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Viraht Sahni

CUNY Graduate School and University Center


Marlina Slamet

Sacred Heart University, slametm@sacredheart.edu

Xiao-Yin Pan

CUNY Graduate School and University Center

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Local effective potential theory: Nonuniqueness of potential and wave function

Viraht Sahni

The Graduate School of the City University of New York, New York, New York 10016

Marlina Slamet

Sacred Heart University, Fairfield, Connecticut 06432

Xiao-Yin Pan

The Graduate School of the City University of New York, New York, New York 10016

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In local effective potential energy theories such as the Hohenberg-Kohn-Sham density functional theory (HKS-DFT) and quantal density functional theory (Q-DFT), electronic systems in their *ground* or *excited* states are mapped to model systems of noninteracting fermions with equivalent density. From these models, the equivalent total energy and ionization potential are also obtained. This paper concerns (i) the *nonuniqueness* of the local effective potential energy function of the model system in the mapping from a *nondegenerate ground* state, (ii) the *nonuniqueness* of the local effective potential energy function in the mapping from a *nondegenerate excited* state, and (iii) in the mapping to a model system in an *excited* state, the *nonuniqueness* of the model system wave function. According to *nondegenerate ground* state HKS-DFT, there exists only *one* local effective potential energy function, obtained as the functional derivative of the unique ground state energy functional, that can generate the *ground* state density. Since the theorems of ground state HKS-DFT cannot be generalized to *nondegenerate excited* states, there could exist different local potential energy functions that generate the *excited* state density. The constrained-search version of HKS-DFT selects one of these functions as the functional derivative of a bidensity energy functional. In this paper, the authors show via Q-DFT that there exist an *infinite* number of local potential energy functions that can generate both the *nondegenerate ground* and *excited* state densities of an interacting system. This is accomplished by constructing model systems in configurations different from those of the interacting system. Further, they prove that the difference between the various potential energy functions lies *solely* in their correlation-kinetic contributions. The component of these functions due to the Pauli exclusion principle and Coulomb repulsion remains the same. The existence of the different potential energy functions as viewed from the perspective of Q-DFT reaffirms that there can be no equivalent to the ground state HKS-DFT theorems for excited states. Additionally, the lack of such theorems for excited states is attributable to correlation-kinetic effects. Finally, they show that in the mapping to a model system in an *excited* state, there is a nonuniqueness of the model system wave function. Different wave functions lead to the same density, each thereby satisfying the *sole* requirement of reproducing the interacting system density. Examples of the nonuniqueness of the potential energy functions for the mapping from both ground and excited states and the nonuniqueness of the wave function are provided for the exactly solvable Hooke's atom. The work of others is also discussed. © 2007 American Institute of Physics. [DOI: 10.1063/1.2733665]

I. INTRODUCTION

This paper is concerned with three aspects of nonuniqueness within local effective potential energy theories such as the Hohenberg-Kohn-Sham density functional theory^{1,2} (HKS-DFT) and quantal density functional theory (Q-DFT).³ (By HKS-DFT, we mean the determination of local effective potential energy functions via functional derivatives of energy functionals of the density.) In local effective potential energy theory,³ a system of electrons in an external field and in their *ground* or *excited* state is mapped into one of *noninteracting* fermions—the model *S* system—with equivalent density $\rho(\mathbf{r})$. The total energy E and ionization potential I are

also obtained from this model system. In this mapping, the model system, therefore, accounts for electron correlations due to the Pauli exclusion principle, Coulomb repulsion, and the correlation contribution to the kinetic energy—the correlation-kinetic effects.

The first facet of the paper concerns the *nonuniqueness* of the *local* effective potential energy of the model fermions in the mapping from a *nondegenerate ground* state of the interacting system. The second concerns the *nonuniqueness* of the local effective potential energy function in the mapping from a *nondegenerate excited* state of the interacting system. The third concerns the nonuniqueness of the wave function of the model fermions in the mapping from a *non-*

degenerate state of the interacting system to a model system in its *excited* state.

For the mapping from a *nondegenerate ground* state of the interacting system, the understanding based on HKS-DFT, a ground state theory, is that there exists *one and only one* local potential energy function that can generate the *ground* state density. As such, this potential energy function is *unique*. Thus, within the context of HKS-DFT as defined above, there is no nonuniqueness of the local effective potential energy function in the mapping from the *ground* state of the interacting system.

It is well known⁴⁻⁶ that the ground state Hohenberg-Kohn theorems cannot be generalized to excited states. This means that there could exist many local effective potential energy functions which generate the excited state density. In the mapping from a *nondegenerate excited* state of the interacting system, the constrained-search extension of HKS-DFT to *excited* states⁷ selects one local effective potential energy function that will generate the excited state density. This identification is, once again, in the context of an energy functional and its functional derivative.

However, via Q-DFT it becomes evident that in the mapping from either a *nondegenerate ground or excited* state of the interacting system, there exist an *infinite* number of local potential energy functions that can generate the corresponding state density. From each of these model systems, the energy E and ionization potential I are also obtained. Further, the difference between the various local potential energy functions is *solely* in their correlation-kinetic contributions. The contribution to these different functions of the Pauli exclusion principle and Coulomb repulsion remains the *same*. Hence, Q-DFT reaffirms that there can be no theorems for excited states similar to those of the ground state HKS-DFT theorems. Additionally, the lack of HKS-DFT theorems for excited states is a direct consequence of correlation-kinetic effects.

The understanding that there exist an infinite number of local effective potential energy functions that can reproduce the ground or excited state density of an interacting system is based on the realization arrived at via Q-DFT that the state of the model system is entirely *arbitrary*. The model system could be in a *ground* or *excited* state. The equations of Q-DFT then guarantee that the interacting system density will be reproduced.

(For completeness, we note the following with regard to the mapping from an interacting system in its *ground* state. It is well known³ that Slater determinants, other than the HKS-DFT determinant, may be constructed to reproduce the ground state density as via the Harriman⁸ construction. However, these Slater determinants are not generated by the self-consistent solution of a differential equation in which the local effective potential energy function is the functional derivative of some energy functional nor are they related to any model S system in an excited state. Thus, although one could envisage the possibility of the density of a model S system in an excited state being the same as the ground state density of an interacting system, there is no rigorous mathematical proof within the context of HKS-DFT of the existence of such a system. In other words, the mathematical basis for the

energy functionals whose functional derivative corresponds to the potential energy of a model system in an excited state and whose density is the ground state density of an interacting system is not yet understood.)

In the mapping from a *nondegenerate ground or excited* state of the interacting system to an S system in an *excited* state, there is a *nonuniqueness* of the wave function of the model fermions. Each of these different wave functions is not necessarily an eigenfunction of the various spin-symmetry operators. However, *each* wave function reproduces the interacting system density, the *sole* requirement of the model system. The different wave functions lead to different Fermi and Coulomb hole charge distributions and therefore to different Pauli and Coulomb energies. The sum of the Fermi and Coulomb holes, the Fermi-Coulomb hole charge, and the corresponding Pauli-Coulomb energy, however, is the *same* for each wave function. Thus, the total energy E as obtained by each wave function is the same.

The outline of the paper is the following. (i) What is meant by local effective potential energy theory in its *general* form is first explained. (ii) The equations of Q-DFT, which allow for the generalization of the definition of local effective potential energy theory beyond the traditional definition, are then given. (iii) Next, the HKS-DFT and Q-DFT understanding of the mapping from a nondegenerate ground state of the interacting system is discussed. An example demonstrating the nonuniqueness of the potential energy of the model fermions reproducing the interacting system ground state density, energy, and ionization potential, as obtained via Q-DFT, is given. (iv) The HKS-DFT and Q-DFT understanding of the mapping from a nondegenerate excited state of the interacting system is discussed next. Again, an example demonstrating the nonuniqueness of the potential energy of the model fermions that reproduce the excited state density, energy, and ionization potential, as obtained via Q-DFT, is given. The work of others with regard to the issue of nonuniqueness of the model system is also discussed for each mapping. (v) It is then proved via Q-DFT that in the mapping from either a nondegenerate ground or excited state of the interacting system, the difference in the potential energy functions of the model fermions is *solely* due to correlation-kinetic effects. (vi) Next, in the mapping from a nondegenerate excited state of the interacting system to a model system with the same excited state configuration, we demonstrate by example the nonuniqueness of the model S system wave function. (vii) Finally, concluding remarks are made.

