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Quantal Density Functional Theory of Excited States

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We explain by quantal density functional theory the physics of mapping from any bound nondegenerate excited state of Schrödinger theory to an S system of noninteracting fermions with equivalent density and energy. The S system may be in a ground or excited state. In either case, the highest occupied eigenvalue is the negative of the ionization potential. We demonstrate this physics with examples. The theory further provides a new framework for calculations of atomic excited states including multiplet structure.

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In this paper we describe time-independent quantal density functional theory (Q-DFT) of singly or multiply excited bound nondegenerate states. This is a description of the physics of mapping from *any* such excited state, say the kth state of Schrödinger theory to that of a system of noninteracting fermions with equivalent density $\rho_k(\mathbf{r})$ and energy E_k. We shall denote such a noninteracting system as an S system, S being a mnemonic for "single Slater" determinant. The rationale for the transformation is that, in determining electronic structure, it is easier to solve N equations for particles in a *local* (multiplicative) potential than to solve the one N-electron Schrödinger equation. The understanding of the physics in turn allows for such calculations to be performed, albeit in an approximate manner. As in ground state Q-DFT [1], the description of the S system is in terms of fields derived from quantal sources. These fields are *separately* representative of electron correlations due to the Pauli exclusion principle, Coulomb repulsion, and correlation-kinetic effects. (Correlation-kinetic effects are a consequence of the difference in kinetic energy between the interacting Schrödinger and noninteracting S systems.) We prove that the potential energy $v_{ee}(\mathbf{r})$ of the noninteracting fermions, representative of *all* the many-body effects, is the work done to move an electron in the force of a conservative field comprised of the sum of the individual fields. Further, the total excited state energy E_k is also expressed in integral virial form in terms of these fields.

We begin by (i) presenting the formal rigorous framework of bound excited state Q-DFT. Within this framework, the model reference system is *arbitrary* in that the S system of noninteracting fermions may either be in (a) its *ground state,* or (b) in an *excited state* with, say, the same configuration as in Schrödinger theory. The difference between these reference systems is accounted for entirely by correlation-kinetic effects. In *either* case, the highest occupied eigenvalue of the S system differential equation is the negative of the ionization potential. We further note that, within this framework, atomic multiplet structure can also be obtained. We then (ii) demonstrate the transformation from an *excited singlet state* of Schrödinger theory to that of an S system in its *ground* state for the exactly solvable Hooke's atom [2]. In this manner, the *exact* separate contributions of the Pauli, Coulomb, and correlation-kinetic effects to the total and potential energy are determined. Next, (iii) we demonstrate the excited S system representation of Q-DFT, and the use of approximate wave functions, by performing self-consistent calculations of various excited states of the Li atom within the Pauli-correlated approximation. In this approximation, only correlations due to the Pauli exclusion principle are considered. We then (iv) propose, within both the ground and excited S system representations, a new calculational scheme for going beyond the Pauli correlated approximation. Finally, (v) we explain via Q-DFT the physics underlying the bidensity energy functional and functional derivative of the Kohn-Sham (KS) DFT of excited states [3], and the differences between the two theories.

The Q-DFT excited state formalism occurs as follows. The Schrödinger equation for the kth excited state is

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

$\hat{T} = -\frac{1}{2}\sum_i \nabla_i^2$, $\hat{V} = \sum_i v(\mathbf{r}_i)$, $\hat{U} = \frac{1}{2}\sum_{i,j}' 1/|\mathbf{r}_i - \mathbf{r}_j|$, where Ψ_k and E_k are a bound nondegenerate excited state wave function and energy, respectively, $\mathbf{X} = \mathbf{x}_1, \ldots, \mathbf{x}_N$, $\mathbf{x} = \mathbf{r}\sigma$, with σ the spin coordinate. The differential virial theorem satisfied by this wave function is

