averaged effective field vanish:

$$\int \rho(\mathbf{r}t)\boldsymbol{\mathcal{F}}^{\mathrm{eff}}(\mathbf{r}t)d\mathbf{r} = 0. \tag{3.95}$$

Further, the contribution of the components $\boldsymbol{\mathcal{E}}_{\mathrm{ee}}(\mathbf{r}t)$, $\boldsymbol{\mathcal{Z}}_{\mathrm{t_c}}(\mathbf{r}t)$, and $\boldsymbol{\mathcal{J}}_{\mathrm{c}}(\mathbf{r}t)$ to the integral also separately vanish. The proofs are similar to those of Sect. 2.8. (See (2.104)–(2.107), and (3.94).) This is the zero force theorem.

The above sum rule is the S system analogue of $\langle \boldsymbol{\mathcal{F}}^{\mathrm{int}} \rangle = 0$ of Schrödinger theory (2.114), and of $\sum'_{i,j} \boldsymbol{F}_{ji} = 0$ of Newton's theory. Note that it is only the electron–interaction $\boldsymbol{\mathcal{E}}_{\mathrm{ee}}(\mathbf{r}t)$ field component that obeys Newton's third law. Hence, the vanishing of its average maybe attributed to it. However, the vanishing of the averaged Correlation–Kinetic $\boldsymbol{\mathcal{Z}}_{\mathrm{t_c}}(\mathbf{r}t)$ and Correlation–Current–Density $\boldsymbol{\mathcal{J}}_{\mathrm{c}}(\mathbf{r}t)$ fields is not a direct consequence of the law. Rather, as in the case of the interacting system, it is a quantum mechanical effect.

Within the framework of the S system then, Ehrenfest's theorem may be stated in terms of the corresponding response of the system $\boldsymbol{\mathcal{J}}_{\mathrm{s}}(\mathbf{r}t)$ as

$$\int \rho(\mathbf{r}t)[\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}t) - \boldsymbol{\mathcal{J}}_{\mathrm{s}}(\mathbf{r}t)]d\mathbf{r} = 0. \tag{3.96}$$

3.2.3 Torque Sum Rule

The S system torque sum rule for the effective field $\boldsymbol{\mathcal{F}}^{\mathrm{eff}}(\mathbf{r}t)$ is

$$\int \rho(\mathbf{r}t)\mathbf{r} \times [\boldsymbol{\mathcal{F}}^{\mathrm{eff}}(\mathbf{r}t) - \boldsymbol{\mathcal{J}}_{\mathrm{c}}(\mathbf{r}t)]d\mathbf{r} = 0. \tag{3.97}$$

Note that in contrast to Schrödinger and Newton's theories, the averaged torque of the effective field does not vanish. It vanishes only when $\boldsymbol{\nabla} \times \mathbf{j}(\mathbf{r}t) = \boldsymbol{\nabla} \times \mathbf{j}_s(\mathbf{r}t) = 0$ because then $\boldsymbol{\nabla} \times [\mathbf{j}_s(\mathbf{r}t) - \mathbf{j}(\mathbf{r}t)] = \boldsymbol{\nabla} \times \boldsymbol{\mathcal{J}}_c(\mathbf{r}t) = 0$, and from the continuity equations $\boldsymbol{\nabla} \cdot [\mathbf{j}_s(\mathbf{r}t) - \mathbf{j}(\mathbf{r}t)] = \boldsymbol{\nabla} \cdot \boldsymbol{\mathcal{J}}_c(\mathbf{r}t) = 0$ because the density $\rho(\mathbf{r}t)$ of the interacting and S systems is the same. Then, from the Helmholtz theorem, $\boldsymbol{\mathcal{J}}_c(\mathbf{r}t) = 0$. When these conditions are met, then the averaged torque of the effective field $\boldsymbol{\mathcal{F}}^{\mathrm{eff}}(\mathbf{r}t)$ vanishes:

$$\int \rho(\mathbf{r}t)\mathbf{r} \times \boldsymbol{\mathcal{F}}^{\mathrm{eff}}(\mathbf{r}t)d\mathbf{r} = 0. \tag{3.98}$$

We provide two proofs of (3.97).

(i) For the first of these proofs apply the operator $\int d\mathbf{r}\rho(\mathbf{r})\mathbf{r} \times$ on the definition (3.69) of $\boldsymbol{\mathcal{F}}^{\mathrm{eff}}(\mathbf{r}t)$ to obtain

$$\int \rho(\mathbf{r}t)\mathbf{r} \times \boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r}t)d\mathbf{r} = \int \rho(\mathbf{r}t)\mathbf{r} \times \boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}t)d\mathbf{r} + \int \rho(\mathbf{r}t)\mathbf{r} \times \boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r}t)d\mathbf{r} + \int \rho(\mathbf{r}t)\mathbf{r} \times \boldsymbol{\mathcal{J}}_{\text{c}}(\mathbf{r}t)d\mathbf{r}. \tag{3.99}$$

That the integral

$$\int \rho(\mathbf{r}t)\mathbf{r} \times \boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}t)d\mathbf{r} = 0 \tag{3.100}$$

is proved by once again employing the symmetry property of the pair-correlation function $h(\mathbf{r}\mathbf{r}'t)$ as in Sect. 2.8. For the proof of

$$\int \rho(\mathbf{r}t)\mathbf{r} \times \boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r}t)d\mathbf{r} = 0, \tag{3.101}$$

we need to show

$$\int \mathbf{r} \times \boldsymbol{z}(\mathbf{r}t)d\mathbf{r} = 0 \qquad \text{and} \qquad \int \mathbf{r} \times \boldsymbol{z}_s(\mathbf{r}t)d\mathbf{r} = 0. \tag{3.102}$$

Consider the component

$$\begin{aligned}\left[\int \mathbf{r} \times \boldsymbol{z}(\mathbf{r}t)d\mathbf{r}\right]_i &= 2\int \sum_{jkl} \epsilon_{ijk} r_j \frac{\partial}{\partial r_l} t_{kl}(\mathbf{r}t; [\gamma])d\mathbf{r} \\ &= -2\sum_{jk} \int \epsilon_{ijk} t_{kj}(\mathbf{r}t; [\gamma])d\mathbf{r} = 0,\end{aligned} \tag{3.103}$$

where we have again employed the vanishing of the tensor at the boundaries at infinity, and the properties $t_{kj}(\mathbf{r}t) = t_{jk}(\mathbf{r}t)$ and $\epsilon_{ijk} = -\epsilon_{ikj}$. This proves the first condition of (3.102). The second is similarly proved. Thus, the torque sum rule of (3.97) is proved.

(ii) The second proof is along the lines of [28] and employs the quantum-mechanical equation of motion for the expectation value of an operator $\hat{Q}(t)$:

$$\frac{d}{dt}\langle \Psi(t)|\hat{Q}(t)|\Psi(t)\rangle = \langle \Psi(t)|\frac{\partial \hat{Q}(t)}{\partial t} - i[\hat{Q}(t), \hat{H}(t)]|\Psi(t)\rangle. \tag{3.104}$$

For the angle operator $\hat{\phi} = \sum_i \mathbf{r}_i \times \mathbf{p}_i$, we have for the difference

$$\begin{aligned}&\frac{d}{dt}[\langle \Psi(t)|\hat{\phi}|\Psi(t)\rangle - \langle \Phi(t)|\hat{\phi}|\Phi(t)\rangle] \\ &\quad = -\int \rho(\mathbf{r}t)\mathbf{r} \times \boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r}t)d\mathbf{r}.\end{aligned} \tag{3.105}$$

Now

$$\frac{d}{dt}\langle\Psi(t)|\hat{\phi}|\Psi(t)\rangle = -i\frac{d}{dt}\int\sum_i \mathbf{r}_i \times \Psi^{\star}(\mathbf{X}t)\nabla_i\Psi(\mathbf{X}t)d\mathbf{X}, \tag{3.106}$$

with a similar equation for the S system so that the left hand of (3.105) is

$$= -\frac{\partial}{\partial t}\int \mathbf{r} \times [\mathbf{j}_s(\mathbf{r}t) - \mathbf{j}(\mathbf{r}t)]d\mathbf{r} \tag{3.107}$$

$$= -\int \rho(\mathbf{r}t)]\mathbf{r} \times \mathcal{J}_c(\mathbf{r}t)d\mathbf{r}. \tag{3.108}$$

Equating (3.105) and (3.108) proves the torque sum rule.

Thus, the torque of the effective field $\mathcal{F}^{\mathrm{eff}}(\mathbf{r}t)$ is *finite*, and due *solely* to Correlation-Current-Density effects represented by the field $\mathcal{J}_c(\mathbf{r}t)$. It is only for cases when $\mathcal{J}_c(\mathbf{r}t) = 0$ does the torque of $\mathcal{F}^{\mathrm{eff}}(\mathbf{r}t)$ vanish. The torque due to the electron-interaction $\mathcal{E}_{\mathrm{ee}}(\mathbf{r}t)$ and Correlation-Kinetic $\mathcal{Z}_{t_c}(\mathbf{r}t)$ fields are proved to *separately* vanish.

3.3 Time-Dependent Quantal Density Functional Theory: Part II

In the previous three sections, we described the Q-DFT mapping of a system of N electrons in an external time-dependent field $\mathcal{F}^{\mathrm{ext}}(\mathbf{r}t) = -\nabla v(\mathbf{r}t)$ to one of noninteracting fermions having the same density $\rho(\mathbf{r}t)$. The choice of the density $\rho(\mathbf{r}t)$, as explained in the Introduction to the chapter, is because it constitutes a basic variable of quantum mechanics as proved by the Runge-Gross theorem [27–29]. That is, the choice of property is governed by the fact that there is a one-to-one relationship between the density $\rho(\mathbf{r}t)$ and the external potential $v(\mathbf{r}t)$. (This mapping is akin to that of time-dependent KS-DFT.) But then in the mapping to the model system, one must account for the Correlation-Current-Density effects.

However, as noted in the Introduction, the current density $\mathbf{j}(\mathbf{r}t)$ is also a basic variable since it too has a one-to-one relationship with the external potential $v(\mathbf{r}t)$. In this section we describe the Q-DFT mapping to a system of noninteracting fermions whose density $\rho(\mathbf{r}t)$ *and* current density $\mathbf{j}(\mathbf{r}t)$ are the same as those of the interacting system of electrons. In other words the response of the two systems is the same. Hence, in this time-dependent Q-DFT one ensures that the model fermions are (a) subject to the same external field $\mathcal{F}^{\mathrm{ext}}(\mathbf{r}t)$, and (b) possess the same basic variables, as that of the interacting system of electrons. The idea that the mapping be such as to reproduce the basic variables leads to an overall consistency within the broader context of Q-DFT. Irrespective of whether the external field includes additionally a time-dependent electric and magnetic field [39], or if the external field is comprised only of an electrostatic and magnetostatic field (see Chap. 9), or just an electrostatic field (see time-independent Q-DFT, Sect. 3.4), the correlations that the model system must account for *in each case* are then *always* only those due to the Pauli exclusion principle, Coulomb repulsion, and Correlation-Kinetic effects.

For this version of time-dependent Q-DFT, we impose the constraints that the interacting electrons and noninteracting model fermions experience the same external field $\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}t) = -\boldsymbol{\nabla} v(\mathbf{r}t)$, and that the response of each system to this field, i.e. the density $\rho(\mathbf{r}t)$ and current densities $(\mathbf{j}(\mathbf{r}t), \mathbf{j}_s(\mathbf{r}t))$ are the same. As a consequence, the Correlation-Current-Density field of (3.38) $\boldsymbol{\mathcal{J}}_c(\mathbf{r}t) = 0$. On imposing the constraints, it then follows from the 'Quantal Newtonian' second laws (3.70) and (3.72) of these systems that the local electron-interaction potential energy $v_{ee}(\mathbf{r}t)$ of the model fermions in the S system differential equation (3.3) is the work done in a conservative effective field $\boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r}t)$:

$$v_{ee}(\mathbf{r}t) = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r}'t) \cdot d\boldsymbol{\ell}' \tag{3.109}$$

where

$$\boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r}t) = \boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}t) + \boldsymbol{\mathcal{Z}}_{\text{t}_\text{c}}(\mathbf{r}t), \tag{3.110}$$

with $\boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}t)$ and $\boldsymbol{\mathcal{Z}}_{\text{t}_\text{c}}(\mathbf{r}t)$ the electron-interaction and Correlation-Kinetic fields as defined in (2.43) and (3.36), respectively. This work done is *path-independent* since $\nabla \times \boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r}t) = 0$. Note that since the effective fields $\boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r}t)$ of (3.69) and (3.110) differ, the corresponding potentials $v_{\text{ee}}(\mathbf{r}t)$ and the orbitals $\phi_i(\mathbf{r}t)$ of the S system differential equation also differ. (Of course, for systems with symmetry such that the field $\boldsymbol{\mathcal{J}}_c(\mathbf{r}t)$ vanishes, i.e. for systems for which both the curl and divergence of the field vanish, the effective field $\boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r}t)$, potential $v_{\text{ee}}(\mathbf{r}t)$, and orbitals $\phi_i(\mathbf{r}t)$ are the same.)

The expressions for the energy, and the various sum rules for $\boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r}t)$ are special cases of those derived previously. For completeness they are the following:

Energy

$$E(t) = T_s(t) + \int \rho(\mathbf{r}t) v(\mathbf{r}t) d\mathbf{r} + E_{\text{ee}}(t) + T_c(t). \tag{3.111}$$

Integral Virial Theorem

$$E_{\text{ee}}(t) + 2T_c(t) = \int \rho(\mathbf{r}t)\mathbf{r} \cdot \boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r}t) d\mathbf{r}. \tag{3.112}$$

Zero Force Sum Rule

$$\int \rho(\mathbf{r}t) \boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r}t) d\mathbf{r} = 0. \tag{3.113}$$

Zero Torque Sum Rule

$$\int \rho(\mathbf{r}t)\mathbf{r} \times \boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r}t) d\mathbf{r} = 0. \tag{3.114}$$

3.4 Time-Independent Quantal Density Functional Theory

We next describe time-independent Quantal Density Functional theory. Consider a system of N electrons in the presence of an *arbitrary* external field $\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}) = -\boldsymbol{\nabla} v(\mathbf{r})$. The theory is a description of the physics of mapping from *any* ground or bound excited, nondegenerate or degenerate *pure* state of the time-independent Schrödinger equation to that of an S system of *noninteracting* fermions such that the equivalent density $\rho(\mathbf{r})$, energy E, and ionization potential I (or electron affinity A) are thereby obtained. It is assumed that the model fermions are subject to the same external field $\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r})$.

3.4.1 The Interacting System and the 'Quantal Newtonian' First Law

The interacting system of N electrons is governed by the time-independent Schrödinger equation (in atomic units $e = \hbar = m = 1$) (see (2.133))

$$\hat{H}\psi(\mathbf{X}) = E\psi(\mathbf{X}) \tag{3.115}$$

where $\psi(\mathbf{X}), E$ are the eigenfunctions and energy eigenvalues, respectively; $\mathbf{X} = \mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N$; $\mathbf{x} = \mathbf{r}\sigma$, $\mathbf{r}$ and σ are the spatial and spin coordinates. (No symbolic differentiation between ground and excited states is made.) The Hamiltonian operator $\hat{H}$ is the sum of the kinetic energy $\hat{T}$, external potential energy $\hat{V}$, and electron-interaction potential energy $\hat{U}$ operators:

$$\hat{H} = \hat{T} + \hat{V} + \hat{U}, \tag{3.116}$$

where

$$\hat{T} = -\frac{1}{2}\sum_i \nabla_i^2 \tag{3.117}$$

$$\hat{V} = \sum_i v(\mathbf{r}_i), \tag{3.118}$$

and

$$\hat{U} = \frac{1}{2}\sum_{i,j}{}' \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \tag{3.119}$$

The energy E is the expectation

$$E = \langle\psi(\mathbf{X})|\hat{H}|\psi(\mathbf{X})\rangle, \tag{3.120}$$

which is a sum of its kinetic T, external potential E_{ext}, and electron-interaction potential E_{ee} energy components:

$$T = \langle\psi(\mathbf{X})|\hat{T}|\psi(\mathbf{X})\rangle, \tag{3.121}$$

$$E_{\text{ext}} = \langle\psi(\mathbf{X})|\hat{V}|\psi(\mathbf{X})\rangle, \tag{3.122}$$

$$E_{\text{ee}} = \langle\psi(\mathbf{X})|\hat{U}|\psi(\mathbf{X})\rangle. \tag{3.123}$$

The 'Quantal Newtonian' first law (see (2.134)) which is the stationary state case of the 'Quantal Newtonian' second law of (2.75) is

$$\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}) + \boldsymbol{\mathcal{F}}^{\text{int}}(\mathbf{r}) = 0, \tag{3.124}$$

where the internal field $\boldsymbol{\mathcal{F}}^{\text{int}}(\mathbf{r})$ is the sum of the electron-interaction $\boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r})$, differential density $\boldsymbol{\mathcal{D}}(\mathbf{r})$, and kinetic $\boldsymbol{\mathcal{Z}}(\mathbf{r})$ fields:

$$\boldsymbol{\mathcal{F}}^{\text{int}}(\mathbf{r}) = \boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}) - \boldsymbol{\mathcal{D}}(\mathbf{r}) - \boldsymbol{\mathcal{Z}}(\mathbf{r}). \tag{3.125}$$

The definition and interpretation of these fields is the same as in Sect. 2.3 but with the quantal sources being time-independent.

3.4.2 The S System and Its 'Quantal Newtonian' First Law

The time-independent Schrödinger equation for the S system of N noninteracting fermions in the same external field $\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}) = -\boldsymbol{\nabla}v(\mathbf{r})$ as that for the interacting system is

$$\Big[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\Big]\phi_i(\mathbf{x}) = \epsilon_i\phi_i(\mathbf{x}); \quad i = 1, \ldots, N, \tag{3.126}$$

with the local effective potential $v_s(\mathbf{r}) = v(\mathbf{r}) + v_{ee}(\mathbf{r})$. Here $v_{ee}(\mathbf{r})$ is the *local* electron-interaction potential energy which ensures that the Slater determinant wave function $\Phi\{\phi_i\}$ of the orbitals $\phi_i(\mathbf{x})$ leads to the same density $\rho(\mathbf{r})$ as that of the interacting system. The potential energy $v_{ee}(\mathbf{r})$ must then incorporate electron correlations due to the Pauli exclusion principle and Coulomb repulsion. It must also account for Correlation-Kinetic effects since the kinetic energy of interacting and noninteracting fermions of the same density $\rho(\mathbf{r})$ differ.

The S system 'Quantal Newtonian' first law is the stationary state case of the 'Quantal Newtonian' second law of (3.72), and is

$$\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}) + \boldsymbol{\mathcal{F}}_s^{\text{int}}(\mathbf{r}) = 0, \tag{3.127}$$

where the corresponding internal field $\boldsymbol{\mathcal{F}}_s^{\text{int}}(\mathbf{r})$ is

$$\boldsymbol{\mathcal{F}}_s^{\text{int}}(\mathbf{r}) = -\nabla v_{ee}(\mathbf{r}) - \boldsymbol{\mathcal{D}}(\mathbf{r}) - \boldsymbol{\mathcal{Z}}_s(\mathbf{r}). \tag{3.128}$$

The definitions of the fields $\boldsymbol{\mathcal{D}}(\mathbf{r})$ and $\boldsymbol{\mathcal{Z}}_s(\mathbf{r})$ are the same as in Sect. 3.1.2 but are obtained by time-independent quantal sources.

The assumed existence of the electron-interaction potential energy $v_{ee}(\mathbf{r})$ implies that there must exist an effective field $\boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r})$ such that

$$\boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r}) = -\nabla v_{ee}(\mathbf{r}). \tag{3.129}$$

This effective field is derived in Sect. 3.4.6.

In time-independent Q-DFT, the state of the model S system of noninteracting fermions is *arbitrary* [1, 2, 5, 10, 11, 14–16, 18, 20]. For the mapping from a pure ground state of the interacting system, it is best to map to an S system that is also in its *ground* state. However, it is possible to map to an S system in an *excited* state with a different electronic configuration. For the mapping from a pure *excited* state of the interacting system, the model S system may be in an *excited* state with the same configuration, or an *excited* state with a different electronic configuration, or in a *ground* state with yet another different electronic configuration. The difference in the electron-interaction potential $v_{ee}(\mathbf{r})$ of these model systems is *solely* due to Correlation-Kinetic effects as will be proved in Sect. 3.4.9 [18, 20]. The fact of the different mappings means that *there exist an infinite number of local electron-interaction potential energy functions* $v_{ee}(\mathbf{r})$ *that can generate a given density* $\rho(\mathbf{r})$.

Another important physical point of note is that whether the mapping is from a ground or excited state of the interacting system, the highest occupied eigenvalue of the model S system, corresponds to the negative of the ionization potential for that state [10, 14, 16, 41–43]. This is the case irrespective of whether the S system is in a ground or excited state. The reason for this is explained in Sect. 3.4.8.

The other critical equations and interpretations governing time-independent Q-DFT follow.

3.4.3 Quantal Sources

The sources: the electron density $\rho(\mathbf{r})$, Dirac density matrix $\gamma_s(\mathbf{rr}')$, and the pair–correlation density $g_s(\mathbf{rr}')$ are defined as in Sect. 3.1.1 as the expectations of the corresponding Hermitian operators taken with respect to the time-independent Slater determinant $\Phi\{\phi_i\}$. The Fermi hole charge $\rho_x(\mathbf{rr}')$ is the nonlocal component of $g_s(\mathbf{rr}')$. The pair–correlation density $g(\mathbf{rr}')$ of the interacting system is obtained from the eigenfunctions $\psi(\mathbf{X})$ of the time-independent Schrödinger equation (3.115) as $g(\mathbf{rr}') = \langle\psi(\mathbf{X})|\hat{P}(\mathbf{rr}')|\psi(\mathbf{X})\rangle/\rho(\mathbf{r})$. The Fermi–Coulomb hole charge $\rho_{xc}(\mathbf{rr}')$ is the nonlocal component of $g(\mathbf{rr}')$. The Coulomb hole $\rho_c(\mathbf{rr}')$ is the difference between the Fermi–Coulomb and Fermi hole charge distributions. The various sum rules satisfied by these sources are the same as those of Sect. 3.1.1. The interacting system density matrix $\gamma(\mathbf{rr}')$ is obtained via the eigenfunctions $\psi(\mathbf{X})$ of the Schrödinger equation (3.115) as the expectation of the density matrix operator as defined in Sect. 2.2.

3.4.4 Fields

The definitions of the S system electron-interaction $\boldsymbol{\mathcal{E}}_{\mathrm{ee,s}}(\mathbf{r})$, Hartree $\boldsymbol{\mathcal{E}}_H(\mathbf{r})$, Pauli $\boldsymbol{\mathcal{E}}_x(\mathbf{r})$, differential density $\boldsymbol{\mathcal{D}}(\mathbf{r})$, and kinetic $\boldsymbol{\mathcal{Z}}_s(\mathbf{r})$ fields are the same as in Sect. 3.1.2 but obtained for stationary-state quantal sources determined as expectations of the appropriate Hermitian operators taken with respect to the Slater determinant $\Phi\{\phi_i\}$ wave function. The definitions of the interacting system electron-interaction $\boldsymbol{\mathcal{E}}_{\mathrm{ee}}(\mathbf{r})$, Hartree $\boldsymbol{\mathcal{E}}_H(\mathbf{r})$, Pauli-Coulomb $\boldsymbol{\mathcal{E}}_{xc}(\mathbf{r})$, differential density $\boldsymbol{\mathcal{D}}(\mathbf{r})$, and kinetic $\boldsymbol{\mathcal{Z}}(\mathbf{r})$ fields are the same as those of Sect. 2.3. Here the stationary-state quantal sources are determined as expectations of the requisite operators taken with respect to the wave function $\psi(\mathbf{X})$ of the time-independent Schrödinger equation (3.115). In a manner similar to the definitions of Sect. 3.1.2, the Coulomb field $\boldsymbol{\mathcal{E}}_c(\mathbf{r})$ is the difference between the Pauli-Coulomb $\boldsymbol{\mathcal{E}}_{xc}(\mathbf{r})$ and Pauli $\boldsymbol{\mathcal{E}}_x(\mathbf{r})$ fields; the Correlation-Kinetic $\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r})$ field is the difference between the kinetic fields $\boldsymbol{\mathcal{Z}}_s(\mathbf{r})$ and $\boldsymbol{\mathcal{Z}}(\mathbf{r})$ of the model fermions and the interacting electrons, respectively.

In the time-independent case, in addition to the Hartree field $\boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r})$, the kinetic field $\boldsymbol{\mathcal{Z}}_{\mathrm{s}}(\mathbf{r})$ is also conservative: $\boldsymbol{\nabla} \times \boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r}) = 0$, and $\boldsymbol{\nabla} \times \boldsymbol{\mathcal{Z}}_{\mathrm{s}}(\mathbf{r}) = 0$, the latter following from the 'Quantal Newtonian' first law of (3.127). The remaining fields $\boldsymbol{\mathcal{E}}_{\mathrm{ee}}(\mathbf{r})$, $\boldsymbol{\mathcal{E}}_{\mathrm{x}}(\mathbf{r})$, $\boldsymbol{\mathcal{E}}_{\mathrm{c}}(\mathbf{r})$, $\boldsymbol{\mathcal{Z}}(\mathbf{r})$, and $\boldsymbol{\mathcal{Z}}_{\mathrm{t_c}}(\mathbf{r})$ are in general not conservative. However, for systems of certain symmetry such as closed–shell atoms, open–shell atoms in the central field approximation, jellium metal clusters and surfaces, etc., these fields are separately conservative: $\boldsymbol{\nabla} \times \boldsymbol{\mathcal{E}}_{\mathrm{ee}}(\mathbf{r}) = 0$, $\boldsymbol{\nabla} \times \boldsymbol{\mathcal{E}}_{\mathrm{x}}(\mathbf{r}) = 0$, $\boldsymbol{\nabla} \times \boldsymbol{\mathcal{E}}_{\mathrm{c}}(\mathbf{r}) = 0$, $\boldsymbol{\nabla} \times \boldsymbol{\mathcal{Z}}(\mathbf{r}) = 0$, and $\boldsymbol{\nabla} \times \boldsymbol{\mathcal{Z}}_{\mathrm{t_c}}(\mathbf{r}) = 0$.

3.4.5 Total Energy and Components

The expressions for the total energy E, and of its components are, of course, the same as for the time-dependent case. Thus, without any symbolic differentiation between ground and excited states, we have

$$E = T_{\mathrm{s}} + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + E_{\mathrm{ee}} + T_{\mathrm{c}}, \tag{3.130}$$

$$= T_{\mathrm{s}} + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + E_{\mathrm{H}} + E_{\mathrm{x}} + E_{\mathrm{c}} + T_{\mathrm{c}}, \tag{3.131}$$

where the S system kinetic energy T_s is the expectation

$$T_s = \sum_{\sigma}\sum_{i}\langle\phi_i(\mathbf{r}\sigma)| - \frac{1}{2}\nabla^2|\phi_i(\mathbf{r}\sigma)\rangle, \tag{3.132}$$

and where in integral virial form the electron–interaction energy E_{ee} is

$$E_{ee} = \int \rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})d\mathbf{r}, \tag{3.133}$$

the Hartree or Coulomb self energy E_H is

$$E_H = \int \rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\mathcal{E}}_H(\mathbf{r})d\mathbf{r}, \tag{3.134}$$

the Pauli (exchange) energy E_x is

$$E_x = \int \rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\mathcal{E}}_x(\mathbf{r})d\mathbf{r}, \tag{3.135}$$

the Coulomb energy E_c is

$$E_c = \int \rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\mathcal{E}}_c(\mathbf{r})d\mathbf{r}, \tag{3.136}$$

and the Correlation–Kinetic energy T_c is

$$T_c = \frac{1}{2}\int \rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r})d\mathbf{r}. \tag{3.137}$$

Note that these expressions are valid whether or not the individual fields are conservative.

The total energy may also be expressed in terms of the eigenvalues ϵ_i of the S system differential equation (3.126). Multiplying (3.126) by $\phi_i^*(\mathbf{r}\sigma)$, summing over all the fermions, and integrating over spatial and spin coordinates leads to

$$T_s = \sum_i \epsilon_i - \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} - \int \rho(\mathbf{r})v_{ee}(\mathbf{r})d\mathbf{r}, \tag{3.138}$$

which on substitution into (3.130) for the total energy E gives

$$E = \sum_i \epsilon_i - \int \rho(\mathbf{r})v_{ee}(\mathbf{r}) + E_{ee} + T_c. \tag{3.139}$$

Note that as in Hartree [44, 45] and Hartree–Fock [46, 47] theory, $E \neq \sum_i \epsilon_i$. This is because the model S system accounts for electron correlations due to the Pauli principle and Coulomb repulsion, and Correlation–Kinetic effects.

3.4.6 Effective Field $\mathcal{F}^{\mathrm{eff}}(\mathbf{r})$ and Electron–Interaction Potential Energy $v_{\mathrm{ee}}(\mathbf{r})$

The effective electron–interaction potential energy $v_{\mathrm{ee}}(\mathbf{r})$ of the model fermions is the work done to move such a fermion from its reference point at infinity to its position at $\mathbf{r}$ in the force of a conservative effective field $\mathcal{F}^{\mathrm{eff}}(\mathbf{r})$:

$$v_{\mathrm{ee}}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \mathcal{F}^{\mathrm{eff}}(\mathbf{r}') \cdot d\boldsymbol{\ell}', \tag{3.140}$$

where

$$\mathcal{F}^{\mathrm{eff}}(\mathbf{r}) = \mathcal{E}_{\mathrm{ee}}(\mathbf{r}) + \mathcal{Z}_{t_c}(\mathbf{r}). \tag{3.141}$$

This work done is *path–independent* since $\nabla \times \mathcal{F}^{\mathrm{eff}}(\mathbf{r}) = 0$. As in the time-dependent case, the proof of these statements follows by equating the time-independent 'Quantal Newtonian' first law for the interacting and S systems (see Appendix A and E) assuming the external potential $v(\mathbf{r})$ and density $\rho(\mathbf{r})$ of the two systems are the same.

Observe that the expression for the time-independent $v_{\mathrm{ee}}(\mathbf{r})$ of (3.140, 3.141) is the same as that of the time-dependent $v_{\mathrm{ee}}(\mathbf{r}t)$ of (3.109, 3.110) of Sect. 3.2 except for the time factor. Recall that in deriving the time-dependent expression we had ensured the external potential $v(\mathbf{r}t)$ of the interacting and noninteracting systems were the same. But we had also ensured that the basic variables of the density $\rho(\mathbf{r}t)$ and current density $\mathbf{j}(\mathbf{r}t)$ of the two systems too were the same. Thus, if the external potential and the basic variables of the interacting and model systems are ensured to be the same, then within Q-DFT the only correlations the model system must account for are those of the Pauli exclusion principle, Coulomb repulsion, and Correlation-Kinetic effects.

Decomposing the electron–interaction field $\mathcal{E}_{\mathrm{ee}}(\mathbf{r})$ into its Hartree $\mathcal{E}_{\mathrm{H}}(\mathbf{r})$, Pauli $\mathcal{E}_{\mathrm{x}}(\mathbf{r})$, and Coulomb $\mathcal{E}_{\mathrm{c}}(\mathbf{r})$ components, and employing the fact that $\mathcal{E}_{\mathrm{H}}(\mathbf{r})$ is conservative, we may write the potential energy $v_{\mathrm{ee}}(\mathbf{r})$ as

$$v_{\mathrm{ee}}(\mathbf{r}) = W_{\mathrm{H}}(\mathbf{r}) + \left(-\int_{\infty}^{\mathbf{r}} \left[\mathcal{E}_{\mathrm{x}}(\mathbf{r}') + \mathcal{E}_{\mathrm{c}}(\mathbf{r}') + \mathcal{Z}_{t_c}(\mathbf{r}')\right] \cdot d\boldsymbol{\ell}'\right), \tag{3.142}$$

where the Hartree potential energy

$$W_{\mathrm{H}}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \tag{3.143}$$

For systems in which the fields $\mathcal{E}_{x}(\mathbf{r})$, $\mathcal{E}_{\mathrm{c}}(\mathbf{r})$, and $\mathcal{Z}_{t_c}(\mathbf{r})$ are separately conservative, we may write the potential energy $v_{\mathrm{ee}}(\mathbf{r})$ as the sum

$$v_{\mathrm{ee}}(\mathbf{r}) = W_{\mathrm{H}}(\mathbf{r}) + W_{\mathrm{x}}(\mathbf{r}) + W_{\mathrm{c}}(\mathbf{r}) + W_{t_c}(\mathbf{r}), \tag{3.144}$$

where $W_{\mathrm{x}}(\mathbf{r})$, $W_{\mathrm{c}}(\mathbf{r})$, and $W_{t_{\mathrm{c}}}(\mathbf{r})$ are the work done, respectively, in the force of these fields:

$$W_{\mathrm{x}}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{E}}_{\mathrm{x}}(\mathbf{r}') \cdot d\boldsymbol{\ell}', \tag{3.145}$$

$$W_{\mathrm{c}}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{E}}_{\mathrm{c}}(\mathbf{r}') \cdot d\boldsymbol{\ell}', \tag{3.146}$$

$$W_{t_{\mathrm{c}}}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{Z}}_{t_{\mathrm{c}}}(\mathbf{r}') \cdot d\boldsymbol{\ell}'. \tag{3.147}$$

Each work done is separately *path–independent*.

Note that if the individual time-dependent and time-independent fields $\boldsymbol{\mathcal{E}}_{\mathrm{x}}(\mathbf{r}t)$ and $\boldsymbol{\mathcal{E}}_{\mathrm{x}}(\mathbf{r})$, etc., are separately conservative, the expressions for the potential energies $v_{\mathrm{ee}}(\mathbf{r}t)$ of (3.79) of Sect. 3.1.5 and (3.109, 3.110) of Sect. 3.3 are the same, and therefore the same as that for $v_{\mathrm{ee}}(\mathbf{r})$ of (3.140, 3.141) except for the time factor. Hence, for systems of such symmetry, the model systems must account for only Pauli, Coulomb and kinetic correlations.

3.4.7 Sum Rules

The sum rules for the effective field $\boldsymbol{\mathcal{F}}^{\mathrm{eff}}(\mathbf{r})$ are a special case of those derived for the time-dependent S system, and their proofs are also the same. The stationary state integral virial theorem is (see (3.92))

$$E_{\mathrm{ee}} + 2T_{\mathrm{c}} = \int \rho(\mathbf{r})\mathbf{r} \cdot \boldsymbol{\mathcal{F}}^{\mathrm{eff}}(\mathbf{r})d\mathbf{r}, \tag{3.148}$$

and is the same as for the time-dependent case. So is the zero force sum rule for the vanishing of the averaged field (see (3.95)):

$$\int \rho(\mathbf{r})\boldsymbol{\mathcal{F}}^{\mathrm{eff}}(\mathbf{r})d\mathbf{r} = 0, \tag{3.149}$$

and of its electron–interaction $\boldsymbol{\mathcal{E}}_{\mathrm{ee}}(\mathbf{r})$ and Correlation–Kinetic $\boldsymbol{\mathcal{Z}}_{t_{\mathrm{c}}}(\mathbf{r})$ components separately. Again, the vanishing of the averaged electron–interaction $\boldsymbol{\mathcal{E}}_{\mathrm{ee}}(\mathbf{r})$ component is attributable to Newton's third law. That of the Correlation–Kinetic component

$\mathcal{Z}_{t_c}(\mathbf{r})$ is not. Finally, in the stationary state case, the averaged torque of the effective field vanishes (see (3.98)):

$$\int \rho(\mathbf{r})\mathbf{r} \times \mathcal{F}^{\text{eff}}(\mathbf{r})d\mathbf{r} = 0, \tag{3.150}$$

as do the averaged torque of its $\mathcal{E}_{\text{ee}}(\mathbf{r})$ and $\mathcal{Z}_{t_c}(\mathbf{r})$ components separately. Once again, it is only the vanishing of averaged torque of the electron–interaction component that may be attributed to Newton's third law.

3.4.8 Highest Occupied Eigenvalue $\epsilon_{\mathbf{m}}$

With the exception of the highest occupied eigenvalue ϵ_{m}, the eigenvalues of the S system differential equation (3.126), both occupied and unoccupied, have no rigorous physical interpretation. The highest eigenvalue ϵ_{m}, however, is equal to the negative of the first ionization potential. This follows from the fact that since the effective potential energy $v_{\text{s}}(\mathbf{r})$ of the model fermions is the same, the asymptotic structure of the S system orbitals $\phi_i(\mathbf{x})$ in the classically forbidden region is governed by their respective eigenvalues. Thus, the asymptotic decay of the density for finite systems for which the eigenvalues are discrete, is due entirely to the highest occupied state $\phi_{\text{m}}(\mathbf{x})$. Asymptotically, the density is then given by

$$\lim_{r\to\infty} \rho(\mathbf{x}) = |\phi_{\text{m}}|^2 \sim \exp\left[-2\sqrt{-2\epsilon_{\text{m}}}r\right]. \tag{3.151}$$

A comparison of this expression with that derived (2.163) for the asymptotic structure of the density for the interacting Schrödinger system shows that

$$\epsilon_{\text{m}} = -I_{\text{k,n}} = E_{\text{n}} - E_{\text{k}}^{N-1}, \tag{3.152}$$

where $E_{\text{n}}, E_{\text{k}}^{N-1}$ are the total energies of the interacting N- and $(N-1)$-electron systems in states n and k respectively. Therefore the highest occupied eigenvalue ϵ_{m} is the negative of the first ionization potential.

Since for the model system, the asymptotic structure of the density is always due solely to the highest occupied orbital ϕ_m, it is irrelevant whether the Q-DFT mapping is such that the system is in a ground or excited state. The corresponding highest occupied eigenvalue ϵ_{m} must then invariably be the negative of the first ionization potential.

3.4.9 *Proof that Nonuniqueness of Effective Potential Energy Is Solely Due to Correlation-Kinetic Effects*

In the mapping from an interacting system in a ground or excited state to model S systems with the same density, it is assumed that the external field $\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}) = -\boldsymbol{\nabla} v(\mathbf{r})$ is the same for both the systems. This in turn leads to the interpretation (3.140, 3.141) for the corresponding electron-interaction potential energy $v_{\mathrm{ee}}(\mathbf{r})$ of the S system. The S systems can be in *different* states and hence with *different* electronic configurations. It is claimed [48, 49] that excited states, other than the lowest excited state of a given symmetry different from the ground state, can be mapped to *different* S systems with the same configuration. (See [31] for further remarks.) Here we prove [2, 18] that the $v_{\mathrm{ee}}(\mathbf{r})$ of the different S systems differ *solely* in their Correlation-Kinetic component. The component due to the Pauli exclusion principle and Coulomb repulsion remains the same.

Consider the mapping from a *ground* or *excited* state of the interacting system with density $\rho(\mathbf{r})$. Next, consider two noninteracting fermion systems S and S' that in the presence of the same external field $\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}) = -\boldsymbol{\nabla} v(\mathbf{r})$, reproduce the same density $\rho(\mathbf{r})$. For the S system, the differential equation and the corresponding local electron-interaction potential $v_{\mathrm{ee}}(\mathbf{r})$ are defined by (3.126) and (3.140), respectively.

For the S' system, the differential equation is

$$[-\frac{1}{2}\nabla^2 + v_s'(\mathbf{r})]\, \phi_i'(\mathbf{x}) = \epsilon_i'\phi_i'(\mathbf{x}), \tag{3.153}$$

where the corresponding local effective potential energy $v_{\mathrm{s}}'(\mathbf{r})$ is

$$v_{\mathrm{s}}'(\mathbf{r}) = v(\mathbf{r}) + v_{\mathrm{ee}}'(\mathbf{r}), \tag{3.154}$$

with $v_{\mathrm{ee}}'(\mathbf{r})$ being the electron-interaction potential energy. The resulting 'Quantal Newtonian' first law is

$$\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}) + \boldsymbol{\mathcal{F}}_s'^{\mathrm{int}}(\mathbf{r}) = 0, \tag{3.155}$$

where $\boldsymbol{\mathcal{F}}_s'^{\mathrm{int}}(\mathbf{r})$ is the internal field of the S' model fermions:

$$\boldsymbol{\mathcal{F}}_s'^{\mathrm{int}}(\mathbf{r}) = -\boldsymbol{\nabla} v_{\mathrm{ee}}'(\mathbf{r}) - \boldsymbol{\mathcal{D}}(\mathbf{r}) - \boldsymbol{\mathcal{Z}}_s'(\mathbf{r}), \tag{3.156}$$

with the definitions of the fields $\boldsymbol{\mathcal{D}}(\mathbf{r})$ and $\boldsymbol{\mathcal{Z}}_s'(\mathbf{r})$ being the same as in Sect. 3.4.4.

A comparison of (3.155) with the interacting system first law of (2.134) then yields

$$v_{\mathrm{ee}}'(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} [\boldsymbol{\mathcal{E}}_{\mathrm{ee}}(\mathbf{r}') + \boldsymbol{\mathcal{Z}}_{t_c}'(\mathbf{r}')] \cdot d\boldsymbol{\ell}', \tag{3.157}$$

where the Correlation-Kinetic field $\mathcal{Z}'_{t_c}(\mathbf{r})$ is

$$\mathcal{Z}'_{t_c}(\mathbf{r}) = \mathcal{Z}'_s(\mathbf{r}) - \mathcal{Z}(\mathbf{r}). \tag{3.158}$$

Here $\mathcal{E}_{\mathrm{ee}}(\mathbf{r})$ and $\mathcal{Z}(\mathbf{r})$ are the electron-interaction and kinetic fields of the interacting system as defined in Chap. 2.

The difference between $v_{\mathrm{ee}}(\mathbf{r})$ and $v'_{\mathrm{ee}}(\mathbf{r})$ of the S and S' systems is then

$$v_{\mathrm{ee}}(\mathbf{r}) - v'_{\mathrm{ee}}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} [\mathcal{Z}_{t_c}(\mathbf{r}') - \mathcal{Z}'_{t_c}(\mathbf{r}')] \cdot d\boldsymbol{\ell}', \tag{3.159}$$

or equivalently

$$v_{\mathrm{ee}}(\mathbf{r}) - v'_{\mathrm{ee}}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} [\mathcal{Z}_s(\mathbf{r}') - \mathcal{Z}'_s(\mathbf{r}')] \cdot d\boldsymbol{\ell}'. \tag{3.160}$$

Note that both (3.159) and (3.160) are independent of the electron-interaction field $\mathcal{E}_{\mathrm{ee}}(\mathbf{r})$. As such the contribution of $\mathcal{E}_{\mathrm{ee}}(\mathbf{r})$ to $v_{\mathrm{ee}}(\mathbf{r})$ and $v'_{\mathrm{ee}}(\mathbf{r})$ is the same.

Thus, the difference between the electron-interaction potential energies of the different S systems arises *solely* due to the difference in their Correlation-Kinetic or equivalently their kinetic fields. This completes the proof.

3.5 Application of Q-DFT to the Ground and First Excited Singlet State of the Hooke's Atom

We next apply Q–DFT to the ground and first excited singlet states of the Hooke's atom (Sect. 2.11). The potential energy $v(\mathbf{r}t)$ of the model fermions due to the external field $\mathcal{F}^{\mathrm{ext}}(\mathbf{r}t)$ is the same as that for the Hooke's atom, and defined by (2.164). Thus, as a consequence of the Harmonic Potential theorem (Sect. 2.9), the properties of the S system for $t > t_0$ are the same as those for the stationary state solution valid for $t \leq t_0$ but translated by a finite value. Hence, it suffices to describe the mappings to the time-independent S systems. We map the stationary *ground* state of the Hooke's atom to an S system in its *ground* state. To demonstrate the *arbitrariness* of the S system, we map the stationary first *excited* singlet state of the Hooke's atom to an S system that is also in a *ground* state. The mappings are such that the densities, energies, and ionization potentials of the interacting Hooke's atom are thereby obtained, with the ionization potentials being the highest occupied eigenvalue of the S system differential equation.

The properties of the ground state S systems are described in the following subsections [5, 10, 11]. The analytical expressions for these properties are given in Appendix C.

3.5.1 S System Wavefunction, Spin–Orbitals, and Density

In the S system ground state, both the model fermions occupy the same 1 s orbital and have opposite spins. Thus, the two one–particle spin–orbitals are

$$\phi_1(\mathbf{x}) = \psi(\mathbf{r})\alpha(\sigma),\ \ \phi_2(\mathbf{x}) = \psi(\mathbf{r})\beta(\sigma), \tag{3.161}$$

where the normalized $\psi(\mathbf{r})$ is the spatial part of the spin–orbital, and $\alpha(\sigma)$, $\beta(\sigma)$ the spin functions. The spin coordinate σ can have only two values ± 1. Following standard convention, the spin functions have only two values 0 and 1 so that $\alpha(1) = 1$, $\alpha(-1) = 0$, $\beta(1) = 0$, $\beta(-1) = 1$. The normalized S system wavefunction is then the Slater determinant

$$\begin{aligned}\Phi(\mathbf{x}_1\mathbf{x}_2) &= \frac{1}{\sqrt{2}}\begin{vmatrix}\phi_1(\mathbf{x}_1) & \phi_1(\mathbf{x}_2)\\ \phi_2(\mathbf{x}_1) & \phi_2(\mathbf{x}_2)\end{vmatrix}\\ &= \frac{1}{\sqrt{2}}\psi(\mathbf{r}_1)\psi(\mathbf{r}_2)\left[\alpha(\sigma_1)\beta(\sigma_2) - \alpha(\sigma_2)\beta(\sigma_1)\right].\end{aligned} \tag{3.162}$$

As the electrons have opposite spins, the density

$$\begin{aligned}\rho(\mathbf{r}) &= \langle\Phi|\hat{\rho}(\mathbf{r})|\Phi\rangle\\ &= \frac{1}{2}\sum_{\substack{\sigma_1,\sigma_2=\pm 1\\ \sigma_1\neq\sigma_2}}\iint \psi^*(\mathbf{r}_1)\psi^*(\mathbf{r}_2)\left[\sum_{i=1}^{2}\delta(\mathbf{r}-\mathbf{r}_i)\right]\psi(\mathbf{r}_1)\psi(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2\\ &\quad\times\left[\alpha(\sigma_1)\beta(\sigma_2) - \alpha(\sigma_2)\beta(\sigma_1)\right]^2\\ &= \iint \psi^*(\mathbf{r}_1)\psi^*(\mathbf{r}_2)\left[\sum_{i=1}^{2}\delta(\mathbf{r}-\mathbf{r}_i)\right]\psi(\mathbf{r}_1)\psi(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2\\ &= 2\psi^*(\mathbf{r})\psi(\mathbf{r}).\end{aligned} \tag{3.163}$$

Thus, the S system orbitals $\psi(\mathbf{r})$ are known in terms of the density $\rho(\mathbf{r})$ as

$$\psi(\mathbf{r}) = \sqrt{\frac{\rho(\mathbf{r})}{2}}. \tag{3.164}$$

Since the wavefunctions $\psi_{00}(\mathbf{r}_1\mathbf{r}_2)$, $\psi_{01}(\mathbf{r}_1\mathbf{r}_2)$, and hence the densities $\rho_{00}(\mathbf{r})$, $\rho_{01}(\mathbf{r})$ of the ground and first excited singlet states of the Hooke's atom, respectively, are known, then so are the orbitals of the corresponding ground state S systems. This allows for all the properties of the S system to be determined exactly.

3.5.2 Pair–Correlation Density; Fermi and Coulomb Hole Charge Distributions

The S system pair–correlation density $g_s(\mathbf{rr}')$ is

$$\begin{aligned} g_s(\mathbf{rr}') &= \langle \Phi | \hat{P}(\mathbf{rr}') | \Phi \rangle / \rho(\mathbf{r}) \\ &= \frac{\sqrt{2}}{\rho(\mathbf{r})} \int \Phi^*(\mathbf{x}_1 \mathbf{x}_2) \hat{P}(\mathbf{rr}') \phi_1(\mathbf{x}_1) \phi_2(\mathbf{x}_2) d\mathbf{X}, \end{aligned} \tag{3.165}$$

where the second step follows as a result of the pair–correlation operator $\hat{P}(\mathbf{rr}')$ being symmetric. Thus,

$$\begin{aligned} & g_s(\mathbf{rr}') \\ &= \frac{1}{\rho(\mathbf{r})} \sum_{\substack{\sigma_1, \sigma_2 = \pm 1 \\ \sigma_1 \neq \sigma_2}} \int \psi^*(\mathbf{r}_1) \psi^*(\mathbf{r}_2) \left[\sum_{\substack{i,j=1 \\ i \neq j}}^{2} \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) \right] \\ &\qquad \psi(\mathbf{r}_1) \psi(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \left[\alpha(\sigma_1) \beta(\sigma_2) - \alpha(\sigma_2) \beta(\sigma_1) \right] \alpha(\sigma_1) \beta(\sigma_2) \\ &= \frac{2 \psi^*(\mathbf{r}) \psi(\mathbf{r}) \psi^*(\mathbf{r}') \psi(\mathbf{r}')}{\rho(\mathbf{r})} \\ &= \frac{\rho(\mathbf{r}')}{2}. \end{aligned} \tag{3.166}$$

Hence, the pair–correlation density of the two model–fermion S system in its ground state is independent of electron position $\mathbf{r}$. Since $g_s(\mathbf{rr}')$ may also be expressed as the sum of the density $\rho(\mathbf{r}')$ and the Fermi hole $\rho_x(\mathbf{rr}')$ (see (3.13)):

$$g_s(\mathbf{rr}') = \rho(\mathbf{r}') + \rho_x(\mathbf{rr}'), \tag{3.167}$$

it is customary in local effective potential energy theory to define a Fermi hole for the two model–fermion system in spite of the fact that the fermions have opposite spin. This Fermi hole is then

$$\rho_x(\mathbf{rr}') = -\frac{\rho(\mathbf{r}')}{2}, \tag{3.168}$$

and is a *local* charge distribution independent of electron position. The ground-state S system Coulomb hole $\rho_c(\mathbf{rr}')$ which is the difference between the Fermi–Coulomb $\rho_{xc}(\mathbf{rr}')$ and Fermi $\rho_x(\mathbf{rr}')$ holes is consequently

$$\rho_c(\mathbf{rr}') = \rho_{xc}(\mathbf{rr}') - \frac{\rho(\mathbf{r}')}{2}, \tag{3.169}$$

and it is a *nonlocal* charge distribution dependent on electron position.

In Fig. 3.1 the Fermi hole $\rho_x(\mathbf{rr}')$ for the ground and excited states is plotted. This charge distribution is spherically symmetric about the nucleus and independent of electron position.

In Figs. 3.2–3.4 the corresponding ground and excited state Coulomb holes are plotted for electron positions at $r = 0, 0.5, 1, 2, 10, 20, 50$, and 200 a.u. The electron position is along the z–axis corresponding to $\theta = 0°$. The cross–sections plotted are those for $\theta' = 0°$ with respect to the electron–nucleus direction. The part of the graph for $r' < 0$ is the structure for $\theta = \pi$ and $r' > 0$. The electron–electron cusp condition is clearly evident in the structure of the Coulomb holes as is their dynamic nature (Figs. 3.2, 3.3). For an electron at the nucleus, the Coulomb holes are spherically symmetric about the electron (Fig. 3.2a). For other electron positions they are not. For asymptotic positions of the electron, the Coulomb holes are once again spherically symmetric about the nucleus (Fig. 3.4). *Furthermore, for these electron positions, they are essentially static charges*. Note that at the electron position, the Coulomb hole for the ground state case is always negative. This is not the case for the excited state for electron positions near the nucleus. The difference is strictly a consequence of the definition of the Fermi hole for the two electron model. The center of mass of the Coulomb holes $\langle \mathbf{r}'\rho_c(\mathbf{rr}')\rangle$ is plotted in Fig. 3.5 a,b. It lies along the nucleus–electron direction, and is on the other side from the electron, approaching the nucleus asymptotically.

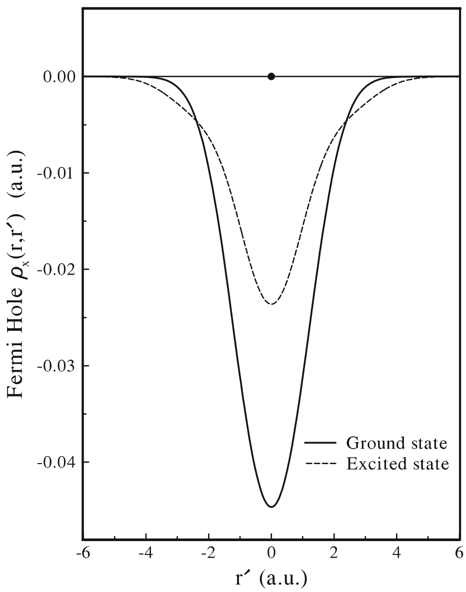


Fig. 3.1 The Fermi hole charge $\rho_x(\mathbf{rr}')$ for the ground and first excited singlet state

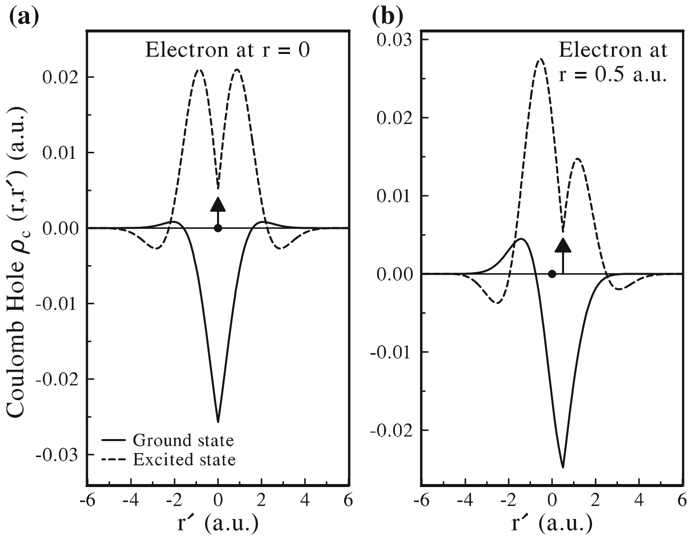


Fig. 3.2 Cross–section through the Coulomb hole charge $\rho_c(\mathbf{rr}')$ for the ground and first excited singlet states. In (**a**) the electron is at the nucleus $r = 0$, and in (**b**) at $r = 0.5$ a.u. The electron, indicated by the *arrow*, is on the z axis corresponding to $\theta = 0°$. The graphs for $r' < 0$ correspond to the structure for $\theta = \pi$, $r' > 0$

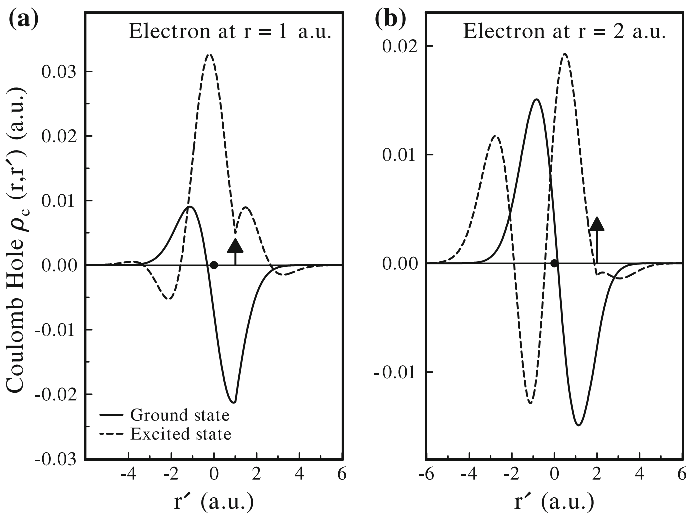


Fig. 3.3 The same as in Fig. 3.2 but for the electron at (**a**) $r = 1$ a.u. and (**b**) $r = 2$ a.u.

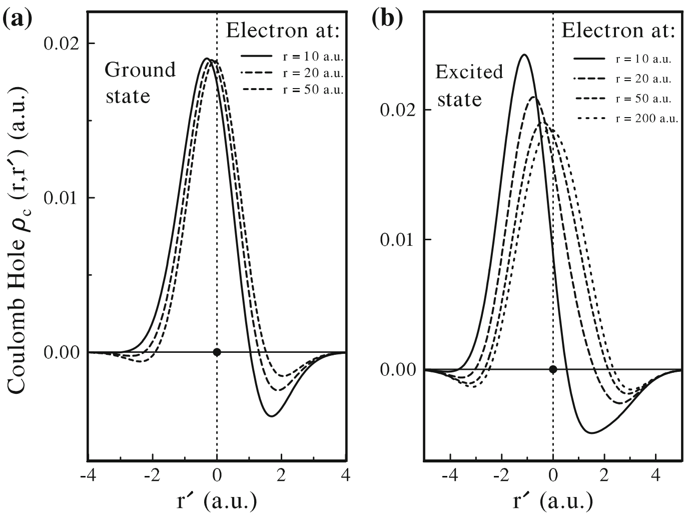
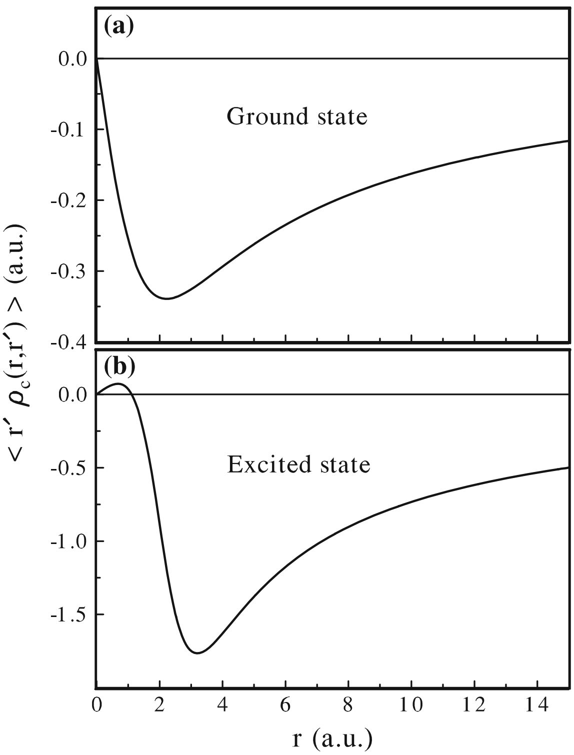


Fig. 3.4 Same as in Fig. 3.2 but for but for electron positions at $r = 10, 20, 50$ and 200 a.u.: (**a**) ground state, (**b**) first excited singlet state

Fig. 3.5 The center of mass $\langle r'\rho_c(\mathbf{rr}')\rangle$ of the Coulomb hole charge: (**a**) ground state, (**b**) first excited singlet state



3.5.3 Hartree, Pauli, and Coulomb Fields $\mathcal{E}_{\mathrm{H}}(\mathbf{r})$, $\mathcal{E}_{\mathrm{x}}(\mathbf{r})$, $\mathcal{E}_{\mathrm{c}}(\mathbf{r})$ and Energies E_{H}, E_{x}, E_{c}

As the interacting and noninteracting system densities are the same, the Hartree fields $\mathcal{E}_{\mathrm{H}}$ and energies E_{H} too are the same. (See Fig. 2.11 and Tables 2.1 and 3.1). For both the ground and excited states, the field $\mathcal{E}_{\mathrm{H}}(\mathbf{r})$ decays asymptotically as $2/r^2$.

The Pauli field $\mathcal{E}_{\mathrm{x}}(\mathbf{r})$ for both states is plotted in Fig. 3.6. This field vanishes at the nucleus because the Fermi hole is spherically symmetric about the electron at that position. Since the total charge of the Fermi hole is negative unity, it decays asymptotically as

$$\mathcal{E}_{\mathrm{x}}(\mathbf{r}) \underset{r\to\infty}{\sim} -\frac{1}{r^2}. \tag{3.170}$$

The merging of the fields asymptotically with the function $-1/r^2$ for both the ground and excited states is evident in the figure. (The asymptotic structure of the fields $\mathcal{E}_{\mathrm{H}}(\mathbf{r})$ and $\mathcal{E}_{\mathrm{x}}(\mathbf{r})$ are to Gaussian accuracy.) The Pauli energy E_{x} for both states as determined from these fields via (3.135) are quoted in Table 3.1. Observe that the magnitude (and sign) of these energies are a reflection of the magnitude (and sign) of the corresponding fields.

The asymptotic structure of the Pauli field $\mathcal{E}_{\mathrm{x}}(\mathbf{r})$ as given by (3.170) is a general result valid for finite systems. It is a consequence of the fact that the Fermi hole charge distribution of total charge unity becomes an essentially static charge localized about the center of mass of the system for asymptotic positions of the electron.

Fig. 3.6 The Pauli field $\mathcal{E}_{\mathrm{x}}(\mathbf{r})$ for the ground and first excited singlet state

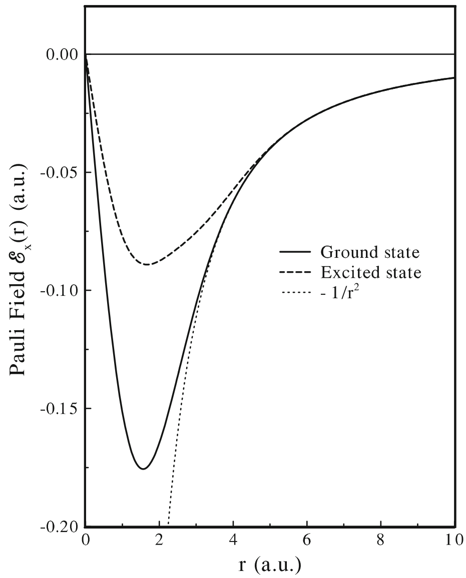


Table 3.1 Q–DFT properties of the *ground* state *S* systems which reproduce the density, total energy, and ionization potential of the ground and first excited singlet states of the Hooke's atom in atomic units

Property	Ground state S system properties	
	Mapping from	
	Ground state[a]	First excited singlet state[b]
E	2.000000	2.280775
T_s	0.635245	0.327471
E_{ext}	0.888141	1.052372
E_H	1.030250	0.722217
E_x	−0.515125	−0.361109
E_c	−0.067682	−0.008966
T_c	0.029173	0.548791
ϵ_m	1.250000	1.710582

[a][5]
[b][11]

The Coulomb fields $\boldsymbol{\mathcal{E}}_c(\mathbf{r})$ for the ground and excited states are plotted in Fig. 3.7. As the Coulomb hole $\rho_c(\mathbf{r}\mathbf{r}')$ is spherically symmetric about the electron position at the nucleus, both fields vanish there. The fields are both positive and negative, reflecting the fact that the total charge of the Coulomb hole is zero. In the classically forbidden region, both the Coulomb fields decay asymptotically as

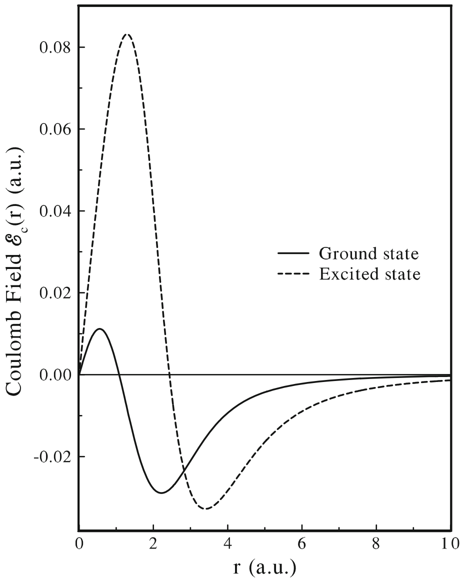


Fig. 3.7 The Coulomb field $\boldsymbol{\mathcal{E}}_c(\mathbf{r})$ for the ground and first excited singlet state

$$\boldsymbol{\mathcal{E}}_{\mathrm{c}}(\mathbf{r}) \underset{r\to\infty}{\sim} -\frac{\delta}{r^4}, \tag{3.171}$$

where the coefficient $\delta = 4$ for the ground state and $\delta = 15.784129$ for the excited state. The Coulomb energy E_{c} for these states as determined from the respective fields via (3.136) are given in Table 3.1. For the ground state, the field $\boldsymbol{\mathcal{E}}_{\mathrm{c}}(\mathbf{r})$ is an order of magnitude smaller than $\boldsymbol{\mathcal{E}}_{\mathrm{x}}(\mathbf{r})$ and consequently so is the Coulomb energy E_{c} in comparison to E_{x}. For the excited state, the positive part of the field $\boldsymbol{\mathcal{E}}_{\mathrm{c}}(\mathbf{r})$ is large, so that the corresponding E_{c} is two-orders of magnitude smaller than the E_{x}. Thus, as may be expected for the excited state, the Coulomb energy E_{c} is very small.

3.5.4 Hartree $\mathbf{W}_{\mathbf{H}}(\mathbf{r})$, Pauli $\mathbf{W}_{\mathbf{x}}(\mathbf{r})$, and Coulomb $\mathbf{W}_{\mathbf{c}}(\mathbf{r})$ Potential Energies

The Hartree $W_{\mathrm{H}}(\mathbf{r})$, Pauli $W_{\mathrm{x}}(\mathbf{r})$, and Coulomb $W_{\mathrm{c}}(\mathbf{r})$ potential energies, calculated as the work done in the Hartree $\boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r})$, Pauli $\boldsymbol{\mathcal{E}}_{\mathrm{x}}(\mathbf{r})$, and Coulomb $\boldsymbol{\mathcal{E}}_{\mathrm{c}}(\mathbf{r})$ fields, are plotted in Figs. 3.8, 3.9, and 3.10, respectively. As these fields vanish at the nucleus, the corresponding potential energies have zero slope there. The fields [$\boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r})$; $\boldsymbol{\mathcal{E}}_{\mathrm{x}}(\mathbf{r})$] are [positive;negative] so that the potential energies [$W_{\mathrm{H}}(\mathbf{r})$; $W_{\mathrm{x}}(\mathbf{r})$] are monotonic with [negative;positive] slope. In contrast, the potential energy $W_{\mathrm{c}}(\mathbf{r})$ is not monotonic since the field $\boldsymbol{\mathcal{E}}_{\mathrm{c}}(\mathbf{r})$ changes sign. Observe that the Coulomb potential energies $W_{\mathrm{c}}(\mathbf{r})$ are an order of magnitude smaller than their Pauli $W_{\mathrm{x}}(\mathbf{r})$ counterparts.

The asymptotic structure of these potential energies are

$$W_{\mathrm{H}}(\mathbf{r}) \underset{r\to\infty}{\sim} \frac{2}{r}, \tag{3.172}$$

$$W_{\mathrm{x}}(\mathbf{r}) \underset{r\to\infty}{\sim} -\frac{1}{r}, \tag{3.173}$$

$$W_{\mathrm{c}}(\mathbf{r}) \underset{r\to\infty}{\sim} -\frac{\eta}{r^3}, \tag{3.174}$$

where $\eta = 4/3$ for the ground state and $\eta = 5.261376$ for the excited state. The merging of $W_{\mathrm{H}}(\mathbf{r})$, $W_{\mathrm{x}}(\mathbf{r})$ with the functions $2/r$, $-1/r$ for both states is evident in Figs. 3.8 and 3.9. The asymptotic structure of $W_{\mathrm{x}}(\mathbf{r})$ is a general result valid for all finite systems. It is also interesting to note that the functional dependence of the asymptotic structure of the fields and potential energies are the same for the ground and excited states. Only the coefficients of the Coulomb field $\boldsymbol{\mathcal{E}}_{\mathrm{c}}(\mathbf{r})$ and potential energy $W_{\mathrm{c}}(\mathbf{r})$ for each state differ.

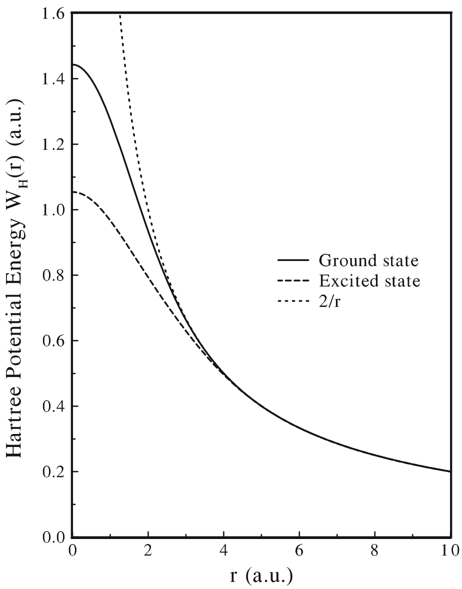


Fig. 3.8 The ground-state *S* system Hartree potential energy $W_{\mathrm{H}}(\mathbf{r})$ for the ground and first excited singlet states of the Hooke's atom

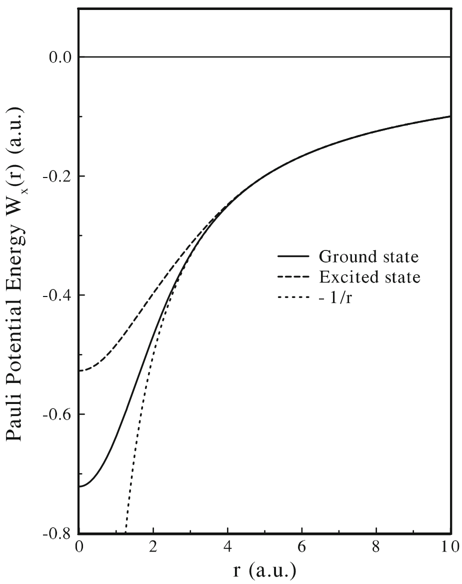


Fig. 3.9 The ground-state *S* system Pauli potential energy $W_{\mathrm{x}}(\mathbf{r})$ for the ground and first excited singlet states of the Hooke's atom

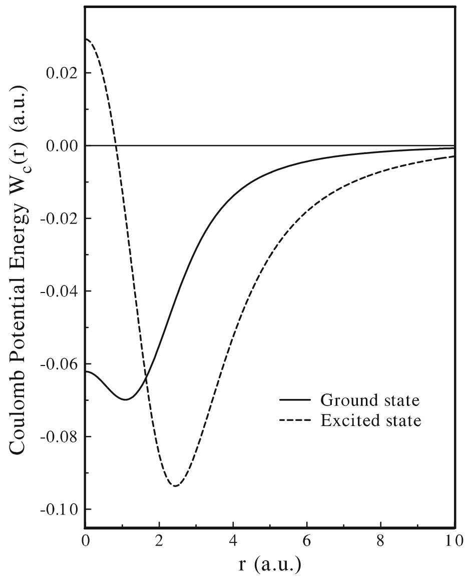


Fig. 3.10 The ground-state S system Coulomb potential energy $W_c(\mathbf{r})$ for the ground and first excited singlet states of the Hooke's atom

3.5.5 Correlation–Kinetic Field $\mathcal{Z}_{t_c}(\mathbf{r})$, Energy T_c, and Potential Energy $W_{t_c}(\mathbf{r})$

The transformation from both the ground and first excited singlet states of the Hooke's atom is to an S system in its *ground* state. Thus, the corresponding S system kinetic–energy–density tensor $t_{s,\alpha\beta}(\mathbf{r}; [\gamma_s])$ for each case is of the form

$$t_{s,\alpha\beta}(\mathbf{r}; [\gamma_s]) = \frac{r_\alpha r_\beta}{r^2} h(r), \tag{3.175}$$

where

$$h(r) = \frac{1}{8\rho}\left(\frac{\partial \rho}{\partial r}\right)^2. \tag{3.176}$$

The expression for the interacting system kinetic–energy–density tensor $t_{\alpha\beta}(\mathbf{r}; [\gamma])$ for the ground and excited state is given by (2.184).

For the ground state case, we compare in Fig. 3.11a the off–diagonal elements of the interacting and noninteracting tensors by plotting the functions $f(r)$ and $h(r)$. Observe that they are essentially the same, vanishing at the nucleus, and decaying in a similar manner asymptotically. In Fig. 3.11b we compare the diagonal elements of the tensors by plotting the functions $h(r)$ and $f(r) + 3k(r)$. Note that the diagonal element of the interacting system tensor is now finite at the nucleus, and that the difference in this element between the two tensors occurs in the interior region of the

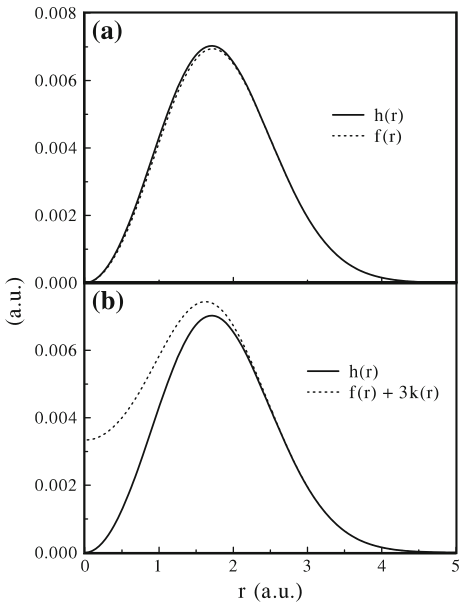


Fig. 3.11 (**a**) Functions $f(r)$ and $h(r)$ of the off–diagonal elements of the interacting and noninteracting system kinetic–energy–density tensors $t_{\alpha\beta}(\mathbf{r}; [\gamma])$ and $t_{s,\alpha\beta}(\mathbf{r}; [\gamma_s])$, respectively. (**b**) The functions $f(r) + 3k(r)$ and $h(r)$ of the diagonal elements of the tensors $t_{\alpha\beta}(\mathbf{r}; [\gamma])$ and $t_{s,\alpha\beta}(\mathbf{r}; [\gamma_s])$, respectively. These plots are for the mapping from the ground state of Hooke's atom

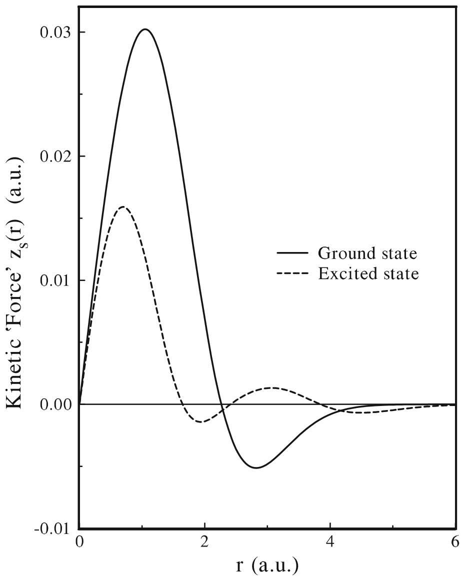


Fig. 3.12 The ground-state S system kinetic 'force' $z_s(\mathbf{r})$ for the mappings from the ground and first excited singlet state of the Hooke's atom

atom. This then is the region from which the correlation contribution to the kinetic energy must arise.

The S system kinetic 'force' $z_s(\mathbf{r})$ for the ground and excited state mappings is plotted in Fig. 3.12. A comparison with the corresponding figure Fig. 2.14 for the 'force' $z(\mathbf{r})$ of the interacting system shows the following. For the mapping from the ground state of Hooke's atom, the 'forces' $z(\mathbf{r})$ and $z_s(\mathbf{r})$ are essentially equivalent. Thus, in this case, the S system kinetic energy T_s is 94 % of the interacting system kinetic energy T (see (3.52)) and Tables 2.1 and 3.1). For the transformation from the excited singlet state to a ground state S system, the 'force' $z_s(\mathbf{r})$ is much smaller in magnitude than the interacting system 'force' $z(\mathbf{r})$. In this case, therefore, T_s is only 37 % of T (see Tables 2.1 and 3.1). (Note that the kinetic energies T_s and T may also be determined from the corresponding kinetic–energy–density tensors as their trace is the kinetic–energy–density.)

The Correlation–Kinetic field $\mathcal{Z}_{t_c}(\mathbf{r})$ for the ground and excited state cases is plotted in Fig. 3.13. For the ground state case, $\mathcal{Z}_{t_c}(\mathbf{r})$ is negligible, so that the Correlation–Kinetic energy T_c obtained from this field via (3.137) is only 6 % of the interacting system kinetic energy T. For the excited state case, the situation is dramatically different: the field $\mathcal{Z}_{t_c}(\mathbf{r})$ is large, and consequently T_c is 63 % of T (see Tables 2.1 and 3.1).

For both the ground and excited state cases, the field $\mathcal{Z}_{t_c}(\mathbf{r})$ decays asymptotically as a positive function:

$$\mathcal{Z}_{t_c}(\mathbf{r}) \underset{r\to\infty}{\sim} \frac{\kappa}{r^3} - \frac{\mu}{r^4}, \tag{3.177}$$

where $\kappa = 1$, $\mu = -8$ for the ground state, and $\kappa = 9.000750$, $\mu = 31.580570$ for the excited state case. (For the ground state, the analytical asymptotic structure of the 'forces' $z(\mathbf{r})$, $z_s(\mathbf{r})$, and the density $\rho(\mathbf{r})$, from which that of $\mathcal{Z}_{t_c}(\mathbf{r})$ is obtained, is given in Appendix C.)

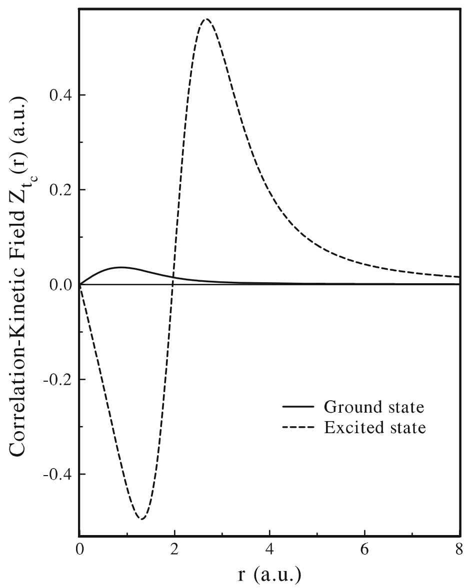


Fig. 3.13 The ground-state S system Correlation–Kinetic field $\mathcal{Z}_{t_c}(\mathbf{r})$ for the mapping from the ground and first excited singlet states of the Hooke's atom

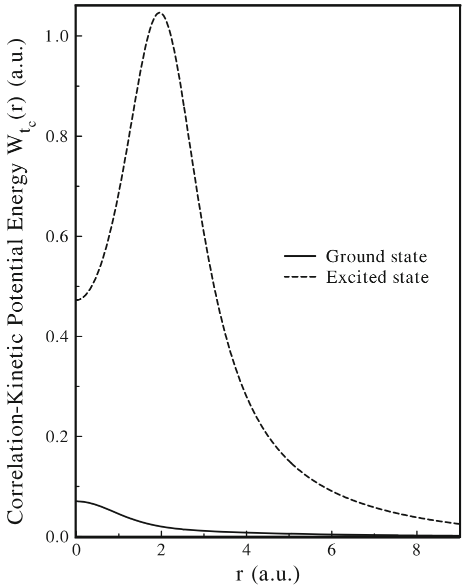


Fig. 3.14 The ground-state S system Correlation–Kinetic potential energy $W_{t_c}(\mathbf{r})$ for the mapping from the ground and first excited singlet state of the Hooke's atom

The structure of the Correlation–Kinetic field $\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r})$ dictates that of the corresponding work done plotted in Fig. 3.14. As the field $\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r})$ vanishes at the nucleus, the potential energy $W_{t_c}(\mathbf{r})$ has zero slope there. For the ground state case, $\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r})$ is positive, so that $W_{t_c}(\mathbf{r})$ is monotonic with negative slope over all space. For the excited state case, $\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r})$ is both positive and negative, so that the resulting $W_{t_c}(\mathbf{r})$ has structure. In both cases, the potential energy $W_{t_c}(\mathbf{r})$ is positive throughout space. In each case, it decays asymptotically as

$$W_{t_c}(\mathbf{r}) \underset{r\to\infty}{\sim} \frac{\alpha}{r^2} - \frac{\beta}{r^3}, \tag{3.178}$$

where $\alpha = 1/2$, $\beta = 8/3$ for the ground state, and $\alpha = 4.500375$, $\beta = 10.526857$ for the excited state.

From these results we see that for the transformation from the *ground* state of an interacting system to an S system in its *ground* state, Correlation–Kinetic effects are small and can reasonably be ignored in a first approximation. On the other hand, for the mapping from an *excited* state of the interacting system to a *ground* state S system, these kinetic correlations are very significant, and must be accounted for in any approximation. In contrast, for this latter case, Coulomb correlations are negligible (see Figs. 3.10 and 3.14), and may be neglected in a first approximation.

3.5.6 Total Energy and Ionization Potential

The total energy E of the ground and first excited state of the Hooke's atom as determined from the corresponding ground-state S system energy components of (3.131) are quoted in Table 3.1. The values of E are the same as obtained by Schrödinger theory for the interacting system given in Table 2.1.

The single eigenvalue ϵ_0 of the ground-state S systems, which is also the maximum eigenvalue ϵ_{m}, corresponds to the negative of the ionization potential for the ground and excited states of the Hooke's atom. This eigenvalue may be determined from the S system differential equation (3.126) via

$$\epsilon = -\frac{1}{2}\frac{\nabla^2\sqrt{\rho(\mathbf{r})}}{\sqrt{\rho(\mathbf{r})}} + v(\mathbf{r}) + v_{\mathrm{ee}}(\mathbf{r}), \tag{3.179}$$

which is an expression valid for arbitrary $\mathbf{r}$, and where the components $W_{\mathrm{H}}(\mathbf{r})$, $W_{\mathrm{x}}(\mathbf{r})$, $W_{\mathrm{c}}(\mathbf{r})$, and $W_{t_{\mathrm{c}}}(\mathbf{r})$ of $v_{\mathrm{ee}}(\mathbf{r})$ of (3.144) are as determined in the previous subsections. Or, it may be determined by substituting the various components of $v_{\mathrm{ee}}(\mathbf{r})$ into the differential equation (3.126), and solving numerically for the single *zero node* orbital and single eigenvalue. The orbital leads to the density, and the eigenvalue quoted in Table 3.1 is the negative of the ionization potential.

In the case of the mapping from the ground state of Hooke's atom, both the Schrödinger wavefunction and the S system orbital are nodeless. In contrast, the singlet excited state wavefunction has a single node. However, we see via Q–DFT that it is possible to obtain the density, total energy, and ionization potential of the excited state from a *nodeless* ground state S system orbital.

3.5.7 Endnote on the Multiplicity of Potentials

We conclude this section by remarks on the multiplicity of local effective potentials. It is evident from Q-DFT and the examples above that there exist an *infinite* number of *local* effective potentials that can generate the density of an interacting system of electrons in a ground or excited state. This is further confirmed by the examples of the Q-DFT mapping of the *ground* state Hooke's atom to an S system in its first *excited* singlet state [16], and that of the mapping from the first *excited* singlet state of the Hooke's atom to an S system also in its first *excited* singlet state [10]. (As it is also possible to map an interacting system of electrons to one of noninteracting bosons having the same density, there exists yet another such local effective potential.)

In the literature of the Hohenberg-Kohn-Sham (HKS) [24, 25] density functional theory, it is stated that there only exists a *unique* local potential that can generate the nondegenerate ground state density of an interacting system. HKS theory is a ground state theory, and as such the mapping can only be to an S system in its ground state. It then follows from the Hohenberg-Kohn theorem, that the corresponding local effective potential must be unique. The theory does not allow for arbitrary mappings to S systems with different configurations. It is from this constrained perspective that the statement of uniqueness is made. Similarly, in excited state density functional theory [50], the mapping from the interacting system is to an S system of the same configuration. Thus, in the context of the configuration-constrained mappings permissible, traditional density functional theory constitutes a special case of Q-DFT.

The above remarks are with reference to the mapping from an interacting system of fermions to one of noninteracting fermions with the same density. Consider now a system of fermions, either interacting or noninteracting, in some external field $\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}) = -\boldsymbol{\nabla} v(\mathbf{r})$. The potential $v(\mathbf{r})$ which then generates via the corresponding Schrödinger equation the nondegenerate ground state density and the density of the lowest excited state of symmetry different from that of the ground state is *unique*. No other potential can generate these densities. This follows, respectively, from the Hohenberg-Kohn [24] and Gunnarsson-Lundqvist [30, 31] theorems. For other excited states of this system, however, there exist other potentials different from $v(\mathbf{r})$ that can generate the same density [31].

3.6 Quantal Density Functional Theory of Degenerate States

The Quantal density functional theory of the mapping from both a *degenerate ground* and *excited* state of the interacting system to one of noninteracting fermions such that the equivalent density, energy and ionization potential are obtained is given in [14] and in Appendix A of ***QDFT2***. The cases of both *pure state* and *ensemble* v-representable densities are considered. The reader is referred to these references for the details, but the following are described in them.

(1) The Q-DFT of the *individual* degenerate *pure* state. For the mapping from a degenerate *ground* or *excited* state, the state of the S system is *arbitrary* in that it may be in a *ground* or *excited* state configuration. In either case, the highest occupied eigenvalue is the negative of the ionization potential.
(2) For the *ground* and *excited* state *ensemble* cases, two different schemes within Q-DFT are described: (a) In the first, the corresponding noninteracting system ensemble density is obtained by constructing g S-systems, where g is the degeneracy of the state. Once again, the g S-systems may either be in a ground or excited state or a combination of the two. (b) In the second, the Q-DFT whereby the ensemble density is obtained from a single noninteracting fermion system whose orbitals could be degenerate is described. The construction of this model system is a consequence of the linearity of the 'Quantal Newtonian' first law. Here the highest occupied eigenvalue is degenerate, and the ensemble density is obtained from the resulting Slater determinants as described in [51]. Again, for the mapping from an excited state, the S system may be in a ground or excited state.

(3) Examples demonstrating the above mappings within Q-DFT are provided.
(4) The above Q-DFT mappings also provide the rigorous physical interpretations of the various Kohn-Sham theory [26, 51–53] degenerate state energy-density and energy-bidensity functionals and of their functional derivatives. (See also Chap. 5.)

3.7 Application of Q-DFT to the Wigner High-Electron-Correlation Regime of Nonuniform Density Systems

The state of matter comprised of a low-electron-density gas in the presence of an external field $\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}) = -\nabla v(\mathbf{r})$ due to a neutralizing *uniform* positive charge (jellium) background was one originally proposed by Wigner [54, 55]. As the electron density becomes lower, the kinetic energy of the electrons becomes negligible in comparison to the electron-interaction potential energy. It is the electron-interaction term of the Hamiltonian that then dominates in the determination of the wave function and leads to a crystallization of the electronic assembly into a body-centered cubic structure. In his work, Wigner also determined the correction to the energy due to the zero-point oscillations of the electrons about the lattice points. The Wigner regime of the electron gas is thus characterized in the literature by a low electronic density and an electron-interaction energy that is much greater than the kinetic energy. This state of matter has been observed experimentally [56–59] in a two-dimensional electron gas on the surface of liquid helium and in GaAs-GaAlAs heterostructures in the presence of strong magnetic fields (The Q-DFT in the presence of an external magnetostatic field is discussed in Chap. 9.)

The Hooke's atom is ideally suited to the application of Q-DFT to the Wigner regime of a *nonuniform* electron gas. The Wigner regime is achieved in this model for weak confinement of the electrons. In contrast, the low-electron-correlation regime is characterized by a confinement such that the kinetic and electron-interaction energies are of the same order of magnitude. The force constant of $k = \frac{1}{4}$ for the ground state and $k = 0.144498$ for the first excited singlet state studied previously corresponds to this regime (see Table 2.1).

A Q-DFT study of the Wigner regime along the lines of Sect. 3.6 has been performed [60, 61] for a value of the force constant $k = 3.00891 \times 10^{-4}$. The corresponding spatial part of the singlet ground-state wave function is

$$\psi_{00}(\mathbf{r}_1, \mathbf{r}_2) = N e^{-\omega R^2} e^{-\frac{1}{4}\omega s^2} \left[1 + \frac{s}{2} + \sum_{j=2}^{4} a_j \left(s\sqrt{\frac{\omega}{2}} \right)^j \right], \tag{3.180}$$

where $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$, $\mathbf{s} = \mathbf{r}_1 - \mathbf{r}_2$, $N = 8.94669 \times 10^{-6}$, $\omega = \sqrt{k} = 1.73462 \times 10^{-2}$, $a_2 = 8.274917$, $a_3 = 4.720056$, and $a_4 = 0.879153$. The Q-DFT mapping is to a ground state of the S system. The results of the study are presented in Table 3.2 together with those of the low-correlation regime corresponding to $k = \frac{1}{4}$ for purposes of comparison. For the details of the calculations, and the structures of the various quantal sources, fields, and potentials, the reader is referred to the original literature. Although there are similarities between the structures of the low- and high-electron-correlation regimes, there are also significant differences as reflected in the analysis below of the results in Table 3.2.

As noted above, the Wigner high electron correlation regime is characterized by a low electron density and an electron-interaction energy E_{ee} greater than the kinetic energy T. The reverse is the case for the low correlation regime. The ratio E_{ee}/T for the high- and low-correlation regimes is 249.3 and 67.3 %, respectively. In comparison with the total energy E, the ratio E_{ee}/E is 43.4 % and 22.4 % respectively. In fact this trend in the difference is reflected in each component of E_{ee}, i.e., in the ratios E_H/E, E_x/E, and E_c/E.

Table 3.2 Q-DFT values for the total E, kinetic T, correlation-kinetic T_c, noninteracting kinetic T_s, external E_{ext}, Hartree E_H, Pauli E_x, Coulomb E_c, and electron-interaction E_{ee} energies, and noninteracting system eigenvalue ϵ in atomic units for the low correlation ($k = \frac{1}{4}$) [5] and high correlation ($k \approx 3.00891 \times 10^{-4}$) regimes [61]. The Q-DFT mapping in each case is from a ground state of the Hooke's atom to an S system in its ground state

Property	$k = \frac{1}{4}$	$k \approx 3.00891 \times 10^{-4}$
E	2.000000	0.1214235
E_{ee}	0.447443	0.052739
T	0.664418	0.021158
E_{ee}/T	67.3 %	249.3 %
T_c	0.029173	0.005700
T_s	0.635245	0.015457
E_{ext}	0.888141	0.047527
E_H	1.030250	0.151474
E_x	−0.515125	−0.075735
E_c	−0.067682	−0.022998
ϵ	1.250000	0.095404
E_{ee}/E	22.4 %	43.4 %
E_H/E	51.5 %	124.7 %
E_x/E	25.8 %	62.4 %
E_c/E	3.4 %	18.9 %
ϵ/E	62.5 %	78.6 %
T/E	33.2 %	17.4 %
T_c/T	4.4 %	26.9 %
T_c/E	1.45 %	4.5 %
$(T_c + E_{ee})/E$	24 %	48 %

A new result discovered by this application of Q-DFT is that in the Wigner regime, not only is the electron-interaction energy E_{ee} very significant, but so is the contribution of electron correlations to the kinetic energy, *viz*., the Correlation-Kinetic energy T_c. Thus, the ratio T_c/T in the Wigner regime is 26.9 %, as opposed to 4.4 % for the low-correlation case. The Correlation-Kinetic energy T_c thus constitutes a significant fraction of the total energy E: the ratio T_c/E is 4.5 % in the Wigner regime, whereas it is only 1.45 % in the low-correlation case. The total contribution of electron correlations to the energy E is $(T_c + E_{ee})$. The ratio $(T_c + E_{ee})/E$ is 48 % for the Wigner and 24 % for the low-correlation regime.

The result for the eigenvalue ϵ of the model S system is also interesting. This eigenvalue, as explained previously, being the highest occupied eigenvalue, is the negative of the ionization potential I. Even though the electrons are more weakly bound to the nucleus in the Wigner regime, the ratio of this eigenvalue ϵ to the total energy E is 78.6 %, whereas for the low-correlation case it is 62.5 %. Thus, in the Wigner regime, the removal energy relative to the total energy is also greater than in the low-electron-correlation case.

Yet another interesting and new result observed is that of the ratio of the kinetic T to the total energy E is reduced from 33.2 % in the low correlation case to 17.4 % in the Wigner regime. The reason for this is the difference of the corresponding kinetic energy densities $t(\mathbf{r})$. In the Wigner regime, there is a *'quantal compression'* of the kinetic energy density $t(\mathbf{r})$ towards the nucleus, whereas there is a *'quantal decompression'* of $t(\mathbf{r})$ away from the nucleus for the low correlation case (see Figs. 15 of [61], and 5 of [60] or Fig. 3.11). For an explanation of the concepts of 'quantal compression' and 'quantal decompression' of the kinetic energy density $t(\mathbf{r})$ for finite nonuniform density systems which in turn lead to the T/E ratios, see [61].

As the density is further diminished, all the above ratios become even more pronounced relative to the low-correlation systems. In the limit of very low density ($k \to 0$), the Correlation-Kinetic energy T_c becomes the zero-point energy of the electrons. Wigner, in his original papers on the uniform electron gas, did explicitly consider the zero-point motion of the electrons. For nonuniform electron gas systems, it is the Correlation-Kinetic energy T_c that is of significance.

What these results indicate is that in addition to characterizing the Wigner regime by a low density and hence a high value of the electron-interaction energy, the regime also be characterized by a high Correlation-Kinetic energy.

3.8 Quantal Density Functional Theory of Hartree–Fock and Hartree Theories

Just as it is possible to construct a Q–DFT for the interacting system defined by the time-independent Schrödinger equation (2.133), it is also possible to construct a Q–DFT for Hartree–Fock (HF) and Hartree (H) theories. In other words, it is possible to construct model systems of noninteracting fermions such that the density and total energy equivalent to those obtained by these theories is obtained. Once again, the existence of these model systems is an assumption.

In Hartree–Fock Theory, the interacting system wavefunction is assumed to be a *single* Slater determinant of spin orbitals, and since the determinant is antisymmetric, electron correlations due to the Pauli exclusion principle are explicitly accounted for within this framework. The Hartree theory wavefunction, which is assumed to be a product of spin orbitals is, however, not antisymmetric, and thus does not obey the Pauli exclusion principle. Instead, the equivalent statement of the principle that no two electrons can occupy the same state is employed in application of the theory. In neither Hartree or Hartree–Fock theory are the effects of Coulomb correlations explicitly incorporated in the wavefunction.

As was the case for the interacting system ground state, a Hohenberg-Kohn theorem of the one-to-one relationship between the Hartree-Fock and Hartree theory ground state densities and the external potential $v(\mathbf{r})$ can be proved [62–64]. Thus, the Hartree-Fock and Hartree theory wavefunctions are functionals of the corresponding densities. This then provides a justification for the construction of the model systems. There is also the simplification of replacing the integral operator of Hartree–Fock theory, and the orbital–dependent (individual electron) potential energies of Hartree theory, by a multiplicative potential energy operator that is the *same* for *all* the model fermions.

In the following subsections the key elements of Hartree–Fock and Hartree theories, and their Q–DFT equivalents, are described. The Q–DFT description is for both ground and excited states for which the Hartree–Fock theory wavefunction is a single Slater determinant of spin orbitals, and the Hartree theory wavefunction a product of them. The spin–orbitals of these wavefunctions are eigenfunctions of the Hartree–Fock or Hartree theory differential equations. [The symbols $\phi_i(\mathbf{x})$, $\rho(\mathbf{r})$ in these subsections indicate the HF, H, and Q–DFT orbitals and density as the case may be.]

The reader is referred to Chaps. 9 and 10 of ***QDFT2*** for the application of the Q-DFT of Hartree and Hartree-Fock theories, respectively, to atoms and mononegative ions.

3.8.1 Hartree–Fock Theory

In Hartree–Fock theory, the wavefunction $\psi(\mathbf{X})$ of the interacting system defined by the Hamiltonian $\hat{H}$ of (2.131) is approximated by $\psi^{\text{HF}}(\mathbf{X})$ which is a Slater determinant $\Phi\{\phi_i\}$ of spin–orbitals $\phi_i(\mathbf{x}) = \psi_i(\mathbf{r})\chi_i(\sigma)$:

$$\psi^{\text{HF}}(\mathbf{X}) = \Phi\{\phi_i\} = \frac{1}{\sqrt{N!}} \ \det \ \phi_i(\mathbf{r}_j\sigma_j). \tag{3.181}$$

From the expectations of the operators $\hat{\rho}(\mathbf{r}), \hat{\gamma}(\mathbf{rr}')$, and $\hat{P}(\mathbf{rr}')$ of (2.12), (2.17) and (2.28) taken with respect to this wavefunction, we have the HF theory quantal sources: the density $\rho(\mathbf{r})$, the Dirac spinless single–particle density matrix $\gamma^{\mathrm{HF}}(\mathbf{rr}')$, and the pair–correlation density $g^{\mathrm{HF}}(\mathbf{rr}')$ to be

$$\rho(\mathbf{r}) = \sum_{\sigma}\sum_{i} |\phi_i(\mathbf{x})|^2, \tag{3.182}$$

$$\gamma^{\mathrm{HF}}(\mathbf{rr}') = \sum_{\sigma}\sum_{i} \phi_i^*(\mathbf{r}\sigma)\phi_i(\mathbf{r}'\sigma), \tag{3.183}$$

and

$$g^{\mathrm{HF}}(\mathbf{rr}') = \rho(\mathbf{r}') + \rho_x^{\mathrm{HF}}(\mathbf{rr}'), \tag{3.184}$$

where the HF theory Fermi hole $\rho_{\mathrm{x}}^{\mathrm{HF}}(\mathbf{rr}')$ is defined as (see (3.14))

$$\rho_{\mathrm{x}}^{\mathrm{HF}}(\mathbf{rr}') = -\frac{|\gamma^{\mathrm{HF}}(\mathbf{rr}')|^2}{2\rho(\mathbf{r})}. \tag{3.185}$$

As the wavefunction is a Slater determinant, these quantal sources satisfy the sum rules of Sect. 3.1.1.

The total energy E^{HF} is the expectation of the interacting system Hamiltonian $\hat{H}$ of (2.131):

$$E^{\mathrm{HF}} = \left\langle \Phi\{\phi_i\}|\hat{H}|\Phi\{\phi_i\}\right\rangle, \tag{3.186}$$

$$= T^{\mathrm{HF}} + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + E_{\mathrm{ee}}^{\mathrm{HF}}, \tag{3.187}$$

where T^{HF} and $E_{\mathrm{ee}}^{\mathrm{HF}}$ are the HF theory kinetic and electron–interaction energies, respectively:

$$T^{\mathrm{HF}} = \sum_i \int \psi_i^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2\right) \psi_i(\mathbf{r})d\mathbf{r}, \tag{3.188}$$

$$E_{\mathrm{ee}}^{\mathrm{HF}} = \frac{1}{2}\iint \frac{\rho(\mathbf{r})g^{\mathrm{HF}}(\mathbf{rr}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'. \tag{3.189}$$

Employing the decomposition of $g^{\mathrm{HF}}(\mathbf{rr}')$ given by (3.184) we may write

$$E_{\mathrm{ee}}^{\mathrm{HF}} = E_{\mathrm{H}} + E_{\mathrm{x}}^{\mathrm{HF}}, \tag{3.190}$$

where the Hartree energy E_{H} is

$$E_{\mathrm{H}} = \frac{1}{2}\iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}', \tag{3.191}$$

and the HF theory exchange or Pauli energy $E_{\mathrm{x}}^{\mathrm{HF}}$ is the energy of interaction between the density and Fermi hole charge:

$$E_{\mathrm{x}}^{\mathrm{HF}} = \frac{1}{2} \iint \frac{\rho(\mathbf{r}) \rho_{\mathrm{x}}^{\mathrm{HF}}(\mathbf{r}\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \tag{3.192}$$

As the energy is a functional of the wavefunction, the best single particle orbitals $\phi_i(\mathbf{x})$ from the total energy perspective are obtained by application of the variational principle for the energy [65] employing the approximate wavefunction $\Phi\{\phi_i\}$. This requires the first order variation of the energy, for arbitrary variations of the wavefunction, to vanish. In HF theory, the orbital $\phi_i(\mathbf{x})$ is varied by an arbitrarily small amount $\delta\phi_i(\mathbf{x})$ such that $\phi_i(\mathbf{x}) \to \phi_i(\mathbf{x}) + \delta\phi_i(\mathbf{x})$, and the stationary condition written as

$$\delta \left[E^{\mathrm{HF}}[\Phi] - \sum_{i,j=1}^{\mathrm{N}} \lambda_{ij} \langle \phi_i | \phi_j \rangle \right] = 0, \tag{3.193}$$

where the $\lambda_{ij} = \lambda_{ji}^*$ are the Langrange multipliers introduced to satisfy the $N(N+1)/2$ orthonormality conditions $\langle \phi_i | \phi_j \rangle = \delta_{ij}$. This leads to the HF equations:

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \sum_{\substack{j=1 \\ j \neq i}}^{\mathrm{N}} \langle \phi_j | \hat{U} | \phi_j \rangle \right] \phi_i(\mathbf{x}) - \sum_{\substack{j=1 \\ j \neq i}}^{\mathrm{N}} \langle \phi_j | \hat{U} | \phi_i \rangle \phi_j(\mathbf{x}) = \sum_{j=1}^{\mathrm{N}} \lambda_{ij} \phi_j(\mathbf{x}), \tag{3.194}$$

where

$$\langle \phi_j | \hat{U} | \phi_i \rangle = \sum_{\sigma'} \int \frac{\phi_j^*(\mathbf{x}') \phi_i(\mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \tag{3.195}$$

Including the self–interaction term in both the third (Hartree) and fourth (exchange) components of the left hand side of (3.194) leads to the definition of the Hermitian exchange operator $\hat{v}_{x,i}(\mathbf{x})$:

$$\hat{v}_{x,i}(\mathbf{x}) \phi_i(\mathbf{x}) = -\sum_{j=1}^{\mathrm{N}} \langle \phi_j | \hat{U} | \phi_i \rangle \phi_j(\mathbf{x}). \tag{3.196}$$

The exchange operator is said to be *nonlocal* because operating with it on $\phi_i(\mathbf{x})$ depends upon the value of $\phi_i(\mathbf{x})$ throughout all space, not just at $\mathbf{x}$, as is evident from (3.196). With the inclusion of the self–interaction term, the resulting Hamiltonian on the left hand side of (3.194) can be readily shown to be Hermitian. Thus, the Lagrange multipliers may be chosen as $\lambda_{ij} = \epsilon_i \delta_{ij}$ with ϵ_i real. This, then leads to the

Hartree–Fock theory eigenvalue equation, which in terms of the spatial component $\psi_i(\mathbf{r})$ is

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + W_{\mathrm{H}}(\mathbf{r})\right]\psi_i(\mathbf{r}) - \sum_{\substack{j=1 \\ \text{spin } j \| \text{spin } i}}^{\mathrm{N}} \left[\int \frac{\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'\right]\psi_j(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \tag{3.197}$$

where $W_{\mathrm{H}}(\mathbf{r})$ is the Hartree potential energy

$$W_{\mathrm{H}}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'. \tag{3.198}$$

It is evident from the integro–differential equation (3.197) that the HF theory effective single particle Hamiltonian is identical for each orbital. (By identical is not meant the same, i.e. the integral exchange operator term is not multiplicative or local.)

In terms of the HF theory eigenvalues ϵ_i, the total energy may then be written as

$$E^{\mathrm{HF}} = \sum_i \epsilon_i - E_{\mathrm{H}} - E_{\mathrm{x}}^{\mathrm{HF}} = \sum_i \epsilon_i - E_{\mathrm{ee}}^{\mathrm{HF}}, \tag{3.199}$$

with E_{H}, $E_{\mathrm{x}}^{\mathrm{HF}}$, and $E_{\mathrm{ee}}^{\mathrm{HF}}$ as defined above.

3.8.2 The Slater–Bardeen Interpretation of Hartree–Fock Theory

Hartree–Fock theory may also be provided a physical interpretation that is due to Slater [22] and Bardeen [66], analogous to that of Hartree theory to be described in Sect. 3.8.5. By multiplying and dividing the exchange term of (3.197) by $\psi_i(\mathbf{r})$, it may be rewritten as

$$\left[\int \frac{\left(-\sum_{\substack{j=1 \\ \text{spin } j \| \text{spin } i}}^{\mathrm{N}} \psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')\psi_j(\mathbf{r})/\psi_i(\mathbf{r})\right)}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'\right]\psi_i(\mathbf{r}). \tag{3.200}$$

The integral in the square parentheses may thus be interpreted as an *orbital–dependent multiplicative* ‘exchange potential energy’

$$v_{x,i}(\mathbf{r}) = \int \frac{\rho_{x,i}(\mathbf{r}\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \tag{3.201}$$

due to the *orbital–dependent Fermi hole* charge distribution $\rho_{x,i}(\mathbf{r}\mathbf{r}')$ at $\mathbf{r}'$ for an electron at $\mathbf{r}$ defined as

$$\rho_{x,i}(\mathbf{r}\mathbf{r}') = - \sum_{\substack{j=1 \\ \text{spin } j \| \text{spin } i}}^{N} \frac{\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')\psi_j(\mathbf{r})}{\psi_i(\mathbf{r})}. \tag{3.202}$$

The orbital–dependent Fermi hole satisfies the same rules as those of the Fermi hole. Thus

$$\int \rho_{x,i}(\mathbf{r}\mathbf{r}')d\mathbf{r}' = -1, \text{(for each electron position } \mathbf{r}) \tag{3.203}$$

$$\rho_{x,i}(\mathbf{r}\mathbf{r}) = -\rho(\mathbf{r})/2, \tag{3.204}$$

$$\rho_{x,i}(\mathbf{r}\mathbf{r}') \leq 0. \tag{3.205}$$

The Hartree–Fock theory eigenvalue equation (3.197) may then be written as

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + W_{\mathrm{H}}(\mathbf{r}) + v_{x,i}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \tag{3.206}$$

and the theory interpreted as *each* electron having a potential energy that is the sum of the external $v(\mathbf{r})$ and Hartree $W_{\mathrm{H}}(\mathbf{r})$ potential energies, which are the same for all the electrons, and an ‘exchange potential energy’ $v_{x,i}(\mathbf{r})$ that depends on the orbital the electron is in. Thus, Hartree–Fock theory may be thought of as being an orbital–dependent theory, with each electron having a *different* potential energy.

In a rigorous sense, the expression for $v_{x,i}(\mathbf{r})$ of (3.201) does not represent a potential energy for nonuniform electron density systems. This is because, as explained more fully in Sect. 10.2 on Slater theory, the orbital–dependent Fermi hole $\rho_{x,i}(\mathbf{r}\mathbf{r}')$ is a *dynamic* charge distribution that depends upon the electron position. The expression would represent a potential energy provided the charge distribution were static and independent of electron position as is the case for the uniform electron gas. Additionally, as is evident from its definition, the orbital–dependent Fermi hole and hence $v_{x,i}(\mathbf{r})$ are singular at the nodes of the orbitals as is the case for atoms. (In Bardeen’s application [66] of this interpretation to the nonuniform density at metal surfaces, the orbitals are nodeless.) Nonetheless, the *function* $v_{x,i}(\mathbf{r})$ represents the effects of the Pauli exclusion principle, and hence the Slater–Bardeen interpretation of Hartree–Fock theory as an orbital–dependent one is reasonable. Of course, for systems for which $v_{x,i}(\mathbf{r})$ is not singular, the interpretation is rigorous.

3.8.3 Theorems in Hartree–Fock Theory

There are four theorems of importance with regard to Hartree–Fock theory which are described next. The reader is referred to the original literature or standard texts for their proofs.

(i) According to Koopmans' theorem [67], the eigenvalues ϵ_i of HF theory may be interpreted as removal energies. The proof *assumes* that the orbitals of the neutral system and those of the resulting ionized system with an electron removed are the same, and that there is no relaxation of the orbitals of the latter. This is rigorously the case for a many electron system with extended orbitals as in a simple metal with s–p band character. Thus, the work function of a metal as obtained in HF theory is the difference in energy between its barrier height and Fermi energy [68]. However, for finite systems such as atoms, there is a relaxation of the orbitals on electron removal. Hence, the interpretation of the eigenvalues as removal energies is not quite rigorous. Consequently, the highest occupied eigenvalue ϵ_{m} of HF theory is not as good an approximation to the experimental ionization potential as that of local effective potential energy theories such as the Pauli–correlated approximation of Q–DFT [2, 69]. The theorem and above remarks are equally valid for the case of the addition of an electron to the neutral system. As such the highest occupied HF theory eigenvalue of negative ions is again not as accurate [2, 70] as the Pauli–correlated approximation of Q–DFT when compared to experimental electron affinities. (See Chap. 10 of ***QDFT2***.)

(ii) For external potential energies that vanish at infinity, the orbitals [71] of HF theory *all* have the *same* asymptotic structure $\psi_i(r)\underset{r\to\infty}{\sim}\exp(-\sqrt{2\epsilon_{\mathrm{m}}}r)$, where ϵ_{m} is the corresponding highest occupied eigenvalue. Thus, all the orbitals contribute to the asymptotic structure of the density in HF theory. Consequently, the relationship between ϵ_{m} and the experimental ionization potential has meaning only within the context of Koopmans' theorem.

(iii) According to Brillouin's theorem [72], if an electron is in an excited state, the matrix element of the Hamiltonian $\hat{H}$ taken with respect to the excited and ground state Slater determinants vanishes.

(iv) As a consequence of Brillouin's theorem, the expectation values of single particle operators taken with respect to the HF theory ground state wavefunction are correct to second order [73, 74] as is the energy.

3.8.4 Q–DFT of Hartree–Fock Theory

In this section we describe the Q–DFT of the model system of noninteracting fermions such that the same density $\rho(\mathbf{r})$ and total energy E^{HF} as that of Hartree–Fock theory is determined. Again, as for the fully interacting system, the existence of such a model S system is an assumption. The corresponding S system differential equation is then

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_{\text{ee}}^{\text{HF}}(\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}); \quad i = 1, \ldots, N, \tag{3.207}$$

where $v_{\text{ee}}^{\text{HF}}(\mathbf{r})$ is the effective electron–interaction potential energy which ensures the orbitals $\phi_i(\mathbf{r})$ generate the HF theory density. Note that these orbitals differ from the HF theory orbitals, and hence the resulting Dirac density matrix $\gamma_s(\mathbf{rr}') = \sum_\sigma \sum_i \phi_i^*(\mathbf{r}\sigma)\phi_i(\mathbf{r}'\sigma)$ is different from $\gamma^{\text{HF}}(\mathbf{rr}')$ of (3.183). The diagonal matrix element of these density matrices which is the density, however, is the same. The Q–DFT description of this model S system constitutes a special case of the fully interacting system case described in Sect. 3.4. Instead of employing the eigenfunctions $\psi_n(\mathbf{X})$ of the time-independent Schrödinger equation to define the quantal sources, fields, and energies, one employs instead the Hartree–Fock theory Slater determinant $\psi^{\text{HF}}(\mathbf{X}) = \Phi\{\phi_i\}$ with $\phi_i(\mathbf{x})$ the corresponding orbitals. This is a consequence of the fact that the HF theory wavefunction $\psi^{\text{HF}}(\mathbf{X})$ satisfies a 'Quantal Newtonian' first law and integral virial theorems [75]. In other words, the form of the time-independent 'Quantal Newtonian' first law (see Appendix A) remains unchanged with the fields now defined instead in terms of the HF theory quantal sources. (The satisfaction of the 'Quantal Newtonian' first law implies that of the integral theorem. The fact that the HF theory wavefunction satisfies the integral virial theorem may also be arrived at independently by scaling arguments [76].) The proof of the Q–DFT description is thus the same as that for the fully interacting case and will not be repeated.

Within Q–DFT, the S system properties are as follows. The potential energy $v_{\text{ee}}^{\text{HF}}(\mathbf{r})$ is the work done to move the model fermion in a conservative field $\boldsymbol{\mathcal{F}}^{\text{HF}}(\mathbf{r})$:

$$v_{\text{ee}}^{\text{HF}}(\mathbf{r}) = -\int_\infty^{\mathbf{r}} \boldsymbol{\mathcal{F}}^{\text{HF}}(\mathbf{r}') \cdot d\boldsymbol{\ell}', \tag{3.208}$$

where

$$\boldsymbol{\mathcal{F}}^{\text{HF}}(\mathbf{r}) = \boldsymbol{\mathcal{E}}_{\text{ee}}^{\text{HF}}(\mathbf{r}) + \boldsymbol{\mathcal{Z}}_{\text{t}_\text{c}}^{\text{HF}}(\mathbf{r}). \tag{3.209}$$

Here the HF theory electron interaction field $\boldsymbol{\mathcal{E}}_{\text{ee}}^{\text{HF}}(\mathbf{r})$ is obtained via Coulomb's law from the pair–correlation density $g^{\text{HF}}(\mathbf{rr}')$ of (3.184):

$$\boldsymbol{\mathcal{E}}_{\text{ee}}^{\text{HF}}(\mathbf{r}) = \int \frac{g^{\text{HF}}(\mathbf{rr}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}' = \boldsymbol{\mathcal{E}}_{\text{H}}(\mathbf{r}) + \boldsymbol{\mathcal{E}}_{\text{x}}^{\text{HF}}(\mathbf{r}), \tag{3.210}$$

with the Hartree $\boldsymbol{\mathcal{E}}_{\text{H}}(\mathbf{r})$ and Pauli $\boldsymbol{\mathcal{E}}_{\text{x}}^{\text{HF}}(\mathbf{r})$ fields being defined as

$$\boldsymbol{\mathcal{E}}_{\text{H}}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}', \tag{3.211}$$

and

$$\boldsymbol{\mathcal{E}}_{\mathrm{x}}^{\mathrm{HF}}(\mathbf{r}) = \int \frac{\rho_{\mathrm{x}}^{\mathrm{HF}}(\mathbf{r}\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}'. \tag{3.212}$$

The Correlation–Kinetic field $\boldsymbol{\mathcal{Z}}_{t_c}^{\mathrm{HF}}(\mathbf{r})$ is defined as the difference between the non-interacting system and HF theory kinetic fields:

$$\boldsymbol{\mathcal{Z}}_{t_c}^{\mathrm{HF}}(\mathbf{r}) = \boldsymbol{\mathcal{Z}}_{\mathrm{s}}(\mathbf{r}) - \boldsymbol{\mathcal{Z}}^{\mathrm{HF}}(\mathbf{r}), \tag{3.213}$$

where the fields $\boldsymbol{\mathcal{Z}}_{\mathrm{s}}(\mathbf{r})$ and $\boldsymbol{\mathcal{Z}}^{\mathrm{HF}}(\mathbf{r})$ are obtained from the corresponding kinetic 'forces' $\mathbf{z}_{\mathrm{s}}(\mathbf{r};[\gamma_{\mathrm{s}}])$ and $\mathbf{z}^{\mathrm{HF}}(\mathbf{r};[\gamma^{\mathrm{HF}}])$:

$$\boldsymbol{\mathcal{Z}}_{\mathrm{s}}(\mathbf{r}) = \frac{\mathbf{z}_{\mathrm{s}}(\mathbf{r};[\gamma_{\mathrm{s}}])}{\rho(\mathbf{r})} \quad \text{and} \quad \boldsymbol{\mathcal{Z}}^{\mathrm{HF}}(\mathbf{r}) = \frac{\mathbf{z}^{\mathrm{HF}}(\mathbf{r};[\gamma^{\mathrm{HF}}])}{\rho(\mathbf{r})}. \tag{3.214}$$

The kinetic 'forces' in turn are derived from the noninteracting and HF theory kinetic–energy–density tensors which are defined in terms of the density matrices $\gamma_{\mathrm{s}}(\mathbf{r}\mathbf{r}')$ and $\gamma^{\mathrm{HF}}(\mathbf{r}\mathbf{r}')$, respectively (see (3.35)).

