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## Coulomb holes and correlation potentials in the helium atom

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In this paper we investigate Coulomb correlation effects in the He atom by studying the structure of the static and dynamic Coulomb hole charge distributions as determined by the analytical 39-parameter correlated wave function of Kinoshita. The static Coulomb hole, which is defined in terms of the radial electron-electron distribution function, shows that as a result of Coulomb repulsion there is a reduction in probability of electron approach within a distance of one atomic unit and an increase in this probability for greater separations. The dynamic Coulomb hole defined directly in terms of the pair-correlation density describes the probability of finding one of the electrons given the position of the other. We thus demonstrate how the two electrons are correlated as a function of the nonuniform density of the atom. We also investigate the correlation potential  $W_c(r)$  of the work formalism, which is the work done to move an electron in the force field of the dynamic Coulomb hole charge. The structure of  $W_c(r)$  is similar to the exchange potential  $W_x(r)$  (which is the work done to move an electron in the force field of the Fermi hole), in that it is attractive, monotonic, and has zero slope at the nucleus. However, as a result of the structure of the Coulomb hole for asymptotic electron positions, and the fact that its total charge is zero, the potential  $W_c(r)$  vanishes rapidly in the classically forbidden region. Thus, the asymptotic structure of the exchange-correlation potential  $W_{xc}(r)$  of the work formalism is that of  $W_x(r)$  which is  $(-1/r)$ . We also determine via the Kinoshita wave function the correlation potential  $\mu_c(r)$  of Kohn-Sham theory, which differs from  $W_c(r)$  in that it also incorporates the effects of the correlation contribution to the kinetic energy. Consequently, it is less attractive than  $W_c(r)$ , but also has zero slope at the nucleus. However, as is known, the potential  $\mu_c(r)$  is nonmonotonic, since it goes positive within the atom, then becomes negative in the classically forbidden region, finally vanishing asymptotically as a negative function. Since the exchange potentials of the work formalism and Kohn-Sham theory are the same for this atom, and because  $W_c(r)$  is strictly representative of Coulomb correlations, we attribute the nonmonotonicity and positiveness of the Kohn-Sham potential  $\mu_c(r)$  to the correlation kinetic energy. This conclusion is consistent with the result that the difference between the correlation energies determined within the work formalism from the dynamic Coulomb hole and Kohn-Sham theory is equal to the correlation contribution to the kinetic energy.

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## I. INTRODUCTION

Electron correlations result from the Pauli exclusion principle as expressed by the requirement that the wave function be antisymmetric in an interchange of the coordinates at any two electrons, and by mutual repulsion as governed by Coulomb's law. There is thus a reduction in density or hole surrounding each electron. This reduction in density at  $r'$  about an electron at  $r$  is the Fermi-Coulomb hole charge distribution  $\rho_{xc}(r, r')$ , the total charge excluded being that of an electron. For the uniform electron gas the Fermi-Coulomb hole is spherically symmetric about and independent of the electron position. In a nonuniform-density system, the Fermi-Coulomb hole charge is not spherically symmetric about the electron. Furthermore, its structure is dependent upon the position of the electron. Thus for such systems

the Fermi-Coulomb hole is a *dynamic* charge whose distribution changes as a function of electron position. Since the Fermi-Coulomb hole represents the correlations between electrons due to the Pauli exclusion principle and Coulomb's law, the lowering of the energy due to these correlations—the exchange-correlation energy—can also be expressed in terms of this charge distribution: it is the energy of interaction between the electron density  $\rho(r)$  and the Fermi-Coulomb hole charge.

The component of the Fermi-Coulomb hole due to Pauli correlations, viz., the Fermi hole charge  $\rho_x(r, r')$ , is defined as that obtained when only these correlations between electrons are assumed present, as in Hartree-Fock theory. Within such an approximation, the reduction in density about each electron due to the Pauli exclusion principle is then explicitly known in terms of the idempotent Dirac density matrix. The Fermi hole thus defined also excludes a total charge of one electron. Since the expression for the Fermi hole in terms of the spin orbitals is exactly known, a considerable number of studies of its structure have been performed for the nonuniform

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density system of atoms [1], molecules [2], and metallic surfaces [3,4].

The Coulomb hole  $\rho_c(\mathbf{r}, \mathbf{r}')$  is then defined as the difference between the Fermi-Coulomb and Fermi hole charge distributions. Since the total charge of both the Fermi-Coulomb and Fermi holes is that of an electron, the total charge of the Coulomb hole is zero. As a consequence, whereas the Fermi hole charge is always negative, representing the reduction in density about the electron in the distribution of other electrons of the same spin, the Coulomb hole is positive as well as negative. The determination of the structure of the Coulomb hole, however, requires a knowledge of the wave function of the system. Although there has been recent work [5] on the pair-correlation density for the Be and Ne atoms and their ions, and of the Coulomb hole for the uniform electron gas [6], there is to our knowledge no systematic study of the Coulomb hole structure for nonuniform-density systems. One purpose of this paper, therefore, is to study the structure of the Coulomb hole  $\rho_c(\mathbf{r}, \mathbf{r}')$  as a function of electron position for the ground state of the He atom. The wave function employed in our calculations is the analytical 39-parameter correlated wave function of Kinoshita [7]. This wave function leads to the same energy as that due to the 1078-parameter wave function of Pekeris [8] to seven significant figures, and to the expectations of various single-particle operators from four to five significant figures. The wave function also satisfies the electron-nucleus [9] cusp condition to three significant figures and the electron-electron [9] cusp condition over most of the atomic region to two significant figures. For purposes of completeness we have also determined the previously studied [10,11] static Coulomb hole  $\rho_c^{\text{static}}(R)$ , where  $R$  is the magnitude of the interelectronic distance.

The dynamic Coulomb hole charge  $\rho_c(\mathbf{r}, \mathbf{r}')$  also constitutes a fundamental quantity in the work formalism [12,13] of electronic structure. In this formalism the wave function  $\Psi$  can in principle be obtained by solution of a Sturm-Liouville-type differential equation whose eigenfunctions form a complete set. The Coulomb hole  $\rho_c(\mathbf{r}, \mathbf{r}')$  is the quantum-mechanical source charge distribution which gives rise to both the correlation energy  $E_c$  and the local potential  $W_c(\mathbf{r})$  representing Coulomb correlations within this formalism. Since the Coulomb hole charge depends upon the electron position, the correlation potential  $W_c(\mathbf{r})$  is the work done to move an electron in the force field  $\mathcal{E}_c(\mathbf{r})$  of this charge. The correlation energy  $E_c$  is in turn the energy of interaction between the density and the Coulomb hole charge. The local potential  $W_x(\mathbf{r})$  representing Pauli correlations and the exchange energy  $E_x$  are similarly defined in terms of the Fermi hole  $\rho_x(\mathbf{r}, \mathbf{r}')$ . The application [13] of the work formalism within the Pauli-correlated approximation to atoms, atomic ions, metallic surfaces, and metallic clusters has led to highly accurate results, and the structure of the exchange potential  $W_x(\mathbf{r})$  for these nonuniform-density systems is known. In this paper we study the structure of the corresponding force field  $\mathcal{E}_c(\mathbf{r})$  and correlation potential  $W_c(\mathbf{r})$  due to the Coulomb hole