$$\nabla v(\mathbf{r}) = -\mathbf{F}_k(\mathbf{r}), \tag{2}$$

where the field $\mathbf{F}_k(\mathbf{r}) = -\mathcal{E}_{ee}(\mathbf{r}) + \mathcal{D}(\mathbf{r}) + \mathcal{Z}(\mathbf{r})$. The electron-interaction field $\mathcal{E}_{ee}(\mathbf{r})$, representative of Pauli and Coulomb correlations, is obtained via Coulomb's law as $\mathcal{E}_{ee}(\mathbf{r}) = \int d\mathbf{r}'\, g(\mathbf{r},\mathbf{r}')(\mathbf{r} - \mathbf{r}')/|\mathbf{r} - \mathbf{r}'|^3$. Its source is the pair-correlation density $g(\mathbf{r},\mathbf{r}') = \langle\Psi_k|\hat{P}(\mathbf{r},\mathbf{r}')|\Psi_k\rangle/\rho_k(\mathbf{r})$, where $\hat{P}(\mathbf{r},\mathbf{r}') = \sum_{i,j}' \delta(\mathbf{r} - \mathbf{r}_i)\delta(\mathbf{r}' - \mathbf{r}_j)$, and the density $\rho_k(\mathbf{r}) = \langle\Psi_k|\hat{\rho}|\Psi_k\rangle$, $\hat{\rho} = \sum_i \delta(\mathbf{r} - \mathbf{r}_i)$. Since $g(\mathbf{r},\mathbf{r}') = \rho_k(\mathbf{r}') + \rho_{xc}(\mathbf{r},\mathbf{r}')$, where $\rho_{xc}(\mathbf{r},\mathbf{r}')$ is the dynamic Fermi-Coulomb hole charge, we can then write $\mathcal{E}_{ee}(\mathbf{r})$ as the sum of the Hartree $\mathcal{E}_{\mathrm{H}}(\mathbf{r})$ and Pauli-Coulomb $\mathcal{E}_{xc}(\mathbf{r})$ fields. The differential density field $\mathcal{D}(\mathbf{r}) = \mathbf{d}(\mathbf{r})/\rho_k(\mathbf{r})$, $\mathbf{d}(\mathbf{r}) = -\frac{1}{4}\nabla\nabla^2\rho_k(\mathbf{r})$, and its source is the density. The kinetic field $\mathcal{Z}(\mathbf{r}) =$

$\mathbf{z}(\mathbf{r},[\gamma_k])/\rho_k(\mathbf{r})$, where the field $\mathbf{z}(\mathbf{r})$ is defined by its component $z_\alpha(\mathbf{r}) = 2\sum_\beta \partial t_{\alpha\beta}(\mathbf{r})/\partial r_\beta$, with $t_{\alpha\beta}(\mathbf{r};[\gamma_k]) = \frac{1}{4}[\partial^2/\partial r'_\alpha \partial r''_\beta + \partial^2/\partial r'_\beta \partial r''_\alpha]\gamma_k(\mathbf{r}',\mathbf{r}'')|_{\mathbf{r}'=\mathbf{r}''=\mathbf{r}}$ the kinetic energy density tensor. Here the source is the spinless single particle density matrix $\gamma_k(\mathbf{r},\mathbf{r}') = \langle\Psi_k|\hat{X}|\Psi_k\rangle$, $\hat{X} = \hat{A} + i\hat{B}$, $\hat{A} = (\frac{1}{2})\sum_j[\delta(\mathbf{r}_j - \mathbf{r})T_j(\mathbf{a}) + \delta(\mathbf{r}_j - \mathbf{r}')T_j(-\mathbf{a})]$, $\hat{B} = -(i/2)\sum_j[\delta(\mathbf{r}_j - \mathbf{r})T_j(\mathbf{a}) - \delta(\mathbf{r}_j - \mathbf{r}')T_j(-\mathbf{a})]$, $T_j(\mathbf{a})$ is a translation operator, and $\mathbf{a} = \mathbf{r}' - \mathbf{r}$.