The Hartree field $\boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r})$ is conservative. The Pauli $\boldsymbol{\mathcal{E}}_{\mathrm{x}}^{\mathrm{HF}}(\mathbf{r})$ and Correlation–Kinetic $\boldsymbol{\mathcal{Z}}_{t_c}^{\mathrm{HF}}(\mathbf{r})$ fields in general are not. Thus, the potential energy $v_{\mathrm{ee}}^{\mathrm{HF}}(\mathbf{r})$ for arbitrary symmetry may be written as

$$v_{\mathrm{ee}}^{\mathrm{HF}}(\mathbf{r}) = W_{\mathrm{H}}(\mathbf{r}) + \left(-\int_{\infty}^{\mathbf{r}} \left[\boldsymbol{\mathcal{E}}_{\mathrm{x}}^{\mathrm{HF}}(\mathbf{r}') + \boldsymbol{\mathcal{Z}}_{t_c}^{\mathrm{HF}}(\mathbf{r}')\right] \cdot d\boldsymbol{\ell}'\right), \tag{3.215}$$

where

$$W_{\mathrm{H}}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'. \tag{3.216}$$

For systems with symmetry such that the fields $\boldsymbol{\mathcal{E}}_{\mathrm{x}}^{\mathrm{HF}}(\mathbf{r})$ and $\boldsymbol{\mathcal{Z}}_{t_c}^{\mathrm{HF}}(\mathbf{r})$ are conservative: $\boldsymbol{\nabla} \times \boldsymbol{\mathcal{E}}_{\mathrm{x}}^{\mathrm{HF}}(\mathbf{r}) = 0$, $\boldsymbol{\nabla} \times \boldsymbol{\mathcal{Z}}_{t_c}^{\mathrm{HF}}(\mathbf{r}) = 0$, we may write $v_{\mathrm{ee}}^{\mathrm{HF}}(\mathbf{r})$ as the sum

$$v_{\mathrm{ee}}^{\mathrm{HF}}(\mathbf{r}) = W_{\mathrm{H}}(\mathbf{r}) + W_{\mathrm{x}}^{\mathrm{HF}}(\mathbf{r}) + W_{t_c}^{\mathrm{HF}}(\mathbf{r}), \tag{3.217}$$

where $W_{\mathrm{x}}^{\mathrm{HF}}(\mathbf{r})$ and $W_{t_c}^{\mathrm{HF}}(\mathbf{r})$ are the separate work done in the Pauli $\boldsymbol{\mathcal{E}}_{\mathrm{x}}^{\mathrm{HF}}(\mathbf{r})$ and Correlation–Kinetic $\boldsymbol{\mathcal{Z}}_{t_c}^{\mathrm{HF}}(\mathbf{r})$ fields:

$$W_{\mathrm{x}}^{\mathrm{HF}}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{E}}_{\mathrm{x}}^{\mathrm{HF}}(\mathbf{r}') \cdot d\boldsymbol{\ell}' \text{ and } W_{t_c}^{\mathrm{HF}}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{Z}}_{t_c}^{\mathrm{HF}}(\mathbf{r}') \cdot d\boldsymbol{\ell}'. \tag{3.218}$$

With the potential energy $v_{\mathrm{ee}}^{\mathrm{HF}}(\mathbf{r})$ defined as in (3.215) or (3.217), solution of the S system differential equation generates orbitals $\phi_i(\mathbf{x})$ which lead to the HF theory density $\rho(\mathbf{r})$.

The HF theory total energy E^{HF} may be expressed in terms of the individual fields as

$$E^{\mathrm{HF}} = T_{\mathrm{s}} + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + E_{\mathrm{ee}}^{\mathrm{HF}} + T_{\mathrm{c}}^{\mathrm{HF}} \tag{3.219}$$

$$= T_{\mathrm{s}} + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + E_{\mathrm{H}} + E_{\mathrm{x}}^{\mathrm{HF}} + T_{\mathrm{c}}^{\mathrm{HF}}, \tag{3.220}$$

where the S system kinetic energy T_{s} is the expectation

$$T_{\mathrm{s}} = \sum_{\sigma}\sum_{i}\langle\phi_i(\mathbf{r}\sigma)| - \frac{1}{2}\nabla^2|\phi_i(\mathbf{r}\sigma)\rangle, \tag{3.221}$$

and where in integral virial form the electron–interaction energy and its components are

$$E_{\mathrm{ee}}^{\mathrm{HF}} = \int \rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\mathcal{E}}_{\mathrm{ee}}^{\mathrm{HF}}(\mathbf{r})d\mathbf{r}, \tag{3.222}$$

$$E_{\mathrm{H}} = \int \rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r})d\mathbf{r}, \tag{3.223}$$

and

$$E_{\mathrm{x}}^{\mathrm{HF}} = \int \rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\mathcal{E}}_{\mathrm{x}}^{\mathrm{HF}}(\mathbf{r})d\mathbf{r}, \tag{3.224}$$

and where the HF theory Correlation–Kinetic energy $T_{\mathrm{c}}^{\mathrm{HF}}$ is

$$T_{\mathrm{c}}^{\mathrm{HF}} = \frac{1}{2}\int \rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\mathcal{Z}}_{t_{\mathrm{c}}}^{\mathrm{HF}}(\mathbf{r})d\mathbf{r}. \tag{3.225}$$

The model system of noninteracting fermions described above determines the same density and energy as that of HF theory. As was the case for the fully interacting system, there is in addition to the electron–interaction term, a Correlation–Kinetic component to both the potential and total energies of these model fermions. This latter component is essential to ensuring the equality of the density and energy to that of HF theory. (Note that the total energy is not determined as the expectation value of the Hamiltonian taken with respect to the S system Slater determinant $\Phi\{\phi_i\}$. Since this wavefunction differs from the HF theory determinant, such an expectation would constitute a rigorous upper bound to the HF theory total energy.)

3.8.5 Hartree Theory

In this approximation, the wavefunction $\Psi(\mathbf{X})$ of the interacting system defined by the Hamiltonian $\hat{H}$ of (2.131) is determined by assuming *each* electron to move in the external field, and the average field due to the charge distribution of all the *other* electrons. Thus, the wavefunction is chosen to be of the form appropriate for independent particles, i.e. a product of spin orbitals:

$$\Psi^{\mathrm{H}}(\mathbf{X}) = \Pi_{i=1}^{\mathrm{N}} \phi_i(\mathbf{x}), \tag{3.226}$$

where $\phi_i(\mathbf{x}) = \psi_i(\mathbf{r})\chi_i(\sigma)$. With the above assumptions, the Hartree theory differential equation may be written directly a

$$\left[-\frac{1}{2}\nabla^2 + v((\mathbf{r}) + \sum_{\substack{j \\ j\neq i}} \int \frac{\phi_j^*(\mathbf{x}')\phi_j(\mathbf{x}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{x}' \right] \phi_i(\mathbf{x}) = \epsilon_i \phi_i(\mathbf{x}); \quad i = 1, \ldots, N. \tag{3.227}$$

The corresponding expression for the total energy E^{H} which is the expectation of the interacting system Hamiltonian $\hat{H}$ of (2.131) is

$$E^{\mathrm{H}} = \langle \Psi^{\mathrm{H}} | \hat{H} | \Psi^{\mathrm{H}} \rangle = T^{\mathrm{H}} + \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + E_{\mathrm{ee}}^{\mathrm{H}}, \tag{3.228}$$

with $\rho(\mathbf{r}) = \sum_\sigma \sum_i |\phi_i(\mathbf{r}\sigma)|^2$ and where T^{H} and $E_{\mathrm{ee}}^{\mathrm{H}}$ are the Hartree theory kinetic and electron–interaction energies, respectively:

$$T^{\mathrm{H}} = \sum_i \int \psi_i^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 \right) \psi_i(\mathbf{r}) d\mathbf{r}, \tag{3.229}$$

$$\mathrm{E}_{\mathrm{ee}}^{\mathrm{H}} = \frac{1}{2} \sum_{\substack{i,j \\ i\neq j}} \iint \frac{|\psi_i(\mathbf{r})|^2 |\psi_j(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \tag{3.230}$$

In terms of the eigenvalues ϵ_i of the Hartree differential equation, the total energy is

$$E^{\mathrm{H}} = \sum_i \epsilon_i - E_{\mathrm{ee}}^{\mathrm{H}}. \tag{3.231}$$

Thus, Hartree theory is an *orbital–dependent* theory in which each electron has a different potential energy. This is analogous to the Slater–Bardeen interpretation of Hartree–Fock theory.

The Hartree theory differential equation may also be rigorously derived by application of the variational principle for the energy. Thus, minimization of the expectation E^{H} with respect to arbitrary variations of the spin–orbitals subject to the *normalization* constraint $\langle \phi_i | \phi_i \rangle = 1$ leads to (3.227) and thereby to the best product type wavefunction from the energy perspective. The Hartree theory Hamiltonian is Hermitian, and therefore the orbitals are orthogonal.

The equations of Hartree theory may be expressed in terms of the corresponding quantal sources by rewriting the density of all but the i th electron as the density of all the electrons minus that of the i th one:

$$\sum_{\substack{j \\ j\neq i}} \sum_{\sigma} |\phi_j(\mathbf{r}\sigma)|^2 = \rho(\mathbf{r}) + q_i(\mathbf{r}\sigma), \tag{3.232}$$

where $q_i(\mathbf{r}\sigma) = -\phi_i^*(\mathbf{r}\sigma)\phi_i(\mathbf{r}\sigma)$. The Hartree theory differential equation is then

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + W_{\mathrm{H}}(\mathbf{r}) + v_i^{\mathrm{SIC}}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}), \tag{3.233}$$

where $W_{\mathrm{H}}(\mathbf{r})$ is the Hartree potential energy (see (3.198), and $v_i^{\mathrm{SIC}}(\mathbf{r})$ the orbital–dependent self–interaction–correction (SIC) potential energy due to the static orbital charge density $q_i(\mathbf{r}\sigma)$:

$$v_i^{\mathrm{SIC}}(\mathbf{r}) = \int \frac{q_i(\mathbf{r}'\sigma)}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{x}'. \tag{3.234}$$

The Hartree theory pair–correlation density $g^{\mathrm{H}}(\mathbf{r}\mathbf{r}')$ which is the expectation of the pair–operator $\hat{P}(\mathbf{r}\mathbf{r}')$ (2.28) taken with respect to $\Psi^{\mathrm{H}}(\mathbf{X})$ is

$$g^{\mathrm{H}}(\mathbf{r}\mathbf{r}') = \rho(\mathbf{r}') + \rho^{\mathrm{SIC}}(\mathbf{r}\mathbf{r}'), \tag{3.235}$$

where $\rho^{\mathrm{SIC}}(\mathbf{r}\mathbf{r}') = -\sum_\sigma \sum_i q_i(\mathbf{r}\sigma)q_i(\mathbf{r}'\sigma)/\rho(\mathbf{r})$. Thus, the Hartree theory electron–interaction energy $E_{\mathrm{ee}}^{\mathrm{H}}$ may be rewritten as

$$E_{\mathrm{ee}}^{\mathrm{H}} = \frac{1}{2}\iint \frac{\rho(\mathbf{r})g^{\mathrm{H}}(\mathbf{r}\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}', \tag{3.236}$$

$$= E_{\mathrm{H}} + E_{\mathrm{H}}^{\mathrm{SIC}}, \tag{3.237}$$

where E_{H} is the Hartree energy (3.191), and $E_{\mathrm{H}}^{\mathrm{SIC}}$ the SIC energy:

$$E_{\mathrm{H}}^{\mathrm{SIC}} = \frac{1}{2}\iint \frac{\rho(\mathbf{r})\rho^{\mathrm{SIC}}(\mathbf{r}\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}'. \tag{3.238}$$

In terms of the eigenvalues the total energy is then

$$E^{\mathrm{H}} = \sum_i \epsilon_i - E_{\mathrm{H}} - E_{\mathrm{H}}^{\mathrm{SIC}}, \tag{3.239}$$

analogous to the total energy expression in HF theory of (3.199).

3.8.6 Q–DFT of Hartree Theory

The Q–DFT description of the model S system of noninteracting fermions whereby the same density $\rho(\mathbf{r})$ and energy E_{H} as that of Hartree theory is obtained, is similar to the corresponding mappings of Schrödinger theory of the fully interacting system and of HF theory. The assumption of existence of such an S system leads to the differential equation for the model fermion spin orbitals $\phi_i(\mathbf{x})$:

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_{\mathrm{ee}}^{\mathrm{H}}(\mathbf{r})\right]\phi_i(\mathbf{x}) = \epsilon_i\phi_i(\mathbf{x}); \quad i = 1, \ldots, N, \tag{3.240}$$

where $v_{\mathrm{ee}}^{\mathrm{H}}(\mathbf{r})$ is the effective electron–interaction potential energy which ensures the orbitals $\phi_i(\mathbf{x})$ lead to the Hartree theory density. The orbitals $\phi_i(\mathbf{x})$ differ from those of Hartree theory so that the corresponding Dirac density matrices differ: $\gamma_{\mathrm{s}}(\mathbf{rr}') = \sum_\sigma \sum_i \phi_i^*(\mathbf{r}\sigma)\phi_i(\mathbf{r}'\sigma) \neq \gamma^{\mathrm{H}}(\mathbf{rr}')$. The diagonal elements of these matrices, however, are the same. Once again, the proof of the Q–DFT description is based on the fact that the Hartree theory wavefunction $\Psi^{\mathrm{H}}(\mathbf{X})$ satisfies the 'Quantal Newtonian' first law and the integral virial theorem, with the fields determined from quantal sources derived from this wavefunction.

Therefore, the potential energy $v_{\mathrm{ee}}^{\mathrm{H}}(\mathbf{r})$ is the work done to move the model fermion in a conservative field $\boldsymbol{\mathcal{F}}^{\mathrm{H}}(\mathbf{r})$:

$$v_{\mathrm{ee}}^{\mathrm{H}}(\mathbf{r}) = -\int_\infty^{\mathbf{r}} \boldsymbol{\mathcal{F}}^{\mathrm{H}}(\mathbf{r}') \cdot d\boldsymbol{\ell}', \tag{3.241}$$

where

$$\boldsymbol{\mathcal{F}}^{\mathrm{H}}(\mathbf{r}) = \boldsymbol{\mathcal{E}}_{\mathrm{ee}}^{\mathrm{H}}(\mathbf{r}) + \boldsymbol{\mathcal{Z}}_{t_c}^{\mathrm{H}}(\mathbf{r}). \tag{3.242}$$

The Hartree electron–interaction field $\boldsymbol{\mathcal{E}}_{\mathrm{ee}}^{\mathrm{H}}(\mathbf{r})$ is obtained from the pair–correlation density $g^{\mathrm{H}}(\mathbf{rr}')$ of (3.235) via Coulomb's law:

$$\boldsymbol{\mathcal{E}}_{\mathrm{ee}}^{\mathrm{H}}(\mathbf{r}) = \int \frac{g^{\mathrm{H}}(\mathbf{rr}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}d\mathbf{r}' \tag{3.243}$$

$$= \boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r}) + \boldsymbol{\mathcal{E}}_{\mathrm{H}}^{\mathrm{SIC}}(\mathbf{r}), \tag{3.244}$$

with $\boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r})$ the Hartree field (see (3.211), and where the SIC $\boldsymbol{\mathcal{E}}_{\mathrm{H}}^{\mathrm{SIC}}(\mathbf{r})$ field is:

$$\boldsymbol{\mathcal{E}}_{\mathrm{H}}^{\mathrm{SIC}}(\mathbf{r}) = \int \frac{\rho^{\mathrm{SIC}}(\mathbf{rr}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}. \tag{3.245}$$

The Correlation–Kinetic field $\boldsymbol{\mathcal{Z}}_{t_c}^{\mathrm{H}}(\mathbf{r})$ is the difference between the noninteracting and Hartree theory kinetic fields:

$$\boldsymbol{\mathcal{Z}}_{t_c}^{\mathrm{H}}(\mathbf{r}) = \boldsymbol{\mathcal{Z}}_{\mathrm{s}}(\mathbf{r}) - \boldsymbol{\mathcal{Z}}^{\mathrm{H}}(\mathbf{r}), \tag{3.246}$$

where

$$\mathcal{Z}_s(\mathbf{r}) = \frac{z_s(\mathbf{r}; [\gamma_s])}{\rho(\mathbf{r})} \;\; \text{and} \;\; \mathcal{Z}^{\mathrm{H}}(\mathbf{r}) = \frac{z^{\mathrm{H}}(\mathbf{r}; [\gamma^{\mathrm{H}}])}{\rho(\mathbf{r})}, \tag{3.247}$$

with $z_s(\mathbf{r}; [\gamma_s])$ and $z^{\mathrm{H}}(\mathbf{r}; [\gamma^{\mathrm{H}}])$ the corresponding kinetic 'forces'. These kinetic 'forces' are derived from the noninteracting and Hartree theory kinetic–energy–density tensors defined in terms of the density matrices $\gamma_s(\mathbf{rr}')$ and $\gamma^{\mathrm{H}}(\mathbf{rr}')$, respectively.

For systems of arbitrary symmetry, the fields $\boldsymbol{\mathcal{E}}^{\mathrm{H}}_{\mathrm{ee}}(\mathbf{r})$ and $\mathcal{Z}^{\mathrm{H}}_{t_c}(\mathbf{r})$ are not necessarily separately conservative. Their sum always is. But as the Hartree field $\boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r})$ is conservative, we may write the potential energy $v^{\mathrm{H}}_{\mathrm{ee}}(\mathbf{r})$ as

$$v^{\mathrm{H}}_{\mathrm{ee}}(\mathbf{r}) = W_{\mathrm{H}}(\mathbf{r}) + \left(-\int_{\infty}^{\mathbf{r}} \left[\boldsymbol{\mathcal{E}}^{\mathrm{SIC}}_{\mathrm{H}}(\mathbf{r}') + \mathcal{Z}^{\mathrm{H}}_{t_c}(\mathbf{r}')\right] \cdot d\boldsymbol{\ell}'\right). \tag{3.248}$$

For systems of symmetry such that $\nabla \times \boldsymbol{\mathcal{E}}^{\mathrm{SIC}}_{\mathrm{H}}(\mathbf{r}) = 0$ and $\boldsymbol{\nabla} \times \mathcal{Z}^{\mathrm{H}}_{t_c}(\mathbf{r}) = 0$, we have

$$v^{\mathrm{H}}_{\mathrm{ee}}(\mathbf{r}) = W_{\mathrm{H}}(\mathbf{r}) + W^{\mathrm{SIC}}_{\mathrm{H}}(\mathbf{r}) + W^{\mathrm{H}}_{t_c}(\mathbf{r}), \tag{3.249}$$

where

$$W^{\mathrm{SIC}}_{\mathrm{H}}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{E}}^{\mathrm{SIC}}_{\mathrm{H}}(\mathbf{r}') \cdot d\boldsymbol{\ell}' \text{ and } W^{\mathrm{H}}_{t_c}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \mathcal{Z}^{\mathrm{H}}_{t_c}(\mathbf{r}') \cdot d\boldsymbol{\ell}'. \tag{3.250}$$

$W^{\mathrm{SIC}}_{\mathrm{H}}(\mathbf{r})$ and $W^{\mathrm{H}}_{t_c}(\mathbf{r})$ are the separate path-independent work done in the fields $\boldsymbol{\mathcal{E}}^{\mathrm{SIC}}_{\mathrm{H}}(\mathbf{r})$ and $\mathcal{Z}^{\mathrm{H}}_{t_c}(\mathbf{r})$, respectively.

The Hartree theory total energy E^{H} may be expressed in terms of the fields as

$$E^{\mathrm{H}} = T_s + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + E^{\mathrm{H}}_{\mathrm{ee}} + T^{\mathrm{H}}_{c} \tag{3.251}$$

$$= T_s + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + E_{\mathrm{H}} + E^{\mathrm{SIC}}_{\mathrm{H}} + T^{\mathrm{H}}_{c}, \tag{3.252}$$

where T_s is the S system kinetic energy (3.221), and where in integral virial form

$$E^{\mathrm{H}}_{\mathrm{ee}} = \int \rho(\mathbf{r})\mathbf{r} \cdot \boldsymbol{\mathcal{E}}^{\mathrm{H}}_{\mathrm{ee}}(\mathbf{r})d\mathbf{r}, \tag{3.253}$$

$$E^{\mathrm{SIC}}_{\mathrm{H}} = \int \rho(\mathbf{r})\mathbf{r} \cdot \boldsymbol{\mathcal{E}}^{\mathrm{SIC}}_{\mathrm{H}}(\mathbf{r})d\mathbf{r}, \tag{3.254}$$

$$T^{\mathrm{H}}_{c} = \frac{1}{2}\int \rho(\mathbf{r})\mathbf{r} \cdot \mathcal{Z}^{\mathrm{H}}_{t_c}(\mathbf{r})d\mathbf{r}, \tag{3.255}$$

and E_{H} is given by (3.223).

The model S system described above leads to the same density and energy as obtained from Hartree theory. Once again note that there is a Correlation–Kinetic component to both the potential energy and total energy of the model fermions. This component is essential to ensuring the equality of the resulting density and total energy to that of Hartree theory.

For the application of the Q–DFT of Hartree theory to atoms for the determination of atomic shell structure and core-valence separation, total energies, and the satisfaction of the *aufbau* principle, see Chap. 9 of ***QDFT2***.

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Chapter 4
Hohenberg–Kohn, Kohn–Sham, and Runge-Gross Density Functional Theories

Abstract The two nondegenerate ground-state theorems of Hohenberg-Kohn (HK) are described with an emphasis on new understandings of the first theorem (HK1) and of its proof. Via HK1, the concept of a basic variable of quantum mechanics, a gauge invariant property knowledge of which uniquely determines the Hamiltonian to within a constant, and hence the wave functions of the system, is developed. HK1 proves that the basic variable is the nondegenerate ground state density. HK1 is generalized via a density preserving unitary transformation to prove the wave function must be a functional of the density and a gauge function of the coordinates in order for the wave function written as a functional to be gauge variant. A corollary proves that degenerate Hamiltonians representing different physical systems but yet possessing the same density cannot be distinguished on the basis of HK1. (This does not constitute a violation of HK1 as the Hamiltonians differ by a constant.) The primacy of the electron number N in the proof of the HK theorems is stressed. The Percus-Levy-Lieb (PLL) constrained-search path from the density to the wave functions is described. It is noted that the HK path is more fundamental, as knowledge of the property that constitutes the basic variable, as gleaned from HK1, is essential for the constrained-search proof of PLL. The Gunnarsson-Lundqvist theorems, the extension of the HK theorems to the lowest excited state of symmetry different from that of the ground state are described. The Runge-Gross (RG) theorems for time-dependent theory, with an emphasis on the first theorem (RG1), are explained. RG1 proves the basic variables to be the density and the current density. A density preserving unitary transformation generalizes RG1 to prove the wave function must be a functional of the density and a gauge function of the coordinates and time. A hierarchy based on gauge functions thereby exists for the fundamental first theorems of density functional theory. A corollary to RG1 similar to that for the time-independent case is proved. Kohn-Sham theory, a ground state theory, which constitutes the mapping from the interacting system to one of noninteracting fermions of the same density, is formulated. As this mapping is based on the HK theorems, the description of the model system is mathematical in that the energy is in terms of functionals of the density, and the local potentials defined as the corresponding functional derivatives.

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Introduction

Hohenberg-Kohn, Kohn-Sham, and Runge-Gross density functional theories in an approximate form are possibly the most extensively employed quantum-mechanical formalisms for the determination of electronic structure in atomic and condensed matter physics, and in quantum chemistry. In this chapter we describe the *in principle* exact framework of these theories. We begin by explaining the two theorems of Hohenberg and Kohn (HK) [1]. We also describe new insights gleaned about the theorems: the primacy of the electron number N to the theory [2]; a corollary to the first theorem [3], [***QDFT1***]; and the generalization of the first theorem to arbitrary density preserving unitary transformations [4], [***QDFT2***]. The theorems of HK then constitute the basis of Kohn-Sham density functional theory (KS-DFT) [5]. The precursor to the HK theorems and KS-DFT is comprised of the work of Thomas [6], Fermi [7], Dirac [8], von Weizscker [9], and Slater [10]. For a description of the precursory material, and for the broader context of Hohenberg-Kohn-Sham density functional theory, the reader is referred to the three original texts on the subject [11–13], and to a more recent one [14]. Slater theory, and its approximations, will be described more fully in Chap. 10.

The first HK theorem defines the concept of a *basic variable* of quantum mechanics in the context of density functional theory. A basic variable is a gauge invariant property, knowledge of which determines uniquely the external potential of the system, hence the Hamiltonian, and by solution of the Schrödinger equation, the ground and excited state wave functions. The theorem proves the *nondegenerate ground state density* $\rho(\mathbf{r})$ to be a basic variable. The proof is for *pure-state* v-representable densities. (These are densities obtained from wave functions that are solutions of the Schrödinger equation for interacting systems.) The knowledge that this density is a basic variable is fundamental to local effective potential energy theories such as KS-DFT and Q-DFT. It is also key [15] to the Percus-Levy-Lieb (PLL) [16–19] constrained-search framework of density functional theory which in turn expands the domain of HK theory to N-representable and *degenerate* ground state densities. The PLL description of density functional theory will also be described in the chapter. (In a later chapter, it will be shown that in the added presence of a uniform magnetostatic field, the basic variables are the nondegenerate ground state density $\rho(\mathbf{r})$ and the *physical* current density $\mathbf{j}(\mathbf{r})$ for fixed canonical orbital and spin angular momentum.)

The fundamental proposition of HK density functional theory, as enunciated by the first HK theorem, is that *all* the properties, both ground and excited state, of a many-electron system in the presence of an external field $\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}) = -\boldsymbol{\nabla} v(\mathbf{r})$, can be determined *exactly* from the nondegenerate ground state density $\rho(\mathbf{r})$, the basic variable. Thus, as will be shown, knowledge of this density uniquely determines the system Hamiltonian to within a constant, and thereby via solution of the Schrödinger equation, the ground and excited state wave functions of the system. Hence, HK density functional theory can be thought of as a means of determining the system wave functions. This is a profound conclusion, one that constitutes a milestone in the development of quantum mechanics. But what this conclusion also achieves is that it shifts the focus from the time-independent Schrödinger theory wave function to that of the system ground state density $\rho(\mathbf{r})$. (The PLL constrained-search method is also a means of determining the Hamiltonian, and thereby the system wave functions, from the ground state density $\rho(\mathbf{r})$. The method, however, requires [15] the *a priori* knowledge that the nondegenerate ground state density $\rho(\mathbf{r})$ is the basic variable, a fact gleaned from the first HK theorem.)

As knowledge of the nondegenerate ground state density $\rho(\mathbf{r})$ determines the wave functions of the system, the wave functions are functionals of this density. Wave functions and Hamiltonians are gauge variant [20] quantities whereas the density is gauge invariant. By a *density preserving* unitary transformation [4], [***QDFT2***] it is shown that the wave function must also be a functional of a gauge function. It is this dependence on the gauge function which ensures that when the wave function is written as a functional it is gauge variant. This also shows that the HK proof is generalized to be valid for each choice of the gauge function. The theorem as originally enunciated is recovered when the gauge function is replaced by a constant. Since for different gauge functions, the physical system remains unchanged, the choice of a vanishing gauge function is equally valid.

As the wave function is a functional of the density $\rho(\mathbf{r})$, properties of the system, obtained as expectation values of Hermitian operators, are unique functionals of this density. The energy is thus such a functional. The second HK theorem which is the application of the variational principle to the energy functional, (for arbitrary variations of the density), then leads to the Euler-Lagrange equation for the nondegenerate ground state density $\rho(\mathbf{r})$. Since the kinetic and electron-interaction energy component functionals of the total energy functional are unknown, they are approximated in the Euler equation. This then harks back to the Thomas, Thomas-Fermi, Thomas-Fermi-Dirac, and Thomas-Fermi-Dirac-von Weizsacker approximations, the equations of which then constitute special cases of the exact Euler-Lagrange equation for the density. The inclusion of terms of higher-order in the gradients of the density for both the kinetic and electron-interaction energy components then makes the solution of the corresponding approximate Euler-Lagrange equation formidable.

Yet another point of note is that in HK density functional theory, the role of the electron number N is primary [2]. The first HK theorem is proved and valid only for fixed N. Further, with regard to the second HK theorem, the variational densities must be such as to integrate to the electron number N. Thus, one must know N prior to solving the Euler-Lagrange equation for the density. (In the chapter on the added presence of a uniform magnetostatic field, which constitutes a new degree of freedom, it will be seen that the parameters characterizing the system are the electron number N and the canonical orbital angular momentum $\mathbf{L}$ and spin momentum $\mathbf{S}$.)

The HK theorems are valid for arbitrary interaction between the electrons. Hence, the theorems are equally applicable to *noninteracting fermions* in their ground state. The energy of the model fermions is once again a functional of the density, and as such there exists a corresponding Euler-Lagrange equation for the density. KS-DFT employs the fact that solution of this Euler-Lagrange equation is equivalent to solving the S system set of single-particle Schrödinger equations for the noninteracting fermions. With the kinetic energy of the noninteracting fermions treated exactly, their potential energy is defined via the equivalence to the Euler-Lagrange equation as the *functional derivative* of the remaining component of the total energy functional taken with respect to the density. Hence, the KS-DFT mapping from the interacting system of electrons to the model S system having the same density is *mathematical* in that it is a description in terms of energy functionals of the density and of their functional derivatives. This description of the S system therefore differs fundamentally from that of the *physical* 'classical' fields and quantal sources perspective of Q-DFT. The existence of the S system within KS-DFT is, once again, an *assumption*. Hohenberg-Kohn and Kohn-Sham density functional theories are ground state theories. Thus, the mapping within KS-DFT is always from the *ground* state of the interacting system to an S system that is also in its *ground* state.

Within Schrödinger theory the variational principle is also applicable to the *lowest excited* state of a given symmetry different from that of the ground state. In the variational procedure, one then restricts the approximate wave functions to have the given excited-state symmetry, and the lowest state of that symmetry is achieved by energy minimization without any orthogonality constraints imposed on the trial wave functions. The trial wave functions are automatically orthogonal to the exact ground state wave function. A corresponding HK theorem for such states can therefore be proved. The proof is for v-representable densities derived from wave functions that have the given excited-state symmetry. Hence, knowledge of the density $\rho^e(\mathbf{r})$ for such an excited state then also determines the external potential $v(\mathbf{r})$ uniquely to within a constant, and thereby the Hamiltonian. Thus, the density $\rho^e(\mathbf{r})$ is also a basic variable of quantum mechanics. This is referred to as the Gunnarsson-Lundqvist (GL) theorem [21, 22]. The excited-state wave function is a functional solely of the density $\rho^e(\mathbf{r})$, and of course of a gauge function to ensure that when written as a functional it is gauge variant. The GL theorem is valid for each choice of gauge function. In addition, all properties are also unique functionals of the density $\rho^e(\mathbf{r})$.

For other excited states, it is known [21, 23, 24] that there is no equivalent of the HK theorem. In other words there is no one-to-one relationship between these excited-state densities $\rho^e(\mathbf{r})$ and the external potential $v(\mathbf{r})$. As knowledge of the density $\rho^e(\mathbf{r})$ of such excited states does not uniquely determine the external potential $v(\mathbf{r})$, the implication is that there could exist *several* potentials $v(\mathbf{r})$ for which the corresponding Schrödinger equations all generate the same excited-state density $\rho^e(\mathbf{r})$. The reader is referred to [22] for an example of the satisfaction of the GL theorem, and for a demonstration of the multiplicity of potentials for excited states other than the lowest excited state.

In spite of the fact that there is no equivalent of the HK theorem for other than the lowest excited state of a symmetry that differs from that of the ground state, the constrained-search approach has been generalized to the individual excited state [24, 25]. The many-body effects are incorporated in a *bidensity* energy functional of the *exact* ground density and the excited state densities. The local potential in the corresponding KS-DFT is then the functional derivative of this bidensity energy functional. The mapping from the excited state of the interacting system to the model system of noninteracting fermions is always to one in an excited state having the *same* electronic configuration. References to other work on excited states in the context of DFT are given in [25].

Time-dependent density functional theory (TD-DFT) is based on the extension by Runge and Gross (RG) [26–28] of the first HK theorem to the time domain. The theorem is valid for external fields $\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}t) = -\boldsymbol{\nabla} v(\mathbf{r}t)$ such that the corresponding potential energy $v(\mathbf{r}t)$ is Taylor expandable about some initial time t_0. The basic ideas parallel those of time-independent theory but with one important difference. The RG theorem shows that in addition to the TD density $\rho(\mathbf{r}t)$, the current density $\mathbf{j}(\mathbf{r}t)$ as defined by (2.39–2.42) is also a basic variable i.e., knowledge of either $\rho(\mathbf{r}t)$ or $\mathbf{j}(\mathbf{r}t)$ uniquely determines the external potential $v(\mathbf{r}t)$ to within a TD function $C(t)$. Unlike TD Q-DFT in which it is possible to map the interacting system to an S system of noninteracting fermions having either the same density $\rho(\mathbf{r}t)$ or one with the same density $\rho(\mathbf{r}t)$ and current density $\mathbf{j}(\mathbf{r}t)$, the focus of TD DFT is solely on the density $\rho(\mathbf{r}t)$. In the time-independent case, the existence of the S system of noninteracting fermions with the same density $\rho(\mathbf{r})$ is an *assumption*. In TD DFT there is the van Leeuven theorem [28, 29] based on the 'Quantal Newtonian' second law [30–32] of (2.75) that purports to prove that such a system exists provided the initial state of the model system reproduces the density and its derivative at the initial time t_0. (As noted in the Introduction to the previous chapter, there has been a critique of this existence theorem, and a response to the critique [4, 33–37].) Again paralleling the *energy* functional of the density $\rho(\mathbf{r})$ and the variational principle for the energy within time-independent theory, RG introduced an *action* functional of the density $\rho(\mathbf{r}t)$ and the stationary-action principle. The potential energy of the model fermions is consequently defined as the functional derivative of the corresponding component of the action functional. It turns out [38] that there is at present no action functional of v-representable densities whose functional derivative corresponds to the potential energy of the noninteracting fermions. (In TD DFT, a v-representable density $\rho(\mathbf{r}t)$ is one derived from the solution of the TD Schrödinger equation in which the external potential energy $v(\mathbf{r}t)$ is Taylor expandable.) An action functional for a broader class of densities that satisfies the constraints on such an action integral has, however been constructed [39–41]. For more recent developments in TD DFT, the reader is referred to [28]. A brief description of the principal tenets of TD DFT is given in the chapter. New insights into the RG theorem are described: a corollary [3], [***QDFT1***] to the theorem; and its generalization [4], [***QDFT2***] via a time-dependent density preserving unitary transformation.

Finally, it has been proved [42, 43] that for electrons in an external time-dependent electromagnetic field, the basic variables are the time-dependent density $\rho(\mathbf{r}t)$ and physical current density $\mathbf{j}(\mathbf{r}t)$. A Q-DFT for such systems has been developed [44].

4.1 The Hohenberg–Kohn Theorems

The Hohenberg-Kohn (HK) theorems are proved for a system of N electrons in an external electrostatic field $\mathcal{F}^{\mathrm{ext}}(\mathbf{r}) = \mathcal{E}(\mathbf{r}) = -\boldsymbol{\nabla} v(\mathbf{r})$. This then is the definition employed (within non-relativistic quantum mechanics) of matter: atoms, molecules, solids, clusters, lower dimensional systems such as heterojunctions, quantum dots, graphene, etc. The Hamiltonian $\hat{H}_N$ of this system of electrons in atomic units ($e = \hbar = m = 1$) is the sum of its kinetic $\hat{T}$, electron-interaction potential energy $\hat{U}$, and external potential energy $\hat{V}$ operator:

$$\hat{H}_N(\mathbf{R}) = \hat{T} + \hat{U} + \hat{V}, \tag{4.1}$$

where

$$\hat{T} = -\frac{1}{2}\sum_{i=1}^{N} \nabla_i^2; \quad \hat{U} = \frac{1}{2}\sum_{i \neq j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}; \quad \hat{V} = \sum_{i=1}^{N} v(\mathbf{r}_i), \tag{4.2}$$

with $\mathbf{R} = \mathbf{r}_1, \ldots, \mathbf{r}_N$.

The corresponding Schrödinger equation is (see (2.133))

$$\hat{H}_N \psi_n(\mathbf{X}) = E_n \psi_n(\mathbf{X}), \tag{4.3}$$

with $[\psi_n(\mathbf{X}), E_n]$ the antisymmetric N electron eigenfunctions and eigenenergies, respectively; $\mathbf{X} = \mathbf{x}_1, \ldots, \mathbf{x}_N$ and $\mathbf{x} = \mathbf{r}\sigma$ with $\mathbf{r}$ and σ the spatial and spin coordinates. The energies E_n are the expectation

$$E_n = \langle \psi_n(\mathbf{X}) | \hat{H}_N | \psi_n(\mathbf{X}) \rangle, \tag{4.4}$$

and the density $\rho_n(\mathbf{r})$ the expectation

$$\rho_n(\mathbf{r}) = \langle \psi_n(\mathbf{X}) | \hat{\rho}(\mathbf{r}) | \psi_n(\mathbf{X}) \rangle, \tag{4.5}$$

with $\rho_n(\mathbf{r})$ the Hermitian density operator of (2.12). The density integrates to the electron number N:

$$\int \rho_n(\mathbf{r}) d\mathbf{r} = N \tag{4.6}$$

The HK theorems are proved for the *nondegenerate ground state* designated as $\{\psi(\mathbf{X}), E, \rho(\mathbf{r})\}$. The theorems are valid for arbitrary external potential $v(\mathbf{r})$ and electron number, but proved for *fixed* N. Following the statement and proof of the first HK theorem we discuss the implications of the theorem.

4.1.1 *The First Hohenberg-Kohn Theorem*

The statement of the first theorem of Hohenberg and Kohn is the following:

Theorem 1 *The nondegenerate ground state density* $\rho(\mathbf{r})$ *determines the external field* $\mathcal{E}(\mathbf{r})$ *or equivalently the external potential* $v(\mathbf{r})$ *to within a trivial additive constant.*

Proof The theorem is proved for nondegenerate ground state densities that are constrained to be *v-representable*. A density is said to be v-representable if it is obtained from an antisymmetric ground state wave function of the time-independent Schrödinger equation (4.3) for arbitrary external potential $v(\mathbf{r})$.

Consider the case of nondegenerate ground states. With the kinetic $\hat{T}$ and electron-interaction $\hat{U}$ potential energy operators known, different external fields with potential energy operators $\hat{V} = \sum_i v(\mathbf{r}_i)$ lead via solution of the time-independent Schrödinger equation to different ground state wavefunctions ψ. (Note that the external potential energies are not restricted to being Coulombic.) This defines the map C between the potential energies $v(\mathbf{r})$ and the wavefunctions ψ (see Fig. 4.1). These different ground state wavefunctions then lead via (4.5) to different ground state densities $\rho(\mathbf{r})$. This establishes the map D between wavefunctions and densities (see Fig. 4.1). The combination (CD) of the maps C and D then maps each potential energy $v(\mathbf{r})$ to a ground state density $\rho(\mathbf{r})$.

The statement of Theorem 1 is that the map (CD) is invertible. In other words, the inverse map $(CD)^{-1}$ ensures that the ground state density $\rho(\mathbf{r})$ then determines the external potential energy $v(\mathbf{r})$ to within an additive constant. To prove the invertibility of map (CD), the separate inverse maps C^{-1} and D^{-1} must exist (see Fig. 4.1). That is, for each ground state wavefunction ψ, there corresponds *one* potential energy $v(\mathbf{r})$. And for each ground state density $\rho(\mathbf{r})$ there exists only *one* ground state wavefunction ψ.

To show the invertibility C^{-1} of map C, what needs be proved is that two different external potential energy operators $\hat{V}$ and $\hat{V}'$ that differ by more than a constant such that $\hat{V} \neq \hat{V}'$ + constant, must lead to different ground state wavefunctions ψ and ψ'. The Schrödinger equations for the operators $\hat{V}$ and $\hat{V}'$ are

$$\hat{H}\psi = (\hat{T} + \hat{U} + \hat{V})\psi = E\psi, \tag{4.7}$$

$$\begin{tikzcd} v(\mathbf{r}) \arrow[r, shift left, "\text{Map C}"] & \Psi(\mathbf{X}) \arrow[l, shift left, "\text{Map C}^{-1}"] \arrow[r, shift left, "\text{Map D}"] & \rho(\mathbf{r}) \arrow[l, shift left, "\text{Map D}^{-1}"] \end{tikzcd}$$

Fig. 4.1 Maps relating the correspondence between external potential energies, ground state wavefunctions, and ground state densities

and

$$\hat{H}'\psi' = (\hat{T} + \hat{U} + \hat{V}')\psi' = E'\psi', \tag{4.8}$$

where E and E' are the respective ground state energies. Now if $\psi = \psi'$, then on subtraction we have

$$(\hat{V} - \hat{V}')\psi = (E - E')\psi. \tag{4.9}$$

As the operators $\hat{V}$ and $\hat{V}'$ are multiplicative (local), the above equation reduces to

$$\hat{V} - \hat{V}' = E - E'. \tag{4.10}$$

Since $(E - E')$ is a constant, (4.10) contradicts the assumption that $\hat{V}$ and $\hat{V}'$ must differ by more that a constant. Thus, for every ground state wavefunction ψ there corresponds a potential energy $v(\mathbf{r})$, and the inverse map C^{-1} is established. A bijective relationship between $v(\mathbf{r})$ and the nondegenerate ground state ψ is consequently proved. The explicit manner by which $v(\mathbf{r})$ is obtained from ψ is via the 'Quantal Newtonian' first law as described in Sect. 2.10. (See also Sect. 4.3.)

To show the invertibility D^{-1} of map D, *one must employ the conclusions of Map C,* i.e. that there exists only one ψ for each $v(\mathbf{r})$. One assumes there exists a ψ and ψ' with $\psi \neq \psi'$ generated from different $v(\mathbf{r})$ and $v'(\mathbf{r})$, respectively, to prove then that $\rho(\mathbf{r}) \neq \rho'(\mathbf{r})$. From the variational principle for the energy we have

$$E = \langle\psi|\hat{H}|\psi\rangle < \langle\psi'|\hat{H}|\psi'\rangle. \tag{4.11}$$

The inequality in (4.11) is justified by our assumption of considering nondegenerate ground states. To see this, recall that according to the variational principle, for $\psi' \neq \psi$, the energy $E \leq \langle\psi'|\hat{H}|\psi'\rangle$. Thus, if $E = \langle\psi'|\hat{H}|\psi'\rangle$, then $H\psi' = E\psi'$, in contradiction of the assumption of nondegeneracy of the ground state. Now

$$\begin{aligned}\langle\psi'|\hat{H}|\psi'\rangle &= \langle\psi'|\hat{T} + \hat{U} + \hat{V}' + \hat{V} - \hat{V}'|\psi'\rangle \\ &= \langle\psi'|\hat{H}'|\psi'\rangle + \langle\psi'|\hat{V} - \hat{V}'|\psi'\rangle \\ &= E' + \int \rho'(\mathbf{r})[v(\mathbf{r}) - v'(\mathbf{r})]d\mathbf{r},\end{aligned} \tag{4.12}$$

so that (4.11) becomes

$$E < E' + \int \rho'(\mathbf{r})[v(\mathbf{r}) - v'(\mathbf{r})]d\mathbf{r}. \tag{4.13}$$

Similarly

$$E' = \langle\psi'|\hat{H}'|\psi'\rangle \; < \; \langle\psi|\hat{H}'|\psi\rangle, \tag{4.14}$$

so that in this instance we obtain

$$E' < E + \int \rho(\mathbf{r})[v'(\mathbf{r}) - v(\mathbf{r})]d\mathbf{r}. \tag{4.15}$$

(Note that the densities $\rho(\mathbf{r})$ and $\rho'(\mathbf{r})$ are v–representable as they are obtained from the solutions of the Schrödinger equation (4.3).) On adding the two inequalities with the assumption that $\rho(\mathbf{r}) = \rho'(\mathbf{r})$, then leads to the contradiction

$$E + E' < E + E'. \tag{4.16}$$

This proves that for each nondegenerate ground state density $\rho(\mathbf{r})$, there exists one and only one ground state wavefunction which would give rise to this density, and hence the inverse map D^{-1} is established. A bijective relationship between the nondegenerate ground state ψ and the density $\rho(\mathbf{r})$ is thus proved.

(Note, however, that there exist an infinite number of antisymmetric N–particle functions $\psi_\rho(\mathbf{X})$ that can lead to the ground state density. Methods for constructing N–particle functions that yield a particular density $\rho(\mathbf{r})$ are described by Gilbert [45], Harriman [46], and Cioslowski [47].) It is also possible to construct [48] antisymmetric functions $\psi_\rho(\mathbf{X})$ that are functionals of functions χ, i.e. $\psi_\rho(\mathbf{X}) = \psi_\rho[\chi](\mathbf{X})$ that also reproduce a given density $\rho(\mathbf{r})$.

Having proved the existence of the inverse maps C^{-1} and D^{-1}, the inverse map $(CD)^{-1}$ ensures that there is a one–to–one correspondence between ground state densities $\rho(\mathbf{r})$ and external potential energies $v(\mathbf{r})$. That is, for each nondegenerate ground state density $\rho(\mathbf{r})$, there exists only *one* external potential energy $v(\mathbf{r})$ that leads to this density. Theorem 1 is thus proved.

4.1.2 Implications of the First Hohenberg-Kohn Theorem

The following are some implications and consequences of the first HK theorem.

1. The first HK theorem can be interpreted as a method for determining the system wave functions $\psi_n(\mathbf{X})$ from the nondegenerate ground state density $\rho(\mathbf{r})$. This is the *HK path* [15] from the density $\rho(\mathbf{r})$ to the Hamiltonian $\hat{H}(\mathbf{R})$ of the system. Knowledge of the density $\rho(\mathbf{r})$ uniquely determines the external potential $v(\mathbf{r})$ to within a constant, and since for fixed electron number N, the kinetic $\hat{T}$ and electron-interaction potential $\hat{U}$ operators are assumed known, so is the Hamiltonian to within a constant. Solution of the Schrdinger equation (4.3) then leads to both the ground and excited state wave functions $\psi_n(\mathbf{X})$ of the system. The HK path in equation form is

$$\rho(\mathbf{r}) \quad \rightarrow \quad v(\mathbf{r}) \quad \rightarrow \quad \hat{H}(\mathbf{R}). \tag{4.17}$$

To understand this mapping, consider the case of the Coulomb external potential $v(\mathbf{r})$. The electron number N is obtained from the ground state density $\rho(\mathbf{r})$ by integration via (4.6), and the potential $v(\mathbf{r})$ via the first HK theorem. The cusps in the electron density which satisfy the electron-nucleus coalescence condition (see Sect. 2.10.2) determine the positions of the nuclei and their charge Z. With the kinetic $\hat{T}$ and potential $\hat{U}$ energy operators known, knowledge of N and $v(\mathbf{r})$ then fully determines the Hamiltonian $\hat{H}$ of (4.1).

2. The statement of the first HK theorem is the basis of the concept of a *basic variable* of quantum mechanics. A basic variable is a *gauge invariant* property whose knowledge uniquely determines the external potential. As there is a bijective relationship between the nondegenerate ground state density $\rho(\mathbf{r})$ and the external potential $v(\mathbf{r})$, the density $\rho(\mathbf{r})$ constitutes a basic variable. (It is this HK definition of a basic variable that must then be employed to determine the corresponding gauge invariant properties when the electrons are subjected to an added external magnetostatic field. The corresponding proof [49] for nondegenerate states with *fixed* canonical angular momentum will be given in Chap. 8.)

3. The fact that knowledge of the nondegenerate ground state density $\rho(\mathbf{r})$ determines the wave functions $\psi_n(\mathbf{X})$ means that the wave functions are functionals of the density: $\psi_n(\mathbf{X}) = \psi_n[\rho(\mathbf{r})]$. Now the wave functions $\psi_n(\mathbf{X})$ are gauge variant [20] whereas the density $\rho(\mathbf{r})$ is gauge invariant. By a density preserving unitary transformation [4], it will be shown in Sect 4.2 that the wave functions must also be functionals of a gauge function $\alpha(\mathbf{R})$, i.e. $\psi_n(\mathbf{X}) = \psi_n[\rho(\mathbf{r}), \alpha(\mathbf{R})]$. In this manner, the wave functions written as functionals will then be gauge variant. Such a unitary transformation also generalizes the first HK theorem to external potential energy operators, that in addition to the standard scalar potential energy operator $v(\mathbf{r})$ also include the momentum and curl-free vector potential energy operators. The theorem as originally formulated by HK then constitutes a special case of this generalization. Since for different gauge functions $\alpha(\mathbf{R})$, the physical system remains unchanged, the choice of vanishing gauge function is equally valid. As such the expectation of any operator $\hat{O}$ is a unique functional of the density:

$$\langle \hat{O} \rangle = O_n[\rho(\mathbf{r})] = \langle \psi_n[\rho(\mathbf{r})] | \hat{O} | \psi_n[\rho(\mathbf{r})] \rangle. \tag{4.18}$$

Thus the energy E_n which is the expectation value of the Hamiltonian $\hat{H}(\mathbf{R})$ is a functional of the density; $E_n = E_n[\rho(\mathbf{r})]$.

Note that although Theorem 1 establishes the fact that the wave function is a functional of the ground state density $\rho(\mathbf{r})$, it does not, however, prescribe the *explicit* dependence of $\psi_n(\mathbf{X})$ on $\rho(\mathbf{r})$. Hence, all the unique expectation value functionals $O_n[\rho(\mathbf{r})]$ are unknown.

4.1.3 *The Second Hohenberg-Kohn Theorem*

The statement and proof of the second Hohenberg-Kohn theorem are given below.

Theorem 2 *The nondegenerate ground state density $\rho(\mathbf{r})$ can be determined from the ground state energy functional $E[\rho]$ via the variational principle by variation only of the density.*

Proof The ground state energy E which is a functional of the density is

$$E \equiv E[\rho] = \langle \psi[\rho] | \hat{H} | \psi[\rho] \rangle. \tag{4.19}$$

Consider a *trial* v–representable ground state density $\tilde{\rho}(\mathbf{r})$. From Theorem 1, this density determines the corresponding external potential energy $\tilde{v}(\mathbf{r})$, and via the resulting Hamiltonian the *trial* wavefunction $\tilde{\psi}[\tilde{\rho}]$. Equivalently, $\tilde{\psi}[\tilde{\rho}]$ is determined from the inverse map D^{-1}. From the variational principle for the energy it follows that

$$\begin{aligned} \tilde{E} \equiv E[\tilde{\rho}] = \langle \tilde{\psi}[\tilde{\rho}] | \hat{H} | \tilde{\psi}[\tilde{\rho}] \rangle &> E \quad \text{for} \quad \tilde{\rho}(\mathbf{r}) \neq \rho(\mathbf{r}) \\ &= E \quad \text{for} \quad \tilde{\rho}(\mathbf{r}) = \rho(\mathbf{r}). \end{aligned} \tag{4.20}$$

Thus, the ground state density $\rho(\mathbf{r})$ can be obtained by minimization of the functional $E[\rho]$ for arbitrary variations $\delta\rho(\mathbf{r})$ of v–representable densities. Introducing a Lagrange multiplier μ to ensure particle number conservation ($\int \rho(\mathbf{r}) d\mathbf{r} = N$), the stationary point is achieved via the variational principle at the vanishing of the first–order variation:

$$\delta \left\{ E[\rho] - \mu \left[\int \rho(\mathbf{r}) d\mathbf{r} - N \right] \right\} = 0. \tag{4.21}$$

Equivalently, the ground state density may be obtained from the corresponding Euler–Lagrange equation

$$\frac{\delta E[\rho]}{\delta \rho(\mathbf{r})} = \mu. \tag{4.22}$$

This proves Theorem 2. □

Separating out the external potential energy component, the ground state energy functional $E[\rho]$ may be written as

$$E[\rho] = \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + F_{\mathrm{HK}}[\rho], \tag{4.23}$$

where the functional

$$F_{\mathrm{HK}}[\rho] = \langle \psi[\rho] | \hat{T} + \hat{U} | \psi[\rho] \rangle. \tag{4.24}$$

Observe, that $F_{\mathrm{HK}}[\rho]$ is *independent* of the external potential energy operator, and depends only on the kinetic $\hat{T}$ and electron–interaction $\hat{U}$ operators. The functional $F_{\mathrm{HK}}[\rho]$ is thus *universal* in that it is the *same* functional for all electronic systems. Furthermore, it is a functional of v–representable densities. However, as the explicit functional dependence of ψ on $\rho(\mathbf{r})$ is unknown, the functional $F_{\mathrm{HK}}[\rho]$ is *unknown*.

An important point of note is that the Lagrange multiplier μ in the Euler–Langrange equation (4.22) has the physical interpretation of being the *chemical potential*. The proof is as follows. The chemical potential $\mu(N)$ is a number that depends on the electron number N. It represents the change in energy $E^{(N)}$ with respect to N:

$$\mu(N) = \frac{\partial E^{(N)}}{\partial N}. \tag{4.25}$$

If $\rho^{(N)}(\mathbf{r})$ is the solution of (4.22) for an N–electron system with ground state energy $E[\rho^{(N)}]$, then the energy difference

$$\begin{aligned} E^{(N+\epsilon)} - E^{(N)} &= E[\rho^{(N+\epsilon)}] - E[\rho^{(N)}] \\ &= \int \frac{\delta E[\rho]}{\delta \rho(\mathbf{r})}|_{\rho^{(N)}} (\rho^{(N+\epsilon)}(\mathbf{r}) - \rho^{(N)}(\mathbf{r}))d\mathbf{r}. \end{aligned} \tag{4.26}$$

Employing (4.22), the right hand side reduces to

$$\begin{aligned} &= \mu(N) \int (\rho^{(N+\epsilon)}(\mathbf{r}) - \rho^{(N)}(\mathbf{r}))d\mathbf{r} \\ &= \mu(N)(N+\epsilon-N) = \mu(N)\epsilon, \end{aligned} \tag{4.27}$$

so that $\lim_{\epsilon\to 0}(E^{(N+\epsilon)} - E^{(N)})/\epsilon = \mu(N)$, which is the desired result.

Finally, the requirement that in the Euler-Lagrange equation (4.21) one employs only v-representable densities is stringent. The conditions for a density to be v-representable are derived [12, 14, 18, 50–55] for extensions of the universal functional $F_{HK}[\rho]$. For v-representability in a lattice system see [56, 57]. The reader is referred to the literature in traditional DFT for further details.

4.1.4 *The Primacy of the Electron Number in Hohenberg-Kohn Theory*

In HK DFT, a key parameter defining the physical system and the consequent basic variable, the nondegenerate ground state density $\rho(\mathbf{r})$, is the electron number N. The density $\rho(\mathbf{r})$ integrates to the electron number N:

$$\int \rho(\mathbf{r})d\mathbf{r} = N. \tag{4.28}$$

(In a later chapter, we will see that in the added presence of a uniform magnetostatic field, another parameter—the canonical orbital angular momentum—is also essential for both the description of the system as well as the properties that constitute the basic variables.) Here we discuss [2] the primacy of the electron number N in HK theory.

As we have seen, in the proof of the HK Theorem 1, the kinetic $\hat{T}$ and electron-interaction potential $\hat{U}$ energy operators are assumed known and kept fixed. It is for *arbitrary local* or *scalar* external potential energy $v(\mathbf{r})$ operators that the proof is formulated. Thus, since the system is comprised of N electrons, the ground state energy E is a functional of the electron number N and the external potential energy operator $v(\mathbf{r})$:

$$E = \langle \psi(\mathbf{X}) | \hat{H}_N | \psi(\mathbf{X}) \rangle \tag{4.29}$$

$$= E[N, v]. \tag{4.30}$$

The statement of HK Theorem 1 that there is a one-to-one correspondence between v-representable nondegenerate ground state densities $\rho(\mathbf{r})$ and the external potential energy operators $v(\mathbf{r})$ to within an additive constant C:$\rho(\mathbf{r}) \leftrightarrow v(\mathbf{r}) + C$, *is only valid for fixed* N.

Employing this theorem, the energy E of (4.30) may then be seen to be a functional of the electron number N and the ground state density $\rho(\mathbf{r})$:

$$E = E[N, \rho]. \tag{4.31}$$

This is an equivalent statement of the postulate that the energy E is a *unique* functional of the ground state density $\rho(\mathbf{r})$. The explicit dependence of the energy E on the electron number N is retained in (4.31) to emphasize its role.

Traditionally, in HK DFT, the electron number N in (4.31) is replaced by $\int \rho(\mathbf{r}) d\mathbf{r}$. By this replacement, the explicit dependence on N is thereby removed. (It is later reintroduced as a constraint in the Euler-Lagrange equation (4.21) for the density.) Thus, in stating that the energy E is a *unique* functional of the ground state density $\rho(\mathbf{r})$, it is the *sole* dependence on the ground state density that is emphasized. Thus, the energy E is written as

$$E\left[\int \rho(\mathbf{r}) d\mathbf{r}, \rho(\mathbf{r})\right] = E[\rho] = \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + F_{HK}[\rho], \tag{4.32}$$

with $F_{HK}[\rho]$ defined by (4.23).

The functional $F_{HK}[\rho]$ is *universal* in the sense that it is independent of both the electron number N and the external potential energy operator $v(\mathbf{r})$. Note the following with regard to the energy functional $E[\rho]$ of (4.32):

(i) The functional $E[\rho]$ via the first term on the right hand side of (4.32) depends *explicitly* on the choice of $v(\mathbf{r})$.

(ii) For an N-electron system, the v-representable densities employed in the functional $E[\rho]$ must all integrate to the electron number N. This is the constraint employed in the application of the HK Theorem 2 according to which the variational principle for the energy may be applied to the functional $E[\rho]$ in terms of arbitrary variations of the density $\rho(\mathbf{r}) + \delta\rho(\mathbf{r})$. On introducing the Lagrange multiplier μ, one obtains the Euler-Lagrange equation (4.21) for the density. The v-representable densities employed in the variational procedure are such that $\int \delta\rho(\mathbf{r})d\mathbf{r} = 0$. The minimum of the energy $E[\rho]$ is achieved for the true ground state density $\rho(\mathbf{r})$. The Lagrange multiplier μ, which was shown to be the chemical potential in the previous section, is determined by the self-consistent solution of the Euler-Lagrange equation (4.21) and the constraint to N-electron number of (4.28).

The above remarks make clear that in spite of the fact that the energy E is a unique functional of the ground state density $\rho(\mathbf{r})$, and that the functional $F_{HK}[\rho]$ is universal, *the knowledge of both* $v(\mathbf{r})$ *and* N *remains fundamental to the determination of the energy* E *of a system. This is the case even if the universal functional* $F_{HK}[\rho]$ *were known*. Hence, in essence, one has returned to the original representation of the energy as a functional of N and $v(\mathbf{r})$ of (4.30). The operator $v(\mathbf{r})$ may be replaced by the density $\rho(\mathbf{r})$ via the HK Theorem 1 as in (4.31), but this density must integrate to N. *Thus, in HK DFT, the role of the electron number* N *is primary. One must know* N *prior to solving the Euler-Lagrange equation for the density* $\rho(\mathbf{r})$, *and from this density the energy* E *from* $E[\rho]$.

4.2 Generalization of the Fundamental Theorem of Hohenberg-Kohn

The fundamental theorem of Hohenberg and Kohn (Theorem 1), of the bijectivity, between the nondegenerate ground state density $\rho(\mathbf{r})$ and the Hamiltonian $\hat{H}(\mathbf{R})$ to within a constant C i.e., $\rho(\mathbf{r}) \leftrightarrow \hat{H}(\mathbf{R}) + C$, is proved for the Hamiltonian $\hat{H}(\mathbf{R})$ of (4.1) and (4.2), where $\mathbf{R} = \mathbf{r}_1, \ldots, \mathbf{r}_N$.

In this Hamiltonian, the external potential energy operator $\hat{V} = \sum_i v(\mathbf{r}_i)$ is a *scalar*. Furthermore, in the proof of the theorem it is *assumed* that the kinetic energy $\hat{T}$ and electron-interaction potential energy $\hat{W}$ operators are known. (The symbol $\hat{U}$ of (4.2) is replaced here by $\hat{W}$.) Thus, in the proof, these operators are kept *fixed*. The theorem is then proved by considering different external potential energy operators $\hat{V}$.

We generalize the theorem of bijectivity by a *density preserving* unitary transformation of the Hamiltonian $\hat{H}(\mathbf{R})$ to Hamiltonians $\hat{H}'(\mathbf{R})$ which in addition to the scalar potential energy $v(\mathbf{r})$ operator also include the momentum $\hat{\mathbf{p}}$ and a curl-free vector potential energy $\hat{\mathbf{A}}(\mathbf{r})$ operator.

4.2.1 The Unitary Transformation

To generalize the fundamental theorem we perform a unitary transformation of the Hamiltonian $\hat{H}(\mathbf{R})$. The unitary operator $\hat{U}$ we employ is

$$\hat{U} = e^{i\alpha(\mathbf{R})}, \tag{4.33}$$

so that the transformed wave function $\psi'(\mathbf{X})$ is

$$\psi'(\mathbf{X}) = \hat{U}^{\dagger}\psi(\mathbf{X}), \tag{4.34}$$

and the transformed density $\rho'(\mathbf{r})$ is

$$\rho'(\mathbf{r}) =< \psi'(\mathbf{X})|\hat{\rho}(\mathbf{r})|\psi'(\mathbf{X}) >= \rho(\mathbf{r}). \tag{4.35}$$

The unitary transformation thus *preserves the density*.

The transformed Hamiltonian $\hat{H}'(\mathbf{R})$ is

$$\hat{H}'(\mathbf{R}) = \hat{U}^{\dagger}\hat{H}(\mathbf{R})\hat{U}, \tag{4.36}$$

so that the transformed time-independent Schrödinger equation is

$$\hat{H}'(\mathbf{R})\psi'(\mathbf{X}) = E'\psi'(\mathbf{X}), \tag{4.37}$$

with $E' = E$ of (4.3). In a unitary transformation, the eigen energies remain unchanged. (That $E' = E$ also follows from the fact that the eigen energies E are unique functionals of the ground state density $\rho(\mathbf{r})$. As the density $\rho(\mathbf{r})$ is invariant in this unitary transformation, the eigen energies of the Hamiltonian $\hat{H}(\mathbf{R})$ and $\hat{H}'(\mathbf{R})$ are the same.)

We next obtain the transformed Hamiltonian $\hat{H}'(\mathbf{R})$. From (4.36)

$$\hat{H}'(\mathbf{R}) = e^{-i\alpha(\mathbf{R})}\sum_i\left(-\frac{1}{2}\nabla_i^2\right)e^{i\alpha(\mathbf{R})} + \hat{V} + \hat{W}. \tag{4.38}$$

Since

$$[\nabla^2, e^{i\alpha}] = \nabla^2 e^{i\alpha} - e^{i\alpha}\nabla^2, \tag{4.39}$$

the Hamiltonian $\hat{H}'(\mathbf{R})$ is

$$\hat{H}'(\mathbf{R}) = -\frac{1}{2}\sum_i\left\{e^{-i\alpha(\mathbf{R})}[\nabla_i^2, e^{i\alpha(\mathbf{R})}] + \nabla_i^2\right\} + \hat{V} + \hat{W} \tag{4.40}$$

or

$$\hat{H}'(\mathbf{R}) = \hat{H}(\mathbf{R}) - \frac{1}{2}\sum_i \left\{ e^{-i\alpha(\mathbf{R})}[\nabla_i^2, e^{i\alpha(\mathbf{R})}] \right\}. \tag{4.41}$$

Next we determine the commutator of (4.40). Employing the commutator relationship

$$\left[\nabla^2, f(\mathbf{r})\right] = \nabla^2 f(\mathbf{r}) + 2\boldsymbol{\nabla} f(\mathbf{r}) \cdot \boldsymbol{\nabla}, \tag{4.42}$$

we have

$$\left[\nabla^2, e^{i\alpha}\right] = \nabla^2 e^{i\alpha} + 2\boldsymbol{\nabla} e^{i\alpha} \cdot \boldsymbol{\nabla}. \tag{4.43}$$

With $\boldsymbol{\nabla} e^{i\alpha} = i e^{i\alpha} \boldsymbol{\nabla}\alpha$, then

$$\begin{aligned} \nabla^2 e^{i\alpha} &= \boldsymbol{\nabla} \cdot \boldsymbol{\nabla} e^{i\alpha} \\ &= -e^{i\alpha}(\boldsymbol{\nabla}\alpha)^2 + i e^{i\alpha} \nabla^2 \alpha. \end{aligned} \tag{4.44}$$

Thus, the commutator

$$\left[\nabla^2, e^{i\alpha}\right] = -e^{i\alpha}(\boldsymbol{\nabla}\alpha)^2 + i e^{i\alpha}\nabla^2\alpha + 2i e^{i\alpha}\boldsymbol{\nabla}\alpha \cdot \boldsymbol{\nabla}, \tag{4.45}$$

and therefore

$$e^{-i\alpha}\left[\nabla^2, e^{i\alpha}\right] = -(\boldsymbol{\nabla}\alpha)^2 + i\nabla^2\alpha + 2i\boldsymbol{\nabla}\alpha \cdot \boldsymbol{\nabla}. \tag{4.46}$$

Employing the vector identity

$$\boldsymbol{\nabla} \cdot (\mathbf{C}\phi) = \boldsymbol{\nabla}\phi \cdot \mathbf{C} + (\boldsymbol{\nabla} \cdot \mathbf{C})\phi, \tag{4.47}$$

we have

$$\boldsymbol{\nabla} \cdot (\boldsymbol{\nabla}\alpha) = \boldsymbol{\nabla}\alpha \cdot \boldsymbol{\nabla} + \nabla^2\alpha, \tag{4.48}$$

so that

$$\nabla^2\alpha = \boldsymbol{\nabla} \cdot \boldsymbol{\nabla}\alpha - \boldsymbol{\nabla}\alpha \cdot \boldsymbol{\nabla}. \tag{4.49}$$

Therefore, on substituting (4.48) into (4.45), we have

$$e^{-i\alpha}\left[\nabla^2, e^{i\alpha}\right] = -(\boldsymbol{\nabla}\alpha)^2 + i\boldsymbol{\nabla} \cdot \boldsymbol{\nabla}\alpha + i\boldsymbol{\nabla}\alpha \cdot \boldsymbol{\nabla}. \tag{4.50}$$

Hence, the transformed Hamiltonian $\hat{H}'(\mathbf{R})$ of (4.40) may be expressed as

$$\hat{H}'(\mathbf{R}) = \hat{H}(\mathbf{R}) + \frac{1}{2}\sum_i \left(\hat{\mathbf{p}}_i \cdot \hat{\mathbf{A}}_i + \hat{\mathbf{A}}_i \cdot \hat{\mathbf{p}}_i + \hat{\mathbf{A}}_i^2\right), \tag{4.51}$$

where $\hat{\mathbf{p}}_i = -i\nabla_i$ is the momentum operator, and where the *vector* potential energy operator is *defined* as $\hat{\mathbf{A}}_i = \nabla_i \alpha(\mathbf{R})$ so that $\nabla \times \mathbf{A}_i = 0$. (It is implicit that for the transformed system, the boundary conditions too are transformed.)

Note that by writing the transformed Hamiltonian $\hat{H}'(\mathbf{R})$ as in (4.51), we emphasize the fact that the operators $\hat{T}$ and $\hat{W}$ are the *same* as those of the untransformed Hamiltonian $\hat{H}(\mathbf{R})$ of (4.1)–(4.2). Thus, we *preserve* the Hohenberg-Kohn assumption that the operators $\hat{T}$ and $\hat{W}$ are *fixed*.

It is evident that $\hat{H}'(\mathbf{R})$ may also be written as

$$\hat{H}'(\mathbf{R}) = \frac{1}{2}\sum_i \left(\hat{\mathbf{p}}_i + \hat{\mathbf{A}}_i\right)^2 + \hat{V} + \hat{W}. \tag{4.52}$$

Note that as is the case for the Hamiltonian $\hat{H}(\mathbf{R})$, there is no magnetic field in the transformed Hamiltonian $\hat{H}'(\mathbf{R})$. The vector potential energy operator $\hat{\mathbf{A}}_i$ as defined above is curl-free.

As we have performed a unitary transformation, the physical system described by $\hat{H}'(\mathbf{R})$ and $\hat{H}(\mathbf{R})$ is the *same*. That $\hat{H}'(\mathbf{R})$ and $\hat{H}(\mathbf{R})$ represent the same physical system may also be seen by performing the following gauge transformation of $\hat{H}(\mathbf{R})$ to obtain $\hat{H}'(\mathbf{R})$. Rewriting $\hat{H}(\mathbf{R})$ as

$$\hat{H}(\mathbf{R}) = \frac{1}{2}\sum_i \left(\hat{\mathbf{p}}_i + \hat{\mathbf{A}}_i\right)^2 \Bigg|_{\hat{A}_i=0} + \hat{V} + \hat{W}, \tag{4.53}$$

such that $\mathbf{B} = \nabla \times \mathbf{A}_i = 0$, we make the transformation $\hat{\mathbf{A}}_i \to \hat{\mathbf{A}}'_i = \hat{\mathbf{A}}_i + \nabla_i \alpha(\mathbf{R})$ with $\hat{\mathbf{A}}_i = 0$ so that $\mathbf{B}' = \nabla \times \hat{\mathbf{A}}'_i = 0$. One then reobtains the Hamiltonian $\hat{H}'(\mathbf{R})$ as written in (4.51). It is well known in quantum mechanics [20] that the above gauge transformation for a Hamiltonian with nonzero but finite magnetic field $\mathbf{B}$ leaves the Schrödinger equation invariant provided the wave functions are related by the gauge transformation $\alpha(\mathbf{R})$ as in (4.34).

4.2.2 *New Insights as a Consequence of the Generalization*

As a consequence of the unitary transformation, there are several new insights that are achieved with regard to the theorem of bijectivity between the ground state density $\rho(\mathbf{r})$ and the Hamiltonian $\hat{H}(\mathbf{R})$ of a system: $\rho(\mathbf{r}) \leftrightarrow \hat{H}(\mathbf{R})$. We describe here these insights together with other clarificatory remarks.

1. The Hamiltonian $\hat{H}'(\mathbf{R})$ of (4.51), (4.52) obtained from the gauge function $\alpha(\mathbf{R})$ is the most *general* form of the Hamiltonian for which the Hohenberg-Kohn theorem is valid. This Hamiltonian includes not only a scalar potential energy operator $v(\mathbf{r}_i)$ but also the momentum operator $\hat{\mathbf{p}}_i = -i\nabla_i$ and a curl-free vector potential energy operator $\hat{\mathbf{A}}_i = \nabla_i \alpha(\mathbf{R})$. The bijectivity of the fundamental theorem in its *general* form is represented pictorially in Fig. 4.2. The figure shows that the bijectivity is

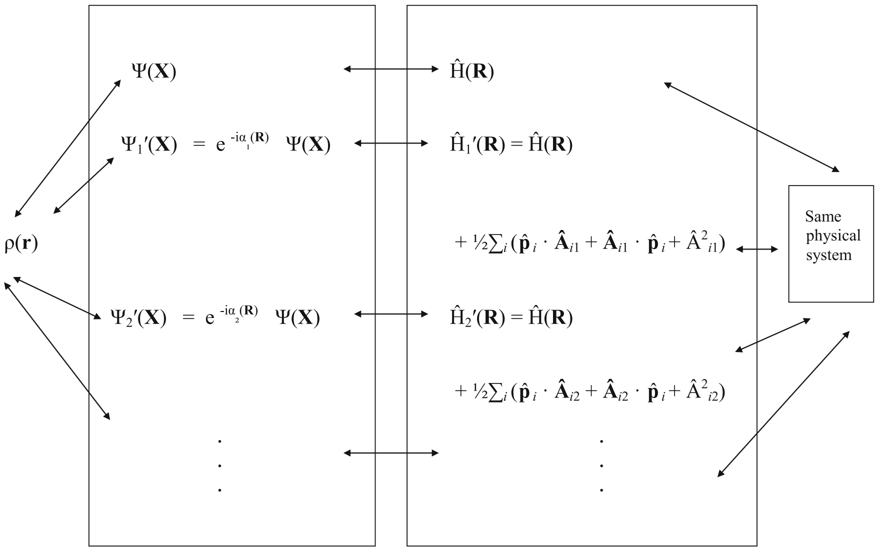

Fig. 4.2 The generalization of the fundamental theorem of Hohenberg and Kohn demonstrating the bijectivity between the nondegenerate ground state density $\rho(\mathbf{r})$ and the Hamiltonians $\hat{H}(\mathbf{R})$ and $\hat{H}_j(\mathbf{R})$ representing that physical system. The figure is drawn for the most general form of the time-independent theorem for which the gauge function is $\alpha_j(\mathbf{R})$. The theorem as originally enunciated is recovered when $\alpha(\mathbf{R}) = \alpha$, a constant

$\rho(\mathbf{r}) \leftrightarrow \hat{H}(\mathbf{R})$ with $\hat{H}(\mathbf{R})$ of (4.1)–(4.2), or equivalently $\rho(\mathbf{r}) \leftrightarrow \hat{H}'_j(\mathbf{R})$ with $\hat{H}'_j(\mathbf{R})$ of (4.51), (4.52), depending on the choice of the gauge function $\alpha_j(\mathbf{R})$. It is emphasized that the Hamiltonian $\hat{H}(\mathbf{R})$ and Hamiltonians $\hat{H}'_j(\mathbf{R})$ all correspond to the *same physical system*.

2. The Hohenberg-Kohn theorem as originally enunciated is recovered as a special case when $\alpha(\mathbf{R}) = \alpha$, a constant (see (4.51) and Fig. 4.2). (As an aside we point out that the more general statement of the bijectivity between the density $\rho(\mathbf{r})$ and the wave function $\psi(\mathbf{X})$, as proved and then employed in the proof of the fundamental theorem, is that the latter is known to within a phase factor α.) Note, that for the special case $\alpha(\mathbf{R}) = \alpha$, there is no constant C present in (4.51). Of course, this must be so because in this case $\hat{H}'_j(\mathbf{R}) = \hat{H}(\mathbf{R})$, and the energies E' and E are equivalent. Therefore the constant C of the Hohenberg-Kohn theorem is arbitrary and *extrinsically* additive. This has also been the understanding since the advent of the theorem. Put another way, the bijectivity $\rho(\mathbf{r}) \leftrightarrow \hat{H}(\mathbf{R})$ or $\rho(\mathbf{r}) \leftrightarrow \hat{H}(\mathbf{R}) + C$ is for the *same physical system* since the constant C simply adjusts the energy reference level. (Note that as will be explained in the Corollary in Sect. 4.8.1, it is possible to construct an *infinite* number of degenerate Hamiltonians $\{H\}$ that differ by an *intrinsic* constant C, represent different physical systems, and which all possess the same density $\rho(\mathbf{r})$. In this case, the density $\rho(\mathbf{r})$ cannot distinguish between the different physical systems, and consequently the theorem of bijectivity is no longer valid.)

3. It becomes evident from the above unitary or gauge transformation that in the general case the wave function $\psi(\mathbf{X})$ must be a functional of both the density $\rho(\mathbf{r})$ as well as the gauge function $\alpha(\mathbf{R})$ i.e., $\psi(\mathbf{X}) = \psi[\rho(\mathbf{r}); \alpha(\mathbf{R})]$. If the wave function $\psi(\mathbf{X})$ was solely a functional of the density $\rho(\mathbf{r})$, then that wave function as a functional of the density would be *gauge invariant* because the density is *gauge invariant*. However, it is well known in quantum mechanics [20] that the Hamiltonian $\hat{H}$ and wave function $\psi(\mathbf{X})$ are *gauge variant*. It is the functional dependence of the wave function functional on the gauge function $\alpha(\mathbf{R})$ that ensures it is gauge variant.

4. Because the bijectivity is between the density $\rho(\mathbf{r})$ and the Hamiltonian representation of the physical system $\hat{H}(\mathbf{R})$, $\hat{H}(\mathbf{R}) + C$, or $\hat{H}'_j(\mathbf{R})$ (see Fig. 4.2), the choice of gauge function is *arbitrary*. Thus the choice $\alpha(\mathbf{R}) = 0$ is equally valid. This provides a deeper understanding of the fundamental theorem of Hohenberg-Kohn. In their original paper [1] they state: "Thus, $v(\mathbf{r})$ is (to within a constant) a unique functional of $\rho(\mathbf{r})$; since, in turn, $v(\mathbf{r})$ fixes H we see that *the full many-particle ground state is a unique functional of* $\rho(\mathbf{r})$." (Our emphases). The statement implies that the many-particle ground state wave function written as a functional is gauge invariant. However, we now understand that their statement is consistent with the fact that the choice of gauge function $\alpha(\mathbf{R}) = 0$ is valid.

5. As a point of information we note that the two Hohenberg-Kohn theorems can be derived employing the original *reductio ad absurdum* argument for a general form of the Hamiltonian $\hat{H} = \hat{H}_0 + \hat{V}$, where $\hat{V}$ is a local potential energy operator, and $\hat{H}_0$ any Hermitian operator defined on the Hilbert space of quadratically integrable functions. The only requirement that $\hat{H}_0$ must have is that it be bounded from below and have normalizable eigen functions. The Hamiltonian $\hat{H}_0$ could contain a magnetic field or a vector potential with vanishing or non-vanishing curl. This form of the generalization of the theorem to be derived in Chap. 8 differs from the generalized form derived via the unitary transformation in a fundamental way. For different Hermitian operators $\hat{H}_0$, the Hamiltonian $\hat{H}$ corresponds to *different* physical systems, and therefore to *different* ground state densities. In the generalization derived via the unitary transformation, the physical system is unchanged and therefore the density is *preserved*.

6. As noted previously, the Hohenberg-Kohn theorems can be proved for different Hamiltonians $\hat{H}$ as for example when different potential energy operators $\hat{W}$ such as the Coulomb or Yukawa interactions are employed. Thus, one can state that the wave function $\psi(\mathbf{X})$ is a functional of the operator $\hat{W}$. The physical systems corresponding to different $\hat{W}$ are different, and hence the density for these different Hamiltonians will be different. However, it is important to note that in proving the Hohenberg-Kohn theorems, the operator $\hat{W}$ is assumed known and kept *fixed* throughout the proof. Hence the statement that the wave function $\psi(\mathbf{X})$ is a functional of both the ground state density $\rho(\mathbf{r})$ and the gauge function $\alpha(\mathbf{R})$ is valid for each Hamiltonian $\hat{H}$ with a *fixed* electron-interaction operator $\hat{W}$.

In conclusion it is reiterated that in the most general case when the gauge function is $\alpha(\mathbf{R})$, the functional dependence of the wave function $\psi(\mathbf{X})$ on the gauge function is important because the corresponding Hamiltonian $\hat{H}'(\mathbf{R})$ of (4.51) explicitly involves the gauge function via the momentum $\hat{\mathbf{p}}_i$ and curl-free vector potential energy $\hat{\mathbf{A}}_i$ operators. This functional dependence hence also enhances the significance of the phase factor in density functional theory in a manner similar to that of quantum mechanics. The understanding that the wave function $\psi(\mathbf{X})$ is a functional of both the density $\rho(\mathbf{r})$ and the gauge function $\alpha(\mathbf{R})$ is fundamental.

4.3 Inverse Maps

In the proof of the first Hohenberg-Kohn theorem, the paths of the maps C and D (see Fig. 4.1) are well defined. For map C, the Schrödinger equation is solved for each external potential energy operator $\hat{V}$ to determine the corresponding nondegenerate ground state wave function ψ. For map D, the density $\rho(\mathbf{r})$ is then obtained from ψ via its definition as the expectation of the density operator. The question we address next is what are the specific paths for the inverse maps C^{-1} and D^{-1}? In other words, what is the path from the wave function ψ to the external potential $v(\mathbf{r})$, and from the density $\rho(\mathbf{r})$ to the wave function ψ?

One approach to the path from the wave function ψ to the external potential $v(\mathbf{r})$ is to obtain the latter by inversion of the Schrdinger equation: $\hat{V} = [(\hat{T} + \hat{U})\psi]/\psi$ to within a constant.

There is, however, another path from ψ to $v(\mathbf{r})$ that is physically insightful. This path follows from the 'Quantal Newtonian' first law of (2.134) and (2.135). Thus, (see 2.136), the external potential $v(\mathbf{r})$ is the work done to move an electron from some reference point at infinity to its position at $\mathbf{r}$ in the force of the conservative internal field $\boldsymbol{\mathcal{F}}^{\text{int}}[\psi](\mathbf{r})$ experienced by the electrons:

$$v(\mathbf{r}) = \int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{F}}^{\text{int}}[\psi](\mathbf{r}') \cdot d\boldsymbol{\ell}' \tag{4.54}$$

where

$$\boldsymbol{\mathcal{F}}^{\text{int}}[\psi](\mathbf{r}) = \boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}) - \boldsymbol{\mathcal{D}}(\mathbf{r}) - \boldsymbol{\mathcal{Z}}(\mathbf{r}), \tag{4.55}$$

with the electron-interaction $\boldsymbol{\mathcal{E}}_{\text{ee}}[\psi](\mathbf{r})$, differential density $\boldsymbol{\mathcal{D}}[\psi](\mathbf{r})$, and kinetic $\boldsymbol{\mathcal{Z}}[\psi](\mathbf{r})$ fields being functionals of the wave function ψ via their respective quantal sources which are expectations of Hermitian operators taken with respect to ψ. These fields, the corresponding 'forces', and the quantal sources defined previously in Chap. 2 are noted here again for completeness. The electron-interaction field $\boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r})$ and 'force' $\mathbf{e}_{\text{ee}}(\mathbf{r})$:

$$\boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}) = \frac{\mathbf{e}_{\text{ee}}(\mathbf{r})}{\rho(\mathbf{r})}; \quad \mathbf{e}_{\text{ee}}(\mathbf{r}) = \int \frac{P(\mathbf{r}\mathbf{r}')(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} d\mathbf{r}', \tag{4.56}$$

with $P(\mathbf{r}\mathbf{r}') = \langle \psi | \hat{P}(\mathbf{r}\mathbf{r}') | \psi \rangle$ the pair function being the quantal source; the differential density field $\boldsymbol{\mathcal{D}}(\mathbf{r})$ and 'force' $d(\mathbf{r})$, with the density $\rho(\mathbf{r})$ the quantal source:

$$\boldsymbol{\mathcal{D}}(\mathbf{r}) = \frac{\mathbf{d}(\mathbf{r})}{\rho(\mathbf{r})}; \quad \mathbf{d}(\mathbf{r}) = -\frac{1}{4}\nabla\nabla^2\rho(\mathbf{r}), \tag{4.57}$$

and the kinetic field $\boldsymbol{\mathcal{Z}}(\mathbf{r})$ and 'force' $z_\alpha(\mathbf{r})$:

$$\boldsymbol{\mathcal{Z}}(\mathbf{r}) = \frac{\mathbf{z}(\mathbf{r}; [\gamma])}{\rho(\mathbf{r})}; \quad \mathbf{z}_\alpha(\mathbf{r}) = 2\sum_\beta \frac{\partial}{\partial r_\beta} t_{\alpha\beta}(\mathbf{r}; [\gamma]), \tag{4.58}$$

with the kinetic-energy-density tensor

$$t_{\alpha\beta}(\mathbf{r}) = \frac{1}{4}\left[\frac{\partial^2}{\partial r'_\alpha \partial r''_\beta} + \frac{\partial^2}{\partial r'_\beta \partial r''_\alpha}\right]\gamma(\mathbf{r}'\mathbf{r}'')\bigg|_{\mathbf{r}'=\mathbf{r}''=r}, \tag{4.59}$$

and where $\gamma(\mathbf{r}\mathbf{r}')$, the reduced single particle density matrix, is the quantal source. Note that the work done (4.54) is *path-independent*. Hence, the path of the inverse map C^{-1}, whereby for each nondegenerate ground state wave function ψ there corresponds a potential energy $v(\mathbf{r})$, is now defined. For examples of the inverse map C^{-1}, and applications of the expression (4.54), see Figs. 2.16 and 2.17.

A consequence of the first HK theorem (see Sect. 4.1.2), is that the nondegenerate ground state wave function ψ is a functional of the density $\rho(\mathbf{r})$, i.e. $\psi = \psi[\rho]$. As also noted there, the explicit dependence of ψ on $\rho(\mathbf{r})$ is unknown. Hence, for the inverse map D^{-1}, there is no explicit formula whereby the ground state wave function ψ can be determined from the ground state density $\rho(\mathbf{r})$, as is the case of (4.54) for the inverse map C^{-1} between ψ and $v(\mathbf{r})$. There is, however, a related question that can be answered. Consider a ground state wave function ψ and the corresponding density $\rho(\mathbf{r})$. As there exist an infinite number of antisymmetric functions ψ_ρ that integrate to this density, how then does one determine the true ground state wave function ψ from amongst these functions? The answer to this query leads to the Percus-Levy-Lieb [15–19] constrained-search path from the density $\rho(\mathbf{r})$ to the wave function ψ and to the Hamiltonian $\hat{H}$. This path, to be described in the following section, is predicated on the *a priori* knowledge that the density $\rho(\mathbf{r})$ is a basic variable of quantum mechanics. The attributes of this path are that it generalizes the first HK theorem to N-representable densities and degenerate states.

4.4 The Percus-Levy-Lieb Constrained-Search Path

As we have seen, the first Hohenberg-Kohn (HK) theorem constitutes a path (see (4.17)) from the nondegenerate ground state density $\rho(\mathbf{r})$ of a system to its Hamiltonian $\hat{H}$. There is a second independent path—*the constrained-search path*—from $\rho(\mathbf{r})$ to $\hat{H}$ due to Percus-Levy-Lieb [15–19] (PLL). Although in the literature, the HK and PLL paths are considered at par with each other, the HK proof is more fundamental, and this is the case in general when the electrons are subject to other external fields such as a magnetostatic field. The reason for this is that it is solely via the proof of bijectivity between the external potentials and certain gauge-invariant properties of the system that determines what constitutes the basic variables of quantum mechanics. Consequently, the PLL proof, which requires the *a priori* knowledge of what the basic variables are, is dependent on the conclusions of an HK-type proof of bijectivity, and is therefore less fundamental. However, once the basic variable has been identified—the nondegenerate ground state density $\rho(\mathbf{r})$—the PLL path shows that it is valid for *degenerate* ground states and N-representable densities, hence broadening the scope of the first HK theorem.

The PLL path from the ground state density $\rho(\mathbf{r})$ to $\hat{H}$ begins with the answer to the question raised at the end of the previous section, *viz.* of the infinite antisymmetric functions ψ_ρ that generate $\rho(\mathbf{r})$, how does one then determine which of these is the true ground state wave function ψ. The answer is as follows. From the variational principle for the energy we have that

$$\langle\psi_\rho|\hat{H}|\psi_\rho\rangle \;\geq\; \langle\psi|\hat{H}|\psi\rangle = E, \tag{4.60}$$

or equivalently

$$\langle\psi_\rho|\hat{T}+\hat{U}|\psi_\rho\rangle \;+\int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \;\geq\; \langle\psi|\hat{T}+\hat{U}|\psi\rangle + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}, \tag{4.61}$$

which in turn is equivalent to

$$\langle\psi_\rho|\hat{T}+\hat{U}|\psi_\rho\rangle \;\geq\; \langle\psi|\hat{T}+\hat{U}|\psi\rangle. \tag{4.62}$$

Thus, of all the antisymmetric functions ψ_ρ that lead to the ground state density $\rho(\mathbf{r})$, the true ground state wave function ψ is that which minimizes the expectation value $\langle\hat{T}+\hat{U}\rangle$. This then can be construed as the mechanism for the inverse map D^{-1}. This mechanism is referred to as the *constrained search path* from the density $\rho(\mathbf{r})$ to the wave function ψ. The search is over all antisymmetric functions ψ_ρ that are constrained to integrate to the ground state density $\rho(\mathbf{r})$.

A comparison of the right hand side of (4.62) with the universal functional $F_{HK}[\rho]$ of (4.24) shows them to be equivalent. Hence, the functional $F_{HK}[\rho]$ may be given the interpretation

$$F_{HK}[\rho] = \inf_{\psi_\rho\to\rho}\langle\psi_\rho|\hat{T}+\hat{U}|\psi_\rho\rangle, \tag{4.63}$$

where the notation $\inf\limits_{\psi_\rho\to\rho}$ means that one searches for the smallest (infimum) value of the expectation $\langle\hat{T}+\hat{U}\rangle$ taken with respect to all the antisymmetric functions ψ_ρ that lead to the ground state density $\rho(\mathbf{r})$. (The set $\{\psi_\rho\}$ is a subset of all functions ψ that could be employed in the expectation. The least value of the expectation for the subset $\{\psi_\rho\}$ is the infimum.) This infimum can be shown to be a minimum [18].

Recall that the variational principle for the energy functional $E[\rho]$ as enunciated by the second HK theorem (see (4.21)), the densities to be varied were v-representable. As also noted, the requirement of v-representability is stringent. The constrained-search definition of $F_{HK}[\rho]$ of (4.63), however, expands the domain of applicability of the second HK theorem to N-representable densities. To see this, one rewrites the variational principle for the energy for all N-particle functions ψ as two nested infima. Thus, the ground state energy E which is

$$E = \inf_{\psi} \, \langle \psi | \hat{T} + \hat{U} + \hat{V} | \psi \rangle \tag{4.64}$$

may be written as

$$E = \inf_{\rho(\mathbf{r})} \left[\inf_{\psi_\rho \to \rho(\mathbf{r})} \langle \psi_\rho | \hat{T} + \hat{U} + \hat{V} | \psi_\rho \rangle \right], \tag{4.65}$$

where the inner infinum is now restricted to all N-particle antisymmetric functions ψ_ρ that yield a given $\rho(\mathbf{r})$, and the outer infinum is a search over all $\rho(\mathbf{r})$. Separating out the external potential energy component, the energy is then

$$E = \inf_{\rho(\mathbf{r})} \left[\inf_{\psi_\rho \to \rho} \langle \psi_\rho | \hat{T} + \hat{U} | \rho \rangle + \int v(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \right] \tag{4.66}$$

which on employing (4.63) is

$$E = \inf_{\rho(\mathbf{r})} \left[F_{HK}[\rho] + \int v(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \right] \tag{4.67}$$

$$= \inf_{\rho(\mathbf{r})} E[\rho], \tag{4.68}$$

with $E[\rho]$ defined by (4.23). The variations in (4.68) are thus over all N-representable densities.

The conditions for a density to be N-representable are those of nonnegativity, normalization, and continuity:

$$\rho(\mathbf{r}) \geq 0; \quad \int \rho(\mathbf{r}) d\mathbf{r} = N; \quad \int |\nabla \rho(\mathbf{r})^{\frac{1}{2}}|^2 d\mathbf{r} < \infty. \tag{4.69}$$

Thus far, when we have referred to a N-representable density, we have stated that it is derived from an N-particle antisymmetric function. However, note that since the density does not contain any information about the Pauli exclusion principle, the same density could correspond to a fermion or boson system. Hence, the functions ψ_ρ need not be restricted to being antisymmetric. They could equally well be symmetric or lack a symmetry. Thus, the constrained-search arguments are valid for a far broader class of functions.

We next address the constrained-search path from the ground state density $\rho(\mathbf{r})$ to the Hamiltonian $\hat{H}$. As explained previously, of all the antisymmetric functions ψ_ρ that yield the density $\rho(\mathbf{r})$, the true wave function ψ is the one that yields the density $\rho(\mathbf{r})$ and obtains the infinum of the expectation value of $\hat{T} + \hat{U}$:

$$\inf_{\psi_\rho \to \rho} \langle \psi_\rho | \hat{T} + \hat{U} | \psi_\rho \rangle. \tag{4.70}$$

This expectation value is *independent* of the external potential $v(\mathbf{r})$. Now according to Levy [19], as ψ cannot be an eigenfunction of more than one $\hat{H}$ with a multiplicative potential, it follows that $\rho(\mathbf{r})$ determines $\hat{H}$ *uniquely* within an additive constant. More explicitly, as the operators $\hat{T}$ and $\hat{U}$ are known, the path from ψ to $\hat{H}$ requires knowledge of the external potential $v(\mathbf{r})$. But with ψ known, the potential $v(\mathbf{r})$ may be obtained by the inverse map C^{-1} as described by (4.54) of Sect. 4.3. Hence, the constrained-search path is

$$\rho(\mathbf{r}) \to \psi \to v \to \hat{H}. \tag{4.71}$$

Note that if more than one ψ satisfies (4.69), then these functions all give the same ground state energy. Thus, when degeneracies exist, the constrained-search path of (4.71) is still valid. Hence, the PLL path encompasses the case of degenerate ground states.

Finally, as noted above, the PLL constrained-search proof for the determination of the wave function ψ (see 4.70) is independent of the external potential $v(\mathbf{r})$. This is a key attribute of the proof. But the proof requires the *a priori* knowledge that $\rho(\mathbf{r})$ is the basic variable. After all the constrained search is over all ψ_ρ that yield $\rho(\mathbf{r})$ and not some other property. As a consequence, there is an *implicit* dependence of the proof on the external potential. This follows from HK via the bijective relationship between the external potential and the basic variable: knowledge of the ground state density $\rho(\mathbf{r})$ uniquely determines $v(\mathbf{r})$ to within a constant. Thus, the PLL proof is intrinsically connected to the specific physical system of interest as defined by the external potential in spite of the fact that one is searching for the infinum of the expectation value of the operators $\hat{T} + \hat{U}$. In this manner, the first HK theorem provides a deeper perspective into the PLL constrained-search proof.

4.5 Kohn–Sham Density Functional Theory

Kohn–Sham density functional theory (KS–DFT) is based on the Hohenberg-Kohn (HK) theorems, and constitutes an alternate description of the mapping from the interacting system to one of noninteracting fermions with the same density $\rho(\mathbf{r})$—the S system. As (HK) theory is a ground state theory, the mapping can only be from a *nondegenerate ground state* of the interacting system to an S system also in its *ground state*.

The starting point of the theory is the *assumption* of existence of the S system. This assumption is referred to as *noninteracting v–representability*. The assumption and terminology mean that the interacting system v–representable densities are also noninteracting v–representable. However, as was the case for the interacting system, the weaker constraint of N–representability suffices.

The basic equations defining the S system are the same as those of Q–DFT of Sect. 3.4. It is the expressions for the total energy E and the electron–interaction potential energy $v_{ee}(\mathbf{r})$, however, that differ in the two theories. The S system Hamiltonian is

$$\hat{H}_s = \hat{T} + \hat{V}_s = \sum_i h_s(\mathbf{r}_i), \tag{4.72}$$

$$\hat{T} = -\frac{1}{2}\sum_i \nabla_i^2; \quad \hat{V}_s = \sum_i v_s(\mathbf{r}_i), \tag{4.73}$$

$$\hat{h}_s(\mathbf{r}) = -\frac{1}{2}\nabla^2 + v_s(\mathbf{r}), \tag{4.74}$$

$$v_s(\mathbf{r}) = v(\mathbf{r}) + v_{ee}(\mathbf{r}). \tag{4.75}$$

The corresponding Schrödinger single particle equations are (see (3.126))

$$\hat{h}_s(\mathbf{r})\phi_i(\mathbf{x}) = \epsilon_i\phi_i(\mathbf{x}); \quad i = 1, \ldots, N, \tag{4.76}$$

the wavefunction is the Slater determinant $\Phi\{\phi_i\}$ of the orbitals $\phi_i(\mathbf{x})$, and the density $\rho(\mathbf{r})$ is obtained from the N *lowest lying* orbitals as

$$\rho(\mathbf{r}) = \sum_{i\sigma} |\phi_i(\mathbf{r}\sigma)|^2. \tag{4.77}$$

From the first Hohenberg–Kohn theorem, it follows that the density $\rho(\mathbf{r})$ uniquely determines the potential energy $v_s(\mathbf{r})$ of the noninteracting fermions (map $(CD)^{-1}$ for the S system) to within a constant, and hence its electron–interaction potential energy $v_{ee}(\mathbf{r})$ component. The Hamiltonian $\hat{H}_s$ is then fully defined, and therefore the corresponding wavefunction $\Phi\{\phi_i\}$ and orbitals $\phi_i(\mathbf{x})$ are functionals of the density: $\phi_i(\mathbf{x}) \equiv \phi_i[\rho]$. Thus, the kinetic energy of the noninteracting fermions is a unique functional of the density:

$$T_s[\rho] = \sum_\sigma \sum_i \langle \phi_i(\mathbf{r}\sigma; [\rho])| - \frac{1}{2}\nabla^2 |\phi_i(\mathbf{r}\sigma; [\rho])\rangle. \tag{4.78}$$

The kinetic energy functional $T_s[\rho]$ may also be provided a PLL *constrained-search* type definition. Consider the map D^{-1} of the S system whereby the ground state density $\rho(\mathbf{r})$ leads to the Slater determinant $\Phi\{\phi_i\}$. Then of the infinite Slater determinants Φ_ρ that lead to $\rho(\mathbf{r})$, how does one determine the Slater determinant

Φ which is the solution of the S system differential equation (4.76)? The answer, obtained by following the procedure of the previous section but for the Hamiltonian $\hat{H}_s$, is

$$T_s[\rho] = \inf_{\Phi_\rho \to \rho} \langle \Phi_\rho | \hat{T} | \Phi_\rho \rangle, \tag{4.79}$$

where the notation $\inf_{\Phi_\rho \to \rho}$ means that one searches for the infimum value of the expectation $\langle \hat{T} \rangle$ taken with respect to all Slater determinants that yield the density $\rho(\mathbf{r})$. The minimum is achieved for the true Slater determinant $\Phi\{\phi_i\}$. The existence of this minimum has been proved [18]. As noted previously, Slater determinants can be constructed to yield a particular density [45–47]. Hence, the constrained search definition of $T_s[\rho]$ is valid for N–representable densities.

The KS–DFT definition of the potential energy $v_{\mathrm{ee}}(\mathbf{r})$ is obtained by application of the variational principle in terms of the density (*HK* Theorem 2) to the corresponding ground state energy functional expression $E[\rho]$ for the S system. This expression is obtained by adding and subtracting the kinetic energy functional $T_s[\rho]$ of the noninteracting fermions from the general ground state energy functional expression (4.23). Thus, the S system energy expression is

$$E[\rho] = T_s[\rho] + \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + E_{\mathrm{ee}}^{\mathrm{KS}}[\rho], \tag{4.80}$$

where

$$E_{\mathrm{ee}}^{\mathrm{KS}}[\rho] = F_{\mathrm{HK}}[\rho] - T_s[\rho], \tag{4.81}$$

which then defines the KS–DFT electron–interaction energy functional $E_{\mathrm{ee}}^{\mathrm{KS}}[\rho]$. As in the previous chapter the ground state energy $E[\rho]$ may be expressed in terms of the eigenvalues ϵ_i of the S system. Thus, with $T_s[\rho]$ obtained as in (3.138) we have

$$E[\rho] = \sum_i \epsilon_i - \int \rho(\mathbf{r}) v_{\mathrm{ee}}(\mathbf{r}) d\mathbf{r} + E_{\mathrm{ee}}^{\mathrm{KS}}[\rho]. \tag{4.82}$$

For the application of the variational principle, the density $\rho(\mathbf{r})$ is varied by a small amount such that $\rho(\mathbf{r}) \to \rho(\mathbf{r}) + \delta\rho(\mathbf{r})$, and the stationary condition is

$$\begin{aligned} \delta E &= E[\rho + \delta\rho] - E[\rho] \\ &= \int \frac{\delta E[\rho]}{\delta\rho(\mathbf{r})} \delta\rho(\mathbf{r}) d\mathbf{r} \\ &= 0. \end{aligned} \tag{4.83}$$

Note that the densities being varied are assumed to be N–representable. Substituting for $E[\rho]$ from (4.80), one obtains

$$\delta T_s[\rho] + \int [v(\mathbf{r}) + v_{\mathrm{ee}}(\mathbf{r})] \delta\rho(\mathbf{r}) d\mathbf{r} = 0, \tag{4.84}$$

where the electron–interaction potential energy $v_{\mathrm{ee}}(\mathbf{r})$ is the functional derivative of $E_{\mathrm{ee}}^{\mathrm{KS}}[\rho]$:

$$v_{\mathrm{ee}}(\mathbf{r}) = \frac{\delta E_{\mathrm{ee}}^{\mathrm{KS}}[\rho]}{\delta\rho(\mathbf{r})}. \tag{4.85}$$

For variations of the orbitals such that $\phi_i(\mathbf{x}) \to \phi_i(\mathbf{x}) + \delta\phi_i(\mathbf{x})$ that lead to variations in the density $\rho(\mathbf{r}) + \delta\rho(\mathbf{r})$, it is readily proved employing (4.76) and the normalization condition of these orbitals that the first order variation

$$\delta T_s[\rho] = -\int v_s(\mathbf{r})\delta\rho(\mathbf{r})d\mathbf{r}. \tag{4.86}$$

Substitution of (4.86) into (4.84) leads to

$$\int [-v_s(\mathbf{r}) + v(\mathbf{r}) + v_{\mathrm{ee}}(\mathbf{r})]\delta\rho(\mathbf{r})d\mathbf{r} = 0. \tag{4.87}$$

Now since the variations $\delta\rho(\mathbf{r})$ are arbitrary within the realm of N–representable densities, we recover (4.75) with the electron–interaction potential energy $v_{\mathrm{ee}}(\mathbf{r})$ defined by the functional derivative (4.85). This is the KS–DFT definition of the local potential energy $v_{\mathrm{ee}}(\mathbf{r})$.

Thus, in KS–DFT, the S system differential (4.76) is solved self–consistently for the orbitals $\phi_i(\mathbf{x})$ from which the ground state density $\rho(\mathbf{r})$ and kinetic energy T_s are obtained. The ground state energy is then determined either from the energy functional $E[\rho]$ of (4.80) or (4.82). If the expectation value functionals $O[\rho]$ of other operators $\hat{O}$ were known, these properties too could then be determined.

In the KS–DFT energy expression $E[\rho]$ of (4.80), $T_s[\rho]$ is the kinetic energy of *noninteracting* fermions whose density is the true ground state density $\rho(\mathbf{r})$. *Hence, the KS electron–interaction energy functional* $E_{\mathrm{ee}}^{\mathrm{KS}}[\rho]$ *and its functional derivative* $v_{\mathrm{ee}}(\mathbf{r})$ *are representative of electron correlations due to the Pauli principle, Coulomb repulsion, and Correlation–Kinetic effects*. Since the Hartree or Coulomb self energy $E_{\mathrm{H}}[\rho]$ functional of the density is known:

$$E_{\mathrm{H}}[\rho] = \frac{1}{2}\iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}', \tag{4.88}$$

the functional $E_{\mathrm{ee}}^{\mathrm{KS}}[\rho]$ is customarily partitioned as

$$E_{\mathrm{ee}}^{\mathrm{KS}}[\rho] = E_{\mathrm{H}}[\rho] + E_{\mathrm{xc}}^{\mathrm{KS}}[\rho], \tag{4.89}$$

which defines the KS 'exchange–correlation' energy functional. From (4.85), the electron–interaction potential energy $v_{\mathrm{ee}}(\mathbf{r})$ within KS–DFT is then

$$v_{\mathrm{ee}}(\mathbf{r}) = v_{\mathrm{H}}(\mathbf{r}) + v_{\mathrm{xc}}(\mathbf{r}), \tag{4.90}$$

where the Hartree potential energy $v_{\mathrm{H}}(\mathbf{r})$ is

$$v_{\mathrm{H}}(\mathbf{r}) = \frac{\delta E_{\mathrm{H}}[\rho]}{\delta\rho(\mathbf{r})} = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}', \tag{4.91}$$

and the KS 'exchange–correlation' potential energy $v_{\mathrm{xc}}(\mathbf{r})$ is defined as

$$v_{\mathrm{xc}}(\mathbf{r}) = \frac{\delta E_{\mathrm{xc}}^{\mathrm{KS}}[\rho]}{\delta\rho(\mathbf{r})}. \tag{4.92}$$

Note that the functional $E_{\mathrm{xc}}^{\mathrm{KS}}[\rho]$ and its functional derivative $v_{\mathrm{xc}}(\mathbf{r})$ are representative of Pauli and Coulomb correlations as well as Correlation–Kinetic effects.

The functional $E_{\mathrm{xc}}^{\mathrm{KS}}[\rho]$ is usually further partitioned into its KS 'exchange' $E_{\mathrm{x}}^{\mathrm{KS}}[\rho]$ and KS 'correlation' $E_{\mathrm{c}}^{\mathrm{KS}}[\rho]$ energy functional components. Thus

$$E_{\mathrm{xc}}^{\mathrm{KS}}[\rho] = E_{\mathrm{x}}^{\mathrm{KS}}[\rho] + E_{\mathrm{c}}^{\mathrm{KS}}[\rho], \tag{4.93}$$

so that the KS 'exchange–correlation' potential energy $v_{\mathrm{xc}}(\mathbf{r})$ is

$$v_{\mathrm{xc}}(\mathbf{r}) = v_{\mathrm{x}}(\mathbf{r}) + v_{\mathrm{c}}(\mathbf{r}), \tag{4.94}$$

where the KS 'exchange' potential energy $v_{\mathrm{x}}(\mathbf{r})$ is defined as the functional derivative

$$v_{\mathrm{x}}(\mathbf{r}) = \frac{\delta E_{\mathrm{x}}^{\mathrm{KS}}[\rho]}{\delta\rho(\mathbf{r})}, \tag{4.95}$$

and the KS 'correlation' potential energy $v_{\mathrm{c}}(\mathbf{r})$ as the functional derivative

$$v_{\mathrm{c}}(\mathbf{r}) = \frac{\delta E_{\mathrm{c}}^{\mathrm{KS}}[\rho]}{\delta\rho(\mathbf{r})}. \tag{4.96}$$

The KS–DFT energy functionals $E_{\mathrm{ee}}^{\mathrm{KS}}[\rho]$, $E_{\mathrm{xc}}^{\mathrm{KS}}[\rho]$, $E_{\mathrm{x}}^{\mathrm{KS}}[\rho]$, $E_{\mathrm{c}}^{\mathrm{KS}}[\rho]$, and their functional derivatives $v_{\mathrm{ee}}(\mathbf{r})$, $v_{\mathrm{xc}}(\mathbf{r})$, $v_{\mathrm{x}}(\mathbf{r})$, $v_{\mathrm{c}}(\mathbf{r})$, respectively, satisfy [58] the following integral virial theorems:

$$E_{\mathrm{ee}}^{\mathrm{KS}}[\rho] + \int \rho(\mathbf{r})\mathbf{r}\cdot\nabla v_{\mathrm{ee}}(\mathbf{r})d\mathbf{r} = -T_{\mathrm{c}}[\rho] \leq 0, \tag{4.97}$$

$$E_{\mathrm{xc}}^{\mathrm{KS}}[\rho] + \int \rho(\mathbf{r})\mathbf{r}\cdot\nabla v_{\mathrm{xc}}(\mathbf{r})d\mathbf{r} = -T_{\mathrm{c}}[\rho] \leq 0, \tag{4.98}$$

$$E_{\mathrm{x}}^{\mathrm{KS}}[\rho] + \int \rho(\mathbf{r})\mathbf{r}\cdot\nabla v_{\mathrm{x}}(\mathbf{r})d\mathbf{r} = 0, \tag{4.99}$$

$$E_{\mathrm{c}}^{\mathrm{KS}}[\rho] + \int \rho(\mathbf{r})\mathbf{r}\cdot\nabla v_{\mathrm{c}}(\mathbf{r})d\mathbf{r} = -T_{\mathrm{c}}[\rho] \leq 0. \tag{4.100}$$

Further, for the KS 'exchange' energy functional $E_{\mathrm{x}}^{\mathrm{KS}}[\rho]$, the Hartree–Fock theory expression for the exchange energy (3.192) is used, but the orbitals $\phi_i(\mathbf{x})$ of the S system are employed instead. This choice for $E_{\mathrm{x}}^{\mathrm{KS}}[\rho]$ is *ad hoc*. Thus,

$$E_{\mathrm{x}}^{\mathrm{KS}}[\rho] = \frac{1}{2}\iint \frac{\rho(\mathbf{r})\rho_{\mathrm{x}}(\mathbf{r}\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}', \tag{4.101}$$

where $\rho_{\mathrm{x}}(\mathbf{r}\mathbf{r}')$ is the ground state S system Fermi hole.

Although it is known that the functional $E_{\mathrm{ee}}^{\mathrm{KS}}[\rho]$ and $E_{\mathrm{xc}}^{\mathrm{KS}}[\rho]$ are representative of Pauli and Coulomb correlations and Correlation–Kinetic effects, KS–DFT does not describe how these correlations are incorporated in the functionals. In addition, it could be erroneously construed that since the Hartree–Fock theory expression is employed for $E_{\mathrm{x}}^{\mathrm{KS}}[\rho]$ of (4.101), and the fact the functional and its functional derivative $v_{\mathrm{x}}(\mathbf{r})$ satisfy the sum rule (4.99) (with T_{c} absent), that $E_{\mathrm{x}}^{\mathrm{KS}}[\rho]$ and $v_{\mathrm{x}}(\mathbf{r})$ are strictly representative of Pauli correlations. Furthermore, as a consequence, the functional $E_{\mathrm{c}}^{\mathrm{KS}}[\rho]$ and its derivative $v_{\mathrm{c}}(\mathbf{r})$ are therefore representative of Coulomb correlations and Correlation–Kinetic effects. This, however, is *not* the case. In the following chapter it will be shown that $E_{\mathrm{x}}^{\mathrm{KS}}[\rho]$ and $v_{\mathrm{x}}(\mathbf{r})$ are representative not only of correlations due to the Pauli exclusion principle, but also of lowest–order Correlation–Kinetic effects. And that the energy functional $E_{\mathrm{c}}^{\mathrm{KS}}[\rho]$ and its functional derivative $v_{\mathrm{c}}(\mathbf{r})$ are therefore representative of Coulomb Correlations and higher–order Correlation–Kinetic effects.

Finally, the functional $T_{\mathrm{s}}[\rho]$ satisfies the sum rule

$$2T_{\mathrm{s}}[\rho] = \int \rho(\mathbf{r})\mathbf{r}\cdot\nabla v_s(\mathbf{r})d\mathbf{r}, \tag{4.102}$$

where $v_{\mathrm{s}}(\mathbf{r})$ is the effective potential energy of the noninteracting fermions as defined by (4.75).

In the literature, it is stated that the local effective potential $v_s(\mathbf{r})$ of KS-DFT is *unique*. This statement, based on the second HK theorem as applied to noninteracting fermions, is correct because in KS-DFT the mapping is from the interacting system in a *ground* state to an S system (having the same density $\rho(\mathbf{r})$) which is also in its *ground* state. However, as we have seen via Q-DFT in Chap. 3, there exist an *infinite* number of local potentials $v_s(\mathbf{r})$ that can generate the ground state density $\rho(\mathbf{r})$ by mapping to S systems that are in *any arbitrary excited* state. The fact of the multiplicity of the local potentials that generate the ground state density cannot be gleaned from HK or KS-DFT because these are ground-state theories.

4.6 Runge-Gross Time-Dependent Density Functional Theory

This section presents a brief survey of the fundamental aspects of Runge-Gross [26] (RG) time-dependent density functional theory (TD DFT) without proofs. For the proof of the RG and other theorems within TD DFT, the reader is referred to [26–28]. The description, however, highlights aspects of the RG theorem not stressed or employed within RG theory.

The basis for TD DFT is the extension by Runge and Gross of Theorem 1 of Hohenberg and Kohn to the time-dependent case. The theory is proved for external fields $\mathcal{F}^{\text{ext}}(\mathbf{r}t) = -\nabla v(\mathbf{r}t)$ for which the potential energy $v(\mathbf{r}t)$ is expandable in a Taylor series about some initial time t_0 which is assumed to be finite. Further, the initial state is not necessarily the ground or any other eigenstate of the initial potential energy $v(\mathbf{r}t_0) = v(\mathbf{r})$. These statements imply that TD DFT is valid for sudden switching on of the external field. It is not valid for fields that are adiabatically switched on in the standard adiabatic hypothesis manner via the switch $e^{\alpha t}$, where α is a small positive constant, beginning at $t_0 = -\infty$. This is because the switch function has an essential singularity at $t_0 = -\infty$, and cannot then be expanded in a Taylor series. The problem can, however, be overcome by switching on the external field at a large negative time such that $\alpha > 1/|t_0|$, which then allows the conditions of the RG theorem to be satisfied.

The RG theorem proves that the density $\rho(\mathbf{r}t)$ and the current density $\mathbf{j}(\mathbf{r}t)$ are both basic variables of quantum mechanics. In other words, there is a one-to-one relationship between the external potential and the basic variables i.e. $\rho(\mathbf{r}t) \leftrightarrow v(\mathbf{r}t)$, and $\mathbf{j}(\mathbf{r}t) \leftrightarrow v(\mathbf{r}t)$. Thus knowledge of either $\rho(\mathbf{r}t)$ or $\mathbf{j}(\mathbf{r}t)$ corresponding to an initial state $\psi(t_0) = \psi_0$ determines the external potential $v(\mathbf{r}t)$ to within an additive purely time-dependent function $C(t)$. As the kinetic $\hat{T}$ and the electron-interaction $\hat{U}$ operators are assumed known, the Hamiltonian $\hat{H}(t)$ is consequently known to within a time-dependent function $C(t)$. The Hamiltonian, via the Schrödinger equation (2.1), then determines the wave function $\psi(t)$ to within a time-dependent phase $\alpha(t)$. In equation form the *RG path* from either basic variable to the Hamiltonian is

$$[\rho(\mathbf{r}t) \text{ or } \mathbf{j}(\mathbf{r}t)] \rightarrow v(\mathbf{r}t) \rightarrow \hat{H}(t). \tag{4.103}$$

The RG theorem as presented in the literature focuses principally on the relationship between the density and the external potential. The proof of the RG theorem is analogous to that of the time-independent case. The theorem is usually stated as: *Two densities $\rho(\mathbf{r}t)$ and $\rho'(\mathbf{r}t)$ evolving from the same initial state $\psi(t_0) = \psi_0$ generated by two external potentials $v(\mathbf{r}t)$* and *$v'(\mathbf{r}t)$ that are Taylor expandable about t_0 are always different provided the potentials differ by more than a purely time-dependent function $C(t)$*, i.e.

$$v(\mathbf{r}t) \neq v'(\mathbf{r}t) + C(t). \tag{4.104}$$

It is first proved that the potentials $v(\mathbf{r}t)$ and $v'(\mathbf{r}t)$ lead to different current densities $\mathbf{j}(\mathbf{r}t)$ and $\mathbf{j}'(\mathbf{r}t)$. This proves that $\mathbf{j}(\mathbf{r}t)$ is a basic variable. Then *employing this fact*, it is further proved that $\rho(\mathbf{r}t) \neq \rho'(\mathbf{r}t)$. Thus, $\rho(\mathbf{r}t)$ is also a basic variable. The fact that $\mathbf{j}(\mathbf{r}t)$ is a basic variable is not further considered or employed in RG theory. (In contrast, as explained in Sect. 3.3, within Q-DFT, both the basic variables $\rho(\mathbf{r}t)$ and $\mathbf{j}(\mathbf{r}t)$ can be employed.)

The consequence of the one–to–one relationship between the density $\rho(\mathbf{r}t)$ and the potential energy $v(\mathbf{r}t)$, is that the wavefunction $\Psi[\Psi_0](t)$ is a functional of the density and the initial state Ψ_0, *unique* to within an arbitrary time-dependent phase factor:

$$\Psi[\Psi_0](t) = \exp[-i\alpha(t)]\widetilde{\Psi}[\rho; \Psi_0](t). \tag{4.105}$$

This means that with $\alpha(t_0) = 0$ but otherwise arbitrary, the wavefunction $\widetilde{\Psi}(t)$ will give the same density $\rho(\mathbf{r}t)$ and have the same initial state $\widetilde{\Psi}(t_0) = \Psi_0$. The expectation value of any operator $\hat{O}(t)$ is therefore a *unique* functional of the density:

$$\langle \hat{O}(t) \rangle = \langle \widetilde{\Psi}[\rho; \Psi_0](t)|\hat{O}(t)|\widetilde{\Psi}[\rho; \Psi_0](t)\rangle, \tag{4.106}$$

with the phase factors canceling out as was the case for the density. In other words, all the properties of a quantum–mechanical system are determined entirely by the density $\rho(\mathbf{r}t)$. The explicit dependence of the wavefunction on the density, however, is not described by the theorem. Hence, the unique functionals of the expectation values are unknown. As a consequence of the RG theorem proof, the above remarks are equally valid for the basic variable $\mathbf{j}(\mathbf{r}t)$.

In time-independent density functional theory, as a consequence of the variational principle of Theorem 2 of Hohenberg and Kohn, the density $\rho(\mathbf{r})$ is determined via the Euler–Lagrange equation (4.22). The basic idea underlying time-dependent theory then is to replace the energy functional $E[\rho]$ of the density $\rho(\mathbf{r})$ by an action functional $A[\rho; \Psi_0]$ of the density $\rho(\mathbf{r}t)$ and the initial state $\Psi(t_0)$. The stationary point of this action functional with respect to variations in $\rho(\mathbf{r}t)$ is thereby determined by solution of the Euler–Lagrange equation

$$\frac{\delta A[\rho; \Psi_0]}{\delta\rho(\mathbf{r}t)} = 0, \tag{4.107}$$

with appropriate boundary conditions.

