

Physics of transformation from Schrödinger theory to Kohn-Sham density-functional theory: Application to an exactly solvable model

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According to Hohenberg-Kohn-Sham density-functional theory (DFT), and its constrained search formulation, the Schrödinger ground-state wave function Ψ is a functional of the ground-state electronic density $\rho(\mathbf{r})$. But the *explicit* functional dependence of Ψ on ρ is unknown. It is, however, possible to describe Kohn-Sham (KS) DFT and its electron-interaction energy functional and functional derivative rigorously in terms of the wave function Ψ . This description involves a conservative field which is a sum of two fields, the first representative of electron correlations due to the Pauli exclusion principle and Coulomb repulsion, and the second of correlation-kinetic effects. The sources of these fields are expectations of Hermitian operators with respect to Ψ . The energy functional is expressed in integral virial form in terms of these fields, whereas the functional derivative is the work done to move an electron in the conservative field of their sum. In this paper we illustrate the physics of transformation from Schrödinger to KS theory by application of this description to a ground state of the exactly solvable Hooke's atom. As such we determine properties such as the pair-correlation density, the Fermi and Coulomb holes, the Schrödinger and KS kinetic-energy-density tensors and kinetic fields, and the electron-interaction and correlation-kinetic fields, potentials, and energies, the majority of these constituent properties of the transformation being obtained analytically. In this manner we demonstrate the separate contributions and significance of each type of electron correlation to the KS electron-interaction energy and its functional derivative. Based on this study and previous work, it is proposed that in the construction of approximate energy functionals and their derivatives for application to more complex systems, it is the fields that be directly approximated. [S1050-2947(98)07904-9]

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I. INTRODUCTION

In this paper, we explain, by example, the physics of transformation from Schrödinger [1] theory to Hohenberg-Kohn-Sham [2] density-functional theory [3]. For a system of N electrons in a local external potential, the Schrödinger equation is a $3N$ -dimensional coupled differential equation. On the other hand, the Kohn-Sham equations comprise N three-dimensional single-particle equations for *noninteracting* fermions bound by the *same* local effective potential. The relationship between the theories is based on two fundamental theorems [2]. First, the Schrödinger system wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ with $\mathbf{x} \equiv \mathbf{r}, \sigma$, is a functional of the ground-state electronic density $\rho(\mathbf{r})$. Thus, the ground-state energy E is such a functional. And second, that the ground-state energy can be obtained by a variational principle involving only the density. Therefore, for arbitrary norm-conserving variations of the density, the exact energy corresponds to that of the ground-state density. According to Hohenberg-Kohn-Sham, therefore, *all* information about the system can be obtained by a knowledge of the ground-state density. The functional $\Psi[\rho]$ is also defined by the constrained search formulation [4] as that antisymmetric function which yields the ground-state density $\rho(\mathbf{r})$ and delivers the minimum of the expectation of the kinetic and electron interaction operators. However, the *explicit* functional dependence of Ψ on $\rho(\mathbf{r})$ is at present unknown. It is, however, possible to describe [5–8] Kohn-Sham density-functional

theory directly in terms of the system wave function Ψ itself. This quantum-mechanical interpretation [5,6] involves fields whose source distributions are expectations of Hermitian operators. These sources, and consequently the fields, are representative of the different electron correlations present. In this manner, a rigorous physical description of Kohn-Sham theory is provided. It is this description, by application to an exactly solvable model system, that we provide in the paper.

The model we consider is Hooke's atom [9], which is comprised of two electrons in an external harmonic oscillator potential. For a certain infinite set of discrete oscillator frequencies, analytical solutions [10,11] of the corresponding Schrödinger equation exist. The model, and a variation [12] of it that incorporates an additional linear electron-interaction term to the Hamiltonian, have been employed for various studies in the literature [12,13]. But as a consequence of the fact that the exact density is known, the model has more recently been used [14] in the context of density-functional theory for testing the accuracy of approximate Kohn-Sham "exchange-correlation" energy functionals and their derivatives (potentials). In our work we employ the ground-state wave function to illustrate the physics, whereby this *interacting* system is transformed to one of *noninteracting* fermions with the same density and energy. Since the wave function is exactly known, the majority of the requisite properties of this transformation are determined *analytically*.

In Sec. II we define properties within conventional Kohn-Sham theory, and briefly describe its quantum-mechanical interpretation. In Sec. III we determine the constituent prop-

erties of the interpretation for the Hooke's atom, and end in Sec. IV with a summary and concluding remarks.

II. DEFINITIONS

A. Definitions within conventional Kohn-Sham theory

In Kohn-Sham (KS) theory, the ground-state energy functional is written as

$$E[\rho] = T_s[\rho] + \int \nu(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + E_{ee}^{\text{KS}}[\rho], \quad (1)$$

where $T_s[\rho]$ is the kinetic energy of noninteracting fermions of density $\rho(\mathbf{r})$, $\nu(\mathbf{r})$ the external potential, and $E_{ee}^{\text{KS}}[\rho]$ the KS electron-interaction energy functional. The functional $E_{ee}^{\text{KS}}[\rho]$ thus incorporates correlations due to the Pauli exclusion principle, Coulomb repulsion, as well as the correlation contribution $T_c[\rho]$ to the kinetic energy. The KS differential equations are

$$\left[-\frac{1}{2}\nabla^2 + \nu(\mathbf{r}) + \nu_{ee}(\mathbf{r})\right]\varphi_i(\mathbf{x}) = \epsilon_i\varphi_i(\mathbf{x}), \quad i = 1, \dots, N, \quad (2)$$

where the local potential $\nu_{ee}(\mathbf{r})$ representing all the electron correlations is defined as the functional derivative

$$\nu_{ee}(\mathbf{r}) = \frac{\delta E_{ee}^{\text{KS}}[\rho]}{\delta \rho(\mathbf{r})}. \quad (3)$$

B. Quantum-mechanical interpretation of Kohn-Sham theory

The quantum-mechanical interpretation [5,6] of KS theory is in terms of a conservative field $\mathcal{F}(\mathbf{r})$ so that $\nabla \times \mathcal{F}(\mathbf{r}) = \mathbf{0}$. The field $\mathcal{F}(\mathbf{r})$ is the sum of its electron-interaction $\mathcal{E}_{ee}(\mathbf{r})$ and correlation-kinetic $\mathcal{Z}_{t_c}(\mathbf{r})$ components:

$$\mathcal{F}(\mathbf{r}) = \mathcal{E}_{ee}(\mathbf{r}) + \mathcal{Z}_{t_c}(\mathbf{r}). \quad (4)$$

The field $\mathcal{E}_{ee}(\mathbf{r})$ is determined by Coulomb's law from the pair-correlation density $g(\mathbf{r}, \mathbf{r}')$ so that

$$\mathcal{E}_{ee}(\mathbf{r}) = \int \frac{g(\mathbf{r}, \mathbf{r}')(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} d\mathbf{r}', \quad (5)$$

where $g(\mathbf{r}, \mathbf{r}') = \langle \Psi | \sum_{i \neq j} \delta(\mathbf{r}_i - \mathbf{r}) \delta(\mathbf{r}_j - \mathbf{r}') | \Psi \rangle / \rho(\mathbf{r})$ is the pair-correlation density.

The field $\mathcal{Z}_{t_c}(\mathbf{r})$ is the difference of two fields $\mathbf{z}_s(\mathbf{r})$ and $\mathbf{z}(\mathbf{r})$, which are derived from the kinetic-energy-density tensors $t_{\alpha\beta}(\mathbf{r})$ and $t_{s,\alpha\beta}(\mathbf{r})$ for the interacting Schrödinger and the noninteracting KS systems, respectively. Thus,

$$\mathcal{Z}_{t_c}(\mathbf{r}) = \frac{1}{\rho(\mathbf{r})} \{ \mathbf{z}_s(\mathbf{r}; [\gamma_s]) - \mathbf{z}(\mathbf{r}; [\gamma]) \}, \quad (6)$$

where the component $z_\alpha(\mathbf{r})$ of the field $\mathbf{z}(\mathbf{r})$ is $z_\alpha(\mathbf{r}) = 2 \sum_\beta (\partial / \partial r_\beta) t_{\alpha\beta}(\mathbf{r}; [\gamma])$, $t_{\alpha\beta}(r; [\gamma]) = \frac{1}{4} (\partial^2 / \partial r'_\alpha \partial r''_\beta + \partial^2 / \partial r'_\beta \partial r''_\alpha) \gamma(\mathbf{r}', \mathbf{r}'') |_{r'=r''=r}$, and $\gamma(\mathbf{r}, \mathbf{r}')$ is the spinless single-particle density matrix [3]. The field $\mathbf{z}_s(\mathbf{r})$ is similarly obtained from the idempotent Dirac density matrix [3] $\gamma_s(\mathbf{r}, \mathbf{r}')$ derived from the KS Slater determinant $\Phi\{\varphi_i\}$.

The KS electron-interaction energy functional $E_{ee}^{\text{KS}}[\rho]$ and its derivative can be expressed in virial form in terms of the fields $\mathcal{E}_{ee}(\mathbf{r})$ and $\mathcal{Z}_{t_c}(\mathbf{r})$:

$$E_{ee}^{\text{KS}}[\rho] = E_{ee}[\rho] + T_c[\rho], \quad (7)$$

where

$$E_{ee}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \mathbf{r} \cdot \mathcal{E}_{ee}(\mathbf{r}) \quad (8)$$

is the quantal electron-interaction energy, and

$$T_c[\rho] = \frac{1}{2} \int d\mathbf{r} \rho(\mathbf{r}) \mathbf{r} \cdot \mathcal{Z}_{t_c}(\mathbf{r}) \quad (9)$$

is the correlation-kinetic energy. The functional derivative $\nu_{ee}(\mathbf{r})$ is the work done to move an electron in the field $\mathcal{F}(\mathbf{r})$:

$$\nu_{ee}(\mathbf{r}) = - \int_{\infty}^{\mathbf{r}} \mathcal{F}(\mathbf{r}') \cdot d\mathbf{l}'. \quad (10)$$

For systems of certain symmetry such as spherically symmetric atoms, nonspherically symmetric atoms in the central field approximation, jellium and structureless pseudopotential metal surfaces, jellium metal clusters, etc., the curl of the fields $\mathcal{E}_{ee}(\mathbf{r})$ and $\mathcal{Z}_{t_c}(\mathbf{r})$ separately vanishes. For such systems we may write $\nu_{ee}(\mathbf{r}) = W_{ee}(\mathbf{r}) + W_{t_c}(\mathbf{r})$, where

$$W_{ee}(\mathbf{r}) = - \int_{\infty}^{\mathbf{r}} \mathcal{E}_{ee}(\mathbf{r}') \cdot d\mathbf{l}' \quad (11)$$

is the work done in the electron-interaction field, and

$$W_{t_c}(\mathbf{r}) = - \int_{\infty}^{\mathbf{r}} \mathcal{Z}_{t_c}(\mathbf{r}') \cdot d\mathbf{l}' \quad (12)$$

is the work done in the correlation-kinetic field.