charge  $\rho_c(\mathbf{r}, \mathbf{r}')$  for the He atom. Once again we assume the wave function known and to be that of Kinoshita, and determine these properties from the resulting Coulomb hole charge. Now in local-potential theories of the He atom, it is possible to define a Fermi hole from which the exchange potential  $W_x(\mathbf{r})$  can then be obtained. As such, comparisons are also made of the exchange  $W_x(\mathbf{r})$ , correlation  $W_c(\mathbf{r})$ , and exchange-correlation  $W_{xc}(\mathbf{r})$  potentials for this atom determined within the work formalism. Such a comparison is important since within this formalism the asymptotic structure of the exchange-correlation potential of all nonuniform-density systems is that of the exchange potential alone. The reason for this is that the total Coulomb hole charge is zero, and consequently there is no force field due to this charge for electron positions asymptotically far from it. Therefore the correlation potential vanishes for these positions of the electron, and the asymptotic structure of the exchange-correlation potential is given by its exchange component due to the unit charge of the Fermi hole. Thus the asymptotic structure of the many-body potential  $W_{xc}(\mathbf{r})$  can be determined by solving the system differential equation in the Pauli-correlated approximation for  $W_x(\mathbf{r})$ . In atoms and molecules the asymptotic structure of  $W_x(\mathbf{r})$  is  $(-1/r)$ . Furthermore, it is meaningful then to compare the highest occupied eigenvalue of this differential equation to experimental ionization potentials, electron affinities, and transition energies. In such a comparison [13] with the corresponding eigenvalue of Hartree-Fock theory, the highest occupied eigenvalue of the work formalism for atoms and negative atomic ions is observed to be consistently superior with respect to experiment. In this paper we explicitly demonstrate that the correlation potential vanishes as the exchange-correlation and exchange potentials approach their asymptotic structure of  $-1/r$ , thereby validating the above argument and observation.

Finally, we compare the potential  $W_c(\mathbf{r})$  with the correlation potential  $\mu_c(\mathbf{r})$  of Hohenberg-Kohn-Sham [14] density-functional theory [15]. We have determined the potential  $\mu_c(\mathbf{r})$  by inverting the Kohn-Sham differential equation as in the work of Almladh and Pedroza [16] but have obtained the density and thereby the Kohn-Sham orbitals via the Kinoshita wave function. The potential thus obtained is the same as that of a Monte Carlo calculation [17]. The correlation potentials  $W_c(\mathbf{r})$  and  $\mu_c(\mathbf{r})$  differ fundamentally in that the former is purely representative of Coulomb correlations whereas the latter [15] incorporates in addition the correlation contribution  $T_c$  to the kinetic energy. Thus, since for the He atom the exchange potentials  $W_x(\mathbf{r})$  and  $\mu_x(\mathbf{r})$  of the work formalism and Kohn-Sham theory, respectively, are the same, the difference between the correlation potentials of the two theories provides an estimate of the correlation-kinetic-energy contribution  $\delta T_c / \delta \rho(\mathbf{r})$  to the Kohn-Sham potential.

In the following section we define and then describe the structure of the static and dynamic Coulomb hole charge distributions for the He atom. We then briefly describe the work formalism and Kohn-Sham theory, and discuss

and compare the corresponding correlation potentials. Finally, we conclude with a summary of our results. For expressions of the relevant properties derived from the Kinoshita wave function we refer the reader to Ref. [18].

## II. COULOMB HOLES

The Schrödinger equation for  $N$  electrons in an external potential  $v_{\text{ext}}(\mathbf{r})$  is

$$\left[ -\frac{1}{2} \sum_i \nabla_i^2 + \sum_i v_{\text{ext}}(\mathbf{r}_i) + \frac{1}{2} \sum_{ij}' \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \Psi = E \Psi, \quad (1)$$

where  $\Psi$  is the electronic wave function and  $E$  the total energy, which is the expectation value of the Hamiltonian. Both the static and dynamic Coulomb holes are defined through the wave function  $\Psi$  via the pair-correlation density  $g(\mathbf{r}, \mathbf{r}')$ , which is the density at  $\mathbf{r}'$  if an electron is assumed to be at  $\mathbf{r}$ . Thus,

$$g(\mathbf{r}, \mathbf{r}') = \frac{\left\langle \Psi \left| \sum_{ij \neq i} \delta(\mathbf{r}_i - \mathbf{r}) \delta(\mathbf{r}_j - \mathbf{r}') \right| \Psi \right\rangle}{\left\langle \Psi \left| \sum_i \delta(\mathbf{r}_i - \mathbf{r}) \right| \Psi \right\rangle}, \quad (2)$$

where the denominator is the density  $\rho(\mathbf{r})$ :

$$\rho(\mathbf{r}) = \left\langle \Psi \left| \sum_i \delta(\mathbf{r}_i - \mathbf{r}) \right| \Psi \right\rangle. \quad (3)$$

Thus the total charge of the pair-correlation density is  $\int g(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = N - 1$ . The pair-correlation density, which incorporates all the electron correlations in its structure, can also be written in terms of the Fermi-Coulomb hole charge  $\rho_{\text{xc}}(\mathbf{r}, \mathbf{r}')$  as

$$g(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r}') + \rho_{\text{xc}}(\mathbf{r}, \mathbf{r}'), \quad (4)$$

so that the total charge of the Fermi-Coulomb hole is then  $\int \rho_{\text{xc}}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = -1$ .

### Static Coulomb hole

The static Coulomb hole  $\rho_c^{\text{static}}(R)$  is defined [11] in terms of the radial electron-electron distribution function  $f(R)$ , which is the probability of finding two electrons at  $\mathbf{r}_1$  and  $\mathbf{r}_2$  a distance  $R = |\mathbf{r}_2 - \mathbf{r}_1|$  apart. In terms of the pair-correlation density  $g(\mathbf{r}, \mathbf{r}')$  this probability can be written as

$$f(R) = \frac{1}{2} \int d\mathbf{r} \rho(\mathbf{r}) \left[ \int g(\mathbf{r}, \mathbf{r} + \mathbf{R}) d\Omega_{\hat{\mathbf{R}}} R^2 \right], \quad (5)$$

where the factor of  $\frac{1}{2}$  ensures the normalization [11] of this distribution function to be the number of electron pairs:

$$\int_0^\infty f(R) dR = \frac{N(N-1)}{2}. \quad (6)$$

The static Coulomb hole  $\rho_c^{\text{static}}(R)$  is defined as the difference

$$\rho_c^{\text{static}}(R) = f(R) - f_x(R), \quad (7)$$

where  $f_x(R)$  is the radial distribution function when only Pauli correlations are assumed present. Since both distribution functions integrate to the number of electron pairs, the total charge

$$\int \rho_c^{\text{static}}(R) dR = 0, \quad (8)$$

and hence  $\rho_c^{\text{static}}(R)$  has no definite sign.

In Fig. 1 we plot the radial distribution functions  $f(R)$  and  $f_x(R)$  for the He atom using the Kinoshita and Hartree-Fock [19] wave functions, respectively, as well as the static Coulomb hole  $\rho_c^{\text{static}}(R)$ . In the region where  $0 < R \leq 1$  a.u. the function  $f(R)$  lies below  $f_x(R)$ , indicating thereby that in this region Coulomb correlations reduce the probability of two electrons being a certain distance apart from that when these correlations are absent. Thus in this region the Coulomb hole is negative. In the region beyond  $R \geq 1$  a.u.,  $f(R)$  lies above  $f_x(R)$  so that the Coulomb hole is positive, indicating that as a result of Coulomb correlations there is an increase in the probability that the electrons are separated by a distance greater than  $\sim 1$  a.u. The structure of the positive part of the hole describes the probability of this separation. Studies [10] of the He isoelectronic sequence  $\text{Li}^+, \text{Be}^{2+}, \dots, \text{Ne}^{8+}$  show that the region in which the Coulomb hole is positive increases with increasing atomic number as it must, but that the structure of the hole remains the same.