II. LOCAL EFFECTIVE POTENTIAL ENERGY THEORY

The basic idea of local effective potential energy theory of electronic structure is the following. Consider a system of N electrons in a *nondegenerate ground or excited* state in some external field $\mathcal{F}^{\text{ext}}(\mathbf{r})$ such that $\mathcal{F}^{\text{ext}}(\mathbf{r}) = -\nabla v(\mathbf{r})$. Note that $v(\mathbf{r})$ is a *local* function. The corresponding time-independent Schrödinger equation is

$$\hat{H}\Psi(\mathbf{X}) = E\Psi(\mathbf{X}), \quad (1)$$

where the Hamiltonian $\hat{H} = \hat{T} + \hat{V} + \hat{U}$, $\hat{T} = -\frac{1}{2}\sum_i \nabla_i^2$, $\hat{V} = \sum_i v(\mathbf{r}_i)$, $\hat{U} = \frac{1}{2}\sum_{i,j} 1/|\mathbf{r}_i - \mathbf{r}_j|$, $\Psi(\mathbf{X})$ is the wave function, E the energy eigenvalue, and $\mathbf{X} = \mathbf{x}_1, \dots, \mathbf{x}_N$, $\mathbf{x} = \mathbf{r}\sigma$, with \mathbf{r} and σ the spatial and spin coordinates of the electron. From the solution $\Psi(\mathbf{X})$, one obtains properties of the system as the expectation of Hermitian operators. Thus, the energy $E = \langle \Psi | \hat{H} | \Psi \rangle = T + E_{\text{ext}} + E_{ee}$ is the sum of the kinetic $T = \langle \Psi | \hat{T} | \Psi \rangle$, external $E_{\text{ext}} = \langle \Psi | \hat{V} | \Psi \rangle$, and electron-interaction $E_{ee} = \langle \Psi | \hat{U} | \Psi \rangle$ energy components; the density $\rho(\mathbf{r}) = \langle \Psi | \hat{\rho} | \Psi \rangle$, where the Hermitian density operator $\hat{\rho} = \sum_i \delta(\mathbf{r} - \mathbf{r}_i)$; the single particle density matrix $\gamma(\mathbf{r}\mathbf{r}') = \langle \Psi | \hat{\gamma} | \Psi \rangle$, $\hat{\gamma} = \hat{A} + i\hat{B}$, where the Hermitian operators $\hat{A} = \frac{1}{2}\sum_j [\delta(\mathbf{r}_j - \mathbf{r})T_j(\mathbf{a}) + \delta(\mathbf{r}_j - \mathbf{r}')T_j(-\mathbf{a})]$, $\hat{B} = -(i/2)\sum_j [\delta(\mathbf{r}_j - \mathbf{r})T_j(\mathbf{a}) - \delta(\mathbf{r}_j - \mathbf{r}')T_j(-\mathbf{a})]$, $T_j(\mathbf{a})$ is a translation operator, and $\mathbf{a} = \mathbf{r}' - \mathbf{r}$. The ionization potential $I = E^{\text{ion}} - E$, where E^{ion} is the energy of the system when it is ionized.

One then *assumes* that a model system of *noninteracting fermions* with *equivalent density* $\rho(\mathbf{r})$ exists. (The model system of *noninteracting bosons* with equivalent density constitutes a special case³ and will not be discussed here.) The corresponding Schrödinger equation for the model fermions is

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right]\phi_i(\mathbf{x}) = \varepsilon_i \phi_i(\mathbf{x}), \quad i = 1, \dots, N, \quad (2)$$

where $v_s(\mathbf{r})$ is the local effective potential energy of each model fermion. On *further assuming* that these model fermions experience the same external field $\mathcal{F}^{\text{ext}}(\mathbf{r})$ as that of the electrons, we can write

$$v_s(\mathbf{r}) = v(\mathbf{r}) + v_{ee}(\mathbf{r}), \quad (3)$$

where $v_{ee}(\mathbf{r})$ is the local electron-interaction potential energy in which all the many-body effects are incorporated. These many-body effects are (i) electron correlations due to the Pauli exclusion principle, (ii) electron correlations due to Coulomb repulsion, and (iii) correlation-kinetic effects which arise due to the difference in kinetic energy between the interacting and noninteracting systems. The wave function $\Phi\{\phi_i\}$ of the model fermions may be a single Slater determinant or a linear combination of Slater determinants. From this wave function, one obtains the density $\rho(\mathbf{r}) = \langle \Phi | \hat{\rho} | \Phi \rangle = \sum_{i,\sigma} |\phi_i(\mathbf{x})|^2$, the Dirac density matrix $\gamma_s(\mathbf{r}\mathbf{r}') = \langle \Phi\{\phi_i\} | \hat{\gamma} | \Phi\{\phi_i\} \rangle = \sum_{i,\sigma} \phi_i^*(\mathbf{r}\sigma)\phi_i(\mathbf{r}'\sigma)$, and the ionization potential $I = -\varepsilon_m$, where ε_m is the highest occupied eigenvalue of Eq. (2).^{3,9-11} The energy E can be determined via Q-DFT and HKS-DFT as explained below.

Thus, by local effective potential energy theory is meant the mapping from the interacting system of electrons, whether in their *ground* or *excited* state, to one of noninteracting fermions with equivalent density $\rho(\mathbf{r})$. Other properties of the interacting system such as the energy and ionization potential can also be obtained from the model system. The issues of this paper are the nonuniqueness of the potential energy $v_s(\mathbf{r})$ or equivalently $v_{ee}(\mathbf{r})$ and of the wave function $\Phi\{\phi_i\}$ of the model fermions.

III. EQUATIONS OF QUANTAL DENSITY FUNCTIONAL THEORY

The equations of Q-DFT (Ref. 3) are based on the integral and differential virial theorems of quantum mechanics. According to Q-DFT, the potential energy $v_{ee}(\mathbf{r})$ is the work done to move the model fermion from the reference point at infinity to its position at \mathbf{r} in the force of an effective conservative field $\mathcal{F}^{\text{eff}}(\mathbf{r})$,

$$v_{ee}(\mathbf{r}) = - \int_{\infty}^{\mathbf{r}} \mathcal{F}^{\text{eff}}(\mathbf{r}') \cdot d\mathbf{l}'. \quad (4)$$

This work done is path independent since $\nabla \times \mathcal{F}^{\text{eff}}(\mathbf{r}) = 0$. The field $\mathcal{F}^{\text{eff}}(\mathbf{r})$ is the sum of an electron-interaction $\mathcal{E}_{ee}(\mathbf{r})$ and correlation-kinetic $\mathcal{Z}_t(\mathbf{r})$ field,

$$\mathcal{F}^{\text{eff}}(\mathbf{r}) = \mathcal{E}_{ee}(\mathbf{r}) + \mathcal{Z}_t(\mathbf{r}). \quad (5)$$

The field $\mathcal{E}_{ee}(\mathbf{r})$ is representative of the Pauli and Coulomb correlations, and the field $\mathcal{Z}_t(\mathbf{r})$ the correlation-kinetic effects. The energy E is then

$$E = T_s + E_{\text{ext}} + E_{ee} + T_c, \quad (6)$$

where

$$T_s = \langle \Phi | \hat{T} | \Phi \rangle = \sum_{\sigma,i} \left\langle \phi_i(\mathbf{r}\sigma) \left| -\frac{1}{2}\nabla^2 \right| \phi_i(\mathbf{r}\sigma) \right\rangle, \quad (7)$$

$$E_{\text{ext}} = \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r}, \quad (8)$$

$$E_{ee} = \int \rho(\mathbf{r})\mathbf{r} \cdot \mathcal{E}_{ee}(\mathbf{r})d\mathbf{r}, \quad (9)$$

$$T_c = \frac{1}{2} \int \rho(\mathbf{r})\mathbf{r} \cdot \mathcal{Z}_t(\mathbf{r})d\mathbf{r}. \quad (10)$$

The field $\mathcal{E}_{ee}(\mathbf{r})$ is obtained from the electron-interaction “force” $\mathbf{e}_{ee}(\mathbf{r})$ as $\mathcal{E}_{ee}(\mathbf{r}) = \mathbf{e}_{ee}(\mathbf{r})/\rho(\mathbf{r})$. The quantal source of the “force” is the pair correlation function $P(\mathbf{r}\mathbf{r}') = \langle \Psi | \hat{P} | \Psi \rangle$, where the Hermitian pair correlation operator is $\hat{P} = \sum_{i,j} \delta(\mathbf{r}_i - \mathbf{r})\delta(\mathbf{r}_j - \mathbf{r}')$. The “force” $\mathbf{e}_{ee}(\mathbf{r})$ in turn is determined via Coulomb’s law as $\mathbf{e}_{ee}(\mathbf{r}) = \int d\mathbf{r}' P(\mathbf{r}\mathbf{r}')(\mathbf{r} - \mathbf{r}')/|\mathbf{r} - \mathbf{r}'|^3$.

The field $\mathcal{Z}_t(\mathbf{r})$ is the difference between the kinetic fields of the noninteracting $\mathcal{Z}_s(\mathbf{r})$ and interacting $\mathcal{Z}(\mathbf{r})$ systems: $\mathcal{Z}_t(\mathbf{r}) = \mathcal{Z}_s(\mathbf{r}) - \mathcal{Z}(\mathbf{r})$. The interacting system field $\mathcal{Z}(\mathbf{r})$ is obtained from the kinetic “force” $\mathbf{z}(\mathbf{r}; \gamma)$ as $\mathcal{Z}(\mathbf{r}) = \mathbf{z}(\mathbf{r}; \gamma)/\rho(\mathbf{r})$. The quantal source of the “force” $\mathbf{z}(\mathbf{r}; \gamma)$ is the single particle density matrix $\gamma(\mathbf{r}\mathbf{r}')$. The force $\mathbf{z}(\mathbf{r}; \gamma)$ is defined in terms of the kinetic-energy-density tensor $t_{\alpha\beta}(\mathbf{r}; \gamma)$ as $z_\alpha(\mathbf{r}) = 2\sum_\beta \partial t_{\alpha\beta}/\partial r_\beta$, where $t_{\alpha\beta}(\mathbf{r}; \gamma) = \frac{1}{4}[\partial^2/\partial r'_\alpha \partial r''_\beta + \partial^2/\partial r'_\beta \partial r''_\alpha]\gamma(\mathbf{r}'\mathbf{r}'')|_{\mathbf{r}'=\mathbf{r}''=\mathbf{r}}$. The field $\mathcal{Z}_s(\mathbf{r}; \gamma_s)$ is similarly defined as $\mathcal{Z}_s(\mathbf{r}) = \mathbf{z}_s(\mathbf{r}; \gamma_s)/\rho(\mathbf{r})$, where $\mathbf{z}_s(\mathbf{r}; \gamma_s)$ in turn is expressed in terms of the corresponding noninteracting system tensor $t_{s,\alpha\beta}(\mathbf{r}; \gamma_s)$ and the Dirac density matrix $\gamma_s(\mathbf{r}\mathbf{r}')$. Thus, $\mathcal{Z}_s(\mathbf{r}; \gamma_s)$ is defined in terms of the orbitals $\phi_i(\mathbf{x})$ of the model system.