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

$$\left[-\tfrac{1}{2}\nabla^2 + v(\mathbf{r}) + v_{ee}(\mathbf{r})\right]\varphi_i(\mathbf{x}) = \epsilon_i\varphi_i(\mathbf{x}), \qquad (3)$$

with $\rho_k(r) = \langle\Phi\{\varphi_i\}|\hat{\rho}|\Phi\{\varphi_i\}\rangle = \sum_{i,\sigma}|\varphi_i(\mathbf{x})|^2$, and $\Phi\{\varphi_i\}$ the *single* Slater determinant of the orbitals $\varphi_i(\mathbf{x})$. The $\varphi_i(\mathbf{x})$ may be the N lowest lying states corresponding to a ground state configuration, or they may be in an excited state with the same configuration as in Schrödinger theory. In either case, the highest occupied eigenvalue $\epsilon_m = -I_k$, the negative of the ionization potential. This follows from the known asymptotic structure of the density. The differential virial theorem satisfied by $\Phi\{\varphi_i\}$ is

$$\nabla v(\mathbf{r}) = -\mathbf{F}_s(\mathbf{r}), \qquad (4)$$

where the field $\mathbf{F}_s(\mathbf{r}) = \nabla v_{ee}(\mathbf{r}) + \mathcal{D}(\mathbf{r}) + \mathcal{Z}_s(\mathbf{r})$, and the kinetic field $\mathcal{Z}_s(\mathbf{r}) = \mathbf{z}_s(\mathbf{r};[\gamma_{s,k}])/\rho_k(\mathbf{r})$. The field $\mathbf{z}_s(\mathbf{r};[\gamma_{s,k}])$ is defined in terms of its source, the Dirac density matrix $\gamma_{s,k}(\mathbf{r},\mathbf{r}') = \langle\Phi\{\varphi_i\}|\hat{X}|\Phi\{\varphi_i\}\rangle = \sum_{i,\sigma}\varphi_i^*(\mathbf{r}\sigma)\varphi_i(\mathbf{r}'\sigma)$ as $z_{s,\alpha}(\mathbf{r}) = 2\sum_\beta \partial t_{s,\alpha\beta}(\mathbf{r})/\partial r_\beta$, where $t_{s,\alpha\beta}(\mathbf{r};[\gamma_{s,k}]) = \frac{1}{4}[\partial^2/\partial r'_\alpha\partial r''_\beta + \partial^2/\partial r'_\beta\partial r''_\alpha] \times \gamma_{s,k}(\mathbf{r}',\mathbf{r}'')|_{\mathbf{r}'=\mathbf{r}''=\mathbf{r}}$.

Equating Eqs. (2) and (4), we have that $v_{ee}(\mathbf{r})$ is the work done to move an electron in the force of the conservative field $\mathcal{F}_k(\mathbf{r})$:

$$v_{ee}(\mathbf{r}) = -\int_\infty^{\mathbf{r}} \mathcal{F}_k(\mathbf{r}')\cdot d\mathbf{l}', \qquad (5)$$

where $\mathcal{F}_k(\mathbf{r}) = \mathcal{E}_{\mathrm{H}}(\mathbf{r}) + \mathcal{E}_{xc}(\mathbf{r}) + \mathcal{Z}_{t_c}(\mathbf{r})$, and $\mathcal{Z}_{t_c}(\mathbf{r}) = \mathcal{Z}_s(\mathbf{r}) - \mathcal{Z}(\mathbf{r})$ is the correlation-kinetic field. To delineate the separate contributions of Pauli and Coulomb correlations, we write $\rho_{xc}(\mathbf{r},\mathbf{r}') = \rho_x(\mathbf{r},\mathbf{r}') + \rho_c(\mathbf{r},\mathbf{r}')$, where $\rho_x(\mathbf{r},\mathbf{r}') = -|\gamma_{s,k}(\mathbf{r},\mathbf{r}')|^2/2\rho_k(\mathbf{r})$ is the Fermi hole with $\int\rho_x(\mathbf{r},\mathbf{r}')\,d\mathbf{r}' = -1$, and $\rho_c(\mathbf{r},\mathbf{r}')$ is the Coulomb hole with $\int\rho_c(\mathbf{r},\mathbf{r}')\,d\mathbf{r}' = 0$. Thus, $\mathcal{F}_k(\mathbf{r}) = \mathcal{E}_{\mathrm{H}}(\mathbf{r}) + \mathcal{E}_x(\mathbf{r}) + \mathcal{E}_c(\mathbf{r}) + \mathcal{Z}_{t_c}(\mathbf{r})$, where $\mathcal{E}_x(\mathbf{r})$ and $\mathcal{E}_c(\mathbf{r})$ are the corresponding Pauli and Coulomb fields. The fields $\mathcal{E}_{xc}(\mathbf{r})$, or $\mathcal{E}_x(\mathbf{r})$ and $\mathcal{E}_c(\mathbf{r})$, and $\mathcal{Z}_{t_c}(\mathbf{r})$ are not necessarily conservative. Their sum always is.