C. Hooke's atom

We consider the singlet ground state of Hooke's atom, for which the external potential $\nu(r) = \frac{1}{2}kr^2$, $k = \frac{1}{4}$. The solution of the Schrödinger equation is then [10,11]

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = C e^{-R^2/2} e^{-r^2/8} (1 + r/2), \quad (13)$$

where $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$, $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$, and $C = 1/[2\pi^{5/4}(5\sqrt{\pi} + 8)^{1/2}] = 0.0291122$ a.u. The resulting analytical expression for the density $\rho(\mathbf{r})$ is given in the Appendix. (See also Kais *et al.* [14].) The corresponding KS theory orbital $\varphi_i(\mathbf{r})$ can be expressed in terms of the density as $\varphi_i(\mathbf{r}) = \sqrt{\rho(\mathbf{r})/2}$; $i = 1, 2$. With the assumption that the functional derivative $\nu_{ee}(\mathbf{r})$ vanishes at infinity, the KS equation can be inverted so that $\nu_{ee}(\mathbf{r})$ can also be written in terms of the density as

$$\nu_{ee}(r) = \epsilon_i + \frac{1}{2} \frac{\nabla^2 \sqrt{\rho(r)}}{\sqrt{\rho(r)}} - \frac{1}{8} r^2, \quad (14)$$

where $\varepsilon_i = 5/4$. Hooke's atom wave function satisfies the electron-electron but not the electron-nucleus cusp condition [15]. Furthermore, for this atom, $\nabla \times \mathcal{E}_{ee}(\mathbf{r}) = \nabla \times \mathbf{Z}_{t_c} = \mathbf{0}$, so that the work done $W_{ee}(\mathbf{r})$ and $W_{t_c}(\mathbf{r})$ are separately path-independent.

III. PROPERTIES OF THE QUANTUM-MECHANICAL INTERPRETATION

For the wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ of Eq. (13), essentially all the constituent properties of the quantum-mechanical interpretation of KS theory have been determined in closed analytical form. The remaining few are semianalytical. These expressions are given in the Appendix. Here we discuss each property separately.

A. Pair-correlation density $g(\mathbf{r}, \mathbf{r}')$

The pair-correlation density, which is the source charge distribution for the electron-interaction component, can be further separated into its local and nonlocal components as $g(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r}') + \rho_{xc}(\mathbf{r}, \mathbf{r}')$, where $\rho_{xc}(\mathbf{r}, \mathbf{r}')$ is the quantal Fermi-Coulomb hole charge distribution with $\int \rho_{xc}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = -1$. The Fermi-Coulomb hole can be further separated [6] into the KS theory Fermi $\rho_x^{\text{KS}}(\mathbf{r}, \mathbf{r}')$ and Coulomb $\rho_c^{\text{KS}}(\mathbf{r}, \mathbf{r}')$ holes as $\rho_{xc}(\mathbf{r}, \mathbf{r}') = \rho_x^{\text{KS}}(\mathbf{r}, \mathbf{r}') + \rho_c^{\text{KS}}(\mathbf{r}, \mathbf{r}')$, where $\rho_x^{\text{KS}}(\mathbf{r}, \mathbf{r}')$ is defined in terms of the KS density matrix $\gamma_s(\mathbf{r}, \mathbf{r}')$ as $\rho_x^{\text{KS}}(\mathbf{r}, \mathbf{r}') = -|\gamma_s(\mathbf{r}, \mathbf{r}')|^2 / 2\rho(\mathbf{r})$. The sum rules satisfied by the Fermi and Coulomb holes are $\int \rho_x^{\text{KS}}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = -1$, $\rho_x^{\text{KS}}(\mathbf{r}, \mathbf{r}') \leq 0$, $\rho_x^{\text{KS}}(\mathbf{r}, \mathbf{r}) = -\rho(\mathbf{r})/2$, and $\int \rho_c^{\text{KS}}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = 0$.

With these definitions we have for the ground state of Hooke's atom $\rho_x^{\text{KS}}(\mathbf{r}, \mathbf{r}') = -\rho(\mathbf{r}')/2$ and $\rho_c^{\text{KS}}(\mathbf{r}, \mathbf{r}') = g(\mathbf{r}, \mathbf{r}') - \rho(\mathbf{r}')/2$. The nonlocal nature of the pair-correlation density in this case is then due to the dynamic Coulomb hole charge. In Fig. 1 we plot the density $\rho(r)$ and the radial probability density $r^2\rho(r)$. Other than the lack of a cusp at the origin, the density (and radial probability density) is similar to that of the He atom, though different in magnitude. Also plotted in the figure are the quantal Fermi-Coulomb $\rho_{xc}(\mathbf{r}, \mathbf{r}')$ and KS Fermi $\rho_x^{\text{KS}}(\mathbf{r}, \mathbf{r}')$ and Coulomb $\rho_c^{\text{KS}}(\mathbf{r}, \mathbf{r}')$ holes for an electron at the nucleus. Observe that the holes are all spherically symmetric about the electron. At the electron position $\mathbf{r}' = \mathbf{r}$ both the Fermi-Coulomb and Coulomb holes exhibit a cusp representative of the electron-electron cusp condition. These holes are also essentially all negative about the electron. The positive part of the Coulomb hole is not evident in the figure.

Since the Fermi hole for this model is independent of electron position, we consider only the Coulomb hole for other electron positions. In Fig. 2 we plot the Coulomb hole for electron positions at $r=0.8$ a.u. in the interior of the atom, and at $r=1.585$ a.u., which corresponds to the maximum of the radial probability density. The electron is along the z axis corresponding to $\theta=0^\circ$. The cross sections through the Coulomb hole correspond to $\theta'=0^\circ$, 45° , and 90° with respect to the electron-nucleus direction. (The graph for $r' < 0$ corresponds to the structure for $\theta=\pi$ and $r' > 0$.) In Fig. 3 we present surface plots of the Coulomb hole along the lines of Pang *et al.* [16] for the electron positions of Fig.

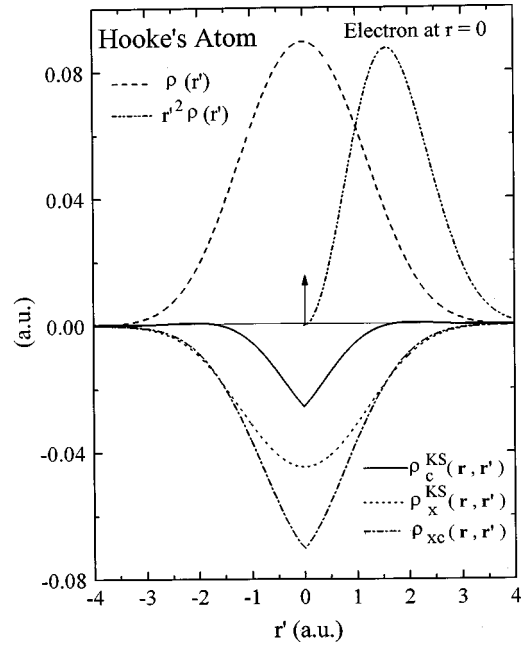


FIG. 1. Density $\rho(r')$ and radial probability density $r^2\rho(r')$. Cross sections through the quantal Fermi-Coulomb $\rho_{xc}(\mathbf{r}, \mathbf{r}')$ and KS theory Fermi $\rho_x^{\text{KS}}(\mathbf{r}, \mathbf{r}')$ and Coulomb $\rho_c^{\text{KS}}(\mathbf{r}, \mathbf{r}')$ holes for an electron at the nucleus (as indicated by the arrow) are also plotted.

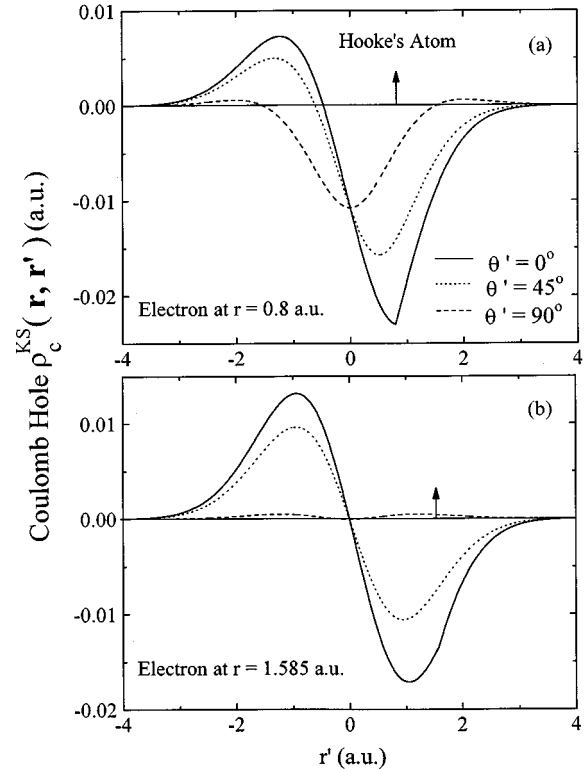


FIG. 2. Cross sections through the structure of the KS Coulomb hole $\rho_c^{\text{KS}}(\mathbf{r}, \mathbf{r}')$ in different directions corresponding to $\theta'=0^\circ$, 45° , and 90° with respect to the nucleus-electron direction. The electron is on the z axis corresponding to $\theta=0^\circ$ at $r=0.8$ a.u. in (a) and at $r=1.585$ a.u. in (b). The plots for $r' < 0$ correspond to the structure for $\theta=\pi$, $r' > 0$.

