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Quantal density-functional theory of excited states: The state arbitrariness of the model noninteracting system

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The quantal density-functional theory (Q-DFT) of nondegenerate excited-states maps the pure state of the Schrödinger equation to one of noninteracting fermions such that the equivalent excited state density, energy, and ionization potential are obtained. The state of the model *S* system is *arbitrary* in that it may be in a ground or excited state. The potential energy of the model fermions differs as a function of this state. The contribution of correlations due to the Pauli exclusion principle and Coulomb repulsion to the potential and total energy of these fermions is independent of the state of the *S* system. The differences are *solely* a consequence of correlation-kinetic effects. Irrespective of the state of the *S* system, the highest occupied eigenvalue of the model fermions is the negative of the ionization potential. In this paper we demonstrate the state arbitrariness of the model system by application of Q-DFT to the first *excited* singlet state of the exactly solvable Hookean atom. We construct two model *S* systems: one in a singlet *ground* state $(1s^2)$, and the other in a singlet first *excited* state $(1s2s)$. In each case, the density and energy determined are equivalent to those of the excited state of the atom, with the highest occupied eigenvalues being the negative of the ionization potential. From these results we determine the corresponding Kohn-Sham density-functional theory (KS-DFT) "exchange-correlation" potential energy for the two S systems. Further, based on the results of the model calculations, suggestions for the KS-DFT of excited states are made.

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I. INTRODUCTION

Time-independent ground-state quantal density-functional theory (Q-DFT) [1–4] is a description of the mapping from a system of electrons in some external field $\mathbf{F}^{ext}(\mathbf{r}) = -\nabla v(\mathbf{r})$ as described by Schrödinger theory to one of *noninteracting* fermions such that the equivalent density $\rho(\mathbf{r})$, energy E, and ionization potential I are obtained. As the effective potential energy $v_s(\mathbf{r})$ of these model fermions is the same, their wave function is a single Slater determinant. The model of noninteracting fermions is referred to as the *S* system. The potential energy $v_s(\mathbf{r})$ is the sum of the external $v(\mathbf{r})$ and electron interaction $v_{ee}(\mathbf{r})$ potential energies, the latter being representative of the many-body correlations the *S* system must account for. These electron correlations are those due to the Pauli exclusion principle, Coulomb repulsion, and correlation-kinetic effects. In Q-DFT, the potential energy $v_{ee}(\mathbf{r})$ is the work done to move a model fermion in the force of a conservative "classical" field. The components of this field are each *separately* representative of the Pauli and Coulomb correlations, and correlation-kinetic effects. The Pauli (exchange), Coulomb (correlation), and correlation-kinetic components of the total energy too are expressed in terms of the corresponding fields. The sources of these fields are quantal in that they are quantum-mechanical expectations of Hermitian operators taken with respect to the Schrödinger and *S* system wave functions. The highest occupied eigenvalue of the *S* system differential equation is the negative of the ionization potential. In this manner, via Q-DFT, it is then possible to study how the different electron correlations in a physical system manifest themselves in the local effective potential-energy framework described by the model *S* system. Irrespective of the symmetry of the interacting system, its energy, density, and ionization potential can be determined from the Q-DFT description of the *S* system.

The Q-DFT description of the mapping from the ground state of the interacting to the model noninteracting *S* system in terms of classical fields and quantal sources differs from that of traditional Kohn-Sham density-functional theory (KS-DFT) [5]. KS-DFT is also a description of the *S* system. This description, however, is in terms of energy functionals of the ground-state density, and of their functional derivatives. Thus, in ground-state KS-DFT, all the many-body correlations are embedded in the KS electron-interaction energy functional $E_{ee}^{KS}[\rho]$ of the ground-state density $\rho(\mathbf{r})$. The corresponding local electron-interaction potential energy $v_{ee}(\mathbf{r})$ of the model fermions is then defined as the functional derivative $\delta E_{ee}^{KS}[\rho]/\delta\rho(\mathbf{r})$. KS-DFT does not describe how the various many-body correlations are incorporated in the functional $E_{ee}^{KS}[\rho]$, and hence how they are represented in its functional derivative. In contrast, within Q-DFT, the contributions due to Pauli, Coulomb, and correlation-kinetic effects to both the potential energy $v_{ee}(\mathbf{r})$ and the total energy are *separately* delineated and explicitly *defined*. (The descriptions in the literature on KS-DFT are usually in terms of the KS "exchange-correlation" energy functional $E_{xc}^{KS}[\rho]$. The sum of this functional and that of the known Hartree self-energy functional $E_H[\rho]$ constitutes the functional $E_{ee}^{KS}[\rho]$. Our discussion is in terms of $E_{ee}^{KS}[\rho]$ because it also includes the Coulomb correlations represented by the Hartree self-energy.)

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In recent works [6,7], we have extended Q-DFT to the case of a *pure nondegenerate excited* state of Schrödinger theory. The excited-state framework is the *same* as that of the ground state, and once again in terms of classical fields and quantal sources. In this case, however, we further proved the mapping to the noninteracting framework is such that the state of the S system is *arbitrary*. The S system may be in a *ground* or *excited* state. *These are different S systems*. The fact that these S systems may be in any arbitrary state and yet lead to the density of the excited state of the interacting system was originally stated by us [6]. The difference in the corresponding electron-interaction potential energy $v_{ee}(\mathbf{r})$ of the model fermions is due *solely* to the correlation-kinetic effects. The Pauli and Coulomb correlation contributions to the potential energy $v_{ee}(\mathbf{r})$ and the corresponding component of the total energy remain the same. Whether the S system is in a ground or excited state, the density and total energy equivalent to that of the *excited* state of Schrödinger theory is obtained. Furthermore, the highest occupied eigenvalue of the S system, whether in a ground or excited state, is equivalent to the negative of the ionization potential energy.

Within KS-DFT, many approaches to excited states have been proposed. All these methods involve energy functionals of a density or bidensity energy functionals, and their functional derivatives, and hence differ from the Q-DFT description. For a brief review, we refer the reader to the work by Dreizler and Gross [8]. Here we note three recent formalisms. The first is based on the energy variational principle for ensembles [9] with unequal weights. The ensemble energy as constructed with the M lowest eigenstates of a system satisfies the variational principle. In other words, the ensemble energy calculated with M approximate wave functions is always greater than or equal to the ensemble energy determined via the M exact eigenstates of the interacting system. It is then proved that the ensemble energy is a functional of the ensemble density $\rho^{ens}(\mathbf{r})$. Thus, in a manner similar to ground state KS-DFT, an electron-interaction energy functional of the ensemble density $E_{ee}^{KS}[\rho^{ens}]$ can be defined. The corresponding effective potential energy of the noninteracting fermions is once again the sum of the external $[v_s(\mathbf{r})]$ and the electron-interaction $[v_{ee}(\mathbf{r})]$ potential energy, where the latter is defined as the functional derivative $\delta E_{ee}^{KS}[\rho^{ens}]/\delta\rho^{ens}(\mathbf{r})$. The excitation energies can then be expressed in terms of the eigenvalues of the noninteracting system differential equation and the functional $E_{ee}^{KS}[\rho^{ens}]$. Again, ensemble KS-DFT of excited states does not describe how the various electron correlations are incorporated into the ensemble-density energy functional $E_{ee}^{KS}[\rho^{ens}]$.