In the quantum-mechanical description of an atom, the probability of an electron being at some position changes as a function of its distance  $r$  from the nucleus. The stat-

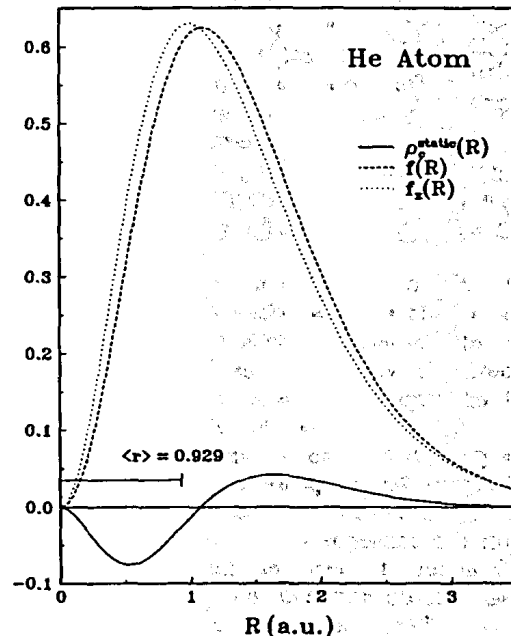


FIG. 1. Static Coulomb hole  $\rho_c^{\text{static}}(R)$  as a function of the interelectronic distance  $R$  for the He atom. The radial electron-electron distribution functions  $f(R)$  and  $f_x(R)$  determined via the Kinoshita and Hartree-Fock wave functions, respectively, are also plotted.

ic Coulomb hole does not describe the effects of Coulomb correlations as a function of this probability or equivalently of the nonuniformity of the electronic density. This is described by the dynamic Coulomb hole charge discussed below.

#### Dynamic Coulomb hole

The dynamic Coulomb hole charge  $\rho_c(\mathbf{r}, \mathbf{r}')$  is defined as the difference

$$\rho_c(\mathbf{r}, \mathbf{r}') = \rho_{xc}(\mathbf{r}, \mathbf{r}') - \rho_x(\mathbf{r}, \mathbf{r}'), \quad (9)$$

where the Fermi hole is determined in an approximation in which only Pauli correlations are considered, such as Hartree-Fock theory or the exchange-only version of the work formalism. As such, the Fermi hole can be expressed in terms of the idempotent Dirac density matrix  $\gamma(\mathbf{r}, \mathbf{r}') = \sum_i \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}')$  as

$$\rho_x(\mathbf{r}, \mathbf{r}') = -|\gamma(\mathbf{r}, \mathbf{r}')|^2 / 2\rho(\mathbf{r}),$$

where  $\gamma(\mathbf{r}, \mathbf{r}) = \rho(\mathbf{r})$  and where the  $\phi_i(\mathbf{r})$  are the spin orbitals generated within the corresponding theory. The Fermi hole satisfies the constraints of charge conservation  $\int \rho_x(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = -1$ , negatively  $\rho_x(\mathbf{r}, \mathbf{r}') \leq 0$ , and value at electron position  $\rho_x(\mathbf{r}, \mathbf{r}) = -\rho(\mathbf{r})/2$ .

For the He atom in its ground state there are no correlations due to the Pauli exclusion principle since the electrons have opposite spin. Thus the determinantal wave function reduces to a product of two spin orbitals. The corresponding pair-correlation density for an electron at  $\mathbf{r}$  is then the density due to the other electron at  $\mathbf{r}'$ , which is half the total density, so that  $g(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r}')/2$ . However, when the pair-correlation density is written as in Eq. (4), it is appropriate to think in terms of a "Fermi hole," which is the negative of the self-interaction term in the density. Therefore for the He atom  $\rho_x(\mathbf{r}, \mathbf{r}') = -\rho(\mathbf{r}')/2$ , which is independent of the electron position. Such a concept derives from local-effective-potential theories in which the pair-correlation density constitutes the fundamental quantity, with both the density and the Fermi or Fermi-Coulomb holes [see Eq. (4)] giving rise to local potentials.

In Fig. 2 we plot a cross section through the Coulomb  $\rho_c(\mathbf{r}, \mathbf{r}')$ , Fermi  $\rho_x(\mathbf{r}, \mathbf{r}')$ , and Fermi-Coulomb  $\rho_{xc}(\mathbf{r}, \mathbf{r}')$  hole charge distributions for an electron at the nucleus  $r=0$  as determined via the Kinoshita wave function. Also plotted for purposes of comparison is the electronic density  $\rho(\mathbf{r}')$ . Observe that for this electron position all the hole charge distributions are spherically symmetric about the electron. At the position of the electron, the holes all also exhibit a cusp. (The cusp in the structure of the Fermi hole is a consequence of the cusp in the density.) At and about the electron position the Fermi-Coulomb hole is more negative than the Fermi hole as must be the case. This is a consequence of the fact that, when Coulomb correlations are introduced, an electron creates a hole about it that is deeper than when only Pauli correlations are present. Thus, in the region about the electron, the Coulomb hole is negative. (This is also the case for all electron positions.) However, near the surface

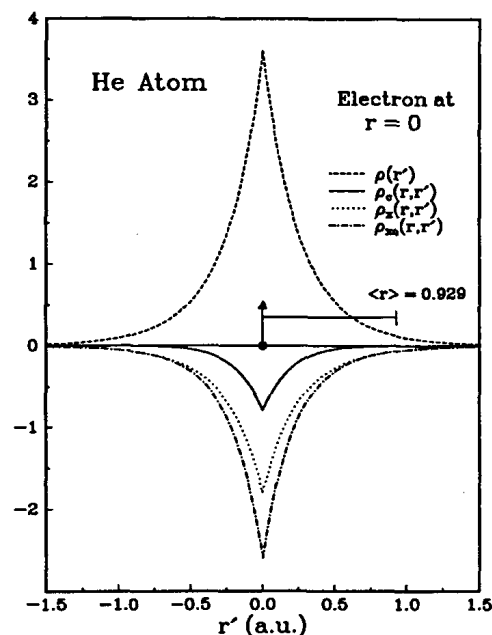


FIG. 2. Cross sections of the Coulomb  $\rho_c(\mathbf{r}, \mathbf{r}')$ , Fermi  $\rho_x(\mathbf{r}, \mathbf{r}')$ , and Fermi-Coulomb  $\rho_{xc}(\mathbf{r}, \mathbf{r}')$  holes for the He atom as determined via the Kinoshita wave function for an electron at the nucleus  $r=0$ , as indicated by the arrow. The nucleus is at the origin. The positive part of the Coulomb hole is not evident on the scale of the figure. The electronic density  $\rho(\mathbf{r}')$  is also plotted.

of the atom ( $\langle r \rangle = 0.929$  a.u.) and in the classically forbidden region, the Fermi-Coulomb hole must lie above the Fermi hole since both these distributions satisfy the same charge conservation constraint. In these regions the Coulomb hole is then positive. (The positive part of the Coulomb hole is not evident on the scale of Fig. 2, but is clearly exhibited in the figures to follow.) Thus the Coulomb hole is both positive and negative, and integrates to a total charge of zero. The positive part of the hole indicates that for an electron at the origin the other electron is outside the surface in the classically forbidden region of the atom.