IV. HKS-DFT AND Q-DFT UNDERSTANDING OF THE MAPPING FROM THE GROUND STATE

Let us first consider our traditional HKS-DFT understanding of the mapping from a *nondegenerate ground state* of the interacting system to a model system also in its *nondegenerate ground state*, i.e., with the lowest orbitals occupied. This understanding comes from the Hohenberg-Kohn theorem 1 (HK1) (Refs. 1 and 3) for the interacting system described by the Schrödinger equation [Eq. (1)].

According to HK1, knowledge of the *ground state density* $\rho(\mathbf{r})$ *uniquely* determines the *local* external potential energy operator $v(\mathbf{r})$ to within an additive constant. Thus, the relationship between $v(\mathbf{r})$ and $\rho(\mathbf{r})$ is bijective: $v(\mathbf{r}) \leftrightarrow \rho(\mathbf{r})$. Now, since the kinetic energy \hat{T} and electron-interaction potential \hat{U} energy operators are known, the Hamiltonian \hat{H} of the system is known. Solution of the Schrödinger equation [Eq. (1)] then leads to the wave function $\Psi(\mathbf{X})$ of the system. The wave function $\Psi(\mathbf{X})$ is thus a functional of the *ground state density*: $\Psi = \Psi[\rho]$. [This is a general statement in that both the *ground* and *excited* state wave functions $\Psi(\mathbf{X})$ are functionals of the *ground state density*.] As such, the expectation of any operator is a *unique* functional of the ground state density $\rho(\mathbf{r})$. Thus, the energy $E = E[\rho] = \langle \Psi[\rho] | \hat{H} | \Psi[\rho] \rangle$ is such a unique functional.

The application of HK1 to the model system of noninteracting fermions in its *ground state* [see Eq. (2)] then leads to the conclusion that knowledge of the ground state density $\rho(\mathbf{r})$ *uniquely* determines the *local* effective potential energy operator $v_s(\mathbf{r})$. Hence, since the advent of HKS-DFT (Refs. 1 and 2), the understanding has been that there is *one and only one* local potential energy function that delivers the ground state density. Since $v(\mathbf{r})$ is predefined [see Eq. (3)], this means that the local electron-interaction potential energy $v_{ee}(\mathbf{r})$ is *unique*. Note that as a consequence of HK1, the corresponding single Slater determinant $\Phi\{\phi_i\}$ wave function is *unique* and that $\Phi\{\phi_i\}$ and the orbitals $\phi_i(\mathbf{x})$ are also functionals of the ground state density.

Another way to state the uniqueness of $v_{ee}(\mathbf{r})$ is through the HKS-DFT ground state energy functional expression, which is

$$E[\rho] = T_s[\rho] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + E_{ee}^{\text{HKS}}[\rho], \quad (11)$$

where $T_s[\rho]$ is the kinetic energy of the model fermions as given by Eq. (7), and $E_{ee}^{\text{HKS}}[\rho]$ is the unique HKS-DFT electron-interaction energy functional in which all the many-body effects described previously are incorporated. In HKS-DFT, the potential energy $v_{ee}(\mathbf{r})$ that generates the ground state density is given by the *functional derivative*

$$v_{ee}(\mathbf{r}) = \delta E_{ee}^{\text{HKS}}[\rho] / \delta \rho(\mathbf{r}), \quad (12)$$

taken at the ground state density. Since $E_{ee}^{\text{HKS}}[\rho]$ is a unique functional, its functional derivative $v_{ee}(\mathbf{r})$ is *unique*. Hence, to reiterate, the understanding based on HKS-DFT is that there is *one and only one* local electron-interaction potential energy function $v_{ee}(\mathbf{r})$ that can generate the ground state density $\rho(\mathbf{r})$.

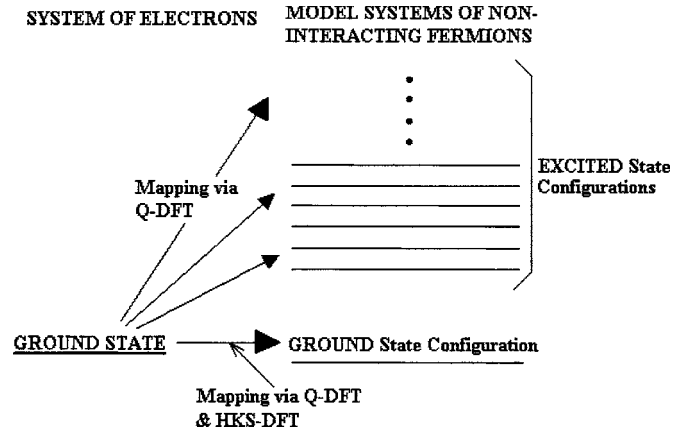


FIG. 1. A pictorial representation of the Q-DFT mapping from the ground state of the interacting system of electrons to model systems of noninteracting fermions in their ground or excited states. The HKS-DFT mapping is only from the ground state of the interacting system to a model system also in its ground state.

It becomes evident from Q-DFT,³ however, that there are an *infinite* number of local electron-interaction potential energy functions $v_{ee}(\mathbf{r})$ that can generate the ground state density. To understand this, recall that the correlation-kinetic field $Z_c(\mathbf{r})$ through its kinetic field $Z_s(\mathbf{r})$ component depends upon the orbitals $\phi_i(\mathbf{x})$ of the model fermion system. Thus, the model system can be constructed to be in its *ground state* with the lowest orbitals occupied. This is equivalent to the mapping within HKS-DFT with the same $v_{ee}(\mathbf{r})$ being obtained. However, in Q-DFT, model systems may also be constructed to be in an *excited state* with excited state orbitals occupied. A pictorial description of these cases is provided in Fig. 1. The correlation-kinetic field $Z_c(\mathbf{r})$ via the differential virial theorem (see proof in Ref. 3) then ensures that the model system, whether in a *ground* or *excited* state configuration, generates the *ground state density* $\rho(\mathbf{r})$ of the interacting system. In either case, the energy E as obtained from Eq. (6) is the *ground state energy*, and the highest occupied eigenvalue $\epsilon_m = -I$. For each model system, there is a different local effective potential energy function $v_s(\mathbf{r})$ and therefore a different electron-interaction potential energy function $v_{ee}(\mathbf{r})$. Therefore, there are an infinite number of functions $v_{ee}(\mathbf{r})$ that can generate the ground state density of the interacting system. Furthermore, the difference between these various functions is *solely* in their correlation-kinetic components. The component of these functions due to the electron-interaction field $\mathcal{E}_{ee}(\mathbf{r})$ and therefore of the correlations due to the Pauli principle and Coulomb repulsion remains the *same*. The proof of this is given in Sec. VI.

[Note that the wave functions of the model systems in the different states are also different, although they all lead to the ground state density $\rho(\mathbf{r})$.]

The nonuniqueness of the electron-interaction potential energy $v_{ee}(\mathbf{r})$ is readily demonstrated via Q-DFT (Ref. 12) for the exactly solvable interacting system of Hooke's atom.¹³⁻¹⁵ Hooke's atom, comprised of two electrons, is similar to the helium atom but with an external potential energy operator in Eq. (1) that is harmonic instead of Coulombic: $v(\mathbf{r}) = (1/2)kr^2$. The mapping via Q-DFT is from a

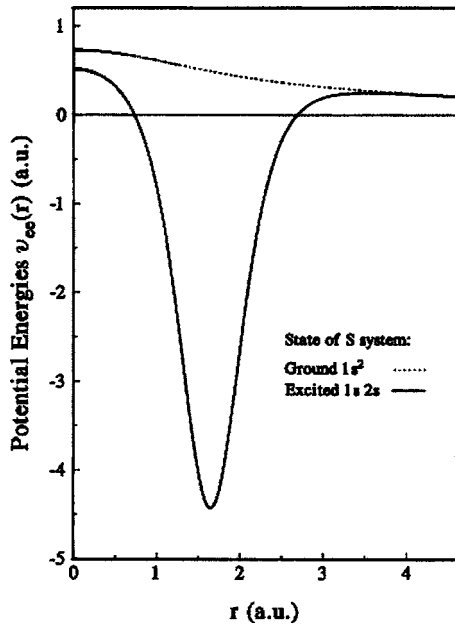


FIG. 2. The mapping from a *ground* state of Hooke's atom to two model S systems, one in its *ground* $1s^2$ state and the other in its *excited* singlet $1s2s$ state. The two corresponding electron-interaction potential energy functions $v_{ee}(\mathbf{r})$ are plotted.