The excited state energy is

$$E_k = T_s + \int\rho_k(\mathbf{r})v(\mathbf{r})\,d\mathbf{r} + E_{ee} + T_c, \qquad (6)$$

where $T_s = \langle\Phi\{\varphi_i\}|\hat{T}|\Phi\{\varphi_i\}\rangle$ is the S system kinetic energy. The electron interaction E_{ee} and correlation-kinetic T_c energies are expressed in terms of the fields in integral virial form as

$$E_{ee} = \int d\mathbf{r}\,\rho_k(\mathbf{r})\mathbf{r}\cdot\mathcal{E}_{ee}(\mathbf{r}) \quad \text{and}$$
$$T_c = \frac{1}{2}\int d\mathbf{r}\,\rho_k(\mathbf{r})\mathbf{r}\cdot\mathcal{Z}_{t_c}(\mathbf{r}). \qquad (7)$$

The energy E_{ee} is the sum of its Hartree E_{H}, Pauli E_x, and Coulomb E_c components with each energy expressed in virial form in terms of the corresponding field.

Equations (3), (5), and (7) define the system of noninteracting fermions, either in their ground state or excited state, that will reproduce the density and energy of any bound nondegenerate excited state of Schrödinger theory. It follows that the differences in the corresponding local potentials are due entirely to correlation-kinetic effects since it is the field $\mathcal{Z}_{t_c}(\mathbf{r})$ that is different. In either case, the ionization potential is the negative of the highest occupied eigenvalue.

In a similar manner, it is possible by Q-DFT to construct S systems which reproduce the density and energy of bound nondegenerate excited states as determined within Hartree-Fock and Hartree theories.

To demonstrate the mapping from an excited state of Schrödinger theory to a ground state of an S system, we consider the first excited singlet state of Hooke's atom which is comprised of two electrons in a harmonic external potential $v(\mathbf{r}) = \frac{1}{2}\omega^2 r^2$. The wave function for this state is

$$\Psi_1(\mathbf{r}_1,\mathbf{r}_2) = C_0 e^{-\omega R^2} e^{-\omega r^2/4}\left[1 + C_1\sqrt{\frac{\omega}{2}}\,r + C_2\left(\frac{\omega}{2}\right)r^2 + C_3\left(\frac{\omega}{2}\right)^{3/2} r^3\right], \qquad (8)$$

where $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$, $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$, $C_0 = 0.026\,100\,5$, $C_1 = 1.146\,884$, $C_2 = -0.561\,569$, $C_3 = -0.489\,647$, and $\omega = 0.380\,129$. The energy $E_1 = 2.280\,775$ a.u. The space orbitals of the corresponding singlet ground state of the S system are $\varphi_i(\mathbf{r}) = \sqrt{\rho_1(\mathbf{r})/2}$, $i = 1, 2$.