Since the Fermi hole for this atom is independent of the electron position, we now focus our attention solely on the structure of the Coulomb hole for the other electron positions considered. In Fig. 3(a) we plot the Coulomb hole for an electron with a radial coordinate of  $r=0.566$  a.u. which is at the maximum of the radial probability density, and in Fig. 3(b) for an electron at  $r=0.8$  a.u. The polar angle  $\theta$  of the electron position is taken to be zero. The polar angles  $\theta'$  of the Coulomb hole charge considered correspond to  $\theta'=0^\circ$ ,  $45^\circ$ , and  $90^\circ$  with respect to the nucleus-electron direction. Since the electron position is along the  $\theta'=0^\circ$  direction, the Coulomb hole (for this spherically symmetric atom) is independent of its azimuthal angle  $\phi'$ . For these electron positions the Coulomb hole is no longer spherically symmetric about the electron. Observe also the cusp in the structure of the Coulomb hole at the position of the elec-

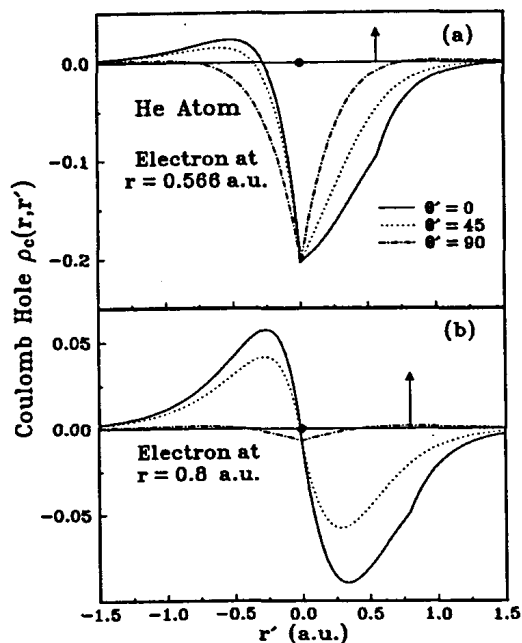


FIG. 3. Coulomb hole  $\rho_c(r,r')$  for the He atom in three different directions corresponding to  $\theta' = 0^\circ$ ,  $45^\circ$ , and  $90^\circ$  with respect to the nucleus-electron direction. The electron position corresponds to a polar angle of  $\theta = 0^\circ$ . In (a) the radial coordinate of the electron, as indicated by the arrow, is at the maximum of the radial probability density for the He atom at  $r = 0.566$  a.u., whereas in (b) the electron is at  $r = 0.8$  a.u.

tron. At and about these positions, the hole is principally negative. Its magnitude at the electron position diminishes with distance from the nucleus as a result of the decrease in the density. However, as the distance of the electron from the nucleus increases, a part of the hole that is positive emerges on the side of the atom opposite to that of the electron. The magnitude of this positive part is seen to increase relative to that of the negative part about the electron, with the positive part moving closer to the nucleus. This indicates that it is more probable for the other electron to be in this region.

In Figs. 4(a)–4(c) we plot the Coulomb hole for an electron in the surface region of the atom at  $r = 1$  a.u., and in the classically forbidden region at  $r = 1.5$  a.u. and  $r = 5$  a.u., respectively. The trends discussed above continue as the distance of the electron from the nucleus increases further. The positive part of the Coulomb hole increases in magnitude about the nucleus, and the negative part around the electron position continues to decrease. For the electron at  $r = 5$  a.u. [Fig. 4(c)], most of the Coulomb hole is positive, localized about the nucleus, and essentially spherically symmetric about it. Thus, if one of the two electrons is in the asymptotic region, the other is localized about the nucleus.

In Fig. 5 we plot the center of mass  $\langle r' \rangle$  of the Coulomb hole  $\rho_c(r,r')$  as a function of electron position. The center of mass lies along the nucleus-electron direc-

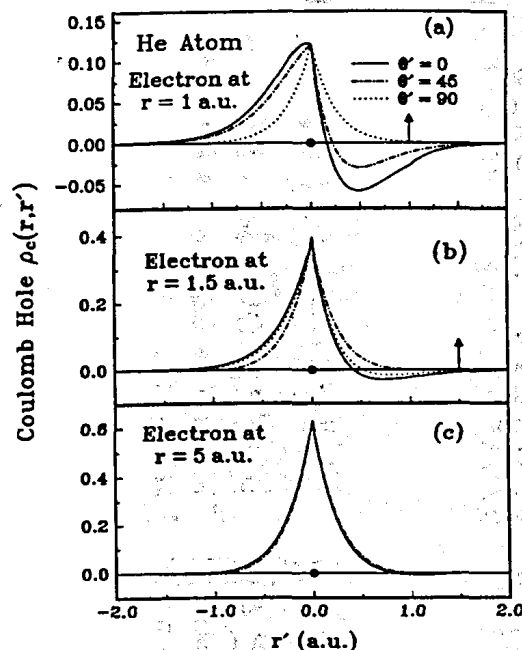


FIG. 4. Same as Fig. 3 except that in (a) the electron is at  $r = 1$  a.u., in (b) at  $r = 1.5$  a.u., and in (c) at  $r = 5$  a.u.

tion. However, it is always on the side of the nucleus opposite to that of the electron, but also always close to the nucleus. For asymptotic positions of the electron, it once again approaches the nucleus. The center of mass of the Fermi hole in this case is at the origin. However, for other atoms (see Fig. 2 of the second reference of [12]), the center of mass of the Fermi hole for the most part lies on the same side of the nucleus as the electron. Furthermore, it follows the electron for positions within the atom, and lies considerably farther from the nucleus prior to approaching the origin for asymptotic electron positions.

As we have seen, the structure of the Coulomb hole charge changes from being essentially negative for electron positions in the deep interior of the atom to being

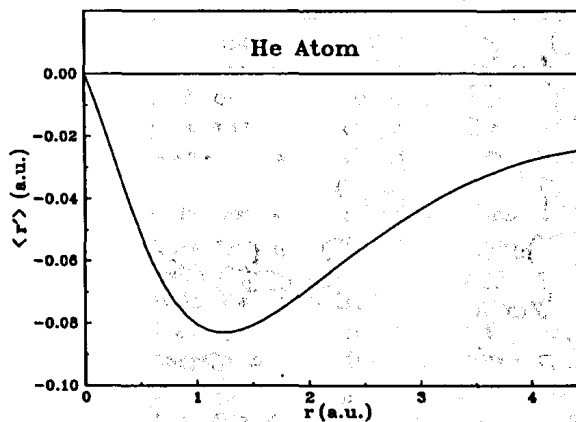


FIG. 5. Center of mass  $\langle r' \rangle$  of the Coulomb hole  $\rho_c(r,r')$  for the He atom as a function of electron position.

essentially positive for asymptotic positions of the electron. This is a direct consequence of the fact that Coulomb repulsion depends upon the distance between the electrons. On the other hand, the Fermi hole is always negative irrespective of the electron position. The negative Fermi hole charge gives rise to a force field  $\mathcal{E}_x(\mathbf{r})$  that is negative, and consequently the exchange potential  $W_x(\mathbf{r})$ , determined as the work done to bring an electron from infinity to its position at  $\mathbf{r}$  in this field, is also always negative. On the other hand, the Coulomb hole charge is both positive and negative, and changes from being nearly all negative to nearly all positive. Does the force field  $\mathcal{E}_c(\mathbf{r})$  due to this charge distribution and the corresponding work done  $W_c(\mathbf{r})$  in this field then go positive in certain regions of space? The structure of the force field due to the Coulomb hole charge and the resulting correlation potential are discussed in the following section.

### III. CORRELATION POTENTIALS

Prior to discussing the structure of the correlation potential  $W_c(\mathbf{r})$  of the work formalism for the He atom, and in order to explain how it differs from the corresponding potential  $\mu_c(\mathbf{r})$  of Kohn-Sham theory, we give a brief outline of the formalism. We then describe the relevant features of Kohn-Sham theory, and finally compare the two correlation potentials.

