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Force field and potential due to the Fermi-Coulomb hole charge for nonspherical-density atoms

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In the work formalism for the determination of electronic structure, the exchange-correlation energy and (local) potential of the electrons both arise via Coulomb's law from the same source, viz., the quantum-mechanical Fermi-Coulomb hole charge. The potential is the work $W_{xc}(\mathbf{r})$ done to move an electron in the field of its Fermi-Coulomb hole and the energy is the interaction energy between the electronic and hole charge densities. For nonsymmetrical electronic density systems for which the curl of the field may not vanish, a local effective exchange-correlation potential $W_{xc}^{\text{eff}}(\mathbf{r})$ is determined from the irrotational component of the field, the solenoidal component being neglected. In this paper we investigate this approximation further to better understand its accuracy for nonspherical density systems by application to a degenerate ground state of the carbon atom within the Pauli-correlated approximation. The results of the non-self-consistent calculations indicate that the solenoidal component of the force field due to the Fermi hole is negligible and *two orders* of magnitude smaller than the irrotational component. Therefore, essentially all the effects of Pauli correlation are accounted for by the latter and the effective exchange potential $W_x^{\text{eff}}(\mathbf{r})$ is thereby an accurate representation of the local exchange potential in the atom. Further, the solenoidal component of the field vanishes at the nucleus, in the classically forbidden region and along certain axes of symmetry. Thus the work $W_x(\mathbf{r})$ in the field of the Fermi hole for such nonspherical atoms is path independent over substantial regions of configuration space. Finally, we discuss the structure of the local many-body potential of nonspherical-density atoms when both Pauli and Coulomb correlations are present.

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I. INTRODUCTION

The electronic charge densities of the majority of atoms in the Periodic Table are non spherically symmetric. However, in most calculations of atomic structure, the atoms are treated within the central-field model wherein these densities are sphericalized by ensemble averaging the different orientations. In order to determine more accurately the properties of atoms, their nonsphericity must be taken into account [1]. To do so in a meaningful manner it is important to understand the nonsphericity of the electronic charge distribution in terms of the correlations between the electrons. In this paper we learn about electron correlations in nonspherical density atoms by investigating further the work formalism for the determination of electronic structure recently proposed by Harbola and Sahni [2].

The formalism has been applied [3] principally within the Pauli-correlated approximation to symmetric systems for which the inhomogeneity of the electronic density is intrinsically one dimensional and to nonspherically symmetric systems for which the density has been so symmetrized. The results for the various ground- and excited-state properties obtained have proved to be accurate when compared with those of other theories, but particularly so in comparison with experiment. We have also recently demonstrated [4] the applicability of the formulation to nonspherical-density atoms. In that work we obtained the structure of the local many-body exchange potential of a nonspherical density atom in different directions as a function of the radial distance from the nucleus. A significant fact learned from this work was that the change from sphericity of the potentials in different directions occurred principally in the intershell region. This explains why the central-field model of atoms is accurate. The present work is a contribution towards an understanding of the work formalism with regard to its accuracy for nonspherical-density atoms. In turn this furthers our understanding of electron correlations and provides an explanation for the structure of the local many-body potential in such systems.

We begin with a brief description of the work formalism. For a system of N electrons in an external potential $v_{\text{ext}}(\mathbf{r})$, the nonrelativistic Schrödinger equation [5] is

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

where $\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)$ and E are the system wave function and energy, respectively. The physics of electron correlation for this inhomogeneous electron gas is described by the structure of the pair-correlation *density* $g(\mathbf{r},\mathbf{r}')$

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defined as

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

where the numerator expectation value represents the probability of simultaneously finding electrons at $\mathbf{r}$ and $\mathbf{r}'$, and the denominator expectation is the electronic density $\rho(\mathbf{r})$. Thus $g(\mathbf{r},\mathbf{r}')$ is the electronic density at $\mathbf{r}'$ when an electron is specified as being at $\mathbf{r}$. The pair-correlation density can further be expressed as the sum of the electronic density $\rho(\mathbf{r})$ and the Fermi-Coulomb hole charge distribution $\rho_{xc}(\mathbf{r},\mathbf{r}')$ at $\mathbf{r}'$ for an electron at $\mathbf{r}$ as

$$g(\mathbf{r},\mathbf{r}')=\rho(\mathbf{r}')-\rho_{xc}(\mathbf{r},\mathbf{r}')\,. \tag{3}$$

Thus the Fermi-Coulomb hole represents the reduction in density about an electron due to correlations resulting from the Pauli exclusion principle and Coulomb repulsion. The total charge of the pair-correlation density is $N-1$ since the Fermi-Coulomb hole is the exclusion of a charge equal in magnitude to that of an electron: $\int\rho_{xc}(\mathbf{r},\mathbf{r}')d\mathbf{r}'=1$.