In a second approach [10], it has been proved that there exists a variational KS-DFT with a minimum principle for the self-consistent determination of an excited state. In this case, the total energy of the kth excited state is a *bidensity* energy functional of the excited $[\rho_k(\mathbf{r})]$ and ground-state $[\rho_0(\mathbf{r})]$ densities. One then defines the corresponding KS electron-interaction energy bidensity functional $E_{ee}^{KS}[\rho,\rho_0]|_{\rho_k}$, with the resulting electron-interaction potential energy $v_{ee}(\mathbf{r})$ of the noninteracting fermions being defined as the functional derivative $\delta E_{ee}^{KS}[\rho,\rho_0]/\delta\rho(\mathbf{r})|_{\rho_k}$ taken at the excited-state density value $\rho_k(\mathbf{r})$. Once again, how the different electron correlations are represented in the energy bidensity functional is not described. Further, the configuration of the noninteracting system constructed *always* corresponds to that of the excited state of the interacting system. In this approach, there can only be *one S* system because the functional derivative at the kth excited-state density value is a *unique* function. [Note that the ground-state density of this S system is not the ground-state density $\rho_0(\mathbf{r})$ of the interacting system.]

A third approach, based on a generalization of the constrained search procedure [11], is the generalized adiabatic connection (GAC) KS-DFT [12]. In this framework, an excited state of the interacting system is adiabatically connected to a particular state of the noninteracting system. The state of the noninteracting fermions, however, is *not arbitrary*, but governed by the adiabatic path. The state could be a ground or excited state. The energy functionals in this instance are generalizations of the constrained search formalism for the ground state, and involve an additional parameter ν. The energy depends upon this parameter, and is a functional of what is referred to as the ρ-stationary density $\rho^{stat}(\mathbf{r})$. In the KS-DFT version, one then defines an electron-interaction energy functional $E_{ee}^{KS}[\rho^{stat},\nu]$ representative of all the many-body effects, with the corresponding electron-interaction potential energy of the noninteracting fermions being the functional derivative $\delta E_{ee}^{KS}[\rho^{stat},\nu]/\delta\rho^{stat}(\mathbf{r})|_{\rho^{stat}(\mathbf{r})=\rho_k(\mathbf{r})}$, where $\rho_k(\mathbf{r})$ is the density of the kth excited state. A further generalization [13] to account for the symmetry problems of KS-DFT involves functionals of symmetrized ρ-stationary densities and the parameter ν.

In this paper we demonstrate, via Q-DFT, the state arbitrariness of the model noninteracting fermion system. The example we consider is that of the first excited nondegenerate singlet state of Hooke's atom [14]. The wave function of this state of the interacting system is known analytically [6,7]. We transform this state described by Schrödinger theory to *two S* systems, one in a singlet *ground* state, and the other in a singlet *excited* state. In each case, the self-consistently determined orbitals lead to the density of the interacting system. The corresponding highest occupied eigenvalues are equivalent to the negative of the ionization potential of this state. In addition, although the noninteracting kinetic and correlation-kinetic energies of the two S systems are different, the equivalent total energy of the interacting system is obtained in each case. The example further demonstrates how the different many-body correlations—Pauli, Coulomb, and correlation-kinetic—contribute to the structure of these different S systems.

As the energy functionals of the different excited-state formalisms within KS-DFT are unknown, one cannot apply these approaches to the solution of the exactly solvable Hooke's atom model. However, from the results obtained via Q-DFT, we determine the KS-DFT "exchange-correlation" potential energy for the two S systems, and arrive at conclusions with regard to the KS-DFT of excited states. For the paper to be self-contained, we briefly describe bound nonde-

generate excited state Q-DFT in Sec. II. The results of transformation to the two S systems are described in Sec. III. These results are then expressed in the language of KS-DFT in Sec. IV. We end with concluding remarks in Sec. V.

For the application to excited states of Q-DFT in both the Pauli-correlated approximation and with the use of an approximate correlation energy functional, we refer the reader to Ref. [15]. For a description of the Q-DFT of *degenerate* states, both *ground* and *excited* states, and for both *pure* state and *ensemble* densities, we refer the reader to our more recent work [16].

II. Q-DFT OF NONDEGENERATE EXCITED STATES

The Schrödinger equation for the kth nondegenerate bound excited state of a system of N electrons in an external field $\mathbf{F}^{ext}(\mathbf{r})=-\boldsymbol{\nabla} v(\mathbf{r})$ is

$$[\hat{T}+\hat{V}+\hat{U}]\Psi_k(\mathbf{X})=E_k\Psi_k(\mathbf{X}), \tag{1}$$

where $\hat{T}=-\frac{1}{2}\Sigma_i\nabla^2$, $\hat{V}=\Sigma_i v(\mathbf{r}_i)$, and $\hat{U}=\frac{1}{2}\Sigma'_{i,j}(1/|\mathbf{r}_i-\mathbf{r}_j|)$ are the kinetic energy, local external potential-energy, and electron-interaction potential energy operators, $\Psi_k(\mathbf{X})$ and E_k are the excited-state wave function and energy, with $\mathbf{X}=\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N$, $\mathbf{x}=\mathbf{r}\sigma$, and σ the spin coordinate. The electronic density of this state is the expectation

$$\rho_k(\mathbf{r})=\langle\Psi_k|\hat{\rho}|\Psi_k\rangle, \tag{2}$$

where $\hat{\rho}=\Sigma_i\delta(\mathbf{r}-\mathbf{r}_i)$ is the density operator. The corresponding spinless single-particle density matrix is the expectation

$$\gamma_k(\mathbf{r}\mathbf{r}')=\langle\Psi_k|\hat{X}|\Psi_k\rangle, \tag{3}$$

where the Hermitian operator $\hat{X}=\hat{A}+i\hat{B}$, $\hat{A}=(1/2)\Sigma_j[\delta(\mathbf{r}_j-\mathbf{r})T_j(\mathbf{a})+\delta(\mathbf{r}_j-\mathbf{r}')T_j(-\mathbf{a})]$, $\hat{B}=-(i/2)\Sigma_j[\delta(\mathbf{r}_j-\mathbf{r})T_j(\mathbf{a})-\delta(\mathbf{r}_j-\mathbf{r}')T_j(-\mathbf{a})]$, $T_j(\mathbf{a})$ is a translation operator, and $\mathbf{a}=\mathbf{r}'-\mathbf{r}$. The ionization potential for this state is $I_k=E_k^{ion}-E_k$, where E_k^{ion} is the energy of the resulting ion when the least bound electron is removed to infinity.