#### The work formalism

The fundamental quantity in the work formalism [12,13] is the pair-correlation density  $g(\mathbf{r}, \mathbf{r}')$  of Eq. (2). It constitutes the quantum-mechanical source charge distribution which gives rise via Coulomb's law to both a local potential  $W(\mathbf{r})$  representing electron correlations and the electron interaction energy  $E_{ee}$ . Since the pair-correlation density is a dynamic (nonlocal) charge distribution which depends upon the electron position, the potential  $W(\mathbf{r})$  is obtained as the work done to bring an electron from infinity to its position at  $\mathbf{r}$  against the force field  $\mathcal{E}(\mathbf{r})$  of this distribution. With the pair-correlation density written as in Eq. (4), the field  $\mathcal{E}(\mathbf{r})$  is the sum of the Hartree  $\mathcal{E}_H(\mathbf{r})$  and exchange-correlation  $\mathcal{E}_{xc}(\mathbf{r})$  fields, where

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

and (10)

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

and the potential  $W(\mathbf{r})$  is the sum of the corresponding Hartree  $W_H(\mathbf{r})$  and the exchange-correlation  $W_{xc}(\mathbf{r})$  potentials defined as the work

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

and (11)

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

respectively. Now since the electronic density  $\rho(\mathbf{r})$  is a static charge distribution, the work done in the Hartree field  $\mathcal{E}_H(\mathbf{r})$  can also be written as

$$W_H(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' . \quad (12)$$

The differential equation governing the system is then

$$\left[ -\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + W_{xc}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}) . \quad (13)$$

This is a Sturm-Liouville differential equation, and as such its solutions form a complete set. Thus the wave function  $\Psi$  can, in principle be obtained [20] as an infinite linear combination of  $N$ -electron Slater determinants  $\Phi\{\phi_i\}$  of the spin orbitals  $\phi_i(\mathbf{r})$  corresponding to the occupied and virtual states of the system:

$$\Psi = \sum_i B_i \Phi\{\phi_i\} , \quad (14)$$

where the  $B_i$  are appropriately chosen coefficients. In the work formalism, therefore, the wave function is obtained self-consistently from a force field that is intrinsic to the system, arising from the pair-correlation density, which in turn is defined in terms of the wave function. The electron interaction energy  $E_{ee}$ , which is the expectation value of the electron-electron interaction operator in the Hamiltonian of Eq. (1), is the energy of interaction between the electronic and pair-correlation densities. With the latter written as in Eq. (4), the energy  $E_{ee}$  is then the sum of the Coulomb self-energy  $E_H$  and the exchange-correlation energy  $E_{xc}$ , where

$$E_H = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

and

$$E_{xc} = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' , \quad (15)$$

so that  $E_{xc}$  is the energy of interaction between the density  $\rho(\mathbf{r})$  and the Fermi-Coulomb hole charge distribution  $\rho_{xc}(\mathbf{r}, \mathbf{r}')$ .

Implicit in the above description of the local potential representing electron correlations is that the work  $W(\mathbf{r})$  in the force field  $\mathcal{E}(\mathbf{r})$  is path independent, or equivalently that the curl of the field vanishes:  $\nabla \times \mathcal{E}(\mathbf{r}) = 0$ . The Hartree potential  $W_H(\mathbf{r})$  is path independent since  $\nabla \times \mathcal{E}_H(\mathbf{r}) = 0$ . The exchange-correlation potential  $W_{xc}(\mathbf{r})$  is rigorously path independent [i.e.,  $\nabla \times \mathcal{E}_{xc}(\mathbf{r}) = 0$ ] for symmetrical-density systems, such as spherically symmetric atoms, jellium metal surfaces and clusters, and nonspherically symmetric systems in the central-field approximation. There is as yet no general proof of the path independence of  $W_{xc}(\mathbf{r})$  for systems of arbitrary symmetry in which the external potential is physically realistic. However, if there are systems for which the curl of the force field  $\mathcal{E}_{xc}(\mathbf{r})$  does not vanish, a local path-independent effective exchange-correlation potential

$W_{xc}^{\text{eff}}(\mathbf{r})$  may be obtained [12,13] from the irrotational component of this force field, the solenoidal component being neglected. Equivalently, the effective potential  $W_{xc}^{\text{eff}}(\mathbf{r})$  arises from a scalar static effective Fermi-Coulomb hole charge  $\rho_{xc}^{\text{eff}}(\mathbf{r}) = (1/4\pi)\nabla \cdot \mathcal{E}_{xc}(\mathbf{r})$  so that

$$W_{xc}^{\text{eff}}(\mathbf{r}) = \int \frac{\rho_{xc}^{\text{eff}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' . \quad (16)$$

The potential  $W_{xc}^{\text{eff}}(\mathbf{r})$  is substituted into the differential equation Eq. (13) which is then solved self-consistently for the determination of the wave function. For systems for which the curl of the force field  $\mathcal{E}_{xc}(\mathbf{r})$  vanishes, the effective potential  $W_{xc}^{\text{eff}}(\mathbf{r})$  is equivalent to  $W_{xc}(\mathbf{r})$ . Thus, for such systems, the work formalism can also be described entirely in terms of the static effective charge  $\rho_{xc}^{\text{eff}}(\mathbf{r})$ , thereby precluding the requirement of performing line integrals.

In the approximation when only Pauli correlations are considered and the wave function is a single Slater determinant of spin orbitals, the system differential equation is the same as Eq. (13) with  $W_{xc}(\mathbf{r})$  replaced by the exchange potential  $W_x(\mathbf{r})$ , which is the work done in the force field of the Fermi hole  $\rho_x(\mathbf{r},\mathbf{r}')$  as defined in terms of the Dirac density matrix. The exchange energy  $E_x$ , in turn, is the energy of interaction between the resulting density and the Fermi hole charge.

With the Coulomb hole charge  $\rho_c(\mathbf{r},\mathbf{r}')$  defined as in Eq. (9), the correlation potential  $W_c(\mathbf{r})$  is the work done to move an electron in its force field  $\mathcal{E}_c(\mathbf{r})$ :

$$W_c(\mathbf{r}) = - \int_{\infty}^{\mathbf{r}} \mathcal{E}_c(\mathbf{r}') \cdot d\mathbf{l}' , \quad (17)$$

where

$$\mathcal{E}_c(\mathbf{r}) = \int \frac{\rho_c(\mathbf{r},\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}' . \quad (18)$$

The correlation energy  $E_c$  is then the interaction energy between the density and the Coulomb hole charge:

$$E_c = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho_c(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' . \quad (19)$$

Note that this definition differs from the quantum-chemistry definition of the correlation energy, which is the difference between the total nonrelativistic and Hartree-Fock theory ground-state energies. It also differs from the Kohn-Sham theory correlation energy defined below. Having described the work formalism, we next determine the correlation potential  $W_c(\mathbf{r})$  for the He atom.

#### Correlation potential of the work formalism

To study the structure of the He atom correlation potential  $W_c(\mathbf{r})$  the Kinoshita wave function again was assumed. The structure of the resulting Coulomb  $\rho_c(\mathbf{r},\mathbf{r}')$ , Fermi  $\rho_x(\mathbf{r},\mathbf{r}')$ , and Fermi-Coulomb  $\rho_{xc}(\mathbf{r},\mathbf{r}')$  hole charge distributions is then as determined previously. The resulting exchange  $\mathcal{E}_x(\mathbf{r})$ , correlation  $\mathcal{E}_c(\mathbf{r})$ , and exchange-correlation  $\mathcal{E}_{xc}(\mathbf{r})$  force fields due to these charge distributions are plotted in Fig. 6. Observe that

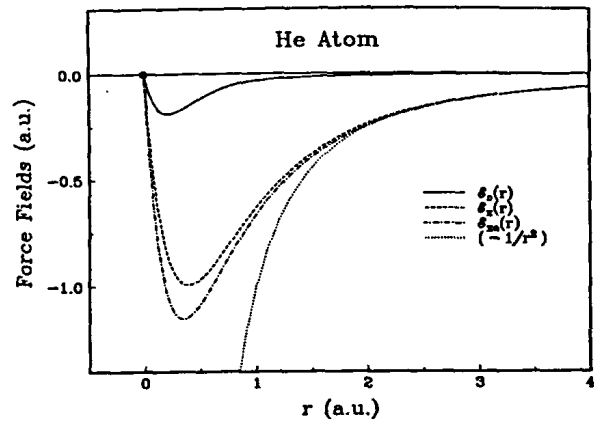


FIG. 6. Force fields  $\mathcal{E}_c(\mathbf{r})$ ,  $\mathcal{E}_x(\mathbf{r})$ , and  $\mathcal{E}_{xc}(\mathbf{r})$  due to the Coulomb, Fermi, and Fermi-Coulomb hole charges, respectively, for the He atom. The function  $(-1/r^2)$  is also plotted.

