Chapter 1
Introduction

In a recent book [1] entitled *Quantal Density Functional Theory*, referred to from now on in abbreviated form as QDFT, I described a new theory of the electronic structure of matter. Quantal density functional theory (Q-DFT) is the description [1–8] of a quantum-mechanical system of electrons in terms of “classical” fields and their quantal sources within the framework of local effective potential energy theory. The theory is based on a similar description of Schrödinger theory in terms of quantal sources and fields [1, 9, 10]. This “classical” description of a quantum-mechanical system is based on the integral and differential virial theorems of quantum mechanics [1–5, 11]. The formal ideas underlying both time-dependent and time-independent Q-DFT as explicated in QDFT are within the Born–Oppenheimer Approximation [12]. As with Schrödinger theory, time-independent Q-DFT is a special case of the time-dependent theory. Q-DFT additionally provides insights into other traditional local effective potential energy theories. Thus, an understanding of Slater theory [13], and a rigorous physical interpretation of the Optimized Potential Method [14, 15] and of Hohenberg–Kohn–Sham density functional theory [16, 17] are also provided in QDFT. (For the rigorous physical interpretation of time-dependent Runge–Gross [18] density functional theory via Q-DFT, the reader is referred to the literature [4–6].) In QDFT, further understandings in terms of electron correlations of the Local Density Approximation of Hohenberg–Kohn–Sham density functional theory and of the discontinuity issue [19] within local effective potential energy theory are also described. Hence, QDFT is comprised of the theoretical foundations of the theory, the further elucidation of the theory by application to the ground and excited states of an exactly solvable interacting model system, its relationship to and physical interpretation of other local effective potential energy theories, and of many fundamental insights arrived at via Q-DFT of the local effective potential energy approach to electronic structure.

This volume is on various approximation methods within and selected applications of time-independent Q-DFT. To understand time-independent Q-DFT, one must first describe Schrödinger theory from the new perspective of “classical” fields and quantal sources. This new perspective on time-independent Schrödinger theory is described in Chap. 2. Thus, in addition to approximation schemes and applications, there are formal in principle components to the book: the description of Schrödinger theory from this “Newtonian” perspective; the extension of
nondegenerate state Q-DFT to degenerate states \[20\]; and the generalization \[21\] of the fundamental theorem of both time-independent density functional theory of Hohenberg–Kohn \[16\] and of its extension to time-dependent phenomenon due to Runge–Gross \[18\]. The book is written to be as independent of QDFT as possible: all the requisite physics, and the corresponding equations and sum rules relevant to time-independent Q-DFT are given in Chap. 3. For the description of time-dependent Q-DFT, and proofs of the formal framework of the theory, however, the reader is referred to QDFT.

Quantal density functional theory (Q-DFT) is a theory of both ground and excited states of a many-electron system. Nondegenerate state Q-DFT is described in Chap. 3, and degenerate state Q-DFT in Appendix A. Q-DFT provides the most general definition of local effective potential energy theory \[22\]. Consider a system of \( N \) electrons in the presence of an arbitrary time-independent external field \( \mathcal{F}^{\text{ext}}(r) \) such that \( \mathcal{F}^{\text{ext}}(r) = -\nabla v(r) \), and in an arbitrary, nondegenerate ground or excited state as described by Schrödinger theory. Q-DFT is the direct mapping from this interacting system of electrons with electron density \( \rho \), as determined by solution of the time-independent Schrödinger equation, to one of \( N \) noninteracting fermions with equivalent density \( \rho \). The model system of noninteracting fermions with equivalent density \( \rho \) is referred to as the \( S \) system. The existence of such \( S \) systems is an assumption. (The mapping to a model system of \( N \) noninteracting bosons with equivalent density \( \rho \) is discussed later.) In the mapping from the interacting electronic to the noninteracting fermion model system the state of the latter is arbitrary. Thus, for example, it is possible via Q-DFT to map an interacting system in its ground state to an \( S \) system, which is also in a ground state (see Fig. 1.1). However, the mapping could be to an \( S \) system in an excited state, again with a density which is the same as that of the interacting system in its ground state (see Fig. 1.1). Similarly, a system of electrons in an excited state can be mapped via Q-DFT to an \( S \) system that is either in its ground state or an excited state of the same configuration as that of the electrons or any other excited state with a different configuration (see Fig. 1.2). From any of these model systems, whether in a ground or excited state, the corresponding total energy \( E \) and ionization potential \( I \) (or electron affinity \( A \)) of the interacting system are also thereby obtained.

As the model fermions of the \( S \) system are noninteracting, the effective potential energy of each fermion in the presence of the external field \( \mathcal{F}^{\text{ext}}(r) \) is the same. As a consequence, this potential energy can be represented in the corresponding Schrödinger equation – the \( S \) system differential equation for the model-fermion single-particle spin-orbitals – by a local (multiplicative) potential energy operator \( v_s(r) \). The resulting wave function of the \( S \) system is then a Slater determinant of these spin-orbitals. This Slater determinantal wave function then leads to the same density \( \rho \) as that of the interacting system, and thereby to all expectations of non-differential Hermitian single-particle operators. Note that since the state of the \( S \) system is arbitrary, and one may construct an \( S \) system in a ground or excited state, there exist in principle an infinite number of local effective potential energy functions \( v_s(r) \) that will generate the density \( \rho \) of the interacting system in question. Additionally, in the mapping to a model system in an excited state, there is also a