The S-system differential equation corresponding to the kth nondegenerate bound excited state is

$$\left[-\frac{1}{2}\nabla^2+v(\mathbf{r})+v_{ee}(\mathbf{r})\right]\phi_i(\mathbf{x})=\epsilon_i\phi_i(\mathbf{x});\quad i=1,\ldots,N, \tag{4}$$

where the *local* electron-interaction potential energy $v_{ee}(\mathbf{r})$, in which all the many-body effects are incorporated, is such that the density $\rho_k(\mathbf{r})$ is obtained as the expectation

$$\rho_k(\mathbf{r})=\langle\Phi\{\phi_i\}|\widehat{\rho_k}|\Phi\{\phi_i\}\rangle=\sum_i\sum_\sigma|\phi_i(\mathbf{r}\sigma)|^2, \tag{5}$$

where $\Phi\{\phi_i\}$ is the Slater determinant of the orbitals $\phi_i(\mathbf{x})$. The occupation of the orbitals $\phi_i(\mathbf{x})$ may either be the N lowest-lying states corresponding to a ground-state configuration, or they may be in an excited-state configuration. The corresponding spinless Dirac density matrix is the expectation

$$\gamma_{s,k}(\mathbf{r}\mathbf{r}')=\langle\Phi\{\phi_i\}|\hat{\mathbf{X}}|\Phi\{\phi_i\}\rangle=\sum_i\sum_\sigma\phi_i^*(\mathbf{r}\sigma)\phi_i(\mathbf{r}'\sigma). \tag{6}$$

Further, whether the S system is in a ground- or excited-state configuration, the highest occupied eigenvalue $\epsilon_m=-I_k$ is the negative of the ionization potential.

The potential energy $v_{ee}(\mathbf{r})$ is the work done to move the model fermion from a reference point at infinity to its position at $\mathbf{r}$ in the force of a *conservative* effective field $\boldsymbol{\mathcal{F}}_k^{eff}(\mathbf{r})$:

$$v_{ee}(\mathbf{r})=-\int_\infty^{\mathbf{r}}\boldsymbol{\mathcal{F}}_k^{eff}(\mathbf{r}')\cdot d\mathbf{l}'. \tag{7}$$

The field $\boldsymbol{\mathcal{F}}_k^{eff}(\mathbf{r})$ is the sum of an electron-interaction field $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$ representative of Pauli and Coulomb correlations, and a correlation-kinetic field $\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r})$ representative of this effect:

$$\boldsymbol{\mathcal{F}}_k^{eff}(\mathbf{r})=\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})+\boldsymbol{\mathcal{Z}}_{t_c}(\mathbf{r}). \tag{8}$$

The field $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$ is obtained via Coulomb's law from the pair-correlation density $g(\mathbf{r}\mathbf{r}')$ which constitutes its quantal source. Thus,

$$\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})=\int\frac{g(\mathbf{r}\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}d\mathbf{r}', \tag{9}$$

where $g(\mathbf{r}\mathbf{r}')=\langle\Psi_k|\hat{P}(\mathbf{r}\mathbf{r}')|\Psi_k\rangle/\rho_k(\mathbf{r})$ and $\hat{P}(\mathbf{r}\mathbf{r}')=\Sigma'_{i,j}\delta(\mathbf{r}_i-\mathbf{r})\delta(\mathbf{r}_j-\mathbf{r}')$ is the pair-correlation operator. The pair-correlation density may further be separated into its local and nonlocal (dynamic) components as

$$g(\mathbf{r}\mathbf{r}')=\rho_k(\mathbf{r}')+\rho_{xc}(\mathbf{r}\mathbf{r}') \tag{10}$$

$$=\rho_k(\mathbf{r}')+\rho_x(\mathbf{r}\mathbf{r}')+\rho_c(\mathbf{r}\mathbf{r}'), \tag{11}$$

where $\rho_{xc}(\mathbf{r}\mathbf{r}')$, $\rho_x(\mathbf{r}\mathbf{r}')$, and $\rho_c(\mathbf{r}\mathbf{r}')$ are the Fermi-Coulomb, Fermi, and Coulomb hole charge distributions. The Fermi hole is defined as $\rho_x(\mathbf{r}\mathbf{r}')=-|\gamma_{s,k}(\mathbf{r}\mathbf{r}')|^2/2\rho_k(\mathbf{r})$, and the Coulomb hole is defined via Eqs. (10) and (11). The sum rules satisfied by these charge distributions are $\int\rho_{xc}(\mathbf{r}\mathbf{r}')d\mathbf{r}'=-1$, $\int\rho_x(\mathbf{r}\mathbf{r}')d\mathbf{r}'=-1$, $\rho_x(\mathbf{r}\mathbf{r}')\leqslant 0$, and $\rho_x(\mathbf{r}\mathbf{r})=-\rho_k(\mathbf{r})/2$, and $\int\rho_c(\mathbf{r}\mathbf{r}')d\mathbf{r}'=0$. The electron-interaction field may then be written in terms of its components as

$$\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})=\boldsymbol{\mathcal{E}}_H(\mathbf{r})+\boldsymbol{\mathcal{E}}_{xc}(\mathbf{r}) \tag{12}$$

$$=\boldsymbol{\mathcal{E}}_H(\mathbf{r})+\boldsymbol{\mathcal{E}}_x(\mathbf{r})+\boldsymbol{\mathcal{E}}_c(\mathbf{r}), \tag{13}$$

where the Hartree $[\boldsymbol{\mathcal{E}}_H(\mathbf{r})]$, Pauli-Coulomb $[\boldsymbol{\mathcal{E}}_{xc}(\mathbf{r})]$, Pauli $[\boldsymbol{\mathcal{E}}_x(\mathbf{r})]$, and Coulomb $[\boldsymbol{\mathcal{E}}_c(\mathbf{r})]$ fields are due to their respective quantal sources $\rho_k(\mathbf{r})$, $\rho_{xc}(\mathbf{r}\mathbf{r}')$, $\rho_x(\mathbf{r}\mathbf{r}')$, and $\rho_c(\mathbf{r}\mathbf{r}')$.

The correlation-kinetic field $\mathcal{Z}_{t_c}(\mathbf{r})$ is the difference of the kinetic fields $\mathcal{Z}(\mathbf{r})$ and $\mathcal{Z}_s(\mathbf{r})$,

$$\mathcal{Z}_{t_c}(\mathbf{r})=\mathcal{Z}_s(\mathbf{r})-\mathcal{Z}(\mathbf{r}), \tag{14}$$

where $\mathcal{Z}(\mathbf{r})=\mathbf{z}(\mathbf{r};[\gamma_k])/\rho_k(\mathbf{r})$ and $\mathcal{Z}_s(\mathbf{r})=\mathbf{z}_s(\mathbf{r};[\gamma_{s,k}])/\rho_k(\mathbf{r})$. The quantal sources of the fields $\mathcal{Z}(\mathbf{r})$ and $\mathcal{Z}_s(\mathbf{r})$ are the single-particle and Dirac density matrices, respectively. The force $\mathbf{z}(\mathbf{r};[\gamma_k])$ is defined in terms of its components as $z_\alpha(\mathbf{r};[\gamma_k])=2\Sigma_\beta\partial t_{\alpha\beta}(\mathbf{r};[\gamma_k])/\partial r_\beta$, where $t_{\alpha\beta}(\mathbf{r};[\gamma_k])=\frac{1}{4}[\partial^2/\partial r'_\alpha\partial r''_\beta+\partial^2/\partial r'_\beta\partial r''_\alpha]\gamma_k(\mathbf{r}'\mathbf{r}'')|_{\mathbf{r}'=\mathbf{r}''=\mathbf{r}}$ is the kinetic-energy tensor. The field $\mathbf{z}_s(\mathbf{r};[\gamma_{s,k}])$ is similarly defined in terms of the *S*-system tensor $t_{\alpha\beta,s}(\mathbf{r};[\gamma_{s,k}])$.