Now according to the work formalism, the *local* potential representing the electron-electron interaction as well as the interaction potential energy *both* arise via Coulomb's law from the same quantum-mechanical source charge distribution, viz., the pair-correlation density. The pair-correlation density is a dynamic charge distribution in that it changes as a function of electron position. Thus the local potential is the work done to move an electron in the force field of the pair-correlation density. The potential energy in turn is the energy of interaction between the electronic and pair-correlation densities. The contribution of the static electron density $\rho(\mathbf{r}')$ term of Eq. (3) leads to the Hartree potential $v_H(\mathbf{r})=\int d\mathbf{r}'\rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$ and to the Coulomb self-energy $E_H=\frac{1}{2}\int\int[\rho(\mathbf{r})\rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|]d\mathbf{r}\,d\mathbf{r}'$. The dynamic Fermi-Coulomb hole charge $\rho_{xc}(\mathbf{r},\mathbf{r}')$ term leads to the exchange-correlation potential $W_{xc}(\mathbf{r})$ and energy E_{xc}. Thus the potential $W_{xc}(\mathbf{r})$ is the work required to bring an electron from infinity to its position at $\mathbf{r}$ against the force field $\mathcal{E}_{xc}(\mathbf{r})$ of the Fermi-Coulomb hole charge:

$$W_{xc}(\mathbf{r})=-\int_\infty^{\mathbf{r}}\mathcal{E}_{xc}(\mathbf{r}')\cdot d\mathbf{l}'\,, \tag{4}$$

where

$$\mathcal{E}_{xc}(\mathbf{r})=\int\frac{\rho_{xc}(\mathbf{r},\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}d\mathbf{r}'\,. \tag{5}$$

The exchange-correlation energy E_{xc} in turn is the energy of interaction between the charge of the electronic density $\rho(\mathbf{r})$ and the Fermi-Coulomb hole charge $\rho_{xc}(\mathbf{r},\mathbf{r}')$:

$$E_{xc}=\tfrac{1}{2}\int\int\frac{\rho(\mathbf{r})\rho_{xc}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}'\,. \tag{6}$$

The properties of the many-electron system are then determined by self-consistent solution of the differential equation

$$[-\tfrac{1}{2}\nabla^2+v_{ext}(\mathbf{r})+v_H(\mathbf{r})+W_{xc}(\mathbf{r})]\phi_i(\mathbf{r})=\epsilon_i\phi_i(\mathbf{r})\,, \tag{7}$$

which is of the Sturm-Liouville type. As such its eigenfunctions form a complete set. Thus the wave function Ψ can, *in principle*, be obtained as an infinite linear combination of Slater determinants of these orbitals. The system energy E, the expectation of the Hamiltonian, is then the sum of the expectation value of the kinetic and external potential operators, the Coulomb self-energy, and the exchange-correlation energy E_{xc}.

In the approximation when only correlations due to the Pauli exclusion principle are considered, and the ground-state wave function Ψ is a Slater determinant of single-particle orbitals $\psi_i(\mathbf{r})$, the pair-correlation density $g_x(\mathbf{r},\mathbf{r}')$ is obtained as

$$g_x(\mathbf{r},\mathbf{r}')=\rho(\mathbf{r}')-\rho_x(\mathbf{r},\mathbf{r}')\,, \tag{8}$$

