

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 **QDFTI**), 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

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 $\mathcal{F}^{\text{ext}}(\mathbf{r}t) : \mathcal{E}(\mathbf{r}t) = -\nabla v(\mathbf{r}t) + \partial[\mathbf{A}(\mathbf{r}t)/c]/\partial t$, $\mathbf{B}(\mathbf{r}t) = \nabla \times \mathbf{A}(\mathbf{r}t)$, 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 $\mathcal{F}^{\text{ext}}(\mathbf{r})$ 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 $\rho(\mathbf{r})$ 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 $v_{\text{ee}}(\mathbf{r})$ of the model fermions is provided a rigorously derived *physical* definition [10–12]. *The potential energy $v_{\text{ee}}(\mathbf{r})$ is the work required at each instant of time to move the model fermion in the force of a conservative effective field $\mathcal{F}^{\text{eff}}(\mathbf{r})$.* As the effective field $\mathcal{F}^{\text{eff}}(\mathbf{r})$ is conservative, the work done is *path-independent*. The field $\mathcal{F}^{\text{eff}}(\mathbf{r})$ is a sum of component fields. These components of $\mathcal{F}^{\text{eff}}(\mathbf{r})$, 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 $\mathcal{F}^{\text{ext}}(\mathbf{r}) = \mathcal{E}(\mathbf{r}) = -\nabla v(\mathbf{r})$, 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 $v_{\text{ee}}(\mathbf{r})$ in

which all the many-body effects are incorporated follows. *The potential energy $v_{ee}(\mathbf{r})$ is the work done to move a model fermion in the force of a conservative effective field $\mathcal{F}^{\text{eff}}(\mathbf{r})$.* As this field is conservative, the work done is *path-independent*. The components of the effective field $\mathcal{F}^{\text{eff}}(\mathbf{r})$ 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 $\mathcal{F}^{\text{ext}}(\mathbf{r}) = \mathcal{E}(\mathbf{r}) = -\nabla v(\mathbf{r})$, 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 $\mathcal{E}(\mathbf{r}) = -\nabla v(\mathbf{r})$ 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 $\alpha(\mathbf{R})$, $\mathbf{R} = \mathbf{r}_1, \dots, \mathbf{r}_N$, 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 $\mathcal{E}(\mathbf{r}) = -\nabla v(\mathbf{r})$ 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 $\mathcal{E}(\mathbf{r})$, 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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Sahni, V.

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