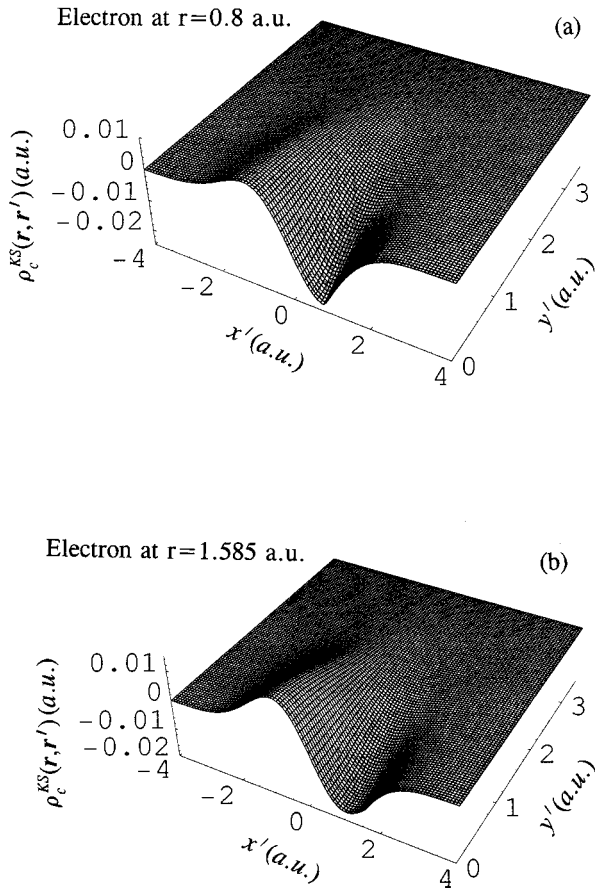


FIG. 3. Surface plots of the Coulomb hole corresponding to the electron positions of Fig. 2. Here x' is the projection of \mathbf{r}' on \mathbf{r} , i.e., $x' = r' \hat{\mathbf{r}} \cdot \hat{\mathbf{r}}'$, and y' is the projection of \mathbf{r}' on the direction perpendicular to \mathbf{r} , i.e., $y' = r' [1 - (\hat{\mathbf{r}}' \cdot \hat{\mathbf{r}})^2]^{1/2}$.

2. These plots are possible due to the spherical symmetry of the model atom. The cuts along the x and y axes correspond to $\theta' = 0^\circ$ and 90° . A study of Figs. 2 and 3 clearly shows the cusp in the Coulomb hole at the electron position, and the fact that it is no longer spherically symmetric about the electron. In Figs. 4 and 5 we consider electron positions near the surface ($\langle r \rangle = 3.489\,025$ a.u.) of the atom at $r = 4.5$ a.u., and in the classically forbidden region at $r = 18$ a.u. Observe that as the electron position from the nucleus increases, the positive part of the Coulomb hole becomes more prominent on the other side of the nucleus [Figs. 2, 3, and 4(a)]. For asymptotic positions of the electron [Figs. 4(b) and 5(b)], the positive part of the hole is concentrated about the nucleus. For these positions the hole becomes essentially a static charge as well as spherically symmetric about the nucleus. In Fig. 6 we plot the center of mass $\langle r' \rangle$ of the Coulomb hole as a function of electron position. The center of mass lies along the nucleus-electron direction, but is on the other side of the nucleus from the electron, approaching the nucleus asymptotically.

A comparison of the structure of Hooke's atom Coulomb hole with that of the He atom [17] shows that, although for certain electron positions there are qualitative differences, the overall structure is strikingly similar, although different in magnitude, in spite of the fact that the external potentials of the two atoms are different. *Ex post facto*, this must be so

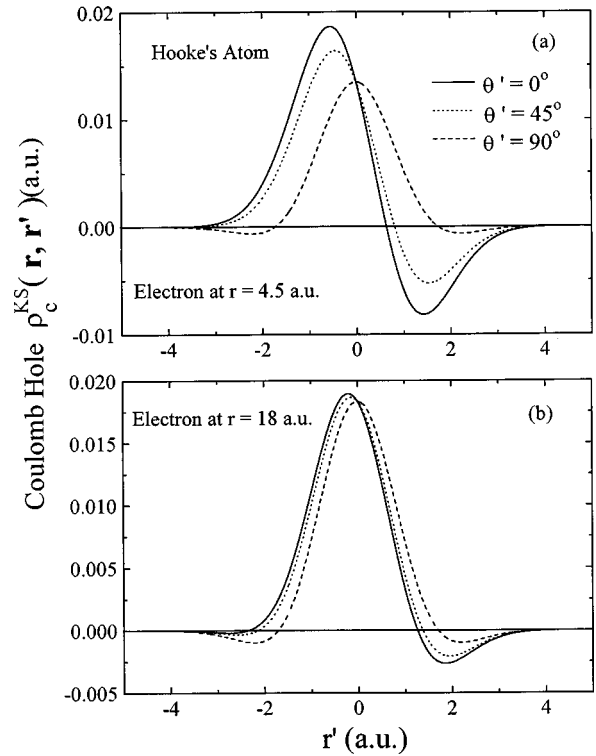


FIG. 4. Same as in Fig. 2 except that in (a) the electron is at $r = 4.5$ a.u., and in (b) at $r = 18$ a.u.

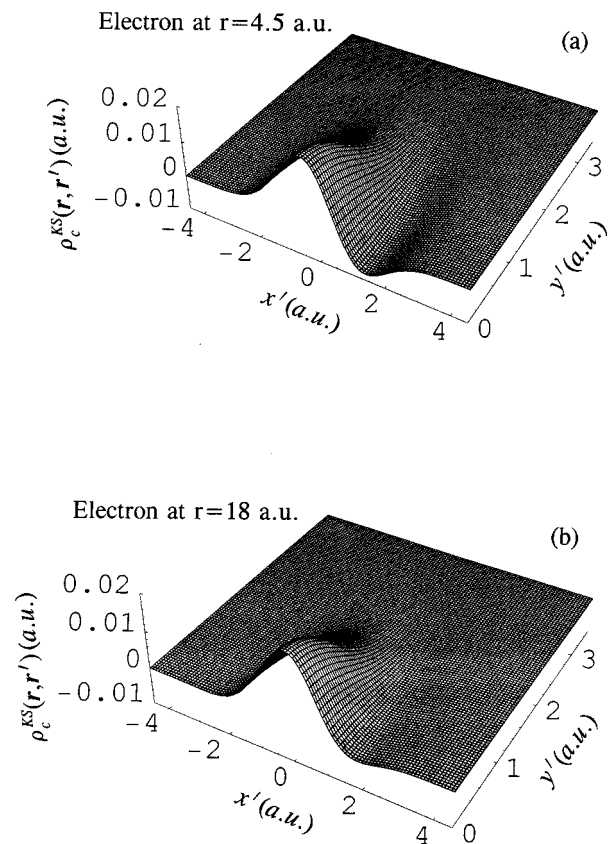


FIG. 5. Surface plots of the Coulomb hole corresponding to the electron positions of Fig. 4.

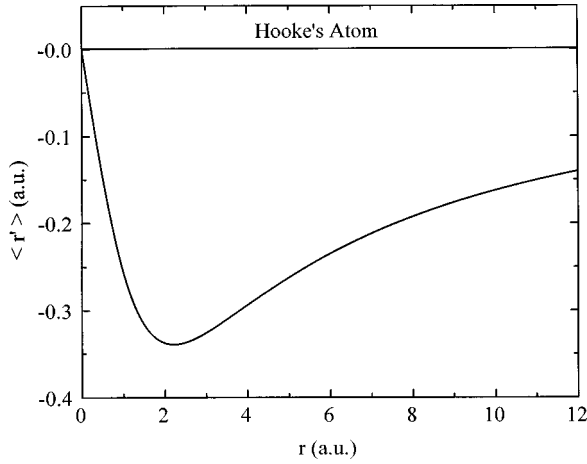


FIG. 6. Center of mass $\langle r' \rangle$ of the KS Coulomb hole $\rho_c^{\text{KS}}(\mathbf{r}, \mathbf{r}')$ as a function of electron position.

since electron repulsion is represented in each case by Coulomb's law. Figures 1–5 are a confirmation of this conclusion.

There is also a striking similarity between the surface plots of Figs. 3 and 5 with those of the pair-correlation function $h(\mathbf{r}, \mathbf{r}') = g(\mathbf{r}, \mathbf{r}')/\rho(\mathbf{r}')$ of the Ne atom plotted by Pang *et al.* [16]. (The comparison is meaningful since for the Hooke's atom $\rho_c^{\text{KS}}(\mathbf{r}, \mathbf{r}') = [h(\mathbf{r}, \mathbf{r}') - \frac{1}{2}]\rho(\mathbf{r}')$ and $\rho(\mathbf{r}')$ is monotonic.) The one qualitative difference which appears is that of the presence of the second shell for the Ne atom. Other than that, the piling of charge on the other side of the nucleus from the electron position, and other characteristics, etc., are all similar.