As the atom in this excited state is spherically symmetric, the potential $v_{ee}(\mathbf{r}) = W_{\mathrm{H}}(\mathbf{r}) + W_x(\mathbf{r}) + W_c(\mathbf{r}) + W_{t_c}(\mathbf{r})$, where W_{H}, W_x, W_c, and W_{t_c} are, respectively, the work done in the fields $\mathcal{E}_{\mathrm{H}}$, $\mathcal{E}_x$, $\mathcal{E}_c$, and $\mathcal{Z}_{t_c}$. This potential, whose components are plotted in Fig. 1, then generates the same density $\rho_1(\mathbf{r})$ and energy E_1 as obtained from Eq. (8). For completeness, $T_s = 0.327\,471$ a.u., $E_{ee} = 0.352\,142$ a.u., $E_{\mathrm{H}} = 0.722\,217$ a.u., $E_x = -0.361\,109$ a.u., $E_c = -0.008\,966$ a.u., and $T_c = 0.548\,791$ a.u. Note that T_c is 63% of $T = \langle\Psi|\hat{T}|\Psi\rangle$. In contrast, in the transformation [1] from the ground state of Hooke's atom, T_c is 4% of T. Hence, correlation-kinetic effects are of much greater significance in the transformation of excited states to ground state systems.

To provide further proof that the S system is in its ground state, we have solved Eq. (3) numerically for the $v_{ee}(\mathbf{r})$ determined and thereby obtained the excited state density from the resulting zero node orbitals generated. Further, the single eigenvalue determined

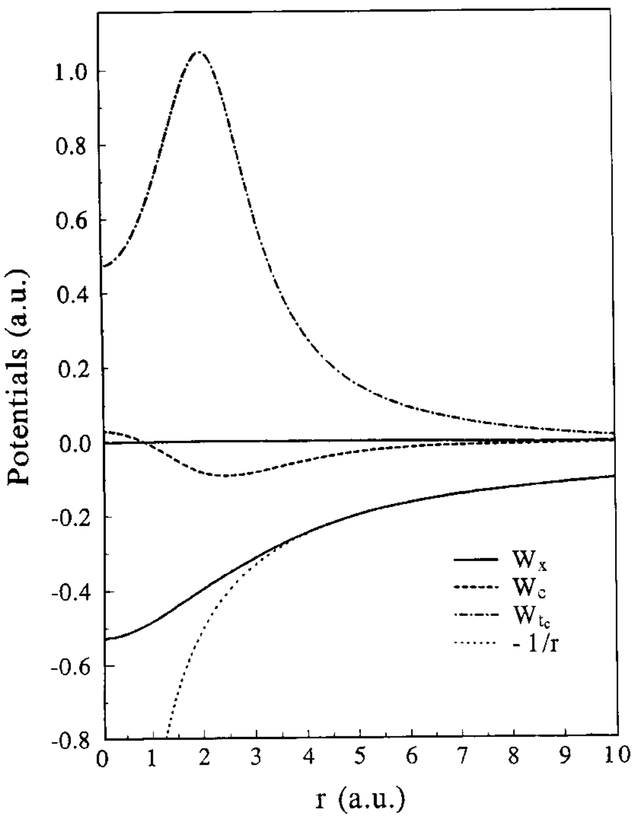

FIG. 1. The Pauli $W_x(\mathbf{r})$, Coulomb $W_c(\mathbf{r})$, and correlation-kinetic $W_{t_c}(\mathbf{r})$ potentials of the first excited singlet state of Hooke's atom.

corresponds to minus the ionization potential: $\epsilon_0 = -I_1 = 1.710\,582$ a.u. Thus, we have demonstrated that it is possible to transform *any* nondegenerate excited state of Schrödinger theory to a ground state of noninteracting fermions with equivalent density, energy, and ionization potential.

We next present self-consistent results for excited states of Li ([He] $3d$, $4d$, $5d$, $4f$, $5f$) within the Pauli-correlated and central-field approximations in which the S system is in an *excited* state with the same configuration as that of the excited state of Schrödinger theory. In this case $v_{ee}(\mathbf{r}) = W_{\mathrm{H}}(\mathbf{r}) + W_x(\mathbf{r})$, with $W_x(\mathbf{r})$ plotted in Fig. 2 for the Li: [He] $4d$, $4f$ states. The inset shows the asymptotic structure where the shell corresponding to the excited state electron is clearly evident. In Table I we present total energies together with those of Hartree-Fock (HF) theory. The Q-DFT results constitute an upper bound, being within 5 ppm of those of the latter. The results of configuration interaction (CI) calculations [4], which expectedly are lower, are also quoted. In Table II, we present the results for the ionization potential as obtained via the highest occupied eigenvalue ϵ_m as well as by total energy differences, together with experimental values [5]. The accuracy of these results speaks for itself. Those of the ϵ_m are because the asymptotic structure of $v_{ee}(\mathbf{r})$ for the fully interacting system is given by the Pauli potential $W_x(\mathbf{r}) \underset{r\to\infty}{\sim} -1/r$.