The basis for the construction of the action functional $A[\rho; \Psi_0]$ is the quantum–mechanical action integral:

$$A[\Psi] = \int_{t_0}^{t_1} \langle \Psi(t)|i\frac{\partial}{\partial t} - \hat{H}(t)|\Psi(t)\rangle dt. \tag{4.108}$$

At the stationary point of this action integral for which $\delta A[\psi] = 0$, the wavefunction $\Psi(t)$ with initial condition $\Psi(t_0)$ satisfies the Schrödinger equation (2.1). The variations $\delta\Psi$ around $\Psi(t)$ are arbitrary but must satisfy [38, 41] the requirement $\delta\Psi(t_0) = \delta\Psi(t_1) = 0$ at the time interval end points, and be such that the real and imaginary parts can be varied independently. Since the wavefunction is a functional of the density, a reasonable (and the original [26]) choice for the action functional $A[\rho; \Psi_0]$ is

$$A[\rho; \Psi_0] = \int_{t_0}^{t_1} \langle \Psi[\rho; \Psi_0](t) | i\frac{\partial}{\partial t} - \hat{H}(t)\Psi[\rho; \Psi_0](t)\rangle dt. \tag{4.109}$$

Unfortunately, this action functional does not satisfy the requirement $\delta A[\rho, \psi_0] = 0$ and therefore cannot be used as the basis for time-dependent density functional theory [28, 38]. (It has been concluded [38] that there is no action functional of v-representable densities whose functional derivative satisfies the Euler-Lagrange equation (4.107).) At present the only action functional free of paradoxes, and which is stationary with respect to variations in the density, is the Keldysh action [39, 40]. This action is general in that it is not restricted to v-representable densities but is valid for the broader class of time-contour densities.

The ideas underlying the Keldysh action are readily extended [40] to the S system of noninteracting fermions with equivalent density $\rho(\mathbf{r}t)$ as defined by (3.1)–(3.4). (As noted in the Introduction, this proof has been critiqued [4, 33–37].) A proof [40] of the existence of such a model system for the time-dependent case, known as the van Leeuwen theorem, based on the Quantal Newtonian Second Law [30–32] of (2.75) has been provided for Taylor expandable external potentials $v(\mathbf{r}t)$. The boundary conditions required for the equivalence of the density $\rho(\mathbf{r}t)$ of the interacting and noninteracting systems in this proof are the following: The initial state $\Phi_0(t_0)$ of the model system must be such that it reproduces the true density and its temporal derivative at the initial time t_0. From the Keldysh action functional $A_s[\rho]$ of the S system, one can then formally define an electron–interaction action functional $A_{\text{ee}}[\rho]$ that is representative of correlations due to the Pauli principle, Coulomb repulsion, Correlation–Kinetic, and Correlation–Current–Density effects. (Recall from Chap. 3 that the interacting and noninteracting system current densities $\mathbf{j}(\mathbf{r}t)$ and $\mathbf{j}_s(\mathbf{r}t)$, respectively, are in general not equivalent. They are equivalent only when both the divergence and curl of the Correlation–Current–Density field $\mathcal{J}_c(\mathbf{r}t)$ of (3.38) vanishes. That $\nabla \cdot \mathcal{J}_c(\mathbf{r}t) = 0$ follows directly from the continuity equation (2.90) since the densities $\rho(\mathbf{r}t)$ of the two systems are the same. However, $\nabla \times \mathcal{J}_c(\mathbf{r}t) \neq 0$ in general. Note that within Q-DFT, it is possible to explicitly account for the difference between the current densities $\mathbf{j}(\mathbf{r}t)$ and $\mathbf{j}_s(\mathbf{r}t)$, and to also construct a model system with equivalent $\rho(\mathbf{r}t)$ and $\mathbf{j}(\mathbf{r}t)$.) The corresponding electron–interaction potential energy $v_{\text{ee}}(\mathbf{r}t)$ of the model system is then defined within (RG)KS–DFT as the functional derivative $v_{\text{ee}}(\mathbf{r}t) = \delta A_{\text{ee}}[\rho]/\delta\rho(\mathbf{r}t)$. The dependence of the action $A_{\text{ee}}[\rho]$ and of its derivative $v_{\text{ee}}(\mathbf{r}t)$ on the various electron correlations is not defined. The physical interpretation of $v_{ee}(\mathbf{r}t)$ in terms of these correlations, however, is given via the Q–DFT definitions as described in Sect. 3.1.5. In KS–DFT, the action functional $A_{ee}[\rho]$ is subdivided into a Hartree $A_{H}[\rho]$ and a KS $A_{xc}[\rho]$ component. The corresponding potential energies $v_{H}(\mathbf{r}t)$ and $v_{xc}(\mathbf{r}t)$ are the functional derivatives $\delta A_{H}[\rho]/\delta\rho(\mathbf{r}t)$ and $\delta A_{xc}[\rho]/\delta\rho(\mathbf{r}t)$, respectively. Finally, $A_{xc}[\rho]$ is further partitioned into a KS 'exchange' $A_{x}[\rho]$ and a KS 'correlation' $A_{c}[\rho]$ action component, with the potential energies $v_{x}(\mathbf{r}t)$ and $v_{c}(\mathbf{r}t)$ being their respective functional derivatives. As in the time-independent case (see Chap. 5), the correlations contributing to these action functionals and their functional derivatives can be rigorously derived [32] via Q–DFT. Thus, for example, the KS 'exchange' potential energy $v_{x}(\mathbf{r}t)$ is representative not only of Pauli correlations, but also of lowest–order Correlation–Kinetic and Correlation–Current–Density contributions. And the KS 'correlation' potential energy $v_{c}(\mathbf{r}t)$ is representative of Coulomb correlations and higher–order Correlation–Kinetic and Correlation–Current–Density effects. We refer the reader to [32] for details. However, it would be best to read the following chapter on the physical meaning in terms of electron correlations of KS 'exchange' and 'correlation' in the time-independent case first.

4.7 Generalization of the Runge-Gross Theorem

In this section we generalize [4] the fundamental theorem of time-dependent (TD) theory due to Runge and Gross [26] (RG) by a *density preserving* unitary or gauge transformation along the lines of Sect. 4.2. New insights as a consequence of the transformation are discussed. This generalization demonstrates the hierarchy that exists in the fundamental theorems of density functional theory, both time-dependent and time-independent.

To make this section self-standing, we redefine the physical system under consideration. The system is comprised of N electrons in a time-dependent external field $\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}t) = -\boldsymbol{\nabla} v(\mathbf{r}t)$, with $v(\mathbf{r}t)$ a *scalar* external potential energy operator. The Schrödinger equation for this system is (the same as (2.1) to (2.5))

$$\hat{H}(\mathbf{R}t)\Psi(\mathbf{X}t) = i\frac{\partial\Psi(\mathbf{X}t)}{\partial t}, \tag{4.110}$$

where $\Psi(\mathbf{X}t)$ is the wave function, $\mathbf{X} = \mathbf{x}_1, \ldots, \mathbf{x}_N$, $\mathbf{x} = \mathbf{r}\sigma$, $\mathbf{r}$ and σ are the spatial and spin coordinates, and $\mathbf{R} = \mathbf{r}_1, \ldots, \mathbf{r}_N$. The Hamiltonian $\hat{H}(\mathbf{R}t)$ is the sum of the kinetic $\hat{T}$, electron-interaction potential energy $\hat{W}$, and external potential energy $\hat{V}$ operators:

$$\hat{H}(\mathbf{R}t) = \hat{T} + \hat{W} + \hat{V}, \tag{4.111}$$

with $\hat{T} = \sum_i (-\frac{1}{2}\nabla_i^2)$; $\hat{W} = \frac{1}{2}\sum'_{i,j} 1/|\mathbf{r}_i - \mathbf{r}_j|$; $\hat{V} = \sum_i v(\mathbf{r}_i t)$. The TD density $\rho(\mathbf{r}t)$ is the expectation

$$\rho(\mathbf{r}t) = \left\langle \Psi(\mathbf{X}t)|\hat{\rho}(\mathbf{r})|\Psi(\mathbf{X}t)\right\rangle, \tag{4.112}$$

where $\hat{\rho}(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i)$ is the density operator.

The RG theorem is proved for the Hamiltonian $\hat{H}(\mathbf{R}t)$ of (4.111). It is proved on the assumption that the scalar operator $v(\mathbf{r}t)$ is Taylor expandable about some initial time t_0. Furthermore, in the proof, the operators $\hat{T}$ and $\hat{W}$, and the initial many-particle state $\Psi(t_0)$, are assumed known and kept *fixed*.

The TD unitary operator $\hat{U}$ we employ is

$$\hat{U} = e^{i\alpha(\mathbf{R}t)}, \tag{4.113}$$

so that the transformed wave function $\Psi'(\mathbf{X}t)$ is

$$\Psi'(\mathbf{X}t) = \hat{U}^{\dagger}\Psi(\mathbf{X}t), \tag{4.114}$$

and the transformed density $\rho'(\mathbf{r}t) =< \Psi'(\mathbf{X}t)|\hat{\rho}(\mathbf{r})|\Psi'(\mathbf{X}t) >= \rho(\mathbf{r}t)$. The unitary transformation thus *preserves* the density. The transformed Schrödinger equation is

$$\hat{H}'(\mathbf{R}t)\Psi'(\mathbf{X}t) = i\frac{\partial\Psi'(\mathbf{X}t)}{\partial t}, \tag{4.115}$$

where the Hamiltonian $\hat{H}'(\mathbf{R}t)$ of the transformed system is

$$\hat{H}'(\mathbf{R}t) = \hat{U}^{\dagger}\hat{H}(\mathbf{R}t)U + \frac{d\alpha(\mathbf{R}t)}{dt} \tag{4.116}$$

$$= \hat{H}(\mathbf{R}t) - \frac{1}{2}\sum_i \left\{\hat{U}^{\dagger}\left[\nabla_i^2, \hat{U}\right]\right\} + \frac{d\alpha(\mathbf{R}t)}{dt}. \tag{4.117}$$

(Note that for the transformed system, the initial state and other boundary conditions too are transformed.) The solution of the commutator of (4.117) is the same as given in Sect. 4.2. Thus, the transformed Hamiltonian $\hat{H}'(\mathbf{R}t)$ is

$$\hat{H}'(\mathbf{R}t) = \hat{H}(\mathbf{R}t) + \frac{d\alpha(\mathbf{R}t)}{dt} + \frac{1}{2}\sum_i(\hat{\mathbf{p}}_i \cdot \hat{\mathbf{A}}_i + \hat{\mathbf{A}}_i \cdot \hat{\mathbf{p}}_i + \hat{\mathbf{A}}_i^2), \tag{4.118}$$

where $\hat{\mathbf{p}}_i = -i\nabla_i$ is the momentum operator, and where the vector potential energy operator is *defined* as $\hat{\mathbf{A}}_i = \nabla_i\alpha(\mathbf{R}t)$ so that $\nabla \times \hat{\mathbf{A}}_i = 0$.

The transformed Hamiltonian may also be written as

$$\hat{H}'(\mathbf{R}t) = \frac{1}{2}\sum_i(\hat{\mathbf{p}}_i + \hat{\mathbf{A}}_i)^2 + \hat{W} + \hat{V}', \tag{4.119}$$

where

$$\hat{V}' = \hat{V} + \frac{d\alpha(\mathbf{R}t)}{dt}. \tag{4.120}$$

Note that as is the case for the Hamiltonian $\hat{H}(\mathbf{R}t)$ of (4.111), there is no magnetic field in the transformed Hamiltonian $\hat{H}'(\mathbf{R}t)$. The vector potential energy operator $\hat{\mathbf{A}}_i$ as defined above is curl-free.

That $\hat{H}(\mathbf{R}t)$ and $\hat{H}'(\mathbf{R}t)$ represent the same physical system may also be seen by performing the following gauge transformation of $\hat{H}(\mathbf{R}t)$ to obtain $\hat{H}'(\mathbf{R}t)$: $\hat{V} \rightarrow \hat{V}' = V + \frac{d\alpha(\mathbf{R}t)}{dt}$ and $\hat{\mathbf{A}}_i \rightarrow \hat{\mathbf{A}}'_i = \hat{\mathbf{A}}_i + \nabla_i \alpha(\mathbf{R}t)$ with $\hat{\mathbf{A}}_i = 0$ so that $\hat{\mathbf{A}}'_i = \nabla_i \alpha(\mathbf{R}t)$ and the magnetic field $\mathbf{B}' = \nabla \times \hat{\mathbf{A}}'_i = 0$. In quantum mechanics it is well known [20] that the more general gauge transformation above with nonzero magnetic field $\mathbf{B}$ leaves the Schrödinger equation invariant provided the wave functions of the original and transformed Hamiltonians are related by the gauge transformation $\alpha(\mathbf{R}t)$ of (4.114).

The Hamiltonian $\hat{H}'(\mathbf{R}t)$ of (4.118), (4.119) is the most general form of the Hamiltonian for which the RG theorem is valid. It includes the scalar potential energy operator $v(\mathbf{r}_i t)$, the TD function $C(\mathbf{R}t) = d\alpha(\mathbf{R}t)/dt$, the momentum operator $\hat{\mathbf{p}}_i$, and the TD curl-free vector potential energy operator $\hat{\mathbf{A}}_i = \nabla_i \alpha(\mathbf{R}t)$. Pictorially the bijectivity of the RG Theorem in its general form is depicted in Fig. 4.3. The

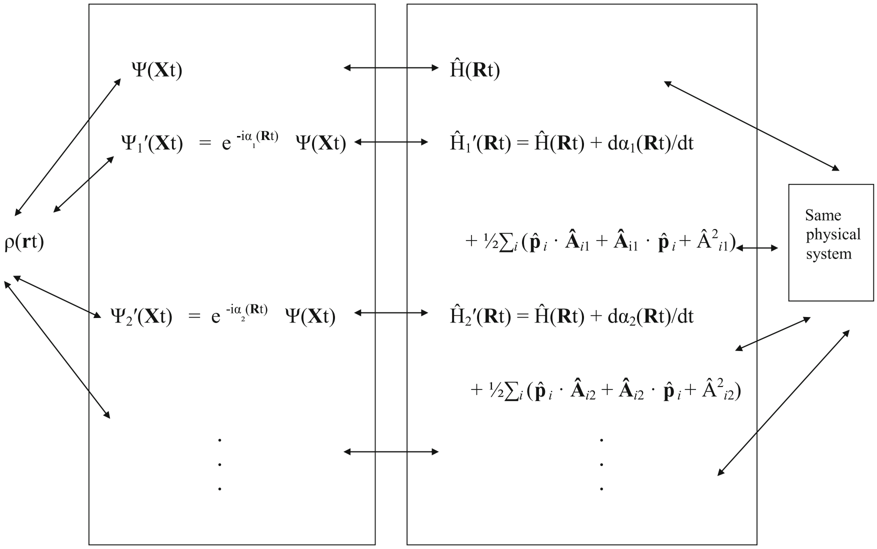

Fig. 4.3 The generalization of the fundamental theorem of density functional theory demonstrating the bijectivity between the density of a physical system and the infinite set of Hamiltonians representing that physical system. The figure is drawn for (**a**) the most general time-dependent form of the gauge function $\alpha(\mathbf{R}t)$. The figure reduces to the RG theorem for (**b**) when $\alpha(\mathbf{R}t) = \alpha(t)$. The figure further reduces to the most general form of the time-independent theorem when (**c**) $\alpha(\mathbf{R}t) = \alpha(\mathbf{R})$. Finally, the Hohenberg-Kohn theorem is recovered for (**d**) when $\alpha(\mathbf{R}t) = \alpha$, a constant

bijectivity is $\rho(\mathbf{r}t) \leftrightarrow \hat{H}(\mathbf{R}t)$ with $\hat{H}(\mathbf{R}t)$ of (4.111), or equivalently $\rho(\mathbf{r}t) \leftrightarrow \hat{H}'_j(\mathbf{R}t)$ with $\hat{H}'_j(\mathbf{R}t)$ of (4.118), (4.119), depending on the gauge function $\alpha_j(\mathbf{R}t)$. The Hamiltonian $\hat{H}(\mathbf{R}t)$ and the Hamiltonian $\hat{H}'(\mathbf{R}t)$ all correspond to the same physical system.

It is evident that the RG theorem in its original form is recovered from the above generalization for the special case when the gauge function $\alpha(\mathbf{R}t) = \alpha(t)$ (see Fig. 4.3). The functions $C(t)$ of RG are linked to the gauge function: $C(t) = d\alpha(t)/dt$. Furthermore, the Hamiltonians $\hat{H}'(\mathbf{R}t) = \hat{H}(\mathbf{R}t) + C(t)$ all correspond to the same physical system because $\hat{H}'(\mathbf{R}t)$ is obtained from $\hat{H}(\mathbf{R}t)$ by a unitary or gauge transformation.

It is also clear from the unitary or gauge transformation that in the *general* case the wave function $\Psi(\mathbf{X}t)$ must be a functional of both the density $\rho(\mathbf{r}t)$ and the gauge function $\alpha(\mathbf{R}t)$ i.e., $\Psi(\mathbf{X}t) = \Psi[\rho(\mathbf{r}t); \alpha(\mathbf{R}t)]$. This functional dependence of the wave function functional on the gauge function $\alpha(\mathbf{R}t)$ ensures that it is gauge variant.

Since the bijectivity is between the density $\rho(\mathbf{r}t)$ of a system and the Hamiltonians representing the same physical system (see Fig. 4.3), the choice of gauge function is arbitrary. Thus, the choice $\alpha(\mathbf{R}t) = 0$ is equally valid. Thus, in the RG case, the choice of $\alpha(t) = 0$ leads to a wave function functional that can be a functional only of the density $\rho(\mathbf{r}t)$.

In the RG case, Fig. 4.3 shows that the bijectivity is between the density $\rho(\mathbf{r}t)$ and the *infinite* number of Hamiltonians $\hat{H}(\mathbf{R}t) + C(t)$ representative of a physical system. Thus, the density uniquely determines the system Hamiltonian to within a function $C(t)$. It is, however, possible to construct [3] as proved in the following section, an *infinite* set of degenerate Hamiltonians $\{\hat{H}\}$ that differ by a function $C(t)$, represent different physical systems, but yet possess the same density $\rho(\mathbf{r}t)$. In such a case, the density $\rho(\mathbf{r}t)$ cannot distinguish between the different physical systems. For such systems, the RG theorem is not valid.

Finally, as a consequence of the unitary or gauge transformation, the following hierarchy exists in the fundamental theorem of density functional theory (see Fig. 4.3). When the gauge function is $\alpha(\mathbf{R}t)$, one obtains the most general form of the time-dependent theorem. For the gauge function $\alpha(t)$, one recovers the original RG theorem. When the gauge function is $\alpha(\mathbf{R})$, one obtains the most general form of the time-independent theorem. Finally, when the gauge function is the constant α, one recovers the original Hohenberg-Kohn theorem. (Note that the function $C(t)$ of the RG theorem does not reduce to the constant C of the Hohenberg-Kohn theorem.) This hierarchy makes the role of the phase factor as significant in density functional theory as it is in quantum mechanics.

4.8 Corollary to the Hohenberg–Kohn and Runge-Gross Theorems

In this section we provide further insight into Theorem 1 of Hohenberg and Kohn (HK), and of its extension to the time-dependent case due to Runge and Gross, by describing a corollary to each theorem [3].

According to Theorem 1 of Hohenberg-Kohn, for a system of N electrons in an external field $\mathcal{F}^{\text{ext}}(\mathbf{r}) = -\nabla v(\mathbf{r})$, the *ground* state electronic density $\rho(\mathbf{r})$ for a nondegerate state determines the external potential energy $v(\mathbf{r})$ uniquely to within an *unknown trivial additive constant C*. Since the kinetic energy $\hat{T}$ and electronic–interaction potential energy $\hat{U}$ operators are known, the Hamiltonian $\hat{H}$ is explicitly known.

For the extension to the time-dependent case, Runge and Gross (RG) [26] prove that for a system of N electrons in a time-dependent external field $\mathcal{F}^{\text{ext}}(\mathbf{r}t) = -\nabla v(\mathbf{r}t)$, such that the potential energy $v(\mathbf{r}t)$ is Taylor–expandable about some initial time t_0, the density $\rho(\mathbf{r}t)$ evolving from some fixed initial state $\Psi(t_0)$, determines the external potential energy uniquely to within an *additive purely time-dependent function C(t)*. Again, as the kinetic and electron–interaction potential energy operators are already defined, the Hamiltonian $\hat{H}(t)$ is known.

In the proofs of these theorems one considers Hamiltonians $\hat{H}/\hat{H}(t)$ that differ by an additive constant *C*/function *C(t)* to be equivalent. In other words, the *physical system* under consideration remains the *same* on addition of this constant/function which is *arbitrary*. Thus, measurements of properties of the system, other than for example the total energy *E/E(t)*, remain invariant. The theorem then proves that *each* density $\rho(\mathbf{r})/\rho(\mathbf{r}t)$ is associated with *one* and *only one* Hamiltonian $\hat{H}/\hat{H}(t)$ or physical system: the density $\rho(\mathbf{r})/\rho(\mathbf{r}t)$ determines that unique Hamiltonian $\hat{H}/\hat{H}(t)$ to within an additive constant *C*/function*C(t)*.

HK/RG, however, did not consider the case of a set of Hamiltonians $\{\hat{H}\}/\{\hat{H}(t)\}$ that represent *different* physical systems which differ by an *intrinsic* constant *C*/function*C(t)*, but which yet have the *same* density $\rho(\mathbf{r})/\rho(\mathbf{r}t)$. By intrinsic constant *C*/function*C(t)* we mean one that is inherent to the system and not extrinsically additive. Thus, this constant *C*/function*C(t)* helps distinguish between the different Hamiltonians in the set $\{\hat{H}\}/\{\hat{H}(t)\}$, and is consequently *not arbitrary*. That the physical systems are *different* could, of course, be confirmed by experiment. Further, the density $\rho(\mathbf{r})/\rho(\mathbf{r}t)$ would then not be able to distinguish between the different Hamiltonians $\{\hat{H}\}/\{\hat{H}(t)\}$ or physical systems, as it is the same for all of them.

In this chapter we construct a *set* of model systems with *different* Hamiltonians $\{\hat{H}\}/\{\hat{H}(t)\}$ that differ by a constant *C*/function*C(t)* but which *all* possess the same density $\rho(\mathbf{r})/\rho(\mathbf{r}t)$. This is the Hooke's species: atom, molecule, all positive molecular ions with number of nuclei $\mathcal{N}$ greater than two. The constants *C*/function*C(t)* contain information about the system, and are essential to distinguishing between the different elements of the species.

The corollary to the HK/RG theorem is as follows: Degenerate Hamiltonians $\{\hat{H}\}/\{\hat{H}(t)\}$ that differ by a constant *C*/function*C(t)* but which represent different physical systems all possessing the same density $\rho(\mathbf{r})/\rho(\mathbf{r}t)$ cannot be distinguished on the basis of the HK/RG theorem. That is, for such systems, the density $\rho(\mathbf{r})/\rho(\mathbf{r}t)$ cannot determine each external potential energy $v(\mathbf{r})/v(\mathbf{r}t)$, and hence each Hamiltonian of the set $\{\hat{H}\}/\{\hat{H}(t)\}$, uniquely.

In the following sections, we describe the Hooke's species for the time-independent and time-dependent cases to prove the above corollary.

4.8.1 Corrollary to the Hohenberg-Kohn Theorem

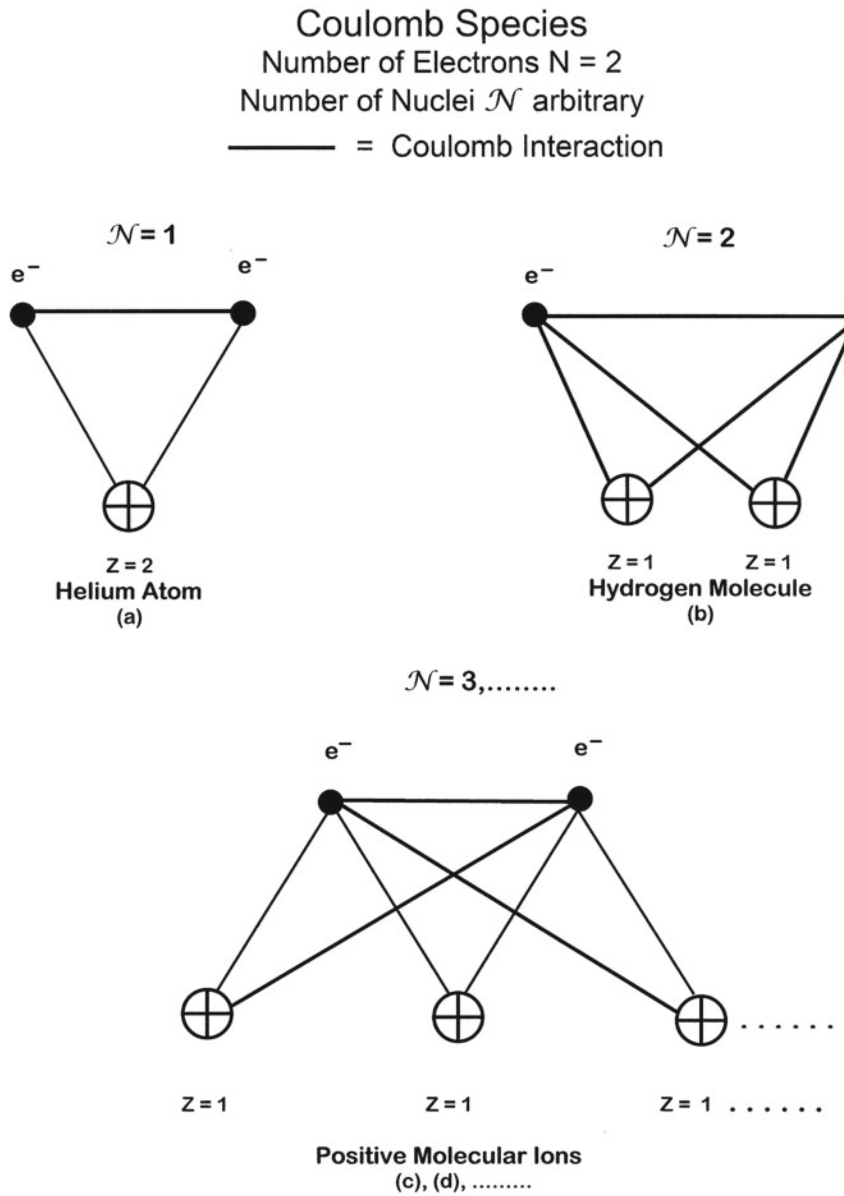

Fig. 4.4 The Coulomb species comprises of two electrons and an arbitrary number $\mathcal{N}$ of nuclei, the interaction between the electrons and between the electrons and nuclei being Coulombic: (**a**) Helium atom; (**b**) Hydrogen molecule; (**c**), (**d**), . . ., Positive molecular ions. Here $\mathcal{N}$ is the number of nuclei, Z the nuclear charge, e^- the electronic charge. Note that each element of the species corresponds to a different physical system

Prior to describing the Hooke's species, let us consider the following Coulomb species of two–electron systems and $\mathcal{N}$ nuclei as shown in Fig. 4.4: the Helium atom($\mathcal{N} = 1$; atomic number $Z = 2$), the Hydrogen molecule ($\mathcal{N} = 2$; atomic number of each nuclei $Z = 1$), and the positive molecular ions ($\mathcal{N} > 2$; atomic number of each nuclei $Z = 1$).

In atomic units, the Hamiltonian of the Coulomb species is

$$\hat{H}_{\mathcal{N}} = \hat{T} + \hat{U} + \hat{V}_{\mathcal{N}}, \tag{4.121}$$

where $\hat{T}$ is the kinetic energy operator:

$$\hat{T} = -\frac{1}{2}\sum_{i=1}^{2} \nabla_i^2, \tag{4.122}$$

$\hat{U}$ the electron–interaction potential energy operator:

$$\hat{U} = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}, \tag{4.123}$$

and $\hat{V}_{\mathcal{N}}$ the external potential energy operator:

$$\hat{V}_{\mathcal{N}} = \sum_{i=1}^{2} v_{\mathcal{N}}(\mathbf{r}_i), \tag{4.124}$$

with

$$v_{\mathcal{N}}(\mathbf{r}) = \sum_{j=1}^{\mathcal{N}} f_C(\mathbf{r} - \mathbf{R}_j). \tag{4.125}$$

where

$$f_C(\mathbf{r} - \mathbf{R}_j) = -\frac{1}{|\mathbf{r} - \mathbf{R}_j|}. \tag{4.126}$$

Here $\mathbf{r}_1$ and $\mathbf{r}_2$ are positions of the electrons, $\mathbf{R}_j (j = 1, \ldots, \mathcal{N})$ the positions of the nuclei, and $f_C(\mathbf{r} - \mathbf{R}_j)$ the Coulomb external potential energy function. Each element of the Coulomb species represents a *different* physical system. (The species could be further generalized by requiring each nuclei to have a different charge.)

Now suppose the ground state density $\rho(\mathbf{r})$ of the Hydrogen molecule were known. Then, according to the HK theorem, this density uniquely determines the external potential energy operator to within an additive constant C:

$$\hat{V}_{\mathcal{N}=2} = -\frac{1}{|\mathbf{r}_1 - \mathbf{R}_1|} - \frac{1}{|\mathbf{r}_1 - \mathbf{R}_2|} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_1|} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_2|}. \tag{4.127}$$

Thus, the Hamiltonian of the Hydrogen molecule is exactly known from the ground state density. Note that in addition to the functional form of the external potential energy, the density also explicitly defines the positions $\mathbf{R}_1$ and $\mathbf{R}_2$ of the nuclei.

The fact that the ground state density determines the external potential energy operator, and hence the Hamiltonian may be understood as follows. Integration of the density leads to the number N of the electrons: $\int \rho(\mathbf{r})d\mathbf{r} = N$. The cusps in the electron density which satisfies the electron–nucleus coalescence condition [59] (see Sect. 2.10.2), determine in turn the position of the $\mathcal{N}$ nuclei and their charge Z. Thus, the external potential energy operator $\hat{V}_{\mathcal{N}} = \sum_i v_{\mathcal{N}}(\mathbf{r}_i)$, and therefore the Hamiltonian $\hat{H}$ are known.

The Hooke's species (see Fig. 4.5) comprise of two electrons coupled harmonically to a variable number $\mathcal{N}$ of nuclei. The electrons are coupled to each nuclei with a different spring constants k_j, $j = 1, \ldots, \mathcal{N}$. The species comprise of the Hooke's atom of Sect. 2.11 ($\mathcal{N} = 1$, atomic number $Z = 2$, spring constant k), the Hooke's molecule ($\mathcal{N} = 2$; atomic number of each nuclei $Z = 1$, spring constants k_1 and k_2), and the Hooke's positive molecular ions ($\mathcal{N} > 2$, atomic number of each nuclei $Z = 1$, spring constants $k_1, k_2, k_3, \ldots, k_{\mathcal{N}}$). The Hamiltonian $\hat{H}_{\mathcal{N}}$ of this species is the same as that of the Coulomb species of (4.121) except that the external potential energy function is $f_H(\mathbf{r} - \mathbf{R}_j)$, where

$$f_H(\mathbf{r} - \mathbf{R}_j) = \frac{1}{2}k_j(\mathbf{r} - \mathbf{R}_j)^2. \tag{4.128}$$

Just as for the Coulomb species, each element of the Hooke's species represents a *different* physical system. Thus, for example, the Hamiltonian for Hooke's atom is

$$\hat{H}_a = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{1}{2}k\left[(\mathbf{r}_1 - \mathbf{R}_1)^2 + (\mathbf{r}_2 - \mathbf{R}_1)^2\right], \tag{4.129}$$

and that of Hooke's molecule is

$$\begin{aligned}\hat{H}_m = &- \frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{1}{2}\left\{k_1\left[(\mathbf{r}_1 - \mathbf{R}_1)^2 + (\mathbf{r}_2 - \mathbf{R}_1)^2\right]\right. \\ &\left. + \, k_2\left[(\mathbf{r}_1 - \mathbf{R}_2)^2 + (\mathbf{r}_2 - \mathbf{R}_2)^2\right]\right\},\end{aligned} \tag{4.130}$$

where $k \neq k_1 \neq k_2$, and so on for the various Hooke's positive molecular ions with $\mathcal{N} > 2$.

For the Hooke's species, however, the external potential energy operator $\hat{V}_{\mathcal{N}}$ which is

$$\hat{V}_{\mathcal{N}} = \frac{1}{2}\sum_{j=1}^{\mathcal{N}}[k_j(\mathbf{r}_1 - \mathbf{R}_j)^2 + k_j(\mathbf{r}_2 - \mathbf{R}_j)^2], \tag{4.131}$$

may be rewritten as

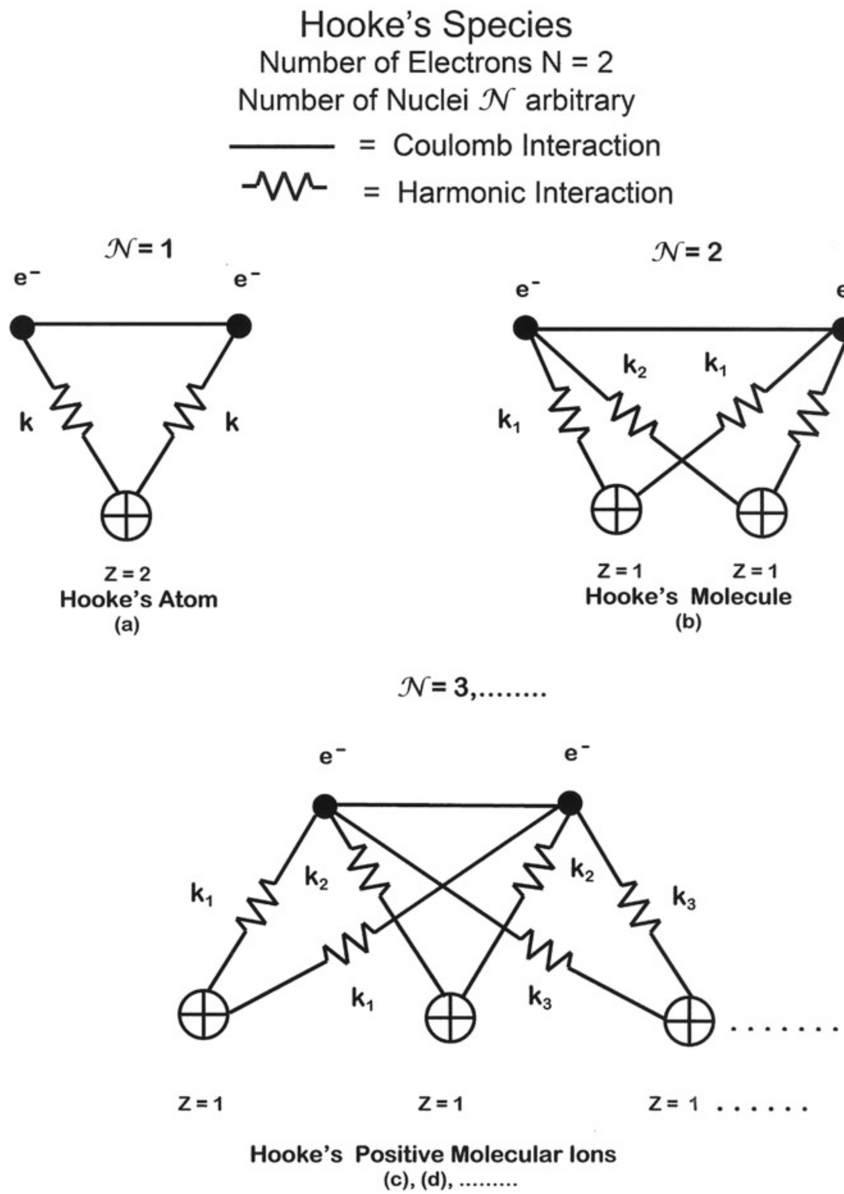

Fig. 4.5 The Hooke's species comprises of two electrons and an arbitrary number $\mathcal{N}$ of nuclei, the interaction between the electrons is Coulombic, and that between the electrons and nuclei is harmonic with spring constant $k, k_1, \ldots, k_{\mathcal{N}}$: (**a**) Hooke's atom; (**b**) Hooke's molecule; (**c**), (**d**), . . . Hooke's positive molecular ions. Here $\mathcal{N}$ is the number of nuclei, Z the nuclear charge, e^- the electronic charge. Note that each element of the species corresponds to a different physical system

$$\hat{V}_{\mathcal{N}}(\mathbf{r}) = \left(\frac{1}{2}\sum_{j=1}^{\mathcal{N}} k_j\right)[(\mathbf{r}_1 - \mathbf{a})^2 + (\mathbf{r}_2 - \mathbf{a})^2] + C(\{k\}, \{\mathbf{R}\}, \mathcal{N}), \tag{4.132}$$

where the translation vector **a** is

$$\mathbf{a} = \sum_{j=1}^{\mathcal{N}} k_j \mathbf{R}_j \Bigg/ \sum_{j=1}^{\mathcal{N}} k_j, \tag{4.133}$$

and the constant $\mathcal{C}$ is

$$C = b - d \tag{4.134}$$

with

$$b = \sum_{j=1}^{\mathcal{N}} k_j \mathbf{R}_j^2. \tag{4.135}$$

$$d = \left(\sum_{j=1}^{\mathcal{N}} k_j \mathbf{R}_j \right)^2 \Bigg/ \sum_{j=1}^{\mathcal{N}} k_j, \tag{4.136}$$

or

$$C = \frac{1}{2} \sum_{i \neq j}^{\mathcal{N}} k_i k_j \left(\mathbf{R}_i - \mathbf{R}_j \right)^2 \Bigg/ \sum_{j=1}^{\mathcal{N}} k_j. \tag{4.137}$$

From (4.132) it is evident that the Hamiltonians $\hat{H}_{\mathcal{N}}$ of the Hooke's species are those of a Hooke's atom $\left(\sum_{j=1}^{\mathcal{N}} k_j = k\right)$, (to within a constant $C(\{k\}, \{\mathbf{R}\}, \mathcal{N})$), whose center of mass is at **a**. The constant C which depends upon the spring constants $\{k\}$, the positions of the nuclei $\{\mathbf{R}\}$, and the number $\mathcal{N}$ of the nuclei, differs from a trivial additive constant in that it is an *intrinsic* part of *each* Hamiltonian $\hat{H}_{\mathcal{N}}$, and distinguishes between the different elements of the species. It does so because the constant $C(\{k\}, \{\mathbf{R}\}, \mathcal{N})$ contains physical information about the system such as the positions $\{\mathbf{R}\}$ of the nuclei.

Now according to the HK theorem, the ground state density determines the external potential energy, and hence the Hamiltonian, to within a constant. Since the density of *each* element of the Hooke's species is that of the Hooke's atom, it can only determine the Hamiltonian of a Hooke's atom and not the constant $C(\{k\}, \{\mathbf{R}\}, \mathcal{N})$. Therefore, it cannot determine the Hamiltonian $\hat{H}_{\mathcal{N}}$ for $\mathcal{N} > 1$. This is reflected by the fact that the density of the elements of the Hooke's species does not satisfy the electron–nucleus coalescence cusp condition. (It is emphasized that although the 'degenerate Hamiltonians' of the Hooke's species have a ground state wavefunction and density that corresponds to that of a Hooke's atom, each element of the species represents a *different* physical system. Thus, for example, a neutron diffraction experiment on the Hooke's molecule and Hooke's positive molecular ions would *all* give different results).

It is also possible to construct a Hooke's species such that the density of each element is the *same*. This is most readily seen for the case when the center of mass is moved to the origin of the coordinate system, i.e. for $\mathbf{a} = 0$. This requires, from (4.133), the product of the spring constants and the coordinates of the nuclei satisfy the condition

$$\sum_{j=1}^{\mathcal{N}} k_j \mathbf{R}_j = 0, \tag{4.138}$$

so that the external potential energy operator is then

$$v_{\mathcal{N}}(\mathbf{r}) = \frac{1}{2}\sum_{j=1}^{\mathcal{N}} k_j \mathbf{r}^2 + \frac{1}{2}\sum_{j=1}^{\mathcal{N}} k_j \mathbf{R}_j^2, \tag{4.139}$$

where $\mathbf{r}$ is the distance to the origin. If the sum $\sum_{j=1}^{\mathcal{N}} k_j$ is then adjusted to equal a particular value of the spring constant k of Hooke's atom:

$$\sum_{j=1}^{\mathcal{N}} k_j = k, \tag{4.140}$$

then the Hamiltonian $\hat{H}_{\mathcal{N}}$ of any element of the species may be rewritten as

$$\hat{H}_{\mathcal{N}}(\{k\}, \{\mathbf{R}\}, \mathcal{N}) = \hat{H}_a(k) + C(\{k\}, \{\mathbf{R}\}, \mathcal{N}), \tag{4.141}$$

where $\hat{H}_a(k)$ is the Hooke's atom Hamiltonian and the constant $C(\{k\}, \{\mathbf{R}\}, \mathcal{N})$ is

$$C(\{k\}, \{\mathbf{R}\}, \mathcal{N}) = \sum_{j=1}^{\mathcal{N}} k_j \mathbf{R}_j^2. \tag{4.142}$$

The solution of the Schrödinger equation and the corresponding density for *each* element of the species are therefore the *same*.

As an example, again consider the case of Hooke's molecule and atom. For Hooke's atom $\mathcal{N} = 1$, $\mathbf{R}_1 = 0$ and let us assume $k = \frac{1}{4}$. Thus, the external potential energy operator is

$$v_a(\mathbf{r}) = \frac{1}{2}kr^2 = \frac{1}{8}r^2. \tag{4.143}$$

For this choice of k, the singlet ground state solution of the time-independent Schrödinger equation ($\hat{H}_{\mathcal{N}}\psi = E_{\mathcal{N}}\psi$) is analytical and given by (2.177):

$$\psi(\mathbf{r}_1\mathbf{r}_2) = De^{-y^2/2}e^{-r^2/8}(1 + r/2), \tag{4.144}$$

where $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, $\mathbf{y} = (\mathbf{r}_1 + \mathbf{r}_2)/2$, and $D = 1/[2\pi^{5/4}(5\sqrt{\pi} + 8)^{1/2}]$. The corresponding ground state density $\rho(\mathbf{r})$ is (see Appendix C)

$$\rho(\mathbf{r}) = \frac{\pi\sqrt{2\pi}}{r} D^2 e^{-r^2/2}\{7r + r^3 + (8/\sqrt{2\pi}) r e^{-r^2/2} + 4(1+r^2) erf(r/\sqrt{2})\}, \tag{4.145}$$

where

$$erf(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-z^2} dz. \tag{4.146}$$

For the Hooke's molecule, $\mathcal{N} = 2$, $\mathbf{R}_1 = -\mathbf{R_2}$, and we choose $k_1 = k_2 = \frac{1}{8}$, so that the external potential energy operator is

$$v_m(\mathbf{r}) = \frac{1}{8}r^2 + \frac{1}{16}(R_1^2 + R_2^2) = \frac{1}{8}r^2 + \frac{1}{8}R^2, \tag{4.147}$$

where $|\mathbf{R}_1| = R$. Thus, the Hamiltonian for Hooke's molecule differs from that of Hooke's atom by only the constant $\frac{1}{8}R^2$, thereby leading to the *same* ground state wave function and density. However, the ground state energy of the two elements of the species differ by $\frac{1}{8}R^2$.

The above example demonstrating the equivalence of the density of the Hooke's atom and molecule is for a specific value of the spring constant k for which the wavefunction happens to be analytical. However, this conclusion is valid for arbitrary value of k for which solutions of the Schrödinger equation exist but are not necessarily analytical. For example, if we assume that for each element of the species ($\mathcal{N} \geq 2$), all the spring constants k_j, $j = 1, 2, \ldots, \mathcal{N}$ are the same and designated by k', then for the three values of k for the Hooke's atom corresponding to $k = \frac{1}{4}, \frac{1}{2}, 1$, the values of k' for which the Hooke's molecule and molecular ion ($\mathcal{N} = 3$) wavefunctions are the same are $k' = \frac{1}{8}, \frac{1}{12}$; $k' = \frac{1}{4}, \frac{1}{6}$; $k' = \frac{1}{2}, \frac{1}{3}$, respectively.

Thus, for the case where the elements of the Hooke's species are all made to have the *same* ground state density $\rho(\mathbf{r})$, the density cannot, on the basis of the HK theorem, distinguish between the different physical elements of the species.

The corollary to the HK theorem, therefore, is as follows:

Corollary 1 *Degenerate time-independent Hamiltonians* $\{\hat{H}\}$ *that represent different physical systems, but which differ by a constant C, and yet possess the same density* $\rho(\mathbf{r})$*, cannot be distinguished on the basis of the Hohenberg–Kohn theorem.*

4.8.2 Corollary to the Runge-Gross Theorem

We next extend the above conclusions to the Runge-Gross theorem. Consider again the Hooke's species, but in this case let us assume that the positions of the nuclei are time-dependent, i.e. $\mathbf{R}_j = \mathbf{R}_j(t)$. This could represent, for example, the zero point motion of the nuclei. For simplicity we consider the spring constant strength to be the same (k') for interaction with all the nuclei. The external potential energy $v_{\mathcal{N}}(\mathbf{r}t)$ for an arbitrary member of the species which now is

$$v_{\mathcal{N}}(\mathbf{r}t) = \frac{1}{2}k' \sum_{j=1}^{\mathcal{N}} (\mathbf{r} - \mathbf{R}_j(t))^2, \tag{4.148}$$

may then be rewritten as

$$v_{\mathcal{N}}(\mathbf{r}t) = \frac{1}{2}\mathcal{N}k'r^2 - k' \sum_{j=1}^{\mathcal{N}} \mathbf{R}_j(t) \cdot \mathbf{r} + \frac{1}{2}k' \sum_{j=1}^{\mathcal{N}} \mathbf{R}_j^2(t), \tag{4.149}$$

where at some initial time t_0, we have $\mathbf{R}_j(t_0) = \mathbf{R}_{j,0}$. (Note that a spatially uniform time-dependent field $\mathbf{F}(t)$ interacting only with the electrons could be further incorporated by adding a term $\mathbf{F}(t) \cdot \mathbf{r}$ to the external potential energy expression.) The Hamiltonian of an element of the species governed by the number of nuclei $\mathcal{N}$ is then

$$\hat{H}_{\mathcal{N}}(\mathbf{r}_1\mathbf{r}_2t) = \hat{H}_{\mathcal{N},0} - k' \sum_{j=1}^{\mathcal{N}} [\mathbf{R}_j(t) - \mathbf{R}_{j,0}] \cdot (\mathbf{r}_1 + \mathbf{r}_2) + C(k', \mathcal{N}, t), \tag{4.150}$$

where $\hat{H}_{\mathcal{N},0}$ is the time-independent Hooke's species Hamiltonian (4.141):

$$\hat{H}_{\mathcal{N},0} = \hat{H}_{\mathcal{N}}(k'), \tag{4.151}$$

and the time-dependent function

$$C(k', \mathcal{N}, t) = k' \sum_{j=1}^{\mathcal{N}} [\mathbf{R}_j^2(t) - \mathbf{R}_{j,0}^2]. \tag{4.152}$$

Note that the function $C(k', \mathcal{N}, t)$ contains physical information about the system: in this case, about the motion of the nuclei about their equilibrium positions. It also differentiates between the different elements of the species.

The solution of the time-dependent Schrödinger equation $\hat{H}_{\mathcal{N}}(t)\Psi(t) = i\partial\Psi(t)/\partial t)$ employing the Harmonic Potential Theorem of Sect. 2.9 is

$$\Psi(\mathbf{r}_1\mathbf{r}_2t) = \exp\{-i\phi(t)\}\exp\left[-i\left\{E_{\mathcal{N},0}t - 2S(t) - 2\frac{d\mathbf{z}}{dt} \cdot \mathbf{y}\right\}\right] \Psi_0(\overline{\mathbf{r}_1}\ \overline{\mathbf{r}_2}), \tag{4.153}$$

where $\overline{\mathbf{r}_i} = \mathbf{r}_i - \mathbf{z}(t)$, $\mathbf{y} = (\mathbf{r}_1 + \mathbf{r}_2)/2$,

$$S(t) = \int_{t_0}^{t} \left[\frac{1}{2}\dot{\mathbf{z}}(t')^2 - \frac{1}{2}k\mathbf{z}(t')^2 \right] dt', \tag{4.154}$$

the shift $\mathbf{z}(t)$ satisfies the classical harmonic oscillator equation

$$\ddot{\mathbf{z}}(t) + k\mathbf{z}(t) - k' \sum_{j=1}^{\mathcal{N}} [\mathbf{R}_j(t) - \mathbf{R}_{j,0}] = 0, \tag{4.155}$$

where the additional phase factor $\phi(t)$ is due to the function $C(k', \mathcal{N}, t)$,

$$\phi(t) = \int_{t_0}^{t} C(k', \mathcal{N}, t')dt', \tag{4.156}$$

and where at the initial time $\Psi(\mathbf{r}_1\mathbf{r}_2t_0) = \Psi_0$ which satisfies $\hat{H}_{\mathcal{N},0}\Psi_0 = E_{\mathcal{N},0}\Psi_0$. Thus, the wave function $\Psi(\mathbf{r}_1\mathbf{r}_2t)$ is the time-independent solution shifted by a time-dependent function $\mathbf{z}(t)$, and multiplied by a phase factor. The explicit contribution of the function $C(k', \mathcal{N}, t)$ to this phase has been separated out. The phase factor cancels out in the determination of the density $\rho(t) = \langle\Psi(t)|\hat{\rho}|\Psi(t)\rangle = \rho(\mathbf{r} - \mathbf{z}(t))$ which is the initial time-independent density $\rho(\mathbf{r}t_0) = \rho_0(\mathbf{r})$ displaced by $\mathbf{z}(t)$.

As in the time-independent case, the 'degenerate Hamiltonians' $\hat{H}_{\mathcal{N}}(\mathbf{r}_1\mathbf{r}_2t)$ of the time-dependent Hooke's species can each be made to generate the *same* density $\rho(\mathbf{r}t)$ by adjusting the spring constant k' such that $\mathcal{N}k' = k$, and provided the density at the initial time t_0 is the *same*. The latter is readily achieved as it constitutes the time-independent Hooke's species case discussed previously.

Thus, we have a set of Hamiltonians describing different physical systems but which can be made to generate the same density $\rho(\mathbf{r}t)$. These Hamiltonians differ by the function $C(k', \mathcal{N}, t)$ that contains information which differentiates between them. In such a case, the density $\rho(\mathbf{r}t)$ cannot distinguish between the different Hamiltonians.

The corollary to the RG theorem, therefore, is as follows.

Corollary 2 *Degenerate time-dependent Hamiltonians $\{\hat{H}(t)\}$ that represent different physical systems, but which differ by a purely time-dependent function $C(t)$, and which all yield the same density $\rho(\mathbf{r}t)$, cannot be distinguished on the basis of the Runge–Gross theorem.*

4.8.3 Endnote

The proof of the HK/RG theorems is general in that it is valid for *arbitrary* local form (Coulombic, Harmonic, Yukawa, oscillatory, etc.) of external potential energy

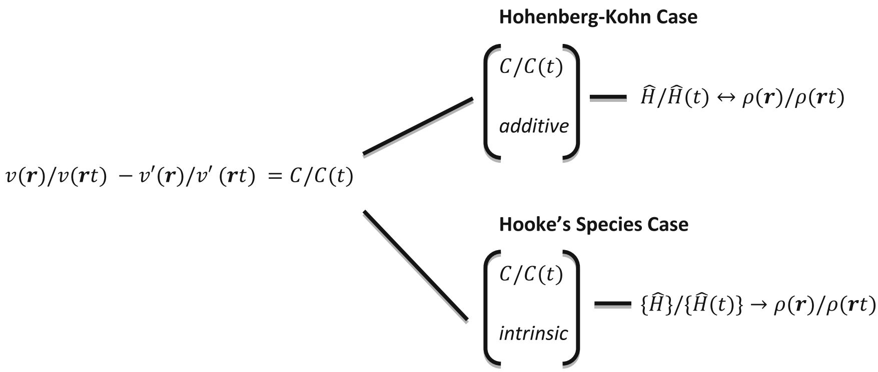

Fig. 4.6 A schematic representation of the Hohenberg-Kohn (and Runge-Gross) theorems, and of the corollary to these theorems

$v(\mathbf{r})/v(\mathbf{r}t)$. (In the time-dependent case, there is the restriction that $v(\mathbf{r}t)$ must be Taylor–expandable about some initial time t_0.) For their proof, HK/RG considered the case of potential energies, and hence Hamiltonians, that differ by an additive constant C/function $C(t)$ to be equivalent:

$$v(\mathbf{r})/v(\mathbf{r}t) - v'(\mathbf{r})/v'(\mathbf{r}t) = C/C(t). \tag{4.157}$$

By equivalent is meant that the density $\rho(\mathbf{r})/\rho(\mathbf{r}t)$ is the same. The fact that the constant C/function $C(t)$ is *additive* means that although the Hamiltonians differ, the physical system, however remains the *same*. The theorem then shows that there is a one–to–one correspondence between a physical system (as described by all these equivalent Hamiltonians), and the corresponding density $\rho(\mathbf{r})/\rho(\mathbf{r}t)$. The relationship between the basic Hamiltonian $\hat{H}/\hat{H}(t)$ describing a particular system and the density $\rho(\mathbf{r})/\rho(\mathbf{r}t)$ is bijective or fully invertible. This case considered by HK/RG is shown schematically in Fig. 4.6 in which the invertibility is indicated by the double–headed arrow.

The case of a set of degenerate Hamiltonians $\{\hat{H}\}/\{\hat{H}(t)\}$ that differ by a constant C/function $C(t)$ that is *intrinsic* such that the Hamiltonians represent *different* physical systems while yet *all* possessing the same density $\rho(\mathbf{r})/\rho(\mathbf{r}t)$, was not considered by HK/RG. In such a case, the density *cannot* uniquely determine the Hamiltonian, and therefore *cannot* differentiate between the different physical systems. This case, also shown schematically in Fig. 4.6, corresponds to the Hooke's species. The relationship between the set of Hamiltonians $\{\hat{H}\}/\{\hat{H}(t)\}$ and the density $\rho(\mathbf{r})/\rho(\mathbf{r}t)$ which is not invertible is indicated by the single–headed arrow.

We conclude by noting that the Hooke's species, in both the time-independent and time-dependent cases, *does not constitute a counter example to the HK/RG theorem.* The reason for this is that the proof of the HK theorem is *independent* of whether the constant C/function $C(t)$ is additive or intrinsic. The Hamiltonians in either case still differ by a constant C/function $C(t)$. A counter example would be one in which Hamiltonians that differ by more than a constant C/function $C(t)$ have the same density $\rho(\mathbf{r})/\rho(\mathbf{r}t)$.

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Chapter 5
Physical Interpretation of Kohn–Sham Density Functional Theory via Quantal Density Functional Theory

Abstract As time-independent ground state Quantal density functional theory (Q-DFT) is a description in terms of 'classical' fields and quantal sources of the mapping from the interacting system of electrons as described by Schrödinger theory to one of noninteracting fermions possessing the same nondegenrate ground state density, it provides a rigorous physical interpretation of the energy functionals and functional derivatives (potentials) of Kohn-Sham (KS) theory. The KS 'exchange-correlation' potential is the work done in a conservative effective field that is the sum of the Pauli-Coulomb and Correlation-Kinetic fields. The KS 'exchange-correlation' energy is the sum of the Pauli-Coulomb and the Correlation-Kinetic energies, these energies being defined in integral virial form in terms of the corresponding fields. Via adiabatic coupling constant perturbation theory applied to Q-DFT, it is shown that KS 'exchange' is representative of electron correlations due to the Pauli Exclusion Principle and lowest-order Correlation-Kinetic effects. KS 'correlation' in turn is representative of Coulomb correlations and second- and higher-order Correlation-Kinetic effects. The Optimized Potential Method (OPM) integro-differential equations are derived. As the OPM is equivalent to KS theory, Q-DFT thus also provides a physical interpretation of the OPM equations. It further provides the interpretation of the energy functionals and functional derivatives (potentials) of the KS Hartree and Hartree-Fock theories.

Introduction

This chapter provides a mathematically rigorous physical interpretation of Kohn-Sham density functional theory (KS-DFT) via Quantal density functional theory (Q-DFT). Q-DFT and KS-DFT are both descriptions of the mapping from the interacting system of electrons as described by Schrödinger theory to one of model noninteracting fermions whereby the same nondegenerate ground state density $\rho(\mathbf{r})$, the energy E, and the ionization potential I (or electron affinity A) as that of the electrons is obtained. Although both Q–DFT and KS–DFT are founded on the Hohenberg-Kohn [1] theorems, their descriptions of the model S system are distinctly different. The framework of KS–DFT [2] is strictly *mathematical* in basis. With the *assumption* of existence of the model system, the theory is in terms of an *energy* functional $E[\rho]$ of the ground state density $\rho(\mathbf{r})$. This energy functional is subdivided into a

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component representing the kinetic energy of the noninteracting fermions, the external potential energy, and an electron-interaction potential energy component $E_{\mathrm{ee}}^{KS}[\rho]$ in which all the many-body effects are incorporated. The local (multiplicative) potential energy of each model fermion is then *defined* through the variational principle of the second Hohenberg-Kohn theorem as the *functional derivative* of the sum of the potential energy components. The electron-interaction energy functional $E_{\mathrm{ee}}^{KS}[\rho]$ and its functional derivative are *implicitly* representative of all the different many-body correlations that the model S system must account for in order to reproduce the density $\rho(\mathbf{r})$, and thereby the energy via the functional $E[\rho]$. In KS–DFT, these electron correlations, as noted previously, are those due to the Pauli exclusion principle, Coulomb repulsion, and Correlation–Kinetic effects. The *explicit* dependence of the potential energy functional and of its functional derivative on the various electron correlations, however, is not described by the theory.

As Q–DFT is a description of the S system in terms of 'classical' fields and quantal sources, it is possible then to provide a rigorous *physical* interpretation of the potential energy functional and its various components, and of their respective functional derivatives. Furthermore, as the fields are separately representative of the different electron correlations, the physical interpretation allows for an explicit understanding of the correlations these functionals and their derivatives are representative of.

In this chapter we describe the rigorous physical interpretation [3, 4] of Kohn–Sham density functional theory. We begin with a description of the physics of the KS electron–interaction energy functional $E_{\mathrm{ee}}^{\mathrm{KS}}[\rho]$, its Hartree $E_{\mathrm{H}}[\rho]$ and 'exchange–correlation' $E_{\mathrm{xc}}^{\mathrm{KS}}[\rho]$ energy components, and of their respective functional derivatives $v_{\mathrm{ee}}(\mathbf{r})$, $v_{\mathrm{H}}(\mathbf{r})$, and $v_{\mathrm{xc}}(\mathbf{r})$. The physics underlying the KS 'exchange' $E_{\mathrm{x}}^{\mathrm{KS}}[\rho]$ and 'correlation' $E_{\mathrm{c}}^{\mathrm{KS}}[\rho]$ energy functionals and their derivatives $v_{\mathrm{x}}(\mathbf{r})$ and $v_{\mathrm{c}}(\mathbf{r})$ is arrived at by application of adiabatic coupling constant perturbation theory. Hence, prior to describing this physics, we explain the adiabatic coupling constant scheme [5–7] as well as the modifications of both Q–DFT and KS–DFT required within this framework for application of the perturbation theory. In this chapter we also explain the physics of the KS–DFT of Hartree–Fock and Hartree theories.

In addition to Q–DFT and KS–DFT, there is [8, 9] a third way [10–12], referred to as the Optimized Potential Method (OPM), whereby the model S system of non-interacting fermions may be constructed. The OPM is also entirely *mathematical* in construct. The starting point of the time-independent OPM is the recognition that the total energy is a functional of the S system orbitals: $E = E[\phi_i]$. The energy is then minimized with respect to arbitrary variations of the S system effective potential energy $v_s(\mathbf{r})$ (see (4.72)–(4.75)). This minimization leads to an integral equation for $v_s(\mathbf{r})$ in terms of the orbitals. The integral equation must then be solved self–consistently together with the S system differential equation. As an additional component to this chapter, the equations of the stationary state OPM will be derived. Having explained the physical interpretation of KS–DFT with all the correlations present, we next provide a physical interpretation of the 'exchange-only' version of the OPM.

As in the time-independent case, a rigorous physical interpretation of the various action functionals and functional derivatives of Runge-Gross [13] time-dependent density functional theory in terms of the various electron correlations is also provided via time–dependent Q–DFT. In fact the time-independent theory interpretations constitute a special case of the time-dependent explanations. The more general case of the latter, however, is not described. The reader is referred to the original literature [14] for the details.

5.1 Interpretation of the Kohn–Sham Electron–Interaction Energy Functional $E_{\mathbf{ee}}^{\mathbf{KS}}[\rho]$ and Its Derivative $v_{\mathbf{ee}}(\mathbf{r})$

A comparison of the general (ground and excited state) Q–DFT expression for the total energy E of (3.130) and the KS–DFT ground state energy functional $E[\rho]$ of (4.80) leads to

$$E_{\rm ee}^{\rm KS}[\rho] = E_{\rm ee} + T_{\rm c}. \tag{5.1}$$

Here $E_{\rm ee}$ is the quantum–mechanical electron–interaction energy expressed in terms of the electron–interaction field $\boldsymbol{\mathcal{E}}_{\rm ee}(\mathbf{r})$ of (4.56) as

$$E_{\rm ee} = \int \rho(\mathbf{r})\mathbf{r} \cdot \boldsymbol{\mathcal{E}}_{\rm ee}(\mathbf{r}) d\mathbf{r}, \tag{5.2}$$

and $T_{\rm c}$ the Correlation–Kinetic energy which in terms of the Correlation–Kinetic field $\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r})$ is

$$T_{\rm c} = \frac{1}{2} \int \rho(\mathbf{r})\mathbf{r} \cdot \boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r}) d\mathbf{r}, \tag{5.3}$$

where

$$\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r}) = \boldsymbol{\mathcal{Z}}_{\rm s}(\mathbf{r}) - \boldsymbol{\mathcal{Z}}(\mathbf{r}), \tag{5.4}$$

with the kinetic field $\boldsymbol{\mathcal{Z}}_{\rm s}(\mathbf{r})$ defined in a manner similar to that of (4.58) for $\boldsymbol{\mathcal{Z}}(\mathbf{r})$ but in terms of the Dirac density matrix $\gamma_{\rm s}(\mathbf{r}\mathbf{r}')$. Thus, the partition of $E_{\rm ee}^{\rm KS}[\rho]$ into its electron–interaction $E_{\rm ee}$ and Correlation–Kinetic $T_{\rm c}$ components is *explicitly* defined via Q–DFT. Recall from Chap. 3, that the fields $\boldsymbol{\mathcal{E}}_{\rm ee}(\mathbf{r})$ and $\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r})$ are not necessarily separately conservative. Their sum always is. However, the expressions for the energy components are valid whether or not the fields are conservative.

Equating the Q–DFT and KS–DFT expressions (3.140) and (4.85) for the electron–interaction potential energy we have

$$v_{\rm ee}(\mathbf{r}) = \frac{\delta E_{\rm ee}^{\rm KS}[\rho]}{\delta \rho(\mathbf{r})} = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{F}}^{\rm eff}(\mathbf{r}') \cdot d\boldsymbol{\ell}', \tag{5.5}$$

with

$$\boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r}) = \boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}) + \boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r}). \tag{5.6}$$

Hence, the physical meaning of the functional derivative $\delta E_{\text{ee}}^{\text{KS}}[\rho]/\delta\rho(\mathbf{r})$ *is that it is the work done to bring the model fermion from some reference point at infinity to its position at* $\mathbf{r}$ *in the force of the conservative field* $\boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r})$. Since $\boldsymbol{\nabla} \times \boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r}) = 0$, this work done is *path independent*. Once again, the electron–interaction and Correlation–Kinetic contributions to the functional derivative $v_{\text{ee}}(\mathbf{r})$ are *explicitly* defined via Q–DFT.

From the above interpretation of the potential energy $v_{\text{ee}}(\mathbf{r})$ we have

$$\boldsymbol{\nabla} v_{\text{ee}}(\mathbf{r}) = \boldsymbol{\nabla}\left(\frac{\delta E_{\text{ee}}^{\text{KS}}[\rho]}{\delta\rho(\mathbf{r})}\right) = -\boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r}), \tag{5.7}$$

or, equivalently employing (5.1) and (5.6) that

$$\boldsymbol{\nabla}\left(\frac{\delta E_{\text{ee}}}{\delta\rho(\mathbf{r})} + \frac{\delta T_{\text{c}}}{\delta\rho(\mathbf{r})}\right) = -(\boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}) + \boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r})). \tag{5.8}$$

This equation relates the functional derivatives of E_{ee} and T_{c} to the component fields $\boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r})$ and $\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r})$. Note, however, that

$$\boldsymbol{\nabla}\left(\frac{\delta E_{\text{ee}}}{\delta\rho(\mathbf{r})}\right) \neq -\boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}), \tag{5.9}$$

and

$$\boldsymbol{\nabla}\left(\frac{\delta T_{\text{c}}}{\delta\rho(\mathbf{r})}\right) \neq -\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r}). \tag{5.10}$$

These inequalities hold whether or not the fields $\boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r})$ and $\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r})$ are conservative. The *equality* of the functional derivatives to the fields is that given by (5.5) or (5.8).

Since the pair–correlation density may also be written as $g(\mathbf{r}\mathbf{r}') = \rho(\mathbf{r}') + \rho_{\text{xc}}(\mathbf{r}\mathbf{r}')$, where $\rho_{\text{xc}}(\mathbf{r}\mathbf{r}')$ is the Fermi–Coulomb hole charge, the electron–interaction field $\boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r})$ of (4.56) may be expressed as the sum of its Hartree $\boldsymbol{\mathcal{E}}_{\text{H}}(\mathbf{r})$ and Pauli–Coulomb $\boldsymbol{\mathcal{E}}_{\text{xc}}(\mathbf{r})$ components:

$$\boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}) = \boldsymbol{\mathcal{E}}_{\text{H}}(\mathbf{r}) + \boldsymbol{\mathcal{E}}_{\text{xc}}(\mathbf{r}), \tag{5.11}$$

where

$$\boldsymbol{\mathcal{E}}_{\text{H}}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}' \;\text{ and }\; \boldsymbol{\mathcal{E}}_{\text{xc}}(\mathbf{r}) = \int \frac{\rho_{\text{xc}}(\mathbf{r}\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}'. \tag{5.12}$$

As the field $\boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r})$ is due to a static or local charge distribution $\rho(\mathbf{r})$, it may be expressed as

$$\boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r}) = -\boldsymbol{\nabla} W_{\mathrm{H}}(\mathbf{r}), \tag{5.13}$$

with the scalar potential energy $W_{\mathrm{H}}(\mathbf{r})$ being

$$W_{\mathrm{H}}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'. \tag{5.14}$$

Thus, $\nabla \times \boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r}) = 0$. Equivalently, the potential energy $W_{\mathrm{H}}(\mathbf{r})$ is the work done in the conservative field $\boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r})$:

$$W_{\mathrm{H}}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r}') \cdot d\boldsymbol{\ell}'. \tag{5.15}$$

A comparison of (4.91) and (5.14) shows that

$$v_{\mathrm{H}}(\mathbf{r}) = W_{\mathrm{H}}(\mathbf{r}). \tag{5.16}$$

Thus, the physical interpretation of the functional derivative $\delta E_{\mathrm{H}}[\rho]/\delta\rho(\mathbf{r})$ is that it is the work done to move a model fermion from its reference point at infinity to its position at $\mathbf{r}$ *in the force of the conservative field* $\boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r})$. Equivalently

$$\boldsymbol{\nabla}\left(\frac{\delta E_{\mathrm{H}}[\rho]}{\delta\rho(\mathbf{r})}\right) = -\boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r}). \tag{5.17}$$

The Hartree energy functional $E_{\mathrm{H}}[\rho]$ of (4.88), which is the energy of self–interaction of the density, may also be expressed in terms of the Hartree field $\boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r})$ as

$$E_{\mathrm{H}} = \int \rho(\mathbf{r})\mathbf{r} \cdot \boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r}) d\mathbf{r}. \tag{5.18}$$

Again, employing the partitioning of the pair–correlation density $g(\mathbf{r}\mathbf{r}')$ into its local and nonlocal components, we can write the quantum–mechanical electron–interaction energy E_{ee} as

$$E_{\mathrm{ee}} = E_{\mathrm{H}} + E_{\mathrm{xc}}, \tag{5.19}$$

where E_{xc} is the Pauli–Coulomb energy. Thus, the KS electron–interaction energy functional (5.1) is

$$E_{\mathrm{ee}}^{\mathrm{KS}} = E_{\mathrm{H}} + E_{\mathrm{xc}} + T_{\mathrm{c}}. \tag{5.20}$$

Comparison with (5.19) then defines the KS 'exchange–correlation' energy functional in terms of the Pauli and Coulomb correlations and Correlation–Kinetic effects as

$$E_{\mathrm{xc}}^{\mathrm{KS}}[\rho] = E_{\mathrm{xc}} + T_{\mathrm{c}}, \tag{5.21}$$

where E_{xc} is expressed in terms of the Pauli–Coulomb field $\boldsymbol{\mathcal{E}}_{\mathrm{xc}}(\mathbf{r})$ as

$$E_{\mathrm{xc}} = \int \rho(\mathbf{r})\mathbf{r} \cdot \boldsymbol{\mathcal{E}}_{\mathrm{xc}}(\mathbf{r}) d\mathbf{r}, \tag{5.22}$$

and with T_{c} as previously defined by (5.3).

The KS 'exchange–correlation' potential energy $v_{\mathrm{xc}}(\mathbf{r})$ *is the work done to bring the model fermion from a reference point at infinity to its position at* $\mathbf{r}$ *in the conservative field* $\boldsymbol{\mathcal{F}}_{\mathrm{xct_c}}(\mathbf{r})$:

$$v_{\mathrm{xc}}(\mathbf{r}) = \frac{\delta E_{\mathrm{xc}}^{\mathrm{KS}}[\rho]}{\delta \rho(\mathbf{r})} = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{F}}_{\mathrm{xct_c}}(\mathbf{r}') \cdot d\boldsymbol{\ell}', \tag{5.23}$$

where

$$\boldsymbol{\mathcal{F}}_{\mathrm{xct_c}}(\mathbf{r}) = \boldsymbol{\mathcal{E}}_{\mathrm{xc}}(\mathbf{r}) + \boldsymbol{\mathcal{Z}}_{\mathrm{t_c}}(\mathbf{r}). \tag{5.24}$$

This follows from (5.5) using the fact that the Hartree field $\boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r})$ is conservative so that $\boldsymbol{\nabla} \times \boldsymbol{\mathcal{F}}_{\mathrm{xct_c}}(\mathbf{r}) = 0$. Equivalently,

$$\boldsymbol{\nabla} v_{\mathrm{xc}}(\mathbf{r}) = \boldsymbol{\nabla}\left(\frac{\delta E_{\mathrm{xc}}^{\mathrm{KS}}[\rho]}{\delta \rho(\mathbf{r})}\right) = -(\boldsymbol{\mathcal{E}}_{\mathrm{xc}}(\mathbf{r}) + \boldsymbol{\mathcal{Z}}_{\mathrm{t_c}}(\mathbf{r})). \tag{5.25}$$

Thus, the KS 'exchange–correlation' energy functional $E_{\mathrm{xc}}^{\mathrm{KS}}[\rho]$ and its functional derivative $v_{\mathrm{xc}}(\mathbf{r})$ can be expressed in terms of the Pauli–Coulomb $\boldsymbol{\mathcal{E}}_{\mathrm{xc}}(\mathbf{r})$ and Correlation–Kinetic $\boldsymbol{\mathcal{Z}}_{\mathrm{t_c}}(\mathbf{r})$ fields. Hence, the dependence of the functional $E_{\mathrm{xc}}^{\mathrm{KS}}[\rho]$ and its derivative $v_{\mathrm{xc}}(\mathbf{r})$ on the *separate* electron correlations due to the Pauli principle, Coulomb repulsion, and Correlation–Kinetic effects is *explicitly* defined within the framework of Q–DFT.

Substituting (5.21) into (5.25) leads to

$$\boldsymbol{\nabla}\left(\frac{\delta E_{\mathrm{xc}}}{\delta \rho(\mathbf{r})} + \frac{\delta T_{\mathrm{c}}}{\delta \rho(\mathbf{r})}\right) = -(\boldsymbol{\mathcal{E}}_{\mathrm{xc}}(\mathbf{r}) + \boldsymbol{\mathcal{Z}}_{\mathrm{t_c}}(\mathbf{r})), \tag{5.26}$$

which relates the functional derivative of the quantum–mechanical exchange–correlation E_{xc} and Correlation–Kinetic T_{c} energies to the fields $\boldsymbol{\mathcal{E}}_{\mathrm{xc}}(\mathbf{r})$ and $\boldsymbol{\mathcal{Z}}_{\mathrm{t_c}}(\mathbf{r})$ that give rise to them, respectively. Again, irrespective of whether the field $\boldsymbol{\mathcal{E}}_{\mathrm{xc}}(\mathbf{r})$ is conservative or not

$$\boldsymbol{\nabla}\left(\frac{\delta E_{\mathrm{xc}}}{\delta \rho(\mathbf{r})}\right) \neq -\boldsymbol{\mathcal{E}}_{\mathrm{xc}}(\mathbf{r}). \tag{5.27}$$

Thus, we see that the mathematical entities of KS–DFT, viz. the electron-interaction energy functional $E_{\mathrm{ee}}^{KS}[\rho]$, its Hartree $E_H[\rho]$ and 'exchange-correlation' $E_{\mathrm{xc}}^{KS}[\rho]$ components, and their respective functional derivatives $v_{\mathrm{ee}}(\mathbf{r})$, $v_H(\mathbf{r})$, and $v_{xc}(\mathbf{r})$ can all be afforded a rigorous physical interpretation.

We next turn to the physical interpretation of the KS ‘exchange’ $E_{\mathrm{x}}^{\mathrm{KS}}[\rho]$ and ‘correlation’ $E_{\mathrm{c}}^{\mathrm{KS}}[\rho]$ energy functionals, and of their respective derivatives $v_{\mathrm{x}}(\mathbf{r})$ and $v_{\mathrm{c}}(\mathbf{r})$ in terms of the various electron correlations. This is achieved [15, 16] via adiabatic coupling constant perturbation theory [17] as applied to both Q–DFT and KS–DFT. The interpretations then follow on comparison of terms of equal order. We begin by first describing the adiabatic coupling constant scheme, and Q–DFT and KS–DFT within this framework.

5.2 Adiabatic Coupling Constant Scheme

In the adiabatic coupling constant (λ) scheme [5–7], the Hamiltonian $\hat{H}^{\lambda}$ is defined as

$$\hat{H}^{\lambda} = \hat{T} + \hat{V}_{\lambda} + \lambda\hat{U}; \quad 0 \leq \lambda \leq 1, \tag{5.28}$$

where $\hat{T}$ and $\hat{U}$ are the usual kinetic and electron interaction operators and where the external potential energy operator $\hat{V}_{\lambda} = \sum_i v_{\lambda}(\mathbf{r}_i)$. The corresponding Schrödinger equation is

$$H^{\lambda}\psi^{\lambda}(\mathbf{X}) = E^{\lambda}\psi^{\lambda}(\mathbf{X}), \tag{5.29}$$

where $\psi^{\lambda}(\mathbf{X})$ is the ground state wavefunction for interaction strength λ. The real interacting system corresponds to $\lambda = 1$. In (5.28), the operator $\hat{V}_{\lambda}$ is constrained so that its addition to $\lambda\hat{U}$ leads to the density for the real system, i.e. the wavefunction $\psi^{\lambda}(\mathbf{X})$ is such that the expectation $\langle\psi^{\lambda}|\hat{\rho}(\mathbf{r})|\psi^{\lambda}\rangle = \rho^{\lambda=1}(\mathbf{r}) = \rho(\mathbf{r})$. Equivalently, the ground state density is independent of λ. For each value of λ, the energy E^{λ} is

$$E^{\lambda} = T^{\lambda} + \int \rho(\mathbf{r})v_{\lambda}(\mathbf{r})d\mathbf{r} + E_{\mathrm{ee}}^{\lambda}, \tag{5.30}$$

where $T^{\lambda} = \langle\psi^{\lambda}|\hat{T}|\psi^{\lambda}\rangle$ is the kinetic energy, and $E_{\mathrm{ee}}^{\lambda} = \langle\psi^{\lambda}|\lambda\hat{U}|\psi^{\lambda}\rangle$, the electron–interaction energy. The equivalent constrained search definition of $\psi^{\lambda}(\mathbf{X})$ is that it is an antisymmetric wavefunction which yields the density $\rho(\mathbf{r})$ and minimizes the expectation $\langle\psi^{\lambda}|\hat{T} + \lambda\hat{U}|\psi^{\lambda}\rangle$.

The $\lambda = 0$ case corresponds to the S system of noninteracting fermions defined by the differential equation (4.76). The potential energy (4.75) of these fermions is $v_s(\mathbf{r}) = v_{\lambda=1}(\mathbf{r}) + v_{\mathrm{ee}}(\mathbf{r})$. Since the density $\rho(\mathbf{r})$ is independent of λ, we may also write

$$v_s(\mathbf{r}) = v_{\lambda}(\mathbf{r}) + v_{\mathrm{ee}}^{\lambda}(\mathbf{r}). \tag{5.31}$$

The ground state energy E^{λ} may then be expressed as

$$E^{\lambda} = T_s + \int \rho(\mathbf{r})v_{\lambda}(\mathbf{r})d\mathbf{r} + E_{\mathrm{ee}}^{\lambda} + T_{\mathrm{c}}^{\lambda} \tag{5.32}$$

or as

$$E^{\lambda} = \sum_i \epsilon_i - \int \rho(\mathbf{r}) v_{\mathrm{ee}}^{\lambda}(\mathbf{r}) d\mathbf{r} + E_{\mathrm{ee}}^{\lambda} + T_{\mathrm{c}}^{\lambda}, \tag{5.33}$$

where $T_{\mathrm{c}}^{\lambda} = T^{\lambda} - T_s$ is the Correlation–Kinetic energy for coupling strength λ.

5.2.1 Q–DFT Within Adiabatic Coupling Constant Framework

The 'Quantal Newtonian' first law and integral virial theorem derived for the fully interacting case are equally valid for the adiabatically coupled system. Thus, the corresponding Q–DFT equations are the same as described in Chap. 3 but with the appropriate λ dependence. (The S system components of these equations remain unchanged.) The Q–DFT equations within the adiabatic coupling constant framework are summarized below.

The pair–correlation density $g^{\lambda}(\mathbf{r}\mathbf{r}')$ quantal source is

$$g^{\lambda}(\mathbf{r}\mathbf{r}') = \langle \psi^{\lambda} | \hat{P}(\mathbf{r}\mathbf{r}') | \psi^{\lambda} \rangle / \rho(\mathbf{r}), \tag{5.34}$$

$$= \rho(\mathbf{r}') + \rho_{\mathrm{xc}}^{\lambda}(\mathbf{r}\mathbf{r}'), \tag{5.35}$$

$$= \rho(\mathbf{r}') + \rho_{\mathrm{x}}(\mathbf{r}\mathbf{r}') + \rho_{\mathrm{c}}^{\lambda}(\mathbf{r}\mathbf{r}'), \tag{5.36}$$

where the Fermi–Coulomb $\rho_{\mathrm{xc}}^{\lambda}(\mathbf{r}\mathbf{r}')$, Fermi $\rho_{\mathrm{x}}(\mathbf{r}\mathbf{r}')$, and Coulomb $\rho_{\mathrm{c}}^{\lambda}(\mathbf{r}\mathbf{r}')$ holes satisfy the charge conservation sum rules

$$\int \rho_{\mathrm{xc}}^{\lambda}(\mathbf{r}\mathbf{r}') d\mathbf{r}' = -1; \int \rho_{\mathrm{x}}(\mathbf{r}\mathbf{r}') d\mathbf{r}' = -1; \int \rho_{\mathrm{c}}^{\lambda}(\mathbf{r}\mathbf{r}') d\mathbf{r}' = 0. \tag{5.37}$$

The Fermi hole $\rho_{\mathrm{x}}(\mathbf{r}\mathbf{r}') = -|\gamma_s(\mathbf{r}\mathbf{r}')|^2 / 2\rho(\mathbf{r})$, where $\gamma_s(\mathbf{r}\mathbf{r}')$ is the S system Dirac density matrix. The spinless single–particle density matrix source of the adiabatically coupled system is $\gamma^{\lambda}(\mathbf{r}\mathbf{r}') = \langle \psi^{\lambda} | \hat{\gamma}(\mathbf{r}\mathbf{r}') | \psi^{\lambda} \rangle$.

The electron–interaction field $\boldsymbol{\mathcal{E}}_{\mathrm{ee}}^{\lambda}(\mathbf{r})$ is then

$$\boldsymbol{\mathcal{E}}_{\mathrm{ee}}^{\lambda}(\mathbf{r}) = \lambda \int \frac{g^{\lambda}(\mathbf{r}\mathbf{r}')(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3}, \tag{5.38}$$

$$= \lambda \boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r}) + \lambda \boldsymbol{\mathcal{E}}_{\mathrm{xc}}^{\lambda}(\mathbf{r}), \tag{5.39}$$

$$= \lambda \boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r}) + \lambda \boldsymbol{\mathcal{E}}_{\mathrm{x}}(\mathbf{r}) + \lambda \boldsymbol{\mathcal{E}}_{\mathrm{c}}^{\lambda}(\mathbf{r}), \tag{5.40}$$

where

$$\boldsymbol{\mathcal{E}}_{\rm H}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}'; \ \boldsymbol{\mathcal{E}}^{\lambda}_{\rm xc}(\mathbf{r}) = \int \frac{\rho^{\lambda}_{\rm xc}(\mathbf{rr}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}'; \tag{5.41}$$

$$\boldsymbol{\mathcal{E}}_{\rm x}(\mathbf{r}) = \int \frac{\rho_{\rm x}(\mathbf{rr}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}'; \ \boldsymbol{\mathcal{E}}^{\lambda}_{\rm c}(\mathbf{r}) = \int \frac{\rho^{\lambda}_{c}(\mathbf{rr}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}'. \tag{5.42}$$

The Correlation–Kinetic field $\boldsymbol{\mathcal{Z}}^{\lambda}_{t_c}(\mathbf{r})$ is

$$\boldsymbol{\mathcal{Z}}^{\lambda}_{t_c}(\mathbf{r}) = \frac{1}{\rho(\mathbf{r})}[\mathbf{z}_s(\mathbf{r}; [\gamma_s]) - \mathbf{z}^{\lambda}(\mathbf{r}; [\gamma^{\lambda}])], \tag{5.43}$$

where the component $z^{\lambda}_{\alpha}(\mathbf{r})$ of the field $\mathbf{z}^{\lambda}(\mathbf{r})$ is $z^{\lambda}_{\alpha} = 2\sum_{\beta} \partial t^{\lambda}_{\alpha\beta}(\mathbf{r})/\partial r_{\beta}$, and $t^{\lambda}_{\alpha\beta}(\mathbf{r})$ is the kinetic energy density tensor $t^{\lambda}_{\alpha\beta}(\mathbf{r}) = \frac{1}{4}(\partial^2/\partial r'_{\alpha}\partial r''_{\beta} + \partial^2/\partial r'_{\beta}\partial r''_{\alpha})$ $\gamma^{\lambda}(\mathbf{r}'\mathbf{r}'')|_{\mathbf{r}'=\mathbf{r}''=\mathbf{r}}$. The field $\mathbf{z}_s(\mathbf{r})$ is similarly derived from the idempotent Dirac density matrix $\gamma_s(\mathbf{rr}')$ via the S-system tensor $t_{s,\alpha\beta}(\mathbf{r})$.

For the system of electrons defined by the Schrödinger equation (5.29), the electron–interaction potential energy $v^{\lambda}_{\rm ee}(\mathbf{r})$ of the S system is the work done to move the model fermion in the conservative field $\boldsymbol{\mathcal{F}}^{\rm eff,\lambda}(\mathbf{r})$:

$$v^{\lambda}_{\rm ee}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{F}}^{\rm eff,\lambda}(\mathbf{r}') \cdot d\boldsymbol{\ell}', \tag{5.44}$$

where

$$\boldsymbol{\mathcal{F}}^{\rm eff,\lambda}(\mathbf{r}) = \boldsymbol{\mathcal{E}}^{\lambda}_{\rm ee}(\mathbf{r}) + \boldsymbol{\mathcal{Z}}^{\lambda}_{t_c}(\mathbf{r}), \tag{5.45}$$

and $\boldsymbol{\nabla} \times \boldsymbol{\mathcal{F}}^{\rm eff,\lambda}(\mathbf{r}) = 0$. For systems of symmetry such that the fields $\boldsymbol{\mathcal{E}}^{\lambda}_{\rm ee}(\mathbf{r})$ and $\boldsymbol{\mathcal{Z}}^{\lambda}_{t_c}(\mathbf{r})$ are separately conservative, the potential energy $v^{\lambda}_{\rm ee}(\mathbf{r})$ may be written as

$$v^{\lambda}_{\rm ee}(\mathbf{r}) = W^{\lambda}_{\rm ee}(\mathbf{r}) + W^{\lambda}_{t_c}(\mathbf{r}) \tag{5.46}$$

$$= \lambda W_{\rm H}(\mathbf{r}) + \lambda W^{\lambda}_{\rm xc}(\mathbf{r}) + W^{\lambda}_{t_c}(\mathbf{r}) \tag{5.47}$$

$$= \lambda W_{\rm H}(\mathbf{r}) + \lambda W_{\rm x}(\mathbf{r}) + \lambda W^{\lambda}_{\rm c}(\mathbf{r}) + W^{\lambda}_{t_c}(\mathbf{r}), \tag{5.48}$$

where $W^{\lambda}_{\rm ee}(\mathbf{r})$, $W_{\rm H}(\mathbf{r})$, $W^{\lambda}_{\rm xc}(\mathbf{r})$, $W_{\rm x}(\mathbf{r})$, $W^{\lambda}_{\rm c}(\mathbf{r})$, $W^{\lambda}_{t_c}(\mathbf{r})$ are, respectively, the work done in the fields $\boldsymbol{\mathcal{E}}^{\lambda}_{\rm ee}(\mathbf{r})$, $\boldsymbol{\mathcal{E}}_{\rm H}(\mathbf{r})$, $\boldsymbol{\mathcal{E}}^{\lambda}_{\rm xc}(\mathbf{r})$, $\boldsymbol{\mathcal{E}}_{\rm x}(\mathbf{r})$, $\boldsymbol{\mathcal{E}}^{\lambda}_{\rm c}(\mathbf{r})$, and $\boldsymbol{\mathcal{Z}}^{\lambda}_{t_c}(\mathbf{r})$. The work done $W_{\rm H}(\mathbf{r})$ in the Hartree field $\boldsymbol{\mathcal{E}}_{\rm H}(\mathbf{r})$ may also be expressed as $W_{\rm H}(\mathbf{r}) = \int d\mathbf{r}'\rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$.

The electron–interaction $E^{\lambda}_{\rm ee}$, Hartree $E^{\lambda}_{\rm H}$, Pauli–Coulomb $E^{\lambda}_{\rm xc}$, Pauli $E^{\lambda}_{\rm x}$, Coulomb $E^{\lambda}_{\rm c}$, and Correlation–Kinetic $T^{\lambda}_{\rm c}$ energies are expressed in integral virial form in terms of the respective fields as:

$$E^{\lambda}_{\rm ee} = \int d\mathbf{r}\rho(\mathbf{r})\mathbf{r} \cdot \boldsymbol{\mathcal{E}}^{\lambda}_{\rm ee}(\mathbf{r}); \tag{5.49}$$

$$E_{\mathrm{H}}^{\lambda} = \lambda E_{\mathrm{H}}, \tag{5.50}$$

with

$$E_{\mathrm{H}} = \int d\mathbf{r}\rho(\mathbf{r})\mathbf{r} \cdot \boldsymbol{\mathcal{E}}_{\mathrm{H}}(\mathbf{r}); \tag{5.51}$$

$$E_{\mathrm{xc}}^{\lambda} = \lambda \int d\mathbf{r}\rho(\mathbf{r})\mathbf{r} \cdot \boldsymbol{\mathcal{E}}_{\mathrm{xc}}^{\lambda}(\mathbf{r}); \tag{5.52}$$

$$E_{\mathrm{x}}^{\lambda} = \lambda E_{\mathrm{x}}, \tag{5.53}$$

with

$$E_{\mathrm{x}} = \int d\mathbf{r}\rho(\mathbf{r})\mathbf{r} \cdot \boldsymbol{\mathcal{E}}_{\mathrm{x}}(\mathbf{r}); \tag{5.54}$$

$$E_{\mathrm{c}}^{\lambda} = \lambda \int d\mathbf{r}\rho(\mathbf{r})\mathbf{r} \cdot \boldsymbol{\mathcal{E}}_{\mathrm{c}}^{\lambda}(\mathbf{r}); \tag{5.55}$$

and

$$T_{\mathrm{c}}^{\lambda} = \frac{1}{2} \int d\mathbf{r}\rho(\mathbf{r})\mathbf{r} \cdot \boldsymbol{\mathcal{Z}}_{t_{\mathrm{c}}}^{\lambda}(\mathbf{r}). \tag{5.56}$$

Note that these energy expressions are valid irrespective of whether or not the individual fields are conservative. Observe that the Hartree E_{H}^{λ} and Pauli E_{x}^{λ} energies scale linearly with λ.

5.2.2 KS–DFT Within Adiabatic Coupling Constant Framework

KS–DFT employs the fact that the wavefunction $\psi^{\lambda}(\mathbf{X})$ of the adiabatically coupled system is a functional of the density $\rho(\mathbf{r})$. Hence, the ground state energy E^{λ} as obtained from the model S system is expressed as

$$E^{\lambda}[\rho] = T_s + \int d\mathbf{r}\rho(\mathbf{r})v_{\lambda}(\mathbf{r}) + E_{\mathrm{ee}}^{\mathrm{KS},\lambda}[\rho], \tag{5.57}$$

where $E_{\mathrm{ee}}^{\mathrm{KS},\lambda}[\rho]$ is the KS electron–interaction energy functional. The energy functional $E_{\mathrm{ee}}^{\mathrm{KS},\lambda}[\rho]$ is further divided into the Hartree $E_{\mathrm{H}}^{\lambda}[\rho]$ and KS 'exchange–correlation' $E_{\mathrm{xc}}^{\mathrm{KS},\lambda}[\rho]$ components, the latter functional being further subdivided into an 'exchange' $E_{\mathrm{x}}^{\mathrm{KS},\lambda}[\rho]$ and 'correlation' $E_{\mathrm{c}}^{\mathrm{KS},\lambda}[\rho]$ component. Thus,

$$E_{\mathrm{ee}}^{\mathrm{KS},\lambda}[\rho] = E_{\mathrm{H}}^{\lambda}[\rho] + E_{\mathrm{xc}}^{\mathrm{KS},\lambda}[\rho], \tag{5.58}$$

$$= E_{\mathrm{H}}^{\lambda}[\rho] + E_{\mathrm{x}}^{\mathrm{KS},\lambda}[\rho] + E_{\mathrm{c}}^{\mathrm{KS},\lambda}[\rho]. \tag{5.59}$$

Here $E_{\mathrm{H}}^{\lambda}[\rho]$, the Coulomb self–energy, is

$$E_{\mathrm{H}}^{\lambda}[\rho] = \lambda E_{\mathrm{H}}[\rho], \tag{5.60}$$

with

$$E_{\mathrm{H}}[\rho] = \frac{1}{2}\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}', \tag{5.61}$$

and [18]

$$E_{\mathrm{x}}^{\mathrm{KS},\lambda}[\rho] = \lambda E_{\mathrm{x}}^{\mathrm{KS}}[\rho], \tag{5.62}$$

with

$$E_{\mathrm{x}}^{\mathrm{KS}}[\rho] = \frac{1}{2}\int \frac{\rho(\mathbf{r})\rho_{\mathrm{x}}(\mathbf{r}\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \tag{5.63}$$

The Hartree functional $E_{\mathrm{H}}[\rho]$ is obviously equivalent to the Q–DFT Hartree energy E_{H} of (5.51). The KS 'exchange' energy functional $E_{\mathrm{x}}^{\mathrm{KS}}[\rho]$ expression is also equivalent to the Q–DFT Pauli energy E_{x} of (5.54) since the source for these energies—the Fermi hole or Dirac density matrix—is the same provided the orbitals are the same. As a consequence, the scaling of these functionals with λ is also linear.

In KS–DFT, the electron–interaction potential energy $v_{\mathrm{ee}}^{\lambda}(\mathbf{r})$ of the S system is defined as the functional derivative of $E_{\mathrm{ee}}^{\mathrm{KS},\lambda}(\mathbf{r})$, so that

$$v_{\mathrm{ee}}^{\lambda}(\mathbf{r}) = \frac{\delta E_{\mathrm{ee}}^{\mathrm{KS},\lambda}[\rho]}{\delta\rho(\mathbf{r})} \tag{5.64}$$

$$= v_{\mathrm{H}}^{\lambda}(\mathbf{r}) + v_{xc}^{\lambda}(\mathbf{r}) \tag{5.65}$$

$$= v_{\mathrm{H}}^{\lambda}(\mathbf{r}) + v_{\mathrm{x}}^{\lambda}(\mathbf{r}) + v_{\mathrm{c}}^{\lambda}(\mathbf{r}), \tag{5.66}$$

where

$$v_{\mathrm{H}}^{\lambda}(\mathbf{r}) = \frac{\delta E_{\mathrm{H}}^{\lambda}[\rho]}{\delta\rho(\mathbf{r})}, \tag{5.67}$$

$$v_{\mathrm{x}}^{\lambda}(\mathbf{r}) = \frac{\delta E_{\mathrm{x}}^{\mathrm{KS},\lambda}[\rho]}{\delta\rho(\mathbf{r})}. \tag{5.68}$$

$$v_{\mathrm{c}}^{\lambda}(\mathbf{r}) = \frac{\delta E_{\mathrm{c}}^{\mathrm{KS},\lambda}[\rho]}{\delta\rho(\mathbf{r})}. \tag{5.69}$$

Here $v_{\mathrm{x}}^{\lambda}(\mathbf{r})$ and $v_{\mathrm{c}}^{\lambda}(\mathbf{r})$ are the KS 'exchange' and 'correlation' potential energies, respectively. From the scaling relationships for $E_{\mathrm{H}}^{\lambda}[\rho]$ and $E_{\mathrm{x}}^{\mathrm{KS},\lambda}[\rho]$, we see that the corresponding functional derivatives also scale linearly [18]:

$$v_{\mathrm{H}}^{\lambda}(\mathbf{r}) = \lambda v_{\mathrm{H}}(\mathbf{r}), \tag{5.70}$$

with

$$v_{\rm H}(\mathbf{r}) = \frac{\delta E_{\rm H}[\rho]}{\delta\rho(\mathbf{r})} = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}', \tag{5.71}$$

and

$$v_{\rm x}^{\lambda}(\mathbf{r}) = \lambda v_{\rm x}(\mathbf{r}), \tag{5.72}$$

with

$$v_{\rm x}(\mathbf{r}) = \frac{\delta E_{\rm x}^{\rm KS}[\rho]}{\delta\rho(\mathbf{r})}. \tag{5.73}$$

As noted previously, the functional derivative $v_{\rm H}(\mathbf{r}) = W_{\rm H}(\mathbf{r})$.

5.2.3 Q–DFT and KS–DFT in Terms of the Adiabatic Coupling Constant Perturbation Expansion

The relationship between the KS 'exchange' $E_{\rm x}^{\rm KS}[\rho]$ and 'correlation' $E_{\rm c}^{\rm KS}[\rho]$ energy functionals, their functional derivatives $v_{\rm x}(\mathbf{r})$ and $v_{\rm c}(\mathbf{r})$, and the fields of Q–DFT is achieved [15, 16] by expressing these fields in terms of the coupling constant perturbation expansion. Thus, the wavefunction $\psi^{\lambda}(\mathbf{X})$ is expanded as

$$\psi^{\lambda}(\mathbf{X}) = \Phi\{\phi_i\}(\mathbf{X}) + \lambda\psi_1(\mathbf{X}) + \lambda^2\psi_2(\mathbf{X}) + \ldots \tag{5.74}$$

where $\Phi\{\phi_i\}$ is the Slater determinant of the S system. The resulting pair–correlation density $g^{\lambda}(\mathbf{r}\mathbf{r}')$ and single–particle density matrix $\gamma^{\lambda}(\mathbf{r}\mathbf{r}')$ are

$$g^{\lambda}(\mathbf{r}\mathbf{r}') = g_s(\mathbf{r}\mathbf{r}') + \lambda g_1^c(\mathbf{r}\mathbf{r}') + \lambda^2 g_2^c(\mathbf{r}\mathbf{r}') + \ldots, \tag{5.75}$$

and

$$\gamma^{\lambda}(\mathbf{r}\mathbf{r}) = \gamma_s(\mathbf{r}\mathbf{r}') + \lambda\gamma_1^c(\mathbf{r}\mathbf{r}') + \lambda^2\gamma_2^c(\mathbf{r}\mathbf{r}') + \ldots, \tag{5.76}$$

where

$$g_s(\mathbf{r}\mathbf{r}') = \rho(\mathbf{r}') + \rho_{\rm x}(\mathbf{r}\mathbf{r}'), \tag{5.77}$$

and $O_1^c(\mathbf{r}\mathbf{r}') = \langle\psi_1|\hat{O}|\psi\rangle + \langle\psi|\hat{O}|\psi_1\rangle$, etc. The fields $\boldsymbol{\mathcal{E}}_{\rm ee}^{\lambda}(\mathbf{r})$ of (5.38) and $\boldsymbol{\mathcal{Z}}_{\rm t_c}^{\lambda}(\mathbf{r})$ of (5.43), which arise from these sources, are then

$$\boldsymbol{\mathcal{E}}_{\rm ee}^{\lambda}(\mathbf{r}) = \lambda\boldsymbol{\mathcal{E}}_{\rm H}(\mathbf{r}) + \lambda\boldsymbol{\mathcal{E}}_{\rm x}(\mathbf{r}) + \lambda^2\boldsymbol{\mathcal{E}}_{\rm c,1}(\mathbf{r}) + \lambda^3\boldsymbol{\mathcal{E}}_{\rm c,2}(\mathbf{r}) + \ldots, \tag{5.78}$$

and

$$\boldsymbol{\mathcal{Z}}_{\rm t_c}^{\lambda}(\mathbf{r}) = -\lambda\boldsymbol{\mathcal{Z}}_{\rm t_c,1}(\mathbf{r}) - \lambda^2\boldsymbol{\mathcal{Z}}_{\rm t_c,2}(\mathbf{r}) - \lambda^3\boldsymbol{\mathcal{Z}}_{\rm t_c,3}(\mathbf{r}) - \ldots, \tag{5.79}$$

where $\boldsymbol{\mathcal{E}}_{c,1}(\mathbf{r}) = \int d\mathbf{r}' g_1^c(\mathbf{r}\mathbf{r}')(\mathbf{r}-\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|^3$ and $\boldsymbol{\mathcal{Z}}_{t_c,1}(\mathbf{r}) = \mathbf{z}(\mathbf{r}; [\gamma_1^c])/\rho(\mathbf{r})$, etc. The expansions of these fields can then be employed in the expressions for the electron–interaction and correlation–kinetic energy and potential energy.

For systems with symmetry such that the individual fields are conservative, the work done $W_{ee}^{\lambda}(\mathbf{r})$ and $W_{t_c}^{\lambda}(\mathbf{r})$ in the fields $\boldsymbol{\mathcal{E}}_{ee}^{\lambda}(\mathbf{r})$ and $Z_{t_c}^{\lambda}(\mathbf{r})$, respectively, may then be expressed as

$$W_{ee}^{\lambda}(\mathbf{r}) = \lambda W_{H}(\mathbf{r}) + \lambda W_{x}(\mathbf{r}) + \lambda^2 W_{c,1}(\mathbf{r}) + \lambda^3 W_{c,2}(\mathbf{r}) + \ldots, \tag{5.80}$$

and

$$W_{t_c}^{\lambda}(\mathbf{r}) = -\lambda W_{t_c,1}(\mathbf{r}) - \lambda^2 W_{t_c,2} - \ldots, \tag{5.81}$$

where $W_{c,1}(\mathbf{r})$, $W_{t_c,1}(\mathbf{r})$, etc. are the work done in the fields $\boldsymbol{\mathcal{E}}_{c,1}(\mathbf{r})$, $Z_{t_c,1}(\mathbf{r})$, respectively, etc.

The scaling relationship for the KS–DFT functionals $E_{H}^{\lambda}[\rho]$ and $E_{x}^{KS,\lambda}[\rho]$ are given in the previous section. It has further been shown [17] that the KS 'correlation' energy functional $E_{c}^{KS,\lambda}[\rho]$ commences in *second order*:

$$E_{c}^{KS,\lambda}[\rho] = \lambda^2 E_{c,2}^{KS}[\rho] + \lambda^3 E_{c,3}^{KS}[\rho] + \ldots, \tag{5.82}$$

so that the KS correlation potential too commences in *second order*:

$$v_{c}^{\lambda}(\mathbf{r}) = \lambda^2 v_{c,2}(\mathbf{r}) + \lambda^3 v_{c,3}(\mathbf{r}) + \ldots, \tag{5.83}$$

where $v_{c,2}(\mathbf{r}) = \delta E_{c,2}^{KS}[\rho]/\delta\rho(\mathbf{r})$, etc., and $E_{c,2}^{KS}[\rho]$ is the $O(\lambda^2)$ KS correlation energy.

From (5.44) we have

$$\nabla v_{ee}^{\lambda}(\mathbf{r}) = -\boldsymbol{\mathcal{F}}^{\mathrm{eff},\lambda}(\mathbf{r}), \tag{5.84}$$

so that on substituting for the field $\boldsymbol{\mathcal{F}}^{\mathrm{eff},\lambda}(\mathbf{r})$ from (5.45) and the KS definition for the potential $v_{ee}(\mathbf{r})$ from (5.66), we have

$$\nabla[v_{H}^{\lambda}(\mathbf{r}) + v_{x}^{\lambda}(\mathbf{r}) + v_{c}^{\lambda}(\mathbf{r})] = -[\boldsymbol{\mathcal{E}}_{ee}^{\lambda}(\mathbf{r}) + \boldsymbol{\mathcal{Z}}_{t_c}^{\lambda}(\mathbf{r})]. \tag{5.85}$$

On substitution of the expansions for the various terms as given in the previous section, and on equating terms of equal order, we obtain the components of the KS potential in terms of the fields as:

$$\nabla v_{H}(\mathbf{r}) = -\boldsymbol{\mathcal{E}}_{H}(\mathbf{r}), \tag{5.86}$$

$$\nabla v_{x}(\mathbf{r}) = -[\boldsymbol{\mathcal{E}}_{x}(\mathbf{r}) - \boldsymbol{\mathcal{Z}}_{t_c,1}(\mathbf{r})], \tag{5.87}$$

$$\nabla v_{c,2}(\mathbf{r}) = -[\boldsymbol{\mathcal{E}}_{c,1}(\mathbf{r}) - \boldsymbol{\mathcal{Z}}_{t_c,2}(\mathbf{r})], \tag{5.88}$$

$$\nabla v_{c,3}(\mathbf{r}) = -[\boldsymbol{\mathcal{E}}_{c,2}(\mathbf{r}) - \boldsymbol{\mathcal{Z}}_{t_c,3}(\mathbf{r})], \ \text{etc.} \tag{5.89}$$

We are now in the position to provide a rigorous interpretation of the KS ‘exchange’ and ‘correlation’ energy functionals and their functional derivatives in terms of the electron correlations that contribute to them. However, prior to explaining the interpretation, note that (5.86) is equivalent to (5.17). The physical reason for this equivalence between the functional derivative $v_H(\mathbf{r})$ and the field $\boldsymbol{\mathcal{E}}_H(\mathbf{r})$ is that the latter is due to the density $\rho(\mathbf{r})$ which is a static charge distribution.

5.3 Interpretation of the Kohn–Sham ‘Exchange’ Energy Functional $E_{\mathbf{x}}^{\mathbf{KS}}[\rho]$ and Its Derivative $v_{\mathbf{x}}(\mathbf{r})$

The physical interpretation of the KS ‘exchange’ potential energy $v_x(\mathbf{r})$ follows from (5.87). It is the work done to move the model fermion in a conservative field $\boldsymbol{\mathcal{R}}(\mathbf{r})$:

$$v_x(\mathbf{r}) = \frac{\delta E_x^{\mathrm{KS}}[\rho]}{\delta\rho(\mathbf{r})} = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{R}}(\mathbf{r}') \cdot d\boldsymbol{\ell}', \tag{5.90}$$

where $\boldsymbol{\mathcal{R}}(\mathbf{r}) = \boldsymbol{\mathcal{E}}_x(\mathbf{r}) - \boldsymbol{\mathcal{Z}}_{\mathrm{t_c},1}(\mathbf{r})$. Since $\nabla \times \boldsymbol{\mathcal{R}}(\mathbf{r}) = 0$, this work done is path independent. The field $\boldsymbol{\mathcal{R}}(\mathbf{r})$, and hence the potential energy $v_x(\mathbf{r})$, is therefore representative *both* of Pauli correlations via the component field $\boldsymbol{\mathcal{E}}_x(\mathbf{r})$, as well as those due to *part* of the Correlation–Kinetic effects through the field $\boldsymbol{\mathcal{Z}}_{\mathrm{t_c},1}(\mathbf{r})$.

For systems with symmetry such that the fields $\boldsymbol{\mathcal{E}}_x(\mathbf{r})$ and $\boldsymbol{\mathcal{Z}}_{\mathrm{t_c},1}(\mathbf{r})$ are separately conservative, we may write

$$v_{\mathrm{x}}(\mathbf{r}) = W_x(\mathbf{r}) + W_{\mathrm{t_c},1}(\mathbf{r}), \tag{5.91}$$

where $W_x(\mathbf{r})$ is the work done in the field $\boldsymbol{\mathcal{E}}_x(\mathbf{r})$ due to the Fermi hole charge, and $W_{\mathrm{t_c},1}(\mathbf{r})$ the work done in the field $\boldsymbol{\mathcal{Z}}_{\mathrm{t_c},1}(\mathbf{r})$.

The KS ‘exchange’ energy functional $E_x^{\mathrm{KS}}[\rho]$ is related to its functional derivative $v_x(\mathbf{r})$ by the virial theorem of (4.99). Substituting (5.87) into this equation leads to

$$E_x^{\mathrm{KS}}[\rho] - \int \rho(\mathbf{r})\mathbf{r} \cdot [\boldsymbol{\mathcal{E}}_x(\mathbf{r}) - \boldsymbol{\mathcal{Z}}_{\mathrm{t_c},1}(\mathbf{r})]d\mathbf{r} = 0. \tag{5.92}$$

Now as noted in Sect. 5.2.2, $E_x^{\mathrm{KS}}[\rho]$ is equivalent to the Q–DFT Pauli energy E_{x} provided the same orbitals are employed in their determination. Thus, using the relationship [19] between E_x and $\boldsymbol{\mathcal{E}}_x(\mathbf{r})$ of (5.54) in the above equation, it follows that

$$\int \rho(\mathbf{r})\mathbf{r} \cdot \boldsymbol{\mathcal{Z}}_{\mathrm{t_c},1}(\mathbf{r})d\mathbf{r} = 0. \tag{5.93}$$

Therefore, although the Correlation–Kinetic field $\boldsymbol{\mathcal{Z}}_{\mathrm{t_c},1}(\mathbf{r})$ contributes *explicitly* to the potential energy $v_x(\mathbf{r})$, it does not contribute directly to the KS ‘exchange’ energy

$E_x^{\mathrm{KS}}[\rho]$. Its contribution to the energy is *implicit* via the orbitals generated by $v_x(\mathbf{r})$. *Hence, the KS–DFT 'exchange' energy functional* $E_x^{\mathrm{KS}}[\rho]$ *and its functional derivative* $v_x(\mathbf{r})$ *are representative of Pauli correlations and lowest–order Correlation–Kinetic effects*.

5.4 Interpretation of the Kohn–Sham 'Correlation' Energy Functional $E_{\mathbf{c}}^{\mathbf{KS}}[\rho]$ and Its Derivative $v_{\mathbf{c}}(\mathbf{r})$

The interpretation of the KS 'correlation' potential energy $v_c(\mathbf{r})$ follows from (5.88)–(5.89), etc. The components $v_{c,2}(\mathbf{r})$, $v_{c,3}(\mathbf{r})$, etc. are separately the work done in a conservative field:

$$v_{c,2}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} [\boldsymbol{\mathcal{E}}_{c,1}(\mathbf{r}') - \boldsymbol{\mathcal{Z}}_{\mathrm{t_c},2}(\mathbf{r}')] \cdot d\boldsymbol{\ell}', \tag{5.94}$$

$$v_{c,3}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} [\boldsymbol{\mathcal{E}}_{c,2}(\mathbf{r}') - \boldsymbol{\mathcal{Z}}_{\mathrm{t_c},3}(\mathbf{r}')] \cdot d\boldsymbol{\ell}', \text{etc.} \tag{5.95}$$

The work done in each order is path independent. Further, *both Coulomb correlation and correlation–kinetic effects contribute to each order of the KS correlation potential energy*.

Next, turning to the energy, observe from (5.56), (5.79) and (5.93) that the Correlation–Kinetic energy T_c also commences in $O(\lambda^2)$;

$$T_c^{\lambda} = -\frac{1}{2}\int d\mathbf{r}\rho(\mathbf{r})\mathbf{r} \cdot [\lambda^2 \boldsymbol{\mathcal{Z}}_{\mathrm{t_c},2}(\mathbf{r}) + \lambda^3 \boldsymbol{\mathcal{Z}}_{\mathrm{t_c},3}(\mathbf{r}) + \dots]. \tag{5.96}$$

Now the KS 'correlation' energy $E_c^{\mathrm{KS},\lambda}[\rho]$ and its functional derivative $v_c^{\lambda}(\mathbf{r})$ are related by the virial theorem (see (4.100))

$$E_c^{\mathrm{KS},\lambda}[\rho] + \int d\mathbf{r}\rho(\mathbf{r})\mathbf{r} \cdot \nabla v_c^{\lambda}(\mathbf{r}) = -T_c^{\lambda}[\rho]. \tag{5.97}$$

On substituting the expansions for the potential energy $v_c^{\lambda}(\mathbf{r})$ (5.83) and Correlation–Kinetic energy T_c^{λ} (5.96) into the virial theorem, we obtain

$$\begin{aligned} E_c^{\mathrm{KS},\lambda}[\rho] + \int d\mathbf{r}\rho(\mathbf{r})\mathbf{r} \cdot \big[&\lambda^2 \nabla v_{c,2}(\mathbf{r}) + \lambda^3 \nabla v_{c,3}(\mathbf{r}) + \dots \\ &- \frac{1}{2}\lambda^2 \boldsymbol{\mathcal{Z}}_{\mathrm{t_c},2}(\mathbf{r}) - \frac{1}{2}\lambda^3 \boldsymbol{\mathcal{Z}}_{\mathrm{t_c},3}(\mathbf{r}) - \dots \big] = 0. \end{aligned} \tag{5.98}$$

However, it has been proved [15] that

$$\int d\mathbf{r}\rho(\mathbf{r})\mathbf{r} \cdot \nabla v_{c,2}(\mathbf{r}) = 0. \tag{5.99}$$

Employing (5.95) and (5.99) in (5.98), we then have

$$\begin{aligned} E_c^{\mathrm{KS},\lambda}[\rho] = \frac{\lambda^2}{2} \int d\mathbf{r}\rho(\mathbf{r})\mathbf{r} \cdot \boldsymbol{\mathcal{Z}}_{\mathrm{t_c},2}(\mathbf{r}) \\ + \lambda^3 \int d\mathbf{r}\rho(\mathbf{r})\mathbf{r} \cdot \left[\boldsymbol{\mathcal{E}}_{c,2}(\mathbf{r}) - \frac{1}{2}\boldsymbol{\mathcal{Z}}_{\mathrm{t_c},3}(\mathbf{r})\right] + \ldots . \end{aligned} \tag{5.100}$$

Comparison with (5.82) then shows that

$$E_{c,2}^{\mathrm{KS}}[\rho] = \frac{1}{2} \int d\mathbf{r}\rho(\mathbf{r})\mathbf{r} \cdot \boldsymbol{\mathcal{Z}}_{\mathrm{t_c},2}(\mathbf{r}), \tag{5.101}$$

$$E_{c,3}^{\mathrm{KS}}[\rho] = \int d\mathbf{r}\rho(\mathbf{r})\mathbf{r} \cdot \left[\boldsymbol{\mathcal{E}}_{c,2}(\mathbf{r}) - \frac{1}{2}\boldsymbol{\mathcal{Z}}_{\mathrm{t_c},3}(\mathbf{r})\right], \tag{5.102}$$

etc. *Thus to leading order, it is only the Correlation–Kinetic effects that contribute to the KS correlation energy. The Coulomb correlations, which contribute explicitly to the potential energy (see* (5.94)*), do not contribute explicitly to the KS correlation energy in this order*. For energy terms beyond the leading order, both Coulomb correlation and Correlation–Kinetic effects contribute.

5.5 Interpretation of the KS–DFT of Hartree–Fock Theory

In a manner similar to the representation of the Schrödinger theory of electrons, there also is a density functional theory representation of Hartree–Fock (HF) theory. In other words, a Hohenberg–Kohn theorem [20] and the constrained search approach [21] can be formulated to prove that the ground state HF theory Slater determinant wavefunction $\psi^{\mathrm{HF}}(\mathbf{X})$ is a functional of the corresponding ground state density $\rho(\mathbf{r})$. Thus, there exists an energy functional $E^{\mathrm{HF}}[\rho]$ that achieves its minimum at the HF theory ground state energy for the HF ground state density $\rho(\mathbf{r})$. (Similar remarks are valid for the Hartree approximation).

In KS–DFT, it is assumed that an S system of noninteracting fermions exists such that the density $\rho(\mathbf{r})$ and energy $E^{\mathrm{HF}}[\rho]$ equivalent to that of HF theory can be obtained. Thus, it is possible to define an electron–interaction energy functional $E_{\mathrm{ee}}^{\mathrm{KSHF}}[\rho]$ such that the ground state energy may be written as

$$E^{\mathrm{HF}}[\rho] = T_s[\rho] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + E_{\mathrm{ee}}^{\mathrm{KSHF}}[\rho], \tag{5.103}$$

with the S system differential equation generating the density being (3.207)

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_{\mathrm{ee}}^{\mathrm{HF}}(\mathbf{r})\right]\phi_i(\mathbf{x}) = \epsilon_i\phi_i(\mathbf{x});\ i = 1, \ldots, N. \tag{5.104}$$

Here $T_s[\rho]$ is the kinetic energy functional of the noninteracting S System fermions of density equivalent to that of HF theory. The corresponding electron–interaction potential energy $v_{\mathrm{ee}}^{\mathrm{HF}}(\mathbf{r})$ of these model fermions that generates the HF theory ground state density via $\rho(\mathbf{r}) = \sum_{i,\sigma}|\phi_i(\mathbf{r}\sigma)|^2$ is then the functional derivative $\delta E_{\mathrm{ee}}^{\mathrm{KSHF}}[\rho]/\delta\rho(\mathbf{r})$.

It is evident from (5.103) that the functional $E_{\mathrm{ee}}^{\mathrm{KSHF}}[\rho]$ is representative of electron correlations due to the Pauli exclusion principle, and Correlation–Kinetic effects that arise due to the difference T_c^{HF} in the HF theory and S system kinetic energies. The physical interpretation of the functional $E_{\mathrm{ee}}^{\mathrm{KSHF}}[\rho]$ and its functional derivative in terms of these correlations then follows from the Q–DFT of HF theory described in Sect. 3.8.4. A comparison of (5.103) with (3.219) shows that

$$E_{\mathrm{ee}}^{\mathrm{KSHF}}[\rho] = E_{\mathrm{ee}}^{\mathrm{HF}} + T_c^{\mathrm{HF}}, \tag{5.105}$$

where $E_{\mathrm{ee}}^{\mathrm{HF}}$ and T_c^{HF} are the HF theory electron–interaction and Correlation–Kinetic energy, respectively. These energies in turn are defined in terms of the corresponding HF theory fields $\boldsymbol{\mathcal{E}}_{\mathrm{ee}}^{\mathrm{HF}}(\mathbf{r})$ and $\boldsymbol{\mathcal{Z}}_{\mathrm{t_c}}^{\mathrm{HF}}(\mathbf{r})$. These fields and energies representative of the different correlations are defined in Sect. 3.8.4.

The functional derivative $v_{\mathrm{ee}}^{\mathrm{HF}}(\mathbf{r})$ (see (3.208)) is the work done to move the model fermion in the conservative field $\boldsymbol{\mathcal{F}}^{\mathrm{HF}}(\mathbf{r})$:

$$v_{\mathrm{ee}}^{\mathrm{HF}}(\mathbf{r}) = \frac{\delta E_{\mathrm{ee}}^{\mathrm{KSHF}}[\rho]}{\delta\rho(\mathbf{r})} = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{F}}^{\mathrm{HF}}(\mathbf{r}')\cdot d\boldsymbol{\ell}', \tag{5.106}$$

where

$$\boldsymbol{\mathcal{F}}^{\mathrm{HF}}(\mathbf{r}) = \boldsymbol{\mathcal{E}}_{\mathrm{ee}}^{\mathrm{HF}}(\mathbf{r}) + \boldsymbol{\mathcal{Z}}_{\mathrm{t_c}}^{\mathrm{HF}}(\mathbf{r}). \tag{5.107}$$

We thus have a rigorous physical interpretation of the KS–DFT of HF theory.