B. Electron-interaction field $\mathcal{E}_{ee}(\mathbf{r})$ and energy $E_{ee}[\rho]$

With the pair-correlation density expressed in terms of its components, the electron-interaction field may be written as $\mathcal{E}_{ee}(\mathbf{r}) = \mathcal{E}_H + \mathcal{E}_{xc}(\mathbf{r})$, where

$$\mathcal{E}_H(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} d\mathbf{r}'$$

and

$$\mathcal{E}_{xc}(\mathbf{r}) = \int \frac{\rho_{xc}(\mathbf{r}, \mathbf{r}')(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} d\mathbf{r}' \quad (15)$$

are the Hartree and Pauli-Coulomb fields, respectively. In turn, the quantal field $\mathcal{E}_{xc}(\mathbf{r})$ is the sum of the KS Pauli $\mathcal{E}_x^{\text{KS}}(\mathbf{r})$ and Coulomb $\mathcal{E}_c^{\text{KS}}(\mathbf{r})$ fields: $\mathcal{E}_{xc}(\mathbf{r}) = \mathcal{E}_x^{\text{KS}}(\mathbf{r}) + \mathcal{E}_c^{\text{KS}}(\mathbf{r})$, where

$$\mathcal{E}_x^{\text{KS}} = \int \frac{\rho_x^{\text{KS}}(\mathbf{r}, \mathbf{r}')(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} d\mathbf{r}'$$

and

$$\mathcal{E}_c^{\text{KS}}(\mathbf{r}) = \int \frac{\rho_c^{\text{KS}}(\mathbf{r}, \mathbf{r}')(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} d\mathbf{r}'. \quad (16)$$

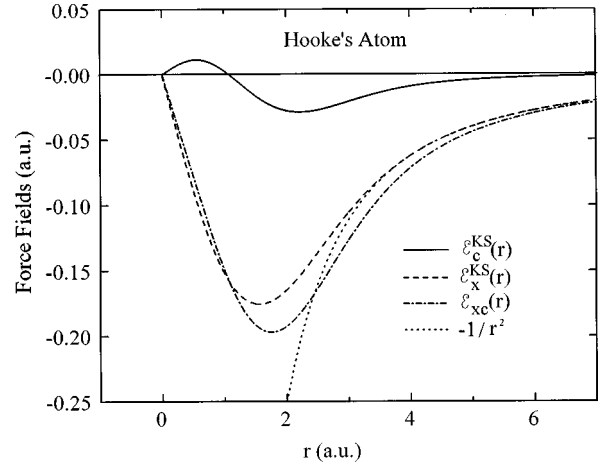


FIG. 7. Quantal Pauli-Coulomb $\mathcal{E}_{xc}(\mathbf{r})$ and KS Pauli $\mathcal{E}_x^{\text{KS}}(\mathbf{r})$ and Coulomb $\mathcal{E}_c^{\text{KS}}(\mathbf{r})$ force fields. The function $-1/r^2$ is also plotted.

The corresponding expressions for the Hartree (Coulomb self-energy) and quantal exchange-correlation energies from Eq. (8) are then

$$E_H[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \mathbf{r} \cdot \mathcal{E}_H(\mathbf{r})$$

and

$$E_{xc}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \mathbf{r} \cdot \mathcal{E}_{xc}(\mathbf{r}). \quad (17)$$

In turn, the KS Pauli $E_x^{\text{KS}}[\rho]$ and Coulomb $U_c^{\text{KS}}[\rho]$ energies are

$$E_x^{\text{KS}}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \mathbf{r} \cdot \mathcal{E}_x^{\text{KS}}(\mathbf{r})$$

and

$$U_c^{\text{KS}}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \mathbf{r} \cdot \mathcal{E}_c^{\text{KS}}(\mathbf{r}). \quad (18)$$

In Fig. 7 we plot the fields $\mathcal{E}_{xc}(\mathbf{r})$, $\mathcal{E}_x^{\text{KS}}(\mathbf{r})$, $\mathcal{E}_c^{\text{KS}}(\mathbf{r})$, and the function $-1/r^2$. [The field $\mathcal{E}_H(\mathbf{r}) = -2\mathcal{E}_x^{\text{KS}}(\mathbf{r})$ is not plotted.] Observe that the fields all vanish at the nucleus. This is because the corresponding source charge distributions, viz., the Fermi-Coulomb, Fermi, and Coulomb holes, are all spherically symmetric about the electron for this electron position (see Fig. 1). The KS Pauli field $\mathcal{E}_x^{\text{KS}}(\mathbf{r})$ is negative throughout space since the Fermi hole is a negative charge distribution. The KS Coulomb field is negative over most of space except the *far interior*. (This contrasts with the case of the He atom [17], for which this field is negative throughout space.) The quantal Pauli-Coulomb field $\mathcal{E}_{xc}(\mathbf{r})$, however, is negative over all space. Note that the fields $\mathcal{E}_{xc}(\mathbf{r})$ and $\mathcal{E}_x^{\text{KS}}(\mathbf{r})$ are an order of magnitude larger than the field $\mathcal{E}_c^{\text{KS}}(\mathbf{r})$. The signs of the various fields and their relative magnitudes are then reflected in the results for the corresponding energies: $E_{ee} = 0.447\,443$ a.u., $E_H = 1.030\,250$ a.u., $E_{xc} = -0.582\,807$ a.u., $E_x^{\text{KS}} = -0.515\,125$ a.u., and $U_c^{\text{KS}} = -0.067\,682\,0$ a.u. The corresponding values [18] for the He atom are $E_{ee} = 0.945\,819$ a.u., $E_H = 2.049\,137$ a.u., $E_{xc} = -1.103\,318$ a.u., $E_x^{\text{KS}} = -1.024\,568$ a.u., and $U_c^{\text{KS}} = -0.078\,750$ a.u.

Note that although the He atom values for E_{ee} and its components E_H , E_{xc} , and E_x^{KS} are about twice the magnitude of those of Hooke's atom, the values of the KS Coulomb energy U_c^{KS} are about the same.

The asymptotic structure of the various fields in the classically forbidden region is

$$\mathcal{E}_{ee}(r) \sim \frac{1}{r^2} - \frac{4}{r^4}, \quad \mathcal{E}_H(r) \sim \frac{2}{r^2}, \quad \mathcal{E}_{xc}(r) \sim -\frac{1}{r^2} - \frac{4}{r^4},$$

$$\mathcal{E}_x^{\text{KS}}(r) \sim -\frac{1}{r^2}, \quad \mathcal{E}_c^{\text{KS}}(r) \sim -\frac{4}{r^4}. \quad (19)$$

The asymptotic structure of the fields $\mathcal{E}_H(\mathbf{r})$ and $\mathcal{E}_x^{\text{KS}}(\mathbf{r})$ are to Gaussian accuracy. The $-1/r^2$ structure of the fields $\mathcal{E}_{xc}(\mathbf{r})$ and $\mathcal{E}_x^{\text{KS}}(\mathbf{r})$ is a general result [6,7] valid for any finite system. It is a consequence of the fact that the total charge of the quantal Fermi-Coulomb and KS Fermi holes is negative unity, and that these charge distributions that are localized about the nucleus become static in the limit of asymptotic positions of the electron.

C. Electron-interaction potential $W_{ee}(\mathbf{r})$

The potential $W_{ee}(\mathbf{r})$, which is the work done in the electron-interaction field $\mathcal{E}_{ee}(\mathbf{r})$, may in turn be written as a sum of the Hartree $W_H(\mathbf{r})$ and quantal Pauli-Coulomb $W_{xc}(\mathbf{r})$ potentials:

$$W_H(\mathbf{r}) = - \int_{\infty}^{\mathbf{r}} \mathcal{E}_H(\mathbf{r}') \cdot d\mathbf{l}'$$

$$\text{and } W_{xc}(\mathbf{r}) = - \int_{\infty}^{\mathbf{r}} \mathcal{E}_{xc}(\mathbf{r}') \cdot d\mathbf{l}'. \quad (20)$$

The KS Pauli $W_x^{\text{KS}}(\mathbf{r})$ and Coulomb $W_c^{\text{KS}}(\mathbf{r})$ potentials may be expressed in a similar manner in terms of the fields $\mathcal{E}_x^{\text{KS}}(\mathbf{r})$ and $\mathcal{E}_c^{\text{KS}}(\mathbf{r})$, respectively. Since the density $\rho(r)$ is a static charge, the potential $W_H(\mathbf{r})$ may also be expressed as $W_H(\mathbf{r}) = \int d\mathbf{r}' \rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$. The Pauli potential $W_x^{\text{KS}}(\mathbf{r}) = -\frac{1}{2}W_H(\mathbf{r})$.

In Fig. 8(a) we plot the potential $W_c^{\text{KS}}(\mathbf{r})$ and in Fig. 8(b) the potentials $W_{xc}(\mathbf{r})$, $W_x^{\text{KS}}(\mathbf{r})$, and the function $-1/r$. Observe that all the potentials have zero slope at the nucleus. This is a result of the fact that the corresponding fields from which these potentials are derived vanish at this electron position. The potentials $W_{xc}(\mathbf{r})$ and $W_x^{\text{KS}}(\mathbf{r})$ are monotonic with positive slope as a result of the fact that the fields $\mathcal{E}_{xc}(\mathbf{r})$ and $\mathcal{E}_x^{\text{KS}}(\mathbf{r})$ are negative. In contrast, the potential $W_c^{\text{KS}}(\mathbf{r})$ is not monotonic since the field $\mathcal{E}_c^{\text{KS}}(\mathbf{r})$ changes sign. Furthermore, the potentials $W_{xc}(\mathbf{r})$ and $W_x^{\text{KS}}(\mathbf{r})$ are an order of magnitude greater than $W_c^{\text{KS}}(\mathbf{r})$ as a result of the magnitudes of the corresponding fields.