all the force fields vanish at the origin. This is a consequence of the fact that, for an electron at the nucleus, the charge distributions  $\rho_c(\mathbf{r},\mathbf{r}')$ ,  $\rho_x(\mathbf{r},\mathbf{r}')$ , and  $\rho_{xc}(\mathbf{r},\mathbf{r}')$  are all spherically symmetric about it. As such there is no force field at the position of the electron. The structure of the correlation field  $\mathcal{E}_c(\mathbf{r})$  in the interior of the atom is similar to the exchange field  $\mathcal{E}_x(\mathbf{r})$ , although it is about an order of magnitude smaller. However, both the fields  $\mathcal{E}_x(\mathbf{r})$  and  $\mathcal{E}_c(\mathbf{r})$  are negative throughout space. This is an interesting result since the corresponding source charge distributions for these fields are strikingly different. The Fermi hole is negative for all electron positions and therefore the field  $\mathcal{E}_x(\mathbf{r})$  is negative throughout. On the other hand, the Coulomb hole is both positive and negative and can be substantially one or the other depending upon the position of the electron. The fact that the correlation field  $\mathcal{E}_c(\mathbf{r})$  is negative is a consequence of the fact that the force field depends not only on the structure of the charge distribution but also on the inverse of the square of the distance between the charge and the electron. Thus the part of the charge that lies farther from the electron contributes less to the field than the charge that is closer. For example, for an electron at  $r=1.5$  a.u., the positive part of the Coulomb hole [see Fig. 4(b)] is much larger in magnitude than its negative part. However, the positive part is localized about the nucleus far from the electron and therefore its contribution to the force field is less than that of the negative charge closer to the electron, with the result that the net force field at the electron position is negative. This explains why the correlation field  $\mathcal{E}_c(\mathbf{r})$  is negative. The fact that the Coulomb hole goes substantially positive for asymptotic positions of the electron does, however, cause the correlation field  $\mathcal{E}_c(\mathbf{r})$  to decay far more rapidly than the exchange field  $\mathcal{E}_x(\mathbf{r})$ . The correlation field  $\mathcal{E}_c(\mathbf{r})$  (see Fig. 6) has essentially vanished by  $r \sim 4$  a.u. whereas the exchange field  $\mathcal{E}_x(\mathbf{r})$  decays asymptotically as  $(-1/r^2)$ . Thus the exchange-correlation field  $\mathcal{E}_{xc}(\mathbf{r})$  is asymptotically the same as its exchange component  $\mathcal{E}_x(\mathbf{r})$ , and decays as  $(-1/r^2)$ . This asymptotic structure may also be understood to be a consequence of the fact that the total charge of the



Coulomb hole is zero, whereas that of the Fermi and Fermi-Coulomb holes is unity, and the fact that all these charge distributions are localized and essentially static about the nucleus for asymptotic positions of the electron.

In Fig. 7 we plot the correlation  $W_c(r)$ , exchange  $W_x(r) = -\frac{1}{2}W_H(r)$ , and exchange-correlation  $W_{xc}(r)$  potentials. Observe that the potentials all approach the nucleus quadratically, and have zero slope at the origin as a consequence of the force fields vanishing there. In the interior of the atom, the structure of  $W_c(r)$  is similar to that of  $W_x(r)$ , but is an order of magnitude smaller. Note that  $W_c(r)$  is negative throughout space and monotonic, and therefore positive work must be done to move an electron against the force field of the Coulomb hole charge. Since the correlation field  $\mathcal{E}_c(r)$  decays rapidly, the correlation potential  $W_c(r)$  is also negligible by  $r \sim 4$  a.u. The exchange  $W_x(r)$  and exchange-correlation  $W_{xc}(r)$  potentials, however, decay asymptotically as  $(-1/r)$ , as they must. This clearly demonstrates that the exchange-correlation potential  $W_{xc}(r)$  of the work formalism reduces to its exchange component  $W_x(r)$  asymptotically. Thus the asymptotic structure of the many-body potential  $W_{xc}(r)$  in the atom can be obtained by solution of the differential equation in the Pauli-correlated approximation. Furthermore, as a consequence, it is meaningful to compare the highest occupied eigenvalue of this differential equation to experiment.

#### Kohn-Sham theory

In Kohn-Sham (KS) theory [15], the ground-state energy  $E$  of Eq. (1), which is a universal functional of the density  $\rho(r)$  is partitioned as follows:

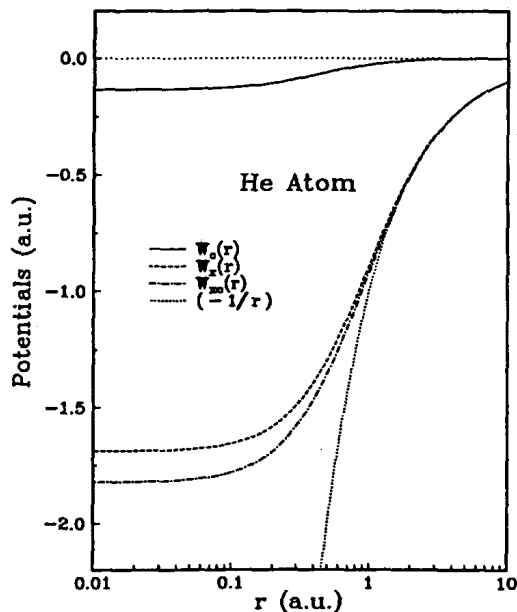


FIG. 7. Work formalism correlation  $W_c(r)$ , exchange  $W_x(r)$ , and exchange-correlation  $W_{xc}(r)$  potentials for the He atom. The function  $(-1/r)$  is also plotted.

$$E[\rho] = T_s[\rho] + E_{\text{ext}}[\rho] + E_H[\rho] + E_{xc}^{\text{KS}}[\rho], \quad (20)$$

where  $T_s[\rho]$  is the kinetic energy of a system of *noninteracting* electrons having the same density distribution as the interacting system,  $E_{\text{ext}}[\rho] = \int v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$  is the expectation of the external potential,  $E_H$  is the Coulomb self-energy of Eq. (15), and  $E_{xc}^{\text{KS}}[\rho]$  is the Kohn-Sham theory exchange-correlation energy. Thus  $E_{xc}^{\text{KS}}[\rho]$  differs from the quantum-mechanical definition of the exchange-correlation energy  $E_{xc}$  of Eq. (15) in that as a result of the above partition it also accounts for the correlation contribution  $T_c[\rho]$  to the kinetic energy.

On application of the variational principle for the energy to the energy functional of Eq. (20) for arbitrary variations of the density, the Kohn-Sham differential equation is obtained:

$$\left[ -\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \mu_{xc}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \quad (21)$$

where the Kohn-Sham exchange-correlation potential  $\mu_{xc}(\mathbf{r})$  is the functional derivative of  $E_{xc}^{\text{KS}}[\rho]$ :

$$\mu_{xc}(\mathbf{r}) = \delta E_{xc}^{\text{KS}}[\rho] / \delta \rho(\mathbf{r}). \quad (22)$$

Thus the potential  $\mu_{xc}(\mathbf{r})$  contains the effects of  $T_c[\rho]$  in its structure. The ground-state density of a closed-shell system is then obtained from a *single* Slater determinant  $\Phi\{\phi_i\}$  of the lowest occupied orbitals  $\phi_i(\mathbf{r})$  of the Kohn-Sham differential equation:

$$\rho(\mathbf{r}) = \left\langle \Phi\{\phi_i\} \left| \sum_i \delta(\mathbf{r}_i - \mathbf{r}) \right| \Phi\{\phi_i\} \right\rangle = \sum_i |\phi_i(\mathbf{r})|^2. \quad (23)$$

With the orbitals  $\phi_i(\mathbf{r})$  and density  $\rho(\mathbf{r})$ , the total energy is then determined from Eq. (20). The highest occupied eigenvalue [21] of the differential equation in turn gives the negative of the removal energy. The functional  $E_{xc}^{\text{KS}}[\rho]$  and consequently the potential  $\mu_{xc}(\mathbf{r})$  are at present unknown. However, for an assumed wave function and thereby known ground-state energy and density, the corresponding Kohn-Sham orbitals  $\phi_i(\mathbf{r})$ , eigenvalues  $\epsilon_i$ , exchange-correlation energy  $E_{xc}^{\text{KS}}[\rho]$ , and potential  $\mu_{xc}(\mathbf{r})$  can all be determined [16,22].