As stated in Sect. (3.8.4), and reiterated here, the S system orbitals $\phi_i(\mathbf{x})$ that generate the HF theory density differ from the HF theory orbitals. Furthermore, Correlation–Kinetic effects contribute to both the total and potential energy of the model fermions.

5.6 Interpretation of the KS–DFT of Hartree Theory

The equations governing the KS–DFT of Hartree theory, following the assumption of existence of an S system such that the equivalent density $\rho(\mathbf{r})$ and ground state energy $E^H[\rho]$ may be obtained, are

$$E^H[\rho] = T_s[\rho] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + E_{\text{ee}}^{\text{KS}H}[\rho], \tag{5.108}$$

and

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_{\text{ee}}^H(\mathbf{r})\right]\phi_i(\mathbf{x}) = \epsilon_i\phi_i(\mathbf{x}); \quad i = 1, \ldots, N. \tag{5.109}$$

$T_s[\rho]$ is the kinetic energy functional of the noninteracting fermions of density $\rho(\mathbf{r})$ equivalent to that of Hartree theory, $E_{\text{ee}}^{\text{KS}H}[\rho]$ the KS electron–interaction energy functional, and $v_{\text{ee}}^H(\mathbf{r})$ the functional derivative $\delta E_{\text{ee}}^{\text{KS}H}[\rho]/\delta\rho(\mathbf{r})$.

The physical interpretation of $E_{\text{ee}}^{\text{KS}H}[\rho]$ and $v_{\text{ee}}^H(\mathbf{r})$ follows from the Q–DFT description of Hartree theory given in Sect. 3.8.6. Thus, a comparison of (5.108) and (3.251) shows that

$$E_{\text{ee}}^{\text{KS}H}[\rho] = E_{\text{ee}}^H + T_c^H \tag{5.110}$$

where E_{ee}^H and T_c^H are the Hartree theory electron–interaction and Correlation–Kinetic energy defined in terms of the corresponding Hartree theory fields $\boldsymbol{\mathcal{E}}_{\text{ee}}^H(\mathbf{r})$ and $\boldsymbol{\mathcal{Z}}_{\text{t}_\text{c}}^H(\mathbf{r})$. The functional derivative $v_{\text{ee}}^H(\mathbf{r})$ (see (3.241)) is the work done to move the model fermion in the conservative field $\boldsymbol{\mathcal{F}}^H(\mathbf{r})$:

$$v_{\text{ee}}^H(\mathbf{r}) = \frac{\delta E_{\text{ee}}^{\text{KS}H}[\rho]}{\delta\rho(\mathbf{r})} = -\int_\infty^{\mathbf{r}} \boldsymbol{\mathcal{F}}^H(\mathbf{r}')\cdot d\boldsymbol{\ell}', \tag{5.111}$$

where

$$\boldsymbol{\mathcal{F}}^H(\mathbf{r}) = \boldsymbol{\mathcal{E}}_{\text{ee}}^H(\mathbf{r}) + \boldsymbol{\mathcal{Z}}_{\text{t}_\text{c}}^H(\mathbf{r}). \tag{5.112}$$

Once again note that the S system and Hartree theory orbitals differ, and that Correlation–Kinetic effects are intrinsic to both the total and potential energy of the model fermions to ensure the equivalence of their density to that of Hartree theory.

5.7 The Optimized Potential Method

The optimized potential method (OPM) is yet another way of constructing the S system of noninteracting fermions. In KS–DFT, the ground state energy E is expressed as a functional of the density $\rho(\mathbf{r})$, and the effective potential energy $v_s(\mathbf{r})$ of the model fermions then defined via the variational minimization of the energy functional $E[\rho]$ with respect to arbitrary variations of the density. Now since the S system orbitals $\phi_i(\mathbf{x})$ are functionals of the density, the energy may also be expressed as a functional of these orbitals: $E = E[\phi_i]$. In the OPM, there is an integral equation that defines the potential energy $v_s(\mathbf{r})$. This equation is obtained by minimization of the functional $E = E[\phi_i]$ with respect to variations of $v_s(\mathbf{r})$. The functional $E = E[\phi_i]$

is, of course, unknown, and consequently the integral equation cannot be solved exactly. However, this equation for the potential energy $v_s(\mathbf{r})$ can be solved in the 'exchange–only' (XO) approximation, which is formally defined as follows [8, 9]. In the XO–OPM, the ground state energy is the expectation of the Hamiltonian:

$$E_{\text{XO}}^{\text{OPM}}[\phi_i] = \langle\Phi|\hat{T} + \hat{U} + \sum_i v(\mathbf{r}_i)|\Phi\rangle, \tag{5.113}$$

taken with respect to that single Slater determinant $\Phi\{\phi_i\}$ which is *constrained* to be a ground state of some noninteracting Hamiltonian of the form $\hat{T} + \sum_i w(\mathbf{r}_i)$ and which simultaneously minimizes the energy as defined by the above expectation. Since this expectation is with respect to a Slater determinant, the *expression* for $E_{\text{XO}}^{\text{OPM}}[\phi_i]$ is the same as that of Hartree–Fock theory, and therefore known. As such the integral equation is entirely in terms of the S system orbitals and eigenvalues, and thereby solvable. (Note, however, that the Hartree–Fock theory determinantal wavefunction differs from that of the XO–OPM since there is no additional constraint on it.) To understand how the integral equation of the OPM comes about, we next derive it in the spin unpolarized XO case.

5.7.1 The 'Exchange–Only' Optimized Potential Method

In the XO–OPM, the noninteracting fermions are subject to the external field $\mathcal{F}^{\text{ext}}(\mathbf{r}) = -\boldsymbol{\nabla} v(\mathbf{r})$, and the wavefunction is assumed to be a Slater determinant $\Phi\{\phi_i\}$ of spin–orbitals $\phi_i(\mathbf{x}) = \psi_i(\mathbf{r})\chi_i(\sigma)$. The differential equation generating these orbitals is further assumed to be

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right]\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r});\ i = 1, \ldots, N, \tag{5.114}$$

where the effective potential energy $v_s(\mathbf{r})$ of the noninteracting fermions is the sum of the external $v(\mathbf{r})$, Hartree $W_H(\mathbf{r})$, and 'exchange' $v_x^{\text{OPM}}(\mathbf{r})$ potential energies:

$$v_s(\mathbf{r}) = v(\mathbf{r}) + W_H(\mathbf{r}) + v_x^{\text{OPM}}(\mathbf{r}), \tag{5.115}$$

where

$$W_H(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \tag{5.116}$$

and $\rho(\mathbf{r}) = \sum_i \sum_\sigma |\phi_i(\mathbf{r}\sigma)|^2$. The expression for the ground state energy $E_{\text{XO}}^{\text{OPM}}[\psi_i]$ is the same as that of Hartree–Fock theory (see Sect. 3.8.1), but in terms of the XO–OPM orbitals. Thus,

$$E_{\mathrm{XO}}^{\mathrm{OPM}}[\psi_i] = \sum_i \int \psi_i^*(\mathbf{r})\Big(-\frac{1}{2}\nabla^2\Big)\psi_i(\mathbf{r})d\mathbf{r} + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + E_H + E_x^{\mathrm{OPM}}, \qquad (5.117)$$

where E_H and E_x^{OPM} are the Hartree and 'exchange' energies, respectively.

$$E_H = \frac{1}{2}\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}', \qquad (5.118)$$

$$E_x^{\mathrm{OPM}} = -\frac{1}{2}\sum_{\substack{i,j \\ \text{spin } j=\text{spin } i}} \int \frac{\psi_i^*(\mathbf{r}')\psi_j^*(\mathbf{r})\psi_i(\mathbf{r})\psi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'. \qquad (5.119)$$

The basic idea of the OPM is to determine the potential energy $v_s(\mathbf{r})$ by variational minimization of the energy $E_{\mathrm{XO}}^{\mathrm{OPM}}$ with respect to arbitrary variations of $v_s(\mathbf{r})$. That is, $v_s(\mathbf{r})$ is varied by a small amount $\delta v_s(\mathbf{r})$ such that $v_s(\mathbf{r}) \to v_s(\mathbf{r}) + \delta v_s(\mathbf{r})$, and the stationary condition determined at the vanishing of the first order variation of the energy:

$$\frac{\delta E_{\mathrm{XO}}^{\mathrm{OPM}}[\psi_i]}{\delta v_s(\mathbf{r})} = 0. \qquad (5.120)$$

This functional derivative may be rewritten using the chain rule for functional differentiation as

$$\frac{\delta E_{\mathrm{XO}}^{\mathrm{OPM}}[\psi_i(\mathbf{r})]}{\delta v_s(\mathbf{r})} = \sum_i \int \frac{\delta E_{\mathrm{XO}}^{\mathrm{OPM}}}{\delta \psi_i(\mathbf{r}')}\frac{\delta \psi_i(\mathbf{r}')}{\delta v_s(\mathbf{r})}d\mathbf{r}' + c.c. = 0. \qquad (5.121)$$

The term $\delta E_{XO}^{\mathrm{OPM}}/\delta\psi_i(\mathbf{r}')$ is simply the Hartree–Fock theory variation so that

$$\frac{\delta E_{\mathrm{XO}}^{\mathrm{OPM}}}{\delta \psi_i(\mathbf{r}')} = \Big[-\frac{1}{2}\nabla^2 + v(\mathbf{r}') + W_H(\mathbf{r}') + v_{x,i}(\mathbf{r}')\Big]\psi_i^*(\mathbf{r}'), \qquad (5.122)$$

where $v_{x,i}(\mathbf{r})$ is the orbital–dependent exchange function of (3.201):

$$v_{x,i}(\mathbf{r}) = \frac{1}{\psi_i^*(\mathbf{r})}\frac{\delta E_x^{\mathrm{OPM}}[\psi_i]}{\delta \psi_i(\mathbf{r})} = -\sum_{\substack{j \\ \text{spin } j=\text{spin } i}} \int \frac{\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')\psi_j(\mathbf{r})}{\psi_i^*(\mathbf{r})|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'. \qquad (5.123)$$

In the XO–OPM case, the function $v_{x,i}(\mathbf{r})$ is known explicitly in terms of the orbitals $\psi_i(\mathbf{r})$. Rewriting the OPM differential equation (5.114) as

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + W_H(\mathbf{r})\right]\psi_i(\mathbf{r}) = [\epsilon_i - v_x^{\mathrm{OPM}}(\mathbf{r})]\psi_i(\mathbf{r}), \tag{5.124}$$

we have

$$\frac{\delta E_{\mathrm{XO}}^{\mathrm{OPM}}}{\delta\psi_i(\mathbf{r}')} = [\epsilon_i - v_x^{\mathrm{OPM}}(\mathbf{r}') + v_{x,i}(\mathbf{r}')]\psi_i^*(\mathbf{r}'). \tag{5.125}$$

To determine the term $\delta\psi_i(\mathbf{r}')/\delta v_s(\mathbf{r})$ in (5.121), we introduce the variations $\delta\psi_i(\mathbf{r}')$ and $\delta v_s(\mathbf{r}')$ in the OPM differential equation (5.114):

$$\delta\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r}')\right]\psi_i(\mathbf{r}') = \delta[\epsilon_i\psi_i(\mathbf{r}')]. \tag{5.126}$$

To first order in δ, we have

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r}') - \epsilon_i\right]\delta\psi_i(\mathbf{r}') = [\delta\epsilon_i - \delta v_s(\mathbf{r}')]\psi_i(\mathbf{r}'). \tag{5.127}$$

The solution to this equation can be expressed in terms of the Green's function $G_i(\mathbf{r}'\mathbf{r}'')$ as

$$\delta\psi_i(\mathbf{r}') = \int G_i(\mathbf{r}'\mathbf{r}'')[\delta\epsilon_i - \delta v_s(\mathbf{r}'')]\psi_i(\mathbf{r}'')d\mathbf{r}'', \tag{5.128}$$

where $G_i(\mathbf{r}'\mathbf{r}'')$, the solution of the differential equation

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r}') - \epsilon_i\right]G_i(\mathbf{r}'\mathbf{r}'') = \delta(\mathbf{r}' - \mathbf{r}''), \tag{5.129}$$

is

$$G_i(\mathbf{r}'\mathbf{r}'') = {\sum_j}' \frac{\psi_j(\mathbf{r}')\psi_j^*(\mathbf{r}'')}{\epsilon_j - \epsilon_i}. \tag{5.130}$$

(The prime on the sum means that the sum over j is restricted to states for which $\epsilon_j \neq \epsilon_i$.) The Green's function $G_i(\mathbf{r}'\mathbf{r}'')$ is thus orthogonal to $\psi_i(\mathbf{r}'')$:

$$\int G_i(\mathbf{r}'\mathbf{r}'')\psi_i(\mathbf{r}'')d\mathbf{r}'' = {\sum_j}' \frac{\psi_j(\mathbf{r}')}{\epsilon_j - \epsilon_i}\int \psi_j^*(\mathbf{r}'')\psi_i(\mathbf{r}'')d\mathbf{r}'' = 0. \tag{5.131}$$

Thus, (5.128) reduces to

$$\delta\psi_i(\mathbf{r}') = -\int G_i(\mathbf{r}'\mathbf{r}'')\delta v_s(\mathbf{r}'')\psi_i(\mathbf{r}'')d\mathbf{r}'', \tag{5.132}$$

so that

$$\frac{\delta\psi_i(\mathbf{r}')}{\delta v_s(\mathbf{r})} = -G_i(\mathbf{r}'\mathbf{r})\psi_i(\mathbf{r}). \tag{5.133}$$

Substituting (5.125) and (5.133) into (5.121) leads to the XO–OPM integral equation

$$\sum_i \int \left[v_x^{\mathrm{OPM}}\left(\mathbf{r}'\right) - v_{x,i}\left(\mathbf{r}'\right)\right]\psi_i^*\left(\mathbf{r}'\right)G_i\left(\mathbf{r}'\mathbf{r}\right)\psi_i(\mathbf{r})d\mathbf{r}' + c.c. = 0, \tag{5.134}$$

where the term proportional to ϵ_i in (5.125) vanishes as a result of the orthogonality condition of (5.131). The integral equation (5.134) is then solved for the 'exchange' potential energy $v_x^{\mathrm{OPM}}(\mathbf{r})$ self consistently with the OPM differential equation (5.114). The energy $E_{\mathrm{XO}}^{\mathrm{OPM}}[\psi_i]$ is obtained from (5.117) via the solutions $\psi_i(\mathbf{r})$.

The XO–OPM is also referred to in the literature [8, 9] as 'exchange–only density functional theory.' The relationship between the XO–OPM and KS–DFT can be established [12] as follows. If the 'exchange' energy $E_x^{\mathrm{OPM}}[\psi_i]$ is a functional of only the density, i.e. $E_x^{\mathrm{OPM}}[\psi_i] = E_x^{\mathrm{OPM}}[\rho]$, then from the definition of the density in terms of the orbitals $\psi_i(\mathbf{r})$ and the chain rule for functional differentiation, the orbital dependent exchange function $v_{x,i}(\mathbf{r})$ of (5.123) is

$$v_{x,i}(\mathbf{r}) = \frac{1}{\psi_i^*(\mathbf{r})}\int \frac{\delta E_x^{\mathrm{OPM}}}{\delta\rho(\mathbf{r}')}\frac{\delta\rho(\mathbf{r}')}{\delta\psi_i(\mathbf{r})}d\mathbf{r}' = \frac{\delta E_x^{\mathrm{OPM}}[\rho]}{\delta\rho(\mathbf{r})}, \tag{5.135}$$

independent of i. Substituting (5.135) into the integral equation (5.134) and employing the orthogonality condition (5.131) then yields

$$v_x^{\mathrm{OPM}}(\mathbf{r}) = \frac{\delta E_x^{\mathrm{OPM}}[\rho]}{\delta\rho(\mathbf{r})}, \tag{5.136}$$

upto a trivial additive constant. This is the definition of $v_x^{\mathrm{OPM}}(\mathbf{r})$ written within the framework of KS–DFT as a functional derivative taken with respect to the density $\rho(\mathbf{r})$.

Note that the XO–OPM 'exchange' energy $E_x^{\mathrm{OPM}}[\psi_i]$ and potential energy $v_x^{\mathrm{OPM}}(\mathbf{r})$ are *not* equivalent to the KS–DFT 'exchange' energy $E_x^{\mathrm{KS}}[\rho]$ and potential energy $v_x(\mathbf{r}) = \delta E_x^{\mathrm{KS}}[\rho]/\delta\rho(\mathbf{r})$ of the fully–interacting system with all correlations present. They would, however, be equivalent if the orbitals and eigenvalues of the fully–interacting system were employed in the expression for $E_x^{\mathrm{OPM}}[\psi_i]$ and the integral equation (5.134) for $v_x^{\mathrm{OPM}}(\mathbf{r})$ instead.

The OPM exchange energy $E_x^{\mathrm{OPM}}[\psi_i]$ and potential energy $v_x^{\mathrm{OPM}}(\mathbf{r})$ satisfy [22] the OPM 'Quantal Newtonian' first law and integral virial theorem:

$$\mathcal{F}^{\mathrm{ext}}(\mathbf{r}) + \mathcal{F}^{\mathrm{int,OPM}}(\mathbf{r}) = 0, \tag{5.137}$$

with

$$\boldsymbol{\mathcal{F}}^{\text{int,OPM}}(\mathbf{r}) = \boldsymbol{\mathcal{E}}_H^{\text{OPM}}(\mathbf{r}) - \nabla v_x^{\text{OPM}}(\mathbf{r}) - \boldsymbol{\mathcal{D}}^{\text{OPM}}(\mathbf{r}) - \boldsymbol{\mathcal{Z}}_s^{\text{OPM}}(\mathbf{r}), \tag{5.138}$$

and

$$E_x^{\text{OPM}}[\psi_i] = \int \rho(\mathbf{r})\mathbf{r} \cdot \nabla v_x^{\text{OPM}}(\mathbf{r})d\mathbf{r}, \tag{5.139}$$

where $\boldsymbol{\mathcal{E}}_H(\mathbf{r})$ is the Hartree field, $\boldsymbol{\mathcal{D}}^{\text{OPM}}(\mathbf{r}) = \mathbf{d}(\mathbf{r})/\rho(\mathbf{r}), \mathbf{d}(\mathbf{r}) = -\frac{1}{4}\nabla\nabla^2\rho(\mathbf{r}), \boldsymbol{\mathcal{Z}}_s^{\text{OPM}}(\mathbf{r}) = \mathbf{z}(\mathbf{r}; [\gamma_s^{\text{OPM}}])/\rho(\mathbf{r})$, $\mathbf{z}(\mathbf{r})$ the kinetic force derived from the OPM kinetic–energy–density tensor $t_{\alpha\beta}(\mathbf{r}; [\gamma_s^{\text{OPM}}])$, and $\gamma_s^{\text{OPM}}(\mathbf{r}\mathbf{r}')$ the OPM Dirac density matrix. It is evident from (5.137) that since $\nabla \times \boldsymbol{\mathcal{F}}^{\text{int,OPM}}(\mathbf{r}) = 0$, and $\nabla \times \boldsymbol{\mathcal{E}}_H(\mathbf{r}) = 0$, $\nabla \times \nabla v_x^{\text{OPM}}(\mathbf{r}) = 0$, $\nabla \times \boldsymbol{\mathcal{D}}(\mathbf{r}) = 0$, that $\nabla \times \boldsymbol{\mathcal{Z}}_s^{\text{OPM}}(\mathbf{r}) = 0$. Thus, within the XO–OPM, each component of the field $\boldsymbol{\mathcal{F}}^{\text{int,OPM}}(\mathbf{r})$ is separately conservative.

The OPM 'Quantal Newtonian' first law and integral virial theorem equations for the fully–correlated case are of the same form as that of XO theory. In these equations, the 'exchange' potential energy $v_x^{\text{OPM}}(\mathbf{r})$ is replaced by $v_{xc}^{\text{OPM}}(\mathbf{r})$. The ground state energy E is assumed to be a functional of the orbitals $\psi_i(\mathbf{r})$, so that in (5.117) $E_{\text{XO}}^{\text{OPM}}[\psi_i]$ is replaced by $E[\psi_i]$, and $E_x^{\text{OPM}}[\psi_i]$ by $E_{xc}^{\text{KS}}[\psi_i]$. That is the KS 'exchange–correlation' energy is now assumed to be a functional of the orbitals $\psi_i(\mathbf{r})$. The derivation of the integral equation for $v_{xc}^{\text{OPM}}(\mathbf{r})$ is the same, but with the explicit form of $v_{x,i}(\mathbf{r})$ replaced by the orbital–dependent exchange–correlation function $v_{xc,i}(\mathbf{r})$ where

$$v_{xc,i}(\mathbf{r}) = \frac{1}{\psi_i^*(\mathbf{r})} \frac{\delta E_{xc}^{\text{KS}}[\psi_i]}{\delta\psi_i(\mathbf{r})}. \tag{5.140}$$

The function $v_{xc,i}(\mathbf{r})$ is not known since the functional $E_{xc}^{\text{KS}}[\psi_i]$ is unknown. Hence, the OPM 'exchange–correlation' potential energy $v_{xc}^{\text{OPM}}(\mathbf{r})$ cannot be determined via solution of the OPM equations. Once again, if the KS 'exchange–correlation' energy functional $E_{xc}^{\text{KS}}[\psi_i]$ is a functional of only the density, i.e. $E_{xc}^{\text{KS}}[\psi_i] = E_{xc}^{\text{KS}}[\rho]$, then by repeating the steps leading to (5.136), it follows that

$$v_{xc}^{\text{OPM}}(\mathbf{r}) \equiv v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}^{\text{KS}}[\rho]}{\delta\rho(\mathbf{r})}, \tag{5.141}$$

to within a trivial additive constant. Thus, $v_{xc}^{\text{OPM}}(\mathbf{r})$ is the KS theory 'exchange–correlation' potential energy $v_{xc}(\mathbf{r})$. The total energy $E[\psi_i]$ is, of course, the ground state energy.

5.8 Physical Interpretation of the Optimized Potential Method

As was the case with KS–DFT, the OPM is strictly a mathematical scheme for the construction of the S system. It obtains the ground state energy $E[\psi_i]$ and the density $\rho(\mathbf{r})$ by determining the effective potential energy $v_s(\mathbf{r})$ of the S system through self–consistent solution of an integral and a differential equation. It does not, for example, describe how the various electron correlations contribute to this potential energy. Consequently, when approximations to the OPM are made, it is not clear what correlations are present. However, as KS–DFT and the OPM are intrinsically equivalent the physical interpretation of the OPM 'exchange–correlation' energy E_{xc}^{OPM} and potential energy $v_{xc}^{\mathrm{OPM}}(\mathbf{r})$, in terms of the electron correlations is the same as described in Sect. 5.1. It is also possible to provide an understanding [22] of the correlations that are intrinsic to the XO–OPM 'exchange' energy E_x^{OPM} and potential energy $v_x^{\mathrm{OPM}}(\mathbf{r})$, and this is described next.

5.8.1 *Interpretation of 'Exchange–Only' OPM*

The XO–OPM 'exchange' energy E_x^{OPM} and potential energy $v_x^{\mathrm{OPM}}(\mathbf{r})$ can also be afforded the interpretation that they each are comprised of a Pauli and Correlation–Kinetic component. This is derived from the Q–DFT perspective via the 'Quantal Newtonian' first law and integral virial theorem. It may also be obtained directly from the XO–OPM integral equation. These derivations involve approximations, and therefore they are not rigorous in the same sense as that of the interpretations of the 'exchange' energy and potential energy of fully–interacting KS theory (Sect. 5.3), or of the corresponding energies of the KS representation of Hartree–Fock theory (Sect. 5.5). The approximations, made on the basis of applications that show them to be extremely accurate, are therefore justified *ex post facto*.

5.8.2 *A. Derivation via Q–DFT*

Let us consider an S system of noninteracting fermions in which Coulomb correlation and Correlation–Kinetic effects are absent. This is the Pauli–Correlated (PC) approximation within Q–DFT discussed more fully in ***QDFT2*** [23]. Thus, within this approximation, only correlations due to the Pauli exclusion principle are considered. Further, let us assume a symmetry such that the inhomogeneity in the density $\rho(\mathbf{r})$ is a function of only one variable. Examples of such systems are closed–shell atoms, open–shell atoms in the central field approximation, and jellium and structureless pseudopotential models of a metal surface.

For such systems, the S system differential equation is

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + W_H(\mathbf{r}) + W_x(\mathbf{r})\right]\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}), \tag{5.142}$$

where

$$W_x(\mathbf{r}) = -\int_\infty^{\mathbf{r}} \boldsymbol{\mathcal{E}}_x(\mathbf{r}')\cdot d\boldsymbol{\ell}', \tag{5.143}$$

is the work done in the field $\boldsymbol{\mathcal{E}}_x(\mathbf{r}) = \int d\mathbf{r}'\rho_x(\mathbf{r}\mathbf{r}')(\mathbf{r}-\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|^3$ due to the Fermi hole $\rho_x(\mathbf{r}\mathbf{r}') = -|\gamma_s(\mathbf{r}\mathbf{r}')|^2/2\rho(\mathbf{r})$, and where $\gamma_s(\mathbf{r}\mathbf{r}')$ is the Dirac density matrix constructed from the orbitals $\psi_i(\mathbf{r})$ of the differential equation (5.142). The corresponding density $\rho(\mathbf{r}) = \gamma_s(\mathbf{r}\mathbf{r})$. The work done $W_x(\mathbf{r})$ is path independent since $\boldsymbol{\nabla}\times\boldsymbol{\mathcal{E}}_x(\mathbf{r}) = 0$ for systems of this symmetry. The exchange energy E_x and potential energy $W_x(\mathbf{r})$ satisfy the integral virial theorem so that

$$E_x = \int \rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\mathcal{E}}_x(\mathbf{r})d\mathbf{r}. \tag{5.144}$$

The corresponding 'Quantal Newtonian' first law is

$$\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}) + \boldsymbol{\mathcal{F}}^{PC} = 0, \tag{5.145}$$

where

$$\boldsymbol{\mathcal{F}}^{PC}(\mathbf{r}) = \boldsymbol{\mathcal{E}}_H(\mathbf{r}) + \boldsymbol{\mathcal{E}}_x(\mathbf{r}) - \boldsymbol{\mathcal{D}}(\mathbf{r}) - \boldsymbol{\mathcal{Z}}_s(\mathbf{r}), \tag{5.146}$$

with the fields $\boldsymbol{\mathcal{D}}(\mathbf{r})$, $\boldsymbol{\mathcal{Z}}(\mathbf{r})$ defined in terms of the density $\rho(\mathbf{r})$ and Dirac density matrix $\gamma_s(\mathbf{r}\mathbf{r}')$ in the usual manner. Since for the symmetry assumed $\boldsymbol{\nabla}\times\boldsymbol{\mathcal{E}}_x(\mathbf{r}) = 0$, it follows from (5.145) that $\boldsymbol{\nabla}\times\boldsymbol{\mathcal{Z}}_s(\mathbf{r}) = 0$.

On equating (5.137) and (5.145) we have

$$\begin{aligned}\boldsymbol{\nabla} v_x^{\text{OPM}}(\mathbf{r}) = &- \left[\boldsymbol{\mathcal{E}}_x(\mathbf{r}) + \boldsymbol{\mathcal{Z}}_{t_c}^{\text{OPM}}(\mathbf{r})\right] \\ &- [\boldsymbol{\mathcal{D}}^{\text{OPM}}(\mathbf{r}) - \boldsymbol{\mathcal{D}}(\mathbf{r})] + \left[\boldsymbol{\mathcal{E}}_H^{\text{OPM}}(\mathbf{r}) - \boldsymbol{\mathcal{E}}_H(\mathbf{r})\right]\end{aligned} \tag{5.147}$$

where

$$\boldsymbol{\mathcal{Z}}_{t_c}^{\text{OPM}}(\mathbf{r}) = \boldsymbol{\mathcal{Z}}_s^{\text{OPM}}\left(r; \left[\gamma_s^{\text{OPM}}\right]\right) - \boldsymbol{\mathcal{Z}}_s\left(\mathbf{r}; [\gamma_s]\right). \tag{5.148}$$

Equation (5.147) is an *exact* relationship between the XO–OPM and the PC approximation of Q–DFT. Next, we *assume* the densities, and therefore the Hartree and derivative density fields of these two schemes to be equivalent. We make *no assumptions* with regard to the fields $\boldsymbol{\mathcal{Z}}_s^{\text{OPM}}(\mathbf{r})$ and $\boldsymbol{\mathcal{Z}}_s(\mathbf{r})$ because $\boldsymbol{\mathcal{Z}}_{t_c}^{\text{OPM}}(\mathbf{r})$ depends upon the difference between the off–diagonal matrix elements of the respective density matrices. Equation (5.147) then reduces to

$$\boldsymbol{\nabla} v_x^{\text{OPM}}(\mathbf{r}) = -[\boldsymbol{\mathcal{E}}_x(\mathbf{r}) + \boldsymbol{\mathcal{Z}}_{t_c}^{\text{OPM}}(\mathbf{r})], \tag{5.149}$$

so that $v_x^{\mathrm{OPM}}(\mathbf{r})$ may be interpreted as the work done in the conservative field $\mathbf{R}^{\mathrm{OPM}}(\mathbf{r})$:

$$v_x^{\mathrm{OPM}}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \mathbf{R}^{\mathrm{OPM}}(\mathbf{r}') \cdot d\boldsymbol{\ell}', \tag{5.150}$$

$$\mathbf{R}^{\mathrm{OPM}}(\mathbf{r}) = \boldsymbol{\mathcal{E}}_x(\mathbf{r}) + \boldsymbol{\mathcal{Z}}_{\mathrm{t_c}}^{\mathrm{OPM}}(\mathbf{r}). \tag{5.151}$$

This work done is path independent. Since $\boldsymbol{\nabla} \times \boldsymbol{\mathcal{E}}_x(\mathbf{r}) = 0$, we have from (5.149) that $\boldsymbol{\nabla} \times \boldsymbol{\mathcal{Z}}_{\mathrm{t_c}}^{\mathrm{OPM}}(\mathbf{r}) = 0$. As both $\boldsymbol{\mathcal{E}}_x(\mathbf{r})$ and $\boldsymbol{\mathcal{Z}}_{\mathrm{t_c}}^{\mathrm{OPM}}(\mathbf{r})$ are separately conservative, we may write $v_x^{\mathrm{OPM}}(\mathbf{r})$ as

$$v_x^{\mathrm{OPM}}(\mathbf{r}) = W_x(\mathbf{r}) + W_{\mathrm{t_c}}^{\mathrm{OPM}}(\mathbf{r}), \tag{5.152}$$

where

$$W_x(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{E}}_x(\mathbf{r}') \cdot d\boldsymbol{\ell}' \quad \text{and}$$
$$W_{\mathrm{t_c}}^{\mathrm{OPM}}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{Z}}_{\mathrm{t_c}}^{\mathrm{OPM}}(\mathbf{r}') \cdot d\boldsymbol{\ell}', \tag{5.153}$$

with $W_x(\mathbf{r})$ and $W_{\mathrm{t_c}}^{\mathrm{OPM}}(\mathbf{r})$ the work done in the fields $\boldsymbol{\mathcal{E}}_x(\mathbf{r})$ and $\boldsymbol{\mathcal{Z}}_{\mathrm{t_c}}^{\mathrm{OPM}}(\mathbf{r})$, respectively.

Next, on substituting for $\boldsymbol{\nabla} v_x^{\mathrm{OPM}}(\mathbf{r})$ from (5.149) into (5.139), the XO–OPM exchange energy may be expressed as

$$E_x^{\mathrm{OPM}}[\psi_i] = \int \rho(\mathbf{r})\mathbf{r} \cdot \left[\boldsymbol{\mathcal{E}}_x(\mathbf{r}) + \boldsymbol{\mathcal{Z}}_{\mathrm{t_c}}^{\mathrm{OPM}}(\mathbf{r})\right] d\mathbf{r}. \tag{5.154}$$

Thus, the 'exchange' energy $E_x^{\mathrm{OPM}}[\psi_i]$ and potential energy $v_x^{\mathrm{OPM}}(\mathbf{r})$ of the XO–OPM are comprised of both a Pauli and a Correlation–Kinetic component. The approximations invoked to arrive at (5.152) and (5.154) are predicated by the results of application to atoms, negative atomic ions, and jellium metal surfaces. For example, the ground state energy of atoms in the PC approximation of Q–DFT [23, 24], lie above those of the XO–OPM [25] by less than 25ppm, the difference for ${}^{35}Br - {}^{86}Rn$ being less than 5ppm. The expectation value of single–particle operators are also essentially equivalent. The structure of the exchange potential energies $W_x(\mathbf{r})$ and $v_x^{\mathrm{OPM}}(\mathbf{r})$ are also essentially the same with both decaying as $-1/r$ in the classically forbidden region, and both being finite with zero slope at the nucleus. They differ only in the intershell region where $W_x(\mathbf{r})$ is monotonic with positive slope whereas $v_x^{\mathrm{OPM}}(\mathbf{r})$ possesses bumps. These bumps and the fact that the XO–OPM ground state energies lie slightly below those of the PC approximation of Q–DFT, are consequently attributable to the Correlation–Kinetic effects. The Correlation–Kinetic energy is therefore negligible [22]. For an analysis of the XO–OPM for arbitrary symmetry, the reader is referred to the original literature [22].

5.8.3 B. Derivation via the XO–OPM Integral Equation

It is also possible to derive [22] an expression for $\nabla v_x^{\mathrm{OPM}}(\mathbf{r})$ in terms of its Pauli field component $\boldsymbol{\mathcal{E}}_{\mathrm{x}}^{\mathrm{OPM}}(\mathbf{r})$ and a correction term to it directly from the XO–OPM integral equation (5.134) by invoking the Sharp–Horton approximations [10]. Once again these approximations are justified *ex post facto* by the results of application [23, 24] to atoms and atomic ions. Following Sharp and Horton, the first of these assumes that the eigenvalues ϵ_j in the denominator of the Green's function of (5.130) do not differ significantly from some average value $\langle\epsilon_i\rangle \neq \epsilon_i$ for all j. In the second approximation, each denominator $(\langle\epsilon_i\rangle - \epsilon_i)$ in the Green's function is replaced by a constant $\Delta\epsilon$ independent of the indices i. Thus, the Green's function becomes

$$G_i(\mathbf{r}\mathbf{r}') = \frac{1}{\Delta\epsilon}\sum_j{}' \psi_j(\mathbf{r})\psi_j^*(\mathbf{r}'), \tag{5.155}$$

which on employing the closure relationship may be rewritten as

$$G_i(\mathbf{r}\mathbf{r}') = \frac{1}{\Delta\epsilon}\left[\delta(\mathbf{r}-\mathbf{r}') - \psi_i(\mathbf{r})\psi_i^*(\mathbf{r}')\right]. \tag{5.156}$$

Substituting this expression for the Green's function into the XO–OPM integral equation leads to

$$\begin{aligned} v_x^{\mathrm{OPM}}(\mathbf{r}) = {} & \frac{\sum_i v_{x,i}(\mathbf{r})\psi_i^*(\mathbf{r})\psi_i(\mathbf{r})}{\sum_i \psi_i^*(\mathbf{r})\psi_i(\mathbf{r})} \\ & + \frac{1}{\sum_i \psi_i^*(\mathbf{r})\psi_i(\mathbf{r})}\sum_i \psi_i^*(\mathbf{r})\psi_i(\mathbf{r}) \\ & \times \int \psi_i^*(\mathbf{r}')[v_x^{\mathrm{OPM}}(\mathbf{r}') - v_{x,i}(\mathbf{r}')]\psi_i(\mathbf{r}')d\mathbf{r}'. \end{aligned} \tag{5.157}$$

On substituting for $v_{x,i}(\mathbf{r})$ from (5.123), the first term on the right hand side may be written as

$$v_x^S(\mathbf{r}) = \int \frac{\rho_x^{\mathrm{OPM}}(\mathbf{r}\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}', \tag{5.158}$$

where $\rho_x^{\mathrm{OPM}}(\mathbf{r}\mathbf{r}') = -|\gamma_s^{\mathrm{OPM}}(\mathbf{r}\mathbf{r}'|^2/2\rho(\mathbf{r})$ is the XO–OPM Fermi hole charge. The function $v_x^S(\mathbf{r})$ is known in the literature as the Slater potential energy [26]. However, as will be explained in Chap. 10, $v_x^S(\mathbf{r})$ does not represent the potential energy of an electron. Hence, it is more appropriate to refer to it as the *Slater function*. The expression for $v_x^{\mathrm{OPM}}(\mathbf{r})$ is then

$$v_x^{\mathrm{OPM}}(\mathbf{r}) = v_x^S(\mathbf{r}) + \sum_i \frac{\rho_i(\mathbf{r})}{\rho(\mathbf{r})}[\langle v_x^{\mathrm{OPM}}(\mathbf{r}) - v_{x,i}(\mathbf{r})\rangle_i], \tag{5.159}$$

where $\rho_i(\mathbf{r}) = \psi_i^*(\mathbf{r})\psi_i(\mathbf{r})$, and the expectation $\langle \ \rangle_i$ taken with respect to $\psi_i(\mathbf{r})$. On taking the gradient of (5.159) we obtain

$$\nabla v_x^{\mathrm{OPM}}(\mathbf{r}) = -\mathcal{E}_x^{\mathrm{OPM}}(\mathbf{r}) + \left\{ \int \frac{\nabla \rho_x(\mathbf{r}\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \sum_i \left(\nabla \frac{\rho_i(\mathbf{r})}{\rho(\mathbf{r})} \right) \times \left[\left\langle v_x^{\mathrm{OPM}}(\mathbf{r}) - v_{x,i}(\mathbf{r}) \right\rangle_i \right] \right\}, \tag{5.160}$$

where

$$\mathcal{E}_x^{\mathrm{OPM}}(\mathbf{r}) = \int \frac{\rho_x^{\mathrm{OPM}}(\mathbf{r}\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}'. \tag{5.161}$$

Equation (5.160) is similar to (5.149) derived via the 'Quantal Newtonian' first law. Thus, the correction term in curly brackets may be thought of as being representative of the kinetic field $\mathcal{Z}_{t_c}^{\mathrm{OPM}}(\mathbf{r})$. (Of course, there is nothing in this derivation that identifies this term as a Correlation–Kinetic field. It is only via comparison with (5.149) that one can relate this field to kinetic effects). Thus, once again $v_x^{\mathrm{OPM}}(\mathbf{r})$ can be interpreted as the work done in a conservative field $[\mathcal{E}_x(\mathbf{r}) - \{\ \}]$ representative of Pauli and Correlation–Kinetic contributions. This work done is path independent since $\nabla \times [\mathcal{E}_x(\mathbf{r}) - \{\ \}] = 0$. On substitution of (5.160) into (5.139) one obtains an expression for $E_x^{\mathrm{OPM}}[\psi_i]$ similar to (5.154). Finally, note that if only the delta function term in the approximate Green's function of (5.156) is retained, then $v_x^{\mathrm{OPM}}(\mathbf{r}) = v_x^S(\mathbf{r})$. Thus, the Slater function can be derived from the XO–OPM integral equation [10]. Slater's original derivation [26] of this function is described in Chap. 10.

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Chapter 6
Quantal Density Functional Theory of the Density Amplitude

Abstract The Quantal density functional theory (Q-DFT) mapping from a system of electrons in an external electrostatic field in any state as described by Schrödinger theory to one of noninteracting bosons in their ground state but with the same density is described. The corresponding Schrödinger equation of the model bosons is for the density amplitude, with the sole eigenvalue being the negative of the ionization potential. Via the 'Quantal Newtonian' first law for the model system, the local potential representative of the many-body effects in this equation is the work done in a conservative effective field. The field is the sum of a component representative of electron correlations due to the Pauli Exclusion Principle and Coulomb repulsion, and another of Correlation-Kinetic effects—the difference between these effects for the interacting fermionic and noninteracting bosonic systems. The corresponding components of the total energy are expressed in integral virial form in terms of the respective fields. The traditional density functional theory definitions of these energies and potentials in terms of energy functionals of the density and their functional derivatives are given. The Levy-Perdew-Sahni definition of the local potential in terms of the wave function written as the product of a marginal and conditional probability amplitude is derived. The maps to the model systems of noninteracting bosons and fermions having the same density are related by the Pauli potential and Pauli kinetic energy. By Q–DFT, it is shown that these energies are not a consequence of the Pauli principle but rather a consequence of kinetic effects of the model systems. The Q–DFT definitions of these energies is given. Finally, the mapping to the model of noninteracting bosons is shown to be a special case of that to noninteracting fermions.

Introduction

In time-independent quantal density functional theory (Q–DFT) and Kohn–Sham density functional theory (KS–DFT), the basic idea is the mapping to the model S system of N *noninteracting fermions* whereby the density $\rho(\mathbf{r})$, the total energy E, and the ionization potential I (or electron affinity A) equivalent to that of the interacting electronic system are obtained. In Q–DFT, which is based on the 'Quantal Newtonian' first law, both the total energy E and the local electron–interaction potential energy $v_{\mathrm{ee}}(\mathbf{r})$ of the model fermions, are defined in terms of 'classical' fields and quantal sources. The potential energy $v_{\mathrm{ee}}(\mathbf{r})$ is the work done to move the model fermion in a conservative effective field. The components of the total energy

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E are expressed in integral virial form in terms of fields associated with these components. The highest occupied eigenvalue of the corresponding S system differential equation is the negative of the ionization potential I. In time-independent KS–DFT, the energy E is expressed in terms of component energy functionals of the ground state density $\rho(\mathbf{r})$. The potential energy $v_{\mathrm{ee}}(\mathbf{r})$ of the model fermions is then defined as the functional derivative of the KS electron–interaction energy functional component. Once again the negative of the ionization potential I is the highest occupied eigenvalue of the S system differential equation. Irrespective of the definition of the potential energy $v_{\mathrm{ee}}(\mathbf{r})$ employed to generate the model fermion orbitals, the S system differential equation must be solved N times to obtain the density $\rho(\mathbf{r})$.

Now consider a system of N *noninteracting bosons* in an external field $\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}) = -\boldsymbol{\nabla} v(\mathbf{r})$. This is the same external field as that of the interacting system of electrons. Let us assume these bosons are in their *ground* state, and that they have the same density $\rho(\mathbf{r})$ as the interacting electronic system. As the bosons occupy the *same* state, their wavefunction $\psi_B(\mathbf{r})$ is defined by the equation

$$N[\psi_B(\mathbf{r})]^2 = \rho(\mathbf{r}), \tag{6.1}$$

so that

$$\psi_B(\mathbf{r}) = \frac{1}{\sqrt{N}}\sqrt{\rho(\mathbf{r})}, \tag{6.2}$$

and the normalization condition is

$$\int [\psi_B(\mathbf{r})]^2 d\mathbf{r} = 1. \tag{6.3}$$

If the Schrödinger equation for the model boson system wavefunction $\psi_B(\mathbf{r})$ which is proportional to the density amplitude $\sqrt{\rho(\mathbf{r})}$ could be derived, then solution of this differential equation would lead directly to the density $\rho(\mathbf{r})$. Note that this differential equation would have to be solved only *once* in order to determine the density. In addition, since the bosons are in their ground state, the wavefunction is nodeless. Furthermore, as the bosons are noninteracting, each has the same potential energy. Therefore, in the differential equation, this potential energy is represented by a *local* (multiplicative) operator. The total ground state energy E could then be determined, for example, by employing the fact that the energy is a functional of the ground state density. We refer to the system of noninteracting bosons whereby the density and energy equivalent to that of the interacting system is obtained as the B system.

The simplest derivation [1] of the B system differential equation and the corresponding total energy expression is via traditional density functional theory, and we describe this first. This derivation is restricted to ground states because density functional theory is a ground state theory. The local potential energy of the noninteracting bosons is $v_B(\mathbf{r}) = v(\mathbf{r}) + v_{\mathrm{ee}}^B(\mathbf{r})$, with $v_{\mathrm{ee}}^B(\mathbf{r})$ defined in this framework as a functional derivative. However, the differential equation may also be derived [1] directly from the Schrödinger equation for the electrons. Thus, the B system differential equation is also valid for excited states of the interacting system. In this second derivation which is described next, the potential energy $v_{\mathrm{ee}}^{B}(\mathbf{r})$ is obtained in terms of a conditional probability amplitude that describes the $(N-1)$ electron system when the position of the remaining electron is fixed. Finally, via the 'Quantal Newtonian' first laws for the interacting and model boson systems, we derive the equations of the corresponding Q–DFT mapping. In this framework, valid for both ground and excited states of the interacting system, the total energy E and the potential energy $v_{\mathrm{ee}}^{B}(\mathbf{r})$ are once again described in terms of 'classical' fields and their quantal sources, with $v_{\mathrm{ee}}^{B}(\mathbf{r})$ being the work done in a conservative effective field. The sole eigenvalue of the B system differential equation is proved to be the chemical potential.

The model S and B systems, which both generate the density $\rho(\mathbf{r})$, are related by what is referred to in the literature [2] as the Pauli kinetic energy T_P and the Pauli potential energy $v_P(\mathbf{r})$. These energies are *not* a consequence of the Pauli exclusion principle as stated in the literature, but depend rather on the difference in the kinetic aspects of the S and B systems as proved below. The traditional density functional theory and Q–DFT definitions of these properties are also given.

6.1 Density Functional Theory of the *B* System

In Hohenberg–Kohn (HK) density functional theory, the nondegenerate ground state energy functional of the density $\rho(\mathbf{r})$ is written as (4.23)

$$E[\rho] = \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + F_{\mathrm{HK}}[\rho], \tag{6.4}$$

where $v(\mathbf{r})$ is the external potential energy, and $F_{\mathrm{HK}}[\rho]$ the universal functional

$$F_{\mathrm{HK}}[\rho] = \langle \psi[\rho] | \hat{T} + \hat{U} | \psi[\rho] \rangle. \tag{6.5}$$

The ground state density is determined by the Euler–Lagrange equation subject to the constraint $\int \rho(\mathbf{r}) d\mathbf{r} = N$:

$$\delta \left(E[\rho] - \mu \int \rho(\mathbf{r}) d\mathbf{r} \right) = 0, \tag{6.6}$$

or

$$\delta E[\rho] / \delta \rho(\mathbf{r}) = \mu, \tag{6.7}$$

where μ is the chemical potential.

Recall that in the KS–DFT description of the S system, the expression for the ground state energy functional is obtained by adding and subtracting from (6.5) the kinetic energy $T_s[\rho]$ of noninteracting fermions with the same density $\rho(\mathbf{r})$. Thus, one obtains (4.80)

$$E[\rho] = T_s[\rho] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + E_{\mathrm{ee}}^{\mathrm{KS}}[\rho], \tag{6.8}$$

with the KS electron–interaction energy functional $E_{\mathrm{ee}}^{\mathrm{KS}}[\rho]$ defined as

$$E_{\mathrm{ee}}^{\mathrm{KS}}[\rho] = F_{\mathrm{HK}}[\rho] - T_s[\rho]. \tag{6.9}$$

The Euler–Lagrange equation for the density is then

$$\frac{\delta T_s[\rho]}{\delta\rho(\mathbf{r})} + v(\mathbf{r}) + \frac{\delta E_{\mathrm{ee}}^{\mathrm{KS}}[\rho]}{\delta\rho(\mathbf{r})} = \mu. \tag{6.10}$$

One could solve this equation if we knew the functional $T_s[\rho]$. However, as the fermions are noninteracting, its solution is equivalent to solving the N single–particle equations of the S system (see (4.76)):

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right]\phi_i(\mathbf{x}) = \epsilon_i\phi_i(\mathbf{x}); \quad i = 1, \ldots, N, \tag{6.11}$$

with the Dirac density matrix being

$$\gamma_s(\mathbf{r}\mathbf{r}') = \sum_\sigma \sum_i \phi_i^*(\mathbf{r}\sigma)\phi_i(\mathbf{r}'\sigma), \tag{6.12}$$

whose diagonal matrix element is the density: $\rho(\mathbf{r}) = \gamma_s(\mathbf{r}\mathbf{r})$. The potential energy $v_s(\mathbf{r})$ of the noninteracting fermions is

$$v_s(\mathbf{r}) = v(\mathbf{r}) + v_{\mathrm{ee}}(\mathbf{r}), \tag{6.13}$$

where

$$v_{\mathrm{ee}}(\mathbf{r}) = \frac{\delta E_{\mathrm{ee}}^{\mathrm{KS}}[\rho]}{\delta\rho(\mathbf{r})}, \tag{6.14}$$

is the electron–interaction potential energy.

In order to construct the B system, let us add and subtract the kinetic energy $T_B[\rho]$ of N *noninteracting bosons* of density $\rho(\mathbf{r})$ in their ground state to the energy functional expression of (6.4). Assuming the mass of the bosons in atomic units is unity, their kinetic energy $T_B[\rho]$ is

$$T_B[\rho] = N \int \psi_B^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2\right) \psi_B(\mathbf{r}) d\mathbf{r}$$
$$= \int \sqrt{\rho(\mathbf{r})} \left(-\frac{1}{2}\nabla^2\right) \sqrt{\rho(\mathbf{r})} d\mathbf{r}. \tag{6.15}$$

Note that in this case the kinetic energy functional of the density is explicitly defined. The B system ground state energy expression is then

$$E[\rho] = T_B[\rho] + \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + E_{\mathrm{ee}}^B[\rho] \tag{6.16}$$

where

$$E_{\mathrm{ee}}^B[\rho] = F_{\mathrm{HK}}[\rho] - T_B[\rho]. \tag{6.17}$$

It is evident from (6.17) that the B system electron–interaction energy functional $E_{\mathrm{ee}}^B[\rho]$ accounts for electron correlations due to the Pauli exclusion principle and Coulomb repulsion as well as Correlation–Kinetic effects. The Correlation–Kinetic effects in turn arise due to the difference in the kinetic energy of the interacting system and that of the noninteracting bosons.

The B system differential equation is obtained by application of the Euler–Lagrange equation to (6.16). Noting that

$$\frac{\delta}{\delta \rho(\mathbf{r})} T_B[\rho] = -\frac{1}{2\sqrt{\rho(\mathbf{r})}} \nabla^2 \sqrt{\rho(\mathbf{r})}, \tag{6.18}$$

substitution of the functional derivative of (6.16) into (6.7) then leads to the B system differential equation for the density amplitude $\sqrt{\rho(\mathbf{r})}$:

$$\left[-\frac{1}{2}\nabla^2 + v_B(\mathbf{r})\right] \sqrt{\rho(\mathbf{r})} = \mu \sqrt{\rho(\mathbf{r})}. \tag{6.19}$$

The potential energy of the bosons $v_B(\mathbf{r})$ is

$$v_B(\mathbf{r}) = v(\mathbf{r}) + v_{\mathrm{ee}}^B(\mathbf{r}), \tag{6.20}$$

with its electron–interaction component $v_{\mathrm{ee}}^B(\mathbf{r})$ obtained as the functional derivative

$$v_{\mathrm{ee}}^B(\mathbf{r}) = \frac{\delta E_{\mathrm{ee}}^B[\rho]}{\delta \rho(\mathbf{r})}. \tag{6.21}$$

Thus, in traditional density functional theory, the B system is described by the equations (6.16) and (6.19), with the potential energy $v_{\mathrm{ee}}^B(\mathbf{r})$ defined by (6.21). The single eigenvalue μ is the chemical potential. Depending upon the direction in which the functional derivative is taken, a statement to be explained more fully in the next chapter, the chemical potential μ is the negative of the ionization energy [3].

The B system differential equation (6.19) for the density amplitude $\sqrt{\rho(\mathbf{r})}$ may also be derived [2, 4–6] via the von Weizsäcker [7] kinetic energy functional $T_W[\rho]$ defined as

$$T_W[\rho] = \frac{1}{8}\int \frac{|\boldsymbol{\nabla}\rho(\mathbf{r})|^2}{\rho(\mathbf{r})} d\mathbf{r}. \tag{6.22}$$

The functional $T_W[\rho]$ is equivalent to the kinetic energy $T_B[\rho]$ of the noninteracting bosons. This is readily seen to be the case since

$$\sqrt{\rho(\mathbf{r})}\left(-\frac{1}{2}\nabla^2\right)\sqrt{\rho(\mathbf{r})} = -\frac{1}{4}\nabla^2\rho(\mathbf{r}) + \frac{1}{8}\frac{|\boldsymbol{\nabla}\rho(\mathbf{r})|^2}{\rho(\mathbf{r})}, \tag{6.23}$$

and the fact that the first term on the right hand side does not contribute to the energy integral because the density vanishes at the surface.

As we have seen, in the construction of the model system, one is free to choose the statistics of the noninteracting particles, as well as their masses and spins. The advantage of choosing noninteracting bosons instead of fermions is that one then obtains a differential equation directly for the density amplitude $\sqrt{\rho(\mathbf{r})}$. This equation is solved *once* to obtain the density. The ground state energy E is then determined from (6.16). The single eigenvalue μ in turn gives the ionization potential. Thus, in principle, the B system constitutes a more computationally efficient framework for the determination of electronic structure than that of the S system.

6.1.1 DFT Definitions of the Pauli Kinetic and Potential Energies

The relationship between the model B and S systems is expressed via the Pauli kinetic energy $T_P[\rho]$ defined as

$$T_P[\rho] = E_{\mathrm{ee}}^{B}[\rho] - E_{\mathrm{ee}}^{KS}[\rho], \tag{6.24}$$

which on substituting for $E_{\mathrm{ee}}^{KS}[\rho]$ and $E_{\mathrm{ee}}^{B}[\rho]$ from (6.9) and (6.17), respectively, leads to

$$T_P[\rho] = T_s[\rho] - T_B[\rho]. \tag{6.25}$$

Hence, it is evident that $T_P[\rho]$ is representative only of kinetic effects. The Pauli potential energy $v_P(\mathbf{r})$ is the functional derivative of $T_P[\rho]$:

$$v_P(\mathbf{r}) = \frac{\delta T_P[\rho]}{\delta\rho(\mathbf{r})} = \frac{\delta T_s[\rho]}{\delta\rho(\mathbf{r})} + \frac{1}{2\sqrt{\rho(\mathbf{r})}}\nabla^2\sqrt{\rho(\mathbf{r})} \tag{6.26}$$

$$= v_{\mathrm{ee}}^{B}(\mathbf{r}) - v_{\mathrm{ee}}(\mathbf{r}) \tag{6.27}$$

$$= v_B(\mathbf{r}) - v_s(\mathbf{r}). \tag{6.28}$$

The Pauli kinetic and potential energies are also related by the integral virial expression [8]

$$T_P[\rho] = -\frac{1}{2}\int \rho(\mathbf{r})\mathbf{r}\cdot\nabla v_P(\mathbf{r})d\mathbf{r}. \tag{6.29}$$

For additional properties of $v_P(\mathbf{r})$ and T_P, we refer the reader to [8, 9].

6.2 Derivation of the Differential Equation for the Density Amplitude from the Schrödinger Equation

In this section we derive [1] the B system differential equation (6.19) for the density amplitude $\sqrt{\rho(\mathbf{r})}$ directly from the Schrödinger equation. As a consequence, the potential energy $v^B_{\text{ee}}(\mathbf{r})$ is expressed as an expectation value taken with respect to a conditional probability amplitude.

We partition the N–electron Hamiltonian of (2.131) as in (2.150):

$$\hat{H} = -\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \sum_{i=2}^{N}\frac{1}{|\mathbf{r}-\mathbf{r}_i|} + \hat{H}^{N-1}, \tag{6.30}$$

where $\hat{H}^{N-1}$ is the $(N-1)$–electron Hamiltonian (2.151). The ground or excited state wavefunction $\psi(\mathbf{X})$ of the time-independent Schrödinger equation (2.133) is factored as [10]

$$\psi(\mathbf{X}) = f(\mathbf{r})\phi\left(\mathbf{X}^{N-1},\sigma|\mathbf{r}\right), \tag{6.31}$$

where $f(\mathbf{r})$ is a marginal probability amplitude for an electron at $\mathbf{r}$, and ϕ^{N-1} $(\mathbf{X}^{N-1},\sigma|\mathbf{r})$ the conditional probability amplitude associated with the other $(N-1)$ electrons at $\mathbf{X}^{N-1}$ when one electron is known to be at $\mathbf{r}$. The conditional amplitude is antisymmetric in the $(N-1)$ electrons, and depends parametrically on the position vector $\mathbf{r}$ and spin coordinate σ of that electron. The normalization condition for the wavefunction then dictates the normalizations

$$\sum_\sigma \int \phi^*\left(\mathbf{X}^{N-1},\sigma|\mathbf{r}\right)\phi\left(\mathbf{X}^{N-1},\sigma|\mathbf{r}\right)d\mathbf{X}^{N-1} = 1 \quad \text{for each} \quad \mathbf{r}, \tag{6.32}$$

and

$$\int f^*(\mathbf{r})f(\mathbf{r})d\mathbf{r} = 1. \tag{6.33}$$

Note that in the normalization condition (6.32), the integration is over the space–spin coordinates of the $(N-1)$ electrons and the spin coordinate σ of the electron at $\mathbf{r}$. (We will assume this to be the case for all the integrations below: $\langle\ \rangle \equiv \sum_\sigma \int d\mathbf{X}^{N-1}$.)

With the wavefunction $\psi(\mathbf{X})$ expressed as by (6.31), the density $\rho(\mathbf{r})$ is (see (2.144))

$$\begin{aligned}\rho(\mathbf{r}) &= N\sum_{\sigma}\int \psi^*(\mathbf{X})\psi(\mathbf{X})d\mathbf{X}^{N-1}\\ &= Nf^*(\mathbf{r})f(\mathbf{r})\sum_{\sigma}\int \phi^*\left(\mathbf{X}^{N-1},\sigma|\mathbf{r}\right)\phi\left(\mathbf{X}^{N-1},\sigma|\mathbf{r}\right)d\mathbf{X}^{N-1}\\ &= Nf^*(\mathbf{r})f(\mathbf{r}),\end{aligned} \tag{6.34}$$

so that the marginal amplitude $f(\mathbf{r})$ is

$$f(\mathbf{r}) = \frac{1}{\sqrt{N}}\sqrt{\rho(\mathbf{r})}. \tag{6.35}$$

(Note that this is the B system wavefunction $\psi_B(\mathbf{r})$.)

Thus, the wavefunction may be expressed as

$$\psi(\mathbf{X}) = \frac{1}{\sqrt{N}}\sqrt{\rho(\mathbf{r})}\phi^{N-1}(\mathbf{X}^{N-1},\sigma|\mathbf{r}). \tag{6.36}$$

With $\hat{H}$ and $\psi(\mathbf{X})$ defined by (6.30) and (6.31) respectively, the Schrödinger equation is

$$\begin{aligned}\left(-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \sum_{i=2}^{N}\frac{1}{|\mathbf{r}-\mathbf{r}_i|} + \hat{H}^{N-1}\right)f(\mathbf{r})\phi(\mathbf{X}^{N-1},\sigma|\mathbf{r})&\\ = E_N f(\mathbf{r})\phi(\mathbf{X}^{N-1},\sigma|\mathbf{r}),&\end{aligned} \tag{6.37}$$

where E_N is the energy of the N–electron system. Multiplying (6.37) by $\phi^*(\mathbf{X}^{N-1}, \sigma|\mathbf{r})$ and performing the integration described above leads to

$$\begin{aligned}\langle\phi| -\frac{1}{2}\nabla^2 + v(\mathbf{r})|\phi\rangle f(\mathbf{r}) + (N-1)\langle\phi|\frac{1}{\mathbf{r}-\mathbf{r}_2}|\phi\rangle f(\mathbf{r})&\\ + \langle\phi|\hat{H}^{N-1}|\phi\rangle f(\mathbf{r}) = E_N f(\mathbf{r}).&\end{aligned} \tag{6.38}$$

Consider next the kinetic energy term

$$\begin{aligned}\langle\phi\left(\mathbf{X}^{N-1},\sigma|\mathbf{r}\right)| -\frac{1}{2}\nabla^2|\phi\left(\mathbf{X}^{N-1},\sigma|\mathbf{r}\right)\rangle f(\mathbf{r}) =&\\ \langle\phi\left(\mathbf{X}^{N-1},\sigma|\mathbf{r}\right)| -\frac{1}{2}\nabla^2|\phi\left(\mathbf{X}^{N-1},\sigma|\mathbf{r}\right)f(\mathbf{r})\rangle.&\end{aligned} \tag{6.39}$$

Using $\nabla^2(AB) = A\nabla^2 B + B\nabla^2 A + 2\boldsymbol{\nabla} A \cdot \boldsymbol{\nabla} B$, we have

$$-\frac{1}{2}\nabla^2(\phi f) = -\frac{1}{2}\left[\phi\nabla^2 f(\mathbf{r}) + f(\mathbf{r})\nabla^2\phi + 2\boldsymbol{\nabla} f(\mathbf{r}) \cdot \boldsymbol{\nabla}\phi\right] \tag{6.40}$$

so that

$$\left\langle\phi\right| - \frac{1}{2}\nabla^2\left|\phi f\right\rangle = -\frac{1}{2}\nabla^2 f(\mathbf{r}) - \frac{1}{2} f(\mathbf{r})\langle\phi|\nabla^2|\phi\rangle - \langle\phi|\boldsymbol{\nabla} f \cdot \boldsymbol{\nabla}\phi\rangle. \tag{6.41}$$

The last term of (6.41) on using (6.32) is

$$\langle\phi|\boldsymbol{\nabla} f \cdot \boldsymbol{\nabla}\phi\rangle = \frac{1}{2}\boldsymbol{\nabla} f \cdot \boldsymbol{\nabla}\langle\phi|\phi\rangle = 0, \tag{6.42}$$

so that (6.38) becomes

$$\left[-\frac{1}{2}\nabla^2 + \widetilde{v}_B(\mathbf{r})\right] f(\mathbf{r}) = E_N f(\mathbf{r}), \tag{6.43}$$

where

$$\widetilde{v}_B(\mathbf{r}) = v(\mathbf{r}) + \int \frac{\widetilde{\rho}^{N-1}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \left\langle\phi\right| - \frac{1}{2}\nabla^2\left|\phi\right\rangle + \langle\phi|\hat{H}^{N-1}|\phi\rangle, \tag{6.44}$$

and $\widetilde{\rho}^{N-1}(\mathbf{r})$ the electron density of that $\phi(\mathbf{X}^{N-1}, \sigma|\mathbf{r})$ associated with the electron at $\mathbf{r}$. Subtracting $E_{N-1} f(\mathbf{r})$ from (6.44), where E_{N-1} is the $(N-1)$–electron system energy, and noting that $f(\mathbf{r}) \sim \sqrt{\rho(\mathbf{r})}$ we recover the B system differential equation

$$\left[-\frac{1}{2}\nabla^2 + v_B(\mathbf{r})\right]\sqrt{\rho(\mathbf{r})} = \mu\sqrt{\rho(\mathbf{r})}, \tag{6.45}$$

with $v_B(\mathbf{r}) = \widetilde{v}_B(\mathbf{r}) - E_{N-1}$, and $\mu = E_N - E_{N-1}$ the negative of the ionization energy. In this manner, the potential energy $v_B(\mathbf{r})$ is expressed in terms of expectation values taken with respect to the conditional probability $\phi(\mathbf{X}^{N-1}, \sigma|\mathbf{r})$.

An important property of the potential energy $v_B(\mathbf{r})$ is obtained as follows. Since

$$\nabla^2\langle\phi|\phi\rangle = 0 \tag{6.46}$$

and

$$\nabla^2\langle\phi|\phi\rangle = 2\langle\boldsymbol{\nabla}\phi \cdot \boldsymbol{\nabla}\phi\rangle + 2\langle\phi|\nabla^2|\phi\rangle, \tag{6.47}$$

we have

$$\left\langle\phi\right| - \frac{1}{2}\nabla^2\left|\phi\right\rangle = \frac{1}{2}\langle\boldsymbol{\nabla}\phi \cdot \boldsymbol{\nabla}\phi\rangle \geq 0, \tag{6.48}$$

because the integrand is positive. Then rewriting the expression for $v_B(\mathbf{r})$ as

$$\begin{aligned} v_B(\mathbf{r}) = v(\mathbf{r}) + \int \frac{\widetilde{\rho}^{N-1}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \\ + \langle \phi(\mathbf{X}^{N-1}, \sigma|r)|\hat{H}^{N-1} - E_{N-1}|\phi(\mathbf{X}^{N-1}, \sigma|\mathbf{r}\rangle \\ + \frac{1}{2}\langle \nabla\phi(\mathbf{X}^{N-1}, \sigma|r) \cdot \nabla\phi(\mathbf{X}^{N-1}, \sigma|\mathbf{r})\rangle, \end{aligned} \tag{6.49}$$

we note that

$$v_B(\mathbf{r}) - v(\mathbf{r}) \geq 0, \tag{6.50}$$

as none of the other terms are negative.

Finally, it can be proved that the kinetic energy T of the interacting system is greater than that of the noninteracting bosons T_B with the same density $\rho(\mathbf{r})$:

$$T \geq T_B. \tag{6.51}$$

From (6.41), (6.42), and (6.48) we have that

$$\left\langle \psi(\mathbf{X})| - \frac{1}{2}\nabla^2|\psi(\mathbf{X})\right\rangle = \left\langle f(\mathbf{r})| - \frac{1}{2}\nabla^2|f(\mathbf{r})\right\rangle + \frac{1}{2}\left\langle \nabla\phi \cdot \nabla\phi \right\rangle, \tag{6.52}$$

so that

$$\langle \psi(\mathbf{X})| - \frac{1}{2}\nabla^2|\psi(\mathbf{X})\rangle \geq \left\langle f(\mathbf{r})| - \frac{1}{2}\nabla^2|f(\mathbf{r})\right\rangle. \tag{6.53}$$

Multiplying both sides of (6.53) by N and using the symmetry of the wavefunction $\psi(\mathbf{X})$ we obtain

$$\langle \psi(\mathbf{X})| - \sum_{i=1}^{N} \frac{1}{2}\nabla_i^2|\psi(\mathbf{X})\rangle \geq \int \sqrt{\rho(\mathbf{r})}\left(-\frac{1}{2}\nabla^2\right)\sqrt{\rho(\mathbf{r})}d\mathbf{r}, \tag{6.54}$$

which proves (6.51).

6.3 Quantal Density Functional Theory of the *B* System

As was the case of the Q–DFT mapping to the S system, the Q–DFT of the B system is in terms of quantal sources and 'classical' fields. The B system, of course, must account for electron correlations due to the Pauli principle and Coulomb repulsion. In addition, as we have seen, the kinetic energy of the noninteracting bosons is different from that of the interacting system. Thus, the B system must also account for Correlation–Kinetic effects. Hence again, the fields describing the B system must be in terms of the properties of both the B and interacting systems. And again, there must exist an effective field $\mathcal{F}_B^{\mathrm{eff}}(\mathbf{r})$ in which the electron–interaction potential energy of the model bosons is $v_{\mathrm{ee}}^B(\mathbf{r})$.

Within Q–DFT the potential energy $v_{\mathrm{ee}}^B(\mathbf{r})$ of the noninteracting bosons is the work done to move a model boson in the conservative effective field $\mathcal{F}_B^{\mathrm{eff}}(\mathbf{r})$:

$$v_{\mathrm{ee}}^B(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \mathcal{F}_B^{\mathrm{eff}}(\mathbf{r}') \cdot d\boldsymbol{\ell}'. \tag{6.55}$$

Since $\nabla \times \mathcal{F}_B^{\mathrm{eff}}(\mathbf{r}) = 0$, this work done is *path–independent*. The effective field $\mathcal{F}_B^{\mathrm{eff}}(\mathbf{r})$ is the sum of the interacting system electron–interaction field $\mathcal{E}_{\mathrm{ee}}(\mathbf{r})$, and a Correlation–Kinetic field $\mathcal{Z}_{t_c}^B(\mathbf{r})$:

$$\mathcal{F}_B^{\mathrm{eff}}(\mathbf{r}) = \mathcal{E}_{\mathrm{ee}}(\mathbf{r}) + \mathcal{Z}_{t_c}^B(\mathbf{r}). \tag{6.56}$$

The field $\mathcal{E}_{\mathrm{ee}}(\mathbf{r})$ is obtained from Coulomb's law from the pair–correlation density $g(\mathbf{r}\mathbf{r}')$ which constitutes its source:

$$\mathcal{E}_{\mathrm{ee}}(\mathbf{r}) = \int \frac{g(\mathbf{r}\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}', \tag{6.57}$$

where $g(\mathbf{r}\mathbf{r}') = \langle \psi(\mathbf{X}) | \hat{P}(\mathbf{r}\mathbf{r}') | \psi(\mathbf{X}) \rangle / \rho(\mathbf{r})$ with $\psi(\mathbf{X})$ the eigenfunctions of the time-independent Schrödinger equation (2.133) and $\hat{P}(\mathbf{r}\mathbf{r}')$ the pair operator of (2.28). The field $\mathcal{Z}_{t_c}^B(\mathbf{r})$ is the difference of two kinetic fields, $\mathcal{Z}_B(\mathbf{r})$ and $\mathcal{Z}(\mathbf{r})$ of the model boson and Schrödinger systems, respectively:

$$\mathcal{Z}_{t_c}^B(\mathbf{r}) = \mathcal{Z}_B(\mathbf{r}) - \mathcal{Z}(\mathbf{r}), \tag{6.58}$$

where

$$\mathcal{Z}_B(\mathbf{r}) = \frac{z_B(\mathbf{r}; [\gamma_B])}{\rho(\mathbf{r})} \quad \text{and} \quad \mathcal{Z}(\mathbf{r}) = \frac{z(\mathbf{r}; [\gamma])}{\rho(\mathbf{r})}. \tag{6.59}$$

The B system kinetic 'force' $z_B(\mathbf{r}; [\gamma_B])$ is defined in terms of the corresponding kinetic–energy–density tensor $t_{B,\alpha\beta}(\mathbf{r})$ as

$$z_{B,\alpha}(\mathbf{r}) = 2 \sum_\beta \frac{\partial}{\partial r_\beta} t_{B,\alpha\beta}(\mathbf{r}; [\gamma_B]), \tag{6.60}$$

with

$$t_{B,\alpha\beta}(\mathbf{r}) = \frac{1}{4} \left[\frac{\partial^2}{\partial r'_\alpha \partial r''_\beta} + \frac{\partial^2}{\partial r'_\beta \partial r''_\alpha} \right] \gamma_B(\mathbf{r}'\mathbf{r}'')|_{\mathbf{r}'=\mathbf{r}''=\mathbf{r}}, \tag{6.61}$$

and where the model boson system density matrix $\gamma_B(\mathbf{r}\mathbf{r}')$ quantal source is

$$\gamma_B(\mathbf{r}\mathbf{r}') = N\psi_B^*(\mathbf{r})\psi_B(\mathbf{r}') = \sqrt{\rho(\mathbf{r})}\sqrt{\rho(\mathbf{r}')}. \tag{6.62}$$

The kinetic 'force' $z(\mathbf{r}; [\gamma])$ is defined similarly in terms of the interacting system density matrix $\gamma(\mathbf{r}\mathbf{r}')$.

The interacting system energy E may then be written as

$$E = T_B + \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + E_{\text{ee}} + T_c^B, \tag{6.63}$$

where the kinetic energy of the bosons T_B is given by (6.15), and the electron–interaction E_{ee} and Correlation–Kinetic T_c^B energies expressed in integral virial form, respectively, are

$$E_{\text{ee}} = \int \rho(\mathbf{r}) \mathbf{r} \cdot \boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}) d\mathbf{r}, \tag{6.64}$$

and

$$T_c^B = \frac{1}{2} \int \rho(\mathbf{r}) \mathbf{r} \cdot \boldsymbol{\mathcal{Z}}_{t_c}^B(\mathbf{r}) d\mathbf{r}. \tag{6.65}$$

The expression for E_{ee} and T_c^B are independent of whether the fields $\boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r})$ and $\boldsymbol{\mathcal{Z}}_{t_c}^B(\mathbf{r})$ are conservative or not. Equations (6.55) and (6.63) constitute the Q–DFT of the B system. These equations are valid for the transformation from both the ground and excited states of the interacting system. Irrespective of the state of the interacting system, the B system is always constructed to be in its ground state.

The proof of the Q–DFT mapping to the B system is as follows. The boson wave function $\psi_B(\mathbf{r})$ of (6.2) is the solution to the differential equation (6.19). It therefore satisfies the 'Quantal Newtonian' first law:

$$\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}) + \boldsymbol{\mathcal{F}}_B^{\text{int}}(\mathbf{r}) = 0 \tag{6.66}$$

where the internal field experienced by each boson is

$$\boldsymbol{\mathcal{F}}_B^{\text{int}}(\mathbf{r}) = -\boldsymbol{\nabla} v_{\text{ee}}^B(\mathbf{r}) - \boldsymbol{\mathcal{D}}(\mathbf{r}) - \boldsymbol{\mathcal{Z}}_B(\mathbf{r}), \tag{6.67}$$

with $\boldsymbol{\mathcal{D}}(\mathbf{r}) = \mathbf{d}(\mathbf{r})/\rho(\mathbf{r})$, $\mathbf{d}(\mathbf{r}) = -\frac{1}{4}\boldsymbol{\nabla}\nabla^2\rho(\mathbf{r})$, and $\boldsymbol{\mathcal{Z}}_B(\mathbf{r})$ is defined by (6.59). Note that $\boldsymbol{\nabla} \times \boldsymbol{\mathcal{Z}}_B(\mathbf{r}) = 0$. The 'Quantal Newtonian' first law for the interacting electrons is (see Sect. 3.4.1)

$$\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}) + \boldsymbol{\mathcal{F}}^{\text{int}}(\mathbf{r}) = 0 \tag{6.68}$$

where the corresponding internal field is

$$\boldsymbol{\mathcal{F}}^{\text{int}}(\mathbf{r}) = \boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}) - \boldsymbol{\mathcal{D}}(\mathbf{r}) - \boldsymbol{\mathcal{Z}}(\mathbf{r}), \tag{6.69}$$

with the components of $\mathcal{F}^{\text{int}}(\mathbf{r})$ as defined above. Equating (6.66) and (6.68) leads to

$$\nabla v_{\text{ee}}^{B}(\mathbf{r}) = -\mathcal{F}_{B}^{\text{eff}}(\mathbf{r}), \tag{6.70}$$

with $\mathcal{F}_{B}^{\text{eff}}(\mathbf{r})$ defined by (6.56). The interpretation of $v_{\text{ee}}^{B}(\mathbf{r})$ as the work done in the field $\mathcal{F}_{B}^{\text{eff}}(\mathbf{r})$ is thus proved. Note that although $\mathcal{F}_{B}^{\text{eff}}(\mathbf{r})$ is conservative, the fields $\boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r})$ and $\boldsymbol{\mathcal{Z}}_{t_c}^{B}(\mathbf{r})$ are in general not curl free. For systems of symmetry such that $\nabla \times \boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}) = 0$ and $\nabla \times \boldsymbol{\mathcal{Z}}_{t_c}^{B}(\mathbf{r}) = 0$, the potential energy $v_{\text{ee}}^{B}(\mathbf{r})$ may by written as

$$v_{\text{ee}}^{B}(\mathbf{r}) = W_{\text{ee}}(\mathbf{r}) + W_{t_c}^{B}(\mathbf{r}), \tag{6.71}$$

where $W_{\text{ee}}(\mathbf{r})$ and $W_{t_c}^{B}(\mathbf{r})$ are respectively the work done in the fields $\boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r})$ and $\boldsymbol{\mathcal{Z}}_{t_c}^{B}(\mathbf{r})$:

$$W_{\text{ee}}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}') \cdot d\boldsymbol{\ell}' \quad \text{and} \quad W_{t_c}^{B}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{Z}}_{t_c}^{B}(\mathbf{r}') \cdot d\boldsymbol{\ell}'. \tag{6.72}$$

The work done $W_{\text{ee}}(\mathbf{r})$ and $W_{t_c}^{B}(\mathbf{r})$ are separately *path-independent*.

The kinetic energy T_B of the noninteracting bosons (6.15) may also be expressed in terms of the kinetic field $\boldsymbol{\mathcal{Z}}_B(\mathbf{r})$ as

$$T_B = -\frac{1}{2}\int \rho(\mathbf{r})\mathbf{r} \cdot \boldsymbol{\mathcal{Z}}_B(\mathbf{r})d\mathbf{r}. \tag{6.73}$$

The integral virial expression for the Correlation–Kinetic energy T_c^{B} of (6.65) then follows by subtracting T_B from the kinetic energy T of the interacting system as given by (2.70).

For two electron systems such as the Helium atom, Hydrogen molecule, and the Hooke's atom, the S system in its ground state and the B system are equivalent. This is because the spatial part of each S system orbital $\phi(\mathbf{x})$ is $\psi(\mathbf{r}) = \psi_B(\mathbf{r}) \propto \sqrt{\rho(\mathbf{r})}$ (see Sect. 3.5). Hence, all the quantal sources, fields etc. of the two systems are the same. The Q–DFT example of the ground state S system description of the ground and first excited singlet states of the Hooke's atom (Sect. 3.5) is therefore also that of the Q–DFT B system representation of these states. The example thus clearly demonstrates that B systems can be constructed for both ground and excited states of the interacting system.

It is also possible to construct B systems whereby the density and total energy of Hartree–Fock and Hartree theories is obtained. The basic Q–DFT equations are the same but with the interacting system pair–correlation density $g(\mathbf{r}\mathbf{r}')$ and density matrix $\gamma(\mathbf{r}\mathbf{r}')$ replaced by the corresponding Hartree–Fock and Hartree theory properties.

6.3.1 Q–DFT Definitions of the Pauli Kinetic and Potential Energy

The Q–DFT definition of the S system electron–interaction potential energy $v_{\mathrm{ee}}(\mathbf{r})$ of (3.126) is given by (3.140):

$$v_{\mathrm{ee}}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{F}}^{\mathrm{eff}}(\mathbf{r}') \cdot d\boldsymbol{\ell}', \tag{6.74}$$

where

$$\boldsymbol{\mathcal{F}}^{\mathrm{eff}}(\mathbf{r}) = \boldsymbol{\mathcal{E}}_{\mathrm{ee}}(\mathbf{r}) + \boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r}), \tag{6.75}$$

with

$$\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r}) = \boldsymbol{\mathcal{Z}}_s(\mathbf{r}) - \boldsymbol{\mathcal{Z}}(\mathbf{r}). \tag{6.76}$$

The S system kinetic field $\boldsymbol{\mathcal{Z}}_s(\mathbf{r})$ is obtained from its quantal source, the Dirac density density matrix $\gamma_s(\mathbf{r}\mathbf{r}')$, from the corresponding kinetic–energy–density tensor $t_{s,\alpha\beta}(\mathbf{r}; [\gamma_s])$. Employing the definition (6.27) for the Pauli potential energy $v_P(\mathbf{r})$, we have then

$$v_P(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \left[\boldsymbol{\mathcal{F}}_B^{\mathrm{eff}}(\mathbf{r}') - \boldsymbol{\mathcal{F}}^{\mathrm{eff}}(\mathbf{r}')\right] \cdot d\boldsymbol{\ell}'. \tag{6.77}$$

But from (6.56) and (6.75)

$$\boldsymbol{\mathcal{F}}_B^{\mathrm{eff}}(\mathbf{r}) - \boldsymbol{\mathcal{F}}^{\mathrm{eff}}(\mathbf{r}) = \boldsymbol{\mathcal{Z}}_B(\mathbf{r}) - \boldsymbol{\mathcal{Z}}_s(\mathbf{r}) = \boldsymbol{\mathcal{Z}}_P(\mathbf{r}), \tag{6.78}$$

so that $v_P(\mathbf{r})$ is the work done in the conservative kinetic field $\boldsymbol{\mathcal{Z}}_P(\mathbf{r})$:

$$v_P(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{Z}}_P(\mathbf{r}') \cdot d\boldsymbol{\ell}'. \tag{6.79}$$

Note that the components $\boldsymbol{\mathcal{Z}}_B(\mathbf{r})$ and $\boldsymbol{\mathcal{Z}}_s(\mathbf{r})$ of $\boldsymbol{\mathcal{Z}}_P(\mathbf{r})$ are each separately conservative so that we may write

$$v_P(\mathbf{r}) = W_k^B(\mathbf{r}) - W_k^S(\mathbf{r}), \tag{6.80}$$

where $W_k^B(\mathbf{r})$ and $W_k^S(\mathbf{r})$ are the work done in the kinetic fields $\boldsymbol{\mathcal{Z}}_B(\mathbf{r})$ and $\boldsymbol{\mathcal{Z}}_s(\mathbf{r})$, respectively:

$$W_k^B(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{Z}}_B(\mathbf{r}') \cdot d\boldsymbol{\ell}' \quad \text{and} \quad W_k^S(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{Z}}_s(\mathbf{r}') \cdot d\boldsymbol{\ell}'. \tag{6.81}$$

Since the kinetic energy of the S system when expressed in terms of $\mathcal{Z}_s(\mathbf{r})$ is

$$T_s = -\frac{1}{2}\int \rho(\mathbf{r})\mathbf{r}\cdot\mathcal{Z}_s(\mathbf{r})d\mathbf{r}, \tag{6.82}$$

we have on employing (6.73) and the definition (6.25) of the Pauli kinetic energy T_P that

$$T_P = -\frac{1}{2}\int \rho(\mathbf{r})\mathbf{r}\cdot\mathcal{Z}_P(\mathbf{r})d\mathbf{r}. \tag{6.83}$$

From their Q–DFT expressions, it is again evident that T_P and $v_P(\mathbf{r})$ are due entirely to kinetic effects. They depend on the kinetic field $\mathcal{Z}_P(\mathbf{r})$ which is the difference between the kinetic fields $\mathcal{Z}_B(\mathbf{r})$ and $\mathcal{Z}_s(\mathbf{r})$ of the noninteracting boson and fermion systems. Since for two electron systems, $\mathcal{Z}_B(\mathbf{r}) = \mathcal{Z}_s(\mathbf{r})$, then $v_P(\mathbf{r}) = 0$ and $T_P = 0$.

6.4 Endnote

As noted previously, for two–electron systems, the S and B model systems are equivalent. It turns out, however, that the B system is a special case of the S system [11]. To see this, let us write the spatial part $\psi_i(\mathbf{r})$ of the S system orbital $\phi_i(\mathbf{x})$ as

$$\psi_i(\mathbf{r}) = \sqrt{\rho(\mathbf{r})}c_i(\mathbf{r}), \quad i = 1,\ 2,\ \ldots,\ N, \tag{6.84}$$

where the coefficients $c_i(\mathbf{r})$ satisfy

$$\sum c_i(\mathbf{r})^2 = 1. \tag{6.85}$$

Then with the choice

$$c_i = 1/\sqrt{N}, \tag{6.86}$$

we see that $\psi_i(\mathbf{r}) \propto \sqrt{\rho(\mathbf{r})}$, and that consequently the model of noninteracting bosons becomes a special case of the noninteracting fermion model.

A consequence of the above fact is that many general properties of the S system then translate over to the B system. For example, it has been proved [11], [***QDFT2***] that the S system electron–interaction potential energy $v_{\text{ee}}(\mathbf{r})$ is finite at the nucleus, irrespective of whether the system is in a ground or excited state or whether the system is an atom, a molecule, or a solid. (There is also a separate proof [12], [***QDFT2***] of the finiteness of $v_{\text{ee}}(\mathbf{r})$ at the nucleus of spherically symmetric systems.) The same is therefore the case for the B system electron–interaction potential energy $v_{\text{ee}}^B(\mathbf{r})$. As another example, to be discussed more fully in the next chapter, the S system potential energy $v_{\text{ee}}(\mathbf{r})$ is discontinuous as the electron number passes through an integer value. Thus, the B system potential energy $v_{\text{ee}}^B(\mathbf{r})$ also exhibits such a discontinuity.

For the application of the Q–DFT of the density amplitude to the Be and Mg atoms see [13], [***QDFT2***]. A key result of the mapping from the interacting electrons to one of noninteracting bosons that are all in the *same* ground state with density $\rho(\mathbf{r})$ is that the Correlation–Kinetic effects become very significant.

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Chapter 7
Quantal Density Functional Theory of the Discontinuity in the Electron–Interaction Potential Energy

Abstract In the mapping from an interacting system of electrons in an external field to one of noninteracting fermions possessing the same density, the local electron-interaction potential of the latter, which incorporates all the many-body effects, exhibits a discontinuity as the electron number passes through an integer value. The origin of the discontinuity is explained, and an expression for it derived in terms of the eigenvalues of the corresponding noninteracting fermion Schrödinger equation. According to Kohn-Sham density functional theory, all the different electron correlations, *viz*. those due to the Pauli Exclusion Principle, Coulomb repulsion, and Correlation-Kinetic effects, contribute to the discontinuity. Via Q–DFT it is shown, both analytically as well as by examples, that neither the Pauli principle nor Coulomb correlations contribute, and that the discontinuity is solely an artifact of Correlation-Kinetic effects.

Introduction

The Quantal and Kohn–Sham density functional theory descriptions of the local effective potential energy theories of the previous chapters have been restricted to the case of integer (N) electronic charge, i.e. $\int \rho(\mathbf{r})d\mathbf{r} = N$. However, in order to understand phenomenon such as the dissociation of molecules [1, 2] so that appropriate integer charge exists on the fragments, or properties such as the band structure of semiconductors [2–5], the framework of these theories must be extended to include the case of fractional charge ($N + \omega$; $0 < \omega < 1$). As a consequence of this extension a fundamental property of the local electron–interaction potential energy $v_{\text{ee}}(\mathbf{r})$ of the S system of noninteracting fermions emerges. It turns out that this potential energy exhibits a discontinuity Δ as the electron number passes through an integer value. Equivalently, as the fractional charge ω vanishes from above

$$\Delta = \lim_{\omega \downarrow 0}[v_{\text{ee}}^{(N+\omega)}(\mathbf{r}) - v_{\text{ee}}^{(N)}(\mathbf{r})]. \tag{7.1}$$

(As the B system of noninteracting bosons is a special case of the S system, the corresponding local electron–interaction potential energy $v_{\text{ee}}^{B}(\mathbf{r})$ also exhibits such a discontinuity.) The existence of the discontinuity then explains the dissociation of molecules and leads to the correct expression for the band gap of semiconductors. Thus, for example, the band gap E_{gap} which is defined as the difference between

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the lowest energy level of the conduction band and the highest energy level of the valence band, can be shown to be given by the expression

$$E_{\text{gap}} = \epsilon_{N+1}^{(N)} - \epsilon_N^{(N)} + \Delta, \tag{7.2}$$

where $\epsilon_m^{(M)}$ is the m th eigenvalue of the S system differential equation (3.126) for M model fermions. It is evident, therefore, that solution of the S system differential equation for the ground state of a semiconductor to determine the difference between the first unoccupied orbital energy $\epsilon_{N+1}^{(N)}$ and the last occupied orbital energy $\epsilon_N^{(N)}$ in itself will not lead to a correct value for the band gap. The addition of the discontinuity Δ is essential to determining the gap accurately.

In Kohn–Sham density functional theory (KS–DFT), the electron–interaction potential energy $v_{\text{ee}}(\mathbf{r})$ is defined as the functional derivative $\delta E_{\text{ee}}^{KS}[\rho]/\delta\rho(\mathbf{r})$, where $E_{\text{ee}}^{KS}[\rho]$ is the Kohn–Sham electron–interaction energy functional. As explained in Chap. 5, this energy functional is representative of electron correlations due to the Pauli exclusion principle, Coulomb repulsion, and Correlation–Kinetic effects. As the dependence of the functional $E_{\text{ee}}^{KS}[\rho]$ on the different electron correlations is unknown, one must therefore conclude from the perspective of KS–DFT, that these correlations *all* contribute to the discontinuity Δ. On the other hand, within Quantal density functional theory (Q–DFT), the contribution of each of these correlations to the potential energy $v_{\text{ee}}(\mathbf{r})$ is delineated, and therefore their *separate* contributions to the discontinuity Δ can be studied. It will be shown [6] in this chapter that Pauli and Coulomb correlations do not contribute to the discontinuity in the limit as the fractional charge vanishes, and that the discontinuity is *solely* a consequence of Correlation–Kinetic effects. Furthermore, for finite fractional charge, irrespective of how small it is, there will always be a contribution to the discontinuity from each type of correlation. The smaller the fractional charge, the smaller the Pauli and Coulomb correlation and greater the Correlation–Kinetic contribution. An analytical expression for the discontinuity Δ in terms of fields representative of Correlation–Kinetic effects for the fractionally charged and integer electron systems is consequently derived.

We begin the chapter by explaining the origin of the discontinuity in the electron–interaction potential energy $v_{\text{ee}}(\mathbf{r})$. Next, an expression for the discontinuity for finite systems is derived in terms of the S system eigenvalues. The Q–DFT of the discontinuity, together with numerical examples explicating the theory, is then described.

7.1 Origin of the Discontinuity of the Electron–Interaction Potential Energy

The understanding of the origin of the discontinuity in the S system electron–interaction potential energy $v_{\text{ee}}(\mathbf{r})$ is due to Perdew et al. [1, 2]. Accordingly, the definition of the ground state energy functional $E[\rho]$ of (4.23) must be extended to densities integrating to fractional particle number. Hence, consider a system with a fractional number of electrons $N + \omega$ whose density is $\rho^{(N+\omega)}(\mathbf{r})$ so that

$$\int \rho^{(N+\omega)}(\mathbf{r})d\mathbf{r} = N + \omega, \quad N = \text{integer}; \quad 0 \leq \omega \leq 1. \tag{7.3}$$

The corresponding ground state energy functional $E^{(N+\omega)}[\rho]$ is then

$$E^{(N+\omega)}[\rho] = \int \rho^{(N+\omega)}(\mathbf{r})v(\mathbf{r})d\mathbf{r} + F_{HK}^{(N+\omega)}[\rho], \tag{7.4}$$

with the universal functional $F_{HK}^{(N+\omega)}[\rho]$ in turn defined as

$$F_{HK}^{(N+\omega)}[\rho] = \min_{\hat{D}\to\rho^{(N+\omega)}} tr\{\hat{D}(\hat{T} + \hat{U})\}. \tag{7.5}$$

In (7.5), the search for the minimum is over all ensemble density matrices $\hat{D}$ constructed from an N- and an $(N+1)$-electron function $(\psi^{(N)}, \psi^{(N+1)})$ which yield the density $\rho^{(N+\omega)}(\mathbf{r})$. (Note that the functions $\psi^{(N)}$ and $\psi^{(N+1)}$ are not necessarily the exact ground state wavefunctions of the N- and $(N+1)$-electron systems.)

The density matrix is thus defined as

$$\hat{D} = \alpha^{(N)}|\psi^{(N)}\rangle\langle\psi^{(N)}| + \alpha^{(N+1)}|\psi^{(N+1)}\rangle\langle\psi^{(N+1)}|, \tag{7.6}$$

with

$$\alpha^{(N)} + \alpha^{(N+1)} = 1. \tag{7.7}$$

It yields the density $\rho^{(N+\omega)}(\mathbf{r})$ via

$$\begin{aligned}\rho^{(N+\omega)}(\mathbf{r}) &= tr\{\hat{D}\hat{\rho}\} \\ &= \alpha^{(N)}\langle\psi^{(N)}|\hat{\rho}|\psi^{(N)}\rangle + \alpha^{(N+1)}\langle\psi^{(N+1)}|\hat{\rho}|\psi^{(N+1)}\rangle \\ &= \alpha^{(N)}\rho^{(N)}(\mathbf{r}) + \alpha^{(N+1)}\rho^{(N+1)}(\mathbf{r}),\end{aligned} \tag{7.8}$$

where $\rho^{(N)}(\mathbf{r})$, $\rho^{(N+1)}(\mathbf{r})$ correspond to the N- and $(N+1)$-electron system ground state densities. Integration of (7.8) then leads to

$$\begin{aligned}N + \omega &= \alpha^{(N)}N + \alpha^{(N+1)}(N+1) \\ &= \left(\alpha^{(N)} + \alpha^{(N+1)}\right)N + \alpha^{(N+1)},\end{aligned} \tag{7.9}$$

which on employing (7.7) yields

$$\alpha^{(N+1)} = \omega \quad \text{and} \quad \alpha^{(N)} = (1-\omega). \tag{7.10}$$

The ensemble density matrix $\hat{D}$ is therefore

$$\hat{D} = (1-\omega)|\psi^{(N)}\rangle\langle\psi^{(N)}| + \omega|\psi^{(N+1)}\rangle\langle\psi^{(N+1)}|, \tag{7.11}$$

and the density $\rho^{(N+\omega)}(\mathbf{r})$ is

$$\rho^{(N+\omega)}(\mathbf{r}) = (1-\omega)\rho^{(N)}(\mathbf{r}) + \omega\rho^{(N+1)}(\mathbf{r}). \tag{7.12}$$

The ground state energy $E^{(N+\omega)}[\rho]$ of the $(N+\omega)$-electron system is then obtained by minimizing the energy functional (7.4) with respect to all densities $\rho^{(N+\omega)}(\mathbf{r})$ that integrate to $(N+\omega)$ electrons.

Thus

$$E^{(N+\omega)}[\rho] = \min_{\substack{\rho^{(N+\omega)}(\mathbf{r})\\ \int\rho^{(N+\omega)}(\mathbf{r})d\mathbf{r}=N+\omega}} \left[\int \rho^{(N+\omega)}(\mathbf{r})v(\mathbf{r})d\mathbf{r} + F_{HK}^{(N+\omega)}[\rho]\right] \tag{7.13}$$

$$= \min_{\substack{\rho^{(N+\omega)}(\mathbf{r})\\ \int\rho^{(N+\omega)}(\mathbf{r})d\mathbf{r}=N+\omega}} \min_{\substack{\psi^{(N)},\psi^{(N+1)}\\ (1-\omega)\rho^{(N)}(\mathbf{r})+\omega\rho^{(N+1)}(\mathbf{r})=\rho^{(N+\omega)}(\mathbf{r})}}$$

$$\times\left[(1-\omega)\langle\psi^{(N)}|\hat{H}|\psi^{(N)}\rangle + \omega\langle\psi^{(N+1)}|\hat{H}|\psi^{(N+1)}\rangle\right]. \tag{7.14}$$

The energy minimum is obtained when $|\psi^{(N)}\rangle$ and $|\psi^{(N+1)}\rangle$ are the *exact* ground state wavefunctions of the N- and $(N+1)$-electron systems. The minimizing density $\rho^{(N+\omega)}(\mathbf{r})$ is then given by (7.8) and the energy minimum of (7.14) is given by

$$E^{(N+\omega)} = (1-\omega)E^{(N)} + \omega E^{(N+1)}, \tag{7.15}$$

where $E^{(N)}$ and $E^{(N+1)}$ are the ground state energies of the N- and $(N+1)$-electron systems. Rewriting (7.15) as

$$\begin{aligned} E^{(N+\omega)} &= \left(E^{(N+1)} - E^{(N)}\right)\omega + E^{(N)} \\ &= -A_N\omega + E^{(N)}, \end{aligned} \tag{7.16}$$

where $A_N = E^{(N)} - E^{(N+1)}$ is the electron affinity of the N-electron system, we see that $E^{(N+\omega)}$ as a function of ω is an equation of a straight line. Thus, the energy $E^{(N+\omega)}$ as a function of the fractional charge consists of straight line segments with possible derivative discontinuities at integer N. Equation (7.16) is plotted [7] in Fig. 7.1 in the range $0 \le \omega \le 1$. In the range $-1 \le \omega \le 0$, the corresponding equation is

$$\begin{aligned} E^{(N+\omega)} &= \left(E^{(N)} - E^{(N-1)}\right)\omega + E^{(N)} \\ &= -I_N\omega + E^{(N)}, \end{aligned} \tag{7.17}$$

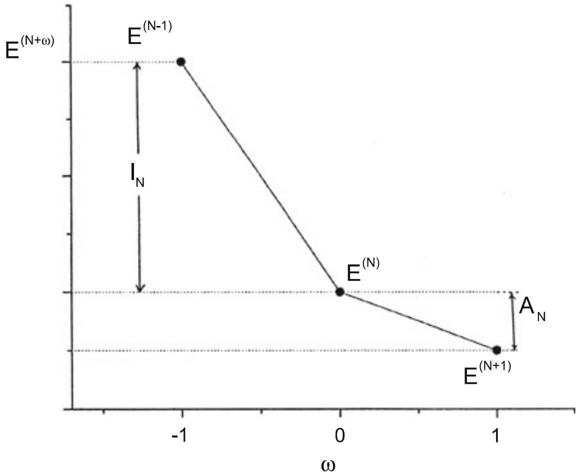


Fig. 7.1 The energy $E^{(N+\omega)}$ of a finite system such as an atom with $(N+\omega)$ electrons as a function of the fractional charge ω [7]

where $I_N = E^{(N-1)} - E^{(N)}$ is the ionization potential of the N-electron system. The straight line of (7.17) is also plotted [7] in Fig. 7.1.

The chemical potential $\mu(N)$ which is the change in the energy as a function of particle number is then (see also Fig. 7.1)

$$\begin{aligned}\mu(N) = \frac{\partial E^{(N+\omega)}}{\partial \omega} &= -I_N \quad \text{for} \quad -1 \leq \omega \leq 0 \\ &= -A_N \quad \text{for} \quad 0 \leq \omega \leq 1.\end{aligned} \tag{7.18}$$

Thus, the chemical potential is discontinuous with discontinuities at integer particle numbers N. As shown in Sect. 4.1, the chemical potential corresponds to the Lagrange multiplier in the Euler–Lagrange equation (4.22) for the density:

$$\frac{\delta}{\delta \rho}\left\{E[\rho] - \mu(N)\int \rho(\mathbf{r}')d\mathbf{r}'\right\} = 0. \tag{7.19}$$

(Note that this equation has now been extended to the case of noninteger charge.) Since the chemical potential is discontinuous, the functional derivative $\delta E[\rho]/\delta\rho(\mathbf{r})$ is discontinuous as the electron number passes through an integer value. With the energy functional $E[\rho]$ written as within KS–DFT (4.80), we see that the S system electron–interaction potential energy $v_{\mathrm{ee}}(\mathbf{r}) = \delta E_{\mathrm{ee}}^{KS}[\rho]/\delta\rho(\mathbf{r})$ is discontinuous. Thus, the origin of the discontinuity in $v_{\mathrm{ee}}(\mathbf{r})$ is the discontinuous nature of the chemical potential as a function of electron number.

7.2 Expression for Discontinuity Δ in Terms of S System Eigenvalues

We next derive [8, 9] an expression for the discontinuity Δ of (7.1) for finite systems. This expression is in terms of the S system eigenvalue of the charge–neutral $(N+1)$-electron system such as an atom, and that of the corresponding N-electron positive ion. We show Δ to be the difference between the highest occupied eigenvalue $\epsilon_{N+1}^{(N+1)}$ of the $(N+1)$-electron system and the $(N+1)$ th eigenvalue $\epsilon_{N+1}^{(N)}$ of the N-electron system. The proof follows.

Consider a fractionally charged $(N+\omega)$ S system with local potential energy $v_s^{(N+\omega)}(\mathbf{r})$. Such a system is defined by the equations

$$\left[-\frac{1}{2}\nabla^2 + v_s^{(N+\omega)}(\mathbf{r})\right]\phi_i^{(N+\omega)}(\mathbf{x}) = \epsilon_i^{(N+\omega)}\phi_i^{(N+\omega)}(\mathbf{x}), \tag{7.20}$$

with

$$\rho^{(N+\omega)}(\mathbf{r}) = \sum_{i=1}^{N}\left|\phi_i^{(N+\omega)}(\mathbf{r})\right|^2 + \omega\left|\phi_{N+1}^{(N+\omega)}(\mathbf{r})\right|^2, \tag{7.21}$$

where the highest occupied orbital has the fractional charge ω. (The spin index σ is suppressed in (7.21).) Equation (7.21) may equivalently be expressed as

$$\rho^{(N+\omega)}(\mathbf{r}) = (1-\omega)\sum_{i=1}^{N}\left|\phi_i^{(N+\omega)}(\mathbf{r})\right|^2 + \omega\sum_{i=1}^{N+1}\left|\phi_i^{(N+\omega)}(\mathbf{r})\right|^2. \tag{7.22}$$

Writing $v_s^{(N+\omega)}(\mathbf{r})$ in terms of its Hartree $v_H^{(N+\omega)}(\mathbf{r})$ and KS 'exchange–correlation' $v_{xc}^{(N+\omega)}(\mathbf{r})$ potentials, we have

$$\begin{aligned} v_s^{(N+\omega)}(\mathbf{r}) &= v(\mathbf{r}) + v_{\text{ee}}^{(N+\omega)}(\mathbf{r}) \\ &= v(\mathbf{r}) + v_H^{(N+\omega)}(\mathbf{r}) + v_{xc}^{(N+\omega)}(\mathbf{r}), \end{aligned} \tag{7.23}$$

where

$$v_H^{(N+\omega)}(\mathbf{r}) = \int \frac{\rho^{(N+\omega)}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'. \tag{7.24}$$

Equations (7.23) and (7.24) then define $v_{xc}^{(N+\omega)}(\mathbf{r})$. Assuming the system under consideration to be finite, we impose the condition that $v_s^{(N+\omega)}(\mathbf{r})$ vanishes at infinity:

$$\lim_{\mathbf{r}\to\infty} v_s^{(N+\omega)}(\mathbf{r}) = 0. \tag{7.25}$$

Since the external and Hartree potential energies also vanish in this limit we then have

$$\lim_{\mathbf{r}\to\infty} v_{xc}^{(N+\omega)}(\mathbf{r}) = 0. \tag{7.26}$$

With this result, the S system orbital densities in general decay asymptotically as

$$|\phi_i(\mathbf{r})|^2 \underset{r\to\infty}{\sim} e^{-2(-2\epsilon_i)^{1/2}r}. \tag{7.27}$$

The highest occupied fractionally charged orbital $\phi_{N+1}^{(N+\omega)}(\mathbf{r})$ has the slowest decay so that the asymptotic structure of the $(N+\omega)$-electron system density is

$$\rho^{(N+\omega)}(\mathbf{r}) \underset{r\to\infty}{\sim} e^{-2(-2\epsilon_{N+1}^{(N+\omega)})^{1/2}r}. \tag{7.28}$$

On the other hand, the asymptotic decay of the N- and $(N+1)$-electron system densities from (2.163) is

$$\rho^{(N)}(\mathbf{r}) \underset{r\to\infty}{\sim} e^{-2(2I_N)^{1/2}r}, \tag{7.29}$$

and

$$\rho^{(N+1)}(\mathbf{r}) \underset{r\to\infty}{\sim} e^{-2(2I_{N+1})^{1/2}r}, \tag{7.30}$$

where I_N and I_{N+1} are the ionization energies for the N- and $(N+1)$-electron systems, respectively. Because the ionization energy for an $(N+1)$-electron system is smaller than that of an N-electron system we have

$$I_{N+1} < I_N, \tag{7.31}$$

and the fact (see (7.12)) that $\rho^{(N+\omega)}(\mathbf{r})$ is a linear combination of $\rho^{(N)}(\mathbf{r})$ and $\rho^{(N+1)}(\mathbf{r})$, we have

$$\rho^{(N+\omega)} \underset{r\to\infty}{\sim} \rho^{(N+1)}(\mathbf{r}) \underset{r\to\infty}{\sim} e^{-2(2I_{N+1})^{1/2}r}. \tag{7.32}$$

A comparison of (7.32) with (7.28) leads to

$$\epsilon_{N+1}^{(N+\omega)} = -I_{N+1} = \epsilon_{N+1}^{(N+1)}, \tag{7.33}$$

where the second equality is a consequence of the fact that the highest occupied eigenvalue of the S system is minus the ionization potential (see Sect. 3.4.8). Equation (7.33) also shows that the highest occupied eigenvalue is independent of the fractional charge ω.

In order to show that $v_s^{(N+\omega)}(\mathbf{r})$ differs from $v_s^{(N)}(\mathbf{r})$ as ω approaches zero from above, let us consider a radius $R(\omega)$ such that

$$\omega\rho^{(N+1)}(R(\omega)) = (1-\omega)\rho^{(N)}(R(\omega)), \tag{7.34}$$

for $r = R(\omega)$. As a consequence of (7.31), $\rho^{(N+1)}(\mathbf{r})$ asymptotically decays more slowly than $\rho^{(N)}(\mathbf{r})$ (see (7.29) and (7.30)). Thus, as ω approaches zero, $R(\omega)$ becomes infinite. For $r < R(\omega)$ and ω approaching zero, the density $\rho^{(N)}(\mathbf{r})$ dominates the ensemble density $\rho^{(N+\omega)}(\mathbf{r})$ of (7.12). Thus, in this region

$$\lim_{\omega \to 0} \rho^{(N+\omega)}(r) = \rho^{(N)}(\mathbf{r}) \quad \text{for} \quad r < R(\omega). \tag{7.35}$$

Therefore, in the region $r < R(\omega)$, both $v_s^{(N+\omega)}(\mathbf{r})$ and $v_s^{(N)}(\mathbf{r})$ generate the same density. As such these potential energies can differ at most by a constant Δ in this region. Since by definition both $v_s^{(N+\omega)}(\mathbf{r})$ and $v_s^{(N)}(\mathbf{r})$ become zero in the limit $r \to \infty$, we have

$$\begin{aligned} v_s^{(N+\omega)}(\mathbf{r}) - v_s^{(N)}(\mathbf{r}) &= \Delta \quad \text{for} \quad r < R(\omega) \\ &= 0 \quad \text{for} \quad r \gg R(\omega). \end{aligned} \tag{7.36}$$

In the limit $\omega \to 0$ the radius $R(\omega)$ becomes infinite and both potentials differ by a constant Δ everywhere. Employing (7.36) in the differential equation (7.20) for the $(N + \omega)$-electron system, and the fact that for small ω in the region $r < R(\omega)$ the orbitals $\phi_i^{(N+\omega)}(\mathbf{x}) \sim \phi_i^{(N)}(\mathbf{x})$, we obtain

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{ee}}^{(N)}(\mathbf{r}) + \Delta \right] \phi_i^{(N)}(\mathbf{x}) = \epsilon_i^{(N+\omega)} \phi_i^{(N)}(\mathbf{x}) \;\; \text{for} \;\; r < R(\omega). \tag{7.37}$$

The corresponding equation for the N-electron system is

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{ee}}^{(N)}(\mathbf{r}) \right] \phi_i^{(N)}(\mathbf{x}) = \epsilon_i^{(N)} \phi_i^{(N)}(\mathbf{x}). \tag{7.38}$$

A comparison of (7.37) and (7.38) shows that

$$\epsilon_i^{(N+\omega)} = \epsilon_i^{(N)} + \Delta \quad \text{for} \quad \omega \to 0. \tag{7.39}$$

In particular for $i = N + 1$ we have

$$\Delta = \lim_{\omega \to 0} \left[\epsilon_{N+1}^{(N+\omega)} - \epsilon_{N+1}^{(N)} \right] = -I_{N+1} - \epsilon_{N+1}^{(N)}, \tag{7.40}$$

where in the last step we have used (7.33). Since

$$v_H^{(N+\omega)}(\mathbf{r}) = v_H^{(N)}(\mathbf{r}) = 0 \quad \text{for} \quad r \to \infty, \tag{7.41}$$

we finally have

$$\begin{aligned}\Delta &= \lim_{\omega\to 0}\left[v_{\mathrm{ee}}^{(N+\omega)}(\mathbf{r}) - v_{\mathrm{ee}}^{(N)}(\mathbf{r})\right]\\ &= \lim_{\omega\to 0}\left[v_{xc}^{(N+\omega)}(\mathbf{r}) - v_{xc}^{(N)}(\mathbf{r})\right]\\ &= \epsilon_{N+1}^{(N+1)} - \epsilon_{N+1}^{(N)},\end{aligned} \tag{7.42}$$

where we have employed $\epsilon_{N+1}^{(N+1)} = -I_{N+1}$. We thus see that the discontinuity Δ is finite. Equation (7.42) is the desired result.

7.3 Correlations Contributing to the Discontinuity According To Kohn–Sham Theory

If in (7.1) one employs the KS–DFT definitions of the potential energies $v_{\mathrm{ee}}^{(N+\omega)}(\mathbf{r})$ and $v_{\mathrm{ee}}^{(N)}(\mathbf{r})$ (or $v_{xc}^{(N+\omega)}(\mathbf{r})$ and $v_{xc}^{(N)}(\mathbf{r})$) as the functional derivatives $\delta E_{\mathrm{ee}}^{KS}[\rho]/\delta\rho(\mathbf{r})|_{N+\omega}$ and $\delta E_{\mathrm{ee}}^{KS}[\rho]/\delta\rho(\mathbf{r})|_{N}$ (or $\delta E_{xc}^{KS}[\rho]/\delta\rho(\mathbf{r})|_{N+\omega}$ and $\delta E_{xc}^{KS}[\rho]/\delta\rho(\mathbf{r})|_{N}$), respectively, one is led to the conclusion that *all* the correlations present—Pauli, Coulomb, and Correlation–Kinetic—contribute to the discontinuity. That this is the case may also be surmised from (7.42), since these eigenvalues are generated via the *full* KS potential energy. In earlier Q–DFT literature [10, 11], it was also implicitly assumed that all the correlations contribute to the discontinuity. What we prove [6] via Q–DFT in the sections to follow is that Pauli and Coulomb correlations do not contribute to the discontinuity, and that this intrinsic property of the S system is *solely* a consequence of Correlation–Kinetic effects.

7.4 Quantal Density Functional Theory of the Discontinuity

For this chapter to be self–contained, we next redefine the fields and potential energies within Q–DFT with minor notational changes in order to distinguish between the N- and $(N+\omega)$-electron systems.

The N-electron Schrödinger equation and that for the corresponding S system are, respectively,

$$\left[-\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i=1}^{N}v(\mathbf{r}_i) + \frac{1}{2}\sum_{i\neq j}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right]\Psi^{(N)}(\mathbf{X}) = E^{(N)}\Psi^{(N)}(\mathbf{X}), \tag{7.43}$$

and

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_{\text{ee}}^{(N)}\right]\phi_i^{(N)}(\mathbf{x}) = \epsilon_i^{(N)}\phi_i^{(N)}(\mathbf{x}), \tag{7.44}$$

where $\Psi^{(N)}(\mathbf{X})$ is the wavefunction, E the ground state energy, and $\phi_i(\mathbf{x})$ and ϵ_i the single particle orbitals and eigenenergies. The density $\rho^{(N)}(\mathbf{r}) = \langle\Psi^{(N)}|\hat{\rho}(\mathbf{r})|\Psi^{(N)}\rangle = \langle\Phi\{\phi_i^{(N)}\}|\hat{\rho}|\Phi\{\phi_i^{(N)}\}\rangle = \sum_{\sigma i}|\phi_i^{(N)}(\mathbf{x})|^2$, where $\hat{\rho}(\mathbf{r})$ is the density operator (2.12), and $\Phi\{\phi_i^{(N)}\}$ the Slater determinant of the orbitals $\phi_i^{(N)}(\mathbf{x})$.

The work $v_{\text{ee}}^{(N)}(\mathbf{r})$ done to move the model fermion from a reference point at infinity to its position at $\mathbf{r}$ in the force of the conservative effective field $\boldsymbol{\mathcal{F}}^{(N)}(\mathbf{r})$ is

$$v_{\text{ee}}^{(N)}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{F}}^{(N)}(\mathbf{r}')\cdot d\boldsymbol{\ell}', \tag{7.45}$$

where

$$\boldsymbol{\mathcal{F}}^{(N)}(\mathbf{r}) = \boldsymbol{\mathcal{E}}_{\text{ee}}^{(N)}(\mathbf{r}) + \boldsymbol{Z}_{t_c}^{(N)}(\mathbf{r}). \tag{7.46}$$

The electron–interaction component field $\boldsymbol{\mathcal{E}}_{\text{ee}}^{(N)}(\mathbf{r})$, which is representative of Pauli and Coulomb correlations, is obtained by Coulomb's law from its nonlocal source charge distribution $g^{(N)}(\mathbf{rr}')$, the pair–correlation density. Thus,

$$\boldsymbol{\mathcal{E}}_{\text{ee}}^{(N)}(\mathbf{r}) = \int \frac{g^{(N)}(\mathbf{rr}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}d\mathbf{r}', \tag{7.47}$$

where $g^{(N)}(\mathbf{rr}') = \langle\Psi^{(N)}|\hat{P}(\mathbf{rr}')|\Psi^{(N)}\rangle/\rho^{(N)}(\mathbf{r})$, and $\hat{P}(\mathbf{rr}')$ is the pair–correlation operator (2.28). The Correlation–Kinetic component field $\boldsymbol{\mathcal{Z}}_{t_c}^{(N)}(\mathbf{r})$ is defined in terms of the kinetic 'forces' $\boldsymbol{z}^{(N)}(\mathbf{r};[\gamma])$ and $\boldsymbol{z}_s^{(N)}(\mathbf{r};[\gamma_s])$ for the interacting and S systems, respectively, as

$$\boldsymbol{\mathcal{Z}}_{t_c}^{(N)}(\mathbf{r}) = \left\{\boldsymbol{z}_s^{(N)}(\mathbf{r};[\gamma_s]) - \boldsymbol{z}^{(N)}(\mathbf{r};[\gamma])\right\}\big/\rho^{(N)}(\mathbf{r}). \tag{7.48}$$

The nonlocal sources of the kinetic 'forces' are the spinless single–particle $\gamma^{(N)}(\mathbf{rr}')$ and Dirac $\gamma_s^{(N)}(\mathbf{rr}')$ density matrices, respectively, where

$$\gamma^{(N)}(\mathbf{rr}') = \langle\Psi^{(N)}|\hat{\gamma}(\mathbf{rr}')|\Psi^{(N)}\rangle \tag{7.49}$$

and

$$\begin{aligned}\gamma_s^{(N)}(\mathbf{rr}') &= \langle\Phi\{\phi_i^{(N)}\}|\hat{\gamma}(\mathbf{rr}')|\Phi\{\phi_i^{(N)}\}\rangle \\ &= \sum_{\sigma i}\phi_i^{(N)*}(\mathbf{r}\sigma)\phi_i^{(N)}(\mathbf{r}'\sigma),\end{aligned} \tag{7.50}$$

and where $\hat{\gamma}(\mathbf{rr}')$ is the density matrix operator (2.17). The kinetic 'forces' are defined such that the component $z_\alpha^{(N)}(\mathbf{r}) = 2\sum_\beta \partial t_{\alpha\beta}(\mathbf{r};[\gamma])/\partial r_\beta$, where $t_{\alpha\beta}(\mathbf{r}) =$

$(\frac{1}{4})[\partial^2/\partial r'_\alpha \partial r''_\beta + \partial^2/\partial r'_\beta \partial r''_\alpha]\gamma^{(N)}(\mathbf{r}'\mathbf{r}'')|_{\mathbf{r}'=\mathbf{r}''=\mathbf{r}}$ is the kinetic–energy–density tensor. The 'force' $z_s^{(N)}(\mathbf{r};[\gamma_s])$ is similarly defined in terms of the S system tensor $t_{s,\alpha\beta}(\mathbf{r})$ and Dirac density matrix $\gamma_s^{(N)}(\mathbf{r}\mathbf{r}')$.