ground state 1^1S of Hooke's atom to two model fermion systems with equivalent density, one in its ground 1^1S state and the other in an excited singlet 2^1S state. A ground state wave function of Hooke's atom $\Psi_{00}(\mathbf{r}_1\mathbf{r}_2)$ is

$$\Psi_{00}(\mathbf{r}_1\mathbf{r}_2) = \xi_0(\mathbf{R})\varphi_0(\mathbf{s}), \quad (13)$$

$$\xi_0(\mathbf{R}) = (2\omega/\pi)^{3/4}e^{-\omega R^2}, \quad (14)$$

$$\varphi_0(\mathbf{s}) = a_{00}e^{-\omega s^2}(1 + \omega s), \quad (15)$$

where $\mathbf{R}=(\mathbf{r}_1+\mathbf{r}_2)/2$, $\mathbf{r}=\mathbf{r}_1-\mathbf{r}_2$, $a_{00}=\omega^{5/4}(3\pi\sqrt{\pi/2}+8\pi\sqrt{\omega}+2\pi\sqrt{2\pi\omega})^{-1/2}=1/14.55670$, $k=1/4$, and $\omega=\sqrt{k}=1/2$. The ground state energy is $E=2$ a.u., and the ionization potential $I_{00}=-1.250$ a.u. For the analytical expression for the density $\rho(\mathbf{r})$, see Appendix C of Ref. 3. In Fig. 2, we plot the two model S system electron-interaction potential energy functions $v_{ee}(\mathbf{r})$ that generate this density. Both model systems lead to the same total energy E via Eq. (6). For the model S system in its ground state, the single eigenvalue $\epsilon_{1s^2}=1.250$ a.u. The two eigenvalues of the model S system in its excited singlet state are $\epsilon_{1s}=-1.799$ a.u. and $\epsilon_{2s}=1.250$ a.u.

For completeness, we note that it is also possible¹⁶ via a constrained-search approach to obtain different local functions $v_s(\mathbf{r})$ that generate the ground state density. The starting point of this approach is an approximate though accurate ground state density obtained from a variationally determined correlated wave function. Given this density, there exist numerical methods whereby a local function $v_s(\mathbf{r})$ [see Eq. (2)], which generates orbitals that reproduce the density, can be constructed self-consistently. With the model fermions occupying either the lowest or various excited states, different local functions $v_s(\mathbf{r})$ can thus be obtained. These

calculations also confirm that there exist many local functions that can generate the ground state density of an interacting system.

Other than the ground state energy functional of Eq. (11) which is unique and whose functional derivative gives rise to the $v_s(\mathbf{r})$ of HKS-DFT, there can be no energy functionals whose functional derivatives correspond to the various other $v_s(\mathbf{r})$. Hence, it is *not possible to learn from ground state HKS-DFT that there exist other local potential energy functions that can generate the ground state density of the interacting system*. The mathematically rigorous understanding that there exist an infinite number of such functions, and the explicit mapping from the interacting to the noninteracting systems to determine these functions, is achieved through Q-DFT.

There also exists a Q-DFT of Hartree-Fock and Hartree theories,³ whereby the density and energy of these theories are obtained. Thus, in a manner similar to that of the fully interacting system, there exist an infinite number of *local* functions that can generate the *exact* Hartree-Fock theory and Hartree theory densities. Most recently, it has been shown¹⁷ that there exist many local functions that can generate the same ground state Hartree-Fock theory density and energy as obtained from a *finite* basis set wave function. More generally, it has been shown¹⁸ that the bijective mapping between the external potential energy $v(\mathbf{r})$ and the wave function $\Psi(\mathbf{X})$ breaks down if the wave function is represented by a finite basis set.

V. HKS-DFT AND Q-DFT UNDERSTANDING OF THE MAPPING FROM AN EXCITED STATE

There is no equivalent HK1 for excited states.⁴⁻⁶ In other words, for the interacting system defined by Eq. (1), knowledge of the excited state density $\rho_e(\mathbf{r})$ does not uniquely determine the external potential energy operator $v(\mathbf{r})$. Thus, there is no one-to-one correspondence between $v(\mathbf{r})$ and $\rho_e(\mathbf{r})$ and therefore no bijective correspondence between the excited state density and the Hamiltonian: $\rho_e(\mathbf{r}) \not\leftrightarrow \hat{H}$. As a consequence, the excited state wave function $\Psi_e(\mathbf{X})$ is *not* a unique functional of the excited state density $\rho_e(\mathbf{r})$: $\Psi_e(\mathbf{X}) \neq \Psi_e[\rho_e]$. Hence, excited state properties are *not* unique functionals of the excited state density. (It has been proved⁶ that HKS-DFT can be generalized to the lowest energy state of a given symmetry, thus encompassing first excited states with symmetries that differ from ground states.)

For the model system of noninteracting fermions, the implication of the lack of HK1 for excited states means that there is *no unique* local effective potential energy function $v_s(\mathbf{r})$ that would generate orbitals leading to the excited state density $\rho_e(\mathbf{r})$.

Using constrained-search arguments, it has been shown⁷ that for a specific excited state k of density ρ_k , there exists a *bidensity* energy functional $E_k[\rho, \rho_g]$, where $\rho_g(\mathbf{r})$ is the *exact* ground state density, whose value at $\rho=\rho_k$ is the energy E_k of that state. For the model system of noninteracting fermions, this means that there exists a *bidensity* electron-interaction energy functional $E_{k,ee}^{\text{HKS}}[\rho, \rho_g]$, whose functional derivative evaluated at the excited state density ρ_k is the local

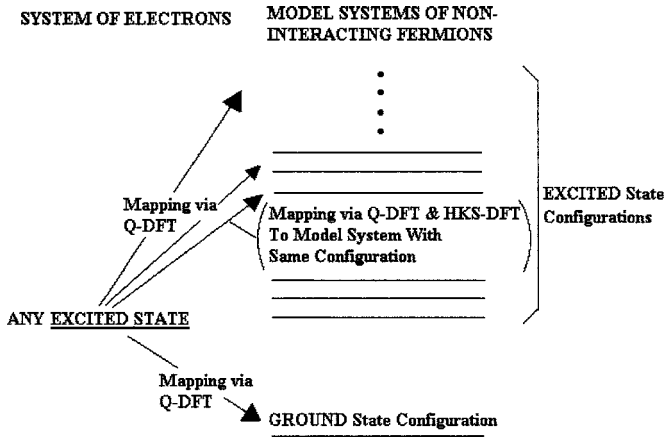


FIG. 3. A pictorial representation of the Q-DFT mapping from any excited state of the interacting system of electrons to model systems of noninteracting fermions in their ground or excited states. The HKS-DFT mapping is only from an excited state of the interacting system to a model system in an excited state of the same configuration.

electron-interaction potential energy function $v_{ee}(\mathbf{r})$ that generates orbitals which reproduce the excited state density,

$$v_{ee}(\mathbf{r}) = \delta E_{k,ee}^{\text{HKS}}[\rho, \rho_g] / \delta \rho(\mathbf{r})|_{\rho=\rho_k}. \quad (16)$$

Note that in this framework, one is mapping to a model system with the *same excited state configuration* as that of the interacting system. In this manner, one local effective potential energy function that generates the excited state density of an interacting system is selected.

Q-DFT is based on the integral and differential virial theorems of quantum mechanics. Hence, just as in quantum mechanics, the framework of Q-DFT as described in Sec. III is the *same* for both ground and excited states. Therefore, for the same reasons as described in Sec. IV, viz., because of the dependence of the Correlation-Kinetic field $Z_{ic}(\mathbf{r})$ on the orbitals of the model system, it is possible to map an interacting system in *any nondegenerate excited* state to model systems of noninteracting fermions that are in a *ground* or *excited* state. In either case, the excited state density $\rho_e(\mathbf{r})$ of the interacting system is generated by the model system. The model system is *not restricted* to being in the same configuration as that of the interacting system. For a pictorial representation, see Fig. 3. The energy obtained from Eq. (6) is $E=E_k$, the energy of the k th excited state of the interacting system. Furthermore, irrespective of whether the model system is constructed to be in a ground or excited state, the highest occupied eigenvalue is the negative of the ionization potential: $\epsilon_m = -I$. Thus, there are an *infinite* number of local effective potential energy functions that can generate the density of an interacting system in an excited state. The difference between these functions lies in their correlation-kinetic contributions. The Pauli and Coulomb correlation components of these functions remain the same. The proof is given in Sec. VI.