For systems of symmetry such that the component fields $\mathcal{E}_{ee}(\mathbf{r})$ and $\mathcal{Z}_{t_c}(\mathbf{r})$ are separately conservative, the potential energy $v_{ee}(\mathbf{r})$ may be expressed as the sum of the separate work done in these fields. Thus

$$v_{ee}(\mathbf{r})=W_{ee}(\mathbf{r})+W_{t_c}(\mathbf{r}) \tag{15}$$

$$=W_H(\mathbf{r})+W_{xc}(\mathbf{r})+W_{t_c}(\mathbf{r}) \tag{16}$$

$$=W_H(\mathbf{r})+W_x(\mathbf{r})+W_c(\mathbf{r})+W_{t_c}(\mathbf{r}), \tag{17}$$

where $W_{ee}(\mathbf{r})$, $W_H(\mathbf{r})$, $W_{xc}(\mathbf{r})$, $W_x(\mathbf{r})$, $W_c(\mathbf{r})$, and $W_{t_c}(\mathbf{r})$ are the work done in the fields $\mathcal{E}_{ee}(\mathbf{r})$, $\mathcal{E}_H(\mathbf{r})$, $\mathcal{E}_{xc}(\mathbf{r})$, $\mathcal{E}_x(\mathbf{r})$, $\mathcal{E}_c(\mathbf{r})$, and $\mathcal{Z}_{t_c}(\mathbf{r})$, respectively.

The excited-state energy is

$$E_k=T_s+\int\rho_k(\mathbf{r})v(\mathbf{r})d\mathbf{r}+E_{ee}+T_c, \tag{18}$$

where $T_s=\langle\Phi\{\phi_i\}|\hat{T}|\Phi\{\phi_i\}\rangle$ is the kinetic energy of the noninteracting fermions. The electron-interaction (E_{ee}) and correlation-kinetic (T_c) energies are expressed in terms of the fields $\mathcal{E}_{ee}(\mathbf{r})$ and $\mathcal{Z}_{t_c}(\mathbf{r})$, respectively, in integral virial form as

$$E_{ee}=\int d\mathbf{r}\rho_k(\mathbf{r})\mathbf{r}\cdot\mathcal{E}_{ee}(\mathbf{r}) \quad\text{and}\quad T_c=\frac{1}{2}\int d\mathbf{r}\rho_k(\mathbf{r})\mathbf{r}\cdot\mathcal{Z}_{t_c}(\mathbf{r}). \tag{19}$$

In our previous work [6] we had proved that the state arbitrariness of the *S* system is reflected entirely through its kinetic field $\mathcal{Z}_s(\mathbf{r})$ or equivalently the correlation-kinetic field $\mathcal{Z}_{t_c}(\mathbf{r})$. The electron-interaction component field $\mathcal{E}_{ee}(\mathbf{r})$ remains the same. Thus, it is the field $\mathcal{Z}_{t_c}(\mathbf{r})$ that is adjusted to ensure that the density, energy, and ionization potential of the interacting system are achieved. [Note that although the field $\mathcal{E}_{ee}(\mathbf{r})$ remains unchanged, its Pauli [$\mathcal{E}_x(\mathbf{r})$] and Coulomb [$\mathcal{E}_c(\mathbf{r})$] components will each be different depending upon the state the *S* system is in.]

III. CONSTRUCTION OF MODEL NONINTERACTING FERMION SYSTEMS

The interacting system we consider is Hooke's atom in its first excited singlet state. Hooke's atom comprises two electrons whose external potential energy is harmonic, $v(\mathbf{r})=\frac{1}{2}kr^2$. The solution of the Schrödinger equation for this state with $k=0.144\,498$ is

$$\Psi_{01}(\mathbf{r}_1\mathbf{r}_2)=C_0e^{-\omega R^2}e^{-\omega r^2/4}\left[1+C_1\sqrt{\frac{\omega}{2}}r+C_2\left(\frac{\omega}{2}\right)r^2+C_3\left(\frac{\omega}{2}\right)^{3/2}r^3\right], \tag{20}$$

where $\mathbf{r}=\mathbf{r}_1-\mathbf{r}_2$, $\mathbf{R}=(\mathbf{r}_1+\mathbf{r}_2)/2$, $\omega=\sqrt{k}=0.380\,129$, $C_0=0.026\,100\,5$, $C_1=1.146\,884$, $C_2=-0.561\,569$, and $C_3=-0.489\,647$. The total energy of this state is $E_{01}=2.280\,775$ a.u., and its ionization potential is $I_{01}=-1.710\,582$ a.u.. The atom in this first excited state is spherically symmetric.

The results of transformation via Q-DFT of this excited state of the interacting system to two model noninteracting fermion systems, one in a singlet *ground* state ($1s^2$) and the other in a singlet first *excited* state ($1s2s$), are described below. The calculations for the transformation to an *S*-system in its ground state are principally analytical since each orbital $\phi_{1s^2}(\mathbf{r})=\sqrt{\rho(\mathbf{r})/2}$, and $\rho(\mathbf{r})$ is known analytically. However, the orbitals and the singlet eigenvalue ϵ_{1s^2} have also been determined independently by numerical solution of the *S*-system differential equation. Additionally, the value of ϵ_{1s^2} has been reconfirmed by taking the expectation value of the *S*-system Hamiltonian. The orbitals $\phi_{1s}(\mathbf{r})$, $\phi_{2s}(\mathbf{r})$, and the corresponding eigenvalues ϵ_{1s}, ϵ_{2s} for transformation to the *S*-system in its excited state are determined by numerical self-consistent solution of the *S*-system differential equation. In this equation, the potential-energy component $W_{ee}(\mathbf{r})$ of the electron-interaction potential energy $v_{ee}(\mathbf{r})$ [see Eq. (15)], which is the same as for the ground-state calculation, remains fixed for each iteration. It is the correlation-kinetic component $W_{t_c}(\mathbf{r})$, which depends upon the orbitals $\phi_{1s}(\mathbf{r})$ and $\phi_{2s}(\mathbf{r})$ through the Dirac density matrix, which changes in each iteration and is determined self-consistently together with the orbitals and eigenvalues. The input potential energy employed to initiate the self-consistency procedure was that of the ground-state calculation. The self-consistency code was designed to converge for solutions with positive eigenvalue for each orbital. Following self-consistency, the eigenvalues ϵ_{1s} and ϵ_{2s} were independently confirmed by taking the expectation of the *S*-system Hamiltonian with the appropriate self-consistently determined orbitals.

In Fig. 1 we plot the ground-state *S* system orbital $\phi_{1s^2}(r)$ and the excited-state *S*-system orbitals $\phi_{1s}(r)$ and $\phi_{2s}(r)$. The node of $\phi_{2s}(r)$ is at 2.4 a.u. The orbital $\phi_{1s^2}(r)$ and orbitals $\phi_{1s}(r)$, $\phi_{2s}(r)$ lead to the same density $\rho(r)$ as that of the singlet excited state of Hooke's atom.