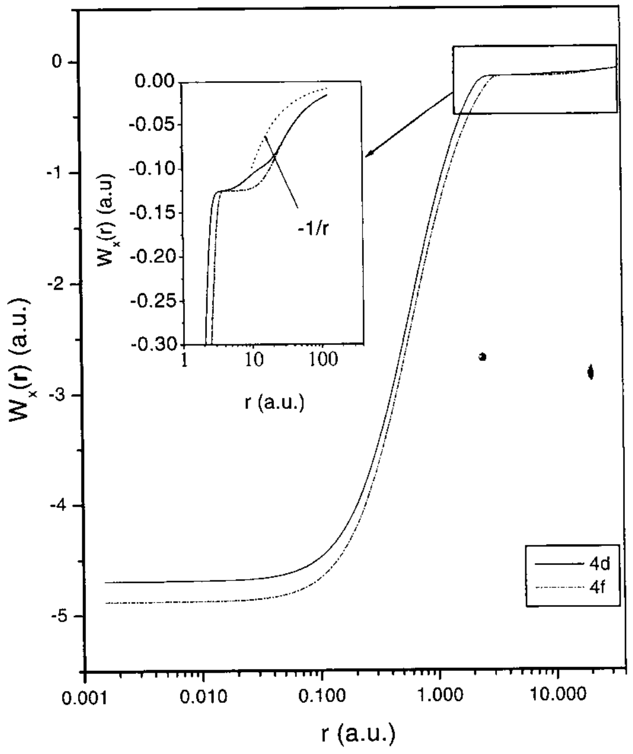

FIG. 2. The Pauli potential $W_x(\mathbf{r})$ of the excited states of Li: [He] $4d$, $4f$.

The Slater determinant of the previous example constitutes an approximate wave function representative only of Pauli correlations. Coulomb correlations and correlation-kinetic effects may additionally be incorporated by assuming an approximate few-parameter correlated wave function. One such choice for a nondegenerate excited state which satisfies the electron-electron cusp condition is [6]

$$\Psi(\mathbf{X};[\rho]) = \Phi\{\varphi_i\}\prod_{i\neq j}\{1 - f(\mathbf{r}_i,\mathbf{r}_j;[\rho]\}. \tag{9}$$

As in the above example, the excited state is identified by the Slater determinant $\Phi\{\varphi_i\}$ of the solutions of the S system differential equation [Eq. (3)] in the *excited* state configuration. The $f(\mathbf{r}_i,\mathbf{r}_j;[\rho])$ is a spinless correlation functional: $f(\mathbf{r}_i,\mathbf{r}_j;[\rho]) = \exp(-\beta^2 r^2)[1 - \chi(R)(1 + r/2)]$, where $\mathbf{r} = \mathbf{r}_i - \mathbf{r}_j$, $\mathbf{R} = (\mathbf{r}_i + \mathbf{r}_j)/2$, $\beta = q\rho^{1/3}(R)$, q is a variational parameter and $\chi(R)$ is determined by

TABLE I. Total energies of the excited states of Li.

	−Total energy (a.u.)		
Li	Q-DFT (Pauli approx.)	HF	CI (Ref. [4])
[He]$3d$	7.291 94	7.291 98	7.335 52
[He]$4d$	7.267 64	7.267 67	7.311 19
[He]$5d$	7.256 40	7.256 42	7.299 93
[He]$4f$	7.267 66	7.267 67	7.311 17
[He]$5f$	7.256 41	7.256 42	7.299 92

TABLE II. Ionization potentials of the excited states of Li.