where $\rho_x(\mathbf{r},\mathbf{r}')=|\gamma(\mathbf{r},\mathbf{r}')|^2/2\rho(\mathbf{r})$ is the Fermi hole charge density at $\mathbf{r}'$ for an electron at $\mathbf{r}$, and $\gamma(\mathbf{r},\mathbf{r}')=\sum_i\psi_i^*(\mathbf{r})\psi_i(\mathbf{r}')$ is the idempotent single-particle density matrix with $\gamma(\mathbf{r},\mathbf{r})=\rho(\mathbf{r})$. The total charge of the Fermi hole is also equal in magnitude to that of an electron $\int\rho_x(\mathbf{r},\mathbf{r}')d\mathbf{r}'=1$, it satisfies the constraints of positivity $\rho_x(\mathbf{r},\mathbf{r}')\geq 0$, and the value at electron position $\rho_x(\mathbf{r},\mathbf{r})=\rho(\mathbf{r})/2$. The corresponding differential equation for the orbitals $\psi_i(\mathbf{r})$ is the same as Eq. (7) with $W_{xc}(\mathbf{r})$ replaced by $W_x(\mathbf{r})$, the work done in the force field of the Fermi hole charge. (We note that in the Pauli-correlated approximation the idempotent single-particle density matrix as defined above differs from the density matrix obtained from the system wave function Ψ.)

Implicit in the above formulation is that the potential $W_{xc}(\mathbf{r})$ is well defined in that it is path independent, or equivalently that the curl of the electric field $\mathcal{E}_{xc}(\mathbf{r})$ vanishes. This is rigorously the case for symmetrical density systems that are intrinsically one dimensional as well as for nonsymmetrical-density systems that are treated approximately as such. For nonsymmetrical density systems for which the curl of the electric field may not vanish [6,7], a well-defined [2,4] local effective exchange-correlation potential $W_{xc}^{\text{eff}}(\mathbf{r})$ (for single simply connected domains) is determined from the irrotational component of the force field. The effective many-body potential and other properties are then determined by self-consistent solution of the differential equation Eq. (7) with $W_{xc}(\mathbf{r})$ replaced by $W_{xc}^{\text{eff}}(\mathbf{r})$.

In this paper we investigate the work formalism further with regard to nonsymmetrical-density systems. In Sec. II we give the definitions of properties of interest, such as the irrotational and solenoidal components of the force field due to the Fermi-Coulomb hole charge, and the scalar and vector source functions which give rise to them respectively. We present in Sec. III the results of application to the degenerate $1s^22s^22p_z^2$ ground state of the carbon atom assuming only correlations between the electrons due to the Pauli exclusion principle. The single-particle orbitals employed in the calculations, which are non-self-consistent, are assumed to be hydrogenic. We thereby demonstrate the accuracy of the formalism for such systems by a comparison of the relative

magnitudes of the irrotational and solenoidal components of the force field due to the Fermi hole charge. Brief details of the derivation and the specific analytical and integral expressions for the various properties are given in the Appendix. Finally, in Sec. IV we summarize what we have learned from our investigation and discuss how these results obtained within the Pauli-correlated approximation contribute to an understanding of the local many-body potential when Coulomb correlation effects are also considered.

II. DEFINITIONS

According to the Helmholtz theorem the most general vector field has both a nonzero divergence and a nonzero curl and can be derived from the negative gradient of a scalar potential and the curl of a vector potential. We can therefore write the electric field $\mathcal{E}_{xc}(\mathbf{r})$ due to the Fermi-Coulomb hole charge distribution of a system for which the curl of the field does not vanish as a sum of its irrotational $\mathcal{E}^I_{xc}(\mathbf{r})$ and solenoidal $\mathcal{E}^S_{sc}(\mathbf{r})$ components. The mathematical statement of Helmholtz's theorem in this case is

$$\mathcal{E}_{xc}(\mathbf{r})=\mathcal{E}^I_{xc}(\mathbf{r})+\mathcal{E}^S_{xc}(\mathbf{r}) \tag{9}$$

$$=-\nabla\int\frac{\nabla'\cdot\mathcal{E}_{xc}(\mathbf{r}')}{4\pi|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'+\nabla\times\int\frac{\nabla'\times\mathcal{E}_{xc}(\mathbf{r}')}{4\pi|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' . \tag{10}$$

The irrotational component of the field is thus the negative gradient of a scalar effective exchange-correlation potential $W^{\rm eff}_{xc}(\mathbf{r})$:

$$\mathcal{E}^I_{xc}(\mathbf{r})=-\nabla W^{\rm eff}_{xc}(\mathbf{r}) , \tag{11}$$

where the scalar potential

$$W^{\rm eff}_{xc}(\mathbf{r})=\int\frac{\rho^{\rm eff}_{xc}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' \tag{12}$$

is seen to arise from a scalar (static) effective Fermi-Coulomb hole source charge $\rho^{\rm eff}_{xc}(\mathbf{r})$ which is

$$\rho^{\rm eff}_{xc}(\mathbf{r})=\frac{1}{4\pi}\nabla\cdot\mathcal{E}_{xc}(\mathbf{r}) . \tag{13}$$