Within the Schrödinger theory framework, the fractionally charged $(N+\omega)$ case is treated in terms of an ensemble of the N- and $(N+1)$-electron systems. Thus, with the ensemble density matrix defined as in (7.11), the pair–correlation density, and the density matrix can be shown to be

$$\begin{aligned} g^{(N+\omega)}(\mathbf{r}\mathbf{r}') &= tr\{\hat{D}\hat{P}\}\big/\rho^{(N+\omega)}(\mathbf{r}) \\ &= \big[(1-\omega)\rho^{(N)}(\mathbf{r})g^{(N)}(\mathbf{r}\mathbf{r}') \\ &\quad + \omega\rho^{(N+1)}(\mathbf{r})g^{(N+1)}(\mathbf{r}\mathbf{r}')\big]\big/\rho^{(N+\omega)}(\mathbf{r}), \end{aligned} \tag{7.51}$$

and

$$\begin{aligned} \gamma^{(N+\omega)}(\mathbf{r}\mathbf{r}') &= tr\{\hat{D}\hat{X}\} \\ &= (1-\omega)\gamma^{(N)}(\mathbf{r}\mathbf{r}') + \omega\gamma^{(N+1)}(\mathbf{r}\mathbf{r}'). \end{aligned} \tag{7.52}$$

The local potential energy $v_{\mathrm{ee}}^{(N+\omega)}(\mathbf{r})$ in (7.23) can be rewritten as the work done in a conservative field $\boldsymbol{\mathcal{F}}^{(N+\omega)}(\mathbf{r})$:

$$v_{\mathrm{ee}}^{(N+\omega)}(\mathbf{r}) = -\int_\infty^{\mathbf{r}} \boldsymbol{\mathcal{F}}^{(N+\omega)}(\mathbf{r}')\cdot d\boldsymbol{\ell}', \tag{7.53}$$

with

$$\boldsymbol{\mathcal{F}}^{(N+\omega)}(\mathbf{r}) = \boldsymbol{\mathcal{E}}_{\mathrm{ee}}^{(N+\omega)}(\mathbf{r}) + \widetilde{\boldsymbol{\mathcal{Z}}}_{t_c}^{(N+\omega)}(\mathbf{r}). \tag{7.54}$$

The electron–interaction field $\boldsymbol{\mathcal{E}}_{\mathrm{ee}}^{(N+\omega)}(\mathbf{r})$ is obtained by Coulomb's law from its source charge $g^{(N+\omega)}(\mathbf{r}\mathbf{r}')$ as

$$\begin{aligned} \boldsymbol{\mathcal{E}}_{\mathrm{ee}}^{(N+\omega)}(\mathbf{r}) &= \big[(1-\omega)\rho^{(N)}(\mathbf{r})\boldsymbol{\mathcal{E}}_{\mathrm{ee}}^{(N)}(\mathbf{r}) \\ &\quad + \omega\rho^{(N+1)}(\mathbf{r})\boldsymbol{\mathcal{E}}_{\mathrm{ee}}^{(N+1)}(\mathbf{r})\big]\big/\rho^{(N+\omega)}(\mathbf{r}). \end{aligned} \tag{7.55}$$

The Correlation–Kinetic field $\widetilde{\mathbf{Z}}_{t_c}^{(N+\omega)}(\mathbf{r})$ is defined as

$$\begin{aligned} \widetilde{\boldsymbol{\mathcal{Z}}}_{t_c}^{(N+\omega)}(\mathbf{r}) &= \big[\widetilde{z}_s^{(N+\omega)}\big(\mathbf{r};\big[\widetilde{\gamma}_s^{(N+\omega)}\big]\big) \\ &\quad - z^{(N+\omega)}\big(\mathbf{r};\big[\gamma^{(N+\omega)}\big]\big)\big]\big/\rho^{(N+\omega)}(\mathbf{r}), \end{aligned} \tag{7.56}$$

where the kinetic 'force' $z^{(N+\omega)}(\mathbf{r})$ is obtained from its source $\gamma^{(N+\omega)}(\mathbf{rr}')$. The S system kinetic 'force' $\widetilde{z}_s^{(N+\omega)}(\mathbf{r})$ is similarly obtained from the density matrix constructed from the orbitals $\phi_i^{(N+\omega)}(\mathbf{x})$ and is

$$\widetilde{\gamma}_s^{(N+\omega)}(\mathbf{rr}') = (1-\omega)\sum_{\sigma,i=1}^{N} \phi_i^{(N+\omega)*}(\mathbf{r}\sigma)\phi_i^{(N+\omega)}(\mathbf{r}'\sigma) + \omega \sum_{\sigma,i=1}^{N+1} \phi_i^{(N+\omega)*}(\mathbf{r}\sigma)\phi_i^{(N+\omega)}(\mathbf{r}'\sigma). \quad (7.57)$$

We next prove that the discontinuity as defined by (7.1) is due to Correlation–Kinetic effects.

7.4.1 *Correlations Contributing to the Discontinuity According To Q–DFT: Analytical Proof*

A. Electron–Interaction Component

We first prove that correlations due to the Pauli exclusion principle and Coulomb repulsion do not contribute to the discontinuity Δ.

From (7.45) and (7.53) we have

$$\nabla \left[v_{\text{ee}}^{(N+\omega)}(\mathbf{r}) - v_{\text{ee}}^{(N)}(\mathbf{r})\right] = -\Delta\boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}) - \Delta\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r}), \quad (7.58)$$

where

$$\Delta\boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}) = \boldsymbol{\mathcal{E}}_{\text{ee}}^{(N+\omega)}(\mathbf{r}) - \boldsymbol{\mathcal{E}}_{\text{ee}}^{(N)}(\mathbf{r}), \quad (7.59)$$

and

$$\Delta\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r}) = \widetilde{\boldsymbol{\mathcal{Z}}}_{t_c}^{(N+\omega)}(\mathbf{r}) - \boldsymbol{\mathcal{Z}}_{t_c}^{(N)}(\mathbf{r}). \quad (7.60)$$

From (7.47) and (7.55), we have

$$\Delta\boldsymbol{\mathcal{E}}_{\text{ee}}([\mathbf{r}]) = \left[\left\{(1-\omega)\rho^{(N)}(\mathbf{r}) - \rho^{(N+\omega)}(\mathbf{r})\right\}\boldsymbol{\mathcal{E}}_{\text{ee}}^{(N)}(\mathbf{r}) + \omega\rho^{(N+1)}(\mathbf{r})\boldsymbol{\mathcal{E}}_{\text{ee}}^{(N+1)}(\mathbf{r})\right]\Big/\rho^{(N+\omega)}(\mathbf{r}). \quad (7.61)$$

Substituting for $(1-\omega)\rho^{(N)}(\mathbf{r}) = \rho^{(N+\omega)}(\mathbf{r}) - \omega\rho^{(N+1)}(\mathbf{r})$ into (7.61) leads to

$$\Delta\boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}) = \omega\rho^{(N+1)}(\mathbf{r})\left[\boldsymbol{\mathcal{E}}_{\text{ee}}^{(N+1)}(\mathbf{r}) - \boldsymbol{\mathcal{E}}_{\text{ee}}^{(N)}(\mathbf{r})\right]\Big/\rho^{(N+\omega)}(\mathbf{r}). \quad (7.62)$$

It follows from (7.62) that $\lim_{\omega\to 0}\Delta\boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}) = 0$. To see this consider the radius $R(\omega)$ defined by (7.34). For $r < R(\omega)$ and small ω, the density $\rho^{(N)}(\mathbf{r})$ dominates the ensemble density $\rho^{(N+\omega)}(\mathbf{r})$. Thus, in this region $\rho^{(N+\omega)}(\mathbf{r}) \sim \rho^{(N)}(\mathbf{r})$, and $\Delta\boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r})$ is linear in ω, and vanishes as $\omega \to 0$. For $\mathbf{r} \gg R(\omega)$, the ensemble density $\rho^{(N+\omega)}(\mathbf{r}) \sim \omega\rho^{(N+1)}(\mathbf{r})$. Substitution into (7.62) shows that the ω's cancel. But in this region the difference $[\boldsymbol{\mathcal{E}}_{\text{ee}}^{(N+1)}(\mathbf{r}) - \boldsymbol{\mathcal{E}}_{\text{ee}}^{(N)}(\mathbf{r})] \sim 1/r^2$ so that $\Delta\boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r})$ once again vanishes. In the region $r \sim R(\omega)$, $\Delta\boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r})$ vanishes essentially linearly with ω. We note, however, that $\Delta\boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r})$ is finite for positive definite ω, irrespective of how small ω is. It is only in the limit of vanishing ω that the Pauli and Coulomb correlation contributions to the discontinuity vanish.

Finally, since the pair-correlation density may be written as $g^{(N)}(\mathbf{r}\mathbf{r}') = \rho^{(N)}(\mathbf{r}') + \rho_{xc}^{(N)}(\mathbf{r}\mathbf{r}')$, where $\rho_{xc}^{(N)}(\mathbf{r}\mathbf{r}')$ is the Fermi–Coulomb hole charge distribution, we have $\Delta\boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}) = \Delta\boldsymbol{\mathcal{E}}_H(\mathbf{r}) + \Delta\mathcal{E}_{xc}(\mathbf{r})$, where $\Delta\boldsymbol{\mathcal{E}}_H(\mathbf{r}) = [\boldsymbol{\mathcal{E}}_H^{(N+\omega)}(\mathbf{r}) - \boldsymbol{\mathcal{E}}_H^{(N)}(\mathbf{r})]$ and $\Delta\mathcal{E}_{xc}(\mathbf{r}) = [\boldsymbol{\mathcal{E}}_{xc}^{(N+\omega)}(\mathbf{r}) - \boldsymbol{\mathcal{E}}_{xc}^{(N)}(\mathbf{r})]$. Here $\boldsymbol{\mathcal{E}}_H^{(N)}$ and $\boldsymbol{\mathcal{E}}_{xc}^{(N)}(\mathbf{r})$ are the Hartree and Pauli–Coulomb fields arising from the component charge distributions $\rho^{(N)}(\mathbf{r}')$ and $\rho_{xc}^{(N)}(\mathbf{r}\mathbf{r}')$, respectively. Since $\Delta\boldsymbol{\mathcal{E}}_H(\mathbf{r}) = \omega[\boldsymbol{\mathcal{E}}_H^{(N+1)}(\mathbf{r}) - \boldsymbol{\mathcal{E}}_H^{(N)}(\mathbf{r})]$, it follows that $\lim_{\omega\to 0}\Delta\boldsymbol{\mathcal{E}}_H(\mathbf{r}) = 0$, and, consequently, the $\lim_{\omega\to 0}\Delta\boldsymbol{\mathcal{E}}_{xc}(\mathbf{r}) = 0$.

B. Correlation–Kinetic Component

Since the quantum–mechanical electron–interaction contribution $\Delta\boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r})$ in (7.58) vanishes in the $\lim \omega \to 0$, we have

$$\lim_{\omega\to 0} \nabla\left[v_{\text{ee}}^{(N+\omega)}(\mathbf{r}) - v_{\text{ee}}^{(N)}(\mathbf{r})\right] = -\Delta\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r}), \tag{7.63}$$

which proves the fact that the discontinuity is strictly a Correlation–Kinetic effect. The discontinuity Δ is then the work done

$$\Delta = -\int_{\infty}^{0}\left[\widetilde{\boldsymbol{\mathcal{Z}}}_{t_c}^{(N+\omega)}(\mathbf{r}') - \boldsymbol{\mathcal{Z}}_{t_c}^{(N)}(\mathbf{r}')\right]\cdot d\boldsymbol{\ell}'. \tag{7.64}$$

From (7.63) it also follows that this work done is *path–independent*. Equation (7.64) is an alternate expression for the discontinuity Δ, in which it is evident that the correlations that contribute to it are solely those due to Correlation–Kinetic effects.

To understand more fundamentally how Correlation–Kinetic effects contribute to the discontinuity, we next explain the structure of $\Delta\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r})$ for small ω. We rewrite $\Delta\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r})$ as

$$\Delta\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r}) = \widetilde{\boldsymbol{\mathcal{Z}}}_{t_c}^{(N+\omega)}(\mathbf{r}) - \boldsymbol{\mathcal{Z}}_{t_c}^{(N)}(\mathbf{r}) \tag{7.65}$$

$$= A + B, \tag{7.66}$$

where

$$A = \frac{1}{\rho^{(N+\omega)}(\mathbf{r})}\widetilde{\boldsymbol{z}}_s^{(N+\omega)}(\mathbf{r}) - \frac{1}{\rho^{(N)}}\boldsymbol{z}_s^{(N)}(\mathbf{r}) \tag{7.67}$$

and

$$B = -\frac{1}{\rho^{(N+\omega)}(\mathbf{r})}\left[(1-\omega)z^{(N)}(\mathbf{r}) + \omega z^{(N+1)}(\mathbf{r})\right] + \frac{1}{\rho^{(N)}(\mathbf{r})}z^{(N)}(\mathbf{r}). \tag{7.68}$$

For $r < R(\omega)$, the region where $\rho^{(N)}(\mathbf{r})$ dominates, $\widetilde{\gamma}_s^{(N+\omega)}(\mathbf{r}\mathbf{r}') \sim \sum_{\sigma,i=1}^{N} \phi_i^{(N)*}(\mathbf{r}\sigma)\phi_i^{(N)}(\mathbf{r}'\sigma)$, so that $\widetilde{z}_s^{(N+\omega)}(\mathbf{r}) \sim z_s^{(N)}(\mathbf{r})$. Therefore, $A = 0$. The term $B = 0$, since the terms linear in ω are negligible. Thus, in this region, $\Delta\mathcal{Z}_{t_c}(\mathbf{r}) = 0$.

In the $\mathbf{r} \to \infty$ limit, both $\widetilde{\mathcal{Z}}_{t_c}^{(N+\omega)}(\mathbf{r})$ and $\mathcal{Z}_{t_c}^{(N)}(\mathbf{r})$ vanish, so that in this region $\Delta\mathcal{Z}_{t_c}(\mathbf{r}) = 0$.

For $\mathbf{r} \gg R(\omega)$, we have $\phi_i^{(N+\omega)}(\mathbf{r}) \to \phi_i^{(N+1)}(\mathbf{r})$, so that $\widetilde{\gamma}_s^{(N+\omega)}(\mathbf{r}\mathbf{r}') \sim \omega \sum_{\sigma,i=1}^{N+1} \phi_i^{(N+1)*}(\mathbf{r}\sigma)\phi_i^{(N+1)}(\mathbf{r}'\sigma)$ and $\widetilde{z}_s^{(N+\omega)}(\mathbf{r}) \sim \omega z_s^{(N+1)}(\mathbf{r})$. Thus $A \sim \{[z_s^{(N+1)}(\mathbf{r})/\rho^{(N+1)}(\mathbf{r})] - [z_s^{(N)}(\mathbf{r})/\rho^{(N)}(\mathbf{r})]\}$ and $B \sim \{[-z^{(N+1)}(\mathbf{r})/\rho^{(N+1)}(\mathbf{r})] + [z^{(N)}(\mathbf{r})/\rho^{(N)}(\mathbf{r})]\}$, so that $\Delta\mathcal{Z}_{t_c}(\mathbf{r}) = \mathcal{Z}_{t_c}^{(N+1)}(\mathbf{r}) - \mathcal{Z}_{t_c}^{(N)}(\mathbf{r})$. Thus, in this region, $\Delta\mathcal{Z}t_c(\mathbf{r})$ is finite. In this limit, as $\omega \to 0$, the radius $R(\omega)$ becomes infinite, and the difference $\Delta\mathcal{Z}_{t_c}(\mathbf{r})$ stabilizes. We next demonstrate the above conclusions via two numerical examples.

7.4.2 Numerical Examples

Example 1. As a demonstration of the above conclusions, we consider the example where the integer system is the He^+ ion (atomic number $Z = 2$, electron number $N = 1$). Its wavefunction, which is hydrogenic, is known, as is the density $\rho^{(N=1)}(\mathbf{r}) \equiv \rho^{(1)}(\mathbf{r})$. The ensemble density $\rho^{(1+\omega)}(\mathbf{r})$ of (7.12) is then

$$\rho^{(1+\omega)}(\mathbf{r}) = (1-\omega)\rho^{(1)}(\mathbf{r}) + \omega\rho^{(2)}(\mathbf{r}), \tag{7.69}$$

where $\rho^{(2)}(\mathbf{r}) \equiv \rho^{(N+1)}(\mathbf{r})$ is the density of the He atom. For the He atom, a highly accurate 491–parameter correlated wavefunction [12] is employed. This wavefunction is accurate upto $r = 24$ a.u. from the nucleus, which in essence is infinity for the atom. Smaller and smaller fractional charge ω is added to the ls shell of the He^+ ion. For the corresponding S system, there is therefore only one orbital $\phi^{(1+\omega)}(\mathbf{r})$. Thus, the ensemble density $\rho^{(1+\omega)}(\mathbf{r})$ in terms of the S system orbitals as given by (7.22) is

$$\begin{aligned}\rho^{(1+\omega)}(\mathbf{r}) &= (1-\omega)|\phi^{(1+\omega)}(\mathbf{r})|^2 + \omega 2|\phi^{(1+\omega)}(\mathbf{r})|^2 \\ &= (1+\omega)|\phi^{(1+\omega)}(\mathbf{r})|^2.\end{aligned} \tag{7.70}$$

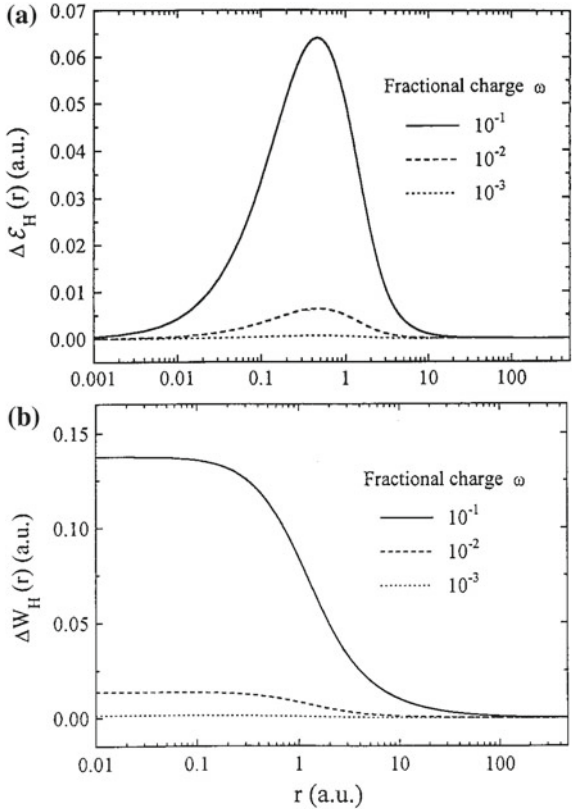


Fig. 7.2 **(a)** Hartree field difference $\Delta\boldsymbol{\mathcal{E}}_H(\mathbf{r})$ for different fractional charge ω. The integer charge system is He^+. **(b)** Work done $\Delta W_H(\mathbf{r})$ in the field $\Delta\boldsymbol{\mathcal{E}}_H$

Thus, from (7.69) and (7.70), we have

$$\phi^{(1+\omega)}(\mathbf{r}) = \left[\frac{(1-\omega)\rho^{(1)}(\mathbf{r}) + \omega\rho^{(2)}(\mathbf{r})}{1+\omega}\right]^{1/2}. \tag{7.71}$$

As the wavefunctions for He^+ and He, and consequently the orbital $\phi^{(1+\omega)}(\mathbf{r})$, are known, all the requisite sources and fields can then be determined for different values of the fractional charge ω.

In Fig. 7.2(a) we plot the Hartree field difference $\Delta\boldsymbol{\mathcal{E}}_H(\mathbf{r})$ for $\omega = 10^{-1}$, 10^{-2}, and 10^{-3}. As the fractional charge diminishes, the difference $\Delta\boldsymbol{\mathcal{E}}_H(\mathbf{r})$ becomes negligible. The corresponding work $\Delta W_H(\mathbf{r}) = -\int_\infty^{\mathbf{r}} \Delta\boldsymbol{\mathcal{E}}_H(\mathbf{r}') \cdot d\boldsymbol{\ell}'$ is constant in the interior as expected (Fig. 7.2(b)), but becomes smaller with decreasing fractional charge, although it is still finite at $\omega = 10^{-3}$. As ω is decreased further, however, both $\Delta\boldsymbol{\mathcal{E}}_H(\mathbf{r})$ and $\Delta W_H(\mathbf{r})$ vanish. Thus the Hartree component of the Coulomb interaction does not contribute to the discontinuity.

In Fig. 7.3(a), the difference in the Pauli–Coulomb fields $\Delta\mathcal{E}_{xc}(\mathbf{r})$ is plotted for fractional charges $\omega = 10^{-5}$, 10^{-8}, and 10^{-10}. As expected, it vanishes in the

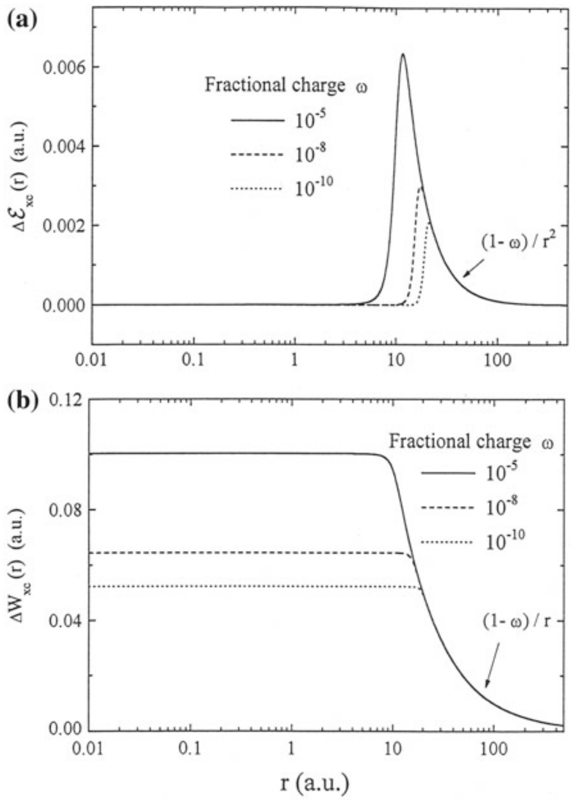


Fig. 7.3 **(a)** Pauli-Coulomb field difference $\Delta\mathcal{E}_{xc}(\mathbf{r})$ for different fractional charge ω. The integer charge system is He^{+}. **(b)** Work done $\Delta W_{xc}(\mathbf{r})$ in the field $\Delta\mathcal{E}_{xc}(\mathbf{r})$

interior, and is peaked in the surface region. It diminishes with decreasing ω, while simultaneously the peak moves further into the classically forbidden region where $\Delta\mathcal{E}_{xc}(\mathbf{r})$ decays as $(1-\omega)/r^2$ for finite ω. Thus, the corresponding work (Fig. 7.3(b)) $\Delta W_{xc}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \Delta\boldsymbol{\mathcal{E}}_{xc}(\mathbf{r}')\cdot d\boldsymbol{\ell}'$ is constant in the interior, with the region where this difference is constant increasing with decreasing ω. Furthermore, as expected the constant value of $\Delta W_{xc}(\mathbf{r})$ also diminishes with decreasing ω. For $\omega = 10^{-10}$ the constant value of $\Delta W_{xc}(\mathbf{r})$ in the interior is 0.052 a.u., Asymptotically, $\Delta W_{xc}(\mathbf{r})$ decays as $(1-\omega)/r$. With vanishing fractional charge, the Pauli–Coulomb contribution to the discontinuity will also vanish.

In Fig. 7.4 we plot the difference $\Delta\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r})$ of the Correlation–Kinetic fields, for fractional charges $\omega = 10^{-2}$, 10^{-5}, 10^{-8}, and 10^{-10} a.u., As expected, this difference vanishes in the interior region. However, in the surface region, these curves are dramatically different from those of Figs. 7.2 and 7.3 in that as the fractional charge ω is decreased, the magnitude of these curves *increases* (Fig. 7.4(a)). With a further decrease in ω, the structure essentially stabilized (Fig. 7.4(b)) and remains finite, while simultaneously moving further out into the classically forbidden region. Thus the constant value of the work $\Delta W_{t_c}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \Delta\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r}')\cdot d\boldsymbol{\ell}'$ *increases* with

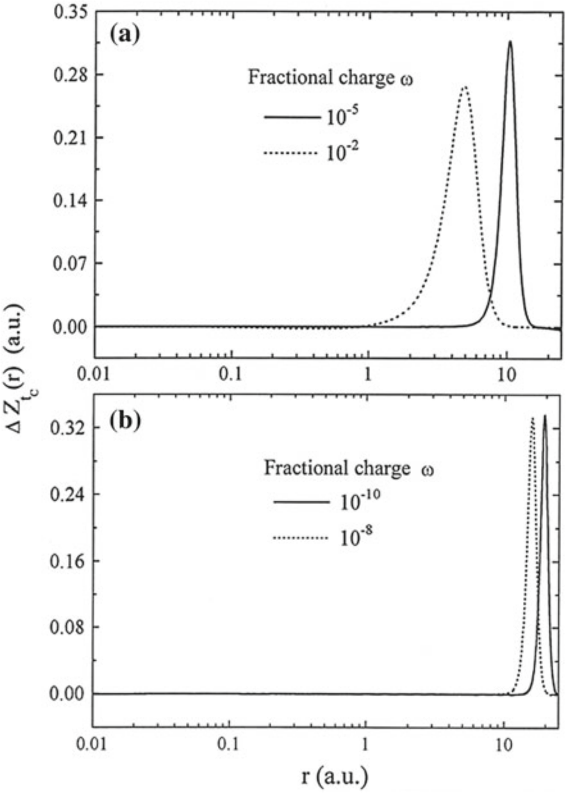
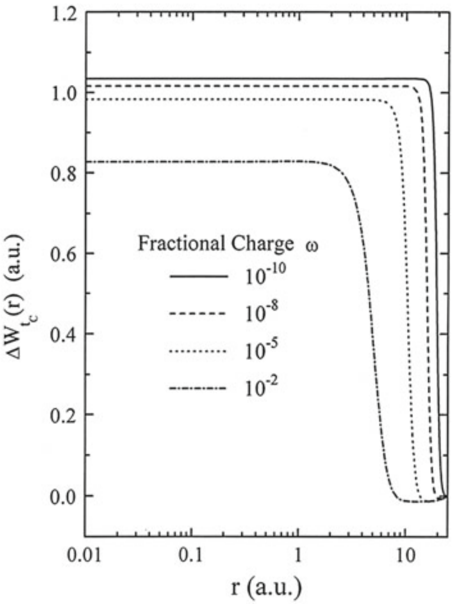


Fig. 7.4 (**a**, **b**) Correlation Kinetic field difference $\Delta\mathcal{Z}_{t_c}(\mathbf{r})$ for difference fractional charge ω. The integer charge system is He^+

decreasing fractional charge (Fig. 7.5), approaching the exact value of the discontinuity Δ from below. This value may be determined from the known result $\Delta = \epsilon_{N+1}^{(N+1)} - \epsilon_{N+1}^{(N)}$ of (7.42), and the fact the highest occupied eigenvalue of the S system corresponds to minus the ionization potential. Taking into consideration the double occupancy of the $1s$ orbital, and that the ionization potentials of He and He^+ are 0.903 and 2 a.u., respectively, we have $\Delta = 1.097$ a.u., The value of ΔW_{t_c} for $\omega = 10^{-10}$ is 1.035 a.u., Adding the value of $\Delta W_{xc} = 0.052$ a.u. for the same ω value, we obtain $\Delta = 1.087$ a.u., which is essentially exact. In the limit of vanishing ω, the contribution from ΔW_{xc} will vanish, and that due to ΔW_{t_c} will equal Δ. This confirms that the discontinuity in the electron–interaction potential energy is solely due to Correlation–Kinetic effects.

Example 2. The calculations in this second example are performed within the Pauli–correlated approximation of Q–DFT [13] as described in Sect. 5.8.1. (see Chap. 6 of ***QDFT2***) (This is also the lowest–order of Q–DFT many–body perturbation theory. See Chap. 18 of ***QDFT2***.) In this approximation, only correlations due to the Pauli exclusion principle are considered beyond the Hartree term. Thus, the corresponding pair–correlation density $g_s^{(N)}(\mathbf{r}\mathbf{r}')$ is determined from a Slater

Fig. 7.5 Work done $\Delta W_{t_c}(\mathbf{r})$ in the field $\Delta \mathcal{Z}_{t_c}(\mathbf{r})$ of Fig. 7.4



determinant $\Phi\{\phi_i^{(N)}\}$ of the S system orbitals $\phi_i^{(N)}(\mathbf{x})$. The local electron–interaction potential energy $v_{\text{ee}}^{(N)}(\mathbf{r})$ of the S system is then $v_{\text{ee}}^{(N)}(\mathbf{r}) = v_H^{(N)}(\mathbf{r}) + W_x^N(\mathbf{r})$, where $W_x^{(N)}(\mathbf{r})$, is the work done in the conservative field $\boldsymbol{\mathcal{E}}_x^{(N)}(\mathbf{r})$due to the S system Fermi hole charge $\rho_x^{(N)}(\mathbf{rr}')$. For the $(N+\omega)$–electron system the Fermi hole charge is

$$\rho_x^{(N+\omega)}(\mathbf{rr}') = g_s^{(N+\omega)}(\mathbf{rr}') - \rho^{(N+\omega)}(\mathbf{r}'), \tag{7.72}$$

where $g_s^{(N+\omega)}(\mathbf{rr}')$ is defined in a manner similar to (7.51) but in terms of the $g_s^{(N)}(\mathbf{rr}')$ and $g_s^{(N+1)}(\mathbf{rr}')$. This is the *ensemble* definition of the Fermi hole. (The use of the nonensemble definition [14] of the Fermi hole: $\rho_x^{(N+\omega)}(\mathbf{rr}') = -|\widetilde{\gamma}_s^{(N+\omega)}(\mathbf{rr}')|^2/2\rho^{(N+\omega)}(\mathbf{r})$, where $\widetilde{\gamma}_s^{(N+\omega)}(\mathbf{rr}')$ is given by (7.57), is inappropriate and will not [10] lead to a discontinuity.)

The integer system we consider in this case is the Na^+ ion (atomic number $Z=11$, electron number $N=10$). In Fig. 7.6 we plot the difference $\Delta\boldsymbol{\mathcal{E}}_x(\mathbf{r}) = \boldsymbol{\mathcal{E}}_x^{(N+\omega)}(\mathbf{r}) - \boldsymbol{\mathcal{E}}_x^{(N)}(\mathbf{r})$ for the Na^+ ion for fractional charge of $\omega = 10^{-5}$, 10^{-10}, 10^{-15} filling the empty $3s$ subshell. These calculations are performed within the spin–unpolarized central field approximation [13]. Observe that the difference vanishes except in the asymptotic region of the atom where it is peaked. Note also that as the fractional charge decreases, this peak moves further into the classically forbidden region as it must. The difference $\Delta\boldsymbol{\mathcal{E}}_x(\mathbf{r})$ also decays asymptotically as $1/r^2$.

In Fig. 7.7 we plot the corresponding Pauli potential $W_x(\mathbf{r})$ for the Na^+ ion for the case of the empty $3s$ subshell (dashed curve), and for the fractionally charged ion with fractional charge $\omega = 10^{-5}$ in the $3s$ subshell (solid curve). The difference

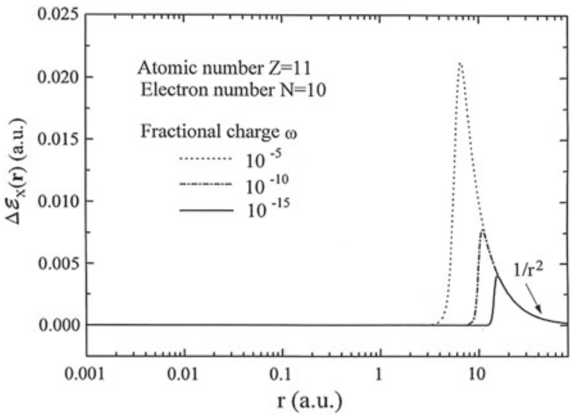


Fig. 7.6 Variation of the difference $\Delta\boldsymbol{\mathcal{E}}_{\mathrm{x}} = \boldsymbol{\mathcal{E}}_{\mathrm{x}}^{(N+\omega)}(\mathbf{r}) - \boldsymbol{\mathcal{E}}_{\mathrm{x}}^{(N)}(\mathbf{r})$ of the Pauli fields $\boldsymbol{\mathcal{E}}_{\mathrm{x}}^{(N+\omega)}(\mathbf{r})$ and $\boldsymbol{\mathcal{E}}_{\mathrm{x}}^{(N)}(\mathbf{r})$ for the $(N+\omega)$ fractionally charged and N-electron Na^+ ions, respectively. The fractional charge of $\omega = 10^{-5}, 10^{-10}, 10^{-15}$, partially fills the empty $3s$ subshell

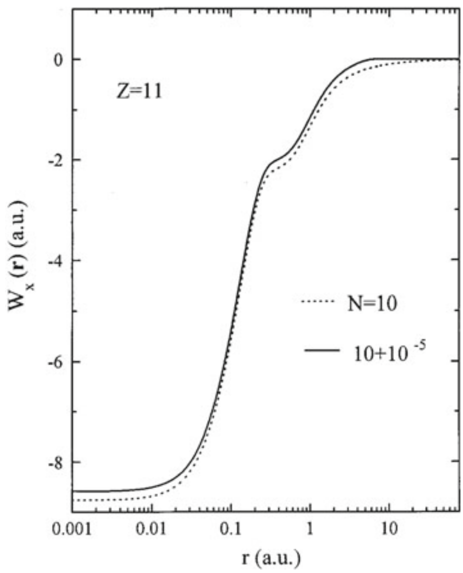


Fig. 7.7 The Pauli potential for the Na^+ ion with integer number $(N = 10)$ of electrons (*dashed curve*), and with fractional charge $(10 + 10^{-5})$ (*solid curve*). The fractional charge 10^{-5} fills the empty $3s$ subshell

$\Delta W_x(\mathbf{r}) = W_x^{(N+\omega)}(\mathbf{r}) - W_x^{(N)}(\mathbf{r})$ of the Pauli potentials for the $(N+\omega)$ fractionally charged and N-electron ions for $\omega = 10^{-5}$, 10^{-10}, 10^{-15} is plotted in Fig. 7.8. As is evident, the difference $\Delta W_x(\mathbf{r})$ is constant except in the asymptotic region where it decays as $1/r$. However, note that the constant value of $\Delta W_x(\mathbf{r})$ continues to diminish with decreasing ω as was the case for $\Delta W_{xc}(\mathbf{r})$ of Fig. 7.3(b). In the limit $\omega \to 0$, the difference $\Delta W_x(\mathbf{r})$ will vanish.

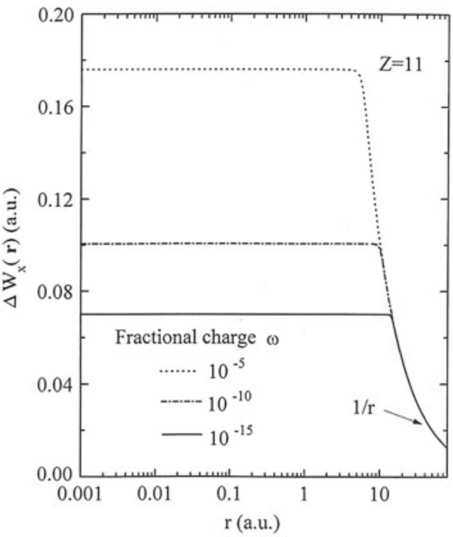


Fig. 7.8 Variation of the difference $\Delta W_x = W_x^{(N+\omega)}(\mathbf{r}) - W_x^{(N)}(\mathbf{r})$ of the Pauli potentials $W_x^{(N+\omega)}(\mathbf{r})$ and $W_x^{(N)}(\mathbf{r})$ for the fractionally charged $(N+\omega)$–and N-electron Na^+ ions respectively

7.5 Endnote

As we have seen, the discontinuity in the S system electron–interaction potential energy $v_{ee}(\mathbf{r})$ as the electron number passes through an integer value is solely due to Correlation–Kinetic effects. The discontinuity is therefore expressed as in (7.64) entirely in terms of fields representative of these correlations. The magnitude of the discontinuity is determined as the work done in a conservative field. Correlations due to the Pauli principle and Coulomb repulsion do not contribute to the discontinuity. Note however, that for finite fractional charge, irrespective of how small it is, there are contributions to the discontinuity from all the three different types of electron correlations. It is only in the limit of vanishing fractional charge that the contributions due to Pauli and Coulomb correlations vanish. Thus an accurate approximation to the discontinuity may be obtained, as in the example above, by summing the contributions of the various correlations as determined for a small value of the fractional charge.

The analysis presented in this chapter also leads to a better understanding of the correlations that contribute to the discontinuity exhibited by the KS–DFT 'exchange' $v_x(\mathbf{r})$ and 'correlation' $v_c(\mathbf{r})$ potential energies. The existence of the discontinuity in $v_x(\mathbf{r})$ has been demonstrated [14] via calculations performed within the 'exchange–only' optimized potential method (see Sect. 5.7.1). As proved in Sect. 5.3, the potential energy $v_x(\mathbf{r})$ is representative of electron correlations due to the Pauli exclusion principle and lowest–order Correlation–Kinetic effects. Since Pauli correlations do not contribute to the discontinuity, it is the lowest–order Correlation–Kinetic component that is responsible for it. The KS–DFT 'correlation' potential energy $v_c(\mathbf{r})$ is in turn representative (Sect. 5.4) of Coulomb correlations and higher–order

Correlation–Kinetic effects. Thus, as Coulomb correlations do not contribute to the discontinuity, the discontinuity in $v_c(\mathbf{r})$ is due to the higher–order Correlation–Kinetic contributions.

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Chapter 8
Generalized Hohenberg-Kohn Theorems in Electrostatic and Magnetostatic Fields

Abstract The Hohenberg-Kohn theorems for a system of N electrons in an external electrostatic field are generalized to the added presence of a uniform magnetostatic field. The theorems are proved for Hamiltonians of both spinless electrons and electrons with spin. It is thereby shown that the basic variables in each case are the nondegenerate ground state density $\rho(\mathbf{r})$ and physical current density $\mathbf{j}(\mathbf{r})$, i.e. knowledge of $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ uniquely determines the external scalar $v(\mathbf{r})$ and vector $\mathbf{A}(\mathbf{r})$ potentials to within a constant and the gradient of a scalar function, respectively. The proofs differ from the original HK proof because the relationship between the potentials $\{v(\mathbf{r}), \mathbf{A}(\mathbf{r})\}$ and the nondegenerate ground state wave function is no longer one-to-one but many-to-one. Further, in addition to the constraint in the original HK proof of fixed electron number N, the constraint of fixed canonical orbital angular momentum $\mathbf{L}$ (for spin less electrons) and the added constraint of fixed spin angular momentum $\mathbf{S}$ (for electrons with spin) is required. The consequence of these proofs to the existing spin and current density functional theories is remarked upon.

Introduction

This chapter is concerned with the generalization [1] of the Hohenberg-Kohn (HK) theorems to the presence of both an external electrostatic $\boldsymbol{\mathcal{E}}(\mathbf{r}) = -\boldsymbol{\nabla} v(\mathbf{r})$ and a magnetostatic $\mathbf{B}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r})$ field, where $v(\mathbf{r})$ and $\mathbf{A}(\mathbf{r})$ are the scalar and vector potentials. The added presence of a magnetostatic field in the context of density functional theory is an active area of theoretical research whose origins lie in the original Kohn-Sham [2] paper. We provide here our most recent understandings and proofs of the corresponding HK theorems. This then leads to the Q-DFT in the presence of these fields as described in the following Chap. 9.

The physics of electrons differ in the added presence of a magnetic field. The corresponding 'Quantal Newtonian' first law for each electron is thus modified [3, 4]. In the law, there is of course the additional Lorentz field contribution to the total external field experienced by each electron. Further, in addition to the components of the internal field representative of the kinetic effects, the density, and the correlations due to the Pauli exclusion principle and Coulomb repulsion, there is also an added component due to the magnetic field. The Schrödinger theory of electrons in the presence of a magnetostatic field $\mathbf{B}(\mathbf{r})$ in terms of 'classical' fields and their

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quantal sources based on the 'Quantal Newtonian' first law will be described fully in the following chapter.

There is yet another fundamental difference in the physics of the electrons in the presence of a magnetostatic field, one that has a particular bearing on the proofs of the corresponding generalized HK theorems. In the case when the only external field is the electrostatic field $\boldsymbol{\mathcal{E}}(\mathbf{r}) = -\boldsymbol{\nabla} v(\mathbf{r})$, HK prove in their first theorem (see Chap. 4), that there is a bijective or *one-to-one* relationship between the external potential $v(\mathbf{r})$ and the nondegenerate ground state wave function ψ. This fact is important because it is then employed to prove a bijective relationship between the wave function ψ and the nondegenerate ground state density $\rho(\mathbf{r})$. Thus, there is a bijective relationship between the external potential $v(\mathbf{r})$ and the density $\rho(\mathbf{r})$. The proof of this theorem is predicated on the *constraint* of *fixed* electron number N [5]. Knowledge of the density $\rho(\mathbf{r})$ then uniquely determines the external potential $v(\mathbf{r})$ to within a constant. Since the kinetic $\hat{T}$ and electron-interaction $\hat{W}$ operators are known, the Hamiltonian is known. Solution of the Schrödinger equation then leads to the ground and excited state wave functions of the system. As such the wave functions of the system are functionals of the nondegenerate ground state density: $\psi = \psi[\rho]$. (The wave function ψ is also a functional of a gauge function $\alpha(\mathbf{R})$ because when written as a functional, it must be gauge variant. (See Chap. 4)) The one-to-one relationship between $\rho(\mathbf{r})$ and the external potential $v(\mathbf{r})$ then defines the gauge invariant property of the density $\rho(\mathbf{r})$ as a *basic variable* of quantum mechanics. As the wave function ψ, and hence the energy $E_v[\rho]$ are functionals of the density $\rho(\mathbf{r})$, the second HK theorem develops an energy variational principle for arbitrary variations of v-representable densities. The corresponding Euler-Lagrange equation is solved for fixed $v(\mathbf{r})$ subject to the constraint of known electron number N (see Table 8.1 for a summary of the theorems).

When both an electrostatic $\boldsymbol{\mathcal{E}}(\mathbf{r}) = -\boldsymbol{\nabla} v(\mathbf{r})$ and a magnetostatic $\mathbf{B}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r})$ field are present, the relationship between the external potentials $\{v(\mathbf{r}), \mathbf{A}(\mathbf{r})\}$ and the nondegenerate ground state wave function ψ is different from that of the original HK case. It turns out that the relationship between $\{v(\mathbf{r}), \mathbf{A}(\mathbf{r})\}$ and ψ can be *many-to-one* [6–10] and even *infinite-to-one* [11, 12]. It is evident then that the proof of bijectivity between any gauge invariant properties and the external potentials $\{v(\mathbf{r}), \mathbf{A}(\mathbf{r})\}$ must also be different. Furthermore, the proof must account for this many-to-one relationship of the potentials $\{v(\mathbf{r}), \mathbf{A}(\mathbf{r})\}$ and the wave function ψ. Such a proof [1] of the bijectivity between the external potentials $\{v(\mathbf{r}), \mathbf{A}(\mathbf{r})\}$ and the gauge invariant properties of the nondegenerate ground state density $\rho(\mathbf{r})$ and the *physical* current density $\mathbf{j}(\mathbf{r})$ is provided for a *uniform* magnetic field. The proof is for $(v, \mathbf{A})$-representable densities $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$. Since the magnetic field constitutes an added degree of freedom, there must be another constraint imposed. When the interaction of the magnetic field is only with the orbital angular momentum, the additional natural *constraint* imposed is that of *fixed* canonical orbital angular momentum $\mathbf{L}$. In the case when the interaction of the magnetic field is with both the orbital and spin angular momentum, the constraint is that of fixed canonical angular momentum $\mathbf{L}$ and spin angular momentum $\mathbf{S}$. Knowledge of $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ then uniquely determines $\{v(\mathbf{r}), \mathbf{A}(\mathbf{r})\}$ to within an arbitrary constant and the gradient of a scalar function, respectively. With the kinetic $\hat{T}$ and electron-interaction $\hat{W}$

Table 8.1 Comparison of Hohenberg-Kohn and Generalized Hohenberg-Kohn theories

Theory	Hohenberg-Kohn DFT	Generalized HK DFT
Parameters characterizing ground state	Electron Number N	Electron Number N Angular momentum $\mathbf{L}$
Relationship between potentials and wave function	One-to-one between $v(\mathbf{r})$ and Ψ	Many-to-one between $\{v(\mathbf{r}), \mathbf{A}(\mathbf{r})\}$ and Ψ
Properties characterizing ground state	Electron density $\rho(\mathbf{r})$	Electron density $\rho(\mathbf{r})$ Physical current density $\mathbf{j}(\mathbf{r})$ Angular momentum $\mathbf{L}$
Bijectivity theorem	For fixed N $\rho(\mathbf{r}) \leftrightarrow v(\mathbf{r})$	For fixed N and $\mathbf{L}$ $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\} \leftrightarrow \{v(\mathbf{r}), \mathbf{A}(\mathbf{r})\}$
Wave function and energy functionals	$\Psi = \Psi[\rho, \alpha]$ For fixed $v : E = E_v[\rho]$	$\Psi = \Psi[\rho, \mathbf{j}, \alpha]$ For fixed $\{v, \mathbf{A}\} : E = E_{v,\mathbf{A}}[\rho, \mathbf{j}]$
Euler equations and constraints	Variational principle for fixed v and known N: $\frac{\delta E_v[\rho]}{\delta \rho} = 0$ $\int \rho(\mathbf{r}) d\mathbf{r} = N$	Variational principle for fixed $\{v, \mathbf{A}\}$ and known $N, \mathbf{L}$: $\left.\frac{\delta E_{v,\mathbf{A}}[\rho,\mathbf{j}]}{\delta \rho}\right\vert_{\mathbf{j}} = 0 \quad \left.\frac{\delta E_{v,\mathbf{A}}[\rho,\mathbf{j}]}{\delta \mathbf{j}}\right\vert_{\rho} = 0$ $\int \rho(\mathbf{r}) d\mathbf{r} = N$ $\int \mathbf{r} \times (\mathbf{j}(\mathbf{r}) - \frac{1}{c}\rho(\mathbf{r})\mathbf{A}(\mathbf{r})) d\mathbf{r} = \mathbf{L}$ $\boldsymbol{\nabla} \cdot \mathbf{j}(\mathbf{r}) = 0$

operators assumed known, the Hamiltonian is known. Solution of the Schrödinger equation then leads to the wave functions of the system. This then is the HK path from the gauge invariant properties $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ to the wave functions ψ. The wave functions ψ are thus functionals of the properties $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$, i.e. $\psi = \psi[\rho, \mathbf{j}]$. Via a density preserving unitary or gauge transformation, it can be shown that the wave functions ψ must also be a functional of a gauge function $\alpha(\mathbf{R})$. This ensures that when ψ is written as a functional it is gauge variant. The basic variables of the quantum mechanics of electrons in the presence of a uniform magnetic field and constant canonical angular momentum are thus $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$.

As the ground state energy is a functional of the basic variables: $E = E_{v,\mathbf{A}}[\rho, \mathbf{j}]$, a variational principle for $E_{v,\mathbf{A}}[\rho, \mathbf{j}]$ exists for arbitrary variations of $(v, \mathbf{A})$-representable densities $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$. The corresponding Euler-Lagrange equations for $\rho(\mathbf{r})$ and $\mathbf{j}(\mathbf{r})$ follow, and these must be solved with the constraints of charge conservation, constant angular momentum, and the vanishing of the divergence of the physical current density via the equation of continuity. Implicit in this variational principle, as in all such energy variational principles, is that *the external potentials remain fixed throughout the variation*.

With the knowledge of the properties that constitute the basic variables, a Percus-Levy-Lieb (PLL) [13] type constrained-search path from the $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ to the nondegenerate or degenerate ground state wave function ψ is then possible. One searches over all N-representable $\psi_{\rho,\mathbf{j}}$ that reproduce $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ and the fixed angular momentum. The minimum of the expectation $\langle \hat{T} + \hat{W} \rangle$ then yields the true function ψ.

Finally, it is possible to map the interacting system of electrons to one of noninteracting fermions within both a Kohn-Sham-type framework and Q-DFT. The latter mapping is described in the following Chap. 9. The generalized HK theorems proved for both spinless electrons and electrons with spin are of particular value for yrast states. These are states of lowest energy for fixed angular momentum. These states have been studied experimentally and theoretically for both bosons and fermions, e.g. rotating trapped Bose-Einstein condensates [14], and harmonically trapped electrons in the presence of a uniform perpendicular magnetic field [15]. The theorems derived are also applicable to all experimentation with a uniform magnetic field such as the magneto-caloric effect [16], the Zeeman effect, cyclotron resonance, magnetoresistance, the de-Haas–van Alphen effect, the Hall effect, the quantum Hall effect, the Meissner effect, nuclear magnetic resonance, etc. The chapter begins with definitions and properties of electrons in a magnetic field. It continues with the proofs of the generalized HK theorems for uniform magnetostatic fields for the cases of the interaction of the field with only the orbital angular momentum, and with both the orbital and spin angular momentum. The chapter concludes with remarks on spin, paramagnetic and other current density functional theories, and an endnote for future work.

8.1 The Classical Hamiltonian and Properties

To obtain the Hamiltonian and other relevant properties of electrons in an external electrostatic and magnetostatic field, we begin with a description of a classical particle in the presence of these fields. This material is in various texts [17–19], but is presented here for purposes of completeness. With this understanding of the classical physics, we then apply the correspondence principle to obtain the resulting properties within quantum mechanics.

8.1.1 Classical Physics

Consider a classical particle of charge Q, mass M, velocity $\mathbf{v}$ in an electrostatic $\mathbf{E} = -\boldsymbol{\nabla}\phi$ and magnetostatic $\mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}$ field where ϕ and $\mathbf{A}$ are the scalar and vector potentials, respectively. The magnetic field definition follows from the Maxwell equation $\boldsymbol{\nabla} \cdot \mathbf{B} = 0$.

Canonical and Physical Momentum

The total or canonical momentum $\mathbf{p}$ is comprised of the sum of its kinetic or physical momentum

$$\mathbf{p}_{\text{physical}} = M\mathbf{v}, \tag{8.1}$$

and its potential or field momentum

$$\mathbf{p}_{\text{field}} = \frac{Q}{c}\mathbf{A}, \tag{8.2}$$

with c the velocity of light. Thus, the canonical momentum is

$$\mathbf{p} = \mathbf{p}_{\text{physical}} + \mathbf{p}_{\text{field}} = M\mathbf{v} + \frac{Q}{c}\mathbf{A}, \tag{8.3}$$

and the physical momentum is

$$\mathbf{p}_{\text{physical}} \equiv \mathbf{\Pi} = \mathbf{p} - \frac{Q}{c}\mathbf{A}. \tag{8.4}$$

(It is the canonical momentum $\mathbf{p}$ on which we impose the canonical commutation relations when we write the quantum mechanical Hamiltonian.) Whereas the physical momentum is gauge invariant, the canonical momentum is gauge variant.

Field Momentum

In the electromagnetic field, the field component of the momentum is obtained from the Poynting's vector [18, 19]:

$$\mathbf{p}_{\text{field}} = \frac{1}{4\pi c}\int \mathbf{E} \times \mathbf{B}\, d\mathbf{r}. \tag{8.5}$$

The field $\mathbf{E}$ at $\mathbf{r}$ due to the charge Q at $\mathbf{r}'$ is $\mathbf{E} = -\nabla\phi$, and satisfies Poisson's equation:

$$\nabla^2\phi = -4\pi Q\delta(\mathbf{r} - \mathbf{r}'). \tag{8.6}$$

Thus,

$$\mathbf{p}_{\text{field}} = -\frac{1}{4\pi c}\int \boldsymbol{\nabla}\phi \times (\boldsymbol{\nabla} \times \mathbf{A})\, d\mathbf{r}. \tag{8.7}$$

Using a standard vector relation, the above volume integral may be written as

$$\int \boldsymbol{\nabla}\phi \times (\boldsymbol{\nabla} \times \mathbf{A})\, d\mathbf{r} = -\int [\mathbf{A} \times \boldsymbol{\nabla} \times (\nabla\phi) - \mathbf{A}\boldsymbol{\nabla} \cdot (\nabla\phi) - (\boldsymbol{\nabla}\phi)\boldsymbol{\nabla} \cdot \mathbf{A}]d\mathbf{r}. \tag{8.8}$$

Since $\boldsymbol{\nabla} \times (\boldsymbol{\nabla}\phi) = 0$, and we can choose the Coulomb or transverse gauge $\boldsymbol{\nabla} \cdot \mathbf{A} = 0$, we have

$$\mathbf{p}_{\text{field}} = -\frac{1}{4\pi c}\int \mathbf{A}\nabla^2\phi \, d\mathbf{r} = \frac{Q}{c}\int \mathbf{A}\delta(\mathbf{r}-\mathbf{r}') \, d\mathbf{r} = \frac{Q}{c}\mathbf{A} \tag{8.9}$$

as noted in (8.2).

In a magnetic field, the kinetic energy of the particle is unchanged. Thus, from (8.3) the kinetic energy is

$$\frac{1}{2}Mv^2 = \frac{1}{2M}(Mv)^2 = \frac{1}{2M}\left(\mathbf{p} - \frac{Q}{c}\mathbf{A}\right)^2. \tag{8.10}$$

Thus, the total energy or Hamiltonian, which is the sum of the kinetic and potential energies of the particle is

$$H = \frac{1}{2M}\left(\mathbf{p} - \frac{Q}{c}\mathbf{A}\right) + Q\phi. \tag{8.11}$$

Rigorous Derivation of Hamiltonian

To determine the Hamiltonian in a more rigorous and general manner, we first require the appropriate Lagrangian for the particle in the electromagnetic field. The Lagrange function in generalized coordinates is [17]

$$L = \frac{1}{2}M\dot{q}^2 - Q\phi(\mathbf{q}) + \frac{Q}{c}\dot{\mathbf{q}} \cdot \mathbf{A}. \tag{8.12}$$

That this Lagrangian is correct is proved by the fact that the Euler-Lagrange equation

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\mathbf{q}}}\right) - \frac{\partial L}{\partial \mathbf{q}} = 0, \tag{8.13}$$

then leads to the correct Lorentz force equation of motion for a charge Q in the electromagnetic field:

$$\mathbf{F} = Q\left(\mathbf{E} + \frac{1}{c}\,\mathbf{v} \times \mathbf{B}\right), \tag{8.14}$$

where

$$\mathbf{E} = -\boldsymbol{\nabla}\phi - \frac{1}{c}\frac{\partial \mathbf{A}}{\partial t} \quad \text{and} \quad \mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}. \tag{8.15}$$

The momentum $\mathbf{p}$ is then

$$\mathbf{p} = \frac{\partial L}{\partial \dot{\mathbf{q}}} = M\dot{\mathbf{q}} + \frac{Q}{c}\mathbf{A}, \tag{8.16}$$

in agreement with (8.3). The Hamiltonian $H(\mathbf{p}, \mathbf{q})$ is [17]

$$H(\mathbf{p}, \mathbf{q}) = \mathbf{p} \cdot \dot{\mathbf{q}} - L \tag{8.17}$$

$$= M\dot{\mathbf{q}}^2 + \frac{Q}{c}\dot{\mathbf{q}} \cdot \mathbf{A} - \frac{1}{2}M\dot{\mathbf{q}}^2 + Q\phi - \frac{Q}{c}\dot{\mathbf{q}} \cdot \mathbf{A} \tag{8.18}$$

$$= \frac{1}{2M}\left(\mathbf{p} - \frac{Q}{c}\mathbf{A}\right)^2 + Q\phi, \tag{8.19}$$

as obtained in (8.11).

Canonical and Physical Angular Momentum

The canonical angular momentum is defined in terms of the canonical momentum as

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}, \tag{8.20}$$

and the kinetic or physical angular momentum as

$$\boldsymbol{\Lambda} = \mathbf{r} \times \boldsymbol{\Pi} = \mathbf{r} \times \left(\mathbf{p} - \frac{Q}{c}\mathbf{A}\right). \tag{8.21}$$

Whereas the canonical angular momentum is gauge variant, the physical angular momentum is gauge invariant.

8.2 The Quantum-Mechanical Hamiltonian and Properties

Consider a system of N electrons in an external electrostatic $\boldsymbol{\mathcal{E}}(\mathbf{r}) = -\boldsymbol{\nabla} v(\mathbf{r})$ and magnetostatic $\mathbf{B}(\mathbf{r}) = \boldsymbol{\nabla} \times \mathbf{A}(\mathbf{r})$ field, where $\{v(\mathbf{r}), \mathbf{A}(\mathbf{r})\}$ are scalar and vector potentials, respectively. In atomic units where we assume the charge of the electron $Q = -e$, with $|e| = \hbar = m = 1$, the Hamiltonian operator, on application of the correspondence principle to the classical Hamiltonian of (8.19), is

$$\hat{H} = \hat{T}_A + \hat{W} + \hat{V}, \tag{8.22}$$

where $\hat{T}_A$ is the *physical* kinetic energy operator:

$$\hat{T}_A = \frac{1}{2}\sum_k \left(\hat{\mathbf{p}}_k + \frac{1}{c}\mathbf{A}(\mathbf{r}_k)\right)^2 \tag{8.23}$$

$$= \hat{T} + \frac{1}{2c}\sum_k \left[\hat{\mathbf{p}}_k \cdot \mathbf{A}(\mathbf{r}_k) + \mathbf{A}(\mathbf{r}_k) \cdot \hat{\mathbf{p}}_k\right] + \frac{1}{2c^2}\sum_k A^2(\mathbf{r}_k), \tag{8.24}$$

with $\hat{T}$ the *canonical* kinetic energy operator:

$$\hat{T} = \frac{1}{2}\sum_k p_k^2; \quad \hat{\mathbf{p}}_k = -i\nabla_{\mathbf{r}_k}, \tag{8.25}$$

with $\hat{\mathbf{p}}_k$ the canonical momentum operator.

The electron-interaction potential energy operator is

$$\hat{W} = \frac{1}{2}\sum_{k,\ell}{}' \frac{1}{|\mathbf{r}_k - \mathbf{r}_l|}, \tag{8.26}$$

and scalar potential energy operator is

$$\hat{V} = \sum_k v(\mathbf{r}_k). \tag{8.27}$$

The time-independent Schrödinger equation is then

$$\hat{H}(\mathbf{R})\psi(\mathbf{X}) = E\psi(\mathbf{X}) \tag{8.28}$$

where $\{\psi(\mathbf{X}), E\}$ are the eigenfunctions and eigenergies of the system with $\mathbf{R} = \mathbf{r}_1, \ldots, \mathbf{r}_N$; $\mathbf{X} = \mathbf{x}_1, \ldots, \mathbf{x}_N$; $\mathbf{x} = \mathbf{r}\sigma$, $\{\mathbf{r}, \sigma\}$ being the spatial and spin coordinates of the electron.

The Hamiltonian operator of (8.22) can be expressed in terms of the *physical current density operator* $\hat{\mathbf{j}}(\mathbf{r})$. To define this operator we revert to the definition of the current density $\mathbf{j}(\mathbf{r})$ of (2.39). In terms of the *physical momentum operator* $\hat{\mathbf{p}}_{\text{physical}} = \left(\hat{\mathbf{p}} + \frac{1}{c}\mathbf{A}\right)$, the physical current density $\mathbf{j}(\mathbf{r})$ is defined as

$$\mathbf{j}(\mathbf{r}) = N\Re\sum_\sigma \int \psi^\star(\mathbf{r}\sigma, \mathbf{X}^{N-1})\left(\hat{\mathbf{p}} + \frac{1}{c}\mathbf{A}(\mathbf{r})\right)\psi(\mathbf{r}\sigma, \mathbf{X}^{N-1})d\mathbf{X}^{N-1}, \tag{8.29}$$

with $\mathbf{X}^{N-1} = \mathbf{x}_2, \ldots, \mathbf{x}_N$. Separating the terms we have

$$\mathbf{j}(\mathbf{r}) = \mathbf{j}_p(\mathbf{r}) + \frac{\mathbf{A}(\mathbf{r})}{c}N\Re\sum_\sigma \int \psi^\star(\mathbf{r}\sigma, \mathbf{X}^{N-1})\psi(\mathbf{r}\sigma, \mathbf{X}^{N-1})d\mathbf{X}^{N-1} \tag{8.30}$$

$$= \mathbf{j}_p(\mathbf{r}) + \frac{1}{c}\rho(\mathbf{r})\mathbf{A}(\mathbf{r}) \tag{8.31}$$

$$= \mathbf{j}_p(\mathbf{r}) + \mathbf{j}_d(\mathbf{r}), \tag{8.32}$$

where $\mathbf{j}_p(\mathbf{r})$ is the paramagnetic component

$$\mathbf{j}_p(\mathbf{r}) = N\Re\sum_\sigma \int \psi^\star(\mathbf{r}\sigma, \mathbf{X}^{N-1})\hat{\mathbf{p}}\psi(\mathbf{r}\sigma, \mathbf{X}^{N-1})d\mathbf{X}^{N-1}, \tag{8.33}$$

(which is the same as that of (2.39)), and $\mathbf{j}_d(\mathbf{r})$ the diamagnetic component.

$$\mathbf{j}_d(\mathbf{r}) = \frac{1}{c}\rho(\mathbf{r})\mathbf{A}(\mathbf{r}). \tag{8.34}$$

Thus, the physical current density operator is (see Sect. 2.2.4)

$$\hat{\mathbf{j}}(\mathbf{r}) = \hat{\mathbf{j}}_p(\mathbf{r}) + \hat{\mathbf{j}}_d(\mathbf{r}), \tag{8.35}$$

with the paramagnetic and diamagnetic component operators defined as

$$\hat{\mathbf{j}}_p(\mathbf{r}) = \frac{1}{2}\sum_k \left[\hat{\mathbf{p}}_k\delta(\mathbf{r}_k - \mathbf{r}) + \delta(\mathbf{r}_k - \mathbf{r})\hat{\mathbf{p}}_k\right], \tag{8.36}$$

$$\hat{\mathbf{j}}_d(\mathbf{r}) = \frac{1}{c}\hat{\rho}(\mathbf{r})\mathbf{A}(\mathbf{r}), \tag{8.37}$$

and where $\hat{\rho}(\mathbf{r})$ is the density operator of (2.12).

Employing the commutator relationship between the momentum operator and any function of the coordinates, we have

$$\hat{\mathbf{p}} \cdot \mathbf{A} - \mathbf{A} \cdot \mathbf{p} = -i\nabla \cdot \mathbf{A}. \tag{8.38}$$

Thus, in the Coulomb gauge $\nabla \cdot \mathbf{A} = 0$, we see that $\hat{\mathbf{p}}$ and $\mathbf{A}(\mathbf{r})$ commute. Using this fact, the physical kinetic energy operator may be written as

$$\hat{T}_A = \hat{T} + \frac{1}{c}\sum_k \mathbf{A}(\mathbf{r}_k) \cdot \hat{\mathbf{p}}_k + \frac{1}{2c^2}\sum_k A^2(\mathbf{r}_k). \tag{8.39}$$

In terms of the paramagnetic $\hat{\mathbf{j}}_p(\mathbf{r})$ and diamagnetic $\hat{\mathbf{j}}_d(\mathbf{r})$ current density operators, the Hamiltonian of (8.22) is then

$$\hat{H} = \hat{T} + \hat{W} + \hat{V} + \frac{1}{c}\int \hat{\mathbf{j}}_p(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r})d\mathbf{r} + \frac{1}{2c^2}\int \hat{\rho}(\mathbf{r})A^2(\mathbf{r})d\mathbf{r}. \tag{8.40}$$

From this expression it is evident that in the presence of a magnetic field, one can define the physical current density operator $\hat{\mathbf{j}}(\mathbf{r})$ of (8.35) as

$$\hat{\mathbf{j}}(\mathbf{r}) = c\,\frac{\partial \hat{H}}{\partial \mathbf{A}(\mathbf{r})} = \hat{\mathbf{j}}_p(\mathbf{r}) + \hat{\mathbf{j}}_d(\mathbf{r}). \tag{8.41}$$

In terms of the operator $\hat{\mathbf{j}}(\mathbf{r})$, the Hamiltonian (8.40) is

$$\hat{H} = \hat{T} + \hat{W} + \hat{V} + \frac{1}{c}\int \hat{\mathbf{j}}(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r})d\mathbf{r} - \frac{1}{2c^2}\int \hat{\rho}(\mathbf{r})A^2(\mathbf{r})d\mathbf{r}. \tag{8.42}$$

Hence, the system energy E which is

$$E = \langle \psi | \hat{H} | \psi \rangle \tag{8.43}$$

may be written in terms either of the paramagnetic $\mathbf{j}_p(\mathbf{r})$ or physical $\mathbf{j}(\mathbf{r})$ current densities as

$$E = T + E_{ee} + V + \frac{1}{c} \int \mathbf{j}_p(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r}) d\mathbf{r} + \frac{1}{2c^2} \int \rho(\mathbf{r}) A^2(\mathbf{r}) d\mathbf{r}, \tag{8.44}$$

or as

$$E = T + E_{ee} + V + \frac{1}{c} \int \mathbf{j}(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r}) d\mathbf{r} - \frac{1}{2c^2} \int \rho(\mathbf{r}) A^2(\mathbf{r}) d\mathbf{r}. \tag{8.45}$$

Here the kinetic T, electron-interaction potential E_{ee} and external scalar potential V energies are the expectations (see Sect. 2.4)

$$T = \langle \psi | \hat{T} | \psi \rangle, \tag{8.46}$$

$$E_{ee} = \langle \psi | \hat{W} | \psi \rangle, \tag{8.47}$$

$$V = \langle \psi | \hat{V} | \psi \rangle, \tag{8.48}$$

and the paramagnetic $\mathbf{j}_p(\mathbf{r})$ and diamagnetic $\mathbf{j}(\mathbf{r})$ current densities the expectations

$$\mathbf{j}_p(\mathbf{r}) = \langle \psi | \hat{\mathbf{j}}_p(\mathbf{r}) | \psi \rangle, \tag{8.49}$$

and

$$\mathbf{j}(\mathbf{r}) = \langle \psi | \hat{\mathbf{j}}(\mathbf{r}) | \psi \rangle, \tag{8.50}$$

respectively.

Finally, as the system is time-independent, the continuity equation for the physical current density $\mathbf{j}(\mathbf{r})$ is

$$\boldsymbol{\nabla} \cdot \mathbf{j}(\mathbf{r}) = \boldsymbol{\nabla} \cdot \mathbf{j}_p + \boldsymbol{\nabla} \cdot \mathbf{j}_d(\mathbf{r}) = 0. \tag{8.51}$$

Unitary Transformation

We next perform a density and physical current density *preserving* unitary transformation [20]. The unitary operator we consider is

$$U = e^{i\alpha(\mathbf{R})}; \quad \alpha(\mathbf{R}) = \sum_j \alpha(\mathbf{r}_j), \tag{8.52}$$

where $\alpha(\mathbf{r})$ is an arbitrary smooth function of position. The transformed (see Sect. 4.2) wave function $\psi'(\mathbf{X})$ and Hamiltonian $\hat{H}'(\mathbf{R})$ of (8.28) are, respectively,

$$\psi'(\mathbf{X}) = U^{\dagger}\psi(\mathbf{X}), \tag{8.53}$$

and

$$\hat{H}' = U^{\dagger}\hat{H}(\mathbf{R})U \tag{8.54}$$
$$= \frac{1}{2}\sum_{k}\left(\hat{\mathbf{p}}_k + \mathbf{A}(\mathbf{r}_k) + \nabla\alpha(\mathbf{r}_k)\right)^2 + \hat{W} + \hat{V}. \tag{8.55}$$

The transformed Schrödinger equation is then

$$\hat{H}'(\mathbf{R})\psi'(\mathbf{X}) = E'\psi'(\mathbf{X}) \tag{8.56}$$

with

$$E' = E. \tag{8.57}$$

Equivalently, if one performs a gauge transformation of the vector potential $\mathbf{A}(\mathbf{r})$ such that

$$\mathbf{A}'(\mathbf{r}) = \mathbf{A}(\mathbf{r}) + \nabla\alpha(\mathbf{r}) \tag{8.58}$$

but let $v'(\mathbf{r}) = v(\mathbf{r})$, the Hamiltonian of (8.22) changes to that of (8.55). Thus, the Hamiltonian is *gauge variant*. Because the physical system remains the same, the wave function $\psi(\mathbf{X})$ must be multiplied by a phase factor $exp[-i\alpha(\mathbf{R})]$, which is (8.52). The system wave function is therefore also *gauge variant*. However, all the physical properties of the system such as the energy E and its individual components T_A, E_{ee}, V, the density $\rho(\mathbf{r})$ and physical current density $\mathbf{j}(\mathbf{r})$ which are all expectations of Hermitian operators remain the same and are *gauge invariant*. The component paramagnetic $\mathbf{j}_p(\mathbf{r})$ and diamagnetic $\mathbf{j}_d(\mathbf{r})$ current densities, on the other hand, are *gauge variant*. The choice of gauge function $\alpha(\mathbf{R})$ is arbitrary because the physical properties of the system remain unchanged: the infinite number of Hamiltonians for different phase factors $\alpha_i(\mathbf{R})$ correspond to the same physical system (see Fig. 1 of [20]). Thus, one can conclude that the wave function $\psi(\mathbf{X})$ is a functional of the gauge function $\alpha(\mathbf{R}) : \psi(\mathbf{X}) = \psi[\alpha(\mathbf{R})](\mathbf{X})$.

Canonical and Physical Angular Momentum

The canonical angular momentum operator $\hat{\mathbf{L}}$ is defined in terms of the canonical momentum operator $\hat{\mathbf{p}}$ as

$$\hat{\mathbf{L}} = \mathbf{r} \times \hat{\mathbf{p}} = \mathbf{r} \times (-i\nabla), \tag{8.59}$$

and the physical angular momentum operator $\hat{\mathbf{\Lambda}}$ in terms of the physical momentum operator $\hat{\mathbf{p}}_{\text{physical}}$ as

$$\hat{\mathbf{\Lambda}} = \mathbf{r} \times \hat{\mathbf{p}}_{\text{physical}} = \mathbf{r} \times \left(\hat{\mathbf{p}} + \frac{1}{c}\mathbf{A} \right) \tag{8.60}$$

The canonical $\mathbf{L}$ and physical $\mathbf{\Lambda}$ angular momentum are defined as the expectations

$$\mathbf{L} = \langle \psi | \hat{\mathbf{L}} | \psi \rangle, \tag{8.61}$$

and

$$\mathbf{\Lambda} = \langle \psi | \hat{\mathbf{\Lambda}} | \psi \rangle, \tag{8.62}$$

respectively.

It is readily seen that the canonical angular momentum is *gauge variant*. Employing the transformed wave function of (8.53) for a single electron, the transformed property

$$\mathbf{L}' = \langle \psi' | \hat{\mathbf{L}} | \psi \rangle = \int \psi'^{\star} (\mathbf{r} \times \hat{\mathbf{p}}) \psi' d\mathbf{r} \tag{8.63}$$

$$= \int \psi^{\star} e^{-i\alpha} [\mathbf{r} \times \hat{\mathbf{p}} \psi'] d\mathbf{r} \tag{8.64}$$

$$= \int \psi^{\star} e^{-i\alpha} [\mathbf{r} \times \{ e^{i\alpha} \hat{\mathbf{p}} \psi + \nabla \alpha \psi' \}] d\mathbf{r} \tag{8.65}$$

$$= \int \psi^{\star} (\mathbf{r} \times \hat{\mathbf{p}}) \psi d\mathbf{r} + \int \psi^{\star} (\mathbf{r} \times \nabla \alpha) \psi d\mathbf{r} \tag{8.66}$$

$$= \mathbf{L} + \int \psi^{\star} (\mathbf{r} \times \nabla \alpha) \psi d\mathbf{r}. \tag{8.67}$$

On the other hand, the physical angular momentum is *gauge invariant*. Employing the transformed wave function of (8.53) for a single electron, and the transformed vector potential of (8.58), the transformed property

$$\mathbf{\Lambda}' = \langle \psi' | \hat{\mathbf{\Lambda}} | \psi' \rangle \tag{8.68}$$

$$= \int \psi^{\star} e^{-i\alpha} \left[\mathbf{r} \times \left(\hat{\mathbf{p}} + \frac{1}{c}\mathbf{A}' \right) \right] \psi' d\mathbf{r}' \tag{8.69}$$

$$= \int \psi^{\star} e^{-i\alpha} \left[\mathbf{r} \times e^{i\alpha} \left(\hat{\mathbf{p}} + \frac{1}{c}\mathbf{A} \right) \psi \right] d\mathbf{r} \tag{8.70}$$

$$= \int \psi^{\star} \left[\mathbf{r} \times \left(\hat{\mathbf{p}} + \frac{1}{c}\mathbf{A} \right) \right] \psi d\mathbf{r} = \mathbf{\Lambda}. \tag{8.71}$$

8.3 Generalized Hohenberg-Kohn Theorems

The Hohenberg-Kohn theorems for N electrons in an external electrostatic field $\boldsymbol{\mathcal{E}}(\mathbf{r}) = -\boldsymbol{\nabla} v(\mathbf{r})$ are extended here to the case of the added presence of a magnetostatic field $\mathbf{B}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r})$. It is proved that for a *uniform* magnetic field and *fixed* canonical angular momentum $\mathbf{L}$, there exists a one-to-one or bijective relationship between the external potentials $\{v(\mathbf{r}), \mathbf{A}(\mathbf{r})\}$ and the nondegenerate ground state density $\rho(\mathbf{r})$ and physical current density $\mathbf{j}(\mathbf{r})$. In other words, the basic variables of quantum mechanics in the presence of a uniform magnetic field are the densities $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$, and the system wave functions ψ are thus functionals of these properties: $\psi = \psi[\rho, \mathbf{j}]$. The proof is for $\{v, \mathbf{A}\}$-representable densities. The proof, however, differs in fundamental ways from that of the proof of the first HK theorem. In order to elucidate these differences, let us first briefly summarize the proof of the first HK theorem of Sect. 4.1 for the Hamiltonian of (4.1)).

In the HK proof, it is first proved (Maps C and C^{-1}) that there is a bijective relationship between the external potential $v(\mathbf{r})$ and the nondegenerate ground state wave function $\psi(\mathbf{X})$. Employing this relationship, it is then proved (Maps D and D^{-1}) that there is a bijective relationship between the wave function $\psi(\mathbf{X})$ and the nondegenerate ground state density $\rho(\mathbf{r})$. Maps D and D^{-1} are established for v-representable densities. (The manner by which this is accomplished is via the assumption that there exists a $\{\psi, E\}$ and a $\{\psi', E'\}$ generated via different potentials $v(\mathbf{r})$ and $v'(\mathbf{r})$, respectively, that lead to the same density $\rho(\mathbf{r})$. This in turn leads to the contradiction $E + E' < E + E'$, thereby proving the bijectivity between $\psi(\mathbf{X})$ and $\rho(\mathbf{r})$. The assumption of existence of a $\psi(\mathbf{X})$ and a $\psi'(\mathbf{X})$ that *differ*, because they arise from different external potentials $v(\mathbf{r})$ and $v'(\mathbf{r})$, is based on and a consequence of Maps C and C^{-1}. Such an assumption would be invalid without the existence of Maps C and C^{-1}.) Thus, knowledge of $\rho(\mathbf{r})$ determines the external potential $v(\mathbf{r})$ to within an additive constant, and thereby the Hamiltonian of the system. In the proof, the electron number N is kept *fixed*.

In the presence of a magnetic field $\mathbf{B}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r})$, the Hamiltonian in terms of the gauge invariant properties $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ is given by (8.42). It would appear that one could prove a one-to-one relationship between these properties and the external potentials $\{v(\mathbf{r}), \mathbf{A}(\mathbf{r})\}$ along the lines of the HK path. However, no such proof is possible as the relationship between the potentials $\{v(\mathbf{r}), \mathbf{A}(\mathbf{r})\}$ and the nondegenerate ground state wave function $\psi(\mathbf{X})$ can be *many-to-one* [6–10] and even *infinite-to-one* [11, 12]:

$$\begin{array}{lll} \{\, v(\mathbf{r}), \mathbf{A}(\mathbf{r})\} & \searrow & \\ \{\, v'(\mathbf{r}), \mathbf{A}'(\mathbf{r})\} & \longrightarrow & \\ \{\, v''(\mathbf{r}), \mathbf{A}''(\mathbf{r})\} & \longrightarrow & \qquad \Psi(\mathbf{X}) \\ \qquad \cdots & \nearrow & \end{array} \tag{8.72}$$

Hence, in these cases, there is no equivalent of the Maps C and C^{-1}, and therefore the original HK path is not possible. The proof that $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ are the basic variables must then differ from the original HK proof. Furthermore, any proof of the bijectivity between $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ and $\{v(\mathbf{r}), \mathbf{A}(\mathbf{r})\}$ must account for the many-to-one relationship between $\{v(\mathbf{r}), \mathbf{A}(\mathbf{r})\}$ and the nondegenerate ground state $\psi(\mathbf{X})$. Finally, because the added presence of a magnetic field $\mathbf{B}(\mathbf{r})$ constitutes an added degree of freedom, there must exist an additional constraint beyond that of fixed electron number N. The constraint is that of fixed canonical angular momentum $\mathbf{L}$.

In the next subsection, we first consider the case of spinless electrons in which the interaction of the magnetic field is only with the orbital angular momentum $\mathbf{L}$ of the electrons. In the subsection that follows we consider the case of electrons with spin. In this case, there is an added term to the Hamiltonian corresponding to the interaction of the magnetic field with the spin angular momentum $\mathbf{S}$. Corresponding to this term of the Hamiltonian, there is (for finite systems), a contribution to the physical current density $\mathbf{j}(\mathbf{r})$ viz. the magnetization current density $\mathbf{j}_m(\mathbf{r})$ component.

8.3.1 Proof of Generalized Hohenberg-Kohn Theorems: Case I: Spinless Electrons

The proof of the first generalized HK theorem of the bijectivity between the nondegenerate ground state $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ and the potentials $\{v(\mathbf{r}), \mathbf{A}(\mathbf{r})\}$ is also by *reductio ad absurdum*. The proof is for $(v, \mathbf{A})$-representable densities $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$. Consider the Hamiltonian $\hat{H}$ of (8.22) or equivalently (8.42) for fixed electron number N and canonical angular momentum $\mathbf{L}$. Let us then consider two different physical systems $\{v, \mathbf{A}\}$ and $\{v', \mathbf{A}'\}$ that generate different nondegenerate ground state wave functions ψ and ψ'. We assume the gauges of the unprimed and primed systems to be the same. Let us further assume that these systems lead to the *same* nondegenerate ground state $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$. We prove this cannot be the case.

From the variational principle for the energy for a nondegenerate ground state

$$E = \langle\psi|\hat{H}|\psi\rangle \;<\; \langle\psi'|\hat{H}|\psi'\rangle. \tag{8.73}$$

Now the term on the right hand side of the inequality may be written as

$$\begin{aligned}
\langle\psi'|\hat{H}|\psi'\rangle &= \langle\psi'|\hat{T} + \hat{U} + \hat{V}' + \frac{1}{c}\int \hat{\mathbf{j}}'(\mathbf{r})\cdot\mathbf{A}'(\mathbf{r})d\mathbf{r} - \frac{1}{2c^2}\int \hat{\rho}(\mathbf{r})A'^2(\mathbf{r})d\mathbf{r}|\psi'\rangle \\
&+ \langle\psi'|\hat{V} - \hat{V}'|\psi'\rangle \\
&+ \langle\psi'|\frac{1}{c}\int [\hat{\mathbf{j}}(\mathbf{r})\cdot\mathbf{A}(\mathbf{r}) - \hat{\mathbf{j}}'(\mathbf{r})\cdot\mathbf{A}'(\mathbf{r})]d\mathbf{r}|\psi'\rangle \\
&- \frac{1}{2c^2}\langle\psi'|\int \hat{\rho}(\mathbf{r})[A^2(\mathbf{r}) - A'^2(\mathbf{r})]d\mathbf{r}|\psi'\rangle.
\end{aligned} \tag{8.74}$$

For the primed system, the physical current density operator is

$$\hat{\mathbf{j}}'(\mathbf{r}) = \hat{\mathbf{j}}_p(\mathbf{r}) + \frac{1}{c}\hat{\rho}(\mathbf{r})\mathbf{A}'(\mathbf{r}), \tag{8.75}$$

so that

$$\mathbf{j}'(\mathbf{r}) = \langle\psi'|\hat{\mathbf{j}}'(\mathbf{r})|\psi'\rangle = \mathbf{j}'_p(\mathbf{r}) + \frac{1}{c}\rho'(\mathbf{r})\mathbf{A}'(\mathbf{r}). \tag{8.76}$$

Employing the original assumption that ψ and ψ' lead to the same $\rho(\mathbf{r})$, we have

$$\langle\psi'|\hat{\mathbf{j}}(\mathbf{r})|\psi'\rangle \;=\; \mathbf{j}'_p(\mathbf{r}) + \frac{1}{c}\rho(\mathbf{r})\mathbf{A}(\mathbf{r}). \tag{8.77}$$

and

$$\langle\psi'|\hat{\mathbf{j}}'(\mathbf{r})|\psi'\rangle \;=\; \mathbf{j}'_p(\mathbf{r}) + \frac{1}{c}\rho(\mathbf{r})\mathbf{A}'(\mathbf{r}). \tag{8.78}$$

Therefore

$$\langle\psi'|\int \hat{\mathbf{j}}(\mathbf{r})\cdot\mathbf{A}(\mathbf{r})d\mathbf{r}|\psi'\rangle \;=\; \int \mathbf{j}'_p(\mathbf{r})\cdot\mathbf{A}(\mathbf{r})d\mathbf{r} + \frac{1}{c}\int \rho(\mathbf{r})A^2(\mathbf{r})d\mathbf{r}, \tag{8.79}$$

and

$$\langle\psi'|\int \hat{\mathbf{j}}'(\mathbf{r})\cdot\mathbf{A}'(\mathbf{r})d\mathbf{r}|\psi'\rangle \;=\; \int \mathbf{j}'_p(\mathbf{r})\cdot\mathbf{A}'(\mathbf{r})d\mathbf{r} + \frac{1}{c}\int \rho(\mathbf{r})A'^2(\mathbf{r})d\mathbf{r}, \tag{8.80}$$

so that in (8.74) the term

$$\begin{aligned}
&\frac{1}{c}\langle\psi'|\int[\hat{\mathbf{j}}(\mathbf{r})\cdot\mathbf{A}(\mathbf{r}) - \hat{\mathbf{j}}'(\mathbf{r})\cdot\mathbf{A}'(\mathbf{r})]d\mathbf{r}|\psi'\rangle \\
&= \frac{1}{c}\int \mathbf{j}'_p(\mathbf{r})\cdot[\mathbf{A}(\mathbf{r}) - \mathbf{A}'(\mathbf{r})]d\mathbf{r} + \frac{1}{c^2}\int \rho(\mathbf{r})[A^2(\mathbf{r}) - A'^2(\mathbf{r})]d\mathbf{r}.
\end{aligned} \tag{8.81}$$

Finally, employing again that $\rho'(\mathbf{r}) = \rho(\mathbf{r})$, the last term of (8.74) is

$$\begin{aligned}
&\frac{1}{2c^2}\langle\psi'|\int \hat{\rho}(\mathbf{r})[A^2(\mathbf{r}) - A'^2(\mathbf{r})]d\mathbf{r}|\psi'\rangle \\
&= \frac{1}{2c^2}\int \rho(\mathbf{r})[A^2(\mathbf{r}) - A'^2(\mathbf{r})]d\mathbf{r}.
\end{aligned} \tag{8.82}$$

Therefore, the inequality of (8.73) is

$$E < E' + \int \rho(\mathbf{r})[v(\mathbf{r}) - v'(\mathbf{r})]d\mathbf{r} + \frac{1}{c}\int \mathbf{j}'_p(\mathbf{r}) \cdot [\mathbf{A}(\mathbf{r}) - \mathbf{A}'(\mathbf{r})]d\mathbf{r} + \frac{1}{2c^2}\int \rho(\mathbf{r})[A^2(\mathbf{r}) - A'^2(\mathbf{r})]d\mathbf{r}. \quad (8.83)$$

On interchanging the primed and unprimed quantities,

$$E' < E + \int \rho(\mathbf{r})[v'(\mathbf{r}) - v(\mathbf{r})]d\mathbf{r} + \frac{1}{c}\int \mathbf{j}_p(\mathbf{r}) \cdot [\mathbf{A}'(\mathbf{r}) - \mathbf{A}(\mathbf{r})]d\mathbf{r} + \frac{1}{2c^2}\int \rho(\mathbf{r})[A'^2(\mathbf{r}) - A^2(\mathbf{r})]d\mathbf{r}. \quad (8.84)$$

On adding the previous two equations one obtains the inequality

$$E + E' < E + E' + \frac{1}{c}\int [\mathbf{j}'_p(\mathbf{r}) - \mathbf{j}_p(\mathbf{r})] \cdot [\mathbf{A}(\mathbf{r}) - \mathbf{A}'(\mathbf{r})]d\mathbf{r}. \quad (8.85)$$

The inequality of (8.85) is a general result.

Consider next the third term on the right hand side of (8.85). With $\mathbf{B}(\mathbf{r}) = B\hat{\mathbf{i}}_z$, $\mathbf{B}'(\mathbf{r}) = B'\hat{\mathbf{i}}_z$, and the symmetric gauge $\mathbf{A}(\mathbf{r}) = \frac{1}{2}\mathbf{B} \times \mathbf{r}$, $\mathbf{A}'(\mathbf{r}) = \frac{1}{2}\mathbf{B}' \times \mathbf{r}$, this term is

$$I = \int \big[\mathbf{j}'_p(\mathbf{r}) - \mathbf{j}_p(\mathbf{r})\big] \cdot \big[\mathbf{A}(\mathbf{r}) - \mathbf{A}'(\mathbf{r})\big]d\mathbf{r} \quad (8.86)$$

$$= \int \big[\mathbf{j}'_p(\mathbf{r}) - \mathbf{j}_p(\mathbf{r})\big] \cdot \big[\frac{1}{2}\Delta\mathbf{B} \times \mathbf{r}\big]d\mathbf{r} \quad (8.87)$$

$$= \frac{1}{2}\Delta\mathbf{B} \cdot \int \mathbf{r} \times \big[\mathbf{j}'_p(\mathbf{r}) - \mathbf{j}_p(\mathbf{r})\big]d\mathbf{r}, \quad (8.88)$$

where $\Delta\mathbf{B} = (B - B')\hat{\boldsymbol{i}}_z$. First consider the integral

$$I_1 = \int \mathbf{r} \times \mathbf{j}_p(\mathbf{r})d\mathbf{r} \quad (8.89)$$

$$= -\frac{i}{2}\sum_k \int \mathbf{r} \times \Big\{\int \Psi^\star(\mathbf{X})\big[\boldsymbol{\nabla}_{\mathbf{r}_k}\delta(\mathbf{r} - \mathbf{r}_k) + \delta(\mathbf{r} - \mathbf{r}_k)\boldsymbol{\nabla}_{\mathbf{r}_k}\big]\Psi(\mathbf{X})d\mathbf{X}\Big\}d\mathbf{r} \quad (8.90)$$

$$= -\frac{i}{2}\sum_k \int d\mathbf{X}\int d\mathbf{r}\Psi^\star(\mathbf{X})\big[\mathbf{r} \times \boldsymbol{\nabla}_{\mathbf{r}_k}\delta(\mathbf{r} - \mathbf{r}_k) + \delta(\mathbf{r} - \mathbf{r}_k)\mathbf{r} \times \boldsymbol{\nabla}_{\mathbf{r}_k}\big]\Psi(\mathbf{X}) \quad (8.91)$$

Next consider the second integral of I_1 of (8.91):

$$I_{12} = -\frac{i}{2}\sum_k \int d\mathbf{X}\Psi^\star(\mathbf{X})\Big[\int d\mathbf{r}\delta(\mathbf{r}-\mathbf{r}_k)\mathbf{r}\times\nabla_{\mathbf{r}_k}\Big]\Psi(\mathbf{X}) \tag{8.92}$$

$$= -\frac{i}{2}\sum_k \int d\mathbf{X}\Psi^\star(\mathbf{X})\mathbf{r}_k\times\nabla_{\mathbf{r}_k}\Psi(\mathbf{X}) \tag{8.93}$$

$$= \frac{1}{2}\int d\mathbf{X}\Psi^\star(\mathbf{X})\Big(\sum_k \mathbf{r}_k\times\mathbf{p}_k\Big)\Psi(\mathbf{X}) \tag{8.94}$$

$$= \frac{1}{2}\int d\mathbf{X}\Psi^\star(\mathbf{X})\sum_k \hat{\mathbf{L}}_k\Psi(\mathbf{X}) \tag{8.95}$$

$$= \frac{1}{2}\mathbf{L}, \tag{8.96}$$

where $\hat{\mathbf{L}}_k = \mathbf{r}_k\times\mathbf{p}_k$ is the canonical orbital angular momentum operator, and $\mathbf{L}$ the total canonical orbital angular momentum defined by (8.95).

The first integral of I_1 of (8.91) is

$$I_{11} = -\frac{i}{2}\sum_k \int d\mathbf{X}\int d\mathbf{r}\Psi^\star(\mathbf{X})\mathbf{r}\times\nabla_{\mathbf{r}_k}\delta(\mathbf{r}-\mathbf{r}_k)\Psi(\mathbf{X}) \tag{8.97}$$

$$= -\frac{i}{2}\sum_k \int d\mathbf{X}\int d\mathbf{r}\Psi^\star(\mathbf{X})\epsilon_{\alpha\beta\gamma}\frac{\partial}{\partial r_{k\gamma}}\big(r_\beta\delta(\mathbf{r}-\mathbf{r}_k)\Psi(\mathbf{X})\big). \tag{8.98}$$

On integrating the inner integral by parts and dropping the surface term, one obtains

$$I_{11} = -\frac{i}{2}\sum_k \int d\mathbf{X}\Big[-\epsilon_{\alpha\beta\gamma}\int d\mathbf{r}\frac{\partial\Psi^\star(\mathbf{X})}{\partial r_{k\gamma}}r_\beta\delta(\mathbf{r}-\mathbf{r}_k)\Psi(\mathbf{X})\Big] \tag{8.99}$$

$$= -\frac{i}{2}\sum_k \int d\mathbf{X}\Big[-\epsilon_{\alpha\beta\gamma}\frac{\partial\Psi^\star(\mathbf{X})}{\partial r_{k\gamma}}r_{k\beta}\Psi(\mathbf{X})\Big]. \tag{8.100}$$

On integrating by parts again, one obtains

$$I_{11} = -\frac{i}{2}\sum_k \epsilon_{\alpha\beta\gamma}\int d\mathbf{X}\Psi^\star(\mathbf{X})\frac{\partial}{\partial r_{k\gamma}}\big(r_{k\beta}\Psi(\mathbf{X})\big) \tag{8.101}$$

$$= -\frac{i}{2}\sum_k \int d\mathbf{X}\Psi^\star(\mathbf{X})\ (\mathbf{r}_k\times\nabla_{\mathbf{r}_k})\Psi(\mathbf{X}) \tag{8.102}$$

$$= \frac{1}{2}\mathbf{L}. \tag{8.103}$$

Hence, the integral I of (8.88) is

$$I = \frac{1}{2}\Delta\mathbf{B}\cdot(\mathbf{L}' - \mathbf{L}). \tag{8.104}$$

If one imposes the constraint that the total canonical orbital angular momentum is *fixed* so that $\mathbf{L} = \mathbf{L}'$, then the integral I of (8.88) vanishes. Hence, (8.85) reduces to the contradiction

$$E + E' < E + E'. \tag{8.105}$$

What this means is that the original assumption ψ and ψ' differ is erroneous, and that there can exist a $\{v, \mathbf{A}\}$ and a $\{v', \mathbf{A}'\}$ with the same nondegenerate ground state wave function. The fact that $\psi = \psi'$ means that

$$\rho(\mathbf{r})\big|_{\psi} = \rho'(\mathbf{r})\big|_{\psi'} \tag{8.106}$$

However, the corresponding physical current densities are not the same:

$$\mathbf{j}(\mathbf{r})\big|_{\psi} \neq \mathbf{j}'(\mathbf{r})\big|_{\psi'}. \tag{8.107}$$

This is because the diamagnetic components are not the same

$$\mathbf{j}_d(\mathbf{r})\big|_{\psi} \neq \mathbf{j}'_d(\mathbf{r})\big|_{\psi'}, \tag{8.108}$$

if one hews to the original assumption that $\mathbf{A}(\mathbf{r})$ is different from $\mathbf{A}'(\mathbf{r})$. This proves that the assumption that there exists a different $\{v', \mathbf{A}'\}$ (with the same N and $\mathbf{L}$) that leads to the same $\{\rho, \mathbf{j}\}$ as that due to $\{v, \mathbf{A}\}$ is incorrect. *This step takes into account the fact that there could exist many* $\{v, \mathbf{A}\}$ *that lead to the same nondegenerate ground state* ψ. Hence, there exists only one $\{v, \mathbf{A}\}$ for fixed N and $\mathbf{L}$ that generates a nondegenerate ground state $\{\rho, \mathbf{j}\}$. The one-to-one relationship between $\{\rho, \mathbf{j}\}$ and $\{v, \mathbf{A}\}$ is therefore proved.

The statement of the first generalized HK theorem is then as follows:

Theorem 1 *For electrons in an external electrostatic field and a uniform magnetostatic field, and for fixed electron number N and orbital angular momentum* $\mathbf{L}$, *the nondegenerate ground state density* $\rho(\mathbf{r})$ *and physical current density* $\mathbf{j}(\mathbf{r})$, *determine the external scalar* $v(\mathbf{r})$ *and vector* $\mathbf{A}(\mathbf{r})$ *potentials to within an additive constant and the gradient of a scalar function, respectively.*

With the kinetic $\hat{T}$ and electron-interaction $\hat{W}$ operators of the electrons known, knowledge of $\{\rho, \mathbf{j}\}$ determines the potentials $\{v, \mathbf{A}\}$ and thereby the Hamiltonian $\hat{H}$. Solution of the Schrödinger equation (8.28) then leads to the wave function $\psi(\mathbf{X})$ of the system. Thus, the HK path to the wave function is

$$\rho(\mathbf{r}), \mathbf{j}(\mathbf{r}) \longrightarrow v(\mathbf{r}), \mathbf{A}(\mathbf{r}) \longrightarrow \hat{H}(\mathbf{R}) \longrightarrow \psi(\mathbf{X}). \tag{8.109}$$

The wave functions $\psi(\mathbf{X})$ are therefore functionals of $\{\rho, \mathbf{j}\}$. As shown in the previous section, the wave functions are also functionals of a gauge function $\alpha(\mathbf{R})$. Hence, the wave functions $\psi(\mathbf{X})$ are functionals of $\{\rho, \mathbf{j}, \alpha\} : \psi(\mathbf{X}) = \psi[\rho, \mathbf{j}, \alpha]$. As $\rho(\mathbf{r})$ and $\mathbf{j}(\mathbf{r})$ are gauge invariant, it is the presence of the gauge function $\alpha(\mathbf{R})$ in the wave function written as a functional that ensures it is gauge variant. As a consequence of the path of (8.109) the basic variables of quantum mechanics in a uniform magnetostatic field are $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$.

With the choice of $\alpha(\mathbf{R}) = 0$, the ground state energy for *fixed angular momentum* can be written as a functional of $\{\rho, \mathbf{j}\}$. Thus,

$$E_{v,\mathbf{A}}[\rho, \mathbf{j}] = \langle \psi[\rho, \mathbf{j}]|\hat{H}(\mathbf{R})|\psi[\rho, \mathbf{j}]\rangle \tag{8.110}$$

$$= F[\rho, \mathbf{j}] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + \frac{1}{c}\int \mathbf{j}(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r})d\mathbf{r}$$
$$- \frac{1}{2c^2}\int \rho(\mathbf{r})A^2(\mathbf{r})d\mathbf{r}, \tag{8.111}$$

where

$$F[\rho, \mathbf{j}] = \langle \psi[\rho, \mathbf{j}]|\hat{T} + \hat{W}|\psi[\rho, \mathbf{j}]\rangle \tag{8.112}$$

is the *universal* internal energy functional. As the ground state energy is a functional of $\{\rho, \mathbf{j}\}$, a variational principle exists for arbitrary variations of $(v, \mathbf{A})$-representable densities $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$. Implicit in such a variational principle, as in all such energy variational principles, is that *the external potentials remain fixed throughout the variation*. The variational character of the energy functional of (8.110) follows from the variational principle:

$$E_{v,\mathbf{A}}[\rho', \mathbf{j}'] \; > \; E_{v,\mathbf{A}}[\rho, \mathbf{j}] \quad \text{for } \{\rho', \mathbf{j}'\} \neq \{\rho, \mathbf{j}\}, \tag{8.113}$$

$$E_{v,\mathbf{A}}[\rho', \mathbf{j}'] \; = \; E_{v,\mathbf{A}}[\rho, \mathbf{j}] \quad \text{for } \{\rho', \mathbf{j}'\} = \{\rho, \mathbf{j}\}. \tag{8.114}$$

Equivalently, the Euler-Lagrange equations that must be solved self-consistently for $\rho(\mathbf{r})$ and $\mathbf{j}(\mathbf{r})$ are

$$\left.\frac{\delta E_{v,\mathbf{A}}[\rho, \mathbf{j}]}{\delta \rho(\mathbf{r})}\right|_{\mathbf{j}(\mathbf{r})} = 0; \quad \left.\frac{\delta E_{v,\mathbf{A}}[\rho, \mathbf{j}]}{\delta \mathbf{j}(\mathbf{r})}\right|_{\rho(\mathbf{r})} = 0 \tag{8.115}$$

subject to the constraints

$$\int \rho(\mathbf{r})d\mathbf{r} = N, \tag{8.116}$$

$$\int \mathbf{r} \times [\mathbf{j}(\mathbf{r}) - \frac{1}{c}\rho(\mathbf{r})\mathbf{A}(\mathbf{r})]d\mathbf{r} = \mathbf{L}, \tag{8.117}$$

$$\boldsymbol{\nabla} \cdot \mathbf{j}(\mathbf{r}) = 0. \tag{8.118}$$

The statement of the second generalized HK theorem is then as follows:
Theorem 2 *The nondegenerate ground state density* $\rho(\mathbf{r})$ *and physical current density* $\mathbf{j}(\mathbf{r})$*, can be determined from the ground state energy functional* $E_{v,\mathbf{A}}[\rho, \mathbf{j}]$ *via the variational principle by variations only of these densities. The constraints on the corresponding Euler-Lagrange equations are the conservation of charge and canonical angular momentum, and the satisfaction of the equation of continuity.*

That the properties $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ for fixed orbital angular momentum $\mathbf{L}$ are the basic variables is most readily seen for the case of $N = 1$. Writing the wave function in polar form

$$\psi(\mathbf{r}) = \Phi(\mathbf{r})e^{i\Theta(\mathbf{r})}, \tag{8.119}$$

with $\Phi(\mathbf{r})$, $\Theta(\mathbf{r})$ real valued, we see that $\rho(\mathbf{r}) = \Phi^2(\mathbf{r})$ and $\mathbf{j}(\mathbf{r}) = \mathbf{j}_p(\mathbf{r}) + \mathbf{j}_d(\mathbf{r})$, $\mathbf{j}_p(\mathbf{r}) = \rho(\mathbf{r})\boldsymbol{\nabla}\Theta(\mathbf{r}), \mathbf{j}_d(\mathbf{r}) = \frac{1}{c}\rho(\mathbf{r})\mathbf{A}(\mathbf{r})$, so that $\frac{1}{c}\mathbf{A}(\mathbf{r}) = \frac{\mathbf{j}(\mathbf{r})}{\rho(\mathbf{r})} - \boldsymbol{\nabla}\Theta(\mathbf{r})$. Thus knowledge of $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ determines the potential $\mathbf{A}(\mathbf{r})$ to within the gradient of a scalar function. Employing this and the fact that one can perform a gauge transformation to eliminate the phase, the one-electron Schrödinger equation can be written as

$$\left[\frac{1}{2}\left(\hat{\mathbf{p}} + \frac{\mathbf{j}(\mathbf{r})}{\rho(\mathbf{r})}\right)^2 + v(\mathbf{r}) - E\right]\rho^{\frac{1}{2}}(\mathbf{r}) = 0, \tag{8.120}$$

from which the potential $v(\mathbf{r})$ can be obtained to within the constant E since $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ are known. (This example is given in [21] but without the added constraint on the angular momentum.)

What is interesting about this example is that the $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ as basic variables are not restricted to being solely the nondegenerate ground state densities. The above arguments are equally valid for $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ corresponding to any state and angular momentum.

For a summary of the generalized HK theorems, and a comparison with the original HK theorems, see Table 8.1.

For other recent work see [22, 23]. The conclusions in [23] are based on the assumption of existence of a HK theorem but one without the requirement of the constraint on the angular momentum.

8.3.2 Proof of Generalized Hohenberg-Kohn Theorems: Case II: Electrons with Spin

When the interaction of the magnetic field is with both the orbital and spin moment of the electrons, the Hamiltonian is

$$\hat{H} = \frac{1}{2}\sum_k \left[\hat{\mathbf{p}}_k + \frac{1}{c}\mathbf{A}(\mathbf{r}_k)\right]^2 + \hat{W} + \hat{V} + \frac{1}{c}\sum_k \mathbf{s}_k \cdot \mathbf{B}(\mathbf{r}_k), \tag{8.121}$$

where $\mathbf{s}_k$ is the electron spin angular momentum vector operator of the kth electron. (The last term is $2\mu_B \sum_k \mathbf{s}_k \cdot \mathbf{B}(\mathbf{r}_k)$, where $\mu_B = e\hbar/2mc$ is the Bohr magneton. We employ the atomic units $|e| = \hbar = m = 1$.) In nonrelativistic quantum mechanics, this term was originally added on *ad hoc* by Pauli to account for the interaction of the magnetic field with the electron spin magnetic moment. Hence, the designation as Schrödinger-Pauli theory. However, for a spin $\frac{1}{2}$ particle, the Hamiltonian can be rigorously derived [24] if one starts with the definition of the kinetic energy operator in the presence of a vector potential to be

$$\hat{T}_A = \frac{1}{2}\left(\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}_{\text{phys}}\right)\left(\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}_{\text{phys}}\right), \tag{8.122}$$

where $\boldsymbol{\sigma}$ is the spin matrix and $\hat{\mathbf{p}}_{\text{phys}} = \hat{\mathbf{p}} + \frac{1}{c}\mathbf{A}$, the physical momentum operator. Substituting this operator, we have

$$\hat{T}_A = \frac{1}{2}\boldsymbol{\sigma} \cdot \left(\hat{\mathbf{p}} + \frac{1}{c}\mathbf{A}\right) \boldsymbol{\sigma} \cdot \left(\hat{\mathbf{p}} + \frac{1}{c}\mathbf{A}\right). \tag{8.123}$$

Employing the vector relation

$$(\boldsymbol{\sigma} \cdot \mathbf{A})(\boldsymbol{\sigma} \cdot \mathbf{B}) = \mathbf{A} \cdot \mathbf{B} + i\boldsymbol{\sigma} \cdot (\mathbf{A} \times \mathbf{B}) \tag{8.124}$$

which holds even with $\mathbf{A}$ and $\mathbf{B}$ being operators, the kinetic energy operator is

$$\hat{T}_A = \frac{1}{2}\left(\hat{\mathbf{p}} + \frac{1}{c}\mathbf{A}\right)^2 + \frac{i}{2}\boldsymbol{\sigma} \cdot \left[\left(\mathbf{p} + \frac{1}{c}\mathbf{A}\right) \times \left(\mathbf{p} + \frac{1}{c}\mathbf{A}\right)\right] \tag{8.125}$$

$$= \frac{1}{2}\left(\hat{\mathbf{p}} + \frac{1}{c}\mathbf{A}\right)^2 + \frac{i}{2}\boldsymbol{\sigma} \cdot \left[\frac{1}{c}\mathbf{A} \times \mathbf{p} + \frac{1}{c}\mathbf{p} \times \mathbf{A}\right]. \tag{8.126}$$

Using the operator relation

$$\hat{\mathbf{p}} \times \mathbf{A} = -i\boldsymbol{\nabla} \times \mathbf{A} - \mathbf{A} \times \mathbf{p}, \tag{8.127}$$

we then arrive at

$$\hat{T}_A = \frac{1}{2}\left(\mathbf{p} + \frac{1}{c}\mathbf{A}\right)^2 + \frac{1}{2c}\boldsymbol{\sigma} \cdot \mathbf{B} \tag{8.128}$$

$$= \frac{1}{2}\left(\hat{\mathbf{p}} + \frac{1}{c}\mathbf{A}\right)^2 + \frac{1}{c}\mathbf{s} \cdot \mathbf{B}, \tag{8.129}$$

where we have employed $\mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}$ and $\mathbf{s} = \frac{1}{2}\boldsymbol{\sigma}$. The spin magnetic moment generated in this way has the correct gyromagnetic ratio $g = 2$ [25]. (Note that the operator $\hat{T}_A$ of (8.122) reduces to $p^2/2$ in the absence of vector potentials.)

The Hamiltonian of (8.121) can also be obtained from the Dirac equation in its nonrelativistic limit.

The Schrödinger-Pauli Hamiltonian of (8.121) may also be written in terms of the density $\hat{\rho}(\mathbf{r})$, physical current density $\hat{\mathbf{j}}(\mathbf{r})$, and local magnetization density $\hat{\mathbf{m}}(\mathbf{r})$ operators as

$$\hat{H} = \hat{T} + \hat{W} + \hat{V}_A - \int \hat{\mathbf{m}}(\mathbf{r}) \cdot \mathbf{B}(\mathbf{r}) d\mathbf{r}, \tag{8.130}$$

where the total external potential operator $\hat{V}_A$ is

$$\hat{V}_A = \hat{V} + \frac{1}{c} \int \hat{\mathbf{j}}(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r}) d\mathbf{r} - \frac{1}{2c^2} \int \hat{\rho}(\mathbf{r}) A^2(\mathbf{r}) d\mathbf{r}, \tag{8.131}$$

and $\hat{\mathbf{m}}(\mathbf{r})$ is defined as

$$\hat{\mathbf{m}}(\mathbf{r}) = -\frac{1}{c} \sum_k \mathbf{s}_k \delta(\mathbf{r}_k - \mathbf{r}). \tag{8.132}$$

The physical current density operator $\hat{\mathbf{j}}(\mathbf{r})$ is the sum of its paramagnetic $\hat{\mathbf{j}}_p(\mathbf{r})$ and diamagnetic $\hat{\mathbf{j}}_d(\mathbf{r})$ components as in (8.35) or (8.41). With the same assumptions made regarding the two different physical systems $\{v, \mathbf{A}; \psi\}$ and $\{v', \mathbf{A}'; \psi'\}$ leading to the same $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ one obtains the inequality

$$\begin{aligned} E + E' < E + E' &+ \int [\mathbf{j}'_p(\mathbf{r}) - \mathbf{j}_p(\mathbf{r})] \cdot [\mathbf{A}(\mathbf{r}) - \mathbf{A}'(\mathbf{r})] d\mathbf{r} \\ &- \int [\mathbf{m}'(\mathbf{r}) - \mathbf{m}(\mathbf{r})] \cdot [\mathbf{B}(\mathbf{r}) - \mathbf{B}'(\mathbf{r})] d\mathbf{r}, \end{aligned} \tag{8.133}$$

with $\mathbf{m}(\mathbf{r})$ the magnetization density being the expectation

$$\mathbf{m}(\mathbf{r}) = \langle \psi | \hat{\mathbf{m}}(\mathbf{r}) | \psi \rangle. \tag{8.134}$$

The inequality is once again a general result.

The third term on the right hand side of (8.133) vanishes if, as in the previous section, a uniform magnetic field is assumed, and the constraint that the orbital angular momentum of the unprimed and primed systems are the same is imposed. Hence next consider the last term of (8.133). With $\mathbf{B}(\mathbf{r}) = B\hat{\mathbf{i}}_z$, the term

$$\int \mathbf{m}(\mathbf{r}) \cdot \mathbf{B}(\mathbf{r}) d\mathbf{r} = B \int m_z(\mathbf{r}) d\mathbf{r}, \tag{8.135}$$

where, with $\mathbf{s}_k \cdot \hat{\mathbf{i}}_z = s_{z,k}$,

$$m_z(\mathbf{r}) = -\frac{1}{c}\sum_{\sigma}\int\sum_{k} s_{z,k}\delta(\mathbf{r}_k - \mathbf{r}) \times \psi^{\star}(\mathbf{r}_k\sigma, \mathbf{X}^{N-1})\psi(\mathbf{r}_k\sigma, \mathbf{X}^{N-1})d\mathbf{X}^{N-1}d\mathbf{r}_k \tag{8.136}$$

$$= -\frac{1}{c}\sum_{\sigma}\int\sum_{k} s_{z,k}\int\psi^{\star}(\mathbf{r}\sigma, \mathbf{X}^{N-1}) \times \psi(\mathbf{r}\sigma, \mathbf{X}^{N-1})d\mathbf{X}^{N-1} \tag{8.137}$$

$$= -\frac{1}{cN}\sum_{\sigma} S_z\gamma(\mathbf{r}\sigma, \mathbf{r}\sigma), \tag{8.138}$$

where $S_z = \sum_k s_{z,k}$ is the z-component of the total spin $\mathbf{S}$, and $\gamma(\mathbf{x}\mathbf{x}') = N\int\psi^{\star}(\mathbf{r}\sigma, \mathbf{X}^{N-1})\psi(\mathbf{r}'\sigma', \mathbf{X}^{N-1})d\mathbf{X}^{N-1}$, the density matrix. Since in the primed system, the spin vectors are different, i.e. some $\mathbf{s}'_k$, we have

$$\int\big[\mathbf{m}'(\mathbf{r}) - \mathbf{m}(\mathbf{r})\big]\cdot\Delta\mathbf{B}(\mathbf{r})d\mathbf{r} = \Delta B\int\big[m'_z(\mathbf{r}) - m_z(\mathbf{r})\big]d\mathbf{r} \tag{8.139}$$

$$= \frac{\Delta B}{cN}\sum_{\sigma}\int\big[S'_z\gamma'(\mathbf{r}\sigma, \mathbf{r}\sigma) - S_z\gamma(\mathbf{r}\sigma, \mathbf{r}\sigma)\big]d\mathbf{r}, \tag{8.140}$$

where $\Delta B = B - B'$. Employing the original assumption that the diagonal matrix elements $\gamma(\mathbf{r}\sigma, \mathbf{r}\sigma)$ of the density matrix $\gamma(\mathbf{x}\mathbf{x}')$ are the same for the unprimed and primed systems we have the right hand side of (8.140) to be

$$\frac{\Delta B}{cN}\sum_{\sigma}\int\big[S'_z - S_z\big]\gamma(\mathbf{r}\sigma, \mathbf{r}\sigma) = 0 \tag{8.141}$$

provided $S'_z = S_z$. Hence, the last term of (8.133) vanishes.

Another way of arriving at this conclusion is by rewriting $m_z(\mathbf{r})$ as [26, 27]

$$m_z(\mathbf{r}) = -\frac{1}{2c}[\rho_\alpha(\mathbf{r}) - \rho_\beta(\mathbf{r})], \tag{8.142}$$

with $\rho_\alpha(\mathbf{r})$, $\rho_\beta(\mathbf{r})$ being the spin-up and spin-down spin densities. The last term of the inequality of (8.133) is then

$$\int[\mathbf{m}'(\mathbf{r}) - \mathbf{m}(\mathbf{r})]\cdot\Delta\mathbf{B}(\mathbf{r})d\mathbf{r} = -\frac{1}{2c}\Delta B\int[\{\rho'_\alpha(\mathbf{r}) - \rho'_\beta(\mathbf{r})\} - \{\rho_\alpha(\mathbf{r}) - \rho_\beta(\mathbf{r})\}]d\mathbf{r}. \tag{8.143}$$

If the z-component of the total spin angular momentum S_z for the unprimed and primed systems are the same, the corresponding spin densities are the same, so that the last term of (8.133) vanishes. More generally, the magnetization densities $\mathbf{m}(\mathbf{r})$ and $\mathbf{m}'(\mathbf{r})$ are the same if the total spin angular momentum $\mathbf{S}$ and $\mathbf{S}'$ are the same.

The vanishing of the last two terms of (8.133) once again leads to the contradiction $E + E' < E + E'$. Employing the same reasoning as in the previous section one concludes that the original assumption that ψ and ψ' differ is erroneous, and that there can exist a $\{v, \mathbf{A}\}$ and a $\{v', \mathbf{A}'\}$ with the same nondegenerate ground state wave function. With $\psi = \psi'$, we have $\rho(\mathbf{r}) = \rho'(\mathbf{r})$, but $\mathbf{j}(\mathbf{r}) \neq \mathbf{j}'(\mathbf{r})$ since $\mathbf{A}(\mathbf{r}) \neq \mathbf{A}'(\mathbf{r})$. This proves that the original assumption that there exists a $\{v', \mathbf{A}'\}$ with the same N, $\mathbf{L}$, and $\mathbf{S}$ as that of $\{v, \mathbf{A}\}$ but leads to the same $\{\rho, \mathbf{j}\}$ to be incorrect. Thus, there can exist only one $\{v, \mathbf{A}\}$ for fixed N, $\mathbf{L}$, and $\mathbf{S}$ that can generate the nondegenerate ground state $\{\rho, \mathbf{j}\}$. The bijective relationship between $\{\rho, \mathbf{j}\}$ and $\{v, \mathbf{A}\}$ for systems defined by the Schrödinger-Pauli Hamiltonian is therefore proved. Note that the proof explicitly accounts for the many-to-one relationship between the potentials $\{v, \mathbf{A}\}$ and the nondegenerate ground state ψ.

In the above proof of bijectivity for the Schrödinger-Pauli Hamiltonian, the definition of the physical current density $\mathbf{j}(\mathbf{r})$ employed was that of (8.29) or equivalently (8.32), viz. one in terms of its paramagnetic and diamagnetic components. However, for finite systems, yet another component—the magnetization current density—due to the electron spin can be introduced [29]. Consider the last term of the Hamiltonian of (8.130):

$$\int \hat{\mathbf{m}}(\mathbf{r}) \cdot \mathbf{B}(\mathbf{r}) d\mathbf{r} = \int \hat{\mathbf{m}}(\mathbf{r}) \cdot (\nabla \times \mathbf{A}(\mathbf{r})) d\mathbf{r} \tag{8.144}$$

$$= \int \mathbf{A}(\mathbf{r}) \cdot (\nabla \times \hat{\mathbf{m}}(\mathbf{r})) d\mathbf{r} + \int \nabla \cdot (\mathbf{A}(\mathbf{r}) \times \hat{\mathbf{m}}(\mathbf{r})) d\mathbf{r}, \tag{8.145}$$

where the vector identity

$$\nabla \cdot (\mathbf{C} \times \mathbf{D}) = \mathbf{D} \cdot (\nabla \times \mathbf{C}) - \mathbf{C} \cdot (\nabla \times \mathbf{D}) \tag{8.146}$$

is employed. The last term of (8.145) may be converted to an integral over a surface: $\int \nabla \cdot (\mathbf{A} \times \hat{\mathbf{m}}) d\mathbf{r} = \int (\mathbf{A} \times \hat{\mathbf{m}}) \cdot d\mathbf{S}$, which vanishes in the usual way for an infinitely distant surface. Thus, the Hamiltonian of (8.130) can be written as

$$\hat{H} = \hat{T} + \hat{W} + \hat{V} + \frac{1}{c} \int \hat{\mathbf{j}}_p(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r}) d\mathbf{r} + \frac{1}{2c^2} \int \hat{\rho}(\mathbf{r}) A^2(\mathbf{r}) d\mathbf{r} + \frac{1}{c} \int \hat{\mathbf{j}}_m(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r}) d\mathbf{r}, \tag{8.147}$$

where the magnetization current density operator $\hat{\mathbf{j}}_m(\mathbf{r})$ is defined as

$$\hat{\mathbf{j}}_m(\mathbf{r}) = -c\nabla \times \hat{\mathbf{m}}(\mathbf{r}). \tag{8.148}$$

Hence the physical current density $\mathbf{j}(\mathbf{r})$ may also be defined as [29]

$$\mathbf{j}(\mathbf{r}) = c\frac{\partial \hat{H}}{\partial \mathbf{A}(\mathbf{r})} = \mathbf{j}_p(\mathbf{r}) + \mathbf{j}_d(\mathbf{r}) + \mathbf{j}_m(\mathbf{r}), \tag{8.149}$$

the sum of the paramagnetic, diamagnetic, and magnetization current densities. Even for this definition of the physical current density $\mathbf{j}(\mathbf{r})$, the proof of bijectivity between $\{\rho, \mathbf{j}\}$ and $\{v, \mathbf{A}\}$ is valid provided the angular momentum $\mathbf{L}$ and $\mathbf{S}$ are fixed. (For spin-compensated systems, the magnetization current density $\mathbf{j}_m(\mathbf{r})$ vanishes.) The corresponding energy variational principle for arbitrary variations of $(v, \mathbf{A})$ representable densities $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ follows together with the constraints of fixed N, $\mathbf{L}$, and $\mathbf{S}$, and the satisfaction of the equation of continuity for the physical current density $\mathbf{j}(\mathbf{r})$.

8.4 Remarks on Spin and Current Density Functional Theories

In the previous section we provided proofs of the generalized HK theorems in the presence of a uniform magnetic field for the cases of both spinless electrons and electrons with spin. There it was shown that for each type of electron, the basic variables were the nondegenerate ground state density $\rho(\mathbf{r})$ and physical current density $\mathbf{j}(\mathbf{r})$, and a subsequent variational principle formulated in terms of these properties. These theorems then constitute a $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ functional theory in a generic sense not to be confused with other existing theories. In the following subsections, we make a few remarks on spin density functional theory (SDFT) [2, 6, 26–28] and the paramagnetic current $\mathbf{j}_p(\mathbf{r})$ density functional theory (CDFT) [30–32]. In neither of these or other similar extensions is the added constraint on the orbital $\mathbf{L}$ or spin $\mathbf{S}$ angular momentum considered.