In Fig. 2 the radial probability density of each orbital [$r^2\rho_{1s^2}(r)$, $r^2\rho_{1s}(r)$, $r^2\rho_{2s}(r)$] is plotted. The ground-state *S* system radial probability density $r^2\rho_{1s^2}(r)$ is equal to the sum of the excited-state *S* system radial probability densities $r^2[\rho_{1s}(r)+\rho_{2s}(r)]$. Each in turn is equivalent to the radial probability density $r^2\rho(r)$ of the interacting system. The

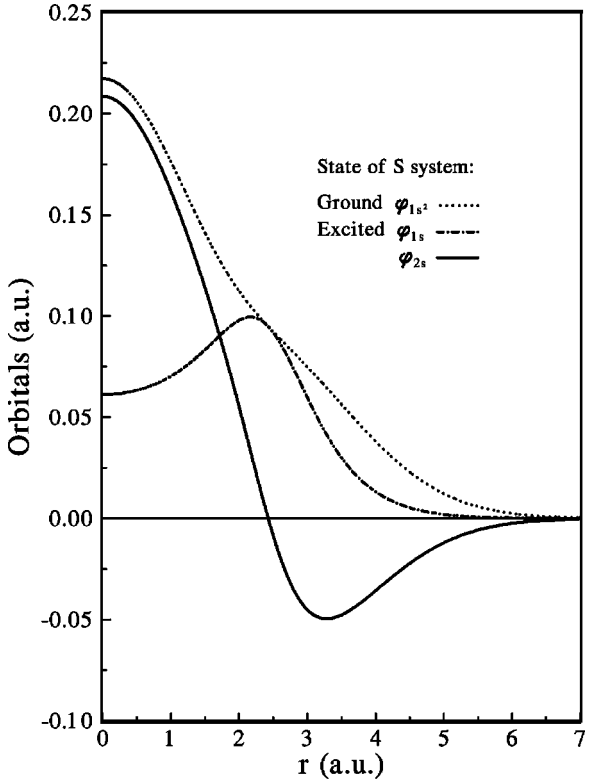

FIG. 1. The orbitals of the S system in its singlet ground state $\phi_{1s^2}(r)$, and its singlet first excited states $\phi_{1s}(r)$ and $\phi_{2s}(r)$.

probability density $r^2\rho_{2s}(r)$ has two maxima, and a minimum at the node. The maximum of $r^2\rho_{1s}(r)$ occurs at the minimum of $r^2\rho_{2s}(r)$, indicating that the region the first model fermion is most likely to be found coincides with the region where the second fermion is least likely to be. Note that $r^2\rho_{1s}(r)$ is negligible for $r>5$ a.u.. As such, the asymptotic structure of the radial probability density, and hence the density, is that of $r^2\rho_{2s}(r)$, and that it coincides with $r^2\rho_{1s^2}(r)$. This is the reason why the eigenvalues ϵ_{1s^2} and ϵ_{2s} are equivalent (see Table I).

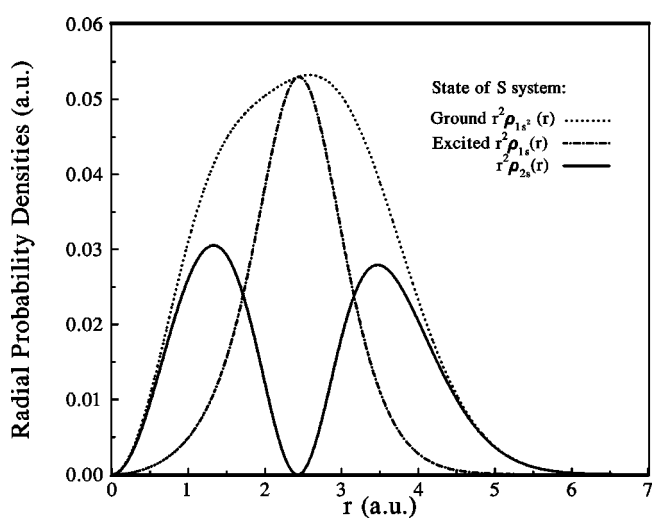

FIG. 2. The radial probability densities $r^2\rho_{1s^2}(r)$, $r^2\rho_{1s}(r)$, and $r^2\rho_{2s}(r)$

TABLE I. The components of the total energy and eigenvalues for the transformation from a singlet first excited state of Hooke's atom to S systems in the singlet ground ($1s^2$) and first excited singlet ($1s2s$) states.

	S systems	
Property (a.u.)	Ground state $1s^2$	Excited state $1s2s$
E_H	0.722217	0.722217
E_x	−0.361109	−0.361109
E_c	−0.008966	−0.008966
E_{ee}	0.352142	0.352142
T_s	0.327471	1.015505
T_c	0.548791	−0.139243
E_{ext}	1.052371	1.052371
E	2.280775	2.280775
Eigenvalues	$\epsilon_{1s^2}=1.711$	$\epsilon_{1s}=0.573$
		$\epsilon_{2s}=1.711$

In Fig. 3, the electron-interaction field $\boldsymbol{\mathcal{E}}_{ee}(r)$, and its Hartree $[\boldsymbol{\mathcal{E}}_H(r)]$, Pauli $[\boldsymbol{\mathcal{E}}_x(r)]$, and Coulomb $[\boldsymbol{\mathcal{E}}_c(r)]$ field components are plotted. [Note that for two electrons in a singlet state within local effective potential-energy theory, one defines $\rho_x(\mathbf{r}\mathbf{r}')=-\rho(\mathbf{r}')/2$, so that $\boldsymbol{\mathcal{E}}_x(\mathbf{r})=-\boldsymbol{\mathcal{E}}_H(\mathbf{r})/2$.] The corresponding potential energy $W_{ee}(r)$, and its Hartree $[W_H(r)]$, Pauli $[W_x(r)]$, and Coulomb $[W_c(r)]$ components are plotted in Fig. 4. The contribution of these potential energies to the electron-interaction potential energy $v_{ee}(r)$ of Eq. (17) remains unchanged irrespective of the state the S system is in. (The fact that the Pauli $[W_x(\mathbf{r})]$ and Coulomb $W_c(\mathbf{r})$ potential energies remain the same is particular to the

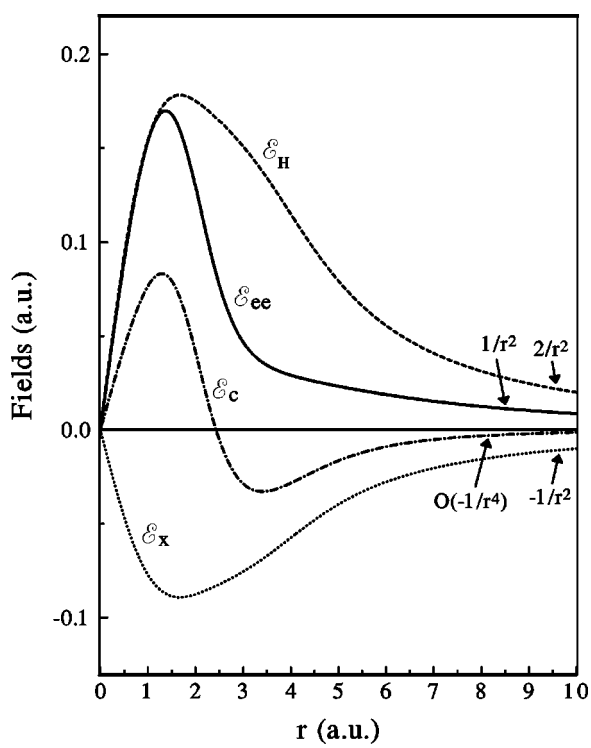

FIG. 3. The electron-interaction field $\boldsymbol{\mathcal{E}}_{ee}(r)$ and its Hartree $[\boldsymbol{\mathcal{E}}_H(r)]$, Pauli $[\boldsymbol{\mathcal{E}}_x(r)]$, and Coulomb $[\boldsymbol{\mathcal{E}}_c(r)]$ field components.