Analogous to the quantum-mechanical definitions, the exchange-correlation energy  $E_{xc}^{\text{KS}}[\rho]$  can also be thought of as the energy of interaction between the density  $\rho(\mathbf{r})$  and the Kohn-Sham Fermi-Coulomb hole charge  $\rho_{xc}^{\text{KS}}(\mathbf{r}, \mathbf{r}')$ . This hole charge, however, differs from the quantum-mechanical hole in that its structure also incorporates the correlation contribution to the kinetic energy. The Kohn-Sham hole charge is defined in terms of the electron-electron-interaction coupling constant  $\lambda$  in integral as [23]

$$\int_0^1 d\lambda g_\lambda(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r}') + \rho_{xc}^{\text{KS}}(\mathbf{r}, \mathbf{r}'), \quad (24)$$

where  $g_\lambda(\mathbf{r}, \mathbf{r}')$  is the pair-correlation density of a hypothetical system in an external potential  $v_{\text{ext},\lambda}(\mathbf{r})$  chosen such that the ground-state density  $\rho_\lambda(\mathbf{r})$

$= \langle \Psi_\lambda | \sum_i \delta(\mathbf{r}_i - \mathbf{r}) | \Psi_\lambda \rangle$  is identical with the true density  $\rho(\mathbf{r})$  for all values of the constant  $\lambda$ . Due to the complexity of its definition  $\rho_{xc}^{KS}(\mathbf{r}, \mathbf{r}')$  has not been determined even for simple nonuniform systems for which the density is known via an accurate wave function.

Since in Kohn-Sham theory the density is obtained from a single Slater determinant, it is meaningful [24] to further partition the energy  $E_{xc}^{KS}[\rho]$  into its exchange  $E_x^{KS}[\rho]$  and correlation  $E_c^{KS}[\rho]$  components. The exchange energy  $E_x^{KS}[\rho]$  is then defined as the energy of interaction between the density  $\rho(\mathbf{r})$  and the Kohn-Sham Fermi hole  $\rho_x^{KS}(\mathbf{r}, \mathbf{r}')$ , where in turn the latter is defined in terms of the idempotent Dirac density matrix formed from the Kohn-Sham orbitals  $\phi_i(\mathbf{r})$ . However, since the functional dependence of  $\rho_x^{KS}(\mathbf{r}, \mathbf{r}')$  on  $\rho(\mathbf{r})$  is unknown, the functional derivative  $\mu_x(\mathbf{r}) = \delta E_x^{KS}[\rho] / \delta \rho(\mathbf{r})$  is also unknown. The correlation energy  $E_c^{KS}[\rho]$  is similarly defined in terms of the density and the Kohn-Sham Coulomb hole  $\rho_c^{KS}(\mathbf{r}, \mathbf{r}')$ , but with the correlation contribution  $T_c[\rho]$  now incorporated in these components of the energy and hole charge distribution. Once again, the functional derivative  $\mu_c(\mathbf{r}) = \delta E_c^{KS}[\rho] / \delta \rho(\mathbf{r})$  is unknown. (It is also possible to partition  $E_{xc}^{KS}[\rho]$  in terms of the exchange energy (and the resulting correlation energy) defined [24] as that obtained from exchange-only Kohn-Sham theory. The corresponding exchange potential is then that obtained by the optimized-potential method [25]. In the present work we do not employ this latter definition.)

#### Correlation potential of Kohn-Sham theory

The correlation potential  $\mu_c(\mathbf{r})$  for the He atom for an assumed density  $\rho(\mathbf{r})$  can be determined either by the methods of Ref. [22] or as in the original work of Almladh and Pedroza [16]. We follow the latter procedure whereby  $\mu_c(\mathbf{r})$  is obtained by inversion of the Kohn-Sham differential equation Eq. (21):

$$\mu_c(\mathbf{r}) = \epsilon + \frac{\nabla^2 \phi}{2\phi} + \frac{2}{r} - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' - \mu_x(\mathbf{r}), \quad (25)$$

where the Kohn-Sham orbital  $\phi(\mathbf{r}) = [\rho(\mathbf{r})/2]^{1/2}$ , the eigenvalue  $\epsilon$  is taken to be the first ionization potential [26], and the expression for the exchange potential  $\mu_x(\mathbf{r})$  is the same as  $W_x(\mathbf{r})$  discussed previously.

A plot of the potential  $\mu_c(\mathbf{r})$  for the density corresponding to the Kinoshita wave function is given in Fig. 8. For purposes of comparison we include in this figure the potential  $W_c(\mathbf{r})$ . Observe (see inset) that  $\mu_c(\mathbf{r})$  also approaches the nucleus quadratically and has zero slope at the origin. As is known,  $\mu_c(\mathbf{r})$  is not a monotonic function and goes positive at  $r \sim 0.3$  a.u., and then decays as a positive function. In recent work [27], however, the use of a 491-term correlated wave function shows that  $\mu_c(\mathbf{r})$  goes negative for  $r > 4$  a.u. and vanishes asymptotically as a negative function. The potential  $\mu_c(\mathbf{r})$  as determined by the Kinoshita wave function also goes negative but for these asymptotic positions of the

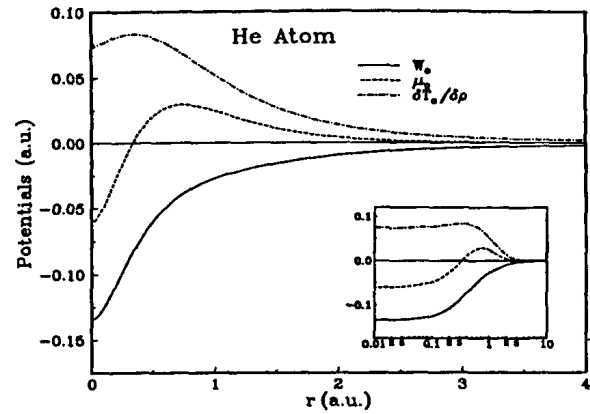


FIG. 8. Correlation potentials  $W_c(\mathbf{r})$  and  $\mu_c(\mathbf{r})$  of the work formalism and Kohn-Sham theory, respectively, for the He atom. The ansatz  $\delta T_c / \delta \rho = \mu_c(\mathbf{r}) - W_c(\mathbf{r})$  is also plotted. The inset is on a logarithmic scale to indicate the structure near the nucleus of the atom.

electron its accuracy is obviously not as great. In contrast,  $W_c(\mathbf{r})$  is monotonic and always negative. Furthermore, in the interior of the atom the potential  $\mu_c(\mathbf{r})$  is less attractive than  $W_c(\mathbf{r})$ .