The nonuniqueness of the electron-interaction potential energy $v_{ee}(\mathbf{r})$ for the mapping from an excited state of the interacting system can also be demonstrated^{3,19-21} via Hooke's atom. In this case, the mapping is from an excited singlet 2^1S state of Hooke's atom to two model S systems,

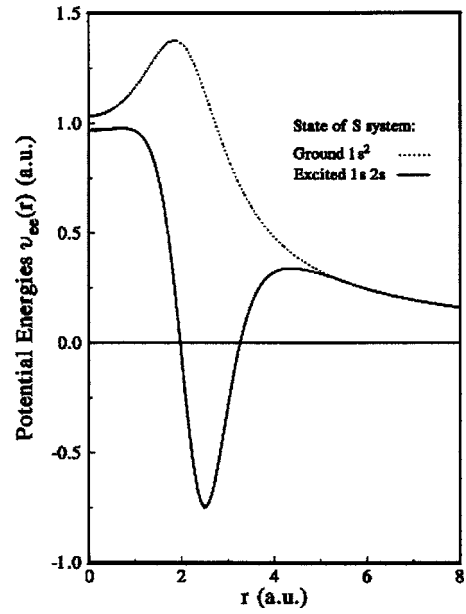


FIG. 4. The mapping from an *excited* singlet 2^1S state of Hooke's atom to two model S systems, one in an *excited* singlet 2^1S state and the other in a *ground* 1^1S singlet state. The two corresponding electron-interaction potential energy functions $v_{ee}(\mathbf{r})$ are plotted.

one in an excited state of the same 2^1S configuration and the other in a ground 1^1S state. An excited singlet state of Hooke's atom $\psi_{01}(\mathbf{r}_1\mathbf{r}_2)$ is

$$\psi_{01}(\mathbf{r}_1\mathbf{r}_2) = \xi_0(\mathbf{R})\varphi_1(\mathbf{s}), \quad (17)$$

$$\varphi_1(\mathbf{s}) = a_{01}e^{-\omega s^2/4} \left[1 + C_1\sqrt{\omega/2}s + C_2\frac{\omega}{2}s^2 + C_3\left(\frac{\omega}{2}\right)^{3/2}s^3 \right], \quad (18)$$

where $a_{01} = \omega^{3/4} [8\sqrt{2}\pi(C_1 + 2C_1C_2 + 2C_3 + 6C_2C_3) + \pi\sqrt{2}\pi(\frac{15}{2}C_2^2 + \frac{105}{4}C_3^2 + 3C_1^2 + 6C_2 + 15C_1C_3 + 2)]^{-1/2} = 1/13.21931$, $C_1 = 1.146884$, $C_2 = -0.561569$, $C_3 = -0.489647$, $k = 0.144498$, and $\omega = \sqrt{k} = 0.380129$. For the analytical expression for the density, see Appendix C of Ref. 3. The energy of this state is $E = 2.281$ a.u., and the ionization potential $I_{01} = -1.711$ a.u. In Fig. 4, we plot the two model S system electron-interaction potential energy functions $v_{ee}(\mathbf{r})$ that generate this density. Both model systems lead to the same total energy E via Eq. (6). The two eigenvalues of the model S system in its excited singlet state are $\epsilon_{1s} = 0.573$ a.u. and $\epsilon_{2s} = 1.711$ a.u. For the model S system in its ground state, the single eigenvalue $\epsilon_{1s,2} = 1.711$ a.u. Note that in the mapping to a model system in its ground state, the number of orbitals to be determined is less than for the mapping to the excited state.

The existence of the different functions $v_s(\mathbf{r})$ that generate the excited state density of an interacting system confirms the lack of HK1 for excited states. Furthermore, *the lack of HK1 for excited states may be attributed to correlation-kinetic effects*. In other words, it is because of the correlation-kinetic component of $v_s(\mathbf{r})$, which changes as a function of the configuration of the model system, that there is no HK1 for excited states.

Recently, it has been shown^{22,23} that for the model noninteracting system in a *fixed excited state configuration*, there

are *different* local effective potential energy functions $v_s(\mathbf{r})$ that generate the *same* density. This further confirms that there is no HK1 for excited states. These different potentials are related to the positive eigenvalues of the nonlocal susceptibility for excited states. It is stated that this relationship is also applicable to interacting systems. However, such a mapping from an interacting system to a model system in a fixed excited state configuration, with different local effective potential energy functions that generate the same density, has not been demonstrated. It is also possible,²³ employing the constrained-search approach of working backward from an excited state density, to construct such different potential energy functions that generate the same density for a fixed excited state configuration. The implication of the work in Refs. 22 and 23 is that in addition to the bidensity energy functional of Ref. 7, there could exist other energy functionals whose functional derivatives correspond to these different local potential energy functions.

It is important to note that the different potential energy functions for *fixed excited state configuration* are *all* equally valid representations of the model system. Neither one of these functions is superior to the rest. This is because each potential energy function satisfies the sole requirement of the local effective potential energy theory that the model system reproduce the density. The fact²³ that one such function satisfies an arbitrarily chosen criterion, such as that proposed in Ref. 7, better than another is irrelevant. In addition, there is no requirement within the local effective potential energy theory that the model S system be created in the image of the interacting system. The *sole* requirement is that the model system reproduces the interacting system density, whether ground or excited and, from this model, allows for the determination of the energy and ionization potential. As noted previously, it is also possible to construct model systems of *noninteracting bosons* that reproduce the density of an interacting system of electrons. In this instance, one is, in fact, employing model particles with properties that are entirely different from those of electrons.

VI. PROOF

In the construction of S systems that reproduce the ground or excited state density of the interacting system, it is *assumed* that the external field $\mathcal{F}^{\text{ext}}(\mathbf{r}) = -\nabla v(\mathbf{r})$ is the *same* for both the interacting and model fermions. This in turn leads³ to the interpretation of Eq. (4) for the corresponding electron-interaction potential energy $v_{ee}(\mathbf{r})$ of the S systems. Here, we prove that the $v_{ee}(\mathbf{r})$ of the different S systems, whether they correspond to S systems in *different* states or whether they are different S systems corresponding to the *same* excited state configuration,^{22,23} 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 state 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 $\mathcal{F}^{\text{ext}}(\mathbf{r}) = -\nabla v(\mathbf{r})$ reproduce the same density $\rho(\mathbf{r})$. For the S system, the differential

equation and the corresponding local effective potential energy $v_s(\mathbf{r})$ are defined by Eqs. (2) and (3), respectively. The electron-interaction potential energy $v_{ee}(\mathbf{r})$ is the work done in Eq. (4).

For the S' system, the differential equation is

$$\left[-\frac{1}{2}\nabla^2 + v'_s(\mathbf{r})\right]\phi'_i(\mathbf{x}) = \epsilon_i\phi'_i(\mathbf{x}), \quad (19)$$

where the corresponding local potential energy $v'_s(\mathbf{r})$ is

$$v'_s(\mathbf{r}) = v(\mathbf{r}) + v'_{ee}(\mathbf{r}), \quad (20)$$

with $v'_{ee}(\mathbf{r})$ being the electron-interaction potential energy. The resulting “quantal Newtonian” first law or differential virial theorem³ is

$$\mathcal{F}^{\text{ext}}(\mathbf{r}) + \mathcal{F}'^{\text{int}}(\mathbf{r}) = 0, \quad (21)$$

where $\mathcal{F}'^{\text{int}}(\mathbf{r})$ is the internal field of the S' model fermions,

$$\mathcal{F}'^{\text{int}}(\mathbf{r}) = -\nabla v'_{ee}(\mathbf{r}) - \mathcal{D}(\mathbf{r}) - \mathcal{Z}'_s(\mathbf{r}), \quad (22)$$

with $\mathcal{Z}'_s(\mathbf{r})$ defined in a manner similar to that of $\mathcal{Z}_s(\mathbf{r})$ but in terms of the S' system orbitals $\phi'_i(\mathbf{x})$. The differential density field $\mathcal{D}(\mathbf{r}) = \mathbf{d}(\mathbf{r})/\rho(\mathbf{r})$, $\mathbf{d}(\mathbf{r}) = -\frac{1}{4}\nabla\nabla^2\rho(\mathbf{r})$, is the same as for the interacting system.

The “quantal Newtonian” first law for the interacting system is

$$\mathcal{F}^{\text{ext}}(\mathbf{r}) + \mathcal{F}^{\text{int}}(\mathbf{r}) = 0, \quad (23)$$

where

$$\mathcal{F}^{\text{int}}(\mathbf{r}) = -\mathcal{E}_{ee}(\mathbf{r}) - \mathcal{D}(\mathbf{r}) - \mathcal{Z}(\mathbf{r}), \quad (24)$$

with $\mathcal{E}_{ee}(\mathbf{r})$ and $\mathcal{Z}(\mathbf{r})$ defined as in Sec. III. A comparison of Eqs. (22) and (24) then yields

$$v'_{ee}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} [\mathcal{E}_{ee}(\mathbf{r}') + \mathcal{Z}'_t(\mathbf{r}')] \cdot d\mathbf{l}', \quad (25)$$

where the correlation-kinetic field $\mathcal{Z}'_t(\mathbf{r})$ is

$$\mathcal{Z}'_t(\mathbf{r}) = \mathcal{Z}'_s(\mathbf{r}) - \mathcal{Z}(\mathbf{r}). \quad (26)$$

The difference between the $v_{ee}(\mathbf{r})$ and $v'_{ee}(\mathbf{r})$ of the S and S' systems is then

$$v_{ee}(\mathbf{r}) - v'_{ee}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} [\mathcal{Z}'_t(\mathbf{r}') - \mathcal{Z}'_t(\mathbf{r}')] \cdot d\mathbf{l}' \quad (27)$$

or equivalently

$$v_{ee}(\mathbf{r}) - v'_{ee}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} [\mathcal{Z}_s(\mathbf{r}') - \mathcal{Z}'_s(\mathbf{r}')] \cdot d\mathbf{l}'. \quad (28)$$

Note that both Eqs. (27) and (28) are independent of the electron-interaction field $\mathcal{E}_{ee}(\mathbf{r})$. As such, the contribution of the field $\mathcal{E}_{ee}(\mathbf{r})$ to both $v_{ee}(\mathbf{r})$ and $v'_{ee}(\mathbf{r})$ is the same. Thus, the difference between the two electron-interaction potential energy functions arises *solely* due to the difference in their correlation-kinetic or equivalently their kinetic fields. This completes the proof.