The asymptotic structures of the potentials may be derived from Eq. (19) to be

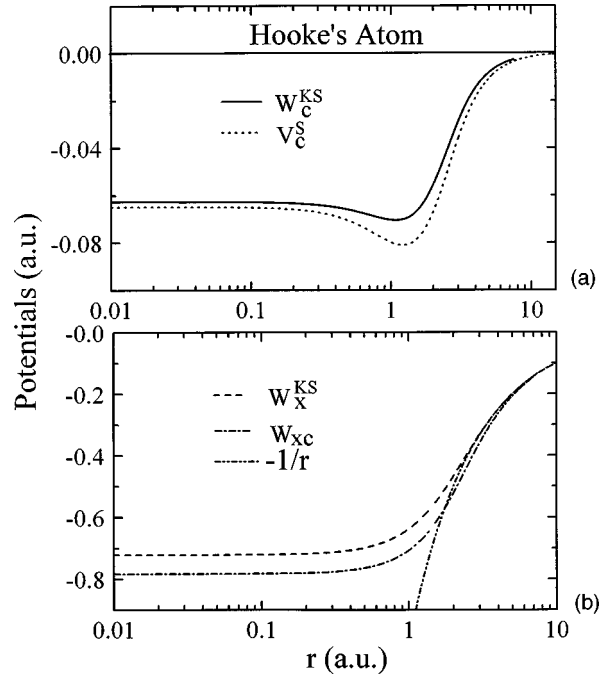


FIG. 8. (a) KS $W_c^{\text{KS}}(\mathbf{r})$ and Slater $V_c^{\text{S}}(\mathbf{r})$ Coulomb potentials. (b) The quantal Pauli-Coulomb $W_{xc}(\mathbf{r})$ and KS Pauli $W_x^{\text{KS}}(\mathbf{r})$ potentials, and the function $-1/r$.

$$W_{ee}(r) \sim \frac{1}{r} - \frac{4}{3r^3}, \quad W_H(r) \sim \frac{2}{r},$$

$$W_{xc}(r) \sim -\frac{1}{r} - \frac{4}{3r^3},$$

$$W_x^{\text{KS}}(r) \sim -\frac{1}{r}, \quad W_c^{\text{KS}}(r) \sim -\frac{4}{3r^3}. \quad (21)$$

Once again, the asymptotic $-1/r$ structure of the potentials $W_{xc}(\mathbf{r})$ and $W_x^{\text{KS}}(\mathbf{r})$ is the same for all finite systems for reasons explained previously. Note that the potential $W_c^{\text{KS}}(\mathbf{r})$ due to the Coulomb hole decays in this case as $O(1/r^3)$. The asymptotic structure of $W_H(\mathbf{r})$ and $W_x^{\text{KS}}(\mathbf{r})$ is again quoted to Gaussian accuracy.

With the Slater electron-interaction potential defined as

$$V_{ee}^{\text{S}}(\mathbf{r}) = \int \frac{g(\mathbf{r}, \mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}', \quad (22)$$

we have also plotted in Fig. 8(a) the Slater correlation potential $V_c^{\text{S}}(\mathbf{r}) = \int d\mathbf{r}' \rho_c^{\text{KS}}(\mathbf{r}, \mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$. [The Slater [19] exchange potential $V_x^{\text{S}}(\mathbf{r}) = \int d\mathbf{r}' \rho_x^{\text{KS}}(\mathbf{r}, \mathbf{r}')/|\mathbf{r}-\mathbf{r}'| = W_x^{\text{KS}}(\mathbf{r})$ since the Fermi hole is a static charge in this model.] In Slater theory, the dynamic nature of the pair-correlation density is not accounted for, and as such $V_c^{\text{S}}(\mathbf{r})$ does not represent the potential energy of an electron. The error of $V_c^{\text{S}}(\mathbf{r})$ in comparison to the work $W_c^{\text{KS}}(\mathbf{r})$ is evident from Fig. 8(a). However, the asymptotic structure of the Slater exchange-correlation potential $V_{xc}^{\text{S}}(\mathbf{r}) = \int d\mathbf{r}' \rho_{xc}(\mathbf{r}, \mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$ is $-1/r$, since the Fermi-Coulomb hole is then essentially a static charge distribution so that $V_{xc}^{\text{S}}(\mathbf{r}) = W_{xc}(\mathbf{r})$ in this limit.

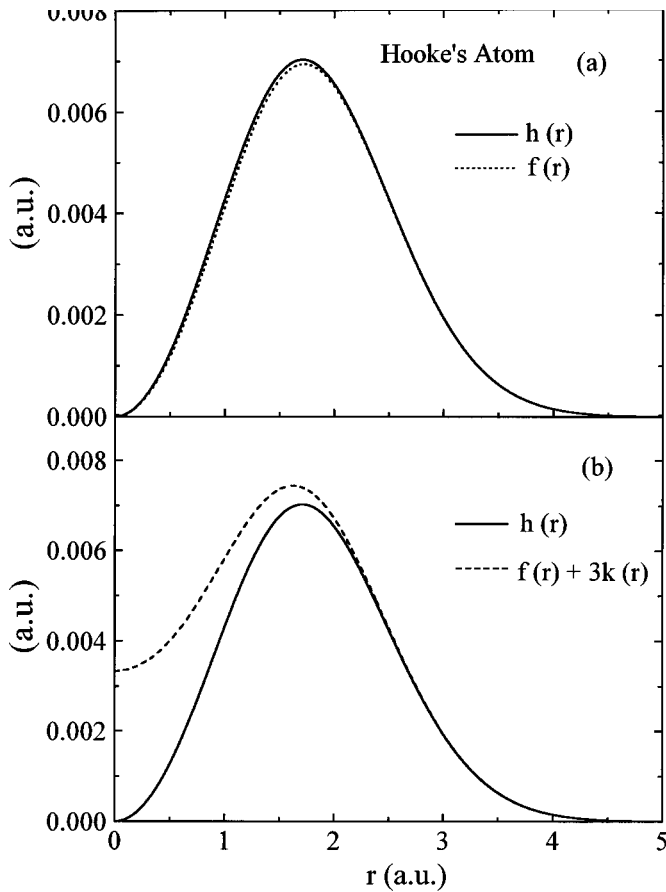


FIG. 9. (a) Functions $f(r)$ and $h(r)$ of the off-diagonal elements of the interacting and noninteracting system kinetic-energy-density tensors $t_{\alpha\beta}(\mathbf{r};[\gamma])$ and $t_{s,\alpha\beta}(\mathbf{r};[\gamma_s])$, respectively. (b) The functions $f(r) + 3k(r)$ and $h(r)$ of the diagonal elements of the tensors $t_{\alpha\beta}(\mathbf{r};[\gamma])$ and $t_{s,\alpha\beta}(\mathbf{r};[\gamma_s])$, respectively.

D. Kinetic-energy-density tensors $t_{\alpha\beta}(\mathbf{r};[\gamma])$ and $t_{s,\alpha\beta}(\mathbf{r};[\gamma_s])$

The source of the correlation-kinetic component is the difference between the kinetic-energy density tensors for the Schrödinger interacting $t_{\alpha\beta}(\mathbf{r};[\gamma])$ and Kohn-Sham noninteracting $t_{s,\alpha\beta}(\mathbf{r};[\gamma_s])$ systems. As a consequence of spherical symmetry, these tensors are of the form

$$t_{\alpha\beta}(\mathbf{r};[\gamma]) = \frac{r_\alpha r_\beta}{r^2} f(r) + \delta_{\alpha\beta} k(r) \quad (23)$$

and

$$t_{s,\alpha\beta}(\mathbf{r};[\gamma_s]) = \frac{r_\alpha r_\beta}{r^2} h(r), \quad (24)$$

respectively, with the functions $f(r)$, $k(r)$, and $h(r)$ given in the Appendix. Since the model is comprised of two electrons of opposite spin in the ground state, $t_{s,\alpha\beta}(\mathbf{r};[\gamma_s])$ is the von Weizsäcker tensor [3]. Note that for the interacting system, there is an additional $\delta_{\alpha\beta} k(r)$ term which contributes only to the diagonal elements of the tensor. We note that, to our knowledge, this is the first time that the kinetic-energy-density tensors for an interacting nonuniform density system and for the equivalent noninteracting system have been determined, and that too analytically.

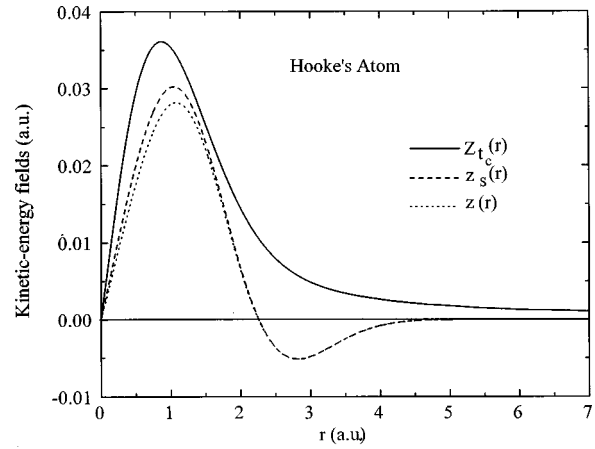


FIG. 10. Correlation-kinetic field $\mathbf{Z}_t(\mathbf{r})$, and its components $\mathbf{z}_s(\mathbf{r};[\gamma_s])$ and $\mathbf{z}(\mathbf{r};[\gamma])$ for the noninteracting and interacting systems.

In Fig. 9(a) we compare the off-diagonal elements of the tensors by plotting the functions $f(r)$ and $h(r)$. Observe that they are essentially the same, vanishing at the nucleus, and decaying in a similar manner asymptotically. In Fig. 9(b) we compare the diagonal elements of the tensors by plotting the functions $h(r)$ and $f(r) + 3k(r)$. Note that the diagonal element of the interacting system tensor is now finite at the nucleus, and that the difference in this element between the two tensors occurs in the interior region of the atom. This then is the region from which the correlation contribution to the kinetic energy must arise.

The trace of the kinetic-energy-density tensor is the kinetic-energy-density $t(\mathbf{r})$. Thus the fact that the interacting and noninteracting system tensors are essentially equivalent implies that the corresponding kinetic energies T and T_s are about the same. The value of $T = \int t(\mathbf{r}) d\mathbf{r} = 0.664\,418$ a.u. and $T_s = \int t_s(\mathbf{r}) d\mathbf{r} = 0.635\,245$ a.u. The difference $T - T_s$ is the correlation-kinetic energy $T_c[\rho]$, which is an order of magnitude smaller.