	Ionization potential (a.u.)			
	$-\varepsilon_m$		$E_k - E_k^{\rm ion}$	
Li	Q-DFT (Pauli approx.)		CI (Ref. [4])	Expt. (Ref. [5])
[He]3*d*	0.055 72	0.055 54	0.055 61	0.055 61
[He]4*d*	0.031 37	0.031 24	0.031 28	0.031 27
[He]5*d*	0.020 08	0.020 00	0.020 02	0.020 01
[He]4*f*	0.031 25	0.031 26	0.031 26	0.031 24
[He]5*f*	0.020 00	0.020 01	0.020 00	0.019 97

the Coulomb hole sum rule. The products of the correlation functional are limited to lowest order since higher-order products of these factors are of less significance. If a ground state S system is constructed, then the excited state is identified in the Slater determinant of Eq. (9) by the corresponding excited but unoccupied orbitals of the S system differential equation. For atomic multiplet structure, the appropriate linear combination of Slater determinants is employed in Eq. (9). We are presently applying this wave function for Q-DFT calculations of excited states.

The origin of the mathematically rigorous framework of Q-DFT of bound excited states presented here harks back to the work of Harbola and Sahni [7], whose ideas were based on physical considerations. The framework, therefore, provides both a justification for, as well as explains, the accuracy of the numerous [8] excited state calculations including singly and multiply excited multiplet structure [8] performed on the basis of these ideas.

Q-DFT and KS DFT differ fundamentally in their description of the S system. In Q-DFT, the total and potential energy of the noninteracting fermions are defined in terms of fields and quantal sources. Within KS DFT, on the other hand, these properties are described, respectively, in terms of an energy functional of the density and of its functional derivative. More recently, KS DFT has been extended [3] to the *individually excited* state. In the corresponding KS DFT representation of the S system, all the many-body effects are incorporated in a *bidensity* electron-interaction functional $E_{ee}^{\rm KS}[\rho,\rho_0]|_{\rho_k}$, where $\rho_0(\mathbf{r})$ is the ground and $\rho_k(\mathbf{r})$ the excited state density. (This functional is different from the KS DFT ground state functional $E_{ee}^{\rm KS}[\rho]|_{\rho_0}$.) The corresponding local electron-interaction potential is defined as the functional derivative $\delta E_{ee}^{\rm KS}[\rho,\rho_0]/\delta\rho(\mathbf{r})|_{\rho_k}$. The S system is assumed to be in an *excited* state. Now, since within Q-DFT it is also possible to obtain the excited state density and energy from an S system in its *ground* state, its scope is broader. The remarkable fact that such an S system can be constructed was previously unknown [9], and provides new mathematical and physical insight into the excited state problem. In particular, we now understand that the arbitrary nature of the reference S system is governed entirely by the correlation-kinetic effect. Further, Q-DFT provides the physical meaning of the functional $E_{ee}^{\rm KS}[\rho,\rho_0]|_{\rho_k}$ and of its derivative. The functional is the sum of E_{ee} and T_c of Eq. (7) as expressed in terms of the electron-interaction $\mathcal{E}_{ee}(\mathbf{r})$ and correlation-kinetic $\mathcal{Z}_{t_c}(\mathbf{r})$ fields, and the functional derivative is the work done in the conservative field $\mathcal{F}_k(\mathbf{r})$ as defined by Eq. (5).

In conclusion, we have explained and demonstrated the physics of mapping from any nondegenerate excited state of Schrödinger theory to an S system of noninteracting fermions with equivalent density and energy. The S system may either be in a ground state or an excited state. In turn, these ideas have led to new methodology for performing excited state calculations including atomic multiplet structure. To further emphasize the arbitrary nature of the reference system, we note that it is also possible within Q-DFT to transform an excited state of Schrödinger theory to a *ground* state of noninteracting bosons with equivalent excited state density, energy, and ionization potential. We discuss the physics of this transformation elsewhere. However, for two electrons, the differential equations for noninteracting fermions and bosons in their ground state are the same, so that the demonstration above of the Hooke's atom is equally an example of the transformation to the system of noninteracting bosons.

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