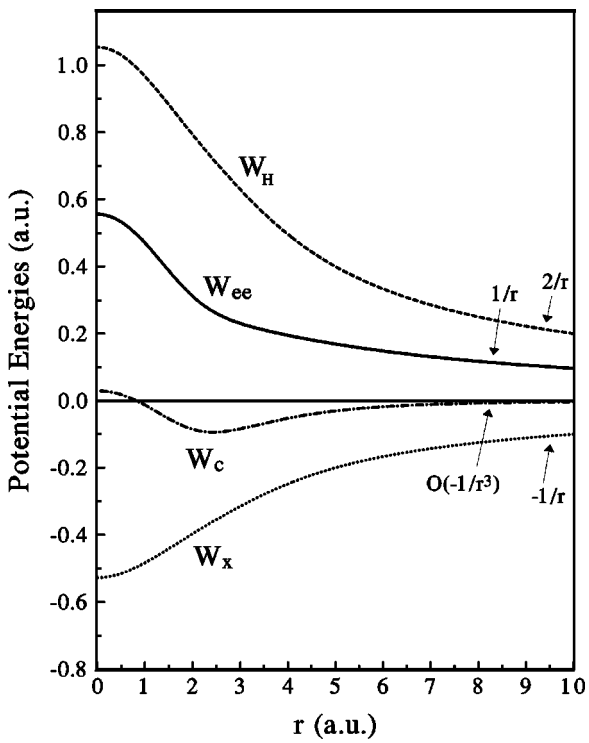

FIG. 4. The potential energy $W_{ee}(r)$, and its Hartree $[W_H(r)]$, Pauli $[W_x(r)]$, and Coulomb $[W_c(r)]$ potential-energy components

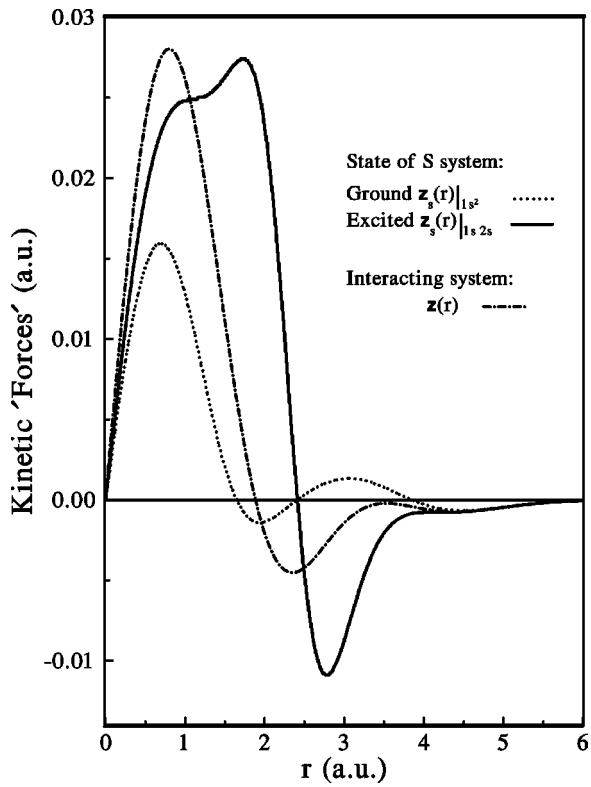

FIG. 5. The kinetic forces $\mathbf{z}(r)$ of the interacting system, and those of the S system $\mathbf{z}_s(r)|_{1s^2}$, $\mathbf{z}_s(r)|_{1s2s}$ in the ground $(1s^2)$ and excited $(1s2s)$ states, respectively.

two-electron case). The electron-interaction energy E_{ee}, and its Hartree (E_H), Pauli (E_x), and Coulomb (E_c) energy component values which remain the same are given in Table I.

It is the kinetic-energy field $\mathcal{Z}_s(r)$ of the noninteracting fermions or equivalently the correlation-kinetic field $\mathcal{Z}_{t_c}(r)$ that differs as a function of the state of the S system. In Fig. 5 we plot the interacting system kinetic "force" $\mathbf{z}(r)$, and ground- and excited-state S system kinetic forces $\mathbf{z}_s(r)|_{1s^2}$, $\mathbf{z}_s(r)|_{1s2s}$. Observe that the force $\mathbf{z}_s(r)|_{1s2s}$ has an additional structure when compared to $\mathbf{z}_s(r)|_{1s^2}$, because both a ground- and an excited-state orbital contribute to it. All the three forces vanish at the nucleus. They also all merge asymptotically. The differences $[\mathbf{z}_s(r)|_{1s^2}-\mathbf{z}(r)]$ and $[\mathbf{z}_s(r)|_{1s2s}-\mathbf{z}(r)]$ between the kinetic forces required for the determination of the corresponding correlation-kinetic fields $\mathcal{Z}_{t_c}(r)|_{1s^2}$ and $\mathcal{Z}_{t_c}(r)|_{1s2s}$, vanish in this region. This cancellation is important because the field $\mathcal{Z}_{t_c}(r)$ is also proportional to $1/\rho_k(r)$. Asymptotically, for large r, the contribution of $1/\rho_k(r)$ is singular. The exact cancellation of the kinetic forces then prevents the correlation-kinetic fields from being singular in the asymptotic region.

The correlation-kinetic fields $\mathcal{Z}_{t_c}(r)|_{1s^2}$, $\mathcal{Z}_{t_c}(r)|_{1s2s}$ are plotted in Fig. 6, and the potential energies $W_{t_c}(r)|_{1s^2}$, $W_{t_c}(r)|_{1s2s}$ in Fig. 7. As expected, the field and potential energy of the system in its excited state have more structure than when in its ground state. The correlation-kinetic fields both vanish at the nucleus, and therefore the potential energies have a zero slope there. Observe that asymptotically the fields are the same (Fig. 6). Thus, in this region, the potential energies are also the same (Fig. 7). Therefore, the effective fields $\mathcal{F}^{eff}_{1s^2}(r)$, $\mathcal{F}^{eff}_{1s2s}(r)$ of Eq. (8), and consequently, the S-system electron-interaction potential energies $v_{ee}(r)|_{1s^2}$, $v_{ee}(r)|_{1s2s}$, as obtained via Eq. (7) or Eq. (17), are the same (Fig. 8), decaying asymptotically as $1/r$. This ensures that the corresponding highest occupied eigenvalues ϵ_{1s^2} and ϵ_{2s} are the same (see Table I). Observe that both the $v_{ee}(r)$ are finite at the nucleus as must be the case [17]. The two potential energies $v_{ee}(r)$ of Fig. 8, one corresponding to the S system in the $1s^2$ state and the other to an S system in the $1s2s$ state, generate the same density $\rho(r)$ as that of the interacting system.