E. Correlation-kinetic field $\mathbf{Z}_t(\mathbf{r})$ and energy $T_c[\rho]$

The field $\mathbf{Z}_t(\mathbf{r})$ defined by Eq. (6) and its components $\mathbf{z}_s(\mathbf{r};[\gamma_s])$ and $\mathbf{z}(\mathbf{r};[\gamma])$ are plotted in Fig. 10. Both components vanish at the nucleus, with $\mathbf{z}_s(\mathbf{r})$ being greater than $\mathbf{z}(\mathbf{r})$ throughout space. As such, $\mathbf{Z}_t(\mathbf{r})$ vanishes at the origin and is positive-definite over all space. In Fig. 11(a) we compare the field $\mathbf{Z}_t(\mathbf{r})$ to the KS Coulomb field $\mathcal{E}_c^{\text{KS}}(\mathbf{r})$ and observe the two to be the same order of magnitude. The correlation-kinetic energy $T_c = 0.029\,1731$ a.u. [see also Eq. (9)] is therefore the same order of magnitude as the KS Coulomb energy $U_c^{\text{KS}}[\rho] = -0.067\,682\,0$ a.u.. (Note that for the He atom $T_c = 0.036\,642\,0$ a.u.)

As noted, the field $\mathbf{Z}_t(\mathbf{r})$ decays asymptotically as a positive function. Its precise asymptotic structure may be obtained from those of the components $\mathbf{z}_s(\mathbf{r})$ and $\mathbf{z}(\mathbf{r})$, which are

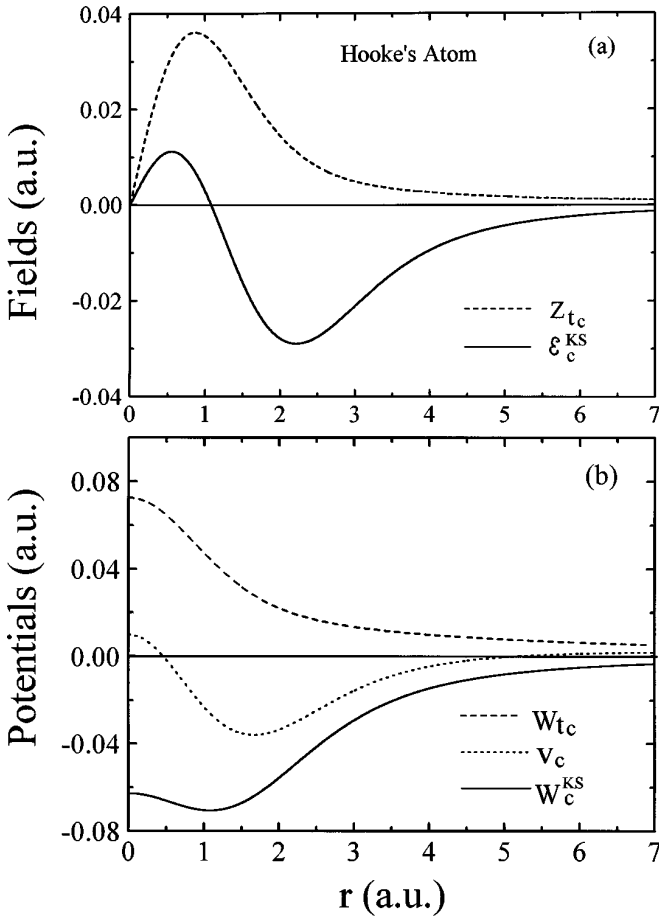


FIG. 11. (a) Correlation-kinetic $Z_{t_c}(\mathbf{r})$ and KS Coulomb $E_c^{KS}(\mathbf{r})$ fields. (b) The correlation-kinetic $W_{t_c}(\mathbf{r})$ and KS Coulomb $W_c^{KS}(\mathbf{r})$ potentials. The functional derivative $\nu_c(\mathbf{r}) = \delta E_c^{KS}[\rho] / \delta \rho(\mathbf{r})$ is also plotted.

$$z_s(r) \sim -\frac{\sqrt{2\pi}\pi C^2}{4} \left(r^5 + 4r^4 - 3r^3 - 24r^2 - 8r + 20 - \frac{20}{r} + \frac{8}{r^2} + \dots \right) e^{-r^2/2} \quad (25)$$

and

$$z(r) \sim -\frac{\sqrt{2\pi}\pi C^2}{4} \left(r^5 + 4r^4 - 3r^3 - 24r^2 - 8r + 20 - \frac{16}{r} - \frac{8}{r^2} + \dots \right) e^{-r^2/2}. \quad (26)$$

Note the cancellation of terms of $O(r^5)$ to $O(r^0)$. The density $\rho(r)$ decays as

$$\rho(r) \sim \sqrt{2\pi}\pi C^2 r^2 \left(1 + \frac{4}{r} \right) e^{-r^2/2}, \quad (27)$$

so that the field $Z_{t_c}(\mathbf{r})$ decays asymptotically as

$$Z_{t_c}(r) \sim \frac{1}{r^3} - \frac{8}{r^4}. \quad (28)$$

The structure of the field $Z_{t_c}(\mathbf{r})$ for the He atom [6] differs from Hooke's model in that it is oscillatory, the difference arising due to the different external potentials. However, for both atoms, the field $Z_{t_c}(\mathbf{r})$ decays as a positive function. We have recently proved [20] that for atoms with a Coulomb external potential, $Z_{t_c}(\mathbf{r})$ decays asymptotically as a positive function of $O(1/r^6)$.

F. Correlation-kinetic potential $W_{t_c}(\mathbf{r})$

The structure of the correlation-kinetic field $Z_{t_c}(\mathbf{r})$ dictates that of the corresponding potential $W_{t_c}(\mathbf{r})$. Since the field $Z_{t_c}(\mathbf{r})$ vanishes at the nucleus, the potential $W_{t_c}(\mathbf{r})$ has zero slope there. Further, the field is positive, so that $W_{t_c}(\mathbf{r})$ is monotonic with negative slope over all space [see Fig. 11(b)]. The potential decays asymptotically as

$$W_{t_c}(r) \sim \frac{1}{2r^2} - \frac{8}{3r^3}. \quad (29)$$

We have also plotted the KS Coulomb potential $W_c^{KS}(\mathbf{r})$ in Fig. 11(b) to show that it is the same order of magnitude as $W_{t_c}(\mathbf{r})$.

G. Conventional Kohn-Sham theory correlation energy

$E_c^{KS}[\rho]$ and its functional derivative $\nu_c(\mathbf{r})$

The KS electron-interaction energy functional $E_{ee}^{KS}[\rho]$ is conventionally written as a sum of the Coulomb self-energy $E_H[\rho]$ and KS exchange-correlation energy $E_{xc}^{KS}[\rho]$, the latter being further split into its exchange $E_x^{KS}[\rho]$ and correlation $E_c^{KS}[\rho]$ components. The corresponding KS Hartree $\nu_H(\mathbf{r})$, exchange-correlation $\nu_{xc}(\mathbf{r})$, exchange $\nu_x(\mathbf{r})$, and correlation $\nu_c(\mathbf{r})$ potentials are, respectively, the functional derivatives of $E_H[\rho]$, $E_{xc}^{KS}[\rho]$, $E_x^{KS}[\rho]$, and $E_c^{KS}[\rho]$. The potential $\nu_H(\mathbf{r})$ is the same as $W_H(\mathbf{r})$ of Eq. (20) expressed in terms of the field $\mathcal{E}_H(\mathbf{r})$. The KS exchange energy $E_x^{KS}[\rho]$, which is defined either via the virial theorem [21] in terms of $\nu_x(\mathbf{r})$, or as the energy of interaction between the density $\rho(\mathbf{r})$ and Fermi hole $\rho_x^{KS}(\mathbf{r}, \mathbf{r}')$, is the same as in Eq. (18) written in terms of the field $\mathcal{E}_x^{KS}(\mathbf{r})$. The potential $\nu_x(\mathbf{r})$, however, is the sum [22,6]

$$\nu_x(\mathbf{r}) = \frac{\delta E_x^{KS}[\rho]}{\delta \rho(\mathbf{r})} = W_x^{KS}(\mathbf{r}) - W_{t_c}^{(1)}(\mathbf{r}), \quad (30)$$

where $W_{t_c}^{(1)}(\mathbf{r})$ is the work done in the field $Z_{t_c}^{(1)}(\mathbf{r}) = \mathbf{z}(\mathbf{r}; [\gamma_1^c]) / \rho(\mathbf{r})$ with $\gamma_1^c(\mathbf{r}, \mathbf{r}')$ being the first-order correction to the KS density matrix $\gamma_s(\mathbf{r}, \mathbf{r}')$ obtained via perturbation theory by an expansion of the wave function Ψ in terms of the electron-interaction coupling constant. The KS exchange potential thus contains part of the correlation-kinetic contribution. [A study of $W_{t_c}^{(1)}(\mathbf{r})$ for atoms and metal surfaces has recently been performed [23].] For Hooke's atom in its ground state, however, $\nu_x(\mathbf{r}) = W_x^{KS}(\mathbf{r})$, so that

$$\nu_c(\mathbf{r}) = \frac{\delta E_c^{KS}[\rho]}{\delta \rho(\mathbf{r})} = W_c^{KS}(\mathbf{r}) + W_{t_c}(\mathbf{r}). \quad (31)$$

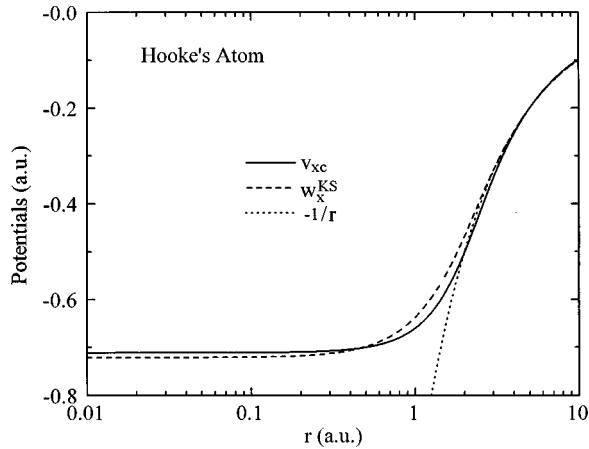


FIG. 12. Comparison of KS Pauli $W_x^{\text{KS}}(\mathbf{r})$ and exchange-correlation $\nu_{\text{xc}}(\mathbf{r}) = \delta E_{\text{xc}}^{\text{KS}}[\rho] / \delta \rho(\mathbf{r})$ potentials. The function $-1/r$ is also plotted.