8.4.1 Remarks on Spin Density Functional Theory

In SDFT it is assumed that the basic variables are the nondegenerate ground state density $\rho(\mathbf{r})$ and the magnetization density $\mathbf{m}(\mathbf{r})$. Equivalently, the assumed basic variables are the density $\rho(\mathbf{r})$ and the electron spin density which is the difference between the spin-up $\rho_\alpha(\mathbf{r})$ and spin-down $\rho_\beta(\mathbf{r})$ densities (see [26, 27] and (8.142)). The basis for this choice is that these properties appear in the corresponding assumed

SDFT Hamiltonian or energy functional. A proof that these properties are the basic variables is then attempted. We comment here on the proof. The Hamiltonian of SDFT is an approximation to the Schrödinger-Pauli Hamiltonian of (8.121) and is assumed to be

$$\hat{H} = \frac{1}{2}\sum_k \hat{\mathbf{p}}_k^2 + \hat{W} + \hat{V} + (1/c)\sum_k \mathbf{B}(\mathbf{r}_k)\cdot\mathbf{s}_k \tag{8.150}$$

$$= \hat{T} + \hat{W} + \hat{V} - \int \mathbf{m}(\mathbf{r})\cdot\mathbf{B}(\mathbf{r})d\mathbf{r}. \tag{8.151}$$

The Hamiltonian corresponds to the energy functional $E[\rho, \mathbf{m}]$ originally proposed by Kohn and Sham [2] to obtain a theory of spin susceptibility. The functional proposed was

$$E[\rho, \mathbf{m}] = \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + E_H[\rho] - \int \mathbf{m}(\mathbf{r})\cdot\mathbf{B}(\mathbf{r})d\mathbf{r} + G[\rho(\mathbf{r}), \mathbf{m}(\mathbf{r})], \tag{8.152}$$

where $E_H[\rho] = \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\rho(\mathbf{r})\rho(\mathbf{r})'/|\mathbf{r}-\mathbf{r}'|$ is the Coulomb self-energy, and $G[\rho, \mathbf{m}(\mathbf{r})]$ a universal functional that includes contributions of the kinetic energy and of the many-body effects. Both the Hamiltonian of (8.150) and energy functional of (8.152) are *ad hoc* and not derivable from first principles: The expressions do not include the field component of the electron momentum, and hence ignore the interaction of the magnetic field with the orbital angular momentum. The contribution of this component to the energy is not insignificant, and is of the same order of magnitude as that of the interaction of the field with the spin angular momentum.

In writing the energy functional of (8.152) it is assumed that the wave function corresponding to the Hamiltonian of (8.150) is a functional of $\{\rho, \mathbf{m}\}$. This, of course, is based on the assumption that there is a one-to-one relationship between $\{\rho, \mathbf{m}\}$ and $\{v, \mathbf{B}\}$ along the lines of the original HK theorem. Subsequently, von Barth and Hedin [6] showed that for noninteracting fermions, the relationship between $\{v, \mathbf{B}\}$ and the nondegenerate ground state wave function was many-to-one, and as such there was no equivalent of Map C for the Hamiltonian of (8.150). Ignoring this fact, and assuming the basic variables to be $\{\rho, \mathbf{m}\}$ these and other authors [6, 28] then focused on Map D between ψ and $\{\rho, \mathbf{m}\}$. As in all reductio ad absurdum type proofs, they begin with the assumption that there exists a $\{v, \mathbf{B}\}$ and a $\{v', \mathbf{B}'\}$ that generate the same $\{\rho, \mathbf{m}\}$. One then has to prove that this statement is incorrect. (Comment: Because the relationship between $\{v, \mathbf{B}\}$ and ψ is many-to-one, there do exist other $\{v', \mathbf{B}'\}$ that lead to the same $\{\rho, \mathbf{m}\}$.) They next assume that there is a ψ and a ψ' with $\psi \neq \psi'$, where $\hat{H}(v, \mathbf{B})\psi = E\psi$ and $\hat{H}'(v', \mathbf{B}')\psi' = E'\psi'$. (Comment: This assumption presupposes the existence of a Map (C, C^{-1}). But there is no Map (C, C^{-1}). Furthermore, there do exist a $\{v, \mathbf{B}\}$ and a $\{v', \mathbf{B}'\}$ that generate the same ψ.) Employing the above two assumptions then leads to the contradiction $E+E' < E+E'$. Thus, these authors conclude (a) that the original assumption that there exists a $\{v, \mathbf{B}\}$ and a $\{v', \mathbf{B}'\}$ that lead to the same $\{\rho, \mathbf{m}\}$ to be incorrect, and (b) that two different nondegenerate ground state ψ and ψ' always lead to $\{\rho, \mathbf{m}\} \neq \{\rho', \mathbf{m}'\}$. Hence, Map (D, D^{-1}) between ψ and $\{\rho, \mathbf{m}\}$ is proved, and consequently ψ is a functional of $\{\rho, \mathbf{m}\}$. It is evident that the error in this solely Map (D, D^{-1})-type proof is the presupposition of the existence of a Map (C, C^{-1}) between $\{v, \mathbf{B}\}$ and ψ. Equivalently, the error is in neglecting the many-to-one relationship between $\{v, \mathbf{B}\}$ and the nondegenerate ground state ψ There is no one-to-one relationship between $\{\rho, \mathbf{m}\}$ and $\{v, \mathbf{B}\}$, and therefore $\{\rho, \mathbf{m}\}$ are not basic variables in the rigorous HK sense.

With the assumption that the basic variables are $\{\rho, \mathbf{m}\}$, a PLL-type proof [26, 27, 33] can, of course, now be formulated. One searches over all antisymmetric functions $\psi_{\rho,\mathbf{m}}$ constrained to reproduce the ground state $\{\rho, \mathbf{m}\}$. The true ground state wave function ψ is that which minimizes the expectation of the operators $\hat{T} + \hat{W}$. (Note that in this minimization process, the magnetic field $\mathbf{B}(\mathbf{r})$ is kept fixed.) But there is an inherent inconsistency in the PLL path for SDFT. Knowledge of the ground state $\{\rho, \mathbf{m}\}$ does not uniquely determine $\{v, \mathbf{B}\}$, and thus does not determine the Hamiltonian.

For completeness, we note that with the assumption of $\{\rho, \mathbf{m}\}$ as the basic variables, there exists a "potential functional" theory [34], and a Legendre transform approach [35, 36] to SDFT.

We conjecture that because of the fundamental significance of the concept of basic variables to a physical system, no HK-type proof can exist for Hamiltonians that are not derivable from the tenets of quantum mechanics.

8.4.2 Remarks on Paramagnetic Current Density Functional Theory

Paramagnetic current $\mathbf{j}_p(\mathbf{r})$ density functional theory (CDFT) [30–32] is with respect to the spinless Hamiltonian of (8.22), which may be rewritten in terms of $\mathbf{j}_p(\mathbf{r})$ as in (8.40). The claim here is that the basic variables are the nondegenerate ground state density $\rho(\mathbf{r})$ and the paramagnetic current density $\mathbf{j}_p(\mathbf{r})$. We remark here on the rational for this choice, and the subsequent proof provided.

(a) At the outset, the choice of physical current density $\mathbf{j}(\mathbf{r})$ as a basic variable is rejected. The reasoning [32] for this is the following: According to the first Hohenberg-Kohn theorem, proved for the $\mathbf{B}(\mathbf{r}) = 0$ case, there is a *unique* one-to-one relationship between the nondegenerate ground state density $\rho(\mathbf{r})$ and the ground state wave function $\psi(\mathbf{X})$. However, in the case of $\mathbf{B}(\mathbf{r}) \neq 0$, because the wave function is gauge variant and can be multiplied by a phase factor, there can be no one-to-one relationship between the physical current density $\mathbf{j}(\mathbf{r})$ which is gauge invariant and the wave function $\psi(\mathbf{X})$. Hence, $\mathbf{j}(\mathbf{r})$ cannot be a basic variable. However, as shown in Sect. 4.2 and [37], *density preserving* gauge transformations can also be applied to the HK Hamiltonian and wave function of (4.1) for the $\mathbf{B}(\mathbf{r}) = 0$ case. The *uniqueness* of the one-to-one relationship between the density $\rho(\mathbf{r})$ and the wave function $\psi(\mathbf{X})$ is for *each* choice of gauge function $\alpha(\mathbf{R})$. If the above reasoning were applied to this case, the corresponding statement would be that there can be no one-to-one relationship between the density $\rho(\mathbf{r})$ which is gauge invariant and the wave function $\psi(\mathbf{X})$ which is gauge variant. As a consequence there would be no density functional theory. The reason for rejecting $\mathbf{j}(\mathbf{r})$ as a basic variable is thus inconsistent with quantum mechanics and the generalization of the first Hoheneberg-Kohn theorem of Sect. 4.2.

(b) As in SDFT, the proof within CDFT that $\{\rho(\mathbf{r}), \mathbf{j}_p(\mathbf{r})\}$ are the basic variables ignores the fundamental physical fact that the relationship between the potentials $\{v(\mathbf{r}), \mathbf{A}(\mathbf{r})\}$ and the nondegenerate ground state wave function $\psi(\mathbf{X})$ is many-to-one. As such the proof, as in SDFT, is based solely on a Map (D, D^{-1})-type argument of a one-to-one relationship between the assumed variables $\{\rho(\mathbf{r}), \mathbf{j}_p(\mathbf{r})\}$ and $\psi(\mathbf{X})$. Hence, the proof is not rigorous in the HK sense as a one-to-one relationship between the variables $\{\rho(\mathbf{r}), \mathbf{j}_p(\mathbf{r})\}$ and the potentials $\{v(\mathbf{r}), \mathbf{A}(\mathbf{r})\}$ is not proved.

(c) The fact [7–10] that there is no one-to-one relationship between $\{\rho(\mathbf{r}), \mathbf{j}_p(\mathbf{r})\}$ and $\{v(\mathbf{r}), \mathbf{A}(\mathbf{r})\}$ means that the former are not basic variables in the rigorous HK sense. Equivalently, the wave function $\psi(\mathbf{X})$ is not a functional of $\{\rho(\mathbf{r}), \mathbf{j}_p(\mathbf{r})\}$. As such $\{\rho(\mathbf{r}), \mathbf{j}_p(\mathbf{r})\}$ cannot determine uniquely all the properties of a system. For example, knowledge of $\{\rho(\mathbf{r}), \mathbf{j}_p(\mathbf{r})\}$ cannot determine the physical current density $\mathbf{j}(\mathbf{r})$. This is because $\mathbf{j}(\mathbf{r}) = \mathbf{j}_p(\mathbf{r}) + \mathbf{j}_d(\mathbf{r})$; $\mathbf{j}_d(\mathbf{r}) = \rho(\mathbf{r})\mathbf{A}(\mathbf{r})/c$ and there are many $\mathbf{A}(\mathbf{r})$ that generate the same $\psi(\mathbf{X})$ and $\mathbf{j}_p(\mathbf{r})$, but *not* the same $\mathbf{j}(\mathbf{r})$.

(d) Again, as in SDFT, the proof presupposes [38, 39] the existence of the generalization of Map (C, C^{-1}) of HK to the $\mathbf{B}(\mathbf{r}) \neq 0$ case. In other words, the starting point of the Map (D, D^{-1})-type proof is the assumption that such a Map (C, C^{-1}) exists. That, of course, is not the case. (A justification [40] of the validity of solely Map (D, D^{-1})-type proofs in fact begins with the assumption of existence of a Map (C, C^{-1}).) (A similar Map (D, D^{-1})-type proof for $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ as the basic variables has also been given [41].)

(e) Finally, for CDFTs corresponding to the Schrödinger-Pauli Hamiltonian of (8.121), the basic variables are assumed [42] to be $\{\rho(\mathbf{r}), \mathbf{j}_p(\mathbf{r}), \mathbf{m}(\mathbf{r})\}$ or [43] $\{\rho(\mathbf{r}), \mathbf{j}_p(\mathbf{r}), \mathbf{m}(\mathbf{r}), \mathbf{j}_{p,m}(\mathbf{r})\}$, where $\mathbf{j}_{p,m}(\mathbf{r})$ are the gauge variant paramagnetic currents of each component of the magnetization density. Once again, these conclusions are based on solely Map (D, D^{-1})-type proofs with no relationship between these properties and the external potentials $\{v(\mathbf{r}), \mathbf{A}(\mathbf{r})\}$ proved.

In summary, the proofs on which SDFT and the various CDFTs are based (a) do not account for the many-to-one relationship between the potentials $\{v(\mathbf{r}), \mathbf{A}(\mathbf{r})\}$ and the nondegenerate ground state wave function $\psi(\mathbf{X})$, and (b) assume the existence of a Map (C, C^{-1}). Thus, although these theories are extensively employed in their respective Kohn-Sham versions, they are not foundationally as strong as the original Hohenberg-Kohn theorems or their generalizations to uniform magnetostatic fields proved here.

8.5 Endnote

For completeness we note that the idea of employing $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ as the basic variables goes back to the work of Ghosh-Dhara [44, 45] who employ these properties without proof that they are basic variables. The relativistic case is discussed by Rajagopal-Callaway [46]. Methods to circumvent the many-to-one relationship between the external potentials and the ground state wave function employing the optimized potential approach have been proposed [47, 48], but the underlying formal issues still persist. Additionally, these methods employ the paramagnetic current density $\mathbf{j}_p(\mathbf{r})$ as a basic variable instead of the physical current density $\mathbf{j}(\mathbf{r})$. However, in none of this or other prior work is the issue of the constraint on the angular momentum considered. Finally, although most experimentation with magnetic fields is done for uniform fields for which the proofs of the generalized Hohenberg-Kohn theorems provided in this chapter are applicable, it would be best to have a more general proof of $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ as the basic variables for arbitrary magnetostatic field. What is learned via the proofs provided here, however, is that the constraint on the constancy of the angular momentum will play a critical role in any such more general proof. The present generalized Hohenberg-Kohn theorems for uniform magnetic fields would then constitute a special case.

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Chapter 9
Quantal-Density Functional Theory in the Presence of a Magnetostatic Field

Abstract Quantal density functional theory (Q–DFT) of electrons in an external electrostatic field is generalized to the added presence of a magnetostatic field. This Q–DFT constitutes the mapping from the interacting system of electrons in an external electrostatic and magnetostatic field in any state as described by Schrödinger theory to one of noninteracting fermions with the same density, physical current density, electron number, and canonical orbital and spin angular momentum. To formulate this Q–DFT, Schrödinger theory from the perspective of the individual electron via the corresponding 'Quantal Newtonian' first law is developed. It is shown that in addition to the external fields, each electron experiences an internal field which is comprised of components representative of electron correlations due to the Pauli exclusion principle and Coulomb interaction, the density, the kinetic effects, and a contribution due to the external magnetic field. These fields are derived from quantal sources that are expectations of Hermitian operators taken with respect to the system wave function. As such the intrinsic self-consistent nature of the Schrödinger equation is demonstrated. With the Schrödinger equation written in self-consistent form, the magnetic field, (in addition to the vector potential of the field component of the momentum), now appears explicitly in it. The 'Quantal Newtonian' first law for the model system of noninteracting fermions is derived. It is shown that if the model fermions are subject to the same external potentials, then the only electron correlations that must be accounted for in the Q–DFT mapping are those of the Pauli principle, Coulomb repulsion and Correlation-Kinetic effects. The resulting local electron-interaction potential within Q–DFT is the work done in an effective field that is the sum of fields representative of these correlations. The corresponding many-body components of the total energy can be expressed in integral virial form in terms of the separate fields. To explicate this Q–DFT, it is applied to a quantum dot as represented by the exactly solvable two-dimensional Hooke's atom in a magnetic field. A key observation is that as a result of the reduction in dimensionality due to the presence of the magnetic field, Correlation-Kinetic effects are significant.

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Introduction

As noted in the previous chapter, the study of the electronic properties of matter in the presence of both an external electrostatic field $\boldsymbol{\mathcal{E}}(\mathbf{r}) = -\boldsymbol{\nabla} v(\mathbf{r})$ and a magneotostatic field $\mathbf{B}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r})$, where $v(\mathbf{r})$ and $\mathbf{A}(\mathbf{r})$ are the scalar and vector potentials, continues to be of interest. Properties such as the Zeeman effect in atoms and molecules, and the magneto-caloric effect, the de Haas - van Alphen effect, the Hall effect, and magnetoresistance in solids, have been studied. The more recent interest has focused on electrons confined to two-dimensions: metal-oxide-semiconductor structures, quantum wells and super lattices, the integer and fractional quantum Hall effects, and quantum dots.

In this chapter, we generalize [1] the Q-DFT of a system of electrons in an external electrostatic field $\boldsymbol{\mathcal{E}}(\mathbf{r}) = -\boldsymbol{\nabla} v(\mathbf{r})$ to now include an external magnetostatic field $\mathbf{B}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r})$. The first issue that must be addressed is what properties constitute the basic variables of quantum mechanics in this case. As shown in the previous chapter (and in [2]), for an external magnetic field that is *uniform*, the basic variables for fixed electron number N and canonical angular momentum $\mathbf{L}$, are the nondegenerate ground state density $\rho(\mathbf{r})$ and the physical current density $\mathbf{j}(\mathbf{r})$. In other words, a bijective relationship between the properties $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ and the potentials $\{v(\mathbf{r}), \mathbf{A}(\mathbf{r})\}$ (to within a constant and the gradient of a scalar function) was proved. There is at present no such proof for *arbitrary* magnetic field $\mathbf{B}(\mathbf{r})$. However, in the presence of an external time-dependent electromagnetic field, it has been proved [3, 4] the basic variables are $\{\rho(\mathbf{r}t), \mathbf{j}(\mathbf{r}t)\}$ with $\mathbf{j}(\mathbf{r}t)$ the physical current density, *i.e.*, there is a one-to-one relationship between $\{\rho(\mathbf{r}t), \mathbf{j}(\mathbf{r}t)\}$ and the potentials $\{v(\mathbf{r}t), \mathbf{A}(\mathbf{r}t)\}$. Extending this conclusion to the time-independent case, we assume that for an arbitrary magnetic field $\mathbf{B}(\mathbf{r})$ and fixed angular momentum $\mathbf{L}$, that the basic variables are $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$.

Q-DFT in the presence of a magnetic field $\mathbf{B}(\mathbf{r})$, constitutes the mapping from the true interacting system of electrons in a nondegenerate ground or excited state to a model S system of noninteracting fermions having the same density $\rho(\mathbf{r})$, physical current density $\mathbf{j}(\mathbf{r})$, and angular momentum $\mathbf{L}$. From the model system, the same total energy E as that of the interacting system may be obtained. The state of the model system is *arbitrary* in that it may be in a ground- or excited-state configuration. The existence of the model fermionic system is an assumption.

To develop this Q-DFT, one needs to first derive [1, 5] the 'Quantal Newtonian' first law for the individual electron for both the interacting and noninteracting systems. For the interacting system, as a result of the presence of the magnetic field $\mathbf{B}(\mathbf{r})$, the total external field $\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r})$ experienced by each electron now has the additional Lorentz field component. The magnetic field $\mathbf{B}(\mathbf{r})$ also contributes a term to the internal field $\boldsymbol{\mathcal{F}}^{\text{int}}(\mathbf{r})$ seen by each electron. For the mapping to the S system, it is assumed that the model fermions are subject to the same external field $\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r})$. The S system is of course designed to reproduce the same $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ and $\mathbf{L}$ as that of the interacting system. With these constraints, it turns out that the contribution of the magnetic field $\mathbf{B}(\mathbf{r})$ to the corresponding internal field $\boldsymbol{\mathcal{F}}_s^{\text{int}}(\mathbf{r})$ experienced by each model fermion, is the same as that of the interacting system. The significant further consequence of these constraints is that the only correlations the model system must account for are those due to the Pauli exclusion principle, Coulomb repulsion, and Correlation-Kinetic effects. These correlations are exactly the same as that of the Q-DFT for the case of $\mathbf{B}(\mathbf{r}) = 0$. (In fact [6], irrespective of the external fields experienced by the interacting electrons, if the model fermions (a) experience the same external fields, and (b) are constrained so as to reproduce the basic variables, then in each case it is only Pauli and Coulomb correlations, and Correlation-Kinetic effects that must be accounted for by the model system. The version of Q-DFT presented here thus differs from that of [1] in that there are no Correlation-Magnetic effects to account for, and is thus simpler. Recall that in time-dependent Q-DFT, the application of these conditions eliminates Correlation-Current-Density effects).

In the sections to follow, we first describe Schrödinger theory from the perspective of the 'Quantal Newtonian' first law. In classical electromagnetic theory, the vector potential $\mathbf{A}(\mathbf{r})$ is introduced to simplify the writing of equations. It is assumed that the magnetic field $\mathbf{B}(\mathbf{r})$ derived from this vector potential is a physical real quantity. In quantum mechanics, it is the vector potential $\mathbf{A}(\mathbf{r})$ that appears explicitly in the Hamiltonian (see (8.22)). (This fact is emphasized, for example, in explaining the Ahranov-Bohm effect [7] in which a vector potential $\mathbf{A}(\mathbf{r})$ exists in a region where there is no magnetic field $\mathbf{B}(\mathbf{r})$.) It is only following the assumption of gauge, e.g. say the Landau gauge $\mathbf{A}(\mathbf{r}) = Bxi_y$ or symmetrical gauge $\mathbf{A}(\mathbf{r}) = \frac{1}{2}\mathbf{B}(\mathbf{r}) \times \mathbf{r}$ that the magnetic field $\mathbf{B}(\mathbf{r})$ then appears in the Schrödinger equation. However, with the Schrödinger equation rewritten via the 'Quantal Newtonian' first law, two important insights are achieved: (a) the intrinsic self-consistent nature of the equation becomes evident, (see also the case for $\mathbf{B}(\mathbf{r}) = 0$ described in Chap. 2), and (b) in addition to the vector potential $\mathbf{A}(\mathbf{r})$, the magnetic field $\mathbf{B}(\mathbf{r})$ now appears naturally in it via the Lorentz field contribution. It is the self-consistent nature of the Schrödinger equation that demands the explicit presence of the magnetic field $\mathbf{B}(\mathbf{r})$ in the Hamiltonian. Next, the model S system of noninteracting fermions having the same $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ and $\mathbf{L}$ is then described from the perspective of the corresponding 'Quantal Newtonian' first law. From these laws for the interacting and model systems, the equations governing Q-DFT are then derived. We conclude the chapter by explicating this Q-DFT by application to an exactly solvable model of a quantum dot as represented by the two-dimensional Hooke's atom [8, 9] in which the electrons are confined to a plane by a magnetic field. The chapter is written to be self-contained.

9.1 Schrödinger Theory and the 'Quantal Newtonian' First Law

Consider a system of N electrons in the presence of an external electrostatic field $\boldsymbol{\mathcal{E}}(\mathbf{r}) = -\boldsymbol{\nabla} v(\mathbf{r})$ and a magnetostatic field $\mathbf{B}(\mathbf{r}) = \boldsymbol{\nabla} \times \mathbf{A}(\mathbf{r})$, where $v(\mathbf{r})$ and $\mathbf{A}(\mathbf{r})$ are the corresponding scalar and vector potentials, respectively. We assume the charge of the electron to be $-e$, and atomic units with $|e| = \hbar = m = 1$. For simplicity of equation writing we further put $c = 1$. (To obtain the expressions in atomic units, replace $\mathbf{A}(\mathbf{r})$ by $\mathbf{A}(\mathbf{r})/c$.) The Hamiltonian $\hat{H}$ is then

$$\hat{H} = \hat{T}_A + \hat{U} + \hat{V}, \tag{9.1}$$

where $\hat{T}_A$ is the *physical* kinetic energy operator:

$$\hat{T}_A = \frac{1}{2}\sum_i (\hat{\mathbf{p}}_i + \mathbf{A}(\mathbf{r_i}))^2 \tag{9.2}$$

$$= \hat{T} + \sum_i \hat{\omega}(\mathbf{r}_i; \mathbf{A}(\mathbf{r}_i)), \tag{9.3}$$

with $\hat{T}$ the *canonical* kinetic energy operator

$$\hat{T} = \sum_i \frac{\hat{p}_i^2}{2} = -\sum_i \frac{1}{2}\nabla_i^2, \tag{9.4}$$

and the operator $\hat{\omega}(\mathbf{r}; \mathbf{A})$ defined as

$$\hat{\omega}(\mathbf{r}; \mathbf{A}(\mathbf{r})) = \frac{1}{2}A^2(\mathbf{r}) - i\hat{\Omega}(\mathbf{r}; \mathbf{A}) \tag{9.5}$$

with

$$\hat{\Omega}(\mathbf{r}; \mathbf{A}(\mathbf{r})) = \frac{1}{2}\{\nabla \cdot \mathbf{A}(\mathbf{r}) + 2\mathbf{A}(\mathbf{r}) \cdot \boldsymbol{\nabla}\}. \tag{9.6}$$

The electron-interaction potential energy operator $\hat{U}$ is

$$\hat{U} = {\sum_{i,j}}' u(\mathbf{r}_i \mathbf{r}_j) = \frac{1}{2}{\sum_{i,j}}' \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \tag{9.7}$$

and the external electrostatic potential energy operator $\hat{V}$ is

$$\hat{V} = \sum_i v(\mathbf{r}_i). \tag{9.8}$$

The time-independent Schrödinger equation is

$$\hat{H}(\mathbf{R}; \mathbf{A})\psi(\mathbf{X}) = E\psi(\mathbf{X}), \tag{9.9}$$

where $\{\psi(\mathbf{X}), E\}$ are the eigenfunctions and eigenenergies of the system, with $\mathbf{R} = \mathbf{r}_1, \ldots, \mathbf{r}_N$; $\mathbf{X} = \mathbf{x}_1, \ldots, \mathbf{x}_N$; $\mathbf{x} = \mathbf{r}\sigma$, $\{\mathbf{r}\sigma\}$ being the spatial and spin coordinates.

The general statement of the 'Quantal Newtonian' first law derived in Appendix F is, of course, the same as (2.134) for the $\mathbf{B}(\mathbf{r}) = 0$ case, viz. that the sum of the external $\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r})$ and internal $\boldsymbol{\mathcal{F}}^{\text{int}}(\mathbf{r})$ fields experienced by each electron vanishes:

$$\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}) + \boldsymbol{\mathcal{F}}^{\text{int}}(\mathbf{r}) = 0. \tag{9.10}$$

The law is valid for arbitrary gauge and derived [1, 5] employing the continuity condition

$$\boldsymbol{\nabla} \cdot \mathbf{j}(\mathbf{r}) = 0. \tag{9.11}$$

The definitions of the fields are as follows. The external field $\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r})$ is the sum of the electrostatic $\boldsymbol{\mathcal{E}}(\mathbf{r})$ and Lorentz $\boldsymbol{\mathcal{L}}(\mathbf{r})$ fields:

$$\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}) = \boldsymbol{\mathcal{E}}(\mathbf{r}) - \boldsymbol{\mathcal{L}}(\mathbf{r}) = -\boldsymbol{\nabla} v(\mathbf{r}) - \boldsymbol{\mathcal{L}}(\mathbf{r}), \tag{9.12}$$

where $\boldsymbol{\mathcal{L}}(\mathbf{r})$ is defined in terms of the Lorentz 'force' $\mathbf{l}(\mathbf{r})$ as

$$\boldsymbol{\mathcal{L}}(\mathbf{r}) = \frac{\mathbf{l}(\mathbf{r})}{\rho(\mathbf{r})}, \tag{9.13}$$

and where

$$\mathbf{l}(\mathbf{r}) = \mathbf{j}(\mathbf{r}) \times \mathbf{B}(\mathbf{r}), \tag{9.14}$$

with its components given as

$$l_\alpha(\mathbf{r}) = \sum_{\beta=1}^{3} \left[j_\beta(\mathbf{r}) \nabla_\alpha A_\beta(\mathbf{r}) - j_\beta(\mathbf{r}) \nabla_\beta A_\alpha(\mathbf{r}) \right]. \tag{9.15}$$

The internal field $\boldsymbol{\mathcal{F}}^{\text{int}}(\mathbf{r})$ is the sum of the electron-interaction $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$, kinetic $\boldsymbol{\mathcal{Z}}(\mathbf{r})$, differential density $\boldsymbol{\mathcal{D}}(\mathbf{r})$, and internal magnetic $\boldsymbol{\mathcal{I}}(\mathbf{r})$ fields:

$$\boldsymbol{\mathcal{F}}^{\text{int}}(\mathbf{r}) = \boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}) - \boldsymbol{\mathcal{Z}}(\mathbf{r}) - \boldsymbol{\mathcal{D}}(\mathbf{r}) - \boldsymbol{\mathcal{I}}(\mathbf{r}). \tag{9.16}$$

These fields are defined in terms of the corresponding 'forces' $\mathbf{e}_{ee}(\mathbf{r})$, $\mathbf{z}(\mathbf{r}; \gamma)$, $\mathbf{d}(\mathbf{r})$, $\mathbf{i}(\mathbf{r}; \mathbf{j}\mathbf{A})$, respectively, as

$$\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}) = \frac{\mathbf{e}_{ee}(\mathbf{r})}{\rho(\mathbf{r})};\ \boldsymbol{\mathcal{Z}}(\mathbf{r}) = \frac{\mathbf{z}(\mathbf{r}; \gamma)}{\rho(\mathbf{r})};\ \boldsymbol{\mathcal{D}}(\mathbf{r}) = \frac{\mathbf{d}(\mathbf{r})}{\rho(\mathbf{r})};\ \boldsymbol{\mathcal{I}}(\mathbf{r}) = \frac{\mathbf{i}(\mathbf{r}; \mathbf{j}\mathbf{A})}{\rho(\mathbf{r})}. \tag{9.17}$$

The electron-interaction 'force' $\mathbf{e}_{ee}(\mathbf{r})$, representative of electron correlations due to the Pauli exclusion principle and Coulomb repulsion, is obtained via Coulomb's law via its quantal source, the pair-correlation function $P(\mathbf{r}\mathbf{r}')$:

$$\mathbf{e}_{ee}(\mathbf{r}) = \int \frac{P(\mathbf{r}\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}'. \tag{9.18}$$

The kinetic 'force' $\mathcal{z}(\mathbf{r};\gamma)$, representative of kinetic effects, is obtained from its quantal source, the reduced single-particle density matrix $\gamma(\mathbf{r}\mathbf{r}')$. It is defined in terms of its components as

$$z_\alpha(\mathbf{r};\gamma) = 2\sum_{\beta=1}^{3} \nabla_\beta t_{\alpha\beta}(\mathbf{r};\gamma), \tag{9.19}$$

where the kinetic energy tensor $t_{\alpha\beta}(\mathbf{r})$ is

$$t_{\alpha\beta}(\mathbf{r};\gamma) = \frac{1}{4}\left(\frac{\partial^2}{\partial r'_\alpha \partial r''_\beta} + \frac{\partial^2}{\partial r'_\beta \partial r''_\alpha}\right)\gamma(\mathbf{r}'\mathbf{r}'')\bigg|_{\mathbf{r}'=\mathbf{r}''=\mathbf{r}}. \tag{9.20}$$

The differential density 'force' $\mathbf{d}(\mathbf{r})$ whose quantal source is the density $\rho(\mathbf{r})$, is defined as

$$\mathbf{d}(\mathbf{r}) = -\frac{1}{4}\boldsymbol{\nabla}\nabla^2\rho(\mathbf{r}). \tag{9.21}$$

Finally, the contribution of the magnetic field to the internal 'force' $\mathbf{i}(\mathbf{r};\mathbf{j}\mathbf{A})$ for which the quantal source is the physical current density $\mathbf{j}(\mathbf{r})$ is defined in terms of its components as

$$i_\alpha(\mathbf{r};\mathbf{j}\mathbf{A}) = \sum_{\beta=1}^{3} \nabla_\beta I_{\alpha\beta}(\mathbf{r};\mathbf{j}\mathbf{A}), \tag{9.22}$$

with

$$I_{\alpha\beta}(\mathbf{r};\mathbf{j}\mathbf{A}) = \big[j_\alpha(\mathbf{r})A_\beta(\mathbf{r}) + j_\beta(\mathbf{r})A_\alpha(\mathbf{r})\big] - \rho(\mathbf{r})A_\alpha(\mathbf{r})A_\beta(\mathbf{r}). \tag{9.23}$$

The fields $\boldsymbol{\mathcal{L}}(\mathbf{r})$, $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$, $\boldsymbol{\mathcal{D}}(\mathbf{r})$, and the sum $[\boldsymbol{\mathcal{Z}}(\mathbf{r})+\boldsymbol{\mathcal{I}}(\mathbf{r})]$ are gauge invariant [5]. The 'forces' and hence the fields arise from local and nonlocal quantal sources such as the density $\rho(\mathbf{r})$, the pair-correlation function $P(\mathbf{r}\mathbf{r}')$, the reduced single-particle density matrix $\gamma(\mathbf{r}\mathbf{r}')$, and the physical current density $\mathbf{j}(\mathbf{r})$, which in turn are expectations of Hermitian operators or the complex sum of Hermitian operators taken with respect to the wave function $\psi(\mathbf{X})$. Thus,

$$\rho(\mathbf{r}) = \langle\psi(\mathbf{X})|\hat{\rho}(\mathbf{r})|\psi(\mathbf{X})\rangle, \tag{9.24}$$

$$P(\mathbf{rr}') = \langle \psi(\mathbf{X}) | \hat{P}(\mathbf{rr}') | \psi(\mathbf{X}) \rangle, \tag{9.25}$$

$$\gamma(\mathbf{rr}') = \langle \psi(\mathbf{X}) | \hat{\gamma}(\mathbf{rr}') | \psi(\mathbf{X}) \rangle, \tag{9.26}$$

$$j(\mathbf{r}) = \langle \psi(\mathbf{X}) | \hat{\mathbf{j}}(\mathbf{r}) | \psi(\mathbf{X}) \rangle = \mathbf{j}_p(\mathbf{r}) + \mathbf{j}_d(\mathbf{r}), \tag{9.27}$$

with $\mathbf{j}_p(\mathbf{r})$ and $\mathbf{j}_d(\mathbf{r})$ the paramagnetic and diamagnetic components, and where the density $\hat{\rho}(\mathbf{r})$, pair-correlation $\hat{P}(\mathbf{rr}')$, single-particle density matrix $\hat{\gamma}(\mathbf{rr}')$, and current density $\hat{\mathbf{j}}(\mathbf{r})$ operators are defined as

$$\hat{\rho}(\mathbf{r}) = \sum_i \delta(\mathbf{r}_i - \mathbf{r}), \tag{9.28}$$

$$\hat{P}(\mathbf{rr}') = \sum_{i,j}{}' \delta(\mathbf{r}_i - \mathbf{r})\delta(\mathbf{r}_j - \mathbf{r}'), \tag{9.29}$$

$$\hat{\gamma}(\mathbf{rr}') = \hat{A} + i\hat{B}, \tag{9.30}$$

$$\hat{A} = \frac{1}{2}\sum_j \big[\delta(\mathbf{r}_j - \mathbf{r})T_j(\mathbf{a}) + \delta(\mathbf{r}_j - \mathbf{r}')T_j(-\mathbf{a})\big], \tag{9.31}$$

$$\hat{B} = -\frac{i}{2}\sum_j \big[\delta(\mathbf{r}_j - \mathbf{r})T_j(\mathbf{a}) - \delta(\mathbf{r}_j - \mathbf{r}')T_j(-\mathbf{a})\big], \tag{9.32}$$

$T_j(\mathbf{a})$ is a translation operator such that $T_j(\mathbf{a})\psi(\ldots\mathbf{r}_j,\ldots) = \psi(\ldots\mathbf{r}_j + \mathbf{a},\ldots)$, and $\mathbf{a} = \mathbf{r}' - \mathbf{r}$, and

$$\hat{\mathbf{j}}(\mathbf{r}) = \hat{\mathbf{j}}_p(\mathbf{r}) + \hat{\mathbf{j}}_d(\mathbf{r}), \tag{9.33}$$

with the paramagnetic current density operator

$$\hat{\mathbf{j}}_p(\mathbf{r}) = \frac{1}{2i}\sum_k \big[\nabla_{\mathbf{r}_k}\delta(\mathbf{r}_k - \mathbf{r}) + \delta(\mathbf{r}_k - \mathbf{r})\nabla_{\mathbf{r}_k}\big], \tag{9.34}$$

and the diamagnetic current density operator

$$\hat{\mathbf{j}}_d = \hat{\rho}(\mathbf{r})\mathbf{A}(\mathbf{r}). \tag{9.35}$$

The 'Quantal Newtonian' first law of (9.10) affords a rigorous physical interpretation of the external electrostatic potential energy $v(\mathbf{r})$: *It is the work done to move* *an electron from some reference point at infinity to its position* $\mathbf{r}$ *in the force of a conservative field* $[\boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r}) - \boldsymbol{\mathcal{L}}(\mathbf{r})]$:

$$v(\mathbf{r}) = \int_{\infty}^{\mathbf{r}} [\boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r}') - \boldsymbol{\mathcal{L}}(\mathbf{r}')] \cdot d\boldsymbol{\ell}'. \tag{9.36}$$

This work done is *path-independent*. Observe that the external potential $v(\mathbf{r})$ is coupled to the internal field $\boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r})$ and the Lorentz field $\boldsymbol{\mathcal{L}}(\mathbf{r})$ experienced by each electron. As these fields are obtained as expectations of Hermitian operators taken with respect to the wave function $\psi(\mathbf{X})$, the potential $v(\mathbf{r})$ is a functional of the wave function: $v(\mathbf{r}) = v[\psi]$. The Schrödinger equation (9.9) can on substitution of (9.36) be written as

$$\left[\frac{1}{2}\sum_i \{\hat{\mathbf{p}}_i + \mathbf{A}(\mathbf{r}_i)\}^2 + \frac{1}{2}\sum_{i,j}{}' \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i \int_{\infty}^{\mathbf{r}_i} \left[\boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r}) - \boldsymbol{\mathcal{L}}(\mathbf{r})\right] \cdot d\boldsymbol{\ell}\right]\psi(\mathbf{X}) = E\psi(\mathbf{X}). \tag{9.37}$$

In this manner, the self-consistent nature of the Schrödinger equation becomes evident. To solve the equation, one begins with an approximation to $\psi(\mathbf{X})$. With this approximate $\psi(\mathbf{X})$ one then determines the fields $\boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r})$ and $\boldsymbol{\mathcal{L}}(\mathbf{r})$ (for an external $\mathbf{B}(\mathbf{r})$), and the work done in the sum of these fields. One then solves the integro-differential equation to determine a new approximate solution $\psi(\mathbf{X})$ and eigenenergy E. This process is continued till self-consistency is achieved to obtain the true $\psi(\mathbf{X})$ and E.

Yet another insightful result is achieved by writing the Schrödinger equation via the ‘Quantal Newtonian’ first law as in (9.37). In texts on quantum mechanics, it is noted that in the presence of an external magnetic field $\mathbf{B}(\mathbf{r})$, it is only the vector potential $\mathbf{A}(\mathbf{r})$ that appears in the Hamiltonian as in (9.1). But since the Lorentz field $\boldsymbol{\mathcal{L}}(\mathbf{r})$ depends on the field $\mathbf{B}(\mathbf{r})$ (see (9.13)), the latter now appears explicitly in the Schrödinger equation. It is the intrinsic self-consistent nature of the equation that demands the dependence on $\mathbf{B}(\mathbf{r})$ to be present in the Hamiltonian. Thus, writing the Schrödinger equation in this manner shows that the magnetic field $\mathbf{B}(\mathbf{r})$ does appear explicitly in it.

The energy E is then the sum of the kinetic T, external E_{ext}, electron-interaction E_{ee}, and internal magnetic contribution I energies:

$$E = E_{\mathrm{ext}} + (T + E_{ee} + I), \tag{9.38}$$

where in integral virial form in terms of the respective fields

$$T = -\frac{1}{2}\int \rho(\mathbf{r})\mathbf{r} \cdot \boldsymbol{\mathcal{Z}}(\mathbf{r}) d\mathbf{r} \tag{9.39}$$

$$E_{\mathrm{ext}} = \int \rho(\mathbf{r})\mathbf{r} \cdot \boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}) d\mathbf{r} \tag{9.40}$$

$$E_{ee} = \int \rho(\mathbf{r})\mathbf{r} \cdot \boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}) d\mathbf{r} \tag{9.41}$$

$$I = \int \rho(\mathbf{r})\mathbf{r} \cdot \boldsymbol{\mathcal{I}}(\mathbf{r}) d\mathbf{r}. \tag{9.42}$$

Finally, by operating on the first law of (9.10) by $\int d\mathbf{r}\rho(\mathbf{r})\mathbf{r}\cdot$ one obtains the integral virial theorem [5, 10]

$$E_{\mathrm{ext}} + E_{ee} + 2T - I = 0. \tag{9.43}$$

The above is a description of the Schrödinger theory of electrons in an external electrostatic and magnetostatic field from the perspective of 'classical' fields and quantal sources as arrived at via the 'Quantal Newtonian' first law for each electron. This perspective gives rise to three insights into the theory not known previously: (a) In addition to the external Lorentz field, each electron also experiences an internal field due to the presence of the magnetic field $\mathbf{B}(\mathbf{r})$; (b) The Schrödinger equation may be written so that its intrinsic self-consistent nature becomes evident; (c) In writing the Schrödinger equation in this manner, the magnetic field $\mathbf{B}(\mathbf{r})$ appears explicitly without having to assume any gauge for the vector potential $\mathbf{A}(\mathbf{r})$ which appears in the equation via the definition of the field component of the electron momentum.

9.2 Quantal Density Functional Theory

As proved in the previous Chap. 8, the basic variables for a system of electrons in an external electrostatic $\boldsymbol{\mathcal{E}}(\mathbf{r}) = -\boldsymbol{\nabla} v(\mathbf{r})$ and a uniform magnetostatic $\mathbf{B}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r})$ field are the nondegenerate ground state density $\rho(\mathbf{r})$ and the physical current density $\mathbf{j}(\mathbf{r})$ for a fixed angular momentum $\mathbf{L}$. Thus, within Q-DFT, one maps the interacting system of electrons to one of *noninteracting* fermions having the same properties. The existence of such a model S system is an assumption. The further assumption made is that the external fields experienced by the model fermions are the same as those of the interacting system. (This Q-DFT is thus akin to that described in Sect. 3.3 in which the model fermions have the same basic variables and experience the same external fields as those of the true interacting electrons. It, therefore, differs from the Q-DFT described in [1].) The advantage gained by the requirement of the same basic variables and external fields is that in the mapping to such a model system, the only correlations that must be accounted for are once again only those due to the Pauli exclusion principle, Coulomb repulsion, and Correlation-Kinetic effects.

The model S system Hamiltonian is then

$$\hat{H}_s = \hat{T}_A + \hat{V}_s = \sum_i \hat{h}_s(\mathbf{r}_i) \tag{9.44}$$

where

$$\hat{T}_A = \frac{1}{2}\sum_i [\hat{\mathbf{p}}_i + \mathbf{A}(\mathbf{r}_i)]^2, \tag{9.45}$$

$$\hat{V}_s = \sum_i v_s(\mathbf{r}_i) = \sum_i [v(\mathbf{r}_i) + v_{ee}(\mathbf{r}_i)], \tag{9.46}$$

with $v_{ee}(\mathbf{r})$ an effective scalar electron-interaction potential in which the many-body correlations are incorporated. Thus,

$$\hat{h}_s(\mathbf{r}) = \frac{1}{2}[\hat{\mathbf{p}} + \mathbf{A}(\mathbf{r})]^2 + v(\mathbf{r}) + v_{ee}(\mathbf{r}), \tag{9.47}$$

and the S system orbital equation is

$$\left\{\frac{1}{2}[\hat{\mathbf{p}} + \mathbf{A}(\mathbf{r})]^2 + v(\mathbf{r}) + v_{ee}(\mathbf{r})\right\}\phi_i(\mathbf{x}) = \epsilon_i \phi_i(\mathbf{x});$$
$$i = 1, \ldots, N, \tag{9.48}$$

and the corresponding wave function is a Slater determinant $\Phi\{\phi_i\}$ of the orbitals $\phi_i(\mathbf{x})$. The $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ as obtained from the S system are the expectations

$$\rho(\mathbf{r}) = \langle \Phi\{\phi_i\}|\hat{\rho}(\mathbf{r})|\Phi\{\phi_i\}\rangle = \sum_\sigma \sum_i \phi_i^\star(\mathbf{r}\sigma)\phi_i(\mathbf{r}'\sigma), \tag{9.49}$$

and

$$\mathbf{j}(\mathbf{r}) = \langle \Phi\{\phi_i\}|\hat{\mathbf{j}}(\mathbf{r})|\Phi\{\phi_i\}\rangle = \mathbf{j}_{p,s}(\mathbf{r}) + \mathbf{j}_{d,s}(\mathbf{r}) \tag{9.50}$$

with

$$\mathbf{j}_{p,s}(\mathbf{r}) = \langle \Phi\{\phi_i\}|\hat{\mathbf{j}}_p(\mathbf{r})|\Phi\{\phi_i\}\rangle \tag{9.51}$$

$$\mathbf{j}_{d,s}(\mathbf{r}) = \langle \Phi\{\phi_i\}|\hat{\mathbf{j}}_d(\mathbf{r})|\Phi\{\phi_i\}\rangle \tag{9.52}$$

with the operators $\hat{\mathbf{j}}(\mathbf{r})$, $\hat{\mathbf{j}}_p(\mathbf{r})$, and $\hat{\mathbf{j}}_d(\mathbf{r})$ defined as in (9.33)–(9.35). (Note that as the orbitals are to be designed such that the $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ of the interacting and model systems are the same, and $\mathbf{A}(\mathbf{r})$ is the same, $\mathbf{j}_{d,s}(\mathbf{r}) = \rho(\mathbf{r})\mathbf{A}(\mathbf{r}) = \mathbf{j}_d(\mathbf{r})$, and therefore $\mathbf{j}_{p,s}(\mathbf{r}) = \mathbf{j}_p(\mathbf{r})$.)

The 'Quantal Newtonian' first law for the S system derived employing the continuity condition of (9.11) is

$$\mathcal{F}^{\text{ext}}(\mathbf{r}) + \mathcal{F}_s^{\text{int}}(\mathbf{r}) = 0, \tag{9.53}$$

where $\mathcal{F}^{\text{ext}}(\mathbf{r})$ is the same as in (9.12) by assumption. The internal field $\mathcal{F}_s^{\text{int}}(\mathbf{r})$ of the S system is

$$\mathcal{F}_s^{\text{int}}(\mathbf{r}) = -\nabla v_{ee}(\mathbf{r}) - \mathcal{Z}_s(\mathbf{r}) - \mathcal{D}(\mathbf{r}) - \mathcal{I}(\mathbf{r}) \tag{9.54}$$

in which the differential density $\mathcal{D}(\mathbf{r})$ and internal magnetic $\mathcal{I}(\mathbf{r})$ field components are the same as for the interacting system (see (9.17), (9.21)–(9.23)) because once again $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ and $\mathbf{A}(\mathbf{r})$ are the same. The S system kinetic field $\mathcal{Z}_s(\mathbf{r})$ is

$$\mathcal{Z}_s(\mathbf{r}) = \frac{z_s(\mathbf{r}; \gamma_s)}{\rho(\mathbf{r})}, \tag{9.55}$$

where the kinetic ‘force’ is defined in terms of its quantal source, the Dirac density matrix $\gamma_s(\mathbf{r}\mathbf{r}')$ as

$$z_{s,\alpha}(\mathbf{r}; \gamma_s) = 2\sum_{\beta=1}^{3} \nabla_\beta t_{s,\alpha\beta}(\mathbf{r}; \gamma_s), \tag{9.56}$$

where the kinetic energy tensor $t_{s,\alpha\beta}(\mathbf{r}; \gamma_s)$ is

$$t_{s,\alpha\beta}(\mathbf{r}; \gamma_s) = \frac{1}{4}\left[\frac{\partial^2}{\partial r'_\alpha \partial r''_\beta} + \frac{\partial^2}{\partial r'_\beta \partial r''_\alpha}\right]\gamma_s(\mathbf{r}'\mathbf{r}'')\bigg|_{\mathbf{r}'=\mathbf{r}''=\mathbf{r}}, \tag{9.57}$$

and the source

$$\gamma_s(\mathbf{r}\mathbf{r}') = \langle \Phi\{\phi_i\}|\hat{\gamma}(\mathbf{r}\mathbf{r}')|\Phi\{\phi_i\}\rangle = \sum_\sigma \sum_i \phi_i^\star(\mathbf{r}\sigma)\phi_i(\mathbf{r}'\sigma). \tag{9.58}$$

Equating the internal fields $\mathcal{F}^{\text{int}}(\mathbf{r})$ and $\mathcal{F}_s^{\text{int}}(\mathbf{r})$ then leads to following rigorous physical interpretation of the local effective potential energy $v_{ee}(\mathbf{r})$. It is *the work done to move a model fermion from some reference point at infinity to its position at* $\mathbf{r}$ *in the force of a conservative effective field* $\mathcal{F}^{\text{eff}}(\mathbf{r})$:

$$v_{ee}(\mathbf{r}) = -\int_\infty^{\mathbf{r}} \mathcal{F}^{\text{eff}}(\mathbf{r}') \cdot d\boldsymbol{\ell}', \tag{9.59}$$

where $\mathcal{F}^{\text{eff}}(\mathbf{r})$ is the sum of the electron-interaction $\mathcal{E}_{ee}(\mathbf{r})$ and correlation-kinetic $\mathcal{Z}_{t_c}(\mathbf{r})$, fields:

$$\mathcal{F}^{\text{eff}}(\mathbf{r}) = \mathcal{E}_{ee}(\mathbf{r}) + \mathcal{Z}_{t_c}(\mathbf{r}), \tag{9.60}$$

and where

$$\mathcal{Z}_{t_c}(\mathbf{r}) = \mathcal{Z}_s(\mathbf{r}) - \mathcal{Z}(\mathbf{r}). \tag{9.61}$$

As in the $\mathbf{B} = 0$ case (see Chap. 2), the field $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$ may be subdivided into its Hartree $\boldsymbol{\mathcal{E}}_H(\mathbf{r})$, Pauli $\boldsymbol{\mathcal{E}}_x(\mathbf{r})$, and Coulomb $\boldsymbol{\mathcal{E}}_c(\mathbf{r})$ field components. The quantal sources for these fields are the density $\rho(\mathbf{r})$, the Fermi hole $\rho_x(\mathbf{r}\mathbf{r}')$, and the Coulomb hole $\rho_c(\mathbf{r}\mathbf{r}')$, respectively. Thus, the effective field may be expressed as

$$\boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r}) = \boldsymbol{\mathcal{E}}_H(\mathbf{r}) + \boldsymbol{\mathcal{E}}_x(\mathbf{r}) + \boldsymbol{\mathcal{E}}_c(\mathbf{r}) + \boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r}), \tag{9.62}$$

with each field being representative of a specific electron correlation. Note that $\nabla \times \boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r}) = 0$ so that the work done $v_{ee}(\mathbf{r})$ is *path-independent*. The individual components of $\boldsymbol{\mathcal{F}}^{\text{eff}}(\mathbf{r})$ are separately curl free for systems with certain symmetry, as in the example of the following section which is one of cylindrical symmetry. The work done in each field is then path-independent.

The total energy E of the interacting electrons can also be written in terms of the model system properties. Splitting the kinetic energy T into its noninteracting T_s and Correlation-Kinetic T_c components, the energy E of the interacting system as given by (8.45) may be written as

$$E = T_s + E_{ee} + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + \int \mathbf{j}(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r})d\mathbf{r} \\ - \frac{1}{2}\int \rho(\mathbf{r})A^2(\mathbf{r})d\mathbf{r} + T_c. \tag{9.63}$$

By multiplying the S system differential equation (9.48) by $\phi_i^\star(\mathbf{x})$ and summing over all the model fermions, the noninteracting system kinetic energy T_s is obtained as

$$T_s = \sum_i \epsilon_i - \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} - \int \rho(\mathbf{r})v_{ee}(\mathbf{r})d\mathbf{r} - \int \mathbf{j}(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r})d\mathbf{r} \\ + \frac{1}{2}\int \rho(\mathbf{r})A^2(\mathbf{r})d\mathbf{r}. \tag{9.64}$$

On substituting (9.64) into (9.63), the expression for the energy E is

$$E = \sum_i \epsilon_i - \int \rho(\mathbf{r})v_{ee}(\mathbf{r})d\mathbf{r} + E_{ee} + T_c, \tag{9.65}$$

where E_{ee} is given by (9.41) and T_c is

$$T_c = \frac{1}{2}\int \rho(\mathbf{r})\mathbf{r} \cdot \boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r})d\mathbf{r}. \tag{9.66}$$

Note that the expression for E and $v_{ee}(\mathbf{r})$ are the same as those of the $\mathbf{B}(\mathbf{r}) = 0$ case of Sects. 3.4.5 and 3.4.6. It is also to be understood that T_s is the kinetic energy of the model fermions having the same density $\rho(\mathbf{r})$ and physical current density $\mathbf{j}(\mathbf{r})$ as that of the interacting system.

On applying $\int d\mathbf{r}\rho(\mathbf{r})\mathbf{r}\cdot$ to (9.60), one obtains the corresponding integral virial theorem for the S system.

$$E_{ee} + 2T_c = \int \rho(\mathbf{r})\mathbf{r} \cdot \mathcal{F}^{\mathrm{eff}}(\mathbf{r})d\mathbf{r}. \tag{9.67}$$

This expression too is the same as the $\mathbf{B}(\mathbf{r}) = 0$ case (see Sect. 3.4.7).

The 'Quantal Newtonian' first law of (9.10) is of course valid for both ground and excited states. Hence, the mapping via Q-DFT is applicable to both ground and excited states of the interacting system. Furthermore, as in the $\mathbf{B}(\mathbf{r}) = 0$ case, the mapping to the S system is arbitrary in that the model fermions may be in a ground or excited state. Thus, once again, there exist an *infinite* number of local potentials $v_s(\mathbf{r})$ that can generate $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ of either a ground or excited state of the interacting system.

Finally, the requirement that the orbital angular momentum $\mathbf{L}$ of the model fermions be the same as for the interacting electrons is automatically satisfied. This is readily seen to be the case from the relation

$$\mathbf{L} = \int \mathbf{r} \times \big(\mathbf{j}(\mathbf{r}) - \rho(\mathbf{r})\mathbf{A}(\mathbf{r})\big)d\mathbf{r}, \tag{9.68}$$

since by construction the $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ are the same, and $\mathbf{A}(\mathbf{r})$ the same by assumption.

9.3 Application of Quantal Density Functional Theory to a Quantum Dot

We next apply Q-DFT in the presence of a magnetostatic field to investigate the properties of a quantum dot. A quantum dot is a two-dimensional electron gas confined to a circular region of approximately tens of Angstroms. It can be thought of as an atom in two-dimensions with a confining external scalar potential that is harmonic. Further confinement is achieved via the presence of a magnetic field. Experimentally, quantum dots may be fabricated from AlAs/AlGaAs heterostructures.

Such a system is well described by the Hooke's atom which is comprised of two electrons in a harmonic external potential of frequency ω_0 in which the electrons are confined to the x-y plane by a magnetic field $\mathbf{B}(\mathbf{r})$ applied in the z-direction [8, 9]. The Hamiltonian for this system (in a.u. with the charge of an electron $= -e$; $|e| = \hbar = m = 1$) is

$$\hat{H} = \sum_{i=1}^{2} \left\{ \frac{1}{2}\left(\hat{\mathbf{p}}_i + \frac{1}{c}\mathbf{A}(\mathbf{r}_i)\right)^2 + \frac{1}{2}\omega_0^2 r_i^2 \right\} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}. \tag{9.69}$$

The procedure for the solution of the corresponding Schrödinger equation $\hat{H}\psi = E\psi$ is the same as described in Sect. 2.11.1 and is valid for any gauge and dimension. With the assumption of the symmetric gauge $\mathbf{A}(\mathbf{r}) = \frac{1}{2}\mathbf{B}(\mathbf{r}) \times \mathbf{r}$, there then exist closed-form analytical solutions to the Schrödinger equation for effective oscillator frequencies $\tilde{\omega} = \sqrt{\omega_0^2 + \omega_L^2}$ belonging to certain denumerably infinite set of values, where $\omega_L = B/2c$ is the Larmor frequency. For $\tilde{\omega} = 1$, the spatial part of the singlet ground state wave function is

$$\psi(\mathbf{r}_1\mathbf{r}_2) = C(1 + r_{12})e^{-\frac{1}{2}(r_1^2+r_2^2)}, \tag{9.70}$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ and $C^2 = 1/\pi^2(3 + \sqrt{2\pi})$. The corresponding ground state energy is $E = 3$ a.u. The total angular momentum $\mathbf{L} = 0$.

For the wave function of (9.70), many properties of the Q-DFT mapping to the model fermion system are obtained in closed analytical or semi-analytical form. These expressions and their asymptotic behavior near and at the nucleus and in the classically forbidden region are given in Appendix G. A derivation of the kinetic-energy-density tensor $t_{\alpha\beta}(\mathbf{r};\gamma)$, which differs from that of Appendix D, is given in Appendix H. We next discuss the individual properties.

9.3.1 *Quantal Sources*

9.3.1.1 Electron Density $\rho(\mathbf{r})$ and Physical Current Density $\mathbf{j}(\mathbf{r})$

The ground state electron density $\rho(\mathbf{r})$ is

$$\rho(\mathbf{r}) = \frac{2}{\pi(3+\sqrt{2\pi})}e^{-r^2}\left\{\sqrt{\pi}e^{-\frac{1}{2}r^2}\left[\left(1+r^2\right)I_0\left(\frac{1}{2}r^2\right) + r^2 I_1\left(\frac{1}{2}r^2\right)\right] + \left(2+r^2\right)\right\}, \tag{9.71}$$

where $I_0(x)$ and $I_1(x)$ are the zeroth- and first-order modified Bessel functions [11]. (Note that the expression given in [12] is incorrect.) The density has cylindrical symmetry: $\rho(\mathbf{r}) = \rho(r)$. The density $\rho(r)$ and the radial probability density $r\rho(r)$ are plotted in Fig. 9.1. As expected for this harmonic external potential, the density does not exhibit a cusp at the nucleus. The asymptotic structure of the density near the nucleus and in the classically forbidden region are given in Appendix G.

As the wave function is real, the paramagnetic current density $\mathbf{j}_p(\mathbf{r}) = 0$. Thus, the physical current density

$$\mathbf{j}(\mathbf{r}) = \frac{1}{c}\rho(\mathbf{r})\mathbf{A}(\mathbf{r}), \tag{9.72}$$

and satisfies the continuity condition $\nabla \cdot \mathbf{j}(\mathbf{r}) = 0$.

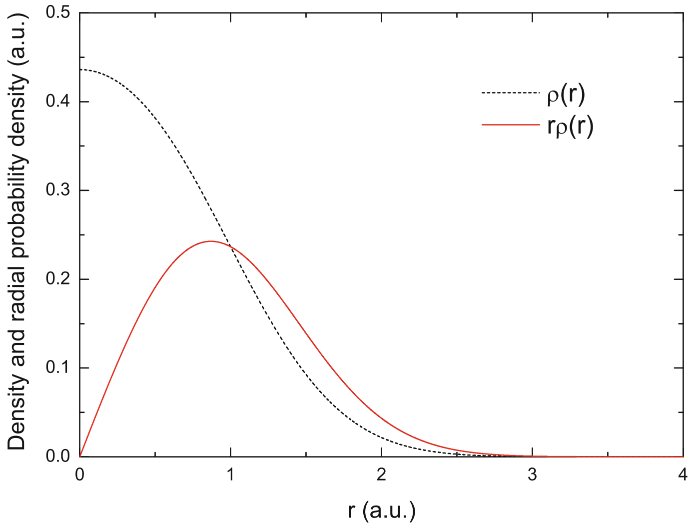

Fig. 9.1 Electron density $\rho(r)$ and radial probability density $r\rho(r)$

For the mapping of the above interacting system in its ground state to an S system also in its ground state, the corresponding S system orbitals $\phi_i(\mathbf{x})$ are of the general form

$$\phi_i(\mathbf{r}) = \sqrt{\frac{\rho(\mathbf{r})}{2}} e^{i\theta(\mathbf{r})}; \qquad i = 1, 2, \tag{9.73}$$

where $\theta(\mathbf{r})$ is an arbitrary real phase factor. The S system paramagnetic current density $\mathbf{j}_{p,s}(\mathbf{r})$ is then

$$\mathbf{j}_{p,s}(\mathbf{r}) = -\rho(\mathbf{r})\boldsymbol{\nabla}\theta(\mathbf{r}). \tag{9.74}$$

As the phase factor is arbitrary, we set $\theta(\mathbf{r}) = 0$, so that $\mathbf{j}_{p,s}(\mathbf{r}) = 0$. This means that the model system then has the same physical current density $\mathbf{j}(\mathbf{r})$. Additionally, the single particle orbitals are $\phi_i(\mathbf{r}) = \sqrt{\rho(\mathbf{r})/2}$. The S system differential equation is then

$$\left[\frac{1}{2}\hat{p}^2 + \frac{1}{2}\tilde{\omega}^2 r^2 + v_{ee}(\mathbf{r})\right]\sqrt{\rho(\mathbf{r})} = \epsilon\sqrt{\rho(\mathbf{r})}, \tag{9.75}$$

were $v_{ee}(\mathbf{r})$ is defined by equations (9.59)–(9.61) and accounts for electron correlations due to the Pauli principle, Coulomb repulsion, and Correlation-Kinetic effects. As the model fermions are in their ground state, the total angular momentum $\mathbf{L} = 0$.

9.3.1.2 Pair-Correlation Density $g(\mathbf{rr}')$, Fermi $\rho_x(\mathbf{rr}')$ and Coulomb $\rho_c(\mathbf{rr}')$ Holes

It is best to study the electron-interaction properties due to the Pauli exclusion principle and Coulomb repulsion via the pair-correlation density $g(\mathbf{rr}')$ which is defined in terms of the quantal source $P(\mathbf{rr}')$ as $g(\mathbf{rr}') = P(\mathbf{rr}')/\rho(\mathbf{r})$. The pair-density may be separated into its local and non-local components as $g(\mathbf{rr}') = \rho(\mathbf{r}') + \rho_{xc}(\mathbf{rr}')$, where $\rho_{xc}(\mathbf{rr}')$ is the Fermi-Coulomb hole charge distribution. In turn $\rho_{xc}(\mathbf{rr}')$ may be further subdivided into its Fermi $\rho_x(\mathbf{rr}')$ and Coulomb $\rho_c(\mathbf{rr}')$ hole charge components. The Fermi hole is defined in terms of the S system Dirac density matrix as $\rho_x(\mathbf{rr}') = -|\gamma_s(\mathbf{rr}')|^2/2\rho(\mathbf{r})$. These charge distributions satisfy the sum rules: $\int g(\mathbf{rr}')d\mathbf{r}' = N - 1$; $\int \rho_{xc}(\mathbf{rr}')d\mathbf{r}' = -1$; $\int \rho_x(\mathbf{rr}')d\mathbf{r}' = -1$; $\rho_x(\mathbf{rr}') \leq 0$; $\rho_x(\mathbf{rr}) = -\rho(\mathbf{r})/2$; $\int \rho_c(\mathbf{rr}')d\mathbf{r}' = 0$.

For the ground state then $\rho_x(\mathbf{rr}') = -\rho(\mathbf{r}')/2$ independent of the electron position $\mathbf{r}$, so that the non-local nature of the pair-correlation density is exhibited by the dynamic Coulomb hole $\rho_c(\mathbf{rr}')$. In Fig. 9.2 cross-sections of the Fermi-Coulomb $\rho_{xc}(\mathbf{rr}')$, Fermi $\rho_x(\mathbf{rr}')$, and Coulomb $\rho_c(\mathbf{rr}')$ holes are plotted for an electron at the nucleus. Observe that for this electron position, all the holes are spherically symmetric about it. Also observe that both the Fermi-Coulomb and Coulomb holes exhibit a cusp at the electron position representative of the two-dimensional electron-electron coalescence condition on the wave function [13] [***QDFT2***].

In Figs. 9.3, 9.4, 9.5, 9.6 cross-sections through the Coulomb hole $\rho_c(\mathbf{rr}')$ in different directions corresponding to $\theta' = 0°, 45°, 90°$ with respect to the nucleus-electron direction are plotted. The electron positions considered, as indicated by arrows, are

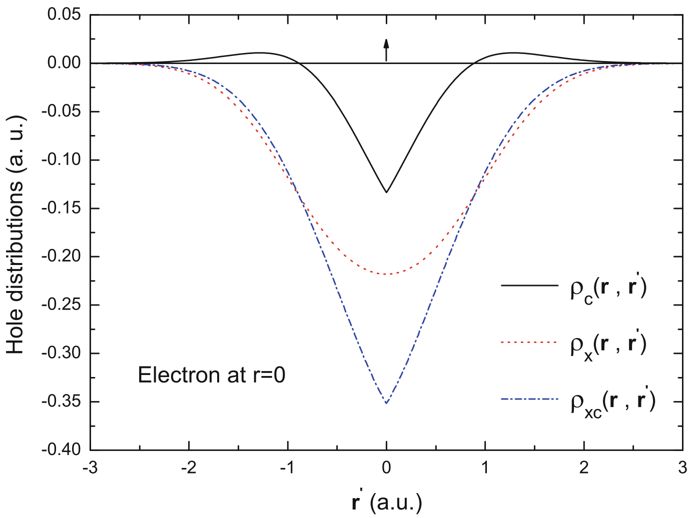

Fig. 9.2 Cross-sections through the quantal Fermi-Coulomb $\rho_{xc}(\mathbf{rr}')$, Fermi $\rho_x(\mathbf{rr}')$, and Coulomb $\rho_c(\mathbf{rr}')$ holes for an electron at the nucleus as indicated by the *arrow*

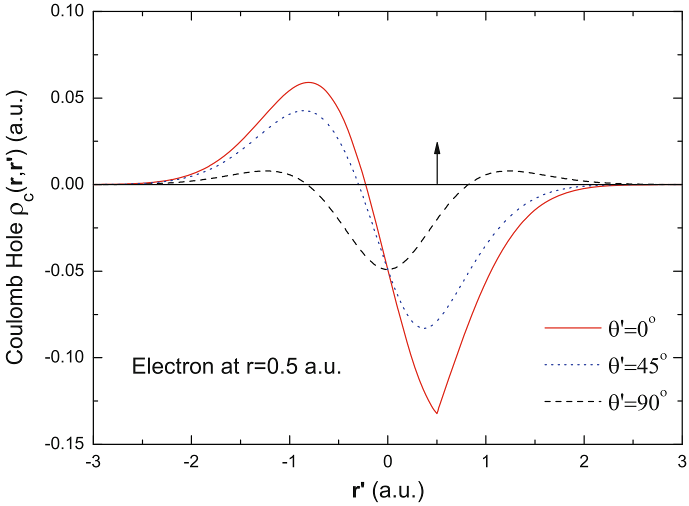

Fig. 9.3 Cross-sections through the Coulomb hole $\rho_c(\mathbf{r}\mathbf{r}')$ in different directions corresponding to $\theta' = 0°, 45°, 90°$ with respect to the nucleus-electron direction. The electron is at $r = 0.5$ a.u.

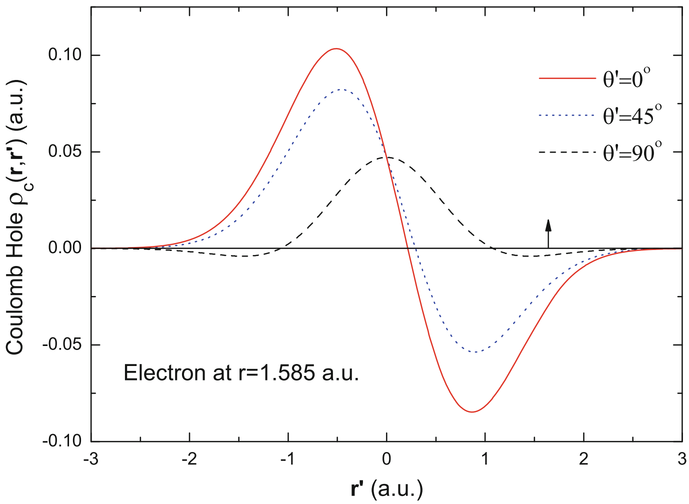

Fig. 9.4 Same as in Fig. 9.3 except that the electron is at $r = 1.585$ a.u.

$\mathbf{r} = 0.5, 1.585, 3.0$, and 18.0 a.u. Observe the dynamic structure of the Coulomb hole and the fact that it is not symmetric about the electron. For asymptotic electron positions (Fig. 9.6), the Coulomb hole becomes more and more spherically symmetric about the nucleus. The cusp [13] [***QDFT2***] in the hole at the electron position is also clearly evident in Fig. 9.3. The Coulomb hole also becomes an essentially static charge distribution for far asymptotic positions of the electron.

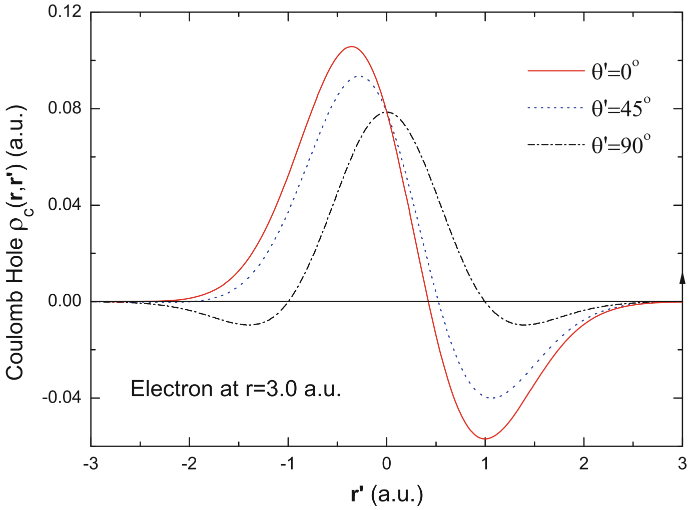

Fig. 9.5 Same as in Fig. 9.3 except that the electron is at $r = 3$ a.u.

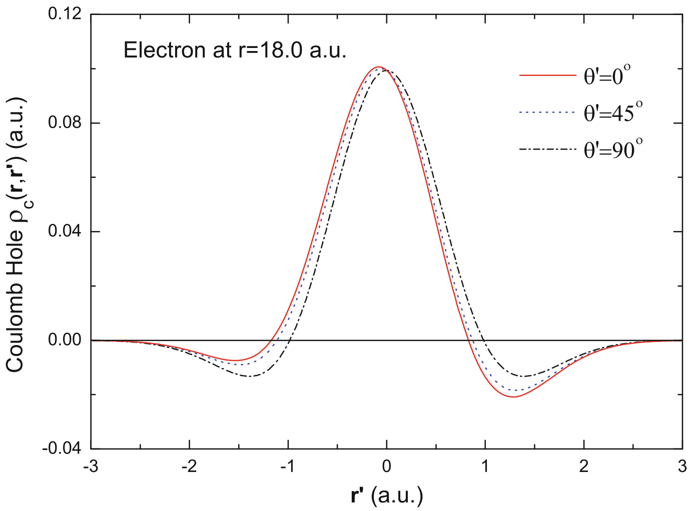

Fig. 9.6 Same as in Fig. 9.3 except that the electron is at $r = 18$ a.u.

9.3.1.3 Single-Particle $\gamma(\mathbf{rr}')$ and Dirac $\gamma_s(\mathbf{rr}')$ Density Matrices

The expressions for the reduced single-particle $\gamma(\mathbf{rr}')$ and Dirac $\gamma_s(\mathbf{rr}')$ density matrices are given in Appendix G.

9.3.2 Fields and Energies

9.3.2.1 Electron-Interaction Field $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$ and Energy E_{ee}

The analytical expression for the electron-interaction field $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$ and the corresponding value of the energy E_{ee} are given in Appendix G (see also Table 9.1). The field $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$ and energy E_{ee} can be split into their Hartree [$\boldsymbol{\mathcal{E}}_H(\mathbf{r})$, E_H], Pauli-Coulomb [$\boldsymbol{\mathcal{E}}_{xc}(\mathbf{r})$, E_{xc}], Pauli [$\boldsymbol{\mathcal{E}}_x(\mathbf{r})$, E_x], and Coulomb [$\boldsymbol{\mathcal{E}}_c(\mathbf{r})$, E_c] components. As the respective quantal sources for the fields are all spherically symmetric about the electron position at the nucleus, all the fields vanish at the origin. The asymptotic structure of the fields in the classically forbidden region is

$$\mathcal{E}_{ee}(r) \underset{r\to\infty}{\sim} \frac{1}{r^2} + \frac{2}{r^3}, \quad \mathcal{E}_H(r) \underset{r\to\infty}{\sim} \frac{2}{r^2} + \frac{5}{r^3}, \quad \mathcal{E}_{xc}(r) \underset{r\to\infty}{\sim} -\frac{1}{r^2} - \frac{3}{r^3}$$
$$\mathcal{E}_x(r) \underset{r\to\infty}{\sim} -\frac{1}{r^2} - \frac{5}{2r^3}, \quad \mathcal{E}_c(r) \underset{r\to\infty}{\sim} -\frac{1}{2r^3}. \tag{9.76}$$

The asymptotic structure is a consequence of the quantal source charge sum rules and the fact that these dynamic charge distributions become static for asymptotic positions of the electron. The asymptotic structure of $\mathcal{E}_{ee}(r)$ near the nucleus is

$$\mathcal{E}_{ee}(r) \underset{r\to 0}{\sim} \frac{1}{2(2+\sqrt{\pi})}\left[\left(4+3\sqrt{\pi}\right)r - \frac{1}{4}\left(13\sqrt{\pi}+16\right)r^3\right]. \tag{9.77}$$

The fields are plotted in Figs. 9.7, 9.8, 9.9. The corresponding energies obtained from these fields are quoted in Table 9.1. It is interesting to note that in contrast to the Hooke's atom in the absence of a magnetic field [14], [Sect. 3.5] for which the Coulomb field is an order of magnitude smaller than the Pauli field, the Coulomb field in the presence of the magnetic field though still smaller is of the same order of magnitude as the corresponding Pauli field. Nevertheless, the Coulomb energy is again an order of magnitude smaller than the Pauli energy (see Table 9.1). The reason for this is that the Coulomb field (see Fig. 9.9) is both positive and negative.

Table 9.1 Quantal density functional theory properties of the ground state S system that reproduces the density, physical current density, and total energy of the Hooke's atom in a magnetic field in a ground state with effective oscillator frequency $\tilde{\omega} = 1$.

Property	Value (a.u.)
E	3.000000
E_{ee}	0.818401
E_H	1.789832
E_{xc}	−0.971431
E_x	−0.894916
E_c	−0.076515
E_{ext}	1.295400
T_s	0.780987
T_c	0.105212
ϵ	2.000000

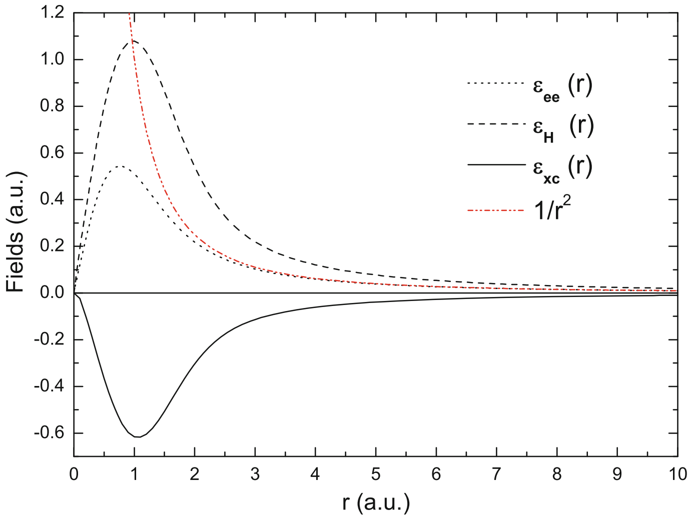

Fig. 9.7 The electron-interaction $\mathcal{E}_{ee}(r)$, and its Hartree $\mathcal{E}_H(r)$ and Pauli-Coulomb $\mathcal{E}_{xc}(r)$ components. The function $1/r^2$ is also plotted

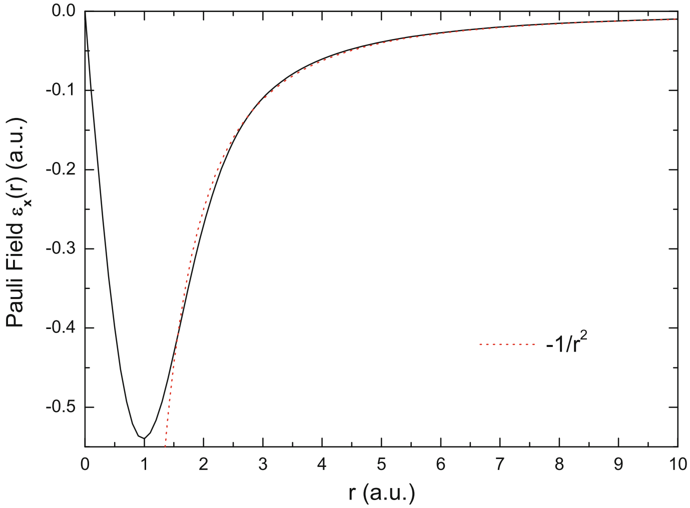

Fig. 9.8 The Pauli field $\mathcal{E}_x(r)$. The function $-1/r^2$ is also plotted

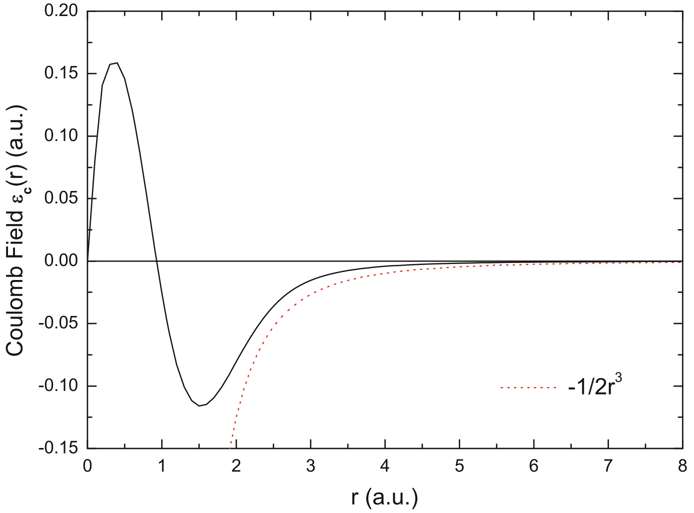

Fig. 9.9 The Coulomb field $\mathcal{E}_c(r)$. The function $-1/2r^3$ is also plotted

Yet another point of contrast is that in the case when the magnetic field is present, the Coulomb field decays asymptotically as $O(-\frac{1}{r^3})$ whereas in the absence of the magnetic field it decays as $O(-\frac{1}{r^4})$.

9.3.2.2 Correlation-Kinetic Field $\mathcal{Z}_{t_c}(\mathbf{r})$ and Energy T_c

The Correlation-Kinetic field $\mathcal{Z}_{t_c}(\mathbf{r})$ and energy T_c are obtained from the interacting and S system kinetic-energy tensors $t_{\alpha\beta}(\mathbf{r};\gamma)$ and $t_{s,\alpha\beta}(\mathbf{r};\gamma_s)$, respectively. As a consequence of the cylindrical symmetry, these tensors are of the form

$$t_{\alpha\beta}(\mathbf{r};\gamma) = \frac{r_\alpha r_\beta}{r^2} f(r) + \delta_{\alpha\beta} k(r) \tag{9.78}$$

and

$$t_{s,\alpha\beta}(\mathbf{r};\gamma_s) = \frac{r_\alpha r_\beta}{r^2} h(r), \tag{9.79}$$

where the functions $f(r)$, $k(r)$, and $h(r)$ are given in Appendix G. For the derivation of $t_{\alpha\beta}(\mathbf{r};\gamma)$ see Appendix H. To compare the off-diagonal matrix elements of the tensors, we plot in Fig. 9.10 the functions $f(r)$ and $h(r)$. Observe that they are extremely close, both vanishing at the nucleus, and decaying in a similar manner asymptotically. Hence, the contribution of the off-diagonal elements to the corresponding kinetic ‘forces’ are similar, and therefore their contribution to the Correlation-Kinetic field $\mathcal{Z}_{t_c}(\mathbf{r})$ very small. To compare the diagonal matrix elements of the tensors, we plot in Fig. 9.11 the functions $f(r) + 2k(r)$ and $h(r)$. Observe that the diagonal matrix element of the interacting system tensor is now finite at the nucleus and differs from

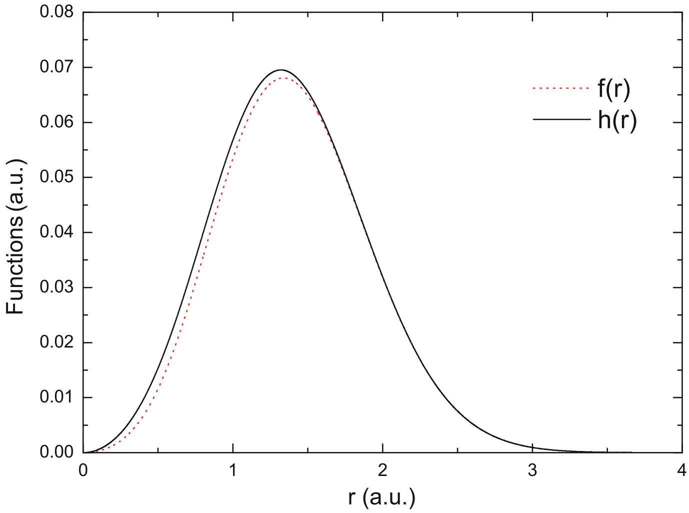

Fig. 9.10 Functions $f(r)$ and $h(r)$ of the off-diagonal elements of the interacting and non-interacting kinetic energy tensors $t_{\alpha\beta}(\mathbf{r};\gamma)$ and $t_{s,\alpha\beta}(\mathbf{r};\gamma_s)$, respectively

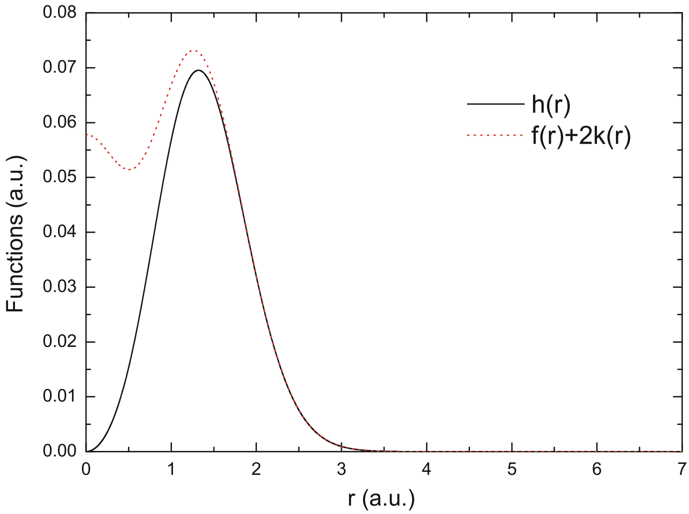

Fig. 9.11 The functions $f(r) + 2k(r)$ and $h(r)$ of the diagonal elements of the tensors $t_{\alpha\beta}(\mathbf{r};\gamma)$ and $t_{s,\alpha\beta}(\mathbf{r};\gamma_s)$, respectively

that of the S system in the interior region of the atom. Hence, the contribution to the Correlation-Kinetic field $\mathcal{Z}_{t_c}(\mathbf{r})$ arises principally from the diagonal matrix elements and from the interior of the atom. This is also the region from which the contribution to the Correlation-Kinetic energy T_c arises.

The expressions for the interacting and S system kinetic 'forces' $z_\alpha(\mathbf{r};\gamma)$ and $z_{s,\alpha}(\mathbf{r};\gamma_s)$, respectively, and their corresponding asymptotic structure are given in

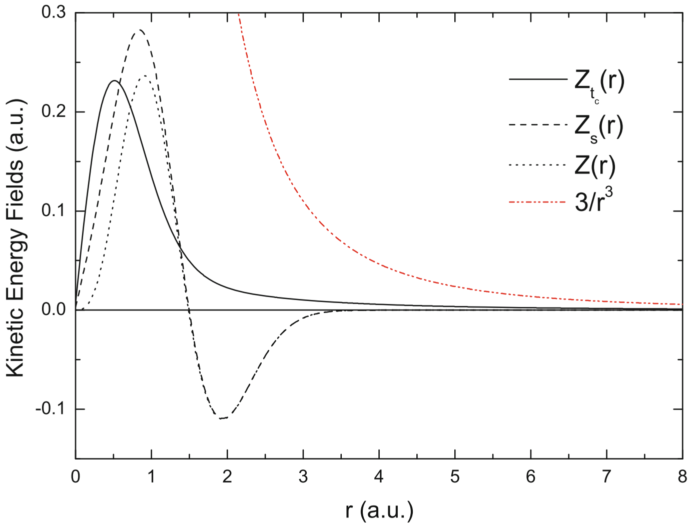

Fig. 9.12 Correlation-Kinetic field $\mathcal{Z}_{t_c}(r)$, and its components $\mathcal{Z}_s(r)$ and $\mathcal{Z}(r)$ for the noninteracting and interacting systems. The function $3/r^3$ is also plotted

Appendix G. The Correlation-Kinetic field $\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r})$ and its components $\boldsymbol{\mathcal{Z}}_s(\mathbf{r})$ and $\boldsymbol{\mathcal{Z}}(\mathbf{r})$ are plotted in Fig. 9.12. Observe that $\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r})$ is positive throughout space. Its asymptotic structure obtained from (G7), (G20) and (G23) is

$$\mathcal{Z}_{t_c}(r) \underset{r\to\infty}{\sim} \frac{3}{r^3} - \frac{12}{r^5}. \tag{9.80}$$

(Note the cancelation of the asymptotic structure of the 'forces' $z(r)$ and $z_s(r)$ from terms of $O(r^5)$ to $O(r^0)$.)

The kinetic energy of the interacting and S systems, T and T_s, may be obtained either from the fields $\boldsymbol{\mathcal{Z}}(\mathbf{r})$ and $\boldsymbol{\mathcal{Z}}_s(\mathbf{r})$, respectively, or from the corresponding system kinetic energy densities $t(\mathbf{r})$ and $t_s(\mathbf{r})$. (The kinetic energy density is the trace of the kinetic energy tensor.) The value of $T = 0.886\,199$ a.u.; $T_s = 0.780\,987$ a.u.; $T_c = 0.105\,212$ a.u. In contrast to the case with no magnetic field [14], [see Table 3.1] for which T_c is an order of magnitude smaller than T_s, in the present case the T_c though still smaller is of the same order of magnitude as T_s.

9.3.3 Potentials

9.3.3.1 Electron-Interaction Potential $W_{ee}(\mathbf{r})$

Due to cylindrical symmetry, the electron-interaction field $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$ is conservative. Hence, the contribution of Pauli and Coulomb correlations $W_{ee}(\mathbf{r})$ to the effective electron-interaction potential energy $v_{ee}(\mathbf{r})$ is the work done in this field:

$$W_{ee}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}') \cdot d\boldsymbol{\ell}'. \tag{9.81}$$

This work done is path-independent. The electron-interaction potential $W_{ee}(\mathbf{r})$ may be further subdivided into its Hartree $W_H(\mathbf{r})$, Pauli-Coulomb $W_{xc}(\mathbf{r})$, Pauli $W_x(\mathbf{r})$ and Coulomb $W_c(\mathbf{r})$ components, each being the work done in the conservative fields $\boldsymbol{\mathcal{E}}_H(\mathbf{r})$, $\boldsymbol{\mathcal{E}}_{xc}(\mathbf{r})$, $\boldsymbol{\mathcal{E}}_x(\mathbf{r})$, and $\boldsymbol{\mathcal{E}}_c(\mathbf{r})$, respectively.

The structure of the individual potentials follows directly from the corresponding fields. Thus, for example, since the field $\boldsymbol{\mathcal{E}}_{xc}(\mathbf{r})$ is negative throughout space and vanishes at the nucleus, the corresponding potential $W_{xc}(\mathbf{r})$ is negative and has zero slope at the nucleus. The asymptotic structure of the potentials follows from (9.76):

$$\begin{aligned} W_{ee}(r) &\underset{r\to\infty}{\sim} \frac{1}{r} + \frac{1}{r^2}, \quad W_H(r) \underset{r\to\infty}{\sim} \frac{2}{r} + \frac{5}{2r^2}, \quad W_{xc}(r) \underset{r\to\infty}{\sim} -\frac{1}{r} - \frac{3}{2r^2} \\ W_x(r) &\underset{r\to\infty}{\sim} -\frac{1}{r} - \frac{5}{4r^2}, \quad W_c(r) \underset{r\to\infty}{\sim} -\frac{1}{4r^2}. \end{aligned} \tag{9.82}$$

Note that the Coulomb potential $W_c(r)$ decays as $O(-1/r^2)$, whereas in the absence of a magnetic field $W_c(\mathbf{r})$ decays as $O(-1/r^3)$.

The potentials $W_H(r)$, $W_{xc}(r)$, $W_x(r)$, $W_c(r)$, and $W_{ee}(r)$ are plotted in Figs. 9.13, 9.14, 9.15, 9.16, 9.18.

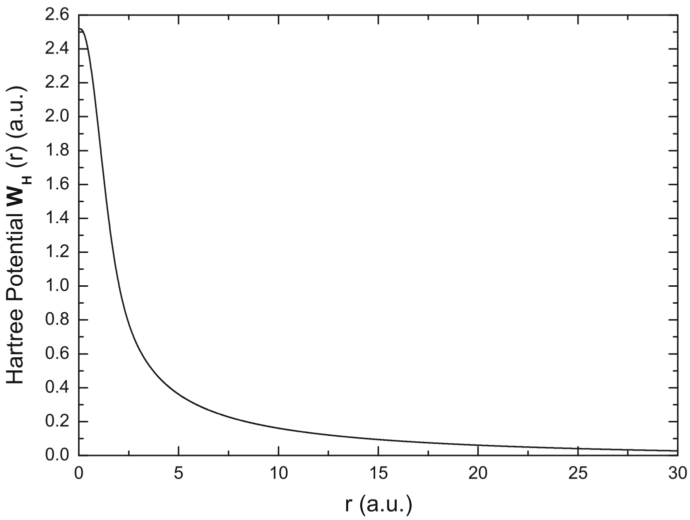

Fig. 9.13 The Hartree potential energy $W_H(r)$

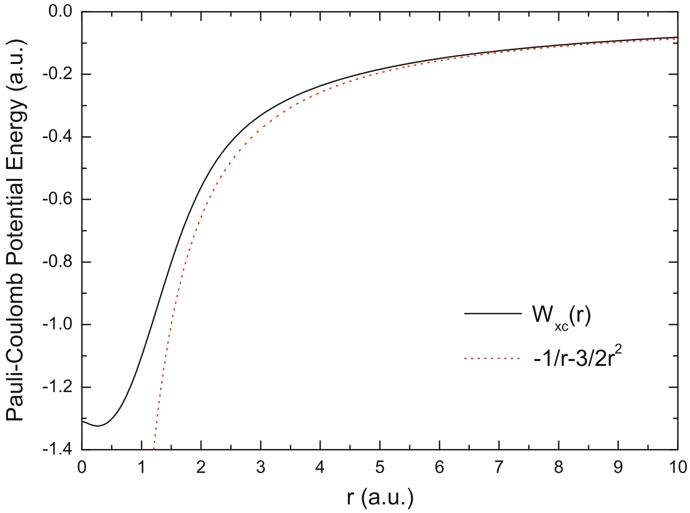

Fig. 9.14 The Pauli-Coulomb potential energy $W_{xc}(r)$. The function $-1/r - 3/2r^2$ is also plotted

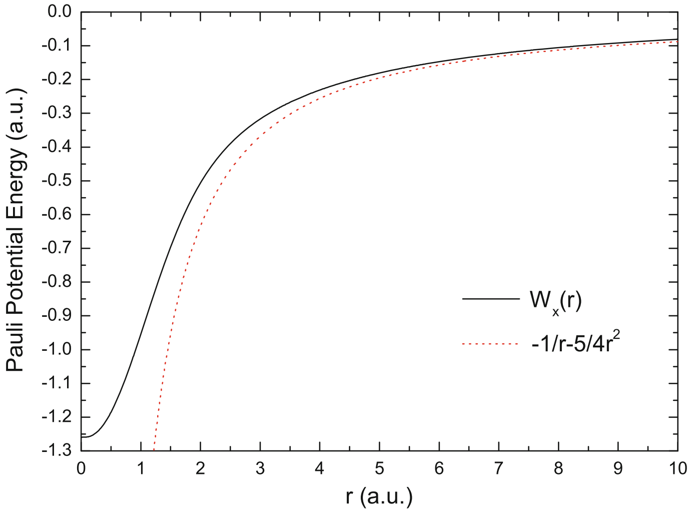

Fig. 9.15 The Pauli potential energy $W_x(r)$. The function $-1/r - 5/4r^2$ is also plotted

9.3.3.2 *Correlation-Kinetic Potential* $W_{t_c}(\mathbf{r})$

Once again, as a consequence of cylindrical symmetry, the correlation-kinetic field $\mathcal{Z}_{t_c}(\mathbf{r})$ is conservative, and therefore the contribution of this effect to the effective electron-interaction potential energy $v_{ee}(\mathbf{r})$ is the work done in this field:

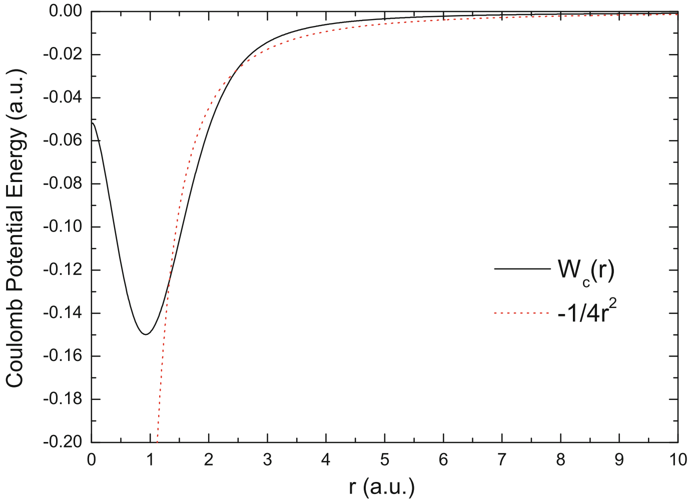

Fig. 9.16 The Coulomb potential energy $W_c(r)$. The function $-1/4r^2$ is also plotted

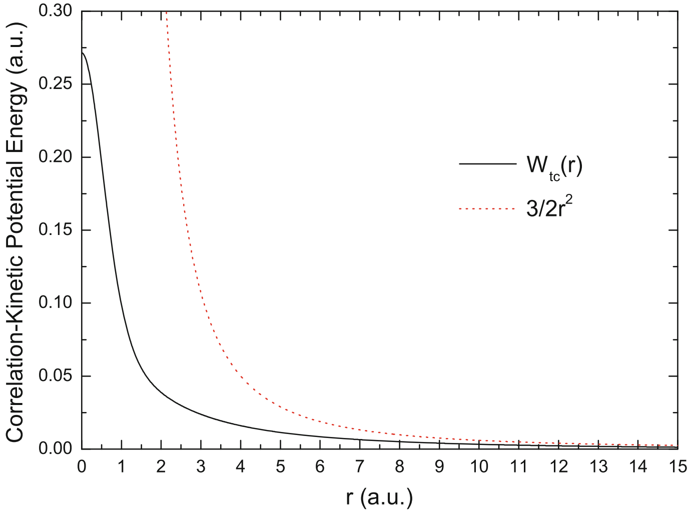

Fig. 9.17 The correlation-kinetic potential energy $W_{t_c}(r)$. The function $3/2r^2$ is also plotted

$$W_{t_c}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \mathcal{Z}_{t_c}(\mathbf{r}') \cdot d\boldsymbol{\ell}'. \tag{9.83}$$

This work done is also path-independent. The potential energy $W_{t_c}(r)$ is plotted in Figs. 9.17, 9.18. It is positive throughout space as a result of the field $\mathcal{Z}_{t_c}(\mathbf{r})$ being

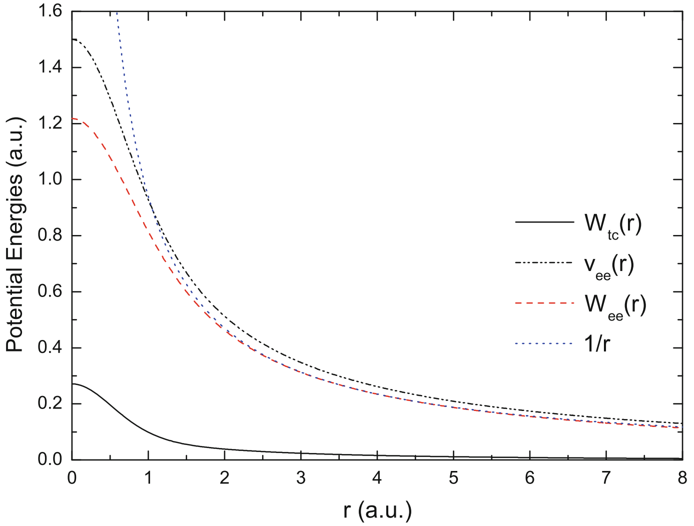

Fig. 9.18 The electron-interaction $W_{ee}(r)$, correlation-kinetic $W_{t_c}(r)$, and effective electron-interaction $v_{ee}(\mathbf{r})$ potential energies. The function $1/r$ is also plotted

positive. Its asymptotic structure obtained from (9.80) is

$$W_{t_c}(r) \underset{r\to\infty}{\sim} \frac{3}{2r^2}. \tag{9.84}$$

It is evident from (9.82) and (9.84) (see also Fig. 9.18) that $W_{t_c}(r)$ decays asymptotically much faster than the electron-interaction potential $W_{ee}(r)$. This decay of $W_{t_c}(\mathbf{r})$ of $O(\frac{1}{r^2})$ is the same as in the absence of a magnetic field.

9.3.3.3 *Effective Electron-Interaction Potential* $v_{ee}(\mathbf{r})$

The effective electron-interaction potential $v_{ee}(\mathbf{r})$ is then the sum of the electron-interaction $W_{ee}(\mathbf{r})$ and Correlation-Kinetic $W_{t_c}(\mathbf{r})$ potentials:

$$v_{ee}(\mathbf{r}) = W_{ee}(\mathbf{r}) + W_{t_c}(\mathbf{r}). \tag{9.85}$$

The potential $v_{ee}(r)$ is plotted in Fig. 9.18. Its structure near the nucleus and in the classically forbidden region are

$$v_{ee}(r) \underset{r\to 0}{\sim} \quad 1.50 - 0.99r^2, \tag{9.86}$$

$$v_{ee}(r) \underset{r\to\infty}{\sim} \frac{1}{r} + \frac{5}{2r^2}. \tag{9.87}$$

Observe (see Figs. 9.16 and 9.17), that the Coulomb $W_c(r)$ and correlation-kinetic $W_{t_c}(r)$ components of $v_{ee}(r)$ are of the same order of magnitude but opposite in sign. Hence, there is a substantial cancelation of these effects in the potential $v_{ee}(r)$. There is also a significant cancelation between the Hartree $W_H(\mathbf{r})$ and Pauli $W_x(\mathbf{r})$ potentials (see Figs. 9.13 and 9.14). It is due to this cancelation that the asymptotic structure of $v_{ee}(r)$ is $1/r$ (see (9.82)), and is due to the residual Hartree potential. The Pauli and Coulomb correlations, and correlation-kinetic effects, all contribute to the term of $O(1/r^2)$ of $v_{ee}(r)$.

9.3.4 Eigenvalue

The eigenvalue ϵ of the S system differential equation (9.75) can be obtained directly from it since the solution $\sqrt{\rho(\mathbf{r})}$ is known. Or it may be determined by writing $v_{ee}(\mathbf{r})$ with $\tilde{\omega} = 1$ as

$$v_{ee}(\mathbf{r}) = \epsilon + \frac{1}{2}\frac{\nabla^2\sqrt{\rho}}{\sqrt{\rho}} - \frac{1}{2}r^2. \tag{9.88}$$

Since $v_{ee}(\mathbf{r})$ vanishes at infinity, and $\nabla^2 = \partial^2/\partial r^2 + (1/r)\partial/\partial r$, we obtain $\epsilon = 2$ a.u.

9.3.5 Single-Particle Expectations

With the density $\rho(\mathbf{r})$ known, the expectations of the single-particle operators $\hat{O} = \sum_i r_i^n, n = 2, 1, -1$ and $\hat{O} = \sum_i \delta(\mathbf{r}_i)$ may be determined and are given in Appendix G.

9.3.6 Concluding Remarks

In the example described above, Q-DFT is applied to a quantum dot as modeled by the Hooke's atom in an external magnetostatic field. Thereby the interacting system is mapped to one of noninteracting fermions possessing the same $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ and angular momentum $\mathbf{L}$. The mapping is from a singlet ground state of the atom to a model system also in its singlet ground state.

The role played by each individual electron correlation is clearly demonstrated in the above application. Thus, for example, Correlation-Kinetic effects contribute positively to the effective electron-interaction potential energy $v_{ee}(\mathbf{r})$ of the model system, whereas the correlations due to Coulomb repulsion contribute negatively. Both these potentials are also of the same order of magnitude. Additionally, it also turns out that the lowest-order contribution of both the Correlation-Kinetic and Coulomb potentials in the classically forbidden region is of $O(1/r^2)$. As a consequence, there is a significant cancellation of the contributions of these two correlations to both the potential energy $v_{ee}(\mathbf{r})$ as well as to the total energy E. In a similar manner, contributions of correlations arising from the Pauli exclusion principle and those due to the Coulomb self-energy, also tend to cancel.

A comparison of the present results with those of the mapping for the Hooke's atom in the absence of a magnetic field [14], [Sect. 3.5] shows both similarities and differences, the latter arising as a consequence of the difference in dimensionality. Thus, for example, the three-dimensional dynamic Coulomb hole for the Hooke's atom exhibits a cusp at the position of the electron thereby indicating the satisfaction of the electron-electron coalescence condition for the wave function in three-dimensions [13, 15–19]. Similarly, the two-dimensional Coulomb hole of the present work exhibits a cusp at each electron position representative of the two-dimensional electron-electron coalescence constraint [13]. On the other hand, the asymptotic decay structure of the corresponding Coulomb fields and potentials in the classically forbidden region differ in spite of the fact that in each case the Coulomb hole satisfies the same sum rule of having a total charge of zero. This difference in the structure is a result of the difference in dimensionality. Another striking difference due to the reduced dimensionality is that Correlation-Kinetic effects which are relatively insignificant in the three-dimensional case are far more significant in two-dimensions. The correlation-kinetic energy in the latter case is greater in magnitude than the Coulomb energy and over ten percent of the Pauli energy. This fact is important in the traditional density functional theory description of the mapping [2], the application of which requires the construction of approximate energy functionals of $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ and their functional derivatives. Contributions due to Correlation-Kinetic effects cannot therefore be ignored in any approximations to the functionals.

Finally, we note that for any two-electron atom in an external magnetostatic field, the mapping from a ground state to a model system in its singlet ground state can be thought of as being to either noninteracting fermions or noninteracting *bosons*. The reason is that the solution of the differential equation for the model system of noninteracting bosons with the same $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ is the density amplitude $\sqrt{\rho(\mathbf{r})}$. This is also the case for the mapping from an excited state of the two-electron atom to a model system in its singlet ground state.

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Chapter 10
Physical Interpretation of the Local Density Approximation and Slater Theory via Quantal Density Functional Theory

Abstract As stationary-state Quantal density functional theory (Q–DFT) is a physical description of the mapping from an interacting system of electrons in an external electrostatic field to one of noninteracting fermions having the same density, it can provide a rigorous physical interpretation of various approximation schemes within local effective potential theory. Here Q–DFT is employed to explain how electron correlations are represented in the local density approximation (LDA) of Kohn-Sham density functional theory (KS-DFT), and to show that the exact Slater 'potential' is unphysical in that it does not represent the potential energy of an electron. According to KS-DFT, it is assumed that the electron correlations within the LDA are those of the uniform electron gas, taken at the local value of the nonuniform density. On the other hand, it is proved via Q-DFT that the correlations within the LDA not only involve the local value of the density but also the gradient of the density at each electron position. This explains the success of the LDA in a more fundamental manner. From basic electrostatics, it is shown that the exact Slater 'potential', and hence the LDA to this 'potential', does not represent a potential energy. The physically correct way to obtain the potential within Slater theory is explained, and shown to be the Pauli-correlated approximation of Q–DFT.

Introduction

In this chapter we explain insights arrived at via Quantal density functional theory (Q–DFT) of two popular approximation schemes within the framework of local effective potential energy theory. The first of these is the local density approximation (LDA) for 'exchange' [1] and 'exchange–correlation' [2] as applied within Kohn–Sham (KS) density functional theory [3]. The second is Slater theory [4] for 'exchange', the LDA within its context [4], and the Slater $X\alpha$ approximation scheme [5]. The LDA and Slater theory are both *ad hoc* formulations.

The description of KS–DFT given in Chap. 4 is the *in principle* exact formulation of the theory. However, as the KS 'exchange–correlation' energy functional $E_{xc}^{KS}[\rho]$ is unknown, it must be approximated in any application of the theory. Thus, approximate KS–DFT means approximating the functional $E_{xc}^{KS}[\rho]$. The LDA is one such

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approximation. The LDA also constitutes the leading term in the majority of approximations to the exact functional $E_{xc}^{KS}[\rho]$ presently employed in the literature, and those that have evolved from the gradient and various generalized gradient expansion approximations. The corresponding 'exchange–correlation' potential energy is the *functional derivative* of the approximate energy functional employed. The approximate functional derivative then generates the orbitals and density within the approximation by self–consistent solution of the corresponding S system differential equation. The ground state energy in turn is determined from the approximate total energy functional expression.

The local density approximation as originally understood is as follows. In the construction of the LDA 'exchange–correlation' energy functional, it is *assumed* that each point of an inhomogeneous electron density system is homogeneous, but with a density corresponding to the local value at that point. In other words, the correlations between the electrons as described by this picture are those of the uniform electron gas. It is *further assumed* that the corresponding approximate functional derivative is also representative of the *same* electron correlations. That is, the correlations assumed in the construction of the approximate energy functional are also those that give rise to the potential energy. Therefore, the LDA wavefunction for the nonuniform electron gas system at *each* electron position is the uniform electron gas wavefunction corresponding to the value of electron density at that position. Thus, within the LDA, the Fermi–Coulomb hole charge distribution at *each* electron position of the nonuniform density system is *spherically symmetric* about that position. (For the uniform electron gas, the Fermi–Coulomb hole charge distribution about an electron is spherically symmetric for *all* electron positions due to translational invariance.) When viewed from the perspective of KS–DFT, the understanding arrived at is that the correlations within the LDA are those of the uniform electron gas. Analysis of results obtained within the LDA are consequently based on this uniform electron gas description of the correlations.

However, when viewed from the field perspective of Q–DFT, it becomes evident that this cannot be the correct representation of the electron correlations in the approximation. The field at *each* electron position due to the spherically symmetric Fermi–Coulomb hole charge distribution *vanishes*. Therefore, the electron cannot have a potential energy as there is no force field present. On the other hand we know that the function represented by the functional derivative in the LDA is well defined and behaved. For the electron to have a potential energy, a force field must exist. A force field can exist at each electron position only if the Fermi–Coulomb hole charge distribution is asymmetric about the electron. It will be shown via Q–DFT in Sect. 10.1 that the LDA goes beyond uniform electron gas theory, and *explicitly* incorporates the non–uniformity of the electron density in its representation of electron correlations [6–9]. The LDA wavefunction thus incorporates, albeit in an approximate manner, the physics apropos to regions where the potential energy is rapidly varying and in the classically forbidden region. As such, the corresponding Fermi–Coulomb hole charge distribution in the LDA is *asymmetric* about the electron at each position in space. The work done in the field of this charge distribution, which is the potential energy of the electron, is then equivalent to the function corresponding to the LDA functional derivative. The representation of electron correlations within the LDA is therefore far more accurate than understood to be the case via KS–DFT.

The electron correlations within the LDA explicitly account for the non–uniformity of the system via a term proportional to the *gradient of the density* at each electron position. This is proved for the case when only correlations due to the Pauli exclusion principle are considered. The analytical expression for the true Fermi hole in the LDA is derived in Appendix I. As an example, the structure of the Fermi hole in the LDA and its spherically symmetric component are then contrasted with the exact Fermi hole in an atom.

The second component of this chapter is concerned with Slater theory [4] and the LDA within its framework. Slater theory is the original local effective potential energy theory. What Slater did was to simplify Hartree–Fock theory by replacing the non–local integral exchange operator in the differential equation by a local (multiplicative) operator. The expression for the total energy, however, remains the same. In Sect. 10.2 the reasoning employed in the construction of the *exact* 'Slater exchange potential' will be described. As will be shown, the 'Slater potential' depends upon the Fermi hole charge distribution $\rho_x(\mathbf{r}\mathbf{r}')$. Thus, although the exchange operator within Slater theory is local, the numerical solution of the corresponding differential equation was at that time still difficult due to the intrinsic non–locality of the Fermi hole distribution. (This is not the case at present, and results for the energy of closed-shell atoms employing the exact 'Slater exchange potential' are obtained and compared to those of Hartree-Fock theory.) Hence, Slater made a further approximation. He approximated the expression for the exact 'Slater exchange potential' by the corresponding expression for the uniform electron gas and assumed it valid for each point of the nonuniform density system. In other words, he constructed the LDA for the exact 'Slater exchange potential'. As this expression for the potential differs by a factor of 2/3 from the Dirac-Gaspar-Kohn-Sham value [1], in later work Slater et al. [5] introduced a parameter α to be determined by the energy variational principle. This $X\alpha$ method is thus intrinsically a LDA.

When Slater theory is viewed from the quantal source and field perspective of Q–DFT, it becomes clear that the 'Slater exchange potential' does not represent the potential energy of an electron. It is, therefore, more appropriate to refer to it as the Slater function. The underlying reason why the Slater function is not a potential energy has to do with the non–local (dynamic) nature of the Fermi hole charge distribution [10–12], as will be explained. The physically incorrect description of the potential energy of an electron representative of Pauli correlations then explains why the results of Slater theory are not accurate.

10.1 The Local Density Approximation in Kohn–Sham Theory

10.1.1 Derivation and Interpretation of Electron Correlations via Kohn–Sham Theory

In the context of Kohn–Sham (KS) density functional theory (see Sect. 4.5), the assumption underlying the LDA is that each point of the nonuniform electron density is uniform but with a density corresponding to the local value at that point. Equivalently, the *wavefunction* $\psi\{\mathbf{r}_1, \ldots, \mathbf{r}_N; \rho(\mathbf{r})\}$ for the nonuniform system at each electron position corresponds to the wavefunction of a uniform electron gas with a density equal to the local value at that position. In the LDA the ground state energy functional of the density $E^{LDA}[\rho]$ is therefore (see 4.80)

$$E^{LDA}[\rho] = T_s[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + E_{\mathrm{ee}}^{LDA}[\rho], \tag{10.1}$$

where $E_{\mathrm{ee}}^{LDA}[\rho]$ is the LDA approximation to the KS electron–interaction energy functional $E_{\mathrm{ee}}^{KS}[\rho]$. The functional $E_{\mathrm{ee}}^{LDA}[\rho]$ is defined as

$$E_{\mathrm{ee}}^{LDA}[\rho] = \frac{1}{2}\iint \frac{\rho(\mathbf{r})g^0\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}', \tag{10.2}$$

where $g^{(0)}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}$ is the pair–correlation density for the uniform electron gas (as indicated by the superscript (0)) corresponding to the local value of the density $\rho(\mathbf{r})$ at $\mathbf{r}$. Since we may subdivide $g^{(0)}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}$ into its local and nonlocal components as

$$g^{(0)}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\} = \rho(\mathbf{r}') + \rho_{xc}^{(0)}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}, \tag{10.3}$$

with $\rho_{xc}^{(0)}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}$ the Fermi–Coulomb hole charge for the uniform system, the energy $E_{\mathrm{ee}}^{LDA}[\rho]$ is

$$E_{\mathrm{ee}}^{LDA}[\rho] = E_H[\rho] + E_{xc}^{LDA}[\rho], \tag{10.4}$$

where the Hartree energy $E_H[\rho]$ is

$$E_H[\rho] = \frac{1}{2}\iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}', \tag{10.5}$$

and the LDA exchange–correlation energy $E_{xc}^{LDA}[\rho]$ is defined as

$$E_{xc}^{LDA}[\rho] = \frac{1}{2}\iint \frac{\rho(\mathbf{r})\rho_{xc}^{(0)}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'. \tag{10.6}$$

In the literature, $E_{xc}^{LDA}[\rho]$ is more commonly expressed as

$$E_{xc}^{LDA}[\rho] = \int \epsilon_{xc}^{(0)}\{\rho(\mathbf{r})\}\rho(\mathbf{r})d\mathbf{r}, \tag{10.7}$$

where $\epsilon_{xc}^{(0)}\{\rho(\mathbf{r})\}$ is the average exchange–correlation energy per electron for the homogeneous electron gas.

The S system differential equation in the LDA is

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_{\mathrm{ee}}^{LDA}(\mathbf{r})\right]\phi_i(\mathbf{x}) = \epsilon_i\phi_i(\mathbf{x}), \quad i = 1, \ldots, N, \tag{10.8}$$

where the LDA electron-interaction potential energy $v_{\mathrm{ee}}^{LDA}(\mathbf{r})$ is

$$v_{\mathrm{ee}}^{LDA}(\mathbf{r}) = v_H(\mathbf{r}) + v_{xc}^{LDA}(\mathbf{r}), \tag{10.9}$$

with the Hartree potential energy $v_H(\mathbf{r})$ as

$$v_H(\mathbf{r}) = \frac{\delta E_H[\rho]}{\delta\rho(\mathbf{r})} = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}', \tag{10.10}$$

and the LDA exchange–correlation potential energy obtained as

$$v_{xc}^{LDA}(\mathbf{r}) = \frac{\delta E_{xc}^{LDA}[\rho]}{\delta\rho(\mathbf{r})} = \frac{d}{d\rho}[\epsilon_{xc}^{(0)}\{\rho(\mathbf{r})\}\rho(\mathbf{r})]. \tag{10.11}$$

The orbitals $\phi_i(\mathbf{x})$ are then employed to determine the kinetic energy T_s and the density $\rho(\mathbf{r})$, with the latter being used to obtain the remaining components of the ground state energy $E^{LDA}[\rho]$ via (10.1).

Since for the uniform electron gas the Fermi–Coulomb hole charge is spherically symmetric about an electron, the hole charge $\rho_{xc}^{(0)}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}$ for the nonuniform electron gas is also spherically symmetric about the electron irrespective of its position. Furthermore, the hole $\rho_{xc}^{(0)}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}$ consequently satisfies the charge conservation constraint of the exact Fermi–Coulomb hole $\int \rho_{xc}(\mathbf{r}\mathbf{r}')d\mathbf{r}' = -1$. It is on the basis of the definitions ((10.2) or (10.6)) of $E_{xc}^{LDA}[\rho]$ and the fact that $\rho_{xc}^{(0)}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}$ by construction satisfies the charge conservation sum rule, that one *assumes* the correlations between the electrons in the LDA to be those of the homogeneous electron gas. As a consequence, the resulting Fermi–Coulomb hole charge is always spherically–symmetric about the electron. However, as will be shown in the following section, this is not the case.