The noninteracting kinetic energy T_s of the two S systems in the different states as quoted in Table I differ significantly. So do the correlation-kinetic energies T_c determined from the fields of Fig. 6 via Eq. (19) (see Table I). However, they both add up to the kinetic energy $T=0.876\,262$ a.u. of the interacting system. The fact that T_s for the S system in the $1s2s$ state is greater than the one in the $1s^2$ state follows from the virial theorem. The $2s$ electron is further from the nucleus (see Fig. 2), and consequently has *higher* external potential energy since $v(\mathbf{r})$ is harmonic. Therefore, via the virial theorem its contribution to T_s is large.

For the S system in the ground $1s^2$ state, $T_c>T_s>0$. In fact, T_c is large and 63% of T. For the S system in the excited $1s2s$ state, $T_c<<T_s$ and $T_c<0$. The fact that T_c is negative is consistent with the structure of the field $\mathcal{Z}_{t_c}(r)|_{1s2s}$ of Fig. 6. The field is negative in two regions of

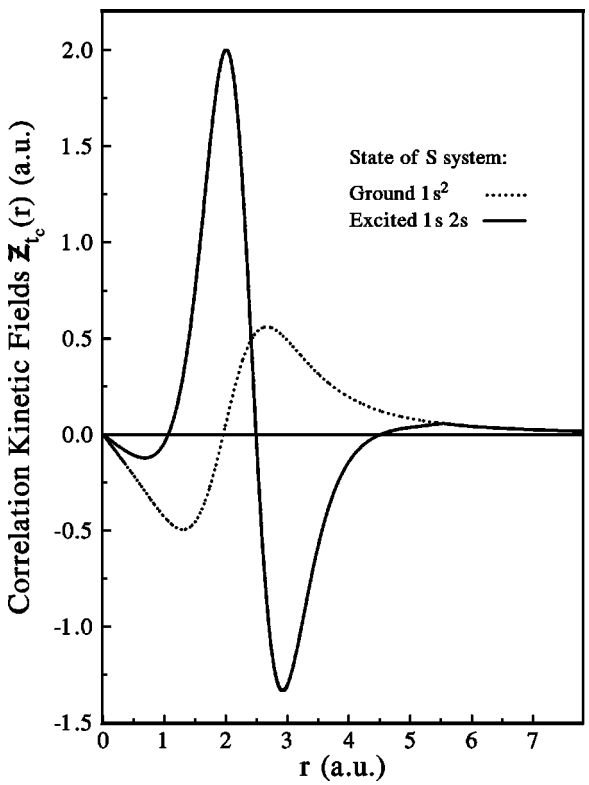

FIG. 6. The correlation-kinetic fields $\mathcal{Z}_{t_c}(r)$ for the S systems in the ground $(1s^2)$ and excited $(1s2s)$ states.

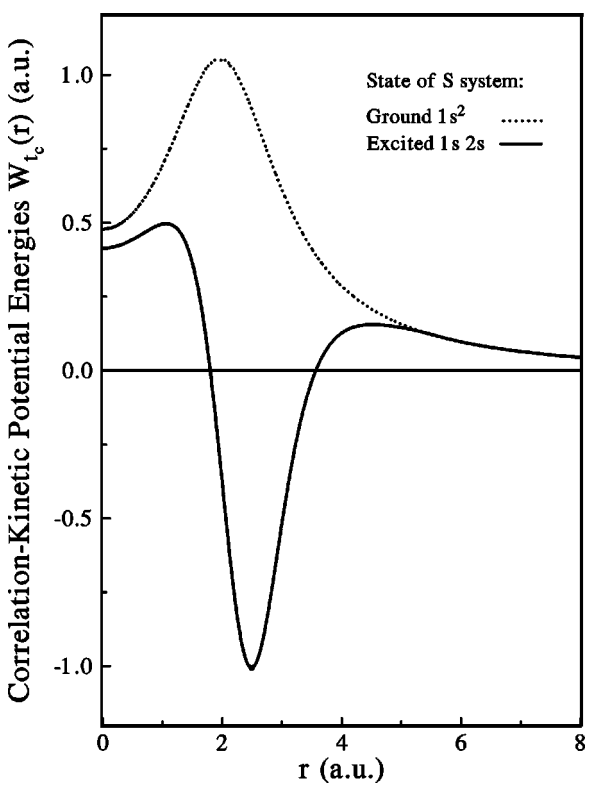

FIG. 7. The correlation-kinetic potential energies $W_{t_c}(r)$ for the S systems in the ground $(1s^2)$ and excited $(1s2s)$ states.

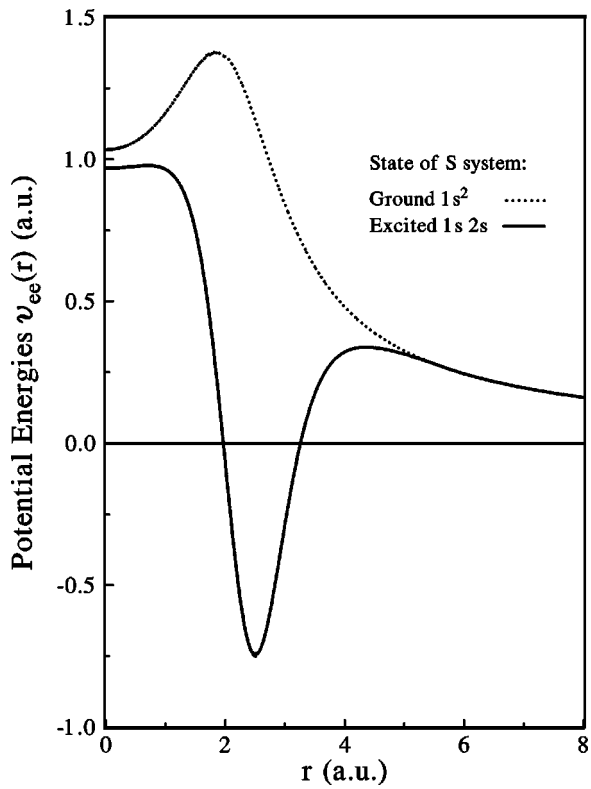

FIG. 8. The electron-interaction potential energies $v_{ee}(r)$ for the S systems in the ground $(1s^2)$ and excited $(1s2s)$ states.

space where the density is also high (Fig. 2). [We have become aware of a recent work [18] on the He atom whereby an S system in a $1s2s$ excited state is constructed to reproduce the density of the corresponding state of the interacting system. In this calculation, an accurate albeit approximate density is assumed, and the S system effective potential energy $v_s(\mathbf{r})$ determined indirectly by one of the standard density-based methods [19]. For this case too the difference $T-T_s=T_c<0$.]