The expression for the effective source charge can be further simplified to read

$$\rho^{\rm eff}_{xc}(\mathbf{r})=\rho_{xc}(\mathbf{r},\mathbf{r})+\frac{1}{4\pi}\int[\nabla\rho_{xc}(\mathbf{r},\mathbf{r}')]\cdot\frac{(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}d\mathbf{r}' . \tag{14}$$

Since the total Fermi-Coulomb hole charge is unity [5], so is the total charge of the effective source: $\int\rho^{\rm eff}_{xc}(\mathbf{r})d\mathbf{r}=1$. The irrotational component of the electric field can also be obtained directly from the scalar effective source charge via Coulomb's law as

$$\mathcal{E}^I_{xc}(\mathbf{r})=\int\frac{\rho^{\rm eff}_{xc}(\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}d\mathbf{r}' . \tag{15}$$

The solenoidal component of the field is the curl of an exchange-correlation vector potential $\mathbf{A}_{xc}(\mathbf{r})$:

$$\mathcal{E}^S_{xc}(\mathbf{r})=\nabla\times\mathbf{A}_{xc}(\mathbf{r}) , \tag{16}$$

where the vector potential

$$\mathbf{A}_{xc}(\mathbf{r})=\int\frac{\mathbf{J}_{xc}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' \tag{17}$$

is due to an exchange-correlation vector vortex source $\mathbf{J}_{xc}(\mathbf{r})$ given as

$$\mathbf{J}_{xc}(\mathbf{r})=\frac{1}{4\pi}\nabla\times\mathcal{E}_{xc}(\mathbf{r}) . \tag{18}$$

The expression for the vector source can be further simplified to read

$$\mathbf{J}_{xc}(\mathbf{r})=\frac{1}{4\pi}\int[\nabla\rho_{xc}(\mathbf{r},\mathbf{r}')]\times\frac{(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}d\mathbf{r}' . \tag{19}$$

Finally, the solenoidal component of the field can also be obtained directly from the vector vortex source as

$$\mathcal{E}^S_{xc}(\mathbf{r})=\int\mathbf{J}_{xc}(\mathbf{r}')\times\frac{(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}d\mathbf{r}' . \tag{20}$$

It is evident that in regions where the vortex source vanishes, the potentials $W^{\rm eff}_{xc}(\mathbf{r})$ and $W_{xc}(\mathbf{r})$ are equivalent. In these regions the work $W_{xc}(\mathbf{r})$ is then path-independent.

In the Pauli-correlated approximation for which the wave function is a Slater determinant of single-particle orbitals $\psi_i(\mathbf{r})$, the expressions for the various properties described above are the same except that they are now derived from the idempotent density matrix $\gamma(\mathbf{r},\mathbf{r}')$. Further, since the Fermi hole charge satisfies the constraint of charge neutrality, so does the effective Fermi hole: $\int\rho^{\rm eff}_x(\mathbf{r})d\mathbf{r}=1$. The effective exchange potential $W^{\rm eff}_x(\mathbf{r})$ is then determined by self-consistent solution of the differential equation

$$[-\tfrac{1}{2}\nabla^2+v_{\rm ext}(\mathbf{r})+v_H(\mathbf{r})+W^{\rm eff}_x(\mathbf{r})]\psi_i(\mathbf{r})=\epsilon_i\psi_i(\mathbf{r}) , \tag{21}$$

which in turn leads to the properties of nonsymmetrical-density systems within this approximation. The solution in this approximation also gives the exact asymptotic structure of the effective exchange-correlation potential $W^{\rm eff}_{xc}(\mathbf{r})$ of the fully correlated system when both Pauli and Coulomb correlations are present. This is because the total Coulomb hole charge and consequently the total effective Coulomb hole charge is zero. (The Coulomb hole can be defined as the difference between the quantum-mechanical Fermi-Coulomb hole $\rho_{xc}(\mathbf{r},\mathbf{r}')$ derived from the pair-correlation density [see Eq. (3)] and the Fermi hole obtained from the idempotent density matrix of the Pauli-correlated approximation.) Therefore, for electron positions asymptotically far from this charge, the force field and correlation potential $W^{\rm eff}_c(\mathbf{r})$ due to this charge vanish. For these electron positions, the differential equation for the fully correlated system reduces to Eq. (21) of the Pauli-correlated case. Thus the asymptotic structure of the exchange potential $W^{\rm eff}_x(\mathbf{r})$ as determined within the latter approximation is equivalent to that of $W^{\rm eff}_{xc}(\mathbf{r})$ of the fully correlated system.