The fact that the correlations in the LDA are not those of the uniform electron gas is best illustrated for the case when only correlations due to the Pauli principle are considered as the expressions for various properties may be determined analytically. The Kohn–Sham LDA equations for the Pauli correlated case are the same as described above but with $E_{xc}^{LDA}[\rho]$, $\rho_{xc}^{(0)}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}$, and $\epsilon_{xc}^{(0)}\{\rho(\mathbf{r})\}$ replaced by $E_x^{LDA}[\rho]$, $\rho_x^{(0)}\{\mathbf{rr}'; \rho(\mathbf{r})\}$, and $\epsilon_x^{(0)}\{\rho(\mathbf{r})\}$. The wavefunction $\Phi^{(0)}\{\mathbf{r}_1, \ldots, \mathbf{r}_N; \rho(\mathbf{r})\}$ for the nonuniform system at *each* electron position is now a Slater determinant of plane waves corresponding to a density equal to the value at that position. The resulting pair–correlation density $g_x^{(0)}\{\mathbf{rr}'; \rho(\mathbf{r})\}$ is then

$$g_x^{(0)}\{\mathbf{rr}'; \rho(\mathbf{r})\} = \rho(\mathbf{r}') + \rho_x^{(0)}\{\mathbf{rr}'; \rho(\mathbf{r})\}, \tag{10.12}$$

where

$$\rho_x^{(0)}\{\mathbf{rr}'; \rho(\mathbf{r})\} = -\frac{1}{2}\rho(\mathbf{r})\left[\frac{9j_1^2(x)}{x}\right] \tag{10.13}$$

is the uniform electron gas Fermi hole [13], $j_1(x)$ is the first–order spherical Bessel function, $x = k_F R$, k_F is the Fermi momentum, $k_F(\mathbf{r}) = [3\pi^2\rho(\mathbf{r})]^{1/3}$ is the local value of the Fermi momentum, and $\mathbf{R} = \mathbf{r}' - \mathbf{r}$. (Recall that the Fermi hole is defined as $\rho_x(\mathbf{rr}') = -|\gamma_s(\mathbf{rr}')|^2/2\rho(\mathbf{r})$, where $\gamma_s(\mathbf{rr}') = \sum_{\sigma,i} \phi_i^*(\mathbf{r}\sigma)\phi_i(\mathbf{r}'\sigma)$ is the Dirac density matrix, and that the hole satisfies the sum rules $\int \rho_x(\mathbf{rr}')d\mathbf{r}' = -1$; $\rho_x(\mathbf{rr}') \leq 0$; $\rho_x(\mathbf{rr}) = -\rho(\mathbf{r})/2$.) The Fermi hole $\rho_x^{(0)}\{\mathbf{rr}'; \rho(\mathbf{r})\}$ is by construction spherically symmetric about the electron irrespective of its position, and satisfies all the sum rules. The expression for the average exchange energy per electron $\epsilon_x^{(0)}\{\rho(\mathbf{r})\}$ assumed valid locally as obtained from uniform electron gas theory [13] is

$$\epsilon_x^{(0)}\{\rho(\mathbf{r})\} = -\frac{3k_F(\mathbf{r})}{4\pi} = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}[\rho(\mathbf{r})]^{1/3}. \tag{10.14}$$

The LDA exchange energy $E_x^{LDA}[\rho]$ is then

$$E_x^{LDA}[\rho] = \frac{1}{2}\iint \frac{\rho(\mathbf{r})\rho_x^{(0)}\{\mathbf{rr}'; \rho(\mathbf{r})\}}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}', \tag{10.15}$$

$$= \int \epsilon_x^{(0)}\{\rho(\mathbf{r})\}\rho(\mathbf{r})d\mathbf{r}, \tag{10.16}$$

$$= -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int \rho^{4/3}(\mathbf{r})d\mathbf{r}, \tag{10.17}$$

and the corresponding LDA exchange potential energy $v_x^{LDA}(\mathbf{r})$ is

$$v_x^{LDA}(\mathbf{r}) = \frac{\delta E_x^{LDA}[\rho]}{\delta\rho(\mathbf{r})} = -\left(\frac{3}{\pi}\right)^{1/3}[\rho(\mathbf{r})]^{1/3} \tag{10.18}$$

$$= -\frac{k_F(\mathbf{r})}{\pi}. \tag{10.19}$$

The resulting LDA electron–interaction potential energy with only Pauli correlations considered $v_{\mathrm{ee}}^{LDAX}(\mathbf{r})$ is therefore

$$v_{ee}^{LDAX}(\mathbf{r}) = v_H(\mathbf{r}) - \frac{k_F(\mathbf{r})}{\pi}. \tag{10.20}$$

Once again, it is on the basis of the definition of the LDA exchange energy $E_x^{LDA}[\rho]$, and the fact that the resulting Fermi hole $\rho_x^{(0)}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}$ by construction satisfies the requisite sum rules, that one *assumes* the electron correlations to be those of the uniform electron gas. This, however, is not how electrons are correlated within the LDA for exchange. We next derive via Q–DFT the explicit *analytical* representation of electron correlations within the local density and Pauli–correlated approximations.

10.1.2 Derivation and Interpretation of Electron Correlations via Quantal Density Functional Theory

We begin our analysis of electron correlations in the LDA via Q–DFT by first considering the case of correlations due to the Pauli exclusion principle. Let us initially analyze via Q–DFT the case when the electron correlations are as described in the previous section by KS theory. In other words we assume the wavefunction to be a Slater determinant of plane waves, and then further assume these uniform electron gas correlations to be valid at each point of the nonuniform density of the system. With this wavefunction, the pair–correlation density $g_x^{(0)}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}$ and Fermi hole $\rho_x^{(0)}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}$ are given by (10.12) and (10.13), respectively. Now since the Fermi hole charge $\rho_x^{(0)}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}$ is *spherically symmetric* about the electron irrespective of its position, there is no contribution of this charge to the force field at the electron position. The force field $\boldsymbol{\mathcal{E}}_{ee}^{(0)}(\mathbf{r})$ of the pair–correlation density $g_x^{(0)}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}$ then arises only from the term $\rho(\mathbf{r}')$ of (10.12) so that

$$\boldsymbol{\mathcal{E}}_{ee}^{(0)}(\mathbf{r}) = \int \frac{g_x^{(0)}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} = \boldsymbol{\mathcal{E}}_H(\mathbf{r}), \tag{10.21}$$

where the Hartree field $\boldsymbol{\mathcal{E}}_H(\mathbf{r})$ is

$$\boldsymbol{\mathcal{E}}_H(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}'. \tag{10.22}$$

Therefore, the corresponding work done $W_{ee}^{(0)}(\mathbf{r})$ in the field $\boldsymbol{\mathcal{E}}_{ee}^{(0)}(\mathbf{r})$ is the Hartree potential energy $v_H(\mathbf{r})$:

$$W_{ee}^{(0)}(\mathbf{r}) = -\int_\infty^{\mathbf{r}} \boldsymbol{\mathcal{E}}_{ee}^{(0)}(\mathbf{r}') \cdot d\boldsymbol{\ell}' \tag{10.23}$$

$$= -\int_\infty^{\mathbf{r}} \boldsymbol{\mathcal{E}}_H(\mathbf{r}') \cdot d\boldsymbol{\ell}' \tag{10.24}$$

$$= \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' = v_H(\mathbf{r}). \tag{10.25}$$

Thus we see that electron correlations as represented by $g_x^{(0)}\{\mathbf{rr}'; \rho(\mathbf{r})\}$ give rise via Coulomb's law to the Hartree potential energy $v_H(\mathbf{r})$. The S system electron–interaction potential energy $v_{\mathrm{ee}}(\mathbf{r}) \equiv W_{\mathrm{ee}}^{(0)}(\mathbf{r}) = v_H(\mathbf{r})$, and the corresponding differential equation is

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_H(\mathbf{r})\right] \phi_i(\mathbf{x}) = \epsilon_i \phi_i(\mathbf{x}), \quad i = 1, \ldots, N, \tag{10.26}$$

with $\rho(\mathbf{r}) = \sum_{\sigma,i} |\phi_i(\mathbf{r}\sigma)|^2$. The resulting electron–interaction energy $E_{\mathrm{ee}}^{(0)}$ which is the energy of interaction between the density and pair–correlation density is then

$$E_{\mathrm{ee}}^{(0)} = \frac{1}{2} \iint \frac{\rho(\mathbf{r}) g_x^{(0)}\{\mathbf{rr}'; \rho(\mathbf{r})\}}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \tag{10.27}$$

$$= E_H[\rho] + E_x^{LDA}[\rho], \tag{10.28}$$

with $E_x^{LDA}[\rho]$ as defined by (10.15)–(10.17). This is the same expression as in KS theory of the previous section. However, the numerical value of $E_{\mathrm{ee}}^{(0)}$ and of the ground state energy is different from that of the KS LDA scheme because the orbitals employed to determine these energies are generated by the differential equation (10.26). The total energy will therefore by an upper bound to the KS LDA ground state energy (See Table 1 of [7]).

What we have learned from the above Q–DFT analysis within the Pauli–correlated approximation is the following. If the electrons of the nonuniform system are assumed correlated at each point as in a uniform electron gas, then the corresponding pair–correlation density $g_x^{(0)}\{\mathbf{rr}'; \rho(\mathbf{r})\}$ gives rise via Coulomb's law to an effective electron–interaction potential energy $v_{\mathrm{ee}}(\mathbf{r})$ that is the Hartree potential energy $v_H(\mathbf{r})$ and not that of (10.20) of the KS LDA scheme. Thus, the corresponding S system differential equation is different. Hence, this is not how electrons are correlated within the LDA of Kohn–Sham theory. The same conclusion is arrived at for the more general case when both Pauli and Coulomb correlations are considered, and the electron correlations represented by the pair–correlation density $g^{(0)}\{\mathbf{rr}'; \rho(\mathbf{r})\}$ of (10.3) obtained from uniform electron gas theory.

Although, as we have seen, the wavefunction corresponding to the LDA in the Pauli–correlated case is not a Slater determinant of plane waves assumed valid locally, it is nevertheless a Slater determinant of single–particle orbitals. Thus, in order to obtain the pair–correlation density $g_x^{LDA}\{\mathbf{rr}'; \rho(\mathbf{r})\}$ in the LDA for exchange, we expand the general expression for $g_s(\mathbf{rr}') = \rho(\mathbf{r}') + \rho_x(\mathbf{rr}')$ in gradients of the density about the uniform electron gas result, and then assume these correlations to be valid at each electron position. To do so one requires the corresponding expansion of the Dirac density matrix $\gamma_s(\mathbf{rr}')$ because both terms of $g_s(\mathbf{rr}')$, viz. the density

$\rho(\mathbf{r}')$ and the Fermi hole $\rho_x(\mathbf{rr}')$ are defined in terms of it. The expression for the expansion of $\gamma_s(\mathbf{rr}')$ to $0(\boldsymbol{\nabla})$ in the gradients of the density is

$$\gamma_s(\mathbf{rr}') = \frac{k_F^3}{\pi^2}\frac{j_1(k_F R)}{k_F R} + \frac{1}{4\pi^2}(\nabla k_F^2 \cdot \hat{\mathbf{R}}) \sin k_F R, \tag{10.29}$$

where $\hat{\mathbf{R}} = \mathbf{R}/R$ and the remaining quantities are as defined previously. The derivation [7] of this result by the Kirzhnits [14] method is given in Appendix I. It is evident from this expression that the lowest–order gradient correction to the density $\rho(\mathbf{r})$ which is the diagonal matrix element $\gamma_s(\mathbf{rr})$, is of $0(\nabla^2)$. The expression for the density to $0(\nabla^2)$ is [15]

$$\rho(\mathbf{r}) = \frac{k_F^3}{3\pi^2} + \frac{1}{24\pi^2}\frac{\nabla^2 k_F^2}{k_F} - \frac{1}{96\pi^2}\frac{(\nabla k_F^2)^2}{k_F^3}. \tag{10.30}$$

The pair–correlation density $g_x^{LDA}\{\mathbf{rr}'; \rho(\mathbf{r})\}$ *is obtained by considering the expansions of* $\gamma_s(\mathbf{rr}')$ *and* $\rho(\mathbf{r})$ *up to terms of* $0(\nabla)$, *and then assuming the resulting expressions to be valid at each point of the nonuniform density system*. Note that the density $\rho(\mathbf{r})$ and the local value of the Fermi momentum $k_F(\mathbf{r})$ are as a result once again related by the uniform electron gas expression: $k_F(\mathbf{r}) = [3\pi^2\rho(\mathbf{r})]^{1/3}$. Thus $g_x^{LDA}\{\mathbf{rr}'; \rho(\mathbf{r})\}$ is given as

$$g_x^{LDA}\{\mathbf{rr}'; \rho(\mathbf{r})\} = \rho(\mathbf{r}') + \rho_x^{(0)}\{\mathbf{rr}'; \rho(\mathbf{r})\} + \rho_x^{(1)}\{\mathbf{rr}'; \rho(\mathbf{r})\}, \tag{10.31}$$

where $\rho_x^{(0)}\{\mathbf{rr}'; \rho(\mathbf{r})\}$ is as given by (10.13) and

$$\rho_x^{(1)}\{\mathbf{rr}'\} = \frac{9}{4}\rho(\mathbf{r})\left[\frac{j_0(x)j_1(x)}{k_F^3}\hat{\mathbf{R}} \cdot \nabla k_F^2\right], \tag{10.32}$$

$j_0(x) = \sin x/x$ is the zeroth–order spherical Bessel function, $\hat{\mathbf{R}} = \mathbf{R}/R$, and where the superscript (1) indicates the expression to be of $O(\nabla)$. To see that $g_x^{LDA}\{\mathbf{rr}'; \rho(\mathbf{r})\}$ is the pair–correlation density in the LDA for exchange, we next determine the potential energy due to this charge distribution via Coulomb's law. Once again the spherically symmetric component $\rho_x^{(0)}\{\mathbf{rr}'; \rho(\mathbf{r})\}$ of this charge does not contribute to the force field at the electron position. However, in addition to $\rho(\mathbf{r}')$, the term $\rho_x^{(1)}\{\mathbf{rr}'; \rho(\mathbf{r})\}$ is also *not spherically symmetric* about the electron position at $\mathbf{r}$, and thus contributes to the force field $\boldsymbol{\mathcal{E}}^{LDAX}(\mathbf{r})$ due to $g_x^{LDA}\{\mathbf{rr}'; \rho(\mathbf{r})\}$. This contribution [16, 17] is $\nabla k_F(\mathbf{r})/\pi$, so that

$$\boldsymbol{\mathcal{E}}^{LDAX}(\mathbf{r}) = \int \frac{g_x^{LDA}\{\mathbf{rr}'; \rho(\mathbf{r})\}(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} d\mathbf{r}' \tag{10.33}$$

$$= \boldsymbol{\mathcal{E}}_H(\mathbf{r}) + \nabla\left(\frac{k_F(\mathbf{r})}{\pi}\right). \tag{10.34}$$

Note that the curl of this force field vanishes, i.e. $\nabla \times \boldsymbol{\mathcal{E}}^{LDAX}(\mathbf{r}) = 0$. The work done $W^{LDAX}(\mathbf{r})$ to move the model fermion in this force field is then

$$W^{LDAX}(\mathbf{r}) = v_H(\mathbf{r}) - \frac{k_F(\mathbf{r})}{\pi}, \tag{10.35}$$

which is the same as the Kohn–Sham electron interaction potential energy $v_{\mathrm{ee}}^{LDAX}(\mathbf{r})$ of (10.20). Thus, the S system differential equation derived from the pair–correlation density $g_x^{LDA}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}$ via Coulomb's law is the same as that of the Kohn–Sham LDA scheme obtained via a functional derivative. Further, the fact that the curl of $\boldsymbol{\mathcal{E}}^{LDAX}(\mathbf{r})$ vanishes explains why the potential energy $v_{\mathrm{ee}}^{LDAX}(\mathbf{r})$ is path–independent. The corresponding expression for the electron–interaction energy component E_{ee}^{LDA} of the total energy obtained from $g_x^{LDA}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}$ is also the same as that of the Kohn–Sham LDA. This energy is the energy of interaction between the density $\rho(\mathbf{r})$ and the pair–correlation density $g_x^{LDA}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}$. However, the non–spherically symmetric component $\rho_x^{(1)}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}$ does not contribute to the energy integral so that

$$E_{\mathrm{ee}}^{LDA} = \frac{1}{2}\iint \frac{\rho(\mathbf{r}) g_x^{LDA}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \tag{10.36}$$

$$= E_H + E_x^{LDA}, \tag{10.37}$$

which is the Kohn–Sham LDA expression. Note that the numerical value of the electron–interaction energy; and therefore of the total ground state energy, is also the same as the Kohn–Sham scheme because the orbitals are identical. Thus, we see that the equations of the local density approximation for exchange of Kohn–Sham theory can be rederived via Q–DFT. The derivation therefore provides a *rigorous physical* interpretation of the approximation. *The local potential energy (functional derivative) representing electron correlations in the LDA for exchange is the work done to move an electron in the force field of the quantum–mechanical source charge distribution* $g_x^{LDA}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}$, *and the electron interaction energy is the energy of interaction between the electronic density and this source charge*. Furthermore, the Q–DFT derivation shows that the source charge $g_x^{LDA}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}$, which is the pair–correlation density in this approximation, contains a term proportional to the gradient of the density. Therefore, the nonuniformity of the electronic density is explicitly accounted for in the representation of electron correlations within the LDA. The existence of the additional correlations, and the fact that it is these correlations which generate the LDA exchange potential energy $v_x^{LDA}(\mathbf{r})$ and orbitals, cannot be gleaned from Kohn–Sham theory.

From the expression for $g_x^{LDA}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}$ of (10.31) it is evident that the Fermi hole in the LDA is given by the expression

$$\rho_x^{LDA}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\} = \rho_x^{(0)}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\} + \rho_x^{(1)}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}. \tag{10.38}$$

This charge distribution is not spherically symmetric about the electron and contains a term proportional to the gradient of the density. The LDA Fermi hole satisfies the constraints of charge neutrality and the value at the electron position since its non–spherical component $\rho_x^{(1)}\{\mathbf{rr}'; \rho(\mathbf{r})\}$ does not contribute to either sum rule. It does not, however, satisfy the constraint of negativity and this is one source of error in the LDA. It is also important to note that it is the nonsymmetric component $\rho_x^{(1)}\{\mathbf{rr}'; \rho(\mathbf{r})\}$ of the LDA Fermi hole charge that generates the force field and thereby the local exchange potential energy $v_x^{LDA}(\mathbf{r})$ and the orbitals of the differential equation in the LDA. However, it is only its symmetric component $\rho_x^{(0)}\{\mathbf{rr}'; \rho(\mathbf{r})\}$ that contributes to the LDA exchange energy E_x^{LDA}. The structure of the LDA Fermi hole $\rho_x^{LDA}\{\mathbf{rr}'; \rho(\mathbf{r})\}$ for the Be atom is described in the following section. The resulting structure of the exchange potential energy $v_x^{LDA}(\mathbf{r})$ and the accuracy of the exchange energy E_x^{LDA} is then explained on the basis of these charge distributions.

When both Pauli and Coulomb correlations are considered, the corresponding LDA Fermi–Coulomb hole charge $\rho_{xc}^{LDA}\{\mathbf{rr}'; \rho(\mathbf{r})\}$ is also not spherically symmetric about the electron, and is the sum of a spherically symmetric component $\rho_{xc}^{(0)}\{\mathbf{rr}'; \rho(\mathbf{r})\}$ obtained from uniform electron gas theory, and a non–spherically symmetric component $\rho_{xc}^{(1)}\{\mathbf{rr}'; \rho(\mathbf{r})\}$ proportional to the first–order in the gradient of the density determined by an expansion about the uniform gas value. The non–spherical component gives rise to the LDA exchange–correlation potential energy $v_{xc}^{LDA}(\mathbf{r})$ and the orbitals, and its spherically symmetric component to the exchange–correlation energy E_{xc}^{LDA}. An expression for the non–spherically symmetric component has not yet been derived.

We thus see that the representation of electron correlations within the LDA are far more physically realistic than understood to be the case via Kohn–Sham theory. The approximation does not correspond to one in which the nonuniform electron gas is considered uniform at each point, but rather one in which the non–uniformity of the electronic density is explicitly accounted for at each electron position. The LDA pair–correlation density $g^{LDA}\{\mathbf{rr}'; \rho(\mathbf{r})\}$ in fact contains a term proportional to the gradient of the density, and may be written as

$$g^{LDA}\{\mathbf{rr}'; \rho(\mathbf{r})\} = g^{(0)}\{\mathbf{rr}'; \rho(\mathbf{r})\} + 0(\nabla\rho), \tag{10.39}$$

with $g^{(0)}\{\mathbf{rr}'; \rho(\mathbf{r})\}$ given by (10.3). From this fact, and from its definition in terms of the corresponding LDA wave function $\psi^{LDA}\{\mathbf{r}_1, \ldots, \mathbf{r}_N; \rho(\mathbf{r})\}$ which is

$$g^{LDA}\{\mathbf{rr}'; \rho(\mathbf{r})\} = \langle\psi^{LDA}|\hat{P}(\mathbf{rr}')|\psi^{LDA}\rangle/\rho(\mathbf{r}), \tag{10.40}$$

with $\hat{P}(\mathbf{rr}')$ the pair–correlation operator, we see that $\psi^{LDA}\{\mathbf{r}_1, \ldots, \mathbf{r}_N; \rho(\mathbf{r})\}$ explicitly incorporates (in an approximate manner) elements of the physics appropriate to regions of space where the effective potential energy is rapidly varying as well as of the classically forbidden region. The fact that the LDA wavefunction possesses these properties is the fundamental reason for the accuracy achieved by the approximation.

The understanding of the LDA achieved via Q–DFT also allows for a more accurate description of the explanation [18, 19] for the success of the LDA given in the past. The starting point of this explanation is also the Kohn–Sham LDA exchange–correlation energy functional $E_{xc}^{LDA}[\rho]$, with the subsequent assumption that the LDA Fermi–Coulomb hole is that derived from uniform electron gas theory, viz. $\rho_{xc}^{(0)}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}$. Further, it is noted that the exact exchange–correlation energy E_{xc} can be written in terms of the spherical average of the true Fermi–Coulomb hole charge $\rho_{xc}(\mathbf{r}\mathbf{r}')$. Thus, E_{xc}, which is defined as

$$E_{xc} = \frac{1}{2}\iint \frac{\rho(\mathbf{r})\rho_{xc}(\mathbf{r}\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}', \tag{10.41}$$

may also be written as

$$E_{xc} = \int \rho(\mathbf{r}) \left[\int_0^\infty \rho_{xc}(\mathbf{r}R) R dR\right] d\mathbf{r}, \tag{10.42}$$

where $\rho_{xc}(\mathbf{r}R)$ is the spherically averaged hole charge:

$$\rho_{xc}(\mathbf{r}R) = \frac{1}{2}\int \rho_{xc}(\mathbf{r}, \mathbf{r}+\mathbf{R}) d\Omega_{\mathbf{R}}, \tag{10.43}$$

with $\mathbf{R} = \mathbf{r}' - \mathbf{r}$. It is then observed that in the interior of atoms where the principal contribution to the energy arises, and in the higher density regions at a metal surface, the spherically–averaged uniform electron gas theory hole is a reasonable approximation to the spherical average of the true hole. The approximate equivalence of these spherically averaged holes is then given as the reason for the accuracy of the atomic ground-state energies achieved by the LDA. However, we know now that the LDA Fermi–Coulomb hole $\rho_{xc}^{LDA}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}$ is a far more accurate representation of electron correlations than that assumed on the basis of Kohn–Sham theory. Thus, although the spherical averages of $\rho_{xc}^{(0)}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}$ and $\rho_{xc}^{LDA}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}$ turn out to be the same, we understand that the spherical average is in fact that of a more accurate representation of the hole charge. This is why the spherical average of the LDA hole in high density regions is a good approximation to that of the exact hole.

10.1.3 Structure of the Fermi Hole in the Local Density Approximation

In this section we apply the above understanding of the electron correlations within the LDA to plot the self–consistently determined structure of the LDA Fermi hole charge for the Be atom. This in turn explains the structure of the corresponding LDA exchange potential energy $v_x^{LDA}(\mathbf{r})$ and the accuracy of various atomic ground-state properties obtained from it. As the explanation of how electrons are correlated in the LDA is achieved via Q–DFT, the LDA results are compared with those of self–consistent calculations performed within the Pauli–correlated approximation of

Table 10.1 Self–consistent ground-state energy E, exchange energy E_x, and highest occupied eigenvalue ϵ_m of the Be atom in the Pauli–correlated approximation as determined within (a) the local density approximation (LDA), (b) Quantal density functional theory (Q–DFT), and (c) Hartree–Fock theory (HF). The energy of (a) is obtained from the ground-state energy expression as written in the LDA for exchange, whereas those of (b) and (c) are the expectation values of the Hamiltonian taken with respect to the Slater determinant of orbitals of the corresponding theory. The negative values of the energies in Rydbergs are quoted. (The experimental ionization potential is 0.685 Ryd)

Property	LDA	Q–DFT[a]	HF[b]
E	14.2233	14.5714	14.5730
E_x	2.2778	2.6665	2.6669
ϵ_m	0.3401	0.6263	0.6185

[a]From [20]
[b]From [21]

Q–DFT (see Sect. 5.8.1 and ***QDFT2***). The orbitals, density, and ground-state energy determined [20] (and ***QDFT2***) within this approximation of Q–DFT are essentially equivalent to those of Hartree–Fock theory [21]. (The difference between the results is an accurate estimate of Correlation-Kinetic effects that arise due to Pauli correlations (see ***QDFT2***)). In Table 10.1 the ground-state energy E, the exchange energy E_x, and the highest occupied eigenvalue ϵ_m for the Be atom as determined within the LDA, Q–DFT, and Hartree–Fock theory are given.

In Fig. 10.1 we plot the LDA Fermi hole $\rho_x^{LDA}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}$ of (10.38) and its spherically symmetric component $\rho_x^{(0)}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}$ of (10.13), and compare it to the Fermi hole $\rho_x(\mathbf{r}\mathbf{r}')$ of Q–DFT. The three electron positions considered (as indicated by arrows) are in the high density regions at the nucleus $r = 0$, and at the positions of maximum radial probability density in the K and L shells which are at $r = 0.266$ a.u. and $r = 2.05$ a.u., respectively. (The electron is along the z-axis corresponding to $\theta = 0°$. The cross-section through the Fermi hole corresponds to $\theta' = 0°$. The graph for $r' < 0$ corresponds to the structure for $\theta = \pi$ and $r' > 0$.) In Fig. 10.2 we plot the Fermi holes for the electron positions in the low probability density regions of the atom at $r = 1.1$ a.u. which is at the position of the intershell minimum of the radial probability density, and at $r = 4.1$ a.u. in the classically forbidden region. Observe in all these figures that the LDA Fermi hole is not spherically symmetric about the electron position. Further, it develops decaying oscillations which indicate that it does not satisfy the constraint of negativity. The positive part of these oscillations have no physical meaning, since the effect of the Pauli exclusion principle is in terms of a reduction in density. In addition, these oscillations though decaying, extend well into the classically forbidden region so that the LDA hole is not located about the nucleus as is the case for the exact hole.

In Fig. 10.3a we plot the LDA force field $\boldsymbol{\mathcal{E}}^{LDAX}(\mathbf{r})$ of (10.34) and the exact Q–DFT field $\boldsymbol{\mathcal{E}}_x(\mathbf{r})$, and in Fig. 10.4 the corresponding exchange potential energies $v_x^{LDA}(\mathbf{r})$ of (10.19) and $W_x(\mathbf{r})$. For an electron at the nucleus, the Q–DFT Fermi hole is spherically symmetric (Fig. 10.1a), so that the corresponding force field $\boldsymbol{\mathcal{E}}_x(\mathbf{r})$ there is zero (Fig. 10.3a). Thus, the potential energy $W_x(\mathbf{r})$ has zero slope at the nucleus.

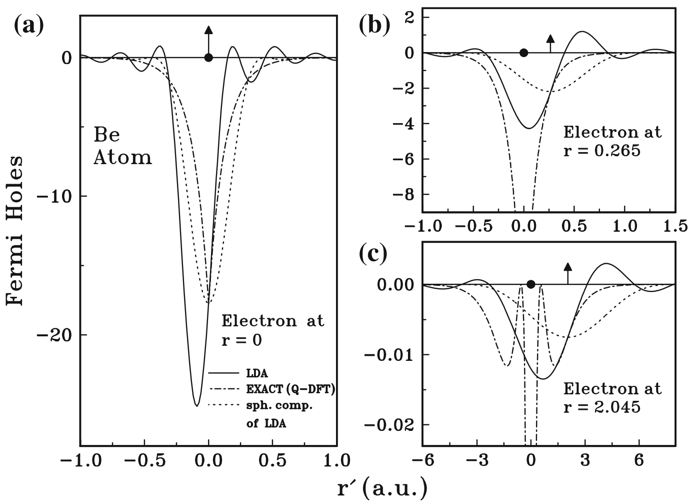

Fig. 10.1 Cross–sections of the Fermi holes for the Be atom for different electron positions. The Fermi holes plotted are those of the local density approximation for exchange (LDA), its spherically symmetric component (sph. comp. of LDA), and that of the Pauli–correlated approximation of Q–DFT. The electron positions, indicted by the *arrow*, are at (**a**) the nucleus, (**b**) and (**c**) at the first and second maximum of the radial probability density corresponding to the K and L shells, respectively, of the LDA for exchange

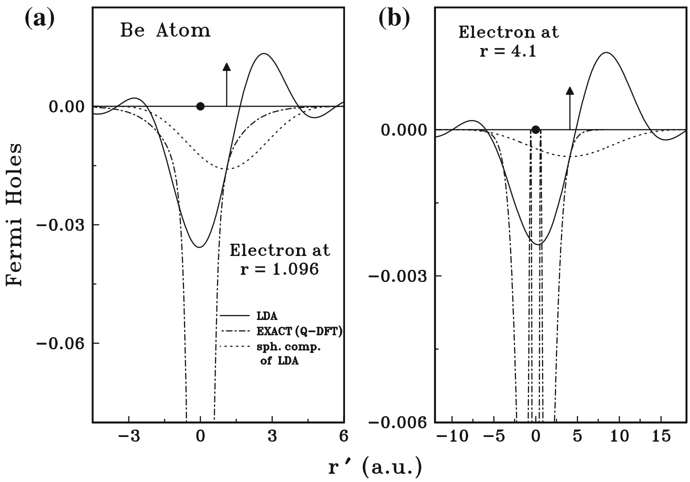

Fig. 10.2 The figure caption is the same as that of Fig. 10.1 except that in (**a**) the electron is at the intershell minimum of the radial probability density, and in (**b**) at a point in the classically forbidden region

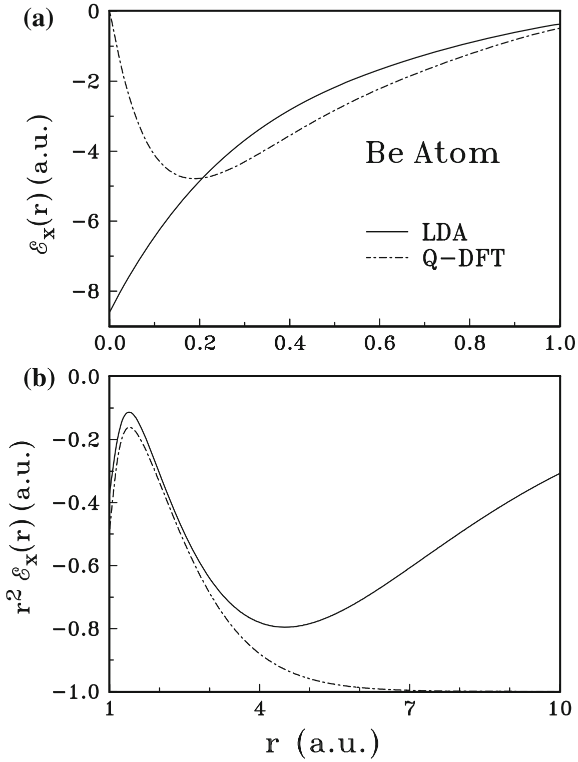

Fig. 10.3 (**a**) The force field $\boldsymbol{\mathcal{E}}^{LDAX}(\mathbf{r})$ for the Be atom obtained within the local density approximation for exchange. The corresponding exact force field $\boldsymbol{\mathcal{E}}_x(\mathbf{r})$ in the Pauli–correlated approximation of Q–DFT is also plotted. (**b**) Plots of $r^2\boldsymbol{\mathcal{E}}_x^{LDAX}(\mathbf{r})$ and $r^2\boldsymbol{\mathcal{E}}_x(\mathbf{r})$

On the other hand, the LDA Fermi hole is not symmetrical about the electron at the nucleus (Fig. 10.1a), and the force field $\boldsymbol{\mathcal{E}}^{LDAX}(\mathbf{r})$ there is finite (Fig. 10.3a). Consequently, the LDA exchange potential energy $v_x^{LDA}(\mathbf{r})$ has a finite slope at the origin. (See Fig. 10.4 and its inset.) (This will also be the case when Coulomb correlations are incorporated within the LDA.)

In the high density regions from which the principal contribution to the energy arises, the LDA hole is a fair approximation to the Q–DFT hole (Fig. 10.1) although it does not possess any of its structure (Fig. 10.1c). Consequently, in the interior of the atom, the potential energy $v_x^{LDA}(\mathbf{r})$ arising from this hole charge is a good approximation to $W_x(\mathbf{r})$ (Fig. 10.4). This explains why the LDA ground state energy is reasonably accurate (2.4 %) in comparison to the Q–DFT and Hartree–Fock theory results (see Table 10.1). On the other hand, the spherically symmetric component of the LDA hole (Fig. 10.1) is not very accurate in this region. Since this is the component that contributes to the exchange energy expression (10.15), it becomes obvious why the LDA exchange energy, for Be is in error by 13 % when compared to the Hartree–Fock theory value (see Table 10.1).

In regions of low probability density and in the classically forbidden region, the LDA Fermi hole is a poor approximation to the exact hole. The amplitude of the first positive oscillation is a substantial fraction of the primary negative part, and

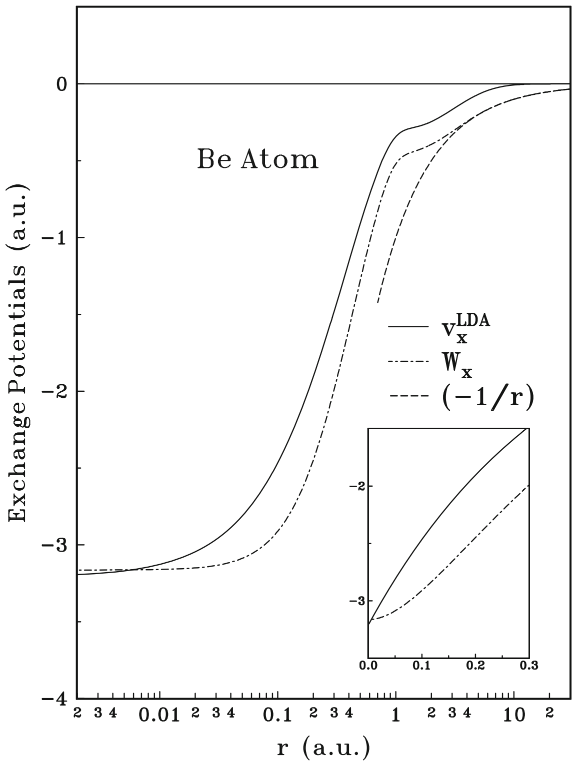

Fig. 10.4 The exchange potential energies $v_x^{LDA}(\mathbf{r})$ and $W_x(\mathbf{r})$ for the Be atom in the local density approximation for exchange and the Pauli–correlated approximation of Q–DFT, respectively. The function $-1/r$ is also plotted

the oscillations extend for substantial distances beyond the surface of the atom. The error in the corresponding force field $\boldsymbol{\mathcal{E}}^{LDAX}(\mathbf{r})$ is therefore significant as may be observed from Fig. 10.3b where we plot $r^2\boldsymbol{\mathcal{E}}^{LDAX}(\mathbf{r})$ and compare it to the exact $r^2\boldsymbol{\mathcal{E}}_x(\mathbf{r})$. Whereas, the Q–DFT result tends asymptotically to -1 as it must, the LDA result approaches zero. Thus, the potential energy $v_x^{LDA}(\mathbf{r})$ is in error in the classically forbidden region, decaying exponentially as does the density, rather than as $-1/r$ (Fig. 10.4). Consequently, the highest occupied eigenvalue of the LDA differential equation is a poor approximation to that of Q–DFT (see Table 10.1) and to the experimental ionization potential which is -0.685 Ryd [20].

The differences between the electron correlations as represented by the pair–correlation densities $g_x^{(0)}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}$, $g_x^{LDA}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}$, and the Q–DFT $g_x(\mathbf{r}\mathbf{r}')$ are also reflected in the structure of the corresponding electron–interaction potential energies $v_H(\mathbf{r})$, $v_{\text{ee}}^{LDAX}(\mathbf{r})$ of (10.20), and $[v_H(\mathbf{r}) + W_x(\mathbf{r})]$, respectively. In Fig. 10.5 we plot these potential energies. Observe the striking difference between $v_H(\mathbf{r})$ and $[v_H(\mathbf{r}) + v_x^{LDA}(\mathbf{r})]$. The effect of the additional correlations represented by the $0(\boldsymbol{\nabla})$ gradient term in $g_x^{LDA}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}$ is obviously significant. Observe also that $[v_H(\mathbf{r}) + v_x^{LDA}(\mathbf{r})]$ is a reasonable approximation to $[v_H(\mathbf{r}) + W_x(\mathbf{r})]$. This again explains why the total ground-state energy in the LDA is as accurate as it is.

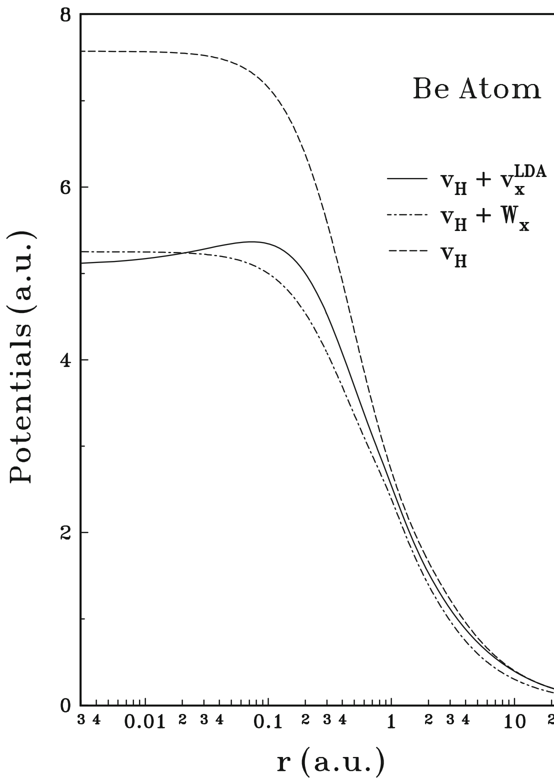

Fig. 10.5 Electron–interaction potential energies $v_H(\mathbf{r})$, $v_{\text{ee}}^{LDAX}(\mathbf{r}) = v_H(\mathbf{r}) + v_x^{LDA}(\mathbf{r})$, and $[v_H(\mathbf{r}) + W_x(\mathbf{r})]$ as determined from their respective source charges $g_x^{(0)}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}$; $g_x^{LDA}\{\mathbf{r}\mathbf{r}'; \rho(\mathbf{r})\}$ and $g_x(\mathbf{r}\mathbf{r}')$

10.1.4 Endnote

The rigorous physical understanding of the LDA of Kohn–Sham theory is therefore as follows. The correlations within this approximation are not those of the uniform electron gas. The correlations in this approximation are determined by expanding the pair–correlation density about the uniform electron gas value to terms of $0(\nabla)$. Thus, it is only the leading term of the expansion that corresponds to the uniform gas expression. Both the local (the density) and nonlocal (the Fermi–Coulomb hole charge) components of the pair density are so expanded. The terms of $0(\nabla)$, which explicitly account for the non–uniformity of the density, appear in the nonlocal part. Thus, the correlations in the approximation are far more accurate than previously understood to be the case. The LDA Fermi–Coulomb hole is not spherically symmetric about the electron. The corresponding LDA exchange–correlation energy $E_{xc}^{LDA}[\rho]$ is the energy of interaction between the density and the LDA Fermi–Coulomb hole charge, and the LDA exchange–correlation potential energy $v_{xc}^{LDA}(\mathbf{r})$ is the work done in the field of this charge distribution. This work done is path independent as the field is conservative. Further, it is the non–spherically symmetric component of this charge that gives rise to the potential energy $v_{xc}^{LDA}(\mathbf{r})$, and its spherically symmetric component that contributes to the energy $E_{xc}^{LDA}[\rho]$.

The graphs of the LDA Fermi hole $\rho_x^{LDA}\{\mathbf{rr}'; \rho(\mathbf{r})\}$ of Figs. 10.1 and 10.2 are a representation of how electrons of parallel spin are correlated in this approximation. It is also evident from these figures that the manner in which the electrons are assumed correlated within the approximation is different from the true correlations. This points to an important difference between approximate KS–DFT and approximation methods within Schrödinger theory and Q–DFT. Approximating the functional $E_{xc}^{KS}[\rho]$ thus means approximating how electrons are correlated in the system. In effect this in turn means that the Hamiltonian of the system is approximated. For approximate KS–DFT, the rigor of the Hohenberg–Kohn theorems is thereby lost. Hence, unlike variational methods within Schrödinger theory and Q–DFT in which the physical system as described by its Hamiltonian remains unchanged, in approximate KS–DFT it is the Hamiltonian that is approximated. The corresponding total energy thus determined may then not constitute a rigorous upper bound to the true value. Total energies that lie below the exact result could be obtained.

Finally, we note that the LDA as practiced does account for Correlation–Kinetic effects, albeit approximately. In the LDA expression for the exchange–correlation energy $E_{xc}^{LDA}[\rho]$ of (10.7), the average exchange–correlation energy per electron $\epsilon_{xc}^{(0)}\{\rho(\mathbf{r})\}$ as determined by solution of the Schrödinger equation for the uniform electron gas is not employed. This is because $\epsilon_{xc}^{(0)}\{\rho(\mathbf{r})\}$ thus obtained does not contain any Correlation–Kinetic contributions as the kinetic energy in the solution of the Schrödinger equation is that of the interacting system. Instead one employs the sum of $\epsilon_x\{\rho(\mathbf{r})\}$ of (10.14) which is the expression derived when only Pauli correlations are considered, and an average 'correlation' energy per electron $\epsilon_c^{(0)}\{\rho(\mathbf{r})\}$. The energy $\epsilon_c^{(0)}\{\rho(\mathbf{r})\}$ is obtained from the difference between the fully–interacting system ground-state energy as determined by solution of the Schrödinger equation for the uniform system and the Hartree–Fock theory energy corresponding to the same density. The $\epsilon_c^{(0)}\{\rho(\mathbf{r})\}$, and therefore the sum $\epsilon_x^{(0)}\{\rho(\mathbf{r})\} + \epsilon_c^{(0)}\{\rho(\mathbf{r})\}$, thereby contain the correlation contribution to the kinetic energy of the uniform electron gas for the particular density.

For a discussion along similar lines of the gradient expansion approximation of KS–DFT, which too is *ad hoc*, the reader is referred to [7].

10.2 Slater Theory

10.2.1 Derivation of the Exact 'Slater Potential'

The reasoning underlying the exact 'Slater potential' $v_x^S(\mathbf{r})$ stems from Slater's interpretation of Hartree–Fock theory as described in Sect. 3.8.2. In this interpretation, Hartree–Fock theory is described as being orbital–dependent so that the potential energy of each electron is different and depends upon the orbital it is in. This orbital dependence results from the orbital–dependent ‘exchange potential energy’ $v_{x,i}(\mathbf{r})$ of (3.201) due to the orbital–dependent Fermi hole $\rho_{x,i}(\mathbf{rr}')$ as defined by (3.202). Slater’s reasoning in deriving the ‘potential’ $v_x^S(\mathbf{r})$ is as follows.

Each orbital–dependent Fermi hole $\rho_{x,i}(\mathbf{rr}')$ satisfies the sum rule of charge neutrality (3.203), value at the electron position (3.204), and negativity (3.205) at each electron position. As such Slater assumed that the $\rho_{x,i}(\mathbf{rr}')$ corresponding to different orbitals i for each electron position were not very different. Based on this assumption, it seems reasonable to use instead a weighted mean of these orbital–dependent Fermi holes, weighting over all electrons of one kind of spin for each electron position. The orbital dependence of these holes and of the resulting ‘potential’ is thereby eliminated.

The weighting factor employed by Slater is the probability $p_i(\mathbf{r})$ that an electron at $\mathbf{r}$ is in the state i:

$$p_i(\mathbf{r}) = \frac{\psi_i^*(\mathbf{r})\psi_i(\mathbf{r})}{\sum_k \psi_k^*(\mathbf{r})\psi_k(\mathbf{r})}. \tag{10.44}$$

The expression for the orbital–dependent Fermi hole $\rho_{x,i}(\mathbf{rr}')$ of (3.202) may be rewritten on multiplying and dividing by $\psi_i^*(\mathbf{r})$ as

$$\rho_{x,i}(\mathbf{rr}') = -\sum_{\substack{j=1 \\ \text{spin } j=\text{spin } i}}^{N} \frac{\psi_i^*(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')\psi_j(\mathbf{r})}{\psi_i^*(\mathbf{r})\psi_i(\mathbf{r})}. \tag{10.45}$$

Slater weighted the $\rho_{x,i}(\mathbf{rr}')$ with the probability $p_i(\mathbf{r})$ over all electrons with the same spin. It turns out the expression derived by this weighting procedure is that of the true Fermi hole charge $\rho_x(\mathbf{rr}')$. In other words, the weighted mean corresponds to the reduction in density at $\mathbf{r}'$ in the distribution of electrons of a particular spin when an electron of the same spin is at $\mathbf{r}$. Thus,

$$\sum_i \rho_{x,i}(\mathbf{rr}')p_i(\mathbf{r}) = -|\gamma_s(\mathbf{rr}')|^2/2\rho(\mathbf{r}) \tag{10.46}$$

$$= \rho_x(\mathbf{rr}'), \tag{10.47}$$

where $\gamma_s(\mathbf{rr}')$ is the Dirac density matrix, with $\gamma_s(\mathbf{rr}) = \rho(\mathbf{r})$.

The exact ‘Slater exchange potential’ $v_x^S(\mathbf{r})$ is defined in terms of the weighted average or Fermi hole $\rho_x(\mathbf{rr}')$ in a manner similar to that of the orbital–dependent exchange potential $v_{x,i}(\mathbf{r})$ of (3.201). The Slater representation of the exchange potential energy is therefore

$$v_x^S(\mathbf{r}) = \int \frac{\rho_x(\mathbf{rr}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'. \tag{10.48}$$

This is a local or multiplicative operator, and replaces the non-local integral exchange operator of Hartree–Fock theory. The resulting differential equation is

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_H(\mathbf{r}) + v_x^S(\mathbf{r})\right]\phi_i(\mathbf{x}) = \epsilon_i\phi_i(\mathbf{x}); \quad i = 1, \ldots, N, \tag{10.49}$$

in which each electron now has the same effective potential energy. Thus Slater theory is a local effective potential energy theory. We refer to this equation as the Hartree–Fock–Slater equation because this was the original approximation made by Slater. (Historically, what is referred to as the Hartree–Fock–Slater equation is when the function $v_x^S(\mathbf{r})$ of (10.48) is replaced in the differential equation by its local density approximation as discussed in Sect. 10.2.4.)

The ground state energy is determined as the expectation value of the Hamiltonian $\hat{H}$ of (2.131) taken with respect to the Slater determinant of the orbitals $\phi_i(\mathbf{x})$ of (10.49). The expression for the energy is therefore the same as that of Hartree–Fock theory. However, as a consequence of the variational principle, the energy thus obtained constitutes an upper bound to the Hartree–Fock theory value because the Hartree–Fock–Slater wavefunction is not the same as the Hartree–Fock theory determinant.

Ground state energies of ten closed–shell atoms as obtained by solution of the Hartree–Fock–Slater equation together with those of Hartree–Fock theory [21] are quoted in Table 10.2. The relative differences between the two in parts per million (ppm) are plotted in Fig. 10.6. Observe that the Slater theory energies are above those of Hartree–Fock theory, the relative difference between the two diminishing with increasing atomic number. This difference varies from 800 ppm for Be to 64 ppm for Xe.

Table 10.2 Ground state energies of closed shell atoms as determined by Slater theory, the Pauli–correlated approximation of Quantal density functional theory (Q–DFT), and Hartree–Fock theory. The negative values of the energies in Rydbergs are quoted

Atom	Slater Theory[a]	Q–DFT[b]	Hartree–Fock Theory[c]
Be	14.561	14.571	14.573
Ne	128.501	128.542	128.547
Mg	199.533	199.606	199.615
Ar	526.703	526.804	526.818
Ca	676.606	676.743	676.758
Zn	1777.576	1777.820	1777.848
Kr	2751.756	2752.030	2752.055
Sr	3131.209	3131.519	3131.546
Cd	5464.700	5465.093	5465.133
Xe	7231.672	7232.101	7232.138

[a]From [12]
[b]From [20]
[c]From [21]

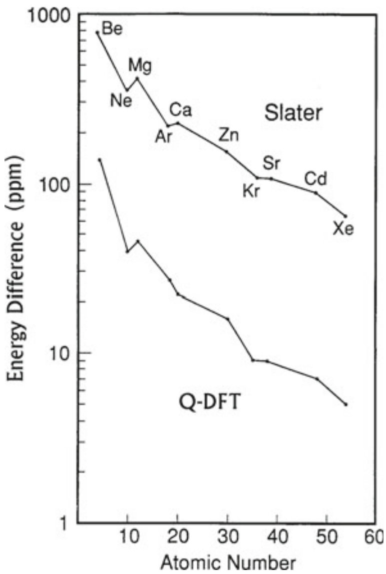

Fig. 10.6 Ground-state energy differences (in parts per million (ppm)) of Slater theory and the Pauli–correlated approximation of Q–DFT taken with respect to the Hartree–Fock theory values

It is an interesting fact that the Slater weighted average of the orbital–dependent Fermi hole $\rho_{x,i}(\mathbf{r}\mathbf{r}')$ turns out to be the Fermi hole $\rho_x(\mathbf{r}\mathbf{r}')$. Furthermore, as the energy expression is the same as that of Hartree–Fock theory, the exchange energy in Slater theory is also the energy of interaction between the corresponding density and Fermi hole charge. However, the assumption by Slater that the orbital–dependent Fermi holes $\rho_{x,i}(\mathbf{r}\mathbf{r}')$ are similar is not correct. A study of these holes shows them to be distinctly different for the uniform electron gas [22] as well as for the nonuniform density system at metal surfaces [22] and in atoms [23].

There is yet another aspect of Slater theory that needs to be addressed. We have seen that Slater's weighting procedure leads to the physically meaningful Fermi hole charge $\rho_x(\mathbf{r}\mathbf{r}')$. In other words, this weighting correctly describes the intrinsic nonlocality that is a consequence of the Pauli exclusion principle. The question that arises is whether Slater theory correctly accounts for this nonlocality of the Fermi hole via its definition of the 'exchange potential' $v_x^S(\mathbf{r})$ of (10.48). In the following section we show why it does not, and therefore why the 'Slater exchange potential' does not represent a potential energy.

10.2.2 Why the 'Slater Exchange Potential' Does Not Represent the Potential Energy of an Electron

The conclusion that the 'Slater exchange potential' does not represent the potential energy of an electron is proved by analogy to classical physics. Let us first consider a static or local charge distribution $Q(\mathbf{r})$ as in Fig. 10.7. The term local is used here

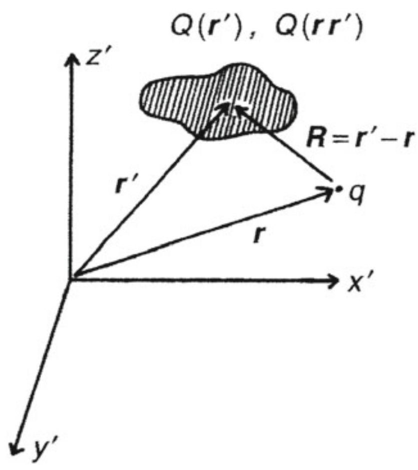

Fig. 10.7 The static $Q(\mathbf{r})$ and dynamic $Q(\mathbf{rr}')$ charge distributions at $\mathbf{r}'$, and the test charge q at $\mathbf{r}$

to indicate that this charge is independent of the position of any external test charge q. The electric field due to this charge distribution is given by Coulomb's law as

$$\boldsymbol{\mathcal{E}}(\mathbf{r}) = \int \frac{Q(\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}'. \tag{10.50}$$

The potential energy $W(\mathbf{r})$ of a test charge q at $\mathbf{r}$ (see Fig. 10.7) in this field is the work done to move it against the force of this field from some reference point, say at infinity, to its position at $\mathbf{r}$:

$$W(\mathbf{r}) = -q \int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{E}}(\mathbf{r}') \cdot d\boldsymbol{\ell}'. \tag{10.51}$$

The electric field $\boldsymbol{\mathcal{E}}(\mathbf{r})$ may also be written as

$$\boldsymbol{\mathcal{E}}(\mathbf{r}) = -\int Q(\mathbf{r}') \left[\boldsymbol{\nabla} \frac{1}{|\mathbf{r}-\mathbf{r}'|} \right] d\mathbf{r}'. \tag{10.52}$$

As the gradient operation is with respect to the coordinate $\mathbf{r}$, it can be pulled out of the integral, so that we may write the field as

$$\boldsymbol{\mathcal{E}}(\mathbf{r}) = -\boldsymbol{\nabla} \int \frac{Q(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' = -\boldsymbol{\nabla} V(\mathbf{r}), \tag{10.53}$$

where

$$V(\mathbf{r}) = \int \frac{Q(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'. \tag{10.54}$$

Thus, the work done $W(\mathbf{r})$ is

$$W(\mathbf{r}) = q\int_{\infty}^{\mathbf{r}} \nabla V(\mathbf{r}') \cdot d\boldsymbol{\ell}' = qV(\mathbf{r}). \tag{10.55}$$

Since $\nabla \times \boldsymbol{\mathcal{E}}(\mathbf{r}) = 0$, the work done $W(\mathbf{r})$ is path–independent. Therefore, $qV(\mathbf{r})$ is the potential energy of the test charge q in the electrostatic field of $Q(\mathbf{r})$.

Next consider a dynamic or nonlocal charge distribution $Q(\mathbf{r}\mathbf{r}')$ whose structure at $\mathbf{r}'$ changes as a function of the position of the test charge q at $\mathbf{r}$ (see Fig. 10.7). (An example of such a changing charge distribution is the charge induced at a metal surface due to a test charge q in the vacuum region outside the metal.) The electric field due to this charge distribution is once again obtained by Coulomb's law as

$$\boldsymbol{\mathcal{E}}(\mathbf{r}) = \int \frac{Q(\mathbf{r}\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}' \tag{10.56}$$

$$= -\int Q(\mathbf{r}\mathbf{r}') \left[\nabla \frac{1}{|\mathbf{r}-\mathbf{r}'|}\right] d\mathbf{r}'. \tag{10.57}$$

Provided the $\nabla \times \boldsymbol{\mathcal{E}}(\mathbf{r}) = 0$ in a simply connected region, the potential energy of a test charge q at $\mathbf{r}$ in this field is the work done to move from infinity to its position at $\mathbf{r}$ against the force of this field:

$$W(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \boldsymbol{\mathcal{E}}(\mathbf{r}') \cdot d\boldsymbol{\ell}'. \tag{10.58}$$

This work done is path–independent. The expressions for the field and work done are, of course, the same as for the case of the static charge.

However, in the case of the dynamic charge $Q(\mathbf{r}\mathbf{r}')$, one cannot pull the gradient operator ∇ in (10.57) outside the integral. Thus, in this case

$$\boldsymbol{\mathcal{E}}(\mathbf{r}) \neq -\nabla V(\mathbf{r}), \tag{10.59}$$

and

$$W(\mathbf{r}) \neq qV(\mathbf{r}), \tag{10.60}$$

where

$$V(\mathbf{r}) = \int \frac{Q(\mathbf{r}\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'. \tag{10.61}$$

One, therefore, cannot interpret $qV(\mathbf{r})$, with $V(\mathbf{r})$ as defined by (10.61) to be the potential energy of the test charge q in the field of the nonlocal charge $Q(\mathbf{r}\mathbf{r}')$. (In the example of a test charge q a distance z from a metal surface, the image potential energy $-q^2/4z$ is obtained as the work done in the field of the induced charge. The $V(\mathbf{r})$ determined from the induced charge via (10.61) leads to the erroneous result of $-q^2/2z$.)

The ‘Slater exchange potential’ $v_x^S(\mathbf{r})$ of (10.48) due to the dynamic quantum–mechanical Fermi hole charge $\rho_x(\mathbf{rr}')$ is similar to the expression for $V(\mathbf{r})$ of (10.61). The reasoning above, taken from classical physics, thus proves that $v_x^S(\mathbf{r})$ cannot be interpreted as a potential energy. It is therefore best to refer to $v_x^S(\mathbf{r})$ as the Slater exchange function.

For the same reasons, the orbital–dependent exchange potential $v_{x,i}(\mathbf{r})$ of (3.201) of Hartree–Fock theory which is expressed similarly in terms of the orbital–dependent Fermi hole $\rho_{x,i}(\mathbf{rr}')$ cannot be interpreted as a potential energy.

Although the principles of classical physics lead to an understanding of Slater's quantum theory, there is an important point of distinction that needs to noted. In the definition of the Fermi $\rho_x(\mathbf{rr}')$ or Fermi–Coulomb $\rho_{xc}(\mathbf{rr}')$ hole charge (at $\mathbf{r}'$), the electron at $\mathbf{r}$ is one of the N electrons of the charge neutral system under consideration whether that system is an atom, a molecule, or a metal with a surface. On the other hand, in the classical physics case, the test charge q is extrinsic to the system. Thus, the overall physical system is no longer charge neutral. This distinction becomes significant when determining the asymptotic structure of the effective potential energy $v_s(\mathbf{r})$ of the S system. Different results and conclusions are arrived at if the electron in the classically forbidden asymptotic region is treated as a test charge rather than as a fermion that is part of the N–electron system [24, 25] (see ***QDFT2***).

10.2.3 Correctly Accounting for the Dynamic Nature of the Fermi Hole

It is evident from the explanation of the previous section that the dynamic nature of the Fermi hole $\rho_x(\mathbf{rr}')$ is correctly accounted for within the framework of local effective potential energy theory by Q–DFT. Accordingly, the field $\boldsymbol{\mathcal{E}}_x(\mathbf{r})$ due to this charge distribution must first be determined:

$$\boldsymbol{\mathcal{E}}_x(\mathbf{r}) = \int \frac{\rho_x(\mathbf{rr}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}'. \tag{10.62}$$

The exchange potential energy $W_x(\mathbf{r})$ is then the work done in this field:

$$W_x(\mathbf{r}) = -\int_\infty^{\mathbf{r}} \boldsymbol{\mathcal{E}}_x(\mathbf{r}') \cdot d\boldsymbol{\ell}'. \tag{10.63}$$

This work done is path–independent provided the field $\boldsymbol{\mathcal{E}}_x(\mathbf{r})$ is conservative. The corresponding differential equation in the Pauli–correlated approximation of Q–DFT is (see also ***QDFT2***)

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_H(\mathbf{r}) + W_x(\mathbf{r})\right]\phi_i(\mathbf{x}) = \epsilon_i\phi_i(\mathbf{x}), \quad i = 1, \ldots, N, \tag{10.64}$$

with the ground state energy determined as the expectation value of the Hamiltonian $\hat{H}$ of (2.131) taken with respect to the Slater determinant $\Phi\{\phi_i\}$ of the orbitals $\phi_i(\mathbf{x})$, or from the integral virial expressions in terms of the various individual fields.

The self–consistently determined Slater exchange function $v_x^S(\mathbf{r})$ and the Q–DFT exchange potential energy $W_x(\mathbf{r})$ for the Argon atom are plotted in Fig. 10.8. (The Pauli field $\boldsymbol{\mathcal{E}}_x(\mathbf{r})$ is conservative for closed–shell atoms.) It is evident that the potential energy $W_x(\mathbf{r})$ is smaller in magnitude than the function $v_x^S(\mathbf{r})$ throughout most of space. It is only in the classically forbidden asymptotic region that they are equivalent, both decaying as $-1/r$. This is because for these asymptotic electron positions, the Fermi hole $\rho_x(\mathbf{rr}')$ is an essentially static charge distribution. For these positions, the Slater exchange function $v_x^S(\mathbf{r})$ expression (10.48) does represent the potential energy of an electron. Therefore, asymptotically, $v_x^S(\mathbf{r})$ is equivalent to $W_x(\mathbf{r})$.

The ground-state energies of ten closed–shell atoms as determined [20] (and ***QDFT2***) in this Pauli–correlated approximation of Q–DFT are also quoted in Table 10.2. These results too constitute an upper bound to the Hartree–Fock theory values. The differences between the results of the two theories plotted in Fig. 10.8 vary from 137 ppm for Be to 5 ppm for Xe. These differences are an order of magnitude smaller than the corresponding differences of Slater theory. Thus, when the physics of the nonlocality of the Fermi hole $\rho_x(\mathbf{rr}')$ is correctly accounted for, results that are essentially equivalent to those of Hartree–Fock theory are obtained. (To obtain the Hartree–Fock theory density and energy within a local effective potential energy framework, Correlation–Kinetic effects must be incorporated as explained in Sect. 3.8.4). The difference between the Q–DFT Pauli-correlated approximation and Hartree–Fock theory results (see Table 10.2 and Fig. 10.6) are an accurate estimate of these Correlation–Kinetic effects.

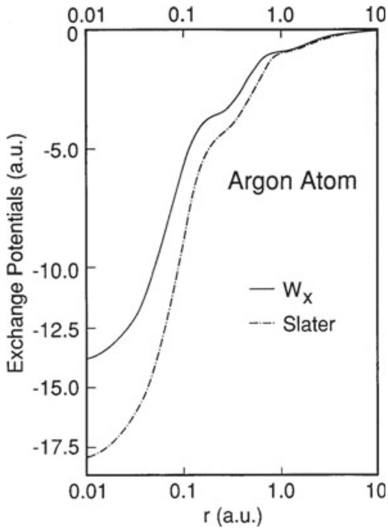

Fig. 10.8 The Slater exchange function $v_x^S(\mathbf{r})$, and the Q–DFT exchange potential energy $W_x(\mathbf{r})$, for the argon atom

10.2.4 The Local Density Approximation in Slater Theory

Although the Slater exchange function $v_x^S(\mathbf{r})$ of (10.48) is a local operator, its determination still requires the self–consistent calculation of the nonlocal Fermi hole charge distribution $\rho_x(\mathbf{r}\mathbf{r}')$. Hence, Slater made a further approximation. He determined the function $v_x^S(\mathbf{r})$ for the uniform electron gas i.e. by employing plane wave orbitals, and then invoked the local density approximation (LDA) on the resulting expression. In other words, he assumed this expression to be valid at each point of the nonuniform density system but for a density corresponding to the local value at that point. The expression for the Slater LDA exchange function $v_x^{S,LDA}(\mathbf{r})$ is

$$v_x^{S,LDA}(\mathbf{r}) = -\frac{3k_F(\mathbf{r})}{2\pi}, \tag{10.65}$$

where the local value of the Fermi momentum $k_F(\mathbf{r})$ and the density $\rho(\mathbf{r})$ are related by the uniform electron gas result of $k_F(\mathbf{r}) = [3\pi^2\rho(\mathbf{r})]^{1/3}$. The expression for $v_x^{S,LDA}(\mathbf{r})$ is then substituted for $v_x^S(\mathbf{r})$ in the Hartree–Fock–Slater differential equation (10.49). This equation is simpler to solve self–consistently as all the nonlocality has now been eliminated. The ground state energy is once again the expectation of the Hamiltonian of (2.131) taken with respect to the determinant of the resulting orbitals.

Note that the Kohn–Sham theory LDA expression for the exchange potential of (10.19) and that of the Slater LDA (10.65) differ by a factor of $2/3$. As a result, Slater introduced a variational parameter α, so that the Slater LDA exchange potential is written as

$$v_x^{S,LDA}(\mathbf{r}) = -\alpha\frac{3k_F(\mathbf{r})}{2\pi}. \tag{10.66}$$

The corresponding Hartree–Fock–Slater differential equation can be solved self–consistently for each value of the parameter till the energy taken as the expectation value of the Hamiltonian of (2.131) is minimized. These results would constitute rigorous upper bounds to the Hartree–Fock theory energy values just as those of the exact 'Slater exchange potential' of Table 10.2. Alternatively, the value of α has been adjusted [26] so as to reproduce the Hartree–Fock theory value. The use of the parameter α in the Slater LDA is referred to as the $X\alpha$ method. For a historical perspective on Slater theory see [27].

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Chapter 11
Epilogue

Abstract The three major pillars of the book are summarized. These are: (a) Schrödinger theory of electronic structure from the perspective of the *individual* electron. This is a new description of the theory in terms of the 'Quantal Newtonian' second and first laws. These laws describe the various external and internal 'classical' fields experienced by each electron, the sources of the fields being quantum-mechanical expectations of Hermitian operators taken with respect to the wave function. The new perspective elucidates the intrinsic self-consistent nature of the Schrödinger equation, and is explicated by examples. (b) Hohenberg-Kohn (HK), Runge-Gross (RG), and Kohn-Sham (KS) density functional theory are described. The emphasis here is on the first theorem of HK which establishes the concept of a basic variable of quantum-mechanics: gauge invariant properties, knowledge of which uniquely determines the external potentials, and thereby the wave functions of the system. There are further understandings of the respective first theorems of HK and RG arrived at via density preserving unitary transformations and corollaries. The theorems of HK are generalized to the added presence of an external uniform magnetostatic field. (The proof of the theorems is rigorous in the HK sense of the relationship between the basic variables and external potentials, but differs from the original proof of HK.) (c) Quantal-density functional theory (Q–DFT) is the principal component of the book. It is the description of the mapping from the interacting system as defined by Schrödinger theory to one of noninteracting fermions or bosons possessing the same basic variables. This mapping is in physical terms of 'classical' fields and quantal sources via the interacting and corresponding model system 'Quantal Newtonian' second and first laws. The theory is generalized to the presence of an external magnetostatic field. Examples of the application of the theory are given. Q–DFT provides the rigorous physical interpretation of the mathematical constructs of KS and other local effective potential theories, and approximations to them. It thereby provides further physical insights into such theories.

As was the case in the first edition, this is a natural point to conclude the book. The book presents the theoretical foundations of Quantal Density Functional Theory (Q–DFT) together with examples that elucidate the theory for both ground and excited states. Time-dependent Q–DFT, and its stationary-state version are described, as is stationary-state Q–DFT in the added presence of a magnetostatic field. Physical insights arrived at via Q–DFT of model noninteracting fermion systems or local

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effective potential energy theory in general, and of other such theories, are explained and demonstrated by example. The overall structure of the book remains the same as in the first edition but with enhancements to each component due to the further understandings achieved over the years and the inclusion of new material. For the various approximation methods and applications of stationary-state Q–DFT, the reader is referred to ***QDFT2***. The book is comprised of three components, which each stand in their own right. The first two of these are foundational to Q–DFT, the principal component.

(a) There is the new description of the Schrödinger theory of electronic structure based on the 'Quantal Newtonian' second and first laws for the individual electron. This is a perspective in terms of 'classical' fields and the quantal sources that give rise to them. The sources are quantum-mechanical in that they are expectations of Hermitian operators taken with respect to the system wave function. Once the quantal sources corresponding to different properties are defined, the quantum-mechanical system can then be described solely in terms of the resulting 'classical' fields. There is a significant degree of new physics that is gleaned from this more tangible perspective: (*i*) In addition to the external time-dependent electric or electrostatic field, each electron experiences an internal field. This internal field is the sum of fields representative of electron correlations due to the Pauli exclusion principle and Coulomb repulsion, the kinetic energy, and the density; (*ii*) As in classical physics, the sum over all the electrons of each component of the internal field is shown to vanish, thereby leading to a new proof of Ehrenfest's theorem, the quantal equivalent to Newton's second law; (*iii*) The external scalar potential $v(\mathbf{r}t)/v(\mathbf{r})$ is shown to arise from a curl-free field and thus its path-independence demonstrated; (*iv*) By writing the external scalar potentials $v(\mathbf{r}t)/v(\mathbf{r})$ via the 'Quantal Newtonian' second and first laws as the known functionals of the wave function, the time-dependent and stationary state Schrödinger equations can be written respectively so as to exhibit their intrinsic self-consistent nature; (*v*) The self-consistent form of the Schrödinger equation then makes it evident that there exist an infinite number of possible solutions to the equation with each possible self-consistent solution leading to a different external scalar potential. In the added presence of an external magnetostatic field $\mathbf{B}(\mathbf{r})$, there are other insights into Schrödinger theory achieved via the new 'classical' field and quantal source perspective: (*vi*) The corresponding 'Quantal Newtonian' first law shows that in addition to the external Lorentz field experienced by each electron, there is an added component to the internal field arising from the magnetic field; (*vii*) The external scalar potential is again shown to arise from a curl-free field and thus its path-independence proved; (*viii*) Once again, via the 'Quantal Newtonian' first law, it is shown that the Schrödinger equation can be written so as to exhibit its intrinsic self-consistent nature; (*ix*) Most significantly, in rewriting the Schrödinger equation in its self-consistent form, the external magnetic field $\mathbf{B}(\mathbf{r})$ now appears explicitly in the equation as opposed to only the vector potential $\mathbf{A}(\mathbf{r})$ as is the case when written in traditional form. It is the self-consistent nature of the Schrödinger equation that demands this be the case. The 'Newtonian' perspective on Schrödinger theory is explicated for a ground and excited state of an exactly solvable model atom in which the electron-electron interaction is Coulombic.

(b) The focus of the second foundational component is on the fundamental theorems of density functional theory: those of Hohenberg-Kohn, their extension to the time-dependent case of Runge-Gross, and on the more recent generalization of the theorems to the added presence of a uniform magnetostatic field $\mathbf{B}(\mathbf{r}) = B\mathbf{i}_z$. In particular, the significance of the first theorem of Hohenberg-Kohn of the bijectivity between the nondegenerate ground state density $\rho(\mathbf{r})$ and the external scalar potential $v(\mathbf{r})$ is noted as the basis of the concept of a basic variable of quantum mechanics. A basic variable is thus defined as a gauge invariant property, knowledge of which determines the external scalar potential, hence the system Hamiltonian, and thereby the wave functions of the system. This is the HK path from the basic variable to the wave functions of Schrödinger theory, an alternate approach to electronic structure. Thus, the stationary state ground state density $\rho(\mathbf{r})$, and the time-dependent density $\rho(\mathbf{r}t)$ are basic variables. The electron number N plays a fundamental role in HK theory as its theorems are proved for fixed N. It is further proved that in the presence of a uniform magnetostatic field, the basic variables for spinless electrons are the nondegenerate ground state density $\rho(\mathbf{r})$ and the physical current density $\mathbf{j}(\mathbf{r})$ for fixed electron number N and canonical angular momentum $\mathbf{L}$. For electrons with spin, the basic variables are the same but for fixed electron number N canonical $\mathbf{L}$ and spin $\mathbf{S}$ angular momentum. These theorems of density functional theory are proved for $v(\mathbf{r})/v(\mathbf{r}t)$-representable and $\{v(\mathbf{r}), \mathbf{A}(\mathbf{r})\}$-representable densities. However, once a basic variable is so identified, it is then possible to extend the domain to N-representable densities and degenerate states via the Percus-Levy-Lieb constrained-search method. With the knowledge that the wave function is a functional of the basic variable or variables, one then employs this fact to write the corresponding Euler-Lagrange variational equations for these properties—the second theorem of the various density functional theories. The second theorem then justifies the mapping of the interacting electronic system to model systems of noninteracting fermions or bosons that possess the same basic variable properties. This then is the Kohn-Sham theory version of local effective potential theory, a description in terms of energy and action functionals of the density, and of their functional derivatives. Generalizations of these theorems obtained via density preserving unitary transformations then lead to further insights into the theorems. In particular, it is shown that the wave function must also be a functional of a gauge function. Only then will the wave function when expressed as a functional be gauge variant. A corollary to the theorem of bijectivity between the density and the external scalar potential of both Hohenberg-Kohn and Runge-Gross leads to a more fundamental understanding of the respective theorems.

(c) Quantal density functional theory (Q–DFT) then evolves from the above foundational understandings. Q–DFT is a local effective potential energy theory, i.e. one that maps the interacting electronic system to one of noninteracting fermions or bosons possessing the same basic variables. It is based on the 'Quantal Newtonian' second and first laws for both the interacting and model noninteracting systems. Hence, in contrast to Kohn-Sham theory, its description of the mapping is in terms of 'classical' fields and their quantal sources. For the mapping which ensures that the model system possesses *all* the same basic variables: $[\{\rho(\mathbf{r}t), \mathbf{j}(\mathbf{r}t)\}$ for the time-dependent case, and $\{\rho(\mathbf{r})\}$ and $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ for the stationary-state case without and with a magnetostatic field], the electron correlations that need be accounted for by the model system *in each case* are those due to the Pauli exclusion principle, Coulomb repulsion and Correlation-Kinetic effects. Within Q–DFT, the contribution of these correlations to the local effective potential of the model system and to the corresponding components of the total energy, are separately delineated and explicitly defined. (If, in the time-dependent case, the mapping to the model system were such as to only ensure that the density $\rho(\mathbf{r}t)$ were the same, as is the case in Runge-Gross theory, then Correlation-Current-Density effects would also have to be accounted for. Within Q–DFT, the contribution of this effect to both the potential and energy is also explicitly defined.) The framework of Q–DFT is general and the *same* for both the ground and excited states. There is, however, an important facet of time-independent Q–DFT that further generalizes local effective potential theory. Within Q–DFT, it is possible to map the interacting system of electrons in either a ground or excited stationary state to a model noninteracting fermion system in an *arbitrary* state with either a ground or excited state configuration. Hence, there exist an *infinite* number of local effective potentials that can generate, for example, the same density as that of the interacting system whether in a ground or excited state. The difference between the potentials is a consequence solely of Correlation-Kinetic effects. Stationary state Kohn-Sham theory is thus seen to be a special case of Q–DFT as the mapping within it from the interacting system can only be to a model system of noninteracting fermions with the same electronic configuration. As is the case in Schrödinger theory, the stationary-state version of Q–DFT constitutes a special case of the time-dependent theory. There are, however, two important points of distinction with Schrödinger theory: (*i*) In Schrödinger theory, the description of the electron correlations due to the antisymmetry of the wave function, or equivalently the Pauli exclusion principle, and those of Coulomb repulsion, are not separable. These correlations perforce are treated together in Schrödinger theory via the quantal source of the pair-correlation density or the pair function. The traditional quantum chemistry manner by which these correlations are separated is by performing a separate Hartree-Fock theory calculation. However, the density as obtained via Hartree-Fock theory differs from that of the fully-interacting electrons, and as such this method of separation is not physically rigorous. Within Q–DFT, the Pauli and Coulomb correlations are separable within the same framework. Further, each correlation component corresponds to the density of the interacting electrons. (*ii*) Within Schrödinger theory, it is not possible to determine the contribution of the electron correlations to the kinetic energy. One simply obtains the total kinetic energy. On the other hand, within Q–DFT, this Correlation-Kinetic contribution can be explicitly determined. Furthermore, the theory ensures that this property corresponds to the density of the interacting system. The Q–DFT description of the mapping in terms of 'classical' fields and quantal sources provides a rigorous physical interpretation to the mathematical framework of Kohn-Sham and Runge-Gross theory. In particular, the manner in which the various electron correlations contribute to the unknown 'exchange-correlation' action and energy functionals of the density, and of their functional derivatives, is explained. The Q–DFT mapping also explains the physics underlying the Local Density Approximation (LDA) of Dirac, Gaspar, and Kohn-Sham, and provides a physical understanding of Slater theory and the Optimized Potential Method. Further insights into the properties of the model noninteracting systems or local effective potential energy theory are also arrived at via Q–DFT. For example, it is shown that Pauli and Coulomb correlations do not contribute to the discontinuity in the local electron-interaction potential as the electron number passes through an integer. The discontinuity is solely a consequence of Correlation-Kinetic effects. Q–DFT, and the various physical insights and interpretations arrived at via the theory, are all explicated by examples.

It is evident from the remarks above that the description of both Schrödinger theory and of its local effective potential energy theory equivalent of Q–DFT in terms of 'classical' fields and quantal sources provides a deeper understanding of the electronic structure of matter. This new perspective is physical, and as such much new physics is gleaned from it. I hope that in reading the book you have enjoyed this different path taken, and the subsequent insights derived therefrom.

Curriculum Vitae

Viraht Sahni received his Bachelor of Technology (Honors) degree in Electrical Engineering from the Indian Institute of Technology, Bombay, India in 1965; his Master of Science in Electrical Engineering (1968) and his Doctor of Philosophy in Physics (1972) from the Polytechnic Institute of Brooklyn, New York, USA. He was a post-doctoral associate at Brooklyn College of the City University of New York (CUNY) from 1972–1974, when he joined Brooklyn College as an Assistant Professor and member of the doctoral faculty of the Graduate School of CUNY. He was a Visiting Research Physicist at the National (now the Kavli) Institute of Theoretical Physics, Santa Barbara, California in 1983. He is presently Professor of Physics at Brooklyn College and the Graduate Center of CUNY. He was appointed Broeklundian Professor of Physics at Brooklyn College from 2001–2011. His principal interests lie in the theoretical foundations of the electronic structure of matter. He has published two books on a newly developed theory of electronic structure: *Quantal Density Functional Theory*, Springer-Verlag, 2004 of which the present volume constitutes the 2nd edition, and *Quantal Density Functional Theory II: Approximation Methods and Applications*, Springer-Verlag, 2010.

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Appendix A
A Derivation of the 'Quantal Newtonian' Second Law

In this Appendix the pure state 'Quantal Newtonian' second law or differential virial theorem [1, 2] is derived.

The time-dependent (TD) Schrödinger equation is

$$\hat{H}(t)\Psi(\mathbf{X}t) \ = \ i\frac{\partial}{\partial t}\Psi(\mathbf{X}t), \tag{A.1}$$

where the Hamiltonian

$$\hat{H}(t) = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i=1}^{N}v(\mathbf{r}_i t) + \frac{1}{2}\sum_{i\neq j}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \tag{A.2}$$

$\mathbf{X} = \mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_\mathrm{N}, \mathbf{x} = \mathbf{r}\sigma$, and σ the spin coordinate. The quantal TD spinless single–particle $\gamma(\mathbf{r}_1\mathbf{r}_1' t)$ and two–particle $\Gamma(\mathbf{r}_1\mathbf{r}_2; \mathbf{r}_1'\mathbf{r}_2', t)$ density matrices are defined respectively as

$$\gamma\left(\mathbf{r}_1\mathbf{r}_1' t\right) \ = \ N\sum_{\sigma}\int \Psi^*\left(\mathbf{r}_1\sigma, \mathbf{X}^{N-1}, t\right)\Psi\left(\mathbf{r}_1'\sigma, \mathbf{X}^{N-1}, t\right)\ d\mathbf{X}^{N-1}, \tag{A.3}$$

$$\begin{aligned}\Gamma\left(\mathbf{r}_1\mathbf{r}_2; \mathbf{r}_1'\mathbf{r}_2', t\right) = \frac{N(N-1)}{2}\sum_{\sigma_1\sigma_2}\int & \Psi^*\left(\mathbf{r}_1\sigma_1\mathbf{r}_2\sigma_2, \mathbf{X}^{N-2}, t\right) \\ & \Psi\left(\mathbf{r}_1'\sigma_1, \mathbf{r}_2'\sigma_2, \mathbf{X}^{N-2}, t\right) d\mathbf{X}^{N-2},\end{aligned} \tag{A.4}$$

where $\mathbf{X}^{N-1} = \mathbf{x}_2, \mathbf{x}_3, \ldots, \mathbf{x}_N$ etc., $d\mathbf{X}^{N-1} = d\mathbf{x}_2, \ldots d\mathbf{x}_N$ etc., and $\int d\mathbf{x} = \sum_\sigma \int d\mathbf{r}$. The diagonal matrix element $\gamma(\mathbf{r}\mathbf{r}t)$ is the TD density $\rho(\mathbf{r}t)$, and the diagonal matrix element $\Gamma(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}', t) \equiv \Gamma(\mathbf{r}\mathbf{r}'t)$ is related to the TD pair–correlation density defined as $g(\mathbf{r}\mathbf{r}'t) = \langle\Psi(t)|\sum_{i\neq j}\delta(\mathbf{r}_i - \mathbf{r})\delta(\mathbf{r}_j - \mathbf{r}')|\Psi(t)\rangle/\rho(\mathbf{r}t)$ by $g(\mathbf{r}\mathbf{r}'t) = 2\Gamma(\mathbf{r}\mathbf{r}'t)/\rho(\mathbf{r}t)$. By writing the wave function as $\Psi(\mathbf{X}t) = \Psi^R(\mathbf{X}t) + i\Psi^I(\mathbf{X}t)$, where $\Psi^R(\mathbf{X}t)$ and $\Psi^I(\mathbf{X}t)$ are its real and imaginary parts, we have on substitution into (A.1)

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$$i\frac{\partial}{\partial t}\Psi^R(t)-\frac{\partial}{\partial t}\Psi^I(t)$$
$$=\left[-\frac{1}{2}\sum_i\nabla_i^2+\sum_i v(\mathbf{r}_i t)+\frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\right]\left(\Psi^R(t)+i\Psi^I(t)\right), \quad (A.5)$$

where the dependence of Ψ on the electronic coordinates $\mathbf{X}$ is implicit. Equating the real parts of (A.5) yields

$$\sum_i v(\mathbf{r}_i t)+\frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}+\frac{1}{\Psi^R(t)}\frac{\partial}{\partial t}\Psi^I(t)=\frac{1}{2\Psi^R(t)}\sum_i\nabla_i^2\Psi^R(t). \quad (A.6)$$

On differentiating (A.6) with respect to $r_{1\alpha}$, where $r_{1\alpha}$ is the α coordinate component of $\mathbf{r}_1$, and then multiplying both sides by $(\Psi^R(t))^2$ we obtain

$$\left\{\frac{\partial}{\partial r_{1\alpha}}\left[v(\mathbf{r}_1 t)+\sum_{j=2}^{N}\frac{1}{|\mathbf{r}_1-\mathbf{r}_j|}\right]\right\}\left(\Psi^R(t)\right)^2+\left(\Psi^R(t)\right)^2\frac{\partial}{\partial r_{1\alpha}}\left(\frac{1}{\Psi^R(t)}\frac{\partial}{\partial t}\Psi^I(t)\right)$$
$$=\frac{1}{2}\sum_{i\beta}\left\{\Psi^R(t)\frac{\partial^3\Psi^R(t)}{\partial r_{i\beta}\partial r_{i\beta}\partial r_{1\alpha}}-\frac{\partial\Psi^R(t)}{\partial r_{1\alpha}}\frac{\partial^2\Psi^R(t)}{\partial r_{i\beta}^2}\right\}. \quad (A.7)$$

Now since

$$\frac{1}{4}\frac{\partial^3(\Psi^R(t))^2}{\partial r_{i\beta}^2\partial r_{1\alpha}}=\frac{1}{2}\frac{\partial^2\Psi^R(t)}{\partial r_{i\beta}^2}\frac{\partial\Psi^R(t)}{\partial r_{1\alpha}}+\frac{\partial\Psi^R(t)}{\partial r_{i\beta}}\frac{\partial^2\Psi^R(t)}{\partial r_{i\beta}\partial r_{1\alpha}}$$
$$+\frac{1}{2}\Psi^R(t)\frac{\partial^3\psi^R(t)}{\partial r_{i\beta}^2\partial r_{1\alpha}}, \quad (A.8)$$

the right side of (A.7) is

$$\frac{1}{2}\sum_{i\beta}\left\{\Psi^R(t)\frac{\partial^3\Psi^R(t)}{\partial r_{i\beta}^2\partial r_{1\alpha}}-\frac{\partial^2\Psi^R(t)}{\partial r_{i\beta}^2}\frac{\partial\Psi^R(t)}{\partial r_{1\alpha}}\right\}$$
$$=\sum_{i\beta}\left\{\frac{1}{4}\frac{\partial^3(\Psi^R(t))^2}{\partial r_{i\beta}^2\partial r_{1\alpha}}-\frac{\partial}{\partial r_{i\beta}}\left(\frac{\partial\Psi^R(t)}{\partial r_{1\alpha}}\frac{\partial\Psi^R(t)}{\partial r_{i\beta}}\right)\right\}. \quad (A.9)$$

Thus (A.7) is

$$\left\{\frac{\partial}{\partial r_{1\alpha}}\left[v(\mathbf{r}_1 t)+\sum_{j=2}^{N}\frac{1}{|\mathbf{r}_1-\mathbf{r}_j|}\right]\right\}\left(\Psi^R(t)\right)^2+\left(\Psi^R(t)\right)^2\frac{\partial}{\partial r_{1\alpha}}\left(\frac{1}{\Psi^R(t)}\frac{\partial}{\partial t}\Psi^I(t)\right)$$
$$=\sum_{i\beta}\left\{\frac{1}{4}\frac{\partial^3(\Psi^R(t))^2}{\partial r_{i\beta}^2\partial r_{1\alpha}}-\frac{\partial}{\partial r_{i\beta}}\left(\frac{\partial\Psi^R(t)}{\partial r_{1\alpha}}\frac{\partial\Psi^R(t)}{\partial r_{i\beta}}\right)\right\}. \quad (A.10)$$

A similar derivation from the imaginary part of (A.5) leads to

$$\left\{\frac{\partial}{\partial r_{1\alpha}}\left[v(\mathbf{r}_1 t)+\sum_{j=2}^{N}\frac{1}{|\mathbf{r}_1-\mathbf{r}_j|}\right]\right\}\left(\Psi^I(t)\right)^2-\left(\Psi^I(t)\right)^2\frac{\partial}{\partial r_{1\alpha}}\left(\frac{1}{\Psi^I(t)}\frac{\partial}{\partial t}\Psi^R(t)\right)$$
$$=\sum_{i\beta}\left\{\frac{1}{4}\frac{\partial^3(\Psi^I(t))^2}{\partial r_{i\beta}^2\partial r_{1\alpha}}-\frac{\partial}{\partial r_{i\beta}}\left(\frac{\partial\Psi^I(t)}{\partial r_{1\alpha}}\frac{\partial\Psi^I(t)}{\partial r_{i\beta}}\right)\right\}. \tag{A.11}$$

Using the fact that

$$\left(\Psi^R(t)\right)^2\frac{\partial}{\partial r_{1\alpha}}\left(\frac{1}{\Psi^R(t)}\frac{\partial}{\partial t}\Psi^I(t)\right)-\left(\Psi^I(t)\right)^2\frac{\partial}{\partial r_{1\alpha}}\left(\frac{1}{\Psi^I(t)}\frac{\partial}{\partial t}\Psi^R(t)\right)$$
$$=\frac{\partial}{\partial t}\left[\Psi^R(t)\frac{\partial}{\partial r_{1\alpha}}\Psi^I(t)-\Psi^I(t)\frac{\partial}{\partial r_{1\alpha}}\Psi^R(t)\right], \tag{A.12}$$

we have on summing (A.10) and (A.11), and then operating by $N\sum_{\sigma_1}\int d\mathbf{X}^{N-1}$ on the resulting equation that

$$N\sum_{\sigma_1}\int d\mathbf{X}^{N-1}\left\{\frac{\partial}{\partial r_{1\alpha}}\left[v(\mathbf{r}_1 t)+\sum_{j=2}^{N}\frac{1}{|\mathbf{r}_1-\mathbf{r}_j|}\right]\right\}|\Psi(t)|^2$$
$$+N\sum_{\sigma_1}\int d\mathbf{X}^{N-1}\frac{\partial}{\partial t}\left\{\Psi^R(t)\frac{\partial}{\partial r_{1\alpha}}\Psi^I(t)-\Psi^I(t)\frac{\partial}{\partial r_{1\alpha}}\Psi^R(t)\right\}$$
$$=\frac{1}{4}N\sum_{\sigma_1}\int d\mathbf{X}^{N-1}\nabla_1^2\frac{\partial}{\partial r_{1\alpha}}|\Psi(t)|^2$$
$$-N\sum_{\sigma_1}\int d\mathbf{X}^{N-1}\frac{\partial}{\partial r_{1\beta}}\sum_{\beta}\left\{\left(\frac{\partial}{\partial r_{1\alpha}}\Psi^R(t)\right)\left(\frac{\partial}{\partial r_{1\beta}}\Psi^R(t)\right)\right.$$
$$\left.+\left(\frac{\partial}{\partial r_{1\alpha}}\Psi^I(t)\right)\left(\frac{\partial}{\partial r_{1\beta}}\Psi^I(t)\right)\right\}$$
$$+N\sum_{\sigma_1}\int d\mathbf{X}^{N-1}\sum_{j=2}^{N}\frac{\partial}{\partial r_{j\beta}}\left\{\frac{1}{4}\frac{\partial}{\partial r_{j\beta}}\frac{\partial}{\partial r_{1\alpha}}|\Psi(t)|^2\right.$$
$$\left.-\left(\frac{\partial}{\partial r_{1\alpha}}\Psi^R(t)\right)\left(\frac{\partial}{\partial r_{j\beta}}\Psi^R(t)\right)-\left(\frac{\partial}{\partial r_{1\alpha}}\Psi^I(t)\right)\left(\frac{\partial}{\partial r_{j\beta}}\Psi^I(t)\right)\right\}. \tag{A.13}$$

On substituting the complex form of the wave function into the expression for $\gamma(\mathbf{r}\mathbf{r}'t)$, the kinetic-energy-density tensor $t_{\alpha\beta}(\mathbf{r}t)$ of (2.53) may be written as

$$t_{\alpha\beta}(\mathbf{r}t) = \frac{1}{2}N\sum_{\sigma}\int d\mathbf{X}^{N-1}\left\{\frac{\partial}{\partial r_\alpha}\Psi^R(\mathbf{r}\sigma,\mathbf{X}^{N-1},t)\frac{\partial}{\partial r_\beta}\Psi^R\left(\mathbf{r}\sigma,\mathbf{X}^{N-1},t\right)\right.$$
$$\left.+\frac{\partial}{\partial r_\beta}\Psi^I(\mathbf{r}\sigma,\mathbf{X}^{N-1},t)\frac{\partial}{\partial r_\alpha}\Psi^I(\mathbf{r}\sigma,\mathbf{X}^{N-1},t)\right\}. \tag{A.14}$$

Employing the definition of $z_\alpha(\mathbf{r}t)$ of (2.52) and the expression for $t_{\alpha\beta}(\mathbf{r}t)$ of (A.14), (A.13) is then

$$N\sum_{\sigma_1}\int d\mathbf{X}^{N-1}\left\{\frac{\partial}{\partial r_{1\alpha}}\left[v(\mathbf{r}_1t)+\sum_{j=2}^{N}\frac{1}{|\mathbf{r}_1-\mathbf{r}_j|}\right]\right\}|\Psi(t)|^2$$
$$+\frac{N}{2}i\sum_{\sigma_1}\frac{\partial}{\partial t}\int d\mathbf{X}^{n-1}\left\{\Psi(t)\frac{\partial}{\partial r_{1\alpha}}\Psi^*(t)-\Psi^*(t)\frac{\partial}{\partial r_{1\alpha}}\Psi(t)\right\}$$
$$=-z_\alpha(\mathbf{r}_1t)+\frac{1}{4}N\sum_{\sigma_1}\int d\mathbf{X}^{N-1}\nabla_1^2\frac{\partial}{\partial r_{1\alpha}}|\Psi(t)|^2$$
$$+N\sum_{\sigma_1}\int d\mathbf{X}^{N-1}\sum_{j=2}^{N}\sum_{\beta}\frac{\partial}{\partial r_{j\beta}}\left\{\frac{1}{4}\frac{\partial}{\partial r_{j\beta}}\frac{\partial}{\partial r_{1\alpha}}|\Psi(t)|^2\right.$$
$$\left.-\left(\frac{\partial}{\partial r_{1\alpha}}\Psi^R(t)\right)\left(\frac{\partial}{\partial r_{j\beta}}\Psi^R(t)\right)-\left(\frac{\partial}{\partial r_{1\alpha}}\Psi^I(t)\right)\left(\frac{\partial}{\partial r_{j\beta}}\Psi^I(t)\right)\right\}, \tag{A.15}$$

where we have employed the relation

$$\Psi(t)\frac{\partial}{\partial r_{1\alpha}}\Psi^*(t)-\Psi^*(t)\frac{\partial}{\partial r_{1\alpha}}\Psi(t)$$
$$=2i\left\{\Psi^I(t)\frac{\partial}{\partial r_{1\alpha}}\Psi^R(t)-\Psi^R(t)\frac{\partial}{\partial r_{1\alpha}}\Psi^I(t)\right\}. \tag{A.16}$$

Since the wavefunction and its derivative vanish at infinity, the last term of (A.15) vanishes on integration over $dr_{j\beta}$. Consequently, (A.15) may be written in terms of the density $\rho(\mathbf{r}t)$, the diagonal matrix element $\Gamma(\mathbf{r}\mathbf{r}'t)$ of the two–particle density matrix, and the current density $\mathbf{j}(\mathbf{r}t)$ of (2.39) as

$$\rho(\mathbf{r}_1t)\frac{\partial}{\partial r_{1\alpha}}v(\mathbf{r}_1t)+2\int d\mathbf{r}_2\Gamma(\mathbf{r}_1\mathbf{r}_2t)\frac{\partial}{\partial r_{1\alpha}}\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}+\frac{\partial}{\partial t}j_\alpha(\mathbf{r}_1t)$$
$$=\frac{1}{4}\nabla^2\frac{\partial}{\partial r_{1\alpha}}\rho(\mathbf{r}_1t)-z_\alpha(\mathbf{r}_1t). \tag{A.17}$$

The 'Quantal Newtonian' second law corresponding to TD Schrödinger theory is then

$$\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}t)+\boldsymbol{\mathcal{F}}^{\text{int}}(\mathbf{r}t)=\boldsymbol{\mathcal{J}}(\mathbf{r}t), \tag{A.18}$$

where

$$\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}t) = -\nabla v(\mathbf{r}t), \tag{A.19}$$

$$\boldsymbol{\mathcal{F}}^{\text{int}}(\mathbf{r}t) = \boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}t) - \boldsymbol{\mathcal{D}}(\mathbf{r}t) - \boldsymbol{\mathcal{Z}}(\mathbf{r}t), \tag{A.20}$$

with the individual fields $\boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}t)$, $\boldsymbol{\mathcal{D}}(\mathbf{r}t)$, $\boldsymbol{\mathcal{Z}}(\mathbf{r}t)$, and $\boldsymbol{\mathcal{J}}(\mathbf{r}t)$ defined in Sect. 2.3.

The pure state ‘Quantal Newtonian’ first law or differential virial theorem for time-independent Schrödinger theory [3–5] in which the external field $\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}) = -\nabla v(\mathbf{r})$, is a special case of the time-dependent law with the time parameter t and current density field $\boldsymbol{\mathcal{J}}(\mathbf{r}t)$ absent. Furthermore, the law is valid for any nondegenerate or degenerate ground or any bound excited state of the time-independent equation. Thus, for the nth eigenstate $\Psi_{\text{n}}(\mathbf{X})$ of the time-independent Schrödinger equation

$$\hat{H}\Psi_{\text{n}}(\mathbf{X}) \;=\; E_{\text{n}}\Psi_{\text{n}}(\mathbf{X}), \tag{A.21}$$

we have the ‘Quantal Newtonian’ first law to be

$$\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}t) + \boldsymbol{\mathcal{F}}_{n}^{\text{int}}(\mathbf{r}t) = 0, \tag{A.22}$$

$$\boldsymbol{\mathcal{F}}_{n}^{\text{ext}}(\mathbf{r}t) = \boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}t) - \boldsymbol{\mathcal{D}}(\mathbf{r}t) - \boldsymbol{\mathcal{Z}}(\mathbf{r}t), \tag{A.23}$$

and where the fields $\boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r})$, $\boldsymbol{\mathcal{D}}(\mathbf{r})$, and $\boldsymbol{\mathcal{Z}}(\mathbf{r})$ are defined as in Sect. 2.3 but for the state $\Psi_{\text{n}}(\mathbf{X})$.

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Appendix B
Derivation of the Harmonic Potential Theorem

In this Appendix, we first prove the Harmonic Potential Theorem (HPT) [1] via the 'operator' method, and then derive [2] the HPT wave function by the Feynman Path–Integral method [3, 4].

B.1 Proof via 'Operator' Method

For the Hamiltonian defined by (2.121)–(2.123), the solution to the time–dependent Schrödinger equation when a shift $\mathbf{y}(t)$ is applied to the electronic coordinates $\mathbf{r}_i$ is written as

$$\Psi_{HPT}(t) = e^{-i(E_n t + NS(t) - N\frac{d\mathbf{y}}{dt}\cdot\mathbf{R})}$$
$$\Psi_n\left[\mathbf{r}_1 - \mathbf{y}(t), \mathbf{r}_2 - \mathbf{y}(t), \ldots, \mathbf{r}_N - \mathbf{y}(t)\right], \tag{B.1}$$

where

$$S(t) = \int_{t_0}^{t}\left[\frac{1}{2}\dot{\mathbf{y}}(t')^2 - \frac{1}{2}\mathbf{y}(t')\cdot\mathbf{K}\cdot\mathbf{y}(t')\right]dt', \tag{B.2}$$

and $\mathbf{R} = (1/N)\sum_i \mathbf{r}_i$. Defining the unitary translation operator $\hat{T}(\mathbf{y}(t))$ as

$$\hat{T}(\mathbf{y}(t)) = e^{-i\mathbf{y}(t)\cdot\sum_i \hat{\mathbf{p}}_i} \tag{B.3}$$

where $\hat{\mathbf{p}}_i = -i\nabla_{\mathbf{r}_i}$, we have

$$\hat{T}(\mathbf{y}(t))\Psi_n(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \Psi_n(\mathbf{r}_1 - \mathbf{y}(t), \mathbf{r}_2 - \mathbf{y}(t), \ldots, \mathbf{r}_N - \mathbf{y}(t)). \tag{B.4}$$

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Thus, with $\mathbf{P} = (1/N)\sum_i \hat{\mathbf{p}}_i$, the wavefunction$\Psi_{HPT}(t)$ may be written as

$$\Psi_{HPT}(t) = e^{-i(E_n t + NS(t) - N\dot{\mathbf{y}}\cdot\mathbf{R})} e^{-iN\mathbf{y}(t)\cdot\mathbf{P}} \Psi_n(\mathbf{r}_1, \ldots, \mathbf{r}_N), \tag{B.5}$$

so that

$$\begin{aligned} i\frac{\partial \Psi_{HPT}(t)}{\partial t} &= \left[E_n + N\dot{S}(t) - N\ddot{\mathbf{y}}(t)\cdot\mathbf{R}\right]\Psi_{HPT}(t) \\ &\quad + Ne^{-i(E_n t + NS(t) - N\dot{\mathbf{y}}(t)\cdot\mathbf{R})}\dot{\mathbf{y}}(t)\cdot\mathbf{P}\Psi_n, \end{aligned} \tag{B.6}$$

where

$$\dot{S}(t) = \frac{1}{2}\dot{\mathbf{y}}(t)^2 - \frac{1}{2}\mathbf{y}(t)\cdot\mathbf{K}\cdot\mathbf{y}(t). \tag{B.7}$$

We next determine

$$\hat{H}(t)\Psi_{HPT}(t) = (\hat{H}_0 - N\mathbf{F}(t)\cdot\mathbf{R})\Psi_{HPT}(t). \tag{B.8}$$

Defining the operators

$$\hat{A}(t) = iN\dot{\mathbf{y}}(t)\cdot\mathbf{R}, \tag{B.9}$$

$$\hat{B}(t) = -iN\mathbf{y}(t)\cdot\mathbf{P}, \tag{B.10}$$

and

$$C(t) = -i(E_n t + NS(t)), \tag{B.11}$$

we have

$$\begin{aligned} \hat{H}_0\Psi_{HPT}(t) &= H_0\, e^{C(t)}\, e^{\hat{A}(t)} e^{\hat{B}(t)}\, \Psi_n \\ &= E_n\Psi_{HPT}(t) + e^{C(t)}\left[\hat{H}_0,\ e^{\hat{A}(t)}\ e^{\hat{B}(t)}\right]\ \Psi_n. \end{aligned} \tag{B.12}$$

Now

$$\left[\hat{H}_0, e^{\hat{A}(t)} e^{\hat{B}(t)}\right] = \left[\hat{H}_0, e^{\hat{A}(t)}\right] e^{\hat{B}(t)} + e^{\hat{A}(t)}\left[\hat{H}_0, e^{\hat{B}(t)}\right], \tag{B.13}$$

$$\left[\hat{H}_0,\ e^{\hat{A}(t)}\right] = \left(\hat{H}_0 - e^{\hat{A}(t)}\hat{H}_0\ e^{-\hat{A}(t)}\right)\ e^{\hat{A}(t)}, \tag{B.14}$$

and

$$e^{\hat{A}(t)}\hat{H}_0 e^{-\hat{A}(t)} = \hat{H}_0 + \left[\hat{A}(t), \hat{H}_0\right] + \frac{1}{2!}\left[\hat{A}(t), [\hat{A}(t), \hat{H}_0]\right] + \ldots. \tag{B.15}$$

Next, we evaluate the various commutators:

$$\left[\hat{A}(t), \hat{H}_0\right] = -N\dot{\mathbf{y}} \cdot \mathbf{P}, \tag{B.16}$$

$$\left[\hat{A}(t), [\hat{A}(t), \hat{H}_0]\right] = N\dot{\mathbf{y}}(t)^2, \tag{B.17}$$

$$\left[\hat{B}(t), \hat{H}_0\right] = -N\mathbf{y}(t) \cdot \mathbf{KR}, \tag{B.18}$$

$$\left[\hat{B}(t), [\hat{B}(t), \hat{H}_0]\right] = N\mathbf{y}(t) \cdot \mathbf{K} \cdot \mathbf{y}(t), \tag{B.19}$$

$$\left[\hat{H}_0, e^{\hat{A}(t)}\right] = \left\{N\dot{\mathbf{y}}(t) \cdot \mathbf{P} - \frac{1}{2}N\dot{\mathbf{y}}(t)^2\right\} e^{\hat{A}(t)}, \tag{B.20}$$

$$\left[\hat{H}_0, e^{\hat{B}(t)}\right] = \left\{N\mathbf{y}(t) \cdot \mathbf{KR} - \frac{1}{2}N\mathbf{y}(t) \cdot \mathbf{K} \cdot \mathbf{y}(t)\right\} e^{\hat{B}(t)}. \tag{B.21}$$

Note that the higher order commutators in (B.15) vanish. Thus, employing the above commutators we have

$$\begin{aligned}\hat{H}_0\Psi_{HPT}(t) &= E_n\Psi_{HPT}(t) + Ne^{C(t)}e^{\hat{A}(t)}\dot{\mathbf{y}} \cdot \mathbf{P}\Psi_n \\ &\quad + N\left\{\frac{1}{2}\dot{\mathbf{y}}(t)^2 + \mathbf{y}(t) \cdot \mathbf{KR} - \frac{1}{2}\mathbf{y}(t) \cdot \mathbf{K} \cdot \mathbf{y}(t)\right\}\Psi_{HPT},\end{aligned} \tag{B.22}$$

and

$$\begin{aligned}i\frac{\partial\Psi_{HPT}(t)}{\partial t} &= E_n\Psi_{HPT} + N\left\{\frac{1}{2}\dot{\mathbf{y}}(t)^2 - \frac{1}{2}\mathbf{y}(t) \cdot \mathbf{K} \cdot \mathbf{y}(t) - \ddot{\mathbf{y}}(t) \cdot \mathbf{R}\right\}\Psi_{HPT} \\ &\quad + Ne^{C(t)}e^{\hat{A}(t)}\dot{\mathbf{y}}(t) \cdot \mathbf{P}\Psi_n,\end{aligned} \tag{B.23}$$

so that

$$\left(\hat{H}(t) - i\frac{\partial}{\partial t}\right)\Psi_{HPT}(t) = \left[\ddot{\mathbf{y}}(t) + \mathbf{K} \cdot \mathbf{y}(t) - \mathbf{F}(t)\right] \cdot \left[\sum_i \mathbf{r}_i\right]\Psi_{HPT}(t), \tag{B.24}$$

which proves the theorem.

B.2 Derivation of Wave Function via Feynman Path-Integral Method

Consider a system of N particles with arbitrary interaction $u(\mathbf{r}_i - \mathbf{r}_j)$ in an external harmonic potential $v(\mathbf{r}) = \frac{1}{2}\mathbf{r} \cdot \mathbf{K} \cdot \mathbf{r}$, with $\mathbf{K}$ the spring constant matrix. The time-independent Schrödinger equation for this system is

$$\hat{H}_0 \Psi_n = E_n^0 \Psi_n, \tag{B.25}$$

where the Hamiltonian $\hat{H}_0$ is

$$\hat{H}_0 = \frac{1}{2m} \sum_i p_i^2 + \frac{1}{2} \sum_i \mathbf{r}_i \cdot \mathbf{K} \cdot \mathbf{r}_i + \sum_{i \neq j} u(\mathbf{r}_i - \mathbf{r}_j), \tag{B.26}$$

and where $\Psi_n(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ and E_n^0 are the n-th eigenstate and eigen energy, respectively. We choose the coordinate system where $\mathbf{K}$ is diagonal: $\mathbf{K} = \mathrm{diag}(k_x, k_y, k_z)$, so that

$$\frac{1}{2} \mathbf{r}_i \cdot \mathbf{K} \cdot \mathbf{r}_i = \frac{1}{2} m (\omega_x^2 x_i^2 + \omega_y^2 y_i^2 + \omega_z^2 z_i^2) \tag{B.27}$$

with $k_x = m\omega_x^2$ etc. A spatially homogenous time-dependent field $\mathbf{E} = -\mathbf{f}(t)/e$ is turned on at $t = 0$. (Assume $\mathbf{f}(t) = 0, t \leq 0$). The corresponding time-dependent Schrödinger equation and Hamiltonian $\hat{H}$ are, respectively,

$$\hat{H}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, t) \Psi_{HPT}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, t) = i\hbar\, \partial \Psi_{HPT}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, t)/\partial t, \tag{B.28}$$

and

$$\hat{H}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, t) = \hat{H}_0 - \mathbf{f}(t) \cdot \sum_j \mathbf{r}_j. \tag{B.29}$$

We next derive that Ψ_{HPT} is

$$\Psi_{HPT}(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N, t) = \exp[-\frac{i}{\hbar}(E_n^0 t + S_0(t) - Nm \frac{d\mathbf{y}}{dt} \cdot \mathbf{R})] \Psi_n(\bar{\mathbf{r}}_1, \bar{\mathbf{r}}_2, \ldots \bar{\mathbf{r}}_N). \tag{B.30}$$

where $\bar{\boldsymbol{r}}_i$ is the shifted coordinate operator, $\mathbf{R}$ the center of mass operator:

$$\bar{\mathbf{r}}_i = \mathbf{r}_i - \mathbf{y}(t), \qquad \mathbf{R} = \frac{1}{N} \sum_i \mathbf{r}_i, \tag{B.31}$$

with $S_0(t)$ the phase angle

$$S_0(t) = N \int_0^t \left[\frac{m}{2} \dot{\mathbf{y}}(t')^2 - \frac{1}{2} \mathbf{y}(t') \cdot \mathbf{K} \cdot \mathbf{y}(t') \right] dt'. \tag{B.32}$$

and where the translation $\mathbf{y}(t)$ satisfies the classical driven harmonic oscillator equation

$$m \ddot{\mathbf{y}}(t) + \mathbf{K} \cdot \mathbf{y}(t) = \mathbf{f}(t). \tag{B.33}$$

Define the center of mass and relative coordinates, and momentum as [2]

$$\mathbf{R}^{(1)} = \mathbf{R} = \frac{1}{N}\sum_i \mathbf{r}_i, \qquad \hat{\mathbf{P}}^{(1)} = \sum_i \hat{\mathbf{p}}_i \tag{B.34}$$

and

$$\begin{aligned} X^{(2)} &= x_1 - x_2, \\ X^{(3)} &= x_1 + x_2 - 2x_3, ..., \\ X^{(N)} &= x_1 + x_2 + ... + x_{N-1} - (N-1)x_N, \end{aligned} \tag{B.35}$$

and similarly for $Y^{(2)}, ...Y^{(N)}$, $Z^{(2)}, ...Z^{(N)}$, and $P^{(2)}, ...P^{(N)}$. The Hamiltonian of (B.29) can be rewritten as

$$\hat{H} = \hat{H}_{CM} + \hat{H}_{rel}, \tag{B.36}$$

where

$$\hat{H}_{CM} = \frac{\hat{\mathbf{P}}^2}{2M} + \frac{M}{2}(\omega_x^2 X^2 + \omega_y^2 Y^2 + \omega_z^2 Z^2) - \mathbf{F}(t)\cdot\mathbf{R}, \tag{B.37}$$

with $M = Nm, \mathbf{F}(t) = N\mathbf{f}(t)$. Here, $\hat{H}_{CM}$ is the Hamiltonian describing the motion of the center of mass only. $\hat{H}_{rel}$ is a function of only the relative coordinates and contains the effects of interaction. For the two-particle system, a closed form analytical expression for $\hat{H}_{rel}$ can be written (see Sect. 2.11). For the general case of N particles, the expression for $\hat{H}_{rel}$ is complicated [2]. However, it can be readily shown that $[\hat{H}_{CM}, \hat{H}_{rel}] = 0$. Thus the center-of-mass and the relative motions are separable. Therefore, the eigenstate of the Hamiltonian is the product of the eigenstates of the center-of-mass and the relative motions:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_N, t) = \Phi(\mathbf{R}, t)\varphi_{rel}(\mathbf{R}^{(2)}, ..., \mathbf{R}^{(N)}). \tag{B.38}$$

The relative motion wave function $\varphi_{rel}(\mathbf{R}^{(2)}, ..., \mathbf{R}^{(N)})$ satisfies

$$\hat{H}_{rel}\varphi_{rel}(\mathbf{R}^{(2)}, ..., \mathbf{R}^{(N)}) = E^0_{rel}\varphi_{rel}(\mathbf{R}^{(2)}, ..., \mathbf{R}^{(N)}), \tag{B.39}$$

where E^0_{rel} is the corresponding eigenvalue. For simplicity, we set $E^0_{rel} = 0$.

It is evident that the external driving force $\mathbf{f}(t)$ does not affect the relative motion, and that it is only the center-of-mass motion which is time-dependent. Thus, we focus our attention on the center-of-mass motion wave function $\Phi(\mathbf{R}, t)$, which satisfies the Schödinger equation

$$i\hbar\frac{\partial\Phi(\mathbf{R}, t)}{\partial t} = (\hat{H}_{CM} + E^0_{rel})\Phi(\mathbf{R}, t) = \hat{H}_{CM}\Phi(\mathbf{R}, t), \tag{B.40}$$

with the initial condition

$$\Phi(\mathbf{R}, 0) = \Phi_n^0(\mathbf{R}) = N H_n(\alpha_x X) H_n(\alpha_y Y) H_n(\alpha_z Z) \exp\left[-\frac{1}{2}(\alpha_x^2 X^2 + \alpha_y^2 Y^2 + \alpha_z^2 Z^2)\right], \tag{B.41}$$

being the n-th state of a three dimensional harmonic oscillator with H_n the corresponding Hermite polynomial, and where $\alpha_i = \left(\frac{M\omega_i}{\hbar}\right)^{\frac{1}{2}}, i = x, y, z$, and N the normalization constant.

It is evident that $\hat{H}_{CM}$ describes a driven oscillator. For convenience, we first consider a driven oscillator in one dimension, with mass M, frequency ω, and external force $F(t)$, the equation-of-motion for which is

$$M\frac{d^2X}{dt^2} + M\omega^2 X(t) - F(t) = 0. \tag{B.42}$$

Employing the path-integral formulation of Feynman, we have

$$\Phi(X, t) = \int_{-\infty}^{+\infty} K(X, t; X_0, 0)\Phi(X_0, 0) dX_0, \tag{B.43}$$

where the initial state

$$\Phi(X_0, 0) = \Phi_n^0(X_0) = N_0 H_n(\alpha_0 X_0) \exp\left\{-\frac{1}{2}\alpha_0^2 X_0^2\right\}, \tag{B.44}$$

with $\alpha_0 = \left(\frac{M\omega}{\hbar}\right)^{\frac{1}{2}}$, $N_0 = \left(\sqrt{\frac{\alpha_0}{\pi}}\frac{1}{2^n n!}\right)^{\frac{1}{2}}$ the normalization constant. The corresponding eigenvalue is $E_{\mathbf{R}}^0 = E_n^0 = \left(n + \frac{1}{2}\right)\hbar\omega$. The propagator for a driven oscillator [5, 6] is,

$$K(X, t; X_0, 0) = \int \exp\left\{\frac{i}{\hbar}S[X(t)]\right\} D[X(t)], \tag{B.45}$$

where

$$S[X(t)] = \int_0^t L(X, \dot{X}, t')dt', \tag{B.46}$$

the classical action functional, and

$$L(X, \dot{X}, t) = \frac{\dot{X}^2}{2M} - \frac{M\omega^2}{2}X^2 + F(t)X, \tag{B.47}$$

the Lagrangian. The propagator can be evaluated analytically,

$$K(X, T; X_0, 0) = \sqrt{\frac{M\omega}{2\pi i\hbar \sin(\omega T)}} \exp\left\{\frac{i}{\hbar} S\right\}, \tag{B.48}$$

where

$$\begin{aligned} S(x_b, t_b; x_a, t_a) &= \frac{M\omega}{2\sin(\omega T)}\left[(x_b^2 + x_a^2)\cos(\omega T) - 2x_a x_b\right] \\ &+ \frac{x_b}{\sin(\omega T)} \int_{t_a}^{t_b} F(t)\sin[\omega(t - t_a)] \\ &+ \frac{x_a}{\sin(\omega T)} \int_{t_a}^{t_b} F(t)\sin[\omega(t_b - t)] \\ &- \frac{1}{M\omega\sin(\omega T)} \int_{t_a}^{t_b}\int_{t_a}^{t} F(t)F(\tau) \\ &\times \sin[\omega(t_b - t)]\sin(\omega(\tau - t_a))]d\tau dt. \end{aligned} \tag{B.49}$$

is the general expression for the action, with $T = t_b - t_a$, $X(t_b) = x_b$, $X(t_a) = x_a$. Notice that here we have set $t_a = 0$, $x_a = 0$. Inserting (B.48) into (B.43), we obtain

$$\begin{aligned} \Phi(X, T) = N_0 &\sqrt{\frac{M\omega}{2\pi i\hbar\sin(\omega T)}} \exp\{\frac{iM}{2\hbar}(c_0 X^2 + 2c_3 X - c_5)\} \\ \times &\int_{-\infty}^{+\infty} \exp\{\frac{iM}{2\hbar}[(c_1 - \frac{\hbar\alpha_0^2}{iM})X_0^2 + 2(c_2 X + c_4)X_0]\} \\ &H_n(\alpha_0 X_0)dX_0, \end{aligned} \tag{B.50}$$

where the coefficients

$$\begin{aligned} &c_0 = c_1 = \omega\cot(\omega T), \qquad c_2 = -\frac{\omega}{\sin(\omega T)}, \qquad c_3 = \frac{\int_0^T F(t)\sin(\omega t)dt}{M\sin(\omega T)}, \\ &c_4 = \frac{\int_0^T F(\tau)\sin[\omega(T - \tau)]d\tau}{M\sin(\omega T)}, \\ &c_5 = \frac{2}{M^2\omega\sin(\omega T)} \int_0^T\int_0^t F(t)F(s)\sin[\omega(t_b - t)]\sin(\omega s)ds dt. \end{aligned} \tag{B.51}$$

Employing the following identity [7]

$$\int_{-\infty}^{+\infty} \exp\{-(x - y)^2\}H_n(ax)dx = \sqrt{\pi}(1 - a^2)^{\frac{n}{2}} H_n\left[ay(1 - a^2)^{-\frac{1}{2}}\right], \tag{B.52}$$

one arrives at

$$\begin{aligned}\Phi(X,T) &= N_0 \exp\left\{\frac{iM}{2\hbar}(c_0X^2+2c_3X-c_5)\right\}\exp\left\{-\frac{\alpha_0^2}{2}(X-y_0(T)^2\right\}\\ &\times H_n[\alpha_0(X-y_0(T))]\\ &\times \exp\left[-i\left(n+\frac{1}{2}\right)\omega T - i\frac{\alpha_0^2}{2}\cot(\omega T)(X-y_0(T))^2\right]\\ &= \exp\left\{-i\frac{E_n^0}{\hbar}T - \frac{i}{2\hbar}\left[Mc_5 + M\omega\cot(wT)y_0(T)^2\right]\right.\\ &\left. + i\frac{M}{\hbar}\dot{y}_0(T)\cdot X\right\}\Phi(X-y_0(T),0),\end{aligned} \tag{B.53}$$

where

$$y_0(T) = \frac{\int_0^T F(t)\sin[\omega(T-t)]dt}{M\omega}, \tag{B.54}$$

which satisfies the classical equation of motion (B.42), with the initial condition $y_0(0)=\dot{y}(0)=0$. Inserting (B.53) into (B.38), we see that the wave function is the shifted initial wave function times a phase factor.