VII. NONUNIQUENESS OF WAVE FUNCTION OF THE S SYSTEM IN AN EXCITED STATE

In the mapping from the *ground*²⁴ or *excited* state of the interacting system to a model S system in an *excited* state, there is a nonuniqueness of the S system wave function. Consider, for example, a two-electron atom and a mapping to an S system in the excited singlet 2^1S state. The singlet 2^1S state means that one electron is in the $1s$ state, and the other of opposite spin in the $2s$ state. There are three different S system wave functions that lead to the *same* density as that of the atom. Two of these are single Slater determinants of the S system orbitals, and the third is a linear combination of these Slater determinants. The linear combination wave function is an eigenfunction of both \hat{S}^2 and \hat{S}_z , where \hat{S} is the spin operator. The single Slater determinants, however, are each only eigenfunctions of \hat{S}_z . Is the former a more appropriate choice of the wave function of the S system? The answer is that it is not more or less appropriate than the single Slater determinants. This is because all that is required of the model system is that it reproduces the density of the interacting system. It is irrelevant from which wave functions the density is obtained. As noted previously, local effective potential energy theory does not require the model system to be constructed in the image of the interacting one. However, based on the choice of the wave functions, the corresponding Fermi and Coulomb holes, and therefore the resulting Pauli and Coulomb energies, will differ. Their sum, the Fermi-Coulomb holes, and the corresponding Pauli-Coulomb energy remain unchanged. (Note that in local effective potential energy theories, such as Q-DFT and HKS-DFT, one defines³ a Fermi hole charge even for singlet states.)

Prior to demonstrating this nonuniqueness, the various charge distributions noted above and the resulting fields, potential energies, and total energy components need to be defined. The quantum-mechanical Fermi-Coulomb hole charge $\rho_{xc}(\mathbf{r}\mathbf{r}')$ is defined as the *nonlocal* component of the pair correlation density $g(\mathbf{r}\mathbf{r}')$: $g(\mathbf{r}\mathbf{r}') = \rho(\mathbf{r}') + \rho_{xc}(\mathbf{r}\mathbf{r}')$. The Fermi hole charge $\rho_x(\mathbf{r}\mathbf{r}')$ is defined as the nonlocal component of the S system pair correlation density $g_s(\mathbf{r}\mathbf{r}')$: $g_s(\mathbf{r}\mathbf{r}') = \rho(\mathbf{r}') + \rho_x(\mathbf{r}\mathbf{r}')$. The nonlocal Coulomb hole charge $\rho_c(\mathbf{r}\mathbf{r}')$ is defined as the difference between $g(\mathbf{r}\mathbf{r}')$ and $g_s(\mathbf{r}\mathbf{r}')$: $\rho_c(\mathbf{r}\mathbf{r}') = g(\mathbf{r}\mathbf{r}') - g_s(\mathbf{r}\mathbf{r}') = \rho_{xc}(\mathbf{r}\mathbf{r}') - \rho_x(\mathbf{r}\mathbf{r}')$. The total charge of $\rho_{xc}(\mathbf{r}\mathbf{r}')$ and $\rho_x(\mathbf{r}\mathbf{r}')$ is negative unity, and that of $\rho_c(\mathbf{r}\mathbf{r}')$ is zero. As a result of these definitions, the electron-interaction field $\mathcal{E}_{ee}(\mathbf{r})$ may be written as the sum of its Hartree $\mathcal{E}_H(\mathbf{r})$ and Pauli-Coulomb $\mathcal{E}_{xc}(\mathbf{r})$ or Pauli $\mathcal{E}_x(\mathbf{r})$ and Coulomb $\mathcal{E}_c(\mathbf{r})$ components: $\mathcal{E}_{ee}(\mathbf{r}) = \mathcal{E}_H(\mathbf{r}) + \mathcal{E}_{xc}(\mathbf{r}) = \mathcal{E}_H(\mathbf{r}) + \mathcal{E}_x(\mathbf{r}) + \mathcal{E}_c(\mathbf{r})$. Assuming the S system to be of symmetry such that the fields $\mathcal{E}_{ee}(\mathbf{r})$ and $\mathcal{Z}_t(\mathbf{r})$ are separately conservative, the potential energy $v_{ee}(\mathbf{r})$ may be written as the sum $v_{ee}(\mathbf{r}) = W_H(\mathbf{r}) + W_{xc}(\mathbf{r}) + W_{t_c}(\mathbf{r}) = W_H(\mathbf{r}) + W_x(\mathbf{r}) + W_c(\mathbf{r}) + W_{t_c}(\mathbf{r})$. Here, the Hartree $W_H(\mathbf{r})$, Pauli-Coulomb $W_{xc}(\mathbf{r})$, Pauli $W_x(\mathbf{r})$, Coulomb $W_c(\mathbf{r})$, and correlation-kinetic $W_{t_c}(\mathbf{r})$ potential energies are, respectively, the work done in the fields $\mathcal{E}_H(\mathbf{r})$, $\mathcal{E}_{xc}(\mathbf{r})$, $\mathcal{E}_x(\mathbf{r})$, $\mathcal{E}_c(\mathbf{r})$, and $\mathcal{Z}_t(\mathbf{r})$. The electron-interaction energy E_{ee} may then be written as a sum of its Hartree E_H , Pauli-Coulomb E_{xc} (or Pauli E_x and Coulomb

E_c), and correlation-kinetic T_c components: $E_{ee} = E_H + E_{xc} + T_c = E_H + E_x + E_c + T_c$.

Consider the *excited* singlet 2^1S state $\psi_{01}(\mathbf{x}_1\mathbf{x}_2)$ of Hooke's atom as defined by Eq. (17). This wave function is an eigenfunction of both the \hat{S}^2 and \hat{S}_z operators. We map this state of the interacting system via Q-DFT to an S system also in its *excited* singlet 2^1S state. The singlet state is as defined above. The self-consistent solution of Eq. (2) that leads to the $v_{ee}(\mathbf{r})$ of Fig. 4 (solid line) generates the two spin-orbitals $\varphi_{1s}(\mathbf{x})$ and $\varphi_{2s}(\mathbf{x})$. The two single Slater determinants

$$\Phi_1(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{1s}(\mathbf{r}_1)\alpha(\sigma_1) & \psi_{1s}(\mathbf{r}_2)\alpha(\sigma_2) \\ \psi_{2s}(\mathbf{r}_1)\beta(\sigma_1) & \psi_{2s}(\mathbf{r}_2)\beta(\sigma_2) \end{vmatrix} \quad (29)$$

and

$$\Phi_2(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{1s}(\mathbf{r}_1)\beta(\sigma_1) & \psi_{1s}(\mathbf{r}_2)\beta(\sigma_2) \\ \psi_{2s}(\mathbf{r}_1)\alpha(\sigma_1) & \psi_{2s}(\mathbf{r}_2)\alpha(\sigma_2) \end{vmatrix}, \quad (30)$$

and the wave function $\Phi_3(\mathbf{x}_1\mathbf{x}_2)$ constructed from the linear combination of these Slater determinants

$$\Phi_3(\mathbf{x}_1\mathbf{x}_2) = \frac{1}{\sqrt{2}}(\Phi_1 - \Phi_2), \quad (31)$$

$$= \frac{1}{2}[\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2) + \psi_{1s}(\mathbf{r}_2)\psi_{2s}(\mathbf{r}_1)] \\ \times [\alpha(\sigma_1)\beta(\sigma_2) - \alpha(\sigma_2)\beta(\sigma_1)], \quad (32)$$

all lead to the same excited state density as that due to $\psi_{01}(\mathbf{x}_1\mathbf{x}_2)$. Furthermore, each wave function leads to the same value for the total energy. The wave function $\Phi_3(\mathbf{x}_1\mathbf{x}_2)$ is an eigenfunction of both \hat{S}^2 and \hat{S}_z , whereas the two single Slater determinants are eigenfunctions only of \hat{S}_z . Furthermore, $\Phi_3(\mathbf{x}_1\mathbf{x}_2)$ is a product of a symmetrical spatial part and an antisymmetric spin part. In standard quantum mechanics, it is this wave function that defines the singlet 2^1S state. However, in local effective potential energy theories, there are no constraints on the S system wave function other than to reproduce the density of the interacting system. Hence, from the perspective of constructing model systems that generate the density, all three wave functions are equally valid.