In Fig. 11(b) we have also plotted the KS correlation potential $\nu_c(\mathbf{r})$. It lies above $W_c^{\text{KS}}(\mathbf{r})$ since it also contains the correlation-kinetic contribution. The corresponding KS correlation energy is $E_c^{\text{KS}}[\rho] = U_c^{\text{KS}}[\rho] + T_c[\rho] = -0.038\,508\,9$ a.u. (The corresponding value of $E_c^{\text{KS}}[\rho]$ for He is $-0.042\,108\,0$ a.u.). Observe [Fig. 11(a)] that the fields $\mathbf{Z}_t(\mathbf{r})$ and $\mathcal{E}_c^{\text{KS}}(\mathbf{r})$ and [Fig. 11(b)] potentials $W_{t_c}(\mathbf{r})$ and $W_c^{\text{KS}}(\mathbf{r})$, and thus the energies $U_c^{\text{KS}}[\rho]$ and $T_c[\rho]$, cancel each other to a great degree. Thus, the KS Pauli potential $W_x^{\text{KS}}(\mathbf{r})$ should be essentially equivalent to the KS exchange-correlation potential $\nu_{\text{xc}}(\mathbf{r})$. That this is the case is shown in Fig. 12 where the potentials $W_x^{\text{KS}}(\mathbf{r})$ and $\nu_{\text{xc}}(\mathbf{r})$ are compared.

H. Asymptotic structure of functional derivative $\nu_{\text{xc}}(\mathbf{r})$ in terms of electron correlations

From the KS equation for Hooke's atom Eq. (14), the asymptotic structure of the functional derivative $\nu_{\text{xc}}(\mathbf{r})$ is [14]

$$\nu_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}^{\text{KS}}[\rho]}{\delta \rho(\mathbf{r})} \underset{r \rightarrow \infty}{\sim} -\frac{1}{r} + \frac{1}{2r^2} - \frac{4}{r^3} + \dots \quad (32)$$

Here the leading $(-1/r)$ term is that of $\nu_x(\mathbf{r})$ or equivalently $W_x^{\text{KS}}(\mathbf{r})$, and therefore due to Pauli correlations. The KS correlation potential then decays as

$$\nu_c(\mathbf{r}) \underset{r \rightarrow \infty}{\sim} \frac{1}{2r^2} - \frac{4}{r^3} + \dots \quad (33)$$

However, from Eqs. (29) and (31), we see that the term of $O(1/r^2)$ of Eq. (33) is a correlation-kinetic contribution. Furthermore, from Eqs. (21) and (29), we observe that the next lower order term $(4/r^3)$ of Eq. (33) is comprised of a Coulomb correlation component of magnitude $(4/3r^3)$ as well as a correlation-kinetic piece of magnitude $(8/3r^3)$. All higher order terms also comprise a sum of Coulomb and correlation-kinetic contributions.

For a Coulomb external potential, $\nu_c(\mathbf{r})$ decays as $-\alpha/2r^4$, where α is the polarizability of the ion. This term is

attributed to Coulomb correlations [24] by comparison with a classical calculation. For completeness we note that at a metal-vacuum interface, both the Pauli $W_x^{\text{KS}}(\mathbf{r})$ and correlation-kinetic $W_{t_c}^{(1)}(\mathbf{r})$ components [see Eq. (30)] contribute [23,25] to the asymptotic structure of the KS exchange potential $\nu_x(\mathbf{r})$ in the classically forbidden and metal bulk regions.

IV. SUMMARY AND CONCLUDING REMARKS

By application to a ground state of Hooke's atom, we have illustrated in this paper how Kohn-Sham density-functional theory can be described in terms of the Schrödinger system wave function Ψ . The transformation requires the construction of two fields $\mathcal{E}_{ee}(\mathbf{r})$ and $\mathbf{Z}_{t_c}(\mathbf{r})$ that in this example are separately conservative, the former representative of correlations due to the Pauli exclusion principle and Coulomb repulsion, and the latter that of correlation-kinetic effects. The structure of these fields then leads to an *a priori* understanding of that of the corresponding potentials and magnitudes of the energies. In this manner, the Kohn-Sham theory exchange-correlation energy functional $E_{\text{xc}}^{\text{KS}}[\rho]$ and its functional derivative $\nu_{\text{xc}}(\mathbf{r})$ can be described in terms of the separate Pauli, Coulomb, and correlation-kinetic contributions. Here we have provided a complete description of the sources, fields, potentials, and energies required for the construction of the equivalent noninteracting Kohn-Sham system.

The following is a summary of our results for Hooke's atom. (i) The representation of electron interaction via the structure of the Coulomb hole is generally similar to that of the He atom. Furthermore, the KS Coulomb U_c^{KS} and correlation-kinetic T_c energies also approximate well the corresponding values for the He atom. As such, it is meaningful to test approximate exchange-correlation energy functionals and derivatives employing this model. (ii) The fact that *both* the Pauli-Coulomb $\mathcal{E}_{\text{xc}}(\mathbf{r})$ and correlation-kinetic $\mathbf{Z}_{t_c}(\mathbf{r})$ fields vanish at the nucleus approaching it linearly indicates that the KS exchange-correlation potential $\nu_{\text{xc}}(\mathbf{r})$ is quadratic with zero slope there. (iii) That both the Pauli-Coulomb $\mathcal{E}_{\text{xc}}(\mathbf{r})$ and Pauli $\mathcal{E}_x^{\text{KS}}(\mathbf{r})$ fields are negative-definite indicates that the corresponding component potentials $W_{\text{xc}}(\mathbf{r})$ and $W_x^{\text{KS}}(\mathbf{r})$ of $\nu_{\text{xc}}(\mathbf{r})$ are monotonic with positive slope. (iv) That the field $\mathbf{Z}_{t_c}(\mathbf{r})$ is positive-definite indicates that the correlation-kinetic component $W_{t_c}(\mathbf{r})$ is monotonic with negative slope. (v) The leading $(-1/r)$ asymptotic structure of $\nu_{\text{xc}}(\mathbf{r})$ is that of $W_x^{\text{KS}}(\mathbf{r})$ and therefore due entirely to Pauli correlations. (vi) The next term of $O(1/r^2)$ is due to correlation-kinetic effects. (vii) Terms of $O(1/r^3)$ and higher are a sum of *both* Coulomb correlation and correlation-kinetic contributions. (viii) The structure of the Coulomb $\mathcal{E}_c^{\text{KS}}(\mathbf{r})$ and correlation-kinetic $\mathbf{Z}_{t_c}(\mathbf{r})$ fields shows these effects to cancel so that the corresponding energies $U_c^{\text{KS}}[\rho]$ and $T_c[\rho]$ are the same order of magnitude and opposite in sign. (ix) As a consequence of the cancellation of the fields $\mathcal{E}_c^{\text{KS}}(\mathbf{r})$ and $\mathbf{Z}_{t_c}(\mathbf{r})$, the Pauli potential $W_x^{\text{KS}}(\mathbf{r})$ is essentially equivalent to the KS exchange-correlation potential $\nu_{\text{xc}}(\mathbf{r})$. (x) The off-diagonal elements of the Schrödinger and Kohn-Sham kinetic-energy density tensors are essen-

tially equivalent. (xi) The diagonal elements of the tensors differ only in the interior region of the atom. They are equivalent elsewhere. As such, the contribution to the correlation-kinetic energy $T_c[\rho]$ arises from this region. (xii) Furthermore, the interacting and noninteracting system kinetic energies are essentially equivalent, so that $T_c[\rho]$ is an order of magnitude smaller.

Since the KS exchange-correlation energy functional $E_{xc}^{KS}[\rho]$ and its functional derivative $v_{xc}(\mathbf{r})$ are unknown, a focus of research has been the development of accurate approximate energy functionals and potentials. The quantum-mechanical interpretation via its application to the He atom as well as the present model calculation suggest another approach to the construction of accurate energy functionals and their derivatives. The idea here is to approximate the Pauli-Coulomb $\mathcal{E}_{xc}(\mathbf{r})$ and correlation-kinetic $\mathcal{Z}_c(\mathbf{r})$ fields since both $E_{xc}^{KS}[\rho]$ and $v_{xc}(\mathbf{r})$ are expressible in terms of them. One constraint on the fields is that their sum be curl-free. Another restriction is that of the known asymptotic structure in the classically forbidden region. Any such approximation would, furthermore, be consistent in that the same total field, and thus the *same* approximate representation of electron correlations, leads to both the energy as well as the potential. The potential could be determined self-consistently until the energy is minimized with respect to any parameters in the fields. The bound thus obtained on the ground-state energy would be rigorous since the Hamiltonian is unchanged, and approximating the fields is equivalent to approximating the system wave function.

Hooke's atom also allows for the concept of an excited state. The excited states for this atom are defined [11] by the number of nodes of the wave function. However, the external potential for the first-excited state with one node is different from that of the ground state with no nodes. Nevertheless, it would be interesting to determine whether an equivalent Kohn-Sham system as described by the quantum-mechanical interpretation for the ground state exists for such an excited state, or how close an approximation such a picture provides. Once again, there would be much to learn, with most properties determinable analytically since the excited state wave functions are known.

ACKNOWLEDGMENTS

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APPENDIX: ANALYTICAL EXPRESSIONS FOR THE GROUND-STATE PROPERTIES OF THE HOOKE'S ATOM

In this appendix we give the analytical and semianalytical expressions for various properties of the Hooke's atom in the ground state corresponding to a spring constant value of $k = 1/4$.