All that remains to prove the HPT is to show the phase factor obtained above is the same as that of Ψ_{HPT} with the shift $y_0(t)$, i.e.

$$\exp\left\{-\frac{i}{2\hbar}\left[Mc_5 + M\omega\cot(wT)y_0(T)^2\right]\right\} = \exp\left\{-\frac{i}{\hbar}S_0[y_0(t)]\right\}, \tag{B.55}$$

where

$$S_0[y_0(t)] = \int_0^T \left[\frac{M}{2}\dot{y}_0^2(t) - \frac{M\omega}{2}y_0^2(t)\right]dt. \tag{B.56}$$

For a general path $y(t)$ which satisfies the classical equation of motion (B.42) with the conditions $y(t_a)=y_a$, $y(t_b)=y_b$, we have

$$\begin{aligned}y(t) &= y_a\cos[\omega(t-t_a)] + \int_{t_a}^t \frac{F(\tau)}{M\omega}\sin[\omega(t-\tau)]d\tau + \\ &\left[\frac{y_b - y_a\cos[\omega(t_b-t_a)] - \int_{t_a}^{t_b}\frac{F(\tau)}{M\omega}\sin[\omega(t_b-\tau)]d\tau}{\sin[\omega(t_b-t_a)]}\right]\\ &\times\sin[\omega(t-t_a)].\end{aligned} \tag{B.57}$$

Notice that

$$\begin{aligned} S_0[y(t)] &= \int_{t_a}^{t_b} [\frac{M}{2}\dot{y}^2(t) - \frac{M\omega}{2} y^2(t)]dt \\ &= \frac{M}{2} y(t)\dot{y}(t)|_{t_a}^{t_b} - \int_{t_a}^{t_b} \frac{1}{2} y(t)F(t)dt. \end{aligned} \tag{B.58}$$

Substituting (B.57) into the two terms on the right hand side of (B.58), we obtain

$$\begin{aligned} \frac{M}{2} y(t)\dot{y}(t)|_{t_a}^{t_b} = \frac{M\omega}{2\sin(\omega T)} \Bigg\{ &(y_a^2 + y_b^2)\cos(\omega T) - 2y_a y_b \\ &+ y_b \int_{t_a}^{t_b} \frac{F(t)}{M\omega} \sin[\omega(t - t_a)]dt \\ &+ y_a \int_{t_a}^{t_b} \frac{F(t)}{M\omega} \sin[\omega(t_b - t)]dt \Bigg\}, \end{aligned} \tag{B.59}$$

and

$$\begin{aligned} \int_{t_a}^{t_b} \frac{1}{2} y(t)F(t)dt = \frac{M\omega}{2\sin(\omega T)} \Bigg\{ &y_b \int_{t_a}^{t_b} \frac{F(t)}{M\omega} \sin[\omega(t - t_a)]dt \\ &+ y_a \int_{t_a}^{t_b} \frac{F(t)}{M\omega} \sin[\omega(t_b - t)]dt \\ &- 2\int_{t_a}^{t_b} d\tau \int_{t_a}^{\tau} dt \frac{F(\tau)}{M\omega}\frac{F(t)}{M\omega} \\ &\times \sin[\omega(t_b - \tau)]\sin[\omega(t - t_a)] \Bigg\}. \end{aligned} \tag{B.60}$$

From (B.58), (B.59) and (B.60), we obtain

$$\begin{aligned} S_0[y(t)] = \frac{M\omega}{2\sin(\omega T)} \Bigg\{ &(y_a^2 + y_b^2)\cos(\omega T) - 2y_a y_b \\ &+ 2\int_{t_a}^{t_b} d\tau \int_{t_a}^{\tau} dt \frac{F(\tau)}{M\omega}\frac{F(t)}{M\omega} \sin[\omega(t_b - \tau)]\sin[\omega(t - t_a)] \Bigg\}. \end{aligned} \tag{B.61}$$

Notice that $y_0(t_a) = y_0(0) = 0$. Thus, we see that (B.55) is correct.

Inserting (B.55) into (B.53), we have

$$\begin{aligned} \Phi(X, T) = \exp &\left\{ -i\frac{E_n^0}{\hbar} T - \frac{i}{\hbar} S_0[y_0(t)] + i\frac{M}{\hbar}\dot{y}_0(T) \cdot X \right\} \\ &\times \Phi_n^0(X - y_0(T)). \end{aligned} \tag{B.62}$$

The three dimensional generalization of the above equation is

$$\Phi(\mathbf{R}, T) = \exp\left\{-i\frac{E_n^0}{\hbar}T - \frac{i}{\hbar}S_0[\mathbf{y}_0(t)] + i\frac{M}{\hbar}\dot{\mathbf{y}}_0(T)\cdot\mathbf{R}\right\}$$
$$\times\ \Phi_n^0(\mathbf{R} - \mathbf{y}_0(T)), \tag{B.63}$$

where $\mathbf{y}_0(t)$ is the classical path satisfying the three dimension equation of motion

$$M\frac{d^2\mathbf{R}}{dt^2} + N\mathbf{K}\cdot\mathbf{R}(t) - \mathbf{F}(t) = 0, \tag{B.64}$$

with initial conditions $\mathbf{y}_0(0) = \dot{\mathbf{y}}(0) = 0$. Inserting (B.63) into (B.38), we obtain the wave function

$$\begin{aligned}\Psi(\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_N, t) &= \exp\left\{-i\frac{E_n^0}{\hbar}t - \frac{i}{\hbar}S_0[\mathbf{y}_0(t)] + i\frac{M}{\hbar}\dot{\mathbf{y}}_0(t)\cdot\mathbf{R}\right\}\\ &\quad\times\ \Phi_n^0(\mathbf{R} - \mathbf{y}_0(t))\varphi_{rel}(\mathbf{R}^{(2)}, ..., \mathbf{R}^{(N)})\\ &= \exp\left\{-i\frac{E_n^0}{\hbar}t - \frac{i}{\hbar}S_0[\mathbf{y}_0(t)] + i\frac{M}{\hbar}\dot{\mathbf{y}}_0(t)\cdot\mathbf{R}\right\}\\ &\quad\times\ \Psi_n(\bar{\mathbf{r}}_1, \bar{\mathbf{r}}_2, ...\bar{\mathbf{r}}_N).\end{aligned} \tag{B.65}$$

As (B.64) is exactly the same as (B.33), we see that the wave function of (B.65) is the same as $\Psi_{HPT}(\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_N, t)$ of (B.30). This then is the derivation of the HPT wave function from first principles.

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Appendix C
Analytical Expressions for the Properties of the Ground and First Excited Singlet States of the Hooke's Atom

In this appendix we give the properties [1, 2] of the ground and first excited singlet states of the Hooke's atom, and of the corresponding S systems in their ground (singlet) state. In other words, the expressions of the latter correspond to the mapping via Q–DFT of the interacting system in the ground and excited state to one of noninteracting fermions in its *ground* state.

C.1 Ground State ($k = 1/4$)

Wavefunction normalization constant $\mathrm{C} = 1/[2\pi^{5/4}(5\sqrt{\pi}+8)^{1/2}] = 0.029112\,\mathrm{a.u.}$

Electron Density $\rho(\mathbf{r})$

$$\rho_{00}(r) = \frac{\pi\sqrt{2\pi}C^2}{r} e^{-r^2/2}\Big\{7r + r^3 + (8/\sqrt{2\pi})re^{-r^2/2} + 4(1+r^2)\mathrm{erf}(r/\sqrt{2})\Big\}, \tag{C.1}$$

where

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-y^2}dy \tag{C.2}$$

is the error function [3].

$$\rho(r) \underset{r\to\infty}{\sim} \sqrt{2\pi}\ \pi\ C^2 r^2\left(1+\frac{4}{r}\right)e^{-r^2/2}. \tag{C.3}$$

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Pair-Correlation Density $g(\mathbf{rr}')$

$$g(\mathbf{rr}') = \frac{C^2}{2\rho(r)} e^{-(r^2+r'^2)/2}(2 + |\mathbf{r} - \mathbf{r}'|)^2. \tag{C.4}$$

Single–Particle Density Matrix $\gamma(\mathbf{r}'\mathbf{r}'')$

$$\gamma(\mathbf{r}'\mathbf{r}'') = 2C^2 e^{-(r'^2+r''^2)/4} \int \left(1 + \frac{|\mathbf{r}' - \mathbf{r}|}{2}\right) \times \left(1 + \frac{|\mathbf{r}'' - \mathbf{r}|}{2}\right) e^{-r^2/2} d\mathbf{r}. \tag{C.5}$$

Dirac Density Matrix $\gamma_s(\mathbf{r}'\mathbf{r}'')$

$$\gamma_s(\mathbf{r}'\mathbf{r}'') = \sqrt{\rho(\mathbf{r}')\rho(\mathbf{r}'')}. \tag{C.6}$$

Kinetic–Energy–Density Tensor $t_{\alpha\beta}(\mathbf{r}; [\gamma])$

$$t_{\alpha\beta}(\mathbf{r}; [\gamma]) = \frac{r_\alpha r_\beta}{r^2} f(r) + \delta_{\alpha\beta} k(r), \tag{C.7}$$

where

$$f(r) = \frac{1}{8}\Bigg(r^2\rho(r) - \frac{4\pi C^2}{r^3} e^{-r^2/2}\Big[\sqrt{2\pi} r^5 - 2\sqrt{2\pi} r^2 \left(1 - r^2\right) \operatorname{erf}\left(r/\sqrt{2}\right) + 4r^3 e^{-r^2/2} - 6\sqrt{\pi}\operatorname{daw}\left(r/\sqrt{2}\right) - \sqrt{2\pi} r (r^2 - 3)\Big]\Bigg), \tag{C.8}$$

$$k(r) = \frac{\left(\sqrt{2\pi}\right)^3 C^2}{4r^3}\left[r - \sqrt{2}\operatorname{daw}\left(r/\sqrt{2}\right)\right] e^{-r^2/2}, \tag{C.9}$$

and

$$\operatorname{daw}(x) = e^{-x^2} \int_0^x e^{t^2} dt \tag{C.10}$$

is Dawson's integral [3].

Kinetic–Energy–Density Tensor $t_{s,\alpha\beta}(r; [\gamma_s])$

$$t_{s,\alpha\beta}(r; [\gamma_s]) = \frac{r_\alpha r_\beta}{r^2} h(r), \tag{C.11}$$

where

$$h(r) = \frac{1}{8\rho}\left(\frac{\partial\rho}{\partial r}\right)^2. \tag{C.12}$$

Electron–Interaction Field $\mathcal{E}_{\mathrm{ee}}(r)$

$$\begin{aligned}\mathcal{E}_{\mathrm{ee}}(r) = \frac{1}{r^2}\frac{C^2\left(\sqrt{2\pi}\right)^3}{2\rho(r)}e^{-r^2/2}\Big\{&(r^2+3)\mathrm{erf}\left(r/\sqrt{2}\right)\\ &-3\sqrt{2/\pi}\,re^{-r^2/2} - 4\sqrt{2}\,\mathrm{daw}\,\left(r/\sqrt{2}\right) + 4r\Big\}.\end{aligned} \tag{C.13}$$

Hartree Field $\mathcal{E}_{\mathrm{H}}(r)$

$$\begin{aligned}\mathcal{E}_{\mathrm{H}}(r) = \frac{1}{r^2}(2\pi C)^2\Big\{&10\pi\,\mathrm{erf}\left(r/\sqrt{2}\right)\\ &-4\sqrt{2\pi}\left(3+r^2\right)e^{-r^2/2}\,\mathrm{erf}\left(r/\sqrt{2}\right) + 16\sqrt{\pi}\,\mathrm{erf}(r)\\ &-8re^{-r^2} - \sqrt{2\pi}\left(10r+r^3\right)e^{-r^2/2}\Big\}.\end{aligned} \tag{C.14}$$

Kinetic 'Force' $z(r;[\gamma])$

$$\begin{aligned}\mathbf{z}(r;[\gamma]) = \frac{\pi\ C^2}{4r^2}e^{-r^2/2}\Big\{&\sqrt{2\pi}r(-r^6+3r^4+8r^2+16)\\ &-4\sqrt{2\pi}(r^6-6r^4+5r^2-2)\mathrm{erf}(r/\sqrt{2})\\ &-8r(r^4-7r^2+2)e^{-r^2/2}\\ &-32\sqrt{\pi}\,\mathrm{daw}(r/\sqrt{2})\Big\}.\end{aligned} \tag{C.15}$$

$$\begin{aligned}\mathbf{z}(r)_{\widetilde{r\to\infty}} - \frac{\sqrt{2\pi}\pi C^2}{4}\Big(&r^5+4r^4-3r^3-24r^2\\ &-8r+20-\frac{16}{r}-\frac{8}{r^2}+\cdots\Big)e^{-r^2/2}.\end{aligned} \tag{C.16}$$

Kinetic 'Force' $z_s(r;[\gamma_s])$

$$\mathbf{z}_s(r;[\gamma_s]) = \frac{1}{2\rho}\left(\frac{\partial\rho}{\partial r}\right)\left[\frac{1}{r}\left(\frac{\partial\rho}{\partial r}\right) - \frac{1}{2\rho}\left(\frac{\partial\rho}{\partial r}\right)^2 + \frac{\partial^2\rho}{\partial r^2}\right]. \tag{C.17}$$

$$\begin{aligned}\mathbf{z}_s(r)_{\widetilde{r\to\infty}} - \frac{\sqrt{2\pi}\pi\ C^2}{4}\Big(&r^5+4r^4-3r^3-24r^2\\ &-8r+20-\frac{20}{r}+\frac{8}{r^2}+\cdots\Big)e^{-r^2/2}.\end{aligned} \tag{C.18}$$

Electron–Interaction Energy E_{ee}

$$E_{\text{ee}} = (4\pi C)^2 \left[\pi/2 + \sqrt{\pi}\right] = 0.447443\,\text{a.u.} \tag{C.19}$$

Hartree or Coulomb Self–Energy E_{H}

$$\begin{aligned} E_{\text{H}} =& 4(2\pi C)^4 \left\{ \frac{20}{3}\pi^2 + \frac{507}{32}\pi^{3/2} + 9\sqrt{3}\pi + 4\sqrt{2\pi} \right. \\ & \left. + \sqrt{\pi}\left(23 \arcsin\frac{7}{9} - 32 \arcsin\frac{1}{3}\right)\right\} = 1.030250\,\text{a.u.} \end{aligned} \tag{C.20}$$

External Energy E_{ext}

$$E_{\text{ext}} = \int \rho(r)\frac{1}{2}kr^2 dr = 2(\pi C)^2[9\pi + 14\sqrt{\pi}] = 0.888141\,\text{a.u.} \tag{C.21}$$

Kinetic Energy $T[\rho]$

$$T[\rho] = \pi^2 C^2[14\pi + 20\sqrt{\pi}] = 0.664418\,\text{a.u.} \tag{C.22}$$

Electron–Interaction Potential Energy $W_{\text{ee}}(r)$

$$\begin{aligned} W_{\text{ee}}(r) = -C^2(\sqrt{2\pi})^3 \int_{\infty}^{r} \frac{1}{2r'^2\rho(r')} e^{-r'^2/2} \Big\{ & (r'^2 + 3)\text{erf}(r'/\sqrt{2}) \\ & -3\sqrt{2/\pi}\,r' e^{-r'^2/2} - 4\sqrt{2}\,\text{daw}(r'/\sqrt{2}) + 4r' \Big\}\, dr'. \end{aligned} \tag{C.23}$$

$$W_{\text{ee}}(0) = 0.65959\,\text{a.u.} \tag{C.24}$$

Hartree Potential Energy $W_{\text{H}}(r)$

$$\begin{aligned} W_{\text{H}}(r) = \frac{(2\pi C)^2\sqrt{2\pi}}{r} \Big\{ & 5\sqrt{2\pi}\,\text{erf}\left(r/\sqrt{2}\right) \\ & - 12e^{-r^2/2}\,\text{erf}\left(r/\sqrt{2}\right) + 8\sqrt{2}\,\text{erf}(r) \\ & + 2\sqrt{2\pi}\,r\left(1 - \text{erf}^2\left(r/\sqrt{2}\right)\right) - re^{-r^2/2} \Big\}. \end{aligned} \tag{C.25}$$

$$W_{\text{H}}(0) = (2\pi C)^2 \left[9\sqrt{2\pi} + 4\pi + 8\right] = 1.442941\,\text{a.u.} \tag{C.26}$$

Slater Electron–Interaction Function $v_{\text{ee}}^{S}(r)$

$$v_{\text{ee}}^{S}(r) = \int \frac{g(\mathbf{r}\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' = \frac{\pi C^2}{r\rho(r)}e^{-r^2/2}\Bigg\{4\sqrt{2\pi}r + 2re^{-r^2/2} + \sqrt{2\pi}\left(5+r^2\right)\operatorname{erf}\left(r/\sqrt{2}\right)\Bigg\}. \tag{C.27}$$

$$v_{\text{ee}}^{S}(0) = \frac{4\left(\sqrt{2\pi}+3\right)}{7\sqrt{2\pi}+16} = 0.656598\,\text{a.u.} \tag{C.28}$$

Expectations

$$\langle r\rangle = \int \rho(r)r\,d\mathbf{r} = 2(2\pi C)^2\left[4\pi + 11\sqrt{2\pi} + 12\right] = 3.489025\,\text{a.u.} \tag{C.29}$$

$$\langle r^2\rangle = \int \rho(r)r^2 d\mathbf{r} = (4\pi C)^2\left[9\pi + 14\sqrt{\pi}\right] = 7.105114\,\text{a.u.} \tag{C.30}$$

$$\left\langle\frac{1}{r}\right\rangle = \int \rho(r)\frac{1}{r}d\mathbf{r} = (2\pi C)^2\left[4\pi + 9\sqrt{2\pi} + 8\right] = 1.442940\,\text{a.u.} \tag{C.31}$$

$$\left\langle\frac{1}{r^2}\right\rangle = \int \rho(r)\frac{1}{r^2}d\mathbf{r} = (2\pi C)^2\Big[11\pi + 8\sqrt{\pi} + 4\sqrt{2\pi}\ln\left(1+\sqrt{2}\right)\Big] = 1.926359\,\text{a.u.} \tag{C.32}$$

$$\langle\delta(\mathbf{r})\rangle = \rho(0) = \pi C^2\left[7\sqrt{2\pi} + 16\right] = 0.089319\text{a.u.} \tag{C.33}$$

C.2 First Excited Singlet State ($k = 0.144498$; $\omega = \sqrt{k} = 0.381029$)

(The Error function and Dawson's integral are given in (C.2) and (C.10), respectively,)

Electron Density $\rho(r)$

$$\rho_{01}(r) = e^{-\omega r^2}\Bigg\{a_0 + a_2r^2 + a_4r^4 + a_6r^6 + (b_0 + b_2r^2 + b_4r^4)e^{-\omega r^2} + \left(\frac{c_{-1}}{r} + c_1r + c_3r^3 + c_5r^5\right)\operatorname{erf}(\sqrt{\omega}r)\Bigg\}, \tag{C.34}$$

Table C.1 The coefficients in the analytical and semianalytical expressions for the density $\rho_{01}(r)$, the kinetic 'force' $\mathbf{z}(r;[\gamma])$, electron–interaction $\boldsymbol{\mathcal{E}}_{\mathrm{ee}}(r)$, and Hartree $\boldsymbol{\mathcal{E}}_{\mathrm{H}}(r)$ fields for the first excited singlet state

	$\rho_{01}(r)$	$\mathbf{z}(r)$	$\boldsymbol{\mathcal{E}}_{\mathrm{ee}}(r)$	$\boldsymbol{\mathcal{E}}_{\mathrm{H}}(r)$
a_{-1}		0.0323711	0.0323711	−0.752256
a_0	0.0252562			
a_1		0.0215704	−0.00423799	−0.0848432
a_2	−0.00156184			
a_3		−0.00892724	0.000280366	−0.0168259
a_4	0.000527316			
a_5		0.0000538074		−0.000880796
a_6	0.00005328761			
a_7		0.000111470		
a_9		−0.00000585396		
b_{-1}		−0.0228867	−0.0223222	−0.215024
b_0	0.00766804			
b_1		0.0258860	−0.000351275	−0.0195676
b_2	−0.000840943			
b_3		−0.00729833	0.0000487625	−0.00424068
b_4	0.000256559			
b_5		0.000796754		
b_7		−0.0000281844		
c_{-2}		0.0328975	0.0320861	−0.990167
c_{-1}	0.0205823			
c_0		−0.00739862	−0.000472655	−0.247069
c_1	0.00620070			
c_2		0.0140838	−0.000313782	−0.0274789
c_3	−0.000550207			
c_4		−0.00672378	0.0000532876	−0.00463420
c_5	0.000280366			
c_6		0.000830180		
c_8		−0.0000307999		

where the coefficients are given in Table C.1.

$$\rho_{01}(r)_{\substack{\sim \\ r\to\infty}} e^{-\omega r^2} \times \left[\frac{b_{-1}}{r} + b_0 + b_1 r + b_2 r^2 + b_3 r^3 + b_4 r^4 + b_5 r^5 + b_6 r^6\right], \tag{C.35}$$

where $b_{-1} = 0.0205823$, $b_0 = 0.0252562$, $b_1 = 0.00620070$, $b_2 = -0.00156184$, $b_3 = -0.000550207$, $b_4 = 0.000527316$, $b_5 = 0.000280366$, $b_6 = 0.0000532876$.

Pair–Correlation Density $g(\mathbf{r}\mathbf{r}')$

$$g(\mathbf{r}\mathbf{r}') = \frac{2C^2}{\rho_{01}(r)} e^{-\omega(r^2+r'^2)}$$
$$\left(1 + C_1\sqrt{\frac{\omega}{2}}|\mathbf{r}-\mathbf{r}'| + C_2\left(\frac{\omega}{2}\right)|\mathbf{r}-\mathbf{r}'|^2 + C_3\left(\frac{\omega}{2}\right)^{3/2}|\mathbf{r}-\mathbf{r}'|^3\right)^2, \tag{C.36}$$

where $C = 0.0261005$, $C_1 = 1.146884$, $C_2 = -0.561569$, $C_3 = -0.489647$.

Single–Particle Density Matrix $\gamma(\mathbf{r}'\mathbf{r}'')$

$$\gamma\left(\mathbf{r}'\mathbf{r}''\right) = 2C^2 e^{-\omega(r'^2+r''^2)/2}$$
$$\times \int \left(1 + C_1\sqrt{\frac{\omega}{2}}|\mathbf{r}'-\mathbf{r}| + C_2\left(\frac{\omega}{2}\right)|\mathbf{r}'-\mathbf{r}|^2 + C_3\left(\frac{\omega}{2}\right)^{3/2}|\mathbf{r}'-\mathbf{r}|^3\right)$$
$$\times \left(1 + C_1\sqrt{\frac{\omega}{2}}|\mathbf{r}''-\mathbf{r}| + C_2\left(\frac{\omega}{2}\right)|\mathbf{r}''-\mathbf{r}|^2\right.$$
$$\left. + C_3\left(\frac{\omega}{2}\right)^{3/2}|\mathbf{r}''-\mathbf{r}|^3\right) e^{-\omega r^2} d\mathbf{r}, \tag{C.37}$$

where $C = 0.0261005$, $C_1 = 1.146884$, $C_2 = -0.561569$, $C_3 = -0.489647$.

Dirac Density Matrix $\gamma_s(\mathbf{r}'\mathbf{r}'')$

$$\gamma_s(\mathbf{r}'\mathbf{r}'') = \sqrt{\rho(\mathbf{r}')\rho(\mathbf{r}'')}. \tag{C.38}$$

Electron–Interaction Field $\mathcal{E}_{\mathrm{ee}}(\mathbf{r})$

$$\mathcal{E}_{\mathrm{ee}}(r) = \frac{e^{-\omega r^2}}{\rho_{01}(r)}\left\{\left(\frac{a_{-1}}{r} + a_1 r + a_3 r^3\right) + \left(\frac{b_{-1}}{r} + b_1 r + b_3 r^3\right)e^{-\omega r^2}\right.$$
$$+ \left(\frac{c_{-2}}{r^2} + c_0 + c_2 r^2 + c_4 r^4\right)\operatorname{erf}(\sqrt{\omega}r)$$
$$\left. - \frac{0.0525039\ \operatorname{daw}(\sqrt{\omega}r)}{r^2}\right\}, \tag{C.39}$$

where all the coefficients are given in Table C.1.

Hartree Field $\mathcal{E}_{\mathrm{H}}(\mathbf{r})$

$$\mathcal{E}_{\mathrm{H}}(r) = e^{-\omega r^2}\left\{\frac{a_{-1}}{r} + a_1 r + a_3 r^3 + a_5 r^5 + \left(\frac{b_{-1}}{r} + b_1 r + b_3 r^3\right)e^{-\omega r^2}\right.$$
$$\left. + \left(\frac{c_{-2}}{r^2} + c_0 + c_2 r^2 + c_4 r^4\right)\ \operatorname{erf}(\sqrt{\omega}r)\right\}$$
$$+ \frac{d_1\ \operatorname{erf}(\sqrt{\omega}r) + d_2\ \operatorname{erf}(\sqrt{2\omega}r)}{r^2}, \tag{C.40}$$

where $d_1 = 1.08130$, $d_2 = 0.918704$, and the other coefficients are given in Table C.1.

Kinetic 'Force' $z(r; [\gamma])$

$$\begin{aligned}\mathbf{z}(r;[\gamma]) = e^{-\omega r^2} \Bigg\{ &\frac{a_{-1}}{r} + a_1 r + a_3 r^3 + a_5 r^5 + a_7 r^7 + a_9 r^9 \\ &+ \left(\frac{b_{-1}}{r} + b_1 r + b_3 r^3 + b_5 r^5 + b_7 r^7 + \right) e^{-\omega r^2} \\ &+ \left(\frac{c_{-2}}{r^2} + c_0 + c_2 r^2 + c_4 r^4 + c_6 r^6 + c_8 r^8 \right) \operatorname{erf}(\sqrt{\omega} r) \\ &- \frac{0.0525039 \operatorname{daw}(\sqrt{\omega} r)}{r^2} \Bigg\},\end{aligned} \tag{C.41}$$

where all the coefficients are given in Table C.1.

Kinetic 'Force' $z_s(r; [\gamma_s])$

$$\mathbf{z}_s\,(r;[\gamma_s]) = \frac{1}{2\rho}\left(\frac{\partial \rho}{\partial r}\right)\left[\frac{1}{r}\left(\frac{\partial \rho}{\partial r}\right) - \frac{1}{2\rho}\left(\frac{\partial \rho}{\partial r}\right)^2 + \left(\frac{\partial^2 \rho}{\partial r^2}\right)\right]. \tag{C.42}$$

Electron–Interaction Potential Energy $W_{\mathrm{ee}}(r)$

$$\begin{aligned}W_{\mathrm{ee}}(r) = -\int_{\infty}^{r} \frac{e^{-\omega r'^2}}{\rho_{01}(r')} \Bigg\{ &\left(\frac{a_{-1}}{r'} + a_1 r' + a_3 r'^3 \right) + \left(\frac{b_{-1}}{r'} + b_1 r' + b_3 r'^3 \right) e^{-\omega r'^2} \\ &+ \left(\frac{c_{-2}}{r'^2} + c_0 + c_2 r'^2 + c_4 r'^4 \right) \operatorname{erf}\left(\sqrt{\omega}\right) r' \\ &- \frac{0.0525039 \operatorname{daw}\left(\sqrt{\omega} r'\right)}{r'^2} \Bigg\} dr',\end{aligned} \tag{C.43}$$

where all the coefficients are given in Table C.2.

$$W_{\mathrm{ee}}(0) = 0.556156\,\text{a.u.} \tag{C.44}$$

Hartree Potential Energy $W_{\mathrm{H}}(r)$

$$\begin{aligned}W_{\mathrm{H}}(r) = e^{-\omega r^2} \Big\{ &a_0 + a_2 r^2 + a_4 r^4 + \left(b_0 + b_2 r^2 + b_4 r^4 \right) e^{-\omega r^2} \\ &+ \left(\frac{c_{-1}}{r} + c_1 r + c_3 r^3 \right) \operatorname{erf}\left(\sqrt{\omega} r\right) \Big\} \\ &+ d + \left(\frac{\mathrm{f}}{r} + g \operatorname{erf}\left(\sqrt{\omega} r\right) \right) \operatorname{erf}\left(\sqrt{\omega} r\right) + \frac{\mathrm{h}}{r} \operatorname{erf}(\sqrt{2\omega} r),\end{aligned} \tag{C.45}$$

Table C.2 The coefficients in the analytical and semianalytical expressions for the electron–interaction $W_{ee}(r)$ and Hartree $W_H(r)$ potential energies for the first excited singlet state

	$W_{ee}(r)$	$W_H(r)$
a_{-1}	0.0323711	
a_o		−0.185855
a_1	−0.00423799	
a_2		−0.0282273
a_3	0.000280366	
a_4		−0.00115855
b_{-1}	−0.0223222	
b_o		−0.0842051
b_1	−0.000351275	
b_2		−0.0151002
b_3	0.0000487625	
b_4		−0.00131433
c_{-2}	0.0320861	
c_{-1}		−0.990167
c_0	−0.000472655	
c_1		−0.0601975
c_2	−0.000313782	
c_3		−0.00609556
c_4	0.0000532876	

where d = 0.320194, f = 1.081298, g = 0.320194, h = 0.918704, and the other coefficients are given in Table C.2.

$$W_H(0) = 1.017414\,\text{a.u.} \tag{C.46}$$

Expectations

$$\langle r \rangle = \int \rho(r) r d\mathbf{r} = 4.971112\,\text{a.u.} \tag{C.47}$$

$$\langle r^2 \rangle = \int \rho(r) r^2 d\mathbf{r} = 14.565898\,\text{a.u.} \tag{C.48}$$

$$\left\langle \frac{1}{r} \right\rangle = \int \rho(r) \frac{1}{r} d\mathbf{r} = 1.053870\,\text{a.u.} \tag{C.49}$$

$$\left\langle \frac{1}{r^2} \right\rangle = \int \rho(r) \frac{1}{r^2} d\mathbf{r} = 0.936753\,\text{a.u.} \tag{C.50}$$

$$\langle \delta(\mathbf{r}) \rangle = \rho(0) = 0.0472434\,\text{a.u.} \tag{C.51}$$

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Appendix D
Derivation of the Kinetic–Energy–Density Tensor for Hooke's Atom in Its Ground State

In this Appendix, we derive the kinetic-energy-density tensor for Hooke's atom in its ground state.

The density matrix for a two–electron system is (see (2.15))

$$\gamma(\mathbf{r}'\mathbf{r}'') = 2\sum_{\sigma}\int \psi^*(\mathbf{r}'\sigma, \mathbf{x}_2)\psi(\mathbf{r}''\sigma, \mathbf{x}_2)d\mathbf{x}_2, \tag{D.1}$$

where $\mathbf{x} = \mathbf{r}, \sigma$ and $\int d\mathbf{x}_2 = \sum_{\sigma_2}\int d\mathbf{r}_2$. Substituting the ground-state wavefunction of (2.177) into the above equation, we obtain,

$$\gamma(\mathbf{r}'\mathbf{r}'') = 2C^2 e^{-(r'^2+r''^2)/4}\int\left[1+\frac{|\mathbf{r}'-\mathbf{r}|}{2}\right] \times\left[1+\frac{|\mathbf{r}''-\mathbf{r}|}{2}\right]e^{-r^2/2}d\mathbf{r}. \tag{D.2}$$

Now let us make the transformation to the coordinates

$$\mathbf{x} = (\mathbf{r}'+\mathbf{r}'')/2, \;\; \mathbf{y} = (\mathbf{r}'-\mathbf{r}'')/2. \tag{D.3}$$

Equation (D.2) then becomes

$$\gamma(\mathbf{r}'\mathbf{r}'') = 2C^2 e^{-(x^2+y^2)/2}\int\left[1+|\mathbf{r}-\mathbf{y}|/2\right] \times\left[1+|\mathbf{r}+\mathbf{y}|/2\right]e^{-|\mathbf{r}+\mathbf{x}|^2/2}d\mathbf{r}. \tag{D.4}$$

Substitution of (D.4) into the time-independent version of the kinetic–energy–density tensor (2.53) then leads to

$$t_{\alpha\beta}(\mathbf{r};[\gamma]) = \frac{1}{8}\left[\frac{\partial^2}{\partial x_\alpha\partial x_\beta} - \frac{\partial^2}{\partial y_\beta\partial y_\alpha}\right]\gamma(\mathbf{r}'\mathbf{r}'')_{\mathbf{x}=\mathbf{r},\mathbf{y}=0}. \tag{D.5}$$

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The first term on the right side of (D.5) can be evaluated readily as

$$\frac{\partial^2}{\partial x_\alpha \partial x_\beta}\gamma(\mathbf{r}'\mathbf{r}'')|_{\mathbf{x}=\mathbf{r},\mathbf{y}=0} = \frac{\partial^2}{\partial r_\alpha \partial r_\beta}\rho(\mathbf{r}). \tag{D.6}$$

After complicated but straightforward algebra, the second term is evaluated as

$$-\frac{1}{2}\frac{\partial^2}{\partial y_\alpha \partial y_\beta}\gamma(\mathbf{r}'\mathbf{r}'')|_{\mathbf{x}=\mathbf{r},\mathbf{y}=0} = \delta_{\alpha\beta}C^2 e^{-r^2/2}I(r) + C^2 e^{-r^2/2}J_{\alpha\beta}(r), \tag{D.7}$$

where the integrals $I(r)$ and $J_{\alpha\beta}(\mathbf{r})$ are defined as

$$I(r) = \int \left[1 + r'/2 - 1/r'\right]\left[1 + r'/2\right] e^{-|\mathbf{r}'+\mathbf{r}|^2/2} d\mathbf{r}', \tag{D.8}$$

$$J_{\alpha\beta}(\mathbf{r}) = \int \frac{r'_\alpha r'_\beta}{r'^3}(1 + r')e^{-|\mathbf{r}+\mathbf{r}'|^2/2} d\mathbf{r}', \tag{D.9}$$

respectively. $J_{\alpha\beta}(\mathbf{r})$ can be further expressed as a sum of two integrals

$$J_{\alpha\beta}(\mathbf{r}) = J_{1\alpha\beta}(\mathbf{r}) + J_{2\alpha\beta}(\mathbf{r}), \tag{D.10}$$

where, respectively,

$$J_{1\alpha\beta}(\mathbf{r}) = \int \frac{r'_\alpha r'_\beta}{r'^3} e^{-|\mathbf{r}'+\mathbf{r}|^2/2} d\mathbf{r}', \tag{D.11}$$

and

$$J_{2\alpha\beta}(\mathbf{r}) = \int \frac{r'_\alpha r'_\beta}{r'^2} e^{-|\mathbf{r}'+\mathbf{r}|^2/2} d\mathbf{r}'. \tag{D.12}$$

The integrals $I(r)$, $J_{1\alpha\beta}(\mathbf{r})$ and $J_{2\alpha\beta}(\mathbf{r})$ are evaluated as

$$I(r) = 2\pi\left\{\frac{5}{4}\sqrt{2\pi} + \sqrt{2\pi}/4r^2 + 2e^{-r^2/2} + \sqrt{2\pi}r\ \mathrm{erf}(r/\sqrt{2})\right\}, \tag{D.13}$$

$$\begin{aligned} J_{1\alpha\beta}(\mathbf{r}) = -2\pi\frac{\partial^2}{\partial r_\alpha \partial r_\beta}&\left\{2e^{-r^2/2} + \sqrt{2\pi}\left(r + \frac{1}{r}\right)\ \mathrm{erf}(r/\sqrt{2})\right\} \\ &+\delta_{\alpha\beta}(2\pi)^{3/2}\frac{1}{r}\ \mathrm{erf}(r/\sqrt{2}), \end{aligned} \tag{D.14}$$

and

$$J_{2\alpha\beta}(\mathbf{r}) = e^{-r^2/2}\sqrt{2}(2\pi)^{3/2}\frac{\partial^2}{\partial r_\alpha \partial r_\beta}\left[e^{r^2/2}\ \mathrm{daw}(r/\sqrt{2})/r\right]. \tag{D.15}$$

Thus, from (D.5–D.7), and (D.10), (D.13–D.15), we obtain

$$t_{\alpha\beta}(\mathbf{r}; [\gamma]) = \frac{r_\alpha r_\beta}{r^2} f(r) + \delta_{\alpha\beta} k(r), \tag{D.16}$$

where $f(r)$ and $k(r)$ are given by (C.8) and (C.9) of Appendix C.

Appendix E
Derivation of the S System 'Quantal Newtonian' Second Law

In this Appendix we derive [1, 2] the TD 'Quantal Newtonian' second law or differential virial theorem for the S system of noninteracting fermions with the same density $\rho(\mathbf{r}t)$ as that of the interacting Schrödinger system. The proof is for arbitrary external field $\mathcal{F}^{\mathrm{ext}}(\mathbf{r}t) = -\boldsymbol{\nabla} v(\mathbf{r}t)$, and not restricted to potential energies $v(\mathbf{r}t)$ that are expandable in a Taylor series about an initial time. The corresponding TD equations for the S system are

$$i\frac{\partial}{\partial t}\phi_j(\mathbf{x}t) = \left[-\frac{1}{2}\nabla^2 + v_{\mathrm{s}}(\mathbf{r}t)\right]\phi_j(\mathbf{x}t), \tag{E.1}$$

where $v_{\mathrm{s}}(\mathbf{r}t) = v(\mathbf{r}t) + v_{\mathrm{ee}}(\mathbf{r}t)$. Writing the orbitals as $\phi_j(\mathbf{x}t) = \phi_j^R(\mathbf{x}t) + i\phi_j^I(\mathbf{x}t)$, where $\phi_j^{\mathrm{R}}(\mathbf{x}t)$ and $\phi_j^{\mathrm{I}}(\mathbf{x}t)$ are its real and imaginary components, we have on equating the real and imaginary parts of the differential equation

$$v_{\mathrm{s}}(\mathbf{r}t) + \frac{1}{\phi_j^{\mathrm{R}}(t)}\frac{\partial}{\partial t}\phi_j^I(t) = \frac{1}{2}\frac{1}{\phi_j^{\mathrm{R}}(t)}\nabla^2\phi_j^{\mathrm{R}}(t), \tag{E.2}$$

$$v_{\mathrm{s}}(\mathbf{r}t) - \frac{1}{\phi_j^{\mathrm{I}}(t)}\frac{\partial}{\partial t}\phi_j^R(t) = \frac{1}{2}\frac{1}{\phi_j^{\mathrm{I}}(t)}\nabla^2\phi_j^{\mathrm{I}}(t). \tag{E.3}$$

Performing operations similar to those for the interacting Schrödinger system in Appendix A leads to

$$\begin{aligned}|\phi_j(t)|^2\frac{\partial}{\partial r_\alpha}v_{\mathrm{s}}(\mathbf{r}t) &+ \frac{\partial}{\partial t}\left\{\phi_j^R(t)\frac{\partial}{\partial r_\alpha}\phi_j^I(t) - \phi_j^I(t)\frac{\partial}{\partial r_\alpha}\phi_j^R(t)\right\}\\ &= \frac{1}{2}\sum_\beta\left\{\frac{\partial^3\phi_j^R(t)}{\partial r_\beta^2\partial r_\alpha}\phi_j^R(t) + \frac{\partial^3\phi_j^I(t)}{\partial r_\beta^2\partial r_\alpha}\phi_j^I(t)\right.\\ &\left.\quad - \frac{\partial^2\phi_j^R(t)}{\partial r_\beta^2}\frac{\partial\phi_j^R(t)}{\partial r_\alpha} - \frac{\partial^2\phi_j^I(t)}{\partial r_\beta^2}\frac{\partial\phi_j^I(t)}{\partial r_\alpha}\right\}.\end{aligned} \tag{E.4}$$

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On using the relations

$$\frac{1}{4}\frac{\partial^3(\phi_j^A(t))^2}{\partial r_\beta^2 \partial r_{1\alpha}} - \frac{\partial}{\partial r_\beta}\left(\frac{\partial \phi_j^A(t)}{\partial r_\alpha}\frac{\partial \phi_j^A(t)}{\partial r_\beta}\right)$$
$$= -\frac{1}{2}\left\{\frac{\partial^2 \phi_j^A(t)}{\partial r_\beta^2}\frac{\partial \phi_j^A(t)}{\partial r_\alpha} - \phi_j^A(t)\frac{\partial^3 \phi_j^A(t)}{\partial r_\beta^2 \partial r_\alpha}\right\}, \tag{E.5}$$

with A = R, I, and

$$\phi_j^R(t)\frac{\partial}{\partial r_\alpha}\phi_j^I(t) - \phi_j^I(t)\frac{\partial}{\partial r_\alpha}\phi_j^R(t)$$
$$= \frac{i}{2}\left\{\phi_j(t)\frac{\partial}{\partial r_\alpha}\phi_j^*(t) - \phi_j^*(t)\frac{\partial}{\partial r_\alpha}\phi_j(t)\right\}, \tag{E.6}$$

in (E.3), we obtain

$$|\phi_j(t)|^2\frac{\partial}{\partial r_\alpha}v_s(\mathbf{r}t) + \frac{i}{2}\frac{\partial}{\partial t}\left\{\phi_j(t)\frac{\partial}{\partial r_\alpha}\phi_j^*(t) - \phi_j^*(t)\frac{\partial}{\partial r_\alpha}\phi_j(t)\right\}$$
$$= \frac{1}{4}\nabla^2\frac{\partial}{\partial r_\alpha}|\phi_j(t)|^2 - \sum_\beta \frac{\partial}{\partial r_\beta}\left\{\frac{\partial \phi_j^R(t)}{\partial r_\alpha}\frac{\partial \phi_j^R(t)}{\partial r_\beta} + \frac{\partial \phi_j^I(t)}{\partial r_\alpha}\frac{\partial \phi_j^I(t)}{\partial r_\beta}\right\}. \tag{E.7}$$

Now, for the noninteracting system

$$t_{s,\alpha\beta}(\mathbf{r}t) = \frac{1}{2}\sum_\sigma\sum_{j=1}^{N}\left\{\frac{\partial \phi_j^R(t)}{\partial r_\alpha}\frac{\partial \phi_j^R(t)}{\partial r_\beta} + \frac{\partial \phi_j^I(t)}{\partial r_\alpha}\frac{\partial \phi_j^I(t)}{\partial r_\beta}\right\}. \tag{E.8}$$

Finally, by operating on (E.7) by $\sum_\sigma \sum_{j=1}^N$, we obtain the TD noninteracting system 'Quantal Newtonian' second law or differential virial theorem as

$$\mathcal{F}^{\text{ext}}(\mathbf{r}t) + \mathcal{F}_s^{\text{int}}(\mathbf{r}t) = \mathcal{J}_s(\mathbf{r}t), \tag{E.9}$$

where

$$\mathcal{F}^{\text{ext}}(\mathbf{r}t) = -\boldsymbol{\nabla} v(\mathbf{r}t), \tag{E.10}$$

and

$$\mathcal{F}_s^{\text{ext}}(\mathbf{r}t) = -\boldsymbol{\nabla} v_{\text{ee}}(\mathbf{r}t) - \mathcal{D}(\mathbf{r}t) - \mathcal{Z}_s(\mathbf{r}t), \tag{E.11}$$

with the individual fields $\mathcal{D}(\mathbf{r}t)$, $\mathcal{Z}_s(\mathbf{r}t)$, and $\mathcal{J}_s(\mathbf{r}t)$ defined in Sect. 3.1.2.

The time-independent 'Quantal Newtonian' second law for the S system [3, 4] in which the external field $\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}) = -\nabla v(\mathbf{r})$ is a special case of the time-dependent theorem with the time parameter t and current density field $\boldsymbol{\mathcal{J}}_s(\mathbf{r}t)$ absent. Furthermore, the theorem is valid for the ground or any bound excited state of the time-independent S system. With no distinction being made for the ground or excited state, the S system differential equation is

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_{\mathrm{ee}}(\mathbf{r})\right]\phi_i(\mathbf{x}) = \epsilon_i\phi_i(\mathbf{x}) \;\;;\;\; i = 1, \ldots, N. \tag{E.12}$$

The corresponding 'Quantal Newtonian' second law is

$$\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}) + \boldsymbol{\mathcal{F}}_s^{\mathrm{int}}(\mathbf{r}) = 0, \tag{E.13}$$

where

$$\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}) = -\boldsymbol{\nabla} v(\mathbf{r}), \tag{E.14}$$

and

$$\boldsymbol{\mathcal{F}}_s^{\mathrm{int}}(\mathbf{r}) = -\boldsymbol{\nabla} v_{\mathrm{ee}}(\mathbf{r}) - \boldsymbol{\mathcal{D}}(\mathbf{r}) - \boldsymbol{\mathcal{Z}}_s(\mathbf{r}), \tag{E.15}$$

and where the fields $\boldsymbol{\mathcal{D}}(\mathbf{r})$ and $\boldsymbol{\mathcal{Z}}_s(\mathbf{r})$ are defined as in Sect. 3.1.2 but for the time-independent case.

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Appendix F
Derivation of the 'Quantal Newtonian' First Law in the Presence of a Magnetic Field

In this appendix we derive [1] the 'Quantal Newtonian' first law in the presence of a magnetostatic field. The method employed is the same as in Appendix A. (This law has also been derived [2] via the equation of motion for the single-particle density matrix.)

Consider the Hamiltonian $\hat{H}$ of (9.1) and the corresponding Schrödinger equation (9.9). Writing the wave function as $\Psi = \Psi^R + i\Psi^I$, where Ψ^R and Ψ^I are the real and imaginary parts, we have on substitution into (9.9)

$$[\hat{U} + \hat{V} + \frac{1}{2}\mathbf{A}^2(\mathbf{r}) - E](\Psi^R + i\Psi^I) = [-\hat{T} + i\hat{\Omega}](\Psi^R + i\Psi^I), \tag{F.1}$$

or, since $\hat{T}$ and $\hat{\Omega}$ have differential operators:

$$\hat{U} + \hat{V} + \frac{1}{2}\mathbf{A}^2(\mathbf{r}) - E = \frac{(-\hat{T}\Psi^R - \hat{\Omega}\Psi^I)}{\Psi^R} = \frac{(-\hat{T}\Psi^I + \hat{\Omega}\Psi^R)}{\Psi^I}. \tag{F.2}$$

With $\nabla_i^2 = \sum_{\beta=1}^{3} \frac{\partial^2}{\partial r_{i\beta}^2}$, we have on differentiating the individual terms on the right hand side of (F.2) with respect to $r_{1\alpha}$

$$\begin{aligned}\frac{\partial}{\partial r_{1\alpha}}[\frac{\hat{T}\Psi^R}{\Psi^R}] = &- \frac{1}{2\Psi^R}\sum_{i=1}^{N}\sum_{\beta=1}^{3}\frac{\partial^3\Psi^R}{\partial r_{i\beta}\partial r_{i\beta}\partial r_{1\alpha}} \\ &+ \frac{1}{2(\Psi^R)^2}\frac{\partial\Psi^R}{\partial r_{1\alpha}}\sum_{i=1}^{N}\sum_{\beta=1}^{3}\frac{\partial^2\Psi^R}{\partial r_{i\beta}^2},\end{aligned} \tag{F.3}$$

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and

$$\frac{\partial}{\partial r_{1\alpha}}\left[\frac{\hat{\Omega}\Psi^I}{\Psi^R}\right] = \sum_{i=1}^{N}\sum_{\beta=1}^{3}\left\{\frac{1}{\Psi^R}\frac{\partial}{\partial r_{1\alpha}}\left(A_{i\beta}\frac{\partial \Psi^I}{\partial r_{i\beta}}\right) - \frac{1}{(\Psi^R)^2}A_{i\beta}\frac{\partial \Psi^I}{\partial r_{i\beta}}\frac{\partial \Psi^R}{\partial r_{1\alpha}}\right\}$$
$$+\frac{1}{2}\sum_{i=1}^{N}\sum_{\beta=1}^{3}\left\{\frac{1}{\Psi^R}\frac{\partial}{\partial r_{1\alpha}}\left(\Psi^I\frac{\partial A_{i\beta}}{\partial r_{i\beta}}\right)\right.$$
$$\left.-\frac{1}{(\Psi^R)^2}\Psi^I\frac{\partial A_{i\beta}}{\partial r_{i\beta}}\frac{\partial \Psi^R}{\partial r_{1\alpha}}\right\}. \tag{F.4}$$

Differentiating the left hand side of (F.2) with respect to $r_{1\alpha}$, employing (F.3) and (F.4), we arrive at

$$\left[\frac{\partial}{\partial r_{1\alpha}}\left\{v(\mathbf{r}_1) + \frac{1}{2}A^2(\mathbf{r}_1) + \sum_{j=2}^{N}u(\mathbf{r}_1,\mathbf{r}_j)\right\}\right](\Psi^R)^2$$
$$= \sum_{i=1}^{N}\sum_{\beta=1}^{3}\left[\frac{1}{2}\Psi^R\frac{\partial^3\Psi^R}{\partial r_{i\beta}\partial r_{i\beta}\partial r_{1\alpha}} - \frac{1}{2}\frac{\partial \Psi^R}{\partial r_{1\alpha}}\frac{\partial^2\Psi^R}{\partial r_{i\beta}^2}\right]$$
$$-\sum_{i=1}^{N}\sum_{\beta=1}^{3}\left[\Psi^R\frac{\partial}{\partial r_{1\alpha}}\left(A_{i\beta}\frac{\partial \Psi^I}{\partial r_{i\beta}}\right) - A_{i\beta}\frac{\partial \Psi^I}{\partial r_{i\beta}}\frac{\partial \Psi^R}{\partial r_{1\alpha}}\right]$$
$$-\frac{1}{2}\sum_{i=1}^{N}\sum_{\beta=1}^{3}\left\{\Psi^R\frac{\partial}{\partial r_{1\alpha}}\left(\Psi^I\frac{\partial A_{i\beta}}{\partial r_{i\beta}}\right) - \Psi^I\frac{\partial A_{i\beta}}{\partial r_{i\beta}}\frac{\partial \Psi^R}{\partial r_{1\alpha}}\right\}. \tag{F.5}$$

The right hand side of (F.5) can be further simplified by using the following relations:

$$\frac{1}{4}\frac{\partial^3\Psi^R\Psi^R}{\partial r_{i\beta}\partial r_{i\beta}\partial r_{1\alpha}} = \frac{1}{2}\frac{\partial^2\Psi^R}{\partial r_{i\beta}^2}\frac{\partial \Psi^R}{\partial r_{1\alpha}} + \frac{\partial \Psi^R}{\partial r_{i\beta}}\frac{\partial^2\Psi^R}{\partial r_{i\beta}\partial r_{1\alpha}}$$
$$+\frac{1}{2}\Psi^R\frac{\partial^3\Psi^R}{\partial r_{i\beta}\partial r_{i\beta}\partial r_{1\alpha}}, \tag{F.6}$$

and

$$-\frac{\partial}{\partial r_{i\beta}}\left[\frac{\partial \Psi^R}{\partial r_{1\alpha}}\frac{\partial \Psi^R}{\partial r_{i\beta}}\right] = -\frac{\partial \Psi^R}{\partial r_{1\alpha}}\frac{\partial^2\Psi^R}{\partial r_{i\beta}\partial r_{i\beta}} - \frac{\partial^2\Psi^R}{\partial r_{1\alpha}\partial r_{i\beta}}\frac{\partial \Psi^R}{\partial r_{i\beta}}. \tag{F.7}$$

Adding (F.6) and (F.7) we obtain

$$\frac{1}{4}\frac{\partial^3\Psi^R\Psi^R}{\partial r_{i\beta}\partial r_{i\beta}\partial r_{1\alpha}} - \frac{\partial}{\partial r_{i\beta}}\left[\frac{\partial \Psi^R}{\partial r_{1\alpha}}\frac{\partial \Psi^R}{\partial r_{i\beta}}\right] = \frac{1}{2}\Psi^R\frac{\partial^3\Psi^R}{\partial r_{i\beta}\partial r_{i\beta}\partial r_{1\alpha}} - \frac{1}{2}\frac{\partial \Psi^R}{\partial r_{1\alpha}}\frac{\partial^2\Psi^R}{\partial r_{i\beta}^2}, \tag{F.8}$$

where the right hand side of (F.8) then corresponds to the terms in the first set of square parenthesis of (F.5).

Thus, (F.5) for the real part of the wave function Ψ^R becomes

$$\left[\frac{\partial}{\partial r_{1\alpha}}\left\{v(\mathbf{r}_1)+\frac{1}{2}A^2(\mathbf{r}_1)+\sum_{j=2}^{N}u(\mathbf{r}_1,\mathbf{r}_j)\right\}\right](\Psi^R)^2$$
$$=\sum_{i=1}^{N}\sum_{\beta=1}^{3}\left\{\frac{1}{4}\frac{\partial^3(\Psi^R\Psi^R)}{\partial r_{i\beta}\partial r_{i\beta}\partial r_{1\alpha}}-\frac{\partial}{\partial r_{i\beta}}\left(\frac{\partial\Psi^R}{\partial r_{1\alpha}}\frac{\partial\Psi^R}{\partial r_{i\beta}}\right)\right\}$$
$$-\sum_{i=1}^{N}\sum_{\beta=1}^{3}\left[\Psi^R\frac{\partial}{\partial r_{1\alpha}}\left(A_{i\beta}\frac{\partial\Psi^I}{\partial r_{i\beta}}\right)-A_{i\beta}\frac{\partial\Psi^I}{\partial r_{i\beta}}\frac{\partial\Psi^R}{\partial r_{1\alpha}}\right]$$
$$-\frac{1}{2}\sum_{i=1}^{N}\sum_{\beta=1}^{3}\left\{\Psi^R\frac{\partial}{\partial r_{1\alpha}}\left(\Psi^I\frac{\partial A_{i\beta}}{\partial r_{i\beta}}\right)-\Psi^I\frac{\partial A_{i\beta}}{\partial r_{i\beta}}\frac{\partial\Psi^R}{\partial r_{1\alpha}}\right\}. \quad (F.9)$$

Similarly, the equation for the imaginary part of the wave function Ψ^I is

$$\left[\frac{\partial}{\partial r_{1\alpha}}\left\{v(\mathbf{r}_1)+\frac{1}{2}A^2(\mathbf{r}_1)+\sum_{j=2}^{N}u(\mathbf{r}_1,\mathbf{r}_j)\right\}\right](\Psi^I)^2$$
$$=\sum_{i=1}^{N}\sum_{\beta=1}^{3}\left\{\frac{1}{4}\frac{\partial^3(\Psi^I\Psi^I)}{\partial r_{i\beta}\partial r_{i\beta}\partial r_{1\alpha}}-\frac{\partial}{\partial r_{i\beta}}\left(\frac{\partial\Psi^I}{\partial r_{1\alpha}}\frac{\partial\Psi^I}{\partial r_{i\beta}}\right)\right\}$$
$$+\sum_{i=1}^{N}\sum_{\beta=1}^{3}\left[\Psi^I\frac{\partial}{\partial r_{1\alpha}}\left(A_{i\beta}\frac{\partial\Psi^R}{\partial r_{i\beta}}\right)-A_{i\beta}\frac{\partial\Psi^R}{\partial r_{i\beta}}\frac{\partial\Psi^I}{\partial r_{1\alpha}}\right]$$
$$+\frac{1}{2}\sum_{i=1}^{N}\sum_{\beta=1}^{3}\left\{\Psi^I\frac{\partial}{\partial r_{1\alpha}}\left(\Psi^R\frac{\partial A_{i\beta}}{\partial r_{i\beta}}\right)-\Psi^R\frac{\partial A_{i\beta}}{\partial r_{i\beta}}\frac{\partial\Psi^I}{\partial r_{1\alpha}}\right\}. \quad (F.10)$$

Note that the terms in the first parenthesis in (F.9) and (F.10) correspond to the derivation in the $\mathbf{B}=0$ case [3]. The terms in the second two parenthesis are the additional terms in the presence of a vector potential.

Adding (F.9), and (F.10) yields

$$\left[\frac{\partial}{\partial r_{1\alpha}}\left\{v(\mathbf{r}_1)+\frac{1}{2}A^2(\mathbf{r}_1)+\sum_{j=2}^{N}u(\mathbf{r}_1,\mathbf{r}_j)\right\}\right]|\Psi|^2$$
$$=\sum_{i=1}^{N}\sum_{\beta=1}^{3}\left\{\frac{1}{4}\frac{\partial^3|\Psi|^2}{\partial r_{i\beta}\partial r_{i\beta}\partial r_{1\alpha}}-\frac{\partial}{\partial r_{i\beta}}\left(\frac{\partial\Psi^R}{\partial r_{1\alpha}}\frac{\partial\Psi^R}{\partial r_{i\beta}}+\frac{\partial\Psi^I}{\partial r_{1\alpha}}\frac{\partial\Psi^I}{\partial r_{i\beta}}\right)\right\}$$
$$+\left[A_{i\beta}\left(\frac{\partial\Psi^I}{\partial r_{i\beta}}\frac{\partial\Psi^R}{\partial r_{1\alpha}}-\frac{\partial\Psi^R}{\partial r_{i\beta}}\frac{\partial\Psi^I}{\partial r_{1\alpha}}\right)+\left(\Psi^I\frac{\partial}{\partial r_{1\alpha}}\left(A_{i\beta}\frac{\partial\Psi^R}{\partial r_{i\beta}}\right)-\Psi^R\frac{\partial}{\partial r_{1\alpha}}\left(A_{i\beta}\frac{\partial\Psi^I}{\partial r_{i\beta}}\right)\right)\right]$$

$$
+\frac{1}{2}\sum_{i=1}^{N}\sum_{\beta=1}^{3}\left\{\Psi^I\frac{\partial}{\partial r_{1\alpha}}\left(\Psi^R\frac{\partial A_{i\beta}}{\partial r_{i\beta}}\right)-\Psi^R\frac{\partial A_{i\beta}}{\partial r_{i\beta}}\frac{\partial \Psi^I}{\partial r_{1\alpha}}\right.
$$
$$
\left.-\Psi^R\frac{\partial}{\partial r_{1\alpha}}\left(\Psi^I\frac{\partial A_{i\beta}}{\partial r_{i\beta}}\right)+\Psi^I\frac{\partial A_{i\beta}}{\partial r_{i\beta}}\frac{\partial \Psi^R}{\partial r_{1\alpha}}\right\}. \tag{F.11}
$$

The terms of the first parenthesis on the right hand side of (F.11) may be rewritten by splitting each term into its $i = 1$ and $i \geq 2$ contributions as

$$
\sum_{i=1}^{N}\sum_{\beta=1}^{3}\frac{1}{4}\frac{\partial}{\partial r_{i\beta}}\frac{\partial}{\partial r_{i\beta}}\frac{\partial}{\partial r_{1\alpha}}|\Psi|^2=\left[\frac{1}{4}\nabla_1^2\frac{\partial}{\partial r_{1\alpha}}|\Psi|^2+\frac{1}{4}\sum_{j=2}^{N}\sum_{\beta=1}^{3}\frac{\partial}{\partial r_{j\beta}}\frac{\partial}{\partial r_{j\beta}}\frac{\partial}{\partial r_{1\alpha}}|\Psi|^2\right], \tag{F.12}
$$

and

$$
\sum_{i=1}^{N}\sum_{\beta=1}^{3}\frac{\partial}{\partial r_{i\beta}}\left(\frac{\partial \Psi^R}{\partial r_{1\alpha}}\frac{\partial \Psi^R}{\partial r_{i\beta}}+\frac{\partial \Psi^I}{\partial r_{1\alpha}}\frac{\partial \Psi^I}{\partial r_{i\beta}}\right)
$$
$$
=\left[\sum_{\beta=1}^{3}\frac{\partial}{\partial r_{1\beta}}\left(\frac{\partial \Psi^R}{\partial r_{1\alpha}}\frac{\partial \Psi^R}{\partial r_{1\beta}}+\frac{\partial \Psi^I}{\partial r_{1\alpha}}\frac{\partial \Psi^I}{\partial r_{1\beta}}\right)\right.
$$
$$
\left.+\sum_{j=2}^{N}\sum_{\beta=1}^{3}\frac{\partial}{\partial r_{j\beta}}\left(\frac{\partial \Psi^R}{\partial r_{1\alpha}}\frac{\partial \Psi^R}{\partial r_{j\beta}}+\frac{\partial \Psi^I}{\partial r_{1\alpha}}\frac{\partial \Psi^I}{\partial r_{j\beta}}\right)\right]. \tag{F.13}
$$

Again, the only new terms in (F.11) that arise on the right hand side due to the presence of the magnetic field or vector potential $\mathbf{A}$ are those of the second two parentheses of (F.11). These terms can be further simplified to

$$
\sum_{i=1}^{N}\sum_{\beta=1}^{3}\left[A_{i\beta}\left(\frac{\partial \Psi^I}{\partial r_{i\beta}}\frac{\partial \Psi^R}{\partial r_{1\alpha}}-\frac{\partial \Psi^R}{\partial r_{i\beta}}\frac{\partial \Psi^I}{\partial r_{1\alpha}}\right)+\left(\Psi^I\frac{\partial}{\partial r_{1\alpha}}\left(A_{i\beta}\frac{\partial \Psi^R}{\partial r_{i\beta}}\right)-\Psi^R\frac{\partial}{\partial r_{1\alpha}}\left(A_{i\beta}\frac{\partial \Psi^I}{\partial r_{i\beta}}\right)\right)\right.
$$
$$
\left.+\Psi^I\frac{\partial A_{i\beta}}{\partial r_{i\beta}}\frac{\partial \Psi^R}{\partial r_{1\alpha}}-\Psi^R\frac{\partial A_{i\beta}}{\partial r_{i\beta}}\frac{\partial \Psi^I}{\partial r_{1\alpha}}\right]. \tag{F.14}
$$

Once again, we split these terms into their $i = 1$ and $i \geq 2$ contributions.

The $i = 1$ term of (F.14) is

$$
\sum_{\beta=1}^{3}\left[A_{1\beta}\left(\frac{\partial \Psi^I}{\partial r_{1\beta}}\frac{\partial \Psi^R}{\partial r_{1\alpha}}-\frac{\partial \Psi^R}{\partial r_{1\beta}}\frac{\partial \Psi^I}{\partial r_{1\alpha}}\right)+\left(\Psi^I\frac{\partial}{\partial r_{1\alpha}}\left(A_{1\beta}\frac{\partial \Psi^R}{\partial r_{1\beta}}\right)-\Psi^R\frac{\partial}{\partial r_{1\alpha}}\left(A_{1\beta}\frac{\partial \Psi^I}{\partial r_{1\beta}}\right)\right)\right]
$$
$$
=\left[\frac{\partial A_{1\beta}}{\partial r_{1\alpha}}\left(\Psi^I\frac{\partial \Psi^R}{\partial r_{1\beta}}-\Psi^R\frac{\partial \Psi^I}{\partial r_{1\beta}}\right)+\left(\frac{\partial}{\partial r_{1\beta}}\left(A_{1\beta}\Psi^I\frac{\partial \Psi^R}{\partial r_{1\alpha}}-A_{1\beta}\Psi^R\frac{\partial \Psi^I}{\partial r_{1\alpha}}\right)\right)\right]. \tag{F.15}
$$

The $i \geq 2$ contribution of (F.14) is

$$= \sum_{i=2}^{N} \sum_{\beta=1}^{3} \frac{\partial}{\partial r_{i\beta}} \left[A_{i\beta} \left(\Psi^I \frac{\partial \Psi^R}{\partial r_{1\alpha}} - \Psi^R \frac{\partial \Psi^I}{\partial r_{1\alpha}} \right) + \Psi^I \frac{\partial A_{i\beta}}{\partial r_{i\beta}} \frac{\partial \Psi^R}{\partial r_{1\alpha}} - \Psi^R \frac{\partial A_{i\beta}}{\partial r_{i\beta}} \frac{\partial \Psi^I}{\partial r_{1\alpha}} \right]. \tag{F.16}$$

We next operate by $N \sum_{\sigma_1} \int d\mathbf{X}^{N-1}$ on (F.11) employing (F.12, F.13, F.15, F.16) for its right hand side. For the left hand side of (F.11) one obtains

$$\frac{\partial}{\partial r_{1\alpha}} \{v(\mathbf{r}_1) + A^2(\mathbf{r}_1)\} \rho(\mathbf{r}_1) + N \sum_{j=2}^{N} \sum_{\sigma_1} \int \frac{\partial u(\mathbf{r}_1 \mathbf{r}_j)}{\partial r_{1\alpha}} |\Psi|^2 d\mathbf{X}^{N-1}. \tag{F.17}$$

For the right hand side of (F.11) we note that the contributions of the second terms of (F.12) and (F.13), and that of the term (F.16) vanish for $|r_j| \to \infty$. Thus, the result of the above operation on the right hand side of (F.11) is

$$\begin{aligned} &\frac{1}{4} \nabla_1^2 \frac{\partial}{\partial r_{1\alpha}} \rho(\mathbf{r}_1) - 2N \sum_{\beta=1}^{3} \sum_{\sigma_1} \int \frac{1}{2} \frac{\partial}{\partial r_{1\beta}} \left(\frac{\partial \Psi^R}{\partial r_{1\alpha}} \frac{\partial \Psi^R}{\partial r_{1\beta}} + \frac{\partial \Psi^I}{\partial r_{1\alpha}} \frac{\partial \Psi^I}{\partial r_{1\beta}} \right) d\mathbf{X}^{N-1} \\ &+ N \sum_{\beta=1}^{3} \sum_{\sigma_1} \int \left[\frac{\partial A_{1\beta}}{\partial r_{1\alpha}} \left(\Psi^I \frac{\partial \Psi^R}{\partial r_{1\beta}} - \Psi^R \frac{\partial \Psi^I}{\partial r_{1\beta}} \right) \right. \\ &\left. + \left\{ \frac{\partial}{\partial r_{1\beta}} \left(A_{1\beta} \Psi^I \frac{\partial \Psi^R}{\partial r_{1\alpha}} - A_{1\beta} \Psi^R \frac{\partial \Psi^I}{\partial r_{1\alpha}} \right) \right\} \right] d\mathbf{X}^{N-1}. \end{aligned} \tag{F.18}$$

It can be readily seen that in the second term of (F.18), the terms within the parenthesis

$$N \sum_{\sigma_1} \int \frac{1}{2} \left(\frac{\partial \Psi^R}{\partial r_{1\alpha}} \frac{\partial \Psi^R}{\partial r_{1\beta}} + \frac{\partial \Psi^I}{\partial r_{1\alpha}} \frac{\partial \Psi^I}{\partial r_{1\beta}} \right) d\mathbf{X}^{N-1} = t_{\alpha\beta}(\mathbf{r}), \tag{F.19}$$

where the kinetic energy tensor $t_{\alpha\beta}(\mathbf{r})$ is

$$t_{\alpha\beta}(\mathbf{r}) = \frac{1}{4} \left(\frac{\partial^2}{\partial r'_\alpha \partial r''_\beta} + \frac{\partial^2}{\partial r'_\beta \partial r''_\alpha} \right) \gamma(\mathbf{r}'\mathbf{r}'') \bigg|_{\mathbf{r}'=\mathbf{r}''=\mathbf{r}}, \tag{F.20}$$

with $\gamma(\mathbf{r}'\mathbf{r}'')$ the reduced single particle density matrix quantal source of (9.26). Thus, the second term of (F.18) is the component $z_\alpha(\mathbf{r})$ of the kinetic 'force' $\mathbf{z}(\mathbf{r}; \gamma)$:

$$z_\alpha(\mathbf{r}) = 2\sum_{\beta=1}^{3} \frac{\partial}{\partial r_\beta} t_{\alpha\beta}(\mathbf{r}). \tag{F.21}$$

The third term of (F.17) may be expressed in terms of the pair-correlation function $P(\mathbf{r}\mathbf{r}')$ of (9.25):

$$N\sum_{j=2}^{N}\sum_{\sigma_1}\int \frac{\partial u(\mathbf{r}_1\mathbf{r}_j)}{\partial r_{1\alpha}}|\Psi|^2 d\mathbf{X}^{N-1} = \int \frac{\partial u(\mathbf{r}\mathbf{r}')}{\partial r_\alpha} P(\mathbf{r}\mathbf{r}')d\mathbf{r}'. \tag{F.22}$$

In vector form (F.22) is

$$\int \nabla u(\mathbf{r}\mathbf{r}')P(\mathbf{r}\mathbf{r}')d\mathbf{r}' = -\int \frac{P(\mathbf{r}\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}d\mathbf{r}' \tag{F.23}$$

$$= -\mathbf{e}_{ee}(\mathbf{r}), \tag{F.24}$$

with $\mathbf{e}_{ee}(\mathbf{r})$ the electron-interaction 'force' as obtained by Coulomb's law.

The last term of (F.18) may be expressed in terms of the paramagnetic current density $\mathbf{j}_p(\mathbf{r})$ as

$$k_\alpha(\mathbf{r};\mathbf{j}_p\mathbf{A}) = \sum_{\beta=1}^{3}\left[\left(\frac{\partial A_{1\beta}}{\partial r_{1\alpha}}\right) j_{p\beta}(\mathbf{r}_1) + \frac{\partial}{\partial r_{1\beta}}\left(A_{1\beta}\, j_{p\alpha}(\mathbf{r}_1)\right)\right]. \tag{F.25}$$

On putting together (F.17) and (F.18) in terms of their further simplifications expressed as 'forces, we have in vector form

$$\rho(\mathbf{r})\left[\nabla v(\mathbf{r}) + \frac{1}{2}\nabla A^2(\mathbf{r})\right] - \mathbf{e}_{ee}(\mathbf{r}) + \mathbf{z}(\mathbf{r};\gamma) + \mathbf{d}(\mathbf{r}) + \mathbf{k}(\mathbf{r};\mathbf{j}_p\mathbf{A}) = 0, \tag{F.26}$$

where the differential density 'force' $\mathbf{d}(\mathbf{r})$ is

$$\mathbf{d}(\mathbf{r}) = -\frac{1}{4}\nabla\nabla^2\rho(\mathbf{r}). \tag{F.27}$$

Equation (F.26) is the differential virial theorem derived by Holas and March [2] via the equation of motion for the single particle density matrix.

Now since the physical current density $\mathbf{j}(\mathbf{r})$ is

$$\mathbf{j}(\mathbf{r}) = \mathbf{j}_p(\mathbf{r}) + \rho(\mathbf{r})\mathbf{A}(\mathbf{r}), \tag{F.28}$$

we have

$$\mathbf{k}(\mathbf{r};\mathbf{j}_p\mathbf{A}) + \frac{1}{2}\rho(\mathbf{r})\nabla A^2(\mathbf{r}) = \mathbf{k}(\mathbf{r};\mathbf{j}\mathbf{A}) - \sum_{\beta=1}^{3}\nabla_\beta[\rho(\mathbf{r})\mathbf{A}(\mathbf{r})A_\beta(\mathbf{r})], \tag{F.29}$$

so that

$$k_\alpha(\mathbf{r}; \mathbf{jA}) = \sum_{\beta=1}^{3}[j_\beta(\mathbf{r})\{\nabla_\alpha A_\beta(\mathbf{r})\} + \nabla_\beta\{A_\beta(\mathbf{r})j_\alpha(\mathbf{r})\}]. \tag{F.30}$$

Equation (F.26) is then

$$\rho(\mathbf{r})\boldsymbol{\nabla} v(\mathbf{r}) - \mathbf{e}_{ee}(\mathbf{r}) + \mathbf{z}(\mathbf{r}; \gamma) + \mathbf{d}(\mathbf{r}) + \mathbf{k}(\mathbf{r}; \mathbf{jA}) - \sum_{\beta=1}^{3}\nabla_\beta[\rho(\mathbf{r})\mathbf{A}(\mathbf{r})A_\beta(\mathbf{r})] = 0. \tag{F.31}$$

The last two terms of (F.31) which are the only terms that depend upon the vector potential *can be afforded a rigorous physical interpretation*. Their sum can be expressed as the sum of a contribution of the external Lorentz 'force' $\mathbf{l}(\mathbf{r})$ and a corresponding contribution $\mathbf{i}(\mathbf{r})$ to the internal 'force'. The Lorentz 'force' $\mathbf{l}(\mathbf{r})$ defined in terms of the physical current density $\mathbf{j}(\mathbf{r})$ is

$$\mathbf{l}(\mathbf{r}) = \mathbf{j}(\mathbf{r}) \times \mathbf{B}(\mathbf{r}). \tag{F.32}$$

With $\mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}$, we have

$$l_\alpha(\mathbf{r}) = \sum_{\beta=1}^{3}[j_\beta(\mathbf{r})\nabla_\alpha A_\beta(\mathbf{r}) - j_\beta(\mathbf{r})\nabla_\beta A_\alpha(\mathbf{r})]. \tag{F.33}$$

The contribution of the magnetic field to the internal force $\mathbf{i}(\mathbf{r})$ is defined via its components as

$$i_\alpha(\mathbf{r}) = \sum_{\beta=1}^{3}\nabla_\beta I_{\alpha\beta}(\mathbf{r}), \tag{F.34}$$

where

$$I_{\alpha\beta}(\mathbf{r}) = [j_\alpha(\mathbf{r})A_\beta(\mathbf{r}) + j_\beta(\mathbf{r})A_\alpha(\mathbf{r})] - \rho(\mathbf{r})A_\alpha(\mathbf{r})A_\beta(\mathbf{r}). \tag{F.35}$$

On applying the continuity condition $\boldsymbol{\nabla} \cdot \mathbf{j}(\mathbf{r}) = \sum_\beta \nabla_\beta j_\beta(\mathbf{r}) = 0$, it is readily seen that

$$l_\alpha(\mathbf{r}) + i_\alpha(\mathbf{r}) = k_\alpha(\mathbf{r}; \mathbf{jA}) - \sum_{\beta=1}^{3}\nabla_\beta[\rho(\mathbf{r})A_\alpha(\mathbf{r})A_\beta(\mathbf{r})]. \tag{F.36}$$

Thus, (F.31) may be written in 'Quantal Newtonian' form in terms of external $\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r})$ and internal $\boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r})$ fields as

$$\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}) + \boldsymbol{\mathcal{F}}^{\mathrm{int}}(\mathbf{r}) = 0 \tag{F.37}$$

with the external field defined as

$$\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}) = \boldsymbol{\mathcal{E}}(\mathbf{r}) - \boldsymbol{\mathcal{L}}(\mathbf{r}) \tag{F.38}$$

where the external electrostatic $\boldsymbol{\mathcal{E}}(\mathbf{r})$ field is

$$\boldsymbol{\mathcal{E}}(\mathbf{r}) = -\boldsymbol{\nabla} v(\mathbf{r}), \tag{F.39}$$

and the magnetostatic Lorentz field $\boldsymbol{\mathcal{L}}(\mathbf{r})$ is

$$\boldsymbol{\mathcal{L}}(\mathbf{r}) = \frac{\mathbf{l}(\mathbf{r})}{\rho(\mathbf{r})}. \tag{F.40}$$

The internal field $\boldsymbol{\mathcal{F}}^{\text{int}}(\mathbf{r})$ is

$$\boldsymbol{\mathcal{F}}^{\text{int}}(\mathbf{r}) = \boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}) - \boldsymbol{\mathcal{Z}}(\mathbf{r}) - \boldsymbol{\mathcal{D}}(\mathbf{r}) - \boldsymbol{\mathcal{I}}(\mathbf{r}), \tag{F.41}$$

where the electron-interaction $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$, kinetic $\boldsymbol{\mathcal{Z}}(\mathbf{r})$, differential density $\boldsymbol{\mathcal{D}}(\mathbf{r})$, and internal magnetic $\boldsymbol{\mathcal{I}}(\mathbf{r})$ fields are defined in terms of their corresponding forces as

$$\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}) = \frac{\mathbf{e}_{ee}(\mathbf{r})}{\rho(\mathbf{r})};\ \boldsymbol{\mathcal{Z}}(\mathbf{r}) = \frac{\mathbf{z}(\mathbf{r};\gamma)}{\rho(\mathbf{r})};\ \boldsymbol{\mathcal{D}}(\mathbf{r}) = \frac{\mathbf{d}(\mathbf{r})}{\rho(\mathbf{r})};\ \boldsymbol{\mathcal{I}}(\mathbf{r}) = \frac{\mathbf{i}(\mathbf{r};\mathbf{jA})}{\rho(\mathbf{r})}. \tag{F.42}$$

Equations (F.37)–(F.42) constitute the 'Quantal Newtonian' first law in the presence of both an external electrostatic and magnetostatic fields.

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Appendix G
Analytical Expressions for the Ground State Properties of the Hooke's Atom in a Magnetic Field

In this appendix we give the Q–DFT analytical and semi-analytical expressions [1] for the mapping from a ground state of the interacting two-dimensional Hooke's atom in a magnetic field [2] as described by the wave function of (9.70) to one of noninteracting fermions in a ground state with equivalent density $\rho(\mathbf{r})$ and physical current density $\mathbf{j}(\mathbf{r})$. The expressions derived are for an effective oscillator frequency $\tilde{\omega} = 1$.

Electron density $\rho(\mathbf{r})$

$$\rho(\mathbf{r}) = 2\pi C^2 e^{-r^2} \left\{ \sqrt{\pi} e^{-\frac{1}{2}r^2} \left[\left(1 + r^2\right) I_0 \left(\frac{1}{2}r^2\right) + r^2 I_1 \left(\frac{1}{2}r^2\right) \right] + (2 + r^2) \right\}, \tag{G.1}$$

with $C^2 = 1/\pi^2(3 + \sqrt{2\pi})$, and where $I_0(x)$ and $I_1(x)$ are the zeroth- and first-order modified Bessel functions $I_\nu(x)$ [3] with

$$I_\nu(x) = \sum_{n=0}^{\infty} \frac{1}{n!\Gamma(n + \nu + 1)} \left(\frac{1}{2}x\right)^{2n+\nu} \tag{G.2}$$

and $\Gamma(x)$ the Gamma function [3]. The asymptotic structure of $\rho(r)$ near the nucleus is

$$\rho(r) \underset{r\to 0}{\sim} \frac{2}{\pi(3 + \sqrt{2\pi})} \left\{ 2 + \sqrt{\pi} - \left(1 + \frac{1}{2}\sqrt{\pi}\right) r^2 - \frac{1}{16}\sqrt{\pi} r^4 + \cdots \right\}, \tag{G.3}$$

with

$$\rho(0) = 0.436132\,\text{a.u.} \tag{G.4}$$

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Employing the asymptotic behavior of the Bessel functions:

$$I_0(z) \underset{r\to\infty}{\sim} \frac{e^z}{\sqrt{2\pi z}} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2z)^n} \frac{\Gamma(n+\frac{1}{2})}{n!\Gamma(-n+\frac{1}{2})} + \frac{e^{-z}}{\sqrt{2\pi z}} \sum_{n=0}^{\infty} \frac{i}{(2z)^n} \frac{\Gamma(n+\frac{1}{2})}{n!\Gamma(-n+\frac{1}{2})}, \tag{G.5}$$

and

$$I_1(z) \underset{r\to\infty}{\sim} \frac{e^z}{\sqrt{2\pi z}} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2z)^n} \frac{\Gamma(n+\frac{3}{2})}{n!\Gamma(-n+\frac{3}{2})} - \frac{e^{-z}}{\sqrt{2\pi z}} \sum_{n=0}^{\infty} \frac{i}{(2z)^n} \frac{\Gamma(n+\frac{3}{2})}{n!\Gamma(-n+\frac{3}{2})}, \tag{G.6}$$

the asymptotic structure of the density in the classically forbidden region is

$$\rho(r) \underset{r\to\infty}{\sim} \frac{2}{\pi(3+\sqrt{2\pi})} e^{-r^2} \left\{ r^2 + 2r + 2 + \frac{1}{2r} + \frac{1}{16r^3} + \cdots \right\}. \tag{G.7}$$

Pair-correlation density $g(\mathbf{r}\mathbf{r}')$

$$g(\mathbf{r}\mathbf{r}') = \frac{2C^2(1+R)^2 e^{-(r^2+r'^2)}}{\rho(\mathbf{r})} \tag{G.8}$$

where $R = |\mathbf{r} - \mathbf{r}'|$.

Single-particle density matrix $\gamma(\mathbf{r}\mathbf{r}')$

$$\gamma(\mathbf{r}\mathbf{r}') = 2C^2 e^{-\frac{1}{2}(r^2+r'^2)} \int (1+|\mathbf{r}-\mathbf{y}|)(1+|\mathbf{r}'-\mathbf{y}|) d\mathbf{y} \tag{G.9}$$

Dirac Density matrix $\gamma_s(\mathbf{r}\mathbf{r}')$

$$\gamma_s = \sqrt{\rho(\mathbf{r})\rho(\mathbf{r}')} \tag{G.10}$$

Electron-interaction field $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$

$$\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}) = \frac{2\pi^{\frac{3}{2}} C^2}{\rho(\mathbf{r})} \frac{\mathbf{r}}{r} e^{-\frac{3}{2}r^2} \left[2I_{\frac{1}{2}}\left(\frac{1}{2}r^2\right) + \frac{3r}{2} I_0\left(\frac{1}{2}r^2\right) - \frac{r}{2} I_1\left(\frac{1}{2}r^2\right) \right] \tag{G.11}$$

Electron-interaction energy E_{ee}

$$E_{ee} = 4\pi^{\frac{5}{2}} C^2 \int_0^{\infty} r^2 e^{-\frac{3}{2}r^2} \left[2I_{\frac{1}{2}}\left(\frac{1}{2}r^2\right) + \frac{3r}{2} I_0\left(\frac{1}{2}r^2\right) - \frac{r}{2} I_1\left(\frac{1}{2}r^2\right) \right] dr \tag{G.12}$$

$$= 4\pi^{\frac{5}{2}} C^2 \left[\frac{\sqrt{2\pi}}{4} + \frac{1}{2} \right] = 0.818401 \text{ a.u.} \tag{G.13}$$

Kinetic energy tensor $t_{\alpha\beta}(\mathbf{r};\gamma)$

$$t_{\alpha\beta}(\mathbf{r};\gamma) = \frac{r_\alpha r_\beta}{r^2} f(r) + \delta_{\alpha\beta} k(r), \tag{G.14}$$

where

$$f(r) = \pi C^2 e^{-r^2} \left\{ r^4 + 1 - \frac{1-e^{-r^2}}{r^2} + \sqrt{\pi} e^{-r^2/2} \left[r^4 I_0\left(\frac{1}{2}r^2\right) + \left(r^4 - r^2\right) I_1\left(\frac{1}{2}r^2\right)\right]\right\}, \tag{G.15}$$

and

$$k(r) = \pi C^2 e^{-r^2} \frac{(1-e^{-r^2})}{2r^2}. \tag{G.16}$$

Kinetic energy tensor $t_{s,\alpha\beta}(\mathbf{r};\gamma_s)$

$$t_{s,\alpha\beta}(\mathbf{r};\gamma_s) = \frac{r_\alpha r_\beta}{r^2} h(r), \tag{G.17}$$

where

$$h(r) = \frac{1}{8\rho(r)} \left(\frac{\partial \rho}{\partial r}\right)^2. \tag{G.18}$$

Kinetic 'force' $z_\alpha(\mathbf{r};\gamma)$

$$\begin{aligned} z_\alpha(\mathbf{r};[\gamma]) &= 2\sum_\beta \nabla_\beta t_{\alpha\beta}(\mathbf{r};[\gamma]) = \frac{2r_\alpha}{r}\left[\frac{\partial(f(r)+k(r))}{\partial r} + \frac{f(r)}{r}\right] \\ &= \frac{2\pi C^2 r_\alpha}{r} e^{-r^2} \left\{ \left[-2r^5 + 5r^3 - 2r + \frac{2(1-e^{-r^2})}{r}\right] \right. \\ &\left. + \sqrt{\pi} e^{-r^2/2} \left[(-2r^5 + 4r^3) I_0\left(\frac{r^2}{2}\right) + (-2r^5 + 6r^3 - r) I_1\left(\frac{r^2}{2}\right)\right]\right\}. \end{aligned} \tag{G.19}$$

$$\begin{aligned} z(r) \underset{r\to\infty}{\sim} 2\pi C^2 e^{-r^2} & \left(-2r^5 - 4r^4 + 5r^3 + 11r^2 - 2r - \frac{33}{8} \right. \\ & \left. + \frac{2}{r} - \frac{15}{33r^2} + \frac{6}{r^3} \right) \end{aligned} \tag{G.20}$$

$$z(r) \underset{r\to 0}{\sim} 2\pi C^2 \left[\left(4 + \frac{15}{4}\sqrt{\pi}\right) r^3 - \left(\frac{17}{3} - \frac{49}{8}\sqrt{\pi}\right) r^5 \right]. \tag{G.21}$$

Kinetic 'force' $z_{s,\alpha}(\mathbf{r};\gamma_s)$

$$z_{s,\alpha}(\mathbf{r};[\gamma_s]) = 2\sum_{\beta}\nabla_\beta t_{\alpha\beta}(\mathbf{r};[\gamma_s]) = \frac{r_\alpha}{2r\rho}\left(\frac{\partial\rho}{\partial r}\right)\left[-\frac{1}{2\rho}\left(\frac{\partial\rho}{\partial r}\right)^2 + \frac{\partial^2\rho}{\partial r^2} + \frac{1}{2r}\left(\frac{\partial\rho}{\partial r}\right)\right]. \tag{G.22}$$

$$z_s(r) \underset{r\to\infty}{\sim} 2\pi c^2 e^{-r^2}\left(-2r^5 - 4r^4 + 5r^3 + 11r^2 - 2r - \frac{33}{8} + \frac{5}{r} - \frac{15}{33r^2} - \frac{5}{r^3}\right). \tag{G.23}$$

$$z_s(r) \underset{r\to 0}{\sim} 0.33r + 0.40r^3 - 0.76r^5. \tag{G.24}$$

Kinetic Energy T

$$T = 2\pi^2C^2[\frac{3}{2} + \frac{3}{8}\sqrt{2\pi}] = 0.886199\,\text{a.u.} \tag{G.25}$$

External Energy E_{ext}

$$E_{ext} = \int \rho(r)\frac{r^2}{2}d\mathbf{r} = 2\pi^2C^2\left[2 + \frac{5\sqrt{2\pi}}{8}\right] = 1.295400\,\text{a.u.} \tag{G.26}$$

Electron-interaction potential $W_{ee}(\mathbf{r})$

$$W_{ee}(\mathbf{r}) = -2\pi^{\frac{3}{2}}C^2\int_\infty^r \frac{1}{\rho(y)}e^{-\frac{3}{2}y^2}\left[2I_{\frac{1}{2}}\left(\frac{y^2}{2}\right) + \frac{3}{2}yI_0(\frac{y^2}{2}) - \frac{1}{2}yI_1\left(\frac{y^2}{2}\right)\right]dy. \tag{G.27}$$

$$W_{ee}(0) = 1.217891\,\text{a.u.} \tag{G.28}$$

Hartree potential $W_H(r)$

In two-dimensions the term $1/|\mathbf{r}-\mathbf{r}'|$ can be rewritten as

$$\begin{aligned}\frac{1}{|\mathbf{r}-\mathbf{r}'|} &= \frac{4}{\pi}\int_0^\infty\left\{\frac{1}{2}I_0(kr_<)K_0(kr_>) + \sum_{m=1}^{\infty}\cos[m(\phi-\phi')]I_m(kr_<)K_m(kr_>)\right\}\\ &= \frac{4}{\pi}\left\{\frac{1}{2r_>}K\left(\frac{r_<^2}{r_>^2}\right) + \sum_{m=1}^{\infty}\sqrt{\pi}\Gamma\left(m+\frac{1}{2}\right)\left(\frac{r_<^2}{r_>^2}\right)^m\cos[m(\phi-\phi')]\right.\\ &\quad\left.\times\, {}_2F_1\left(\frac{1}{2},\frac{1}{2}+m,m+1;\frac{r_<^2}{r_>^2}\right)\frac{1}{2r_>\Gamma(m+1)}\right\},\end{aligned} \tag{G.29}$$

where $r_<(r_>)$ is the smaller (larger)of r and r', I_i and K_i are the modified Bessel functions of $i-th$ order, ${}_2F_1(a,b,c;x)$ is the Hypergeometric function [3], and

$K(x)$ is the complete elliptic integral of the first kind [3]

$$K(k) = \int_0^1 dt[(1-t^2)(1-kt^2)]^{-1/2} = \frac{\pi}{2}\,{}_2F_1\left(\frac{1}{2}, \frac{1}{2}, 1; k\right). \qquad \text{(G.30)}$$

Using the above equations and performing the angular integral, we obtain

$$\begin{aligned} W_H(\mathbf{r}) &= \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \\ &= 4\int_0^r dr' \frac{r'}{r}\rho(r')K\left(\frac{r'^2}{r^2}\right) + 4\int_r^\infty dr' \rho(r') K\left(\frac{r^2}{r'^2}\right). \end{aligned} \qquad \text{(G.31)}$$

Expectations

$$\begin{aligned} \langle r\rangle &= \int \rho(r) r d\mathbf{r} \\ &= 4\pi^2 C^2 \int e^{-r^2}\left\{2r^2 + r^4 + \sqrt{\pi}e^{-\frac{r^2}{2}}\left[(r^2+r^4)I_0\left(\frac{1}{2}r^2\right) + r^4 I_1\left(\frac{1}{2}r^2\right)\right]\right\} dr \\ &= 4\pi^2 C^2\left[\frac{7}{8}\sqrt{\pi} + \frac{\sqrt{6}\pi}{18}\left({}_2F_1\left(\frac{3}{4}, \frac{5}{4}, 1, \frac{1}{9}\right) + {}_2F_1\left(\frac{5}{4}, \frac{7}{4}, 1, \frac{1}{9}\right)\right) + \frac{5\sqrt{6}\pi}{216}{}_2F_1\left(\frac{7}{4}, \frac{9}{4}, 2, \frac{1}{9}\right)\right] \\ &= 2.037\,89\,\text{a.u.} \end{aligned} \qquad \text{(G.32)}$$

$$\begin{aligned} \langle r^2\rangle &= \int \rho(r) r^2 d\mathbf{r} \\ &= 4\pi^2 C^2 \int e^{-r^2}\left\{2r^3 + r^5 + \sqrt{\pi}e^{-\frac{r^2}{2}}\left[(r^3+r^5)I_0\left(\frac{1}{2}r^2\right) + r^5 I_1\left(\frac{1}{2}r^2\right)\right]\right\} dr \\ &= 4\pi^2 C^2\left[2 + \frac{3\sqrt{\pi}}{8\sqrt{2}} + \frac{19\sqrt{\pi}}{32\sqrt{2}} + \frac{9\sqrt{\pi}}{32\sqrt{2}}\right] \\ &= 4\pi^2 C^2\left[2 + \frac{5\sqrt{2\pi}}{8}\right] \\ &= 2.590\,8\,\text{a.u.} \end{aligned} \qquad \text{(G.33)}$$

$$\begin{aligned} \langle\frac{1}{r}\rangle &= \int \rho(r)\frac{1}{r} d\mathbf{r} \\ &= 4\pi^2 C^2 \int e^{-r^2}\left\{2 + r^2 + \sqrt{\pi}e^{-\frac{r^2}{2}}\left[(1+r^2)I_0\left(\frac{1}{2}r^2\right) + r^2 I_1\left(\frac{1}{2}r^2\right)\right]\right\} dr \\ &= 4\pi^2 C^2[\frac{5}{4}\sqrt{\pi} + \frac{\sqrt{6}}{6}\pi{}_2F_1(\frac{1}{4}, \frac{3}{4}, 1, \frac{1}{9}) + \frac{\sqrt{6}}{18}\pi{}_2F_1(\frac{3}{4}, \frac{5}{4}, 1, \frac{1}{9}) + \frac{\sqrt{6}}{72}\pi{}_2F_1(\frac{5}{4}, \frac{7}{4}, 2, \frac{1}{9})] \\ &= 2.996\,87\text{ a.u.} \end{aligned} \qquad \text{(G.34)}$$

$$\langle\delta(\mathbf{r})\rangle = \rho(0) = 2\pi C^2[2+\sqrt{\pi}] = 0.436132\,\text{a.u.} \qquad \text{(G.35)}$$

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Appendix H
Derivation of the Kinetic-Energy-Density Tensor for the Ground State of Hooke's Atom in a Magnetic Field

In this appendix we provide an alternate derivation [1, 2] to that given in Appendix D for the kinetic-energy-density tensor $t_{\alpha\beta}[\mathbf{r};\gamma]$. We consider here the case of the ground state of Hooke's atom in a magnetic field for which the expression for $t_{\alpha\beta}[\mathbf{r};\gamma]$ is given in Appendix G, (G.14)–(G.16). The tensor $t_{\alpha\beta}[\mathbf{r};\gamma]$ is defined as

$$t_{\alpha\beta}[\mathbf{r};\gamma] = \frac{1}{4}\left[\frac{\partial^2}{\partial r_{p\alpha}\partial r_{q\beta}} + \frac{\partial^2}{\partial r_{p\beta}\partial r_{q\alpha}}\right]\gamma(\mathbf{r}_p\mathbf{r}_q)\bigg|_{\mathbf{r}_p=\mathbf{r}_q=\mathbf{r}} \tag{H.1}$$

where the single-particle density matrix is

$$\gamma(\mathbf{r}_p\mathbf{r}_q) = 2\int \psi^{\star}(\mathbf{r}_p\mathbf{r}_2)\psi(\mathbf{r}_q\mathbf{r}_2)d\mathbf{r}_2. \tag{H.2}$$

The spatial part of the singlet ground state wave function (see (9.70)) is

$$\psi(\mathbf{r}_p\mathbf{r}_2) = C(1 + |\mathbf{r}_2 - \mathbf{r}_p|)e^{-\frac{1}{2}(r_p^2+r_2^2)}, \tag{H.3}$$

with $C = 1/\pi^2(3+\sqrt{2\pi})$. Due to the symmetry of $\mathbf{r}_q$ and $\mathbf{r}_p$ in $\gamma(\mathbf{r}_p\mathbf{r}_q)$ and the fact that the wave function is real, the tensor of (H.1) reduces to

$$t_{\alpha\beta}[\mathbf{r};\gamma] = \int \frac{\partial\psi(\mathbf{r}_p\mathbf{r}_2)}{\partial r_{p\alpha}}\frac{\partial\psi(\mathbf{r}_q\mathbf{r}_2)}{\partial r_{q\beta}}d\mathbf{r}_2\bigg|_{\mathbf{r}_p=\mathbf{r}_q=\mathbf{r}}. \tag{H.4}$$

Substituting the wavefunction of (H.3) into (H.4) and employing the relations

$$\frac{\partial|\mathbf{r}_2-\mathbf{r}_p|}{\partial r_{p\alpha}} = -\frac{(r_{2\alpha}-r_{p\alpha})}{|\mathbf{r}_2-\mathbf{r}_p|}, \tag{H.5}$$

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and

$$\frac{\partial}{\partial r_{p\alpha}} e^{-\frac{1}{2}(r_p^2+r_2^2)} = -r_{p\alpha} e^{-\frac{1}{2}(r_p^2+r_2^2)}, \tag{H.6}$$

the resulting $t_{\alpha\beta}[\mathbf{r};\gamma]$ is a sum of 4 terms listed below:

$$\text{Term 1} = C^2 e^{-r^2} \int \frac{(r_{2\alpha}-r_\alpha)(r_{2\beta}-r_\beta)}{|\mathbf{r}_2-\mathbf{r}|^2} e^{-r_2^2} d\mathbf{r}_2, \tag{H.7}$$

$$\text{Term 2} = C^2 e^{-r^2} r_\beta \int \frac{(r_{2\alpha}-r_\alpha)}{|\mathbf{r}_2-\mathbf{r}|}(1+|\mathbf{r}_2-\mathbf{r}|) e^{-r_2^2} d\mathbf{r}_2, \tag{H.8}$$

$$\text{Term 3} = C^2 e^{-r^2} r_\alpha \int \frac{(r_{2\beta}-r_\beta)}{|\mathbf{r}_2-\mathbf{r}|}(1+|\mathbf{r}_2-\mathbf{r}|) e^{-r_2^2} d\mathbf{r}_2, \tag{H.9}$$

$$\text{Term 4} = C^2 e^{-r^2} r_\alpha r_\beta \int (1+|\mathbf{r}_2-\mathbf{r}|)^2 e^{-r_2^2} d\mathbf{r}_2, \tag{H.10}$$

$$= \frac{1}{2} r_\alpha r_\beta \rho(r), \tag{H.11}$$

where $\rho(r)$ is the electron density given in (G.1).

Next in (H.7) transform the coordinates to $\mathbf{r}_3 = \mathbf{r}_2 - \mathbf{r}$. Then

$$\text{Term 1} = C^2 e^{-r^2} \int \frac{r_{3\alpha} r_{3\beta}}{r_3^2} e^{-(r^2+r_3^2+2\mathbf{r}\cdot\mathbf{r}_3)} d\mathbf{r}_3. \tag{H.12}$$

Since

$$r_{3\alpha} r_{3\beta} e^{-2\mathbf{r}\cdot\mathbf{r}_3} = \frac{1}{4} \frac{\partial^2}{\partial r_\alpha \partial r_\beta} e^{-2\mathbf{r}\cdot\mathbf{r}_3}, \tag{H.13}$$

then

$$\text{Term 1} = \frac{2\pi}{4} C^2 e^{-2r^2} \frac{\partial^2}{\partial r_\alpha \partial r_\beta} \int_0^\infty \frac{1}{r_3} e^{-r_3^2} I_0(2rr_3) dr_3, \tag{H.14}$$

where

$$\int_0^{2\pi} e^{-2rr_3\cos\theta_3} d\theta_3 = 2\pi I_0(2rr_3), \tag{H.15}$$

and $I_0(r)$ the zeroth-order Bessel function. To eliminate the singularity at $r_3 = 0$, employ

$$\frac{\partial}{\partial r_\beta} I_0(2rr_3) = \frac{2r_\beta r_3}{r} I_1(2rr_3), \tag{H.16}$$

where $I_1(r)$ is the first-order Bessel function. Thus, we have

$$\text{Term 1} = \pi C^2 e^{-2r^2} \frac{\partial}{\partial r_\alpha}\left[\frac{r_\beta}{r}\int_0^\infty e^{-r_3^2} I_1(2rr_3)dr_3\right] \tag{H.17}$$

$$= \pi C^2 e^{-2r^2} \frac{\partial}{\partial r_\alpha}\left[r_\beta f_1(r)\right], \tag{H.18}$$

where

$$f_1(r) = \frac{e^{r^2}-1}{2r^2}. \tag{H.19}$$

Now for a general function $f(r)$,

$$\frac{\partial}{\partial r_\alpha}[r_\beta f(r)] = \delta_{\alpha\beta} f(r) + \frac{r_\alpha r_\beta}{r}\frac{\partial f(r)}{\partial r}. \tag{H.20}$$

Thus, (H.18) is

$$\text{Term 1} = \delta_{\alpha\beta}[\pi C^2 e^{-2r^2} f_1(r)] + \frac{r_\alpha r_\beta}{r}\left[\pi C^2 e^{-2r^2}\frac{\partial f_1(r)}{\partial r}\right]. \tag{H.21}$$

The steps to obtain Terms 2 and 3, which are identical, are the same as described above: apply the coordinate transformation, employ $r_{3\beta}\exp(-2\mathbf{r}\cdot\mathbf{r}_3) = -(\frac{1}{2})\partial [\exp -2\mathbf{r}\cdot\mathbf{r}_3]/\partial r_\beta$, and $r_\beta \partial f(r)/\partial r_\alpha = (r_\alpha r_\beta/r)\partial f(r)/\partial r$ where $f(r)$ is any function of r, to obtain

$$\text{Term }(2+3) = -\left(\frac{r_\alpha r_\beta}{r}\right)\left[2\pi C^2 e^{-2r^2}\frac{\partial f_2(r)}{\partial r}\right], \tag{H.22}$$

where

$$f_2(r) = \frac{1}{2}e^{r^2} + \frac{\sqrt{\pi}}{2}e^{\frac{1}{2}r^2} I_0\left(\frac{r^2}{2}\right). \tag{H.23}$$

On summing (H.11), (H.21) and (H.22), one obtains (G.14) for $t_{\alpha\beta}(\mathbf{r};\gamma)$.

References

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Appendix I
Derivation of the Pair–Correlation Density in the Local Density Approximation for Exchange

In this appendix we derive [1] the analytical expression for the pair–correlation density $g_x^{LDA}\{\mathbf{rr}'; \rho(\mathbf{r})\}$ in the local density approximation (LDA) for exchange by the method of Kirzhnits [2].

For a Slater determinant $\Phi\{\phi_i\}$ of orbitals $\phi_i(\mathbf{r})$, the pair–correlation density $g_x(\mathbf{rr}') = \rho(\mathbf{r}') + \rho_x(\mathbf{rr}')$. Both the density $\rho(\mathbf{r})$ and the Fermi hole charge $\rho_x(\mathbf{rr}')$ are defined in terms of the idempotent Dirac density matrix $\gamma_s(\mathbf{rr}')$, which with the spin index suppressed is

$$\gamma_s(\mathbf{rr}') = \sum_{j:\epsilon_j \leq \epsilon_F} \phi_j^*(\mathbf{r})\phi_j(\mathbf{r}'). \tag{I.1}$$

Thus, $\rho(\mathbf{r}) = \gamma_s(\mathbf{rr})$, and

$$\rho_x(\mathbf{rr}') = -|\gamma_s(\mathbf{rr}')|^2/2\rho(\mathbf{r}). \tag{I.2}$$

The orbitals $\phi_j(\mathbf{r})$ are in turn solutions of the S system type differential equation:

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}), \tag{I.3}$$

with $v_s(\mathbf{r})$ a local multiplicative operator. Therefore, to obtain $g_x^{LDA}\{\mathbf{rr}'; \rho(\mathbf{r})\}$, one must expand the density matrix $\gamma_s(\mathbf{rr}')$ in gradients of the density about the uniform electron gas result.

The density matrix is first written in terms of the Fermi energy ϵ_F as

$$\begin{aligned}\gamma_s(\mathbf{rr}') &= \sum_{j=1}^{\infty} \Theta(\epsilon_F - \epsilon_j)\phi_j^*(\mathbf{r})\phi_j(\mathbf{r}') \\ &= \sum_{j=1}^{\infty} \Theta(\epsilon_F - \hat{t} - \hat{v}_s)\phi_j^*(\mathbf{r})\phi_j(\mathbf{r}'),\end{aligned} \tag{I.4}$$

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where $\Theta(x)$ is the step function, and $\hat{t} = -\frac{1}{2}\nabla^2$ the kinetic energy operator. Defining the operator $\hat{T}_F(\mathbf{r}) = \frac{1}{2}k_F^2(\mathbf{r})$ for the local Fermi energy $T_F(\mathbf{r}) = \epsilon_F - v_s(\mathbf{r})$, the density matrix can then be written as

$$\gamma_s(\mathbf{rr}') = \Theta(\hat{T}_F - \hat{t}) \sum_{j=1}^{\infty} \phi_j^*(\mathbf{r})\phi_j(\mathbf{r}'). \tag{I.5}$$

Employing the completeness of the single–particle orbitals $\phi_j(\mathbf{r})$ i.e. $\sum_{j=1}^{\infty} \phi_j(\mathbf{r})\phi_j^*(\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$ together with the representation of the delta function $\delta(\mathbf{r} - \mathbf{r}')$ in terms of plane–wave orbitals one obtains

$$\gamma_s(\mathbf{rr}') = \frac{2}{(2\pi)^3} \int d\mathbf{k} \Theta(\hat{T}_F - \hat{t}) e^{i\mathbf{k}\cdot\mathbf{r}} e^{-i\mathbf{k}\cdot\mathbf{r}'}, \tag{I.6}$$

where the factor of 2 is for the spin. The step function $\Theta(\hat{T}_F - \hat{t}) \equiv \Theta(\hat{k}_F^2 - \hat{k}^2)$ can simply be written as $f(\hat{a} + \hat{b})$, where $f = \Theta$, $\hat{a} = -\hat{k}^2 = \nabla^2$, and $\hat{b} = k_F^2(\mathbf{r})$. Thus (I.6) becomes

$$\gamma_s(\mathbf{rr}') = \frac{2}{(2\pi)^3} \int d\mathbf{k} f(\hat{a} + \hat{b}) e^{i\mathbf{k}\cdot\mathbf{r}} e^{-i\mathbf{k}\cdot\mathbf{r}'}. \tag{I.7}$$

This leads to a mathematical problem of the following general nature: given the eigenfunction $|a\rangle$ of an operator $\hat{a}$, where $\hat{a}|a\rangle = a|a\rangle$ with $|a\rangle = e^{i\mathbf{k}\cdot\mathbf{r}}$ and $a = -k^2$, how can one compute the quantity $f(\hat{a} + \hat{b})|a\rangle$ if the operator $\hat{a}$ does not commute with $\hat{b} : [\hat{a}, \hat{b}] \neq 0$. To tackle this problem, $f(\hat{a} + \hat{b})|a\rangle$ is rewritten in terms of its Laplace (or Fourier) transformation as

$$f(\hat{a} + \hat{b})|a\rangle = \int d\tau F(\tau) \hat{E}(\tau)|a\rangle, \tag{I.8}$$

where τ is a real (or imaginary) parameter, and $\hat{E}(\tau) = e^{\tau(\hat{a}+\hat{b})}$. Since $\hat{a}$ does not commute with $\hat{b}$, the operator $\hat{E}(\tau)$ does not simply equal to $(e^{\tau\hat{a}}e^{\tau\hat{b}})$ nor $(e^{\tau\hat{b}}e^{\tau\hat{a}})$. Thus, a supplementary operator $\hat{K}$ is introduced such that $\hat{E}(\tau)$ can be put into normal form, which means a product in which all $\hat{\boldsymbol{k}}$ operators are to the right of the $\hat{\boldsymbol{r}}$ operators, so that the $\hat{\boldsymbol{k}}$ and $\hat{\boldsymbol{r}}$ operators can be treated as classical variables:

$$\hat{E}(\tau) = e^{\tau(\hat{a}+\hat{b})} = e^{\tau\hat{b}} \hat{K}(\tau) e^{\tau\hat{a}}. \tag{I.9}$$

Thus

$$\hat{E}(\tau)|a\rangle = e^{\tau\hat{b}} \hat{K}(\tau) e^{\tau\hat{a}}|a\rangle = e^{\tau\hat{b}} \hat{K}(\tau) e^{\tau a}|a\rangle, \tag{I.10}$$

and consequently

$$\hat{E}(\tau)|a\rangle = e^{\tau(a+\hat{b})}\hat{K}(\tau)|a\rangle. \tag{I.11}$$

Note that the eigenvalue a has now replaced the operator $\hat{a}$ in the argument of the exponential function, and consequently it now commutes with the operator $\hat{b}$ such that the dependence on the commutators $[\hat{a}, \hat{b}]$ appears only in the operator $\hat{K}(\tau)$.

Now in order to determine $\hat{K}(\tau)$, one must first determine an expression for the differential equation of $\hat{K}(\tau)$ by differentiating both sides of (I.9) with respect to τ. One then obtains

$$\frac{\partial \hat{K}}{\partial \tau} = e^{-\tau\hat{b}}\hat{a}e^{\tau\hat{b}}\hat{K} - \hat{K}\hat{a}. \tag{I.12}$$

The expansion of $\hat{K}$ in powers of τ is obtained by expanding both of the exponential functions of (I.12) in a Taylor series. This results in the expansion

$$\begin{aligned} e^{-\tau\hat{b}}\hat{a}e^{\tau\hat{b}} &= \left(1 - \tau\hat{b} + \frac{1}{2!}\tau^2\hat{b}^2 - \frac{1}{3!}\tau^3\hat{b}^3 + \cdots\right) \\ &\quad \hat{a}\left(1 + \tau\hat{b} + \frac{1}{2!}\tau^2\hat{b}^2 + \frac{1}{3!}\tau^3\hat{b}^3 + \cdots\right) \\ &= \hat{a} - \tau\left[\hat{b}, \hat{a}\right] + \frac{\tau^2}{2!}\left[\hat{b}, \left[\hat{b}, \hat{a}\right]\right] - \cdots \end{aligned} \tag{I.13}$$

In general form

$$e^{-\tau\hat{b}}\hat{a}e^{\tau\hat{b}} = \sum_{n=0}^{\infty}\frac{(-\tau)^n}{n!}\left[\hat{b}, \left[\hat{b}, \left[\hat{b}, \ldots, \left[\hat{b}, \hat{a}\right]\right]\ldots\right]\right] \;\; n \text{ times}. \tag{I.14}$$

By substituting (I.13) into (I.12) one obtains

$$\frac{\partial \hat{K}}{\partial \tau} = \left(\hat{a} - \tau\left[\hat{b}, \hat{a}\right] + \frac{\tau^2}{2!}\left[\hat{b}, \left[\hat{b}, \hat{a}\right]\right] - \cdots\right)\hat{K} - \hat{K}\hat{a}. \tag{I.15}$$

The solution $\hat{K}(\tau)$ of this differential equation is determined via iteration whereby the $(i+1)$th order solution of $\hat{K}$ is obtained from the ith order solution by substituting the latter into the right hand side of (I.15), and then integrating the differential equation. Thus $\hat{K}_{i+1} = \int(\partial\hat{K}_{i+1}/\partial\tau)d\tau = \int \hat{O}K_i d\tau$, where $\hat{O}\hat{K}_i$ is the entire right hand side of (I.15) with $\hat{K}_i$ substituted in it. The zeroth order solution of $\hat{K}$ implies that there is no dependence on the commutator $[\hat{b}, \hat{a}]$, and thus it is determined by substituting $\tau = 0$ into (I.9), which results in: $\hat{K}_0 = 1$. The first order solution of $\hat{K}$ which implies that only the commutator $[\hat{b}, \hat{a}]$ is considered to be non-zero, is then obtained as the integral over $\int d\tau$ of (I.12) which is then

$$\begin{aligned}\frac{\partial \hat{K}_1}{\partial \tau} &= \left(\hat{a} - \tau\left[\hat{b}, \hat{a}\right]\right)\hat{K}_0 - \hat{K}_0\hat{a} \\ &= -\tau\left[\hat{b}, \hat{a}\right],\end{aligned} \tag{I.16}$$

and which results in

$$\hat{K}_1(\tau) = 1 - \frac{1}{2}\tau^2\left[\hat{b}, \hat{a}\right]. \tag{I.17}$$

Then by using (I.8), (I.11), and (I.17) one obtains

$$\begin{aligned}f\left(\hat{a} + \hat{b}\right)|a\rangle &= \left(\int d\tau F(\tau) e^{\tau\left(a+\hat{b}\right)}\right)|a\rangle \\ &\quad - \frac{1}{2}\left(\int d\tau F(\tau)\tau^2 e^{\tau\left(a+\hat{b}\right)}\right)\left[\hat{b}, \hat{a}\right]|a\rangle.\end{aligned} \tag{I.18}$$

Since the parameter τ acts as an operator for differentiating the function f with respect to its argument, the right hand side of (I.18) can be rewritten as

$$f\left(\hat{a} + \hat{b}\right)|a\rangle = f\left(a + \hat{b}\right)|a\rangle - \frac{1}{2}f''\left(a + \hat{b}\right)\left[\hat{b}, \hat{a}\right]|a\rangle, \tag{I.19}$$

where

$$\begin{aligned} f\left(a + \hat{b}\right) &= \Theta\left(k_F^2 - k^2\right), \\ f'\left(a + \hat{b}\right) &= \delta\left(k_F^2 - k^2\right), \\ \text{and}\quad f''\left(a + \hat{b}\right) &= \delta'\left(k_F^2 - k^2\right). \end{aligned} \tag{I.20}$$

The commutator $[\hat{b}, \hat{a}]$ acting on $|a\rangle$ in the second term of the right hand side of (I.19), i.e. $[\hat{b}, \hat{a}]|a\rangle = -[k_F^2, \hat{k}^2]e^{ik\cdot\mathbf{r}}$, is evaluated by employing the relationship $\hat{\boldsymbol{k}} = \frac{1}{i}\nabla$ so that

$$\left[\hat{b}, \hat{a}\right]|a\rangle = -\left(\nabla^2 k_F^2 + 2i\nabla k_F^2 \cdot \mathbf{k}\right)e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{I.21}$$

Since we are interested in determining the density matrix $\gamma_s(\mathbf{r}\mathbf{r}')$ only to lowest order in ∇, we drop the first term in the parentheses. Then by using (I.7), (I.19)–(I.21) we obtain

$$\begin{aligned}&\gamma_s(\mathbf{r}\mathbf{r}') \\ &= \frac{2}{(2\pi)^3}\int dk\left(\Theta(k_F^2 - k^2) + \frac{1}{2}\delta'(k_F^2 - k^2)2i\nabla k_F^2 \cdot \mathbf{k}\right)e^{i\mathbf{k}\cdot(\mathbf{r}-[\mathbf{r}')}.\end{aligned} \tag{I.22}$$

The integral of this equation can easily be solved by shifting the origin of the position vector $\mathbf{r}'$ to the tip of the position vector $\mathbf{r}$, such that $\boldsymbol{R} = \mathbf{r}' - \mathbf{r}$, and then choosing the direction of $\boldsymbol{R}$ along the z-axis such that $\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}') = -kR\cos\theta$. The first term of the integral of (I.22) is evaluated in a straight forward manner, and results in

$$\frac{2}{(2\pi)^3} \int d\mathbf{k} \Theta(k_F^2 - k^2) e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} = \frac{k_F^3 j_1(k_F R)}{\pi^2 k_F R}, \tag{I.23}$$

where

$$j_1(\mathbf{x}) = \frac{\sin x - x\cos x}{x^2} \tag{I.24}$$

is the first–order spherical Bessel function. The second term of the integral of (I.22) is evaluated by partial integration and by rewriting

$$\delta'(k_F^2 - k^2) = -\frac{1}{2k}\frac{\partial}{\partial k}\delta(k_F^2 - k^2) \tag{I.25}$$

in order to first eliminate the first derivative of the delta function. Then by employing the relation

$$\delta[f(\mathbf{x})] = \sum_i \frac{\delta(x - x_i)}{|f'(x_i)|}, \tag{I.26}$$

where $f(x_i) = 0$, $f'(x_i) \neq 0$, we have

$$\delta(k_F^2 - k^2) = \frac{\delta(k - k_F)}{2k_F} + \frac{\delta(k + k_F)}{2k_F}. \tag{I.27}$$

The second delta function on the right does not contribute to the integral so that finally one obtains

$$\begin{aligned} \frac{2}{(2\pi)^3} \int d\mathbf{k} \left(\frac{1}{2}\delta'(k_F^2 - \mathbf{k}^2) 2i \boldsymbol{\nabla} k_F^2 \cdot \mathbf{k}\right) e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} \\ = (\boldsymbol{\nabla} k_F^2 \cdot \boldsymbol{R}) \sin(k_F R)/4\pi^2. \end{aligned} \tag{I.28}$$

Thus, to first order in ∇, the Dirac density matrix is

$$\gamma_s(\mathbf{r}\mathbf{r}') = \frac{k_F^3}{\pi^2}\frac{j_1(k_F R)}{k_F R} + \frac{1}{4\pi^2}(\boldsymbol{\nabla} k_F^2 \cdot \hat{\boldsymbol{R}}) \sin(k_F R), \tag{I.29}$$

with $\hat{\boldsymbol{R}} = \boldsymbol{R}/R$. It is thus evident from (I.29) that the density $\rho(\mathbf{r}) = \gamma_s(\mathbf{r}\mathbf{r})$ is of $O(\nabla^2)$ to lowest order in the gradients of the density. Since $j_1(x) \sim x/3$ for small x, then to $O(\nabla^2)$ the density $\rho(\mathbf{r})$ and local Fermi momentum $k_F(\mathbf{r})$ are related by the first term of (I.29), so that $\rho(\mathbf{r}) = k_F^3(\mathbf{r})/3\pi^2$ which is the uniform electron gas relationship.

Finally by considering the expansions of $\gamma_s(\mathbf{rr}')$ and $\rho(\mathbf{r}')$ to terms of $0(\boldsymbol{\nabla})$ assumed valid locally, one obtains from (I.28), (I.2) and (I.29) the expression for the LDA pair–correlation density as

$$g_x^{LDA}\{\mathbf{rr}'; \rho(\mathbf{r})\} = \frac{k_F^3(\mathbf{r}')}{3\pi^2} + \rho_x^{LDA}\{\mathbf{rr}'; \rho(\mathbf{r})\} \tag{I.30}$$

where the Fermi hole in the LDA is given by

$$\rho_x^{LDA}\left\{\mathbf{rr}'; \rho(\mathbf{r})\right\} = -\frac{\rho(\mathbf{r})}{2}\left[\frac{9j_1^2(k_F R)}{(k_F R)^2} + \frac{9j_0(k_F R)j_1(k_F R)}{2k_F^3}(\hat{\boldsymbol{R}} \cdot \boldsymbol{\nabla} k_F^2)\right], \tag{I.31}$$

and where

$$j_0(x) = \frac{\sin x}{x} \tag{I.32}$$

is the zeroth–order spherical Bessel function.

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