IV. RESULTS EXPRESSED IN KOHN-SHAM THEORY TERMS

The results derived via Q-DFT can be expressed in the language of KS-DFT. For the transformation from the kth excited state of the interacting system to an S system in an excited state, the KS-DFT electron-interaction bidensity energy functional is written [10] as

$$E_{ee}^{KS}[\rho,\rho_0]|_{\rho=\rho_k}=E_H[\rho]|_{\rho=\rho_k}+E_{xc}^{KS}[\rho,\rho_0]|_{\rho=\rho_k}, \quad (21)$$

where $\rho_0(\mathbf{r})$, $\rho_k(\mathbf{r})$ are the ground- and excited-state densities, and $E_H[\rho]$ is the Hartree energy functional:

$$E_H[\rho]=\frac{1}{2}\int\int\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}', \quad (22)$$

and $E_{xc}^{KS}[\rho,\rho_0]$ the unknown-excited-state KS "exchange-correlation" energy bidensity functional. The corresponding electron-interaction potential energy is

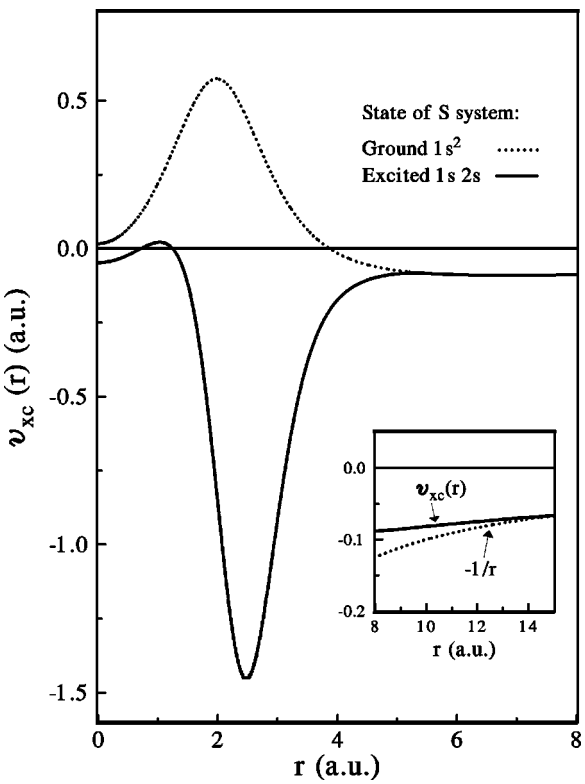

FIG. 9. The KS-DFT "exchange-correlation" potential energies $v_{xc}(r)$ for the S systems in the ground $(1s^2)$ and excited $(1s2s)$ states.

$$v_{ee}(\mathbf{r})=\left.\frac{\delta E_{ee}^{KS}[\rho,\rho_0]}{\delta\rho(\mathbf{r})}\right|_{\rho=\rho_k}=v_H(\mathbf{r})+v_{xc}(\mathbf{r}), \qquad (23)$$

where $v_H(\mathbf{r})=\delta E_H[\rho]/\delta\rho(\mathbf{r})|_{\rho=\rho_k}=\int d\mathbf{r}'\rho_k(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$ and $v_{xc}(\mathbf{r})=\delta E_{xc}^{KS}[\rho,\rho_0]/\delta\rho(\mathbf{r})|_{\rho=\rho_k}$ the KS "exchange-correlation" potential energy. As $v_{ee}(\mathbf{r})$ and $v_H(\mathbf{r})=W_H(\mathbf{r})$ are known via Q-DFT (Figs. 8 and 4), we plot in Fig. 9 $v_{xc}(\mathbf{r})$ for the S system in the $1s2s$ state. Note that this is the *exact* functional derivative for this excited state. It decays as $-1/r$, and is finite at the nucleus. The value (from Table I) of the KS energy $E_{xc}^{KS}[\rho,\rho_0]|_{\rho=\rho_k}=E_x+E_c+T_c=-0.509\,318$ a.u.

The answer to the question of how one transforms an excited state of the interacting system to one of noninteracting fermions in a *ground* state with equivalent density within the framework of KS-DFT is unknown. The GAC formulation [12] depends explicitly on the adiabatic path. The end point is not necessarily a ground state. One cannot employ the KS ground-state energy functional since it represents the ground state of the interacting system and not an excited state. Neither can one employ the excited-state bidensity energy functional because its functional derivative is unique to an S system in an excited state. Hence, let us *assume* that there exists an energy functional of the excited-state density that allows one within the context of KS-DFT to transform an excited state of the interacting system to an S system in its ground state. One may then define a corresponding KS exchange-correlation energy functional $E_{xc}^{KS(e\to g)}[\rho,\rho_0]|_{\rho=\rho_k}$ and the potential energy $v_{xc}(\mathbf{r})=\delta E_{xc}^{KS(e\to g)}[\rho,\rho_0]/\delta\rho(\mathbf{r})|_{\rho=\rho_k}$. Again, as the $v_{ee}(\mathbf{r})$ and $v_H(\mathbf{r})$ potential energies of the S system in the ground $(1s^2)$ state are known via Q-DFT (Figs. 8 and 4), the function $v_{xc}(\mathbf{r})$ may be determined, and is plotted in Fig. 9. It too decays as $-1/r$ asymptotically, and is also finite at the nucleus. The value (from Table I) of the energy $E_{xc}^{KS(e\to g)}[\rho_k,\rho_0]=0.178\,716$ a.u.

V. CONCLUDING REMARKS

In the Q-DFT of excited states, the mapping from a pure nondegenerate excited state of Schrödinger theory to one of noninteracting fermions with the same density is such that the state of the model S system is arbitrary. It may be in a ground state or in an excited state with the same or different configuration from that of the interacting system. In this paper we have demonstrated the state arbitrariness of the S system by transforming the first *excited* state of Hooke's atom to S systems in a singlet *ground* state $(1s^2)$ and a singlet first *excited* state $(1s2s)$. As expected, the kinetic energy T_s of the S system in its excited state is closer to the kinetic energy T of the interacting system. Equivalently, the magnitude of the correlation-kinetic energy T_c for the excited state S system is less. This is of relevance to the construction of the bidensity energy functional $E[\rho,\rho_0]$ of KS-DFT. In ground-state KS-DFT, the correlation-kinetic energy T_c contribution is small [3] compared to T_s. For excited state KS-DFT, it is then best to construct the S system to be in the same configuration as that of the interacting system.

An important property of the noninteracting systems is that their highest occupied eigenvalue is the negative of the ionization potential irrespective of the state the S system is in. This implies that the effective potential energy $v_s(\mathbf{r})$ of these S systems must vanish asymptotically in the classically forbidden region in the same manner. As the Pauli and Coulomb correlation contribution to the electron-interaction potential energy $v_{ee}(\mathbf{r})$ remains unchanged, this further means that the correlation-kinetic contribution must asymptotically be the same for each S system. This is explicitly demonstrated in the example studied in the paper. Over the rest of the atom, however, the correlation-kinetic fields and potential energies differ significantly. It follows, therefore, that the correlation-kinetic component is critical to ensuring the equivalence of the highest occupied eigenvalue of the S system in different configurations.

ACKNOWLEDGMENTS

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