A. The single Slater determinant case

The two single Slater determinants $\Phi_1(\mathbf{x}_1\mathbf{x}_2)$ and $\Phi_2(\mathbf{x}_1\mathbf{x}_2)$ lead to the same expression for the Fermi hole $\rho_x^{\text{SD}}(\mathbf{r}\mathbf{r}')$, where the superscript SD stands for single determinant. In Fig. 5, the Fermi hole $\rho_x^{\text{SD}}(\mathbf{r}\mathbf{r}')$ is plotted for electron positions at $r=0, 0.5, 1.0, 2.0,$ and 7.0 a.u. (In the figure, a cross section of the holes is plotted. The electron is along the z axis corresponding to $\theta=0^\circ$. The cross sections plotted correspond to $\theta'=0^\circ$ with respect to the nucleus-electron direction. The graph for $r'<0$ is the structure for $\theta'=\pi$ and $r'>0$.) These holes are negative with a total charge of negative unity. Further, they are spherically symmetric about the nucleus for all electron positions because the orbitals $\psi_{1s}(\mathbf{r})$ and $\psi_{2s}(\mathbf{r})$ are spherically symmetric. The corresponding Coulomb holes $\rho_c^{\text{SD}}(\mathbf{r}\mathbf{r}')$ for these electron positions are plotted in Fig. 6. With the exception of the electron position at

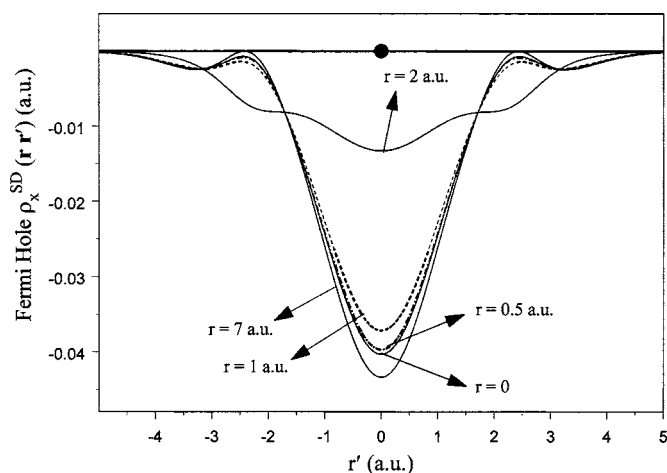


FIG. 5. Cross section of the Fermi holes $\rho_x^{\text{SD}}(\mathbf{r}, \mathbf{r}')$ as a function of electron position at $\mathbf{r}=0, 0.5, 1.0, 2.0,$ and 7.0 a.u. as determined from a single Slater determinant (SD).

the nucleus, the Coulomb holes are not spherically symmetric about the nucleus. The holes are both positive and negative, with total charge of zero. Observe the cusps in the Coulomb holes at the electron position evident for electron positions near the nucleus.

The Pauli $\mathcal{E}_x(\mathbf{r})$ and Coulomb $\mathcal{E}_c(\mathbf{r})$ fields determined from the Fermi $\rho_x^{\text{SD}}(\mathbf{r}, \mathbf{r}')$ and Coulomb $\rho_c^{\text{SD}}(\mathbf{r}, \mathbf{r}')$ holes, respectively, are plotted in Fig. 7. For comparison, the electron interaction $\mathcal{E}_{ee}(\mathbf{r})$ and its Hartree $\mathcal{E}_H(\mathbf{r})$ component are also plotted. The asymptotic structure of these fields is also given in the figures. The Pauli field $\mathcal{E}_x(\mathbf{r})$ is negative, as expected because its quantal source charge $\rho_x^{\text{SD}}(\mathbf{r}, \mathbf{r}')$ is negative. The Coulomb field $\mathcal{E}_c(\mathbf{r})$ is both positive and negative because of its quantal source $\rho_c^{\text{SD}}(\mathbf{r}, \mathbf{r}')$. Observe that both fields $\mathcal{E}_x(\mathbf{r})$ and $\mathcal{E}_c(\mathbf{r})$ exhibit shell structure.

The Pauli $W_x(\mathbf{r})$ and Coulomb $W_c(\mathbf{r})$ potential energies together with the electron interaction $W_{ee}(\mathbf{r})=W_H(\mathbf{r})+W_x(\mathbf{r})+W_c(\mathbf{r})$ and its Hartree $W_H(\mathbf{r})$ component as determined from their respective fields are plotted in Fig. 8. Because the fields $\mathcal{E}_x(\mathbf{r})$ and $\mathcal{E}_c(\mathbf{r})$ vanish at the nucleus, the potential energies $W_x(\mathbf{r})$ and $W_c(\mathbf{r})$ have zero slope there.

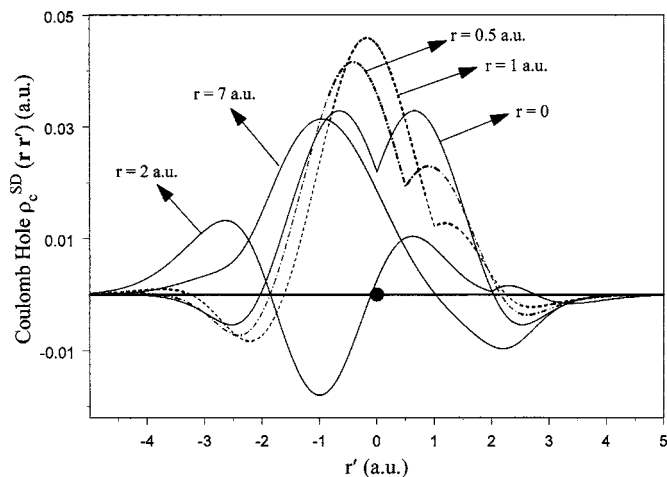


FIG. 6. Cross section of the Coulomb holes $\rho_c^{\text{SD}}(\mathbf{r}, \mathbf{r}')$ for electron position at $\mathbf{r}=0, 0.5, 1.0, 2.0,$ and 7.0 a.u. with the Fermi hole $\rho_x^{\text{SD}}(\mathbf{r}, \mathbf{r}')$ as determined from a single Slater determinant (SD).

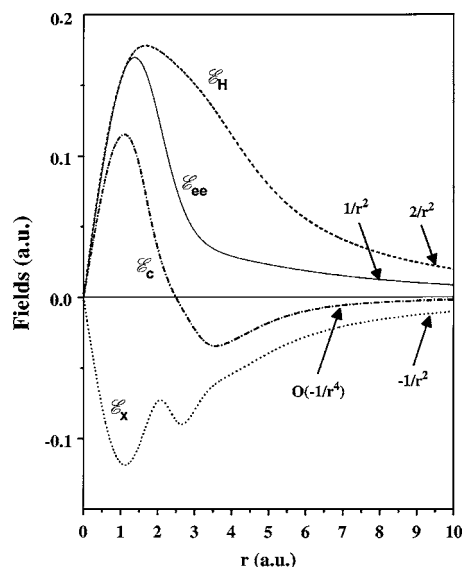


FIG. 7. The electron-interaction $\mathcal{E}_{ee}(\mathbf{r})$ field and its Hartree $\mathcal{E}_H(\mathbf{r})$, Pauli $\mathcal{E}_x(\mathbf{r})$, and Coulomb $\mathcal{E}_c(\mathbf{r})$ field components. The fields $\mathcal{E}_x(\mathbf{r})$ and $\mathcal{E}_c(\mathbf{r})$ are a consequence of the Fermi hole $\rho_x^{\text{SD}}(\mathbf{r}, \mathbf{r}')$ determined via a single Slater determinant.

The two shells are also evident in the $W_x(\mathbf{r})$ and $W_c(\mathbf{r})$ curves. The asymptotic structure of the various potential energy functions is indicated in the figure.

The corresponding Pauli E_x and Coulomb E_c energies are quoted in Table I indicated by (SD). Note that the Pauli energy is two orders of magnitude greater than the Coulomb energy. The other components of the total energy are also noted in the table.

B. The linear combination of Slater determinant case

For the wave function $\Phi_3(\mathbf{x}_1, \mathbf{x}_2)$ formed by a linear combination of $\Phi_1(\mathbf{x}_1, \mathbf{x}_2)$ and $\Phi_2(\mathbf{x}_1, \mathbf{x}_2)$, the expression for the Fermi hole $\rho_x^{\text{LCD}}(\mathbf{r}, \mathbf{r}')$ denoted by LCD differs from that of $\rho_x^{\text{SD}}(\mathbf{r}, \mathbf{r}')$ and, hence, so does the corresponding Coulomb hole $\rho_c^{\text{LCD}}(\mathbf{r}, \mathbf{r}')$. The Fermi $\rho_x^{\text{LCD}}(\mathbf{r}, \mathbf{r}')$ and Coulomb $\rho_c^{\text{LCD}}(\mathbf{r}, \mathbf{r}')$

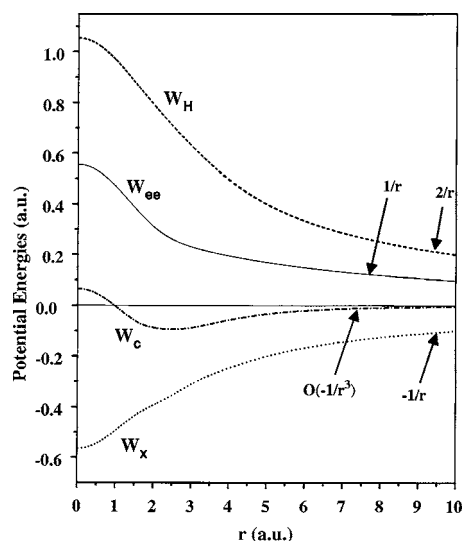


FIG. 8. The electron interaction $W_{ee}(\mathbf{r})$ potential energy, and its Hartree $W_H(\mathbf{r})$, Pauli $W_x(\mathbf{r})$, and Coulomb $W_c(\mathbf{r})$ components determined as the work done in the corresponding fields of Fig. 7.

TABLE I. The component of the total energy for the mapping from an excited singlet 2^1S state of Hooke's atom to an S system in its first excited singlet 2^1S state. The Pauli E_x energy as determined from a single Slater determinant (SD) and from a linear combination of Slater determinants (LCD), and the corresponding Coulomb E_c energies are also quoted.