1. Electron density $\rho(r)$

$$\rho(r) = \frac{\pi\sqrt{2\pi}C^2}{r} e^{-r^2/2} \{7r + r^3 + (8/\sqrt{2\pi})re^{-r^2/2} + 4(1+r^2)\text{erf}(r/\sqrt{2})\}, \quad (\text{A1})$$

where

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-y^2} dy \quad (\text{A2})$$

is the error function [26].

2. Pair-correlation density $g(\mathbf{r}, \mathbf{r}')$

$$g(\mathbf{r}, \mathbf{r}') = \frac{C^2}{2\rho(r)} e^{-(r^2+r'^2)/2} (2 + |\mathbf{r} - \mathbf{r}'|)^2. \quad (\text{A3})$$

3. Electron-interaction field $\mathcal{E}_{ee}(\mathbf{r})$

$$\mathcal{E}_{ee}(r) = \frac{1}{r^2} \frac{C^2(\sqrt{2\pi})^3}{2\rho(r)} e^{-r^2/2} \{(r^2+3)\text{erf}(r/\sqrt{2}) - 3\sqrt{2/\pi}re^{-r^2/2} - 4\sqrt{2}\text{daw}(r/\sqrt{2}) + 4r\}, \quad (\text{A4})$$

where

$$\text{daw}(x) = e^{-x^2} \int_0^x e^{t^2} dt \quad (\text{A5})$$

is Dawson's integral [26].

4. Hartree field $\mathcal{E}_H(\mathbf{r})$

$$\mathcal{E}_H(r) = \frac{1}{r^2} (2\pi C)^2 \{10\pi \text{erf}(r/\sqrt{2}) - 4\sqrt{2\pi}(3+r^2)e^{-r^2/2}\text{erf}(r/\sqrt{2}) + 16\sqrt{\pi} \text{erf}(r) - 8re^{-r^2} - \sqrt{2\pi}(10r+r^3)e^{-r^2/2}\}. \quad (\text{A6})$$

5. Electron-interaction energy E_{ee}

$$E_{ee} = (4\pi C)^2 [\pi/2 + \sqrt{\pi}] = 0.447\,443 \text{ a.u.} \quad (\text{A7})$$

6. Coulomb self-energy E_H

$$E_H = 4(2\pi C)^4 \left\{ \frac{20}{3}\pi^2 + \frac{507}{32}\pi^{3/2} + 9\sqrt{3}\pi + 4\sqrt{2\pi} + \sqrt{\pi}(23 \arcsin \frac{7}{9} - 32 \arcsin \frac{1}{3}) \right\} = 1.030\,250 \text{ a.u.} \quad (\text{A8})$$

7. External energy E_{ext}

$$E_{\text{ext}} = \int \rho(r) \frac{1}{2} kr^2 dr = 2(\pi C)^2 [9\pi + 14\sqrt{\pi}] = 0.888\,141 \text{ a.u.} \quad (\text{A9})$$

8. Electron-interaction potential $W_{ee}(\mathbf{r})$

$$W_{ee}(r) = -C^2(\sqrt{2\pi})^3 \int_{\infty}^r \frac{1}{2r'^2 \rho(r')} e^{-r'^2/2} \{ (r'^2 + 3) \operatorname{erf}(r'/\sqrt{2}) - 3\sqrt{2/\pi} r' e^{-r'^2/2} - 4\sqrt{2} \operatorname{daw}(r'/\sqrt{2}) + 4r' \} dr', \quad (\text{A10})$$

$$W_{ee}(0) = 0.659\,59 \text{ a.u.} \quad (\text{A11})$$

9. Hartree potential $W_H(\mathbf{r})$

$$W_H(r) = \frac{(2\pi C)^2 \sqrt{2\pi}}{r} \{ 5\sqrt{2\pi} \operatorname{erf}(r/\sqrt{2}) - 12e^{-r^2/2} \operatorname{erf}(r/\sqrt{2}) + 8\sqrt{2} \operatorname{erf}(r) + 2\sqrt{2\pi} r (1 - \operatorname{erf}^2(r/\sqrt{2})) - r e^{-r^2/2} \}. \quad (\text{A12})$$

$$W_H(0) = (2\pi C)^2 [9\sqrt{2\pi} + 4\pi + 8] = 1.442\,941 \text{ a.u.} \quad (\text{A13})$$

10. Slater electron-interaction potential $V_{ee}^S(\mathbf{r})$

$$V_{ee}^S(r) = \frac{\pi C^2}{r\rho(r)} e^{-r^2/2} \{ 4\sqrt{2\pi} r + 2r e^{-r^2/2} + \sqrt{2\pi} (5 + r^2) \operatorname{erf}(r/\sqrt{2}) \}. \quad (\text{A14})$$

$$V_{ee}^S(0) = \frac{4(\sqrt{2\pi} + 3)}{7\sqrt{2\pi} + 16} = 0.656\,598 \text{ a.u.} \quad (\text{A15})$$

11. Single-particle density matrix $\gamma(\mathbf{r}', \mathbf{r}'')$

$$\gamma(\mathbf{r}', \mathbf{r}'') = 2C^2 e^{-1/4(r'^2 + r''^2)} \int \left(1 + \frac{|\mathbf{r}' - \mathbf{r}|}{2} \right) \times \left(1 + \frac{|\mathbf{r}'' - \mathbf{r}|}{2} \right) e^{-r^2/2} d\mathbf{r}. \quad (\text{A16})$$

12. Dirac density matrix $\gamma_s(\mathbf{r}', \mathbf{r}'')$

$$\gamma_s(\mathbf{r}', \mathbf{r}'') = \sqrt{\rho(\mathbf{r}') \rho(\mathbf{r}'')}. \quad (\text{A17})$$

13. Kinetic-energy-density tensor $t_{\alpha\beta}(\mathbf{r}; [\gamma])$

$$t_{\alpha\beta}(\mathbf{r}; [\gamma]) = \frac{r_{\alpha} r_{\beta}}{r^2} f(r) + \delta_{\alpha\beta} k(r), \quad (\text{A18})$$

where

$$f(r) = \frac{1}{8} \left(r^2 \rho(r) - \frac{4\pi C^2}{r^3} e^{-r^2/2} [\sqrt{2\pi} r^5 - 2\sqrt{2\pi} r^2 (1 - r^2) \operatorname{erf}(r/\sqrt{2}) + 4r^3 e^{-r^2/2} - 6\sqrt{\pi} \operatorname{daw}(r/\sqrt{2}) - \sqrt{2\pi} r (r^2 - 3)] \right) \quad (\text{A19})$$

and

$$k(r) = \frac{(\sqrt{2\pi})^3 C^2}{4r^3} [r - \sqrt{2} \operatorname{daw}(r/\sqrt{2})] e^{-r^2/2}. \quad (\text{A20})$$

14. Kinetic-energy-density tensor $t_{s,\alpha\beta}(\mathbf{r}; [\gamma_s])$

$$t_{s,\alpha\beta}(\mathbf{r}; [\gamma_s]) = \frac{r_{\alpha} r_{\beta}}{r^2} h(r), \quad (\text{A21})$$

where

$$h(r) = \frac{1}{8\rho} \left(\frac{\partial \rho}{\partial r} \right)^2. \quad (\text{A22})$$

15. Kinetic field $z(\mathbf{r}; [\gamma])$

$$z(\mathbf{r}; [\gamma]) = \frac{\pi C^2}{4r^2} e^{-r^2/2} \{ \sqrt{2\pi} r (-r^6 + 3r^4 + 8r^2 + 16) - 4\sqrt{2\pi} (r^6 - 6r^4 + 5r^2 - 2) \operatorname{erf}(r/\sqrt{2}) - 8r(r^4 - 7r^2 + 2) e^{-r^2/2} - 32\sqrt{\pi} \operatorname{daw}(r/\sqrt{2}) \}. \quad (\text{A23})$$

16. Kinetic field $z_s(\mathbf{r}; [\gamma_s])$

$$z_s(\mathbf{r}; [\gamma_s]) = \frac{1}{2\rho} \left(\frac{\partial \rho}{\partial r} \right) \left[\frac{1}{r} \left(\frac{\partial \rho}{\partial r} \right) - \frac{1}{2\rho} \left(\frac{\partial \rho}{\partial r} \right)^2 + \frac{\partial^2 \rho}{\partial r^2} \right]. \quad (\text{A24})$$

17. Kinetic energy $T[\rho]$

$$T[\rho] = \pi^2 C^2 [14\pi + 20\sqrt{\pi}] = 0.664\,418 \text{ a.u.} \quad (\text{A25})$$

18. Expectations

$$\langle r \rangle = \int \rho(r) r d\mathbf{r} = 2(2\pi C)^2 [4\pi + 11\sqrt{2\pi} + 12] = 3.489\,025 \text{ a.u.} \quad (\text{A26})$$

$$\langle r^2 \rangle = \int \rho(r) r^2 d\mathbf{r} = (4\pi C)^2 [9\pi + 14\sqrt{\pi}] = 7.105\,114 \text{ a.u.} \quad (\text{A27})$$

$$\left\langle \frac{1}{r} \right\rangle = \int \rho(r) \frac{1}{r} d\mathbf{r} = (2\pi C)^2 [4\pi + 9\sqrt{2\pi} + 8] = 1.442\,940 \text{ a.u.} \quad (\text{A28})$$

$$\left\langle \frac{1}{r^2} \right\rangle = \int \rho(r) \frac{1}{r^2} d\mathbf{r} = (2\pi C)^2 [11\pi + 8\sqrt{\pi} + 4\sqrt{2\pi} \ln(1 + \sqrt{2})] = 1.926\,359 \text{ a.u.} \quad (\text{A29})$$

$$\langle \delta(\mathbf{r}) \rangle = \rho(0) = \pi C^2 [7\sqrt{2\pi} + 16] = 0.089\,319 \text{ a.u.} \quad (\text{A30})$$

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