It is thus evident that the structure of the Kohn-Sham Coulomb hole  $\rho_c^{KS}(\mathbf{r}, \mathbf{r}')$  is different from that of the quantum-mechanical Coulomb hole  $\rho_c(\mathbf{r}, \mathbf{r}')$  described in the previous section. It is, however, difficult to infer the structure of  $\rho_c^{KS}(\mathbf{r}, \mathbf{r}')$  from that of the potential  $\mu_c(\mathbf{r})$  via Coulomb's law. This is because the potential  $W_c(\mathbf{r})$  determined as the work done in the force field of either  $\rho_c(\mathbf{r}, \mathbf{r}')$  or  $\rho_c^{KS}(\mathbf{r}, \mathbf{r}')$  does not [12,28] satisfy the Kohn-Sham theory correlation sum rule [29]

$$E_c^{KS}[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) \mathbf{r} \cdot \nabla \mu_c(\mathbf{r}) = -T_c[\rho] < 0. \quad (26)$$

On substitution of either of the above  $W_c(\mathbf{r})$  for  $\mu_c(\mathbf{r})$  into the sum rule, the left-hand side vanishes. This implies that the contribution of  $T_c[\rho]$  to  $\rho_c^{KS}(\mathbf{r}, \mathbf{r}')$  and thus to  $\mu_c(\mathbf{r})$  cannot be described by Coulomb's law, or, equivalently, the components of  $\rho_c^{KS}(\mathbf{r}, \mathbf{r}')$  due to  $T_c[\rho]$  do not contribute to the resulting force field. (They do, however, contribute to the Kohn-Sham correlation energy  $E_c^{KS}[\rho]$ .) Now the potential  $W_c(\mathbf{r})$  due to the Coulomb hole  $\rho_c(\mathbf{r}, \mathbf{r}')$  is strictly representative of Coulomb correlations whereas  $\mu_c(\mathbf{r})$  includes in addition the correlation contribution  $T_c[\rho]$  to the kinetic energy. [This is consistent with  $\mu_c(\mathbf{r})$  being less attractive than  $W_c(\mathbf{r})$ .] Thus it is reasonable to assume that the difference  $[\mu_c(\mathbf{r}) - W_c(\mathbf{r})]$  is a good approximation to  $\delta T_c[\rho] / \delta \rho(\mathbf{r})$ , the contribution of  $T_c[\rho]$  to  $\mu_c(\mathbf{r})$ . The result of this ansatz for  $\delta T_c / \delta \rho$  is also plotted in Fig. 8. Observe that it is of the same order of magnitude as  $\mu_c(\mathbf{r})$ , and also not monotonic. It is, however, positive over the entire range of the figure. The fact that  $\delta T_c / \delta \rho$  is a significant fraction of  $\mu_c(\mathbf{r})$  is reflected in the corresponding values of the energies  $T_c[\rho]$  and  $E_c^{KS}[\rho]$ . From Eq. (20),  $E_c^{KS}[\rho] = -0.0422$  a.u. whereas from Eq. (19) of the

work formalism  $E_c = -0.0787$  a.u. Once again, since the exchange energies of Kohn-Sham theory and the work formalism are the same, we have  $T_c[\rho] = E_c^{KS}[\rho] - E_c = 0.0365$  a.u. This value for  $T_c[\rho]$  is the same as that determined by Ludeña *et al.* [30] by means of local scaling transformations.

For completeness we note that Levy and Perdew [29] (1985) have provided explanations for the nonmonotonicity and positiveness of the Kohn-Sham correlation potential  $\mu_c(\mathbf{r})$ . For a tightly bound closed-shell atom they show that to leading order ( $e^4$ ) in the electronic charge  $e$  in perturbation theory, the integral term in the sum rule Eq. (26) vanishes, and thus  $\mu_c(\mathbf{r})$  cannot be monotonic since  $\rho(\mathbf{r})$  is everywhere positive. The value of the integral turns out to be 0.0057 a.u., which is small. To explain that  $\mu_c(\mathbf{r})$  goes positive in certain regions of space, they employ the theorem [21] that the highest occupied eigenvalue of the Kohn-Sham differential equation is the negative of the first ionization potential. On comparing the highest occupied eigenvalue of exchange-only Kohn-Sham theory to the ionization potential they find that the former is more negative than the latter for many atoms. Thus, in order to satisfy the ionization potential theorem, they conclude that the expectation value of  $\mu_c(\mathbf{r})$  taken with respect to the highest occupied orbital is often positive. The present analysis shows the *physical* source of the nonmonotonicity and positiveness of  $\mu_c(\mathbf{r})$  to be the correlation contribution to the kinetic energy. The purely Coulomb correlation component of  $\mu_c(\mathbf{r})$  is well described by  $W_c(\mathbf{r})$  just as the exchange potential  $\mu_x(\mathbf{r})$  of Kohn-Sham theory is well described [12,13] by  $W_x(\mathbf{r})$ .

#### IV. CONCLUSION

In this paper we have investigated Coulomb correlation effects in the He atom by studying the structure of the static and dynamic Coulomb hole charge distributions as determined by the correlated wave function of Kinoshita. The static Coulomb hole, which is defined in terms of the radial electron-electron distribution function, shows that due to Coulomb repulsion there is a decrease in probability that the two electrons will be separated by a distance less than 1 a.u., and an increase in this probability for greater separations. The dynamic Coulomb hole, which is defined directly in terms of the pair-correlation density, describes the probability of finding one of the electrons, given the position of the other. In contrast to the Fermi hole, which is negative over the entire region of the atom irrespective of electron position, the dynamic Coulomb hole is both negative and positive. At and about the test electron, the Coulomb hole is always negative, indicating the reduction in density about it due to Coulomb repulsion. The positive part of the Coulomb hole then gives the positional probability of the other electron. By studying the structure of the dynamic Coulomb hole as a function of electron position, we have

explained how the two electrons are correlated as a function of the nonuniform density of the atom.

We have also investigated the structure of the correlation potential  $W_c(\mathbf{r})$  of the work formalism as determined by Coulomb's law from the dynamic Coulomb hole charge distribution. Although the structure of the Coulomb hole is strikingly different from that of the Fermi hole, the structure of  $W_c(\mathbf{r})$  is similar to the exchange potential  $W_x(\mathbf{r})$  due to the Fermi hole: it is negative, has zero slope at the nucleus, and is monotonic, but is an order of magnitude smaller. Since the total charge of the Coulomb hole is zero, and because it is principally positive and localized about the nucleus for asymptotic electron positions, the potential  $W_c(\mathbf{r})$  decays rapidly in this region. Thus the asymptotic structure of the exchange-correlation potential  $W_{xc}(\mathbf{r})$  is that of the exchange potential  $W_x(\mathbf{r})$  which is  $(-1/r)$ . These results then affirm that the asymptotic structure of the many-body potential  $W_{xc}(\mathbf{r})$  can be obtained by solution within the Pauli-correlated approximation of the work formalism.

The structure of  $W_c(\mathbf{r})$  also sheds light on the physics underlying the structure of the correlation potential  $\mu_c(\mathbf{r})$  of Kohn-Sham theory. The latter potential contains in addition the correlation contribution  $T_c[\rho]$  to the kinetic energy and is thus less attractive. Further, it is not monotonic as it goes positive within the atom and then becomes negative again in the classically forbidden region, vanishing asymptotically as a negative function. Since the potential  $W_c(\mathbf{r})$  is strictly representative of Coulomb correlations and is everywhere negative and monotonic, the nonmonotonically and positiveness of the Kohn-Sham correlation potential  $\mu_c(\mathbf{r})$  can be attributed to the correlation kinetic energy. (Note that for the He atom the Kohn-Sham theory and work formalism exchange potentials are the same, being negative and monotonic.)

Finally, since accurate Monte Carlo-generated wave functions for atoms up to 20 electrons are now being determined, similar studies of the Coulomb hole and correlation potentials within the framework of the work formalism and Kohn-Sham theory can be performed. Simultaneously we also propose to determine the wave function by self-consistent solution of the work formalism differential equation. A comparison with the Monte Carlo-generated results would then provide an estimate of the number of configurations required to achieve the same degree of accuracy.

#### ACKNOWLEDGMENTS

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