Property (a.u.)	S system in 2^1S state
E_{ext}	1.052 371
E_{ee}	0.352 142
E_H	0.722 217
E_x	-0.361 109 (SD) -0.337 265(LCD)
E_c	-0.008 966 (SD) -0.032 810(LCD)
T_s	1.015 505
T_c	-0.139 243
E	2.280 775

holes are plotted in Figs. 9 and 10, respectively, for electron positions at $r=0, 0.5, 1.0, 2.0,$ and 7.0 a.u. These holes, of course, differ from those of the single determinant case of Figs. 5 and 6. However, their general features regarding symmetry, cusps, etc., are similar.

The corresponding fields and potential energies are plotted in Figs. 11 and 12. The shell structure in the plots of the fields $\mathcal{E}_x(\mathbf{r})$ and $\mathcal{E}_c(\mathbf{r})$ and the potential energies $W_x(\mathbf{r})$ and $W_c(\mathbf{r})$ are more dramatic in this case. The asymptotic structure of the various individual components, of course, remains the same.

The Pauli E_x and Coulomb E_c energies are quoted in Table I indicated by LCD. These energies differ from their single determinant counterparts. In this case, however, the Coulomb energy E_c is only an order of magnitude less than E_x . The sum of E_x and E_c is the same as that for the single determinant example, as must be the case.

We conclude this section by noting that if the excited singlet 2^1S state of the interacting system had been mapped to an S system in an excited triplet 2^3S state, there would once again be three wave functions that lead to the *same* density. Two of these would be single Slater determinants,

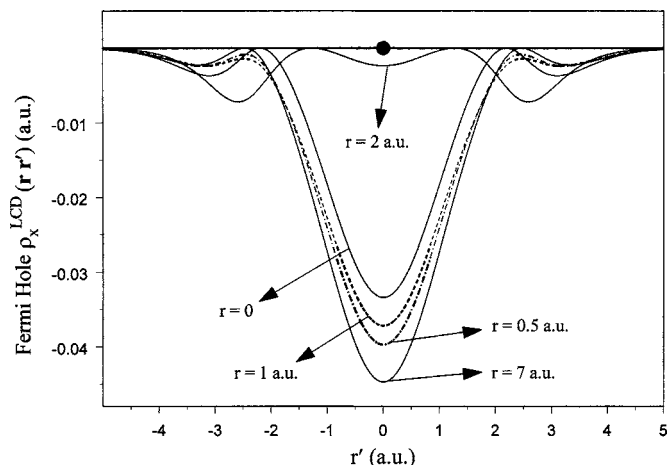


FIG. 9. Cross section of the Fermi holes $\rho_x^{\text{LCD}}(\mathbf{r}, \mathbf{r}')$ as a function of electron position at $\mathbf{r}=0, 0.5, 1.0, 2.0,$ and 7.0 a.u. as determined by the linear combination of Slater determinants (LCD).

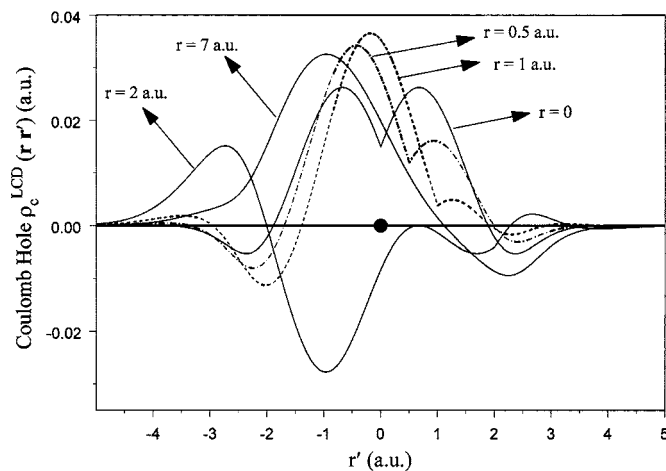


FIG. 10. Cross section of the Coulomb holes $\rho_c^{\text{LCD}}(\mathbf{r}, \mathbf{r}')$ for electron position at $\mathbf{r}=0, 0.5, 1.0, 2.0,$ and 7.0 a.u. when the Fermi hole is determined by the linear combination of Slater determinants (LCD).

and the third a linear combination of the first two. All three wave functions are eigenfunctions of \hat{S}^2 and \hat{S}_z . They are all written as a product of an antisymmetrical spatial function and a symmetric spin function. Within the framework of local effective potential energy theory, each wave function is equally valid.

In this case, the three wave functions also each lead to the same expression for the Fermi hole and hence to that of the Coulomb hole. Hence, the corresponding Pauli and Coulomb fields, potential energies, and components of the total energy are also all the same.

VIII. CONCLUDING REMARKS

The idea of determining electronic structure from orbitals generated from a local effective potential energy function is originally due to Slater.²⁵ In this paper, our understanding

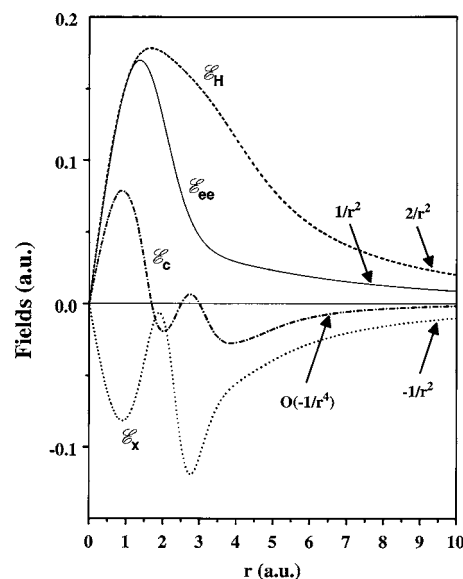


FIG. 11. The electron-interaction $\mathcal{E}_{ee}(\mathbf{r})$ field and its Hartree $\mathcal{E}_H(\mathbf{r})$, Pauli $\mathcal{E}_x(\mathbf{r})$, and Coulomb $\mathcal{E}_c(\mathbf{r})$ field components. The fields $\mathcal{E}_x(\mathbf{r})$ and $\mathcal{E}_c(\mathbf{r})$ are a consequence of the Fermi hole $\rho_x^{\text{LCD}}(\mathbf{r}, \mathbf{r}')$ determined via a linear combination of Slater determinants.

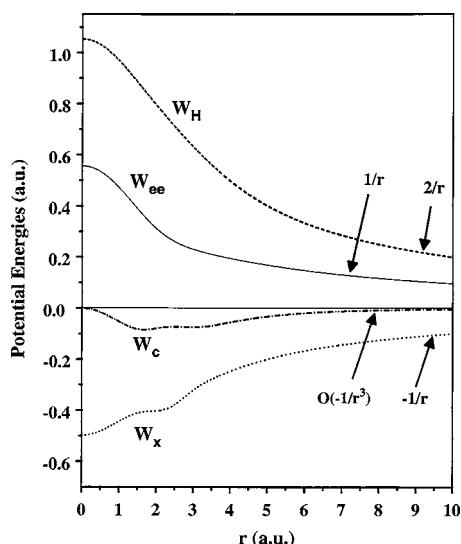


FIG. 12. The electron interaction $W_{ee}(\mathbf{r})$ potential energy and its Hartree $W_H(\mathbf{r})$, Pauli $W_x(\mathbf{r})$, and Coulomb $W_c(\mathbf{r})$ components determined as the work done in the corresponding field of Fig. 11.

of what constitutes local effective potential energy theory is generalized. Within the context of the ground state HKS-DFT, the understanding is that in the mapping from a *nondegenerate* ground state of the interacting system to a model S system of noninteracting fermions in its ground state, there exists *one and only one* local effective potential energy function that could generate the corresponding density. In the mapping from a *nondegenerate* excited state of the interacting system to a model system in the same electronic configuration, the constrained-search HKS-DFT selects one local effective potential energy function that generates the same excited state density. Via Q-DFT, we now understand that there exist an *infinite* number of such functions that can generate the ground or excited state density of an interacting system. These *different* functions correspond to the model S system being in different states, both *ground* and *excited*. Hence, the configuration of the model system need not be the same as that of the interacting one. From each model system, the corresponding total energy and ionization potential of the interacting system are also obtained, the latter being the negative of the highest occupied eigenvalue. It has also been noted by others that in the mapping from an excited state of the interacting system to a *fixed excited* state configuration of the model S system, there can exist different local functions that generate the excited state density.

The difference between the various local effective potential energy functions, whether the model system is in different states or for a fixed excited state configuration, lies *solely* in their correlation-kinetic component. The components of these functions that represent the correlations due to the Pauli exclusion principle and Coulomb repulsion remain the same.

The fact that in the mapping from an *excited* state of the interacting system, there exist many local functions that generate the same density, confirming the well-known lack of

equivalent HKS-DFT ground state theorems for *excited* states. Additionally, we now understand that this is a direct consequence of correlation-kinetic effects.

Finally, in the mapping from either a ground or excited state of the interacting system to an S system in an excited state, there is a nonuniqueness of the model system wave function. Although some of these wave functions are not eigenfunctions of all the spin-symmetry operators, they each generate the same density as that of the interacting system, the *sole* requirement of local effective potential energy theory.

For a discussion of the mapping via Q-DFT from *degenerate ground* and *excited* states of the interacting system to model systems of noninteracting fermions, we refer the reader to Ref. 26.

Finally, we emphasize that in the local effective potential energy theory, the model system of noninteracting fermions is just that, a model system. The model should not be construed as being a replica of the true interacting system. All that is required of the model is that it reproduce the density of the interacting system and thereby the total energy and ionization potential.

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