III. RESULTS AND ANALYSIS

We next apply the above formalism within the Pauli-correlated approximation in a non-self-consistent calculation to the open-shell carbon atom. We assume the atom to be in its degenerate $1s^2 2s^2 2p_z^2$ ground state and the single-particle solutions $\psi_i(\mathbf{r})$ of Eq. (21) to be hydrogenic so that

$$\psi_{1s}(r)=\frac{1}{\sqrt{\pi}}Z^{3/2}e^{-Zr},$$
$$\psi_{2s}(r)=\frac{1}{2\sqrt{2\pi}}Z^{3/2}\left[1-\frac{Z}{2}r\right]e^{-Zr/2}, \tag{22}$$
$$\psi_{2p_z}(r,\theta)=\frac{1}{4\sqrt{2\pi}}Z^{5/2}r\cos\theta e^{-Zr/2},$$

with $Z=6$. (The choice of these orbitals implies that there exists some hypothetical external potential such that the effective potential seen by the electrons is central. The assumption that the atom is in a degenerate state is a means to simulate the non-sphericity of the density of an open-shell atom for which the effective potential is not central.) The electronic density $\rho(\mathbf{r})$ thus has azimuthal symmetry and depends only on the coordinates $[(r,\theta)\equiv q]$. The highly nonspherically symmetric structure of the density $\rho(\mathbf{r})$ is evident in Fig. 1 where the radial probability density $r^2\rho(q)$ is plotted for different directions corresponding to $\theta=0°$, 30°, 60°, and 90°. The Fermi hole $\rho_x(\mathbf{r},\mathbf{r}')\equiv\rho_x(q,q')$ is also independent of the azimuthal angles ϕ and ϕ'. Thus the electric field $\mathcal{E}_x(\mathbf{r})$ due to the Fermi hole charge is independent of the angle ϕ and does not have an azimuthal component. [This is also the case for the irrotational $\mathcal{E}_x^I(\mathbf{r})$ and solenoidal $\mathcal{E}_x^S(\mathbf{r})$ components of the field.] The electric field is thus $\mathcal{E}_x(q)=\hat{\mathbf{i}}_r\mathcal{E}_{x,r}(q)+\hat{\mathbf{i}}_\theta\mathcal{E}_{x,\theta}(q)$, so that its curl is also independent of ϕ and only has an azimuthal component: $\nabla\times\mathcal{E}_x=\hat{\mathbf{i}}_\phi[\nabla\times\mathcal{E}_x(q)]_\phi$.

In Fig. 2 we plot the curl of the electric field (or equivalently the vortex source) as a function of the radial distance r from the nucleus for different angles θ. The curl vanishes for $\theta=0°$, but its magnitude increases [Fig. 2 (a)] with increasing values of θ reaching a maximum for $\theta=60°$. With a further increase in θ [Fig. 2(b)] the magnitude of the curl decreases vanishing once again for $\theta=90°$. Observe that the curl of the electric field is finite

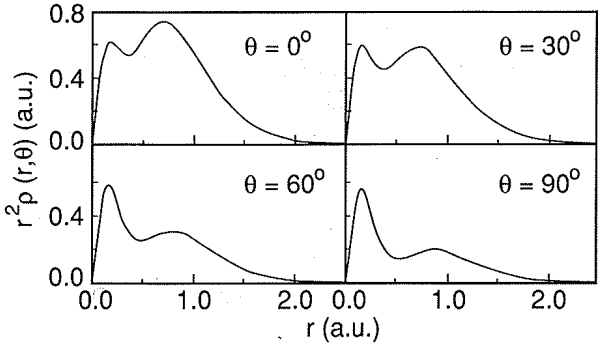

FIG. 1. The radial probability density $r^2\rho(r,\theta)$ as a function of the radial distance r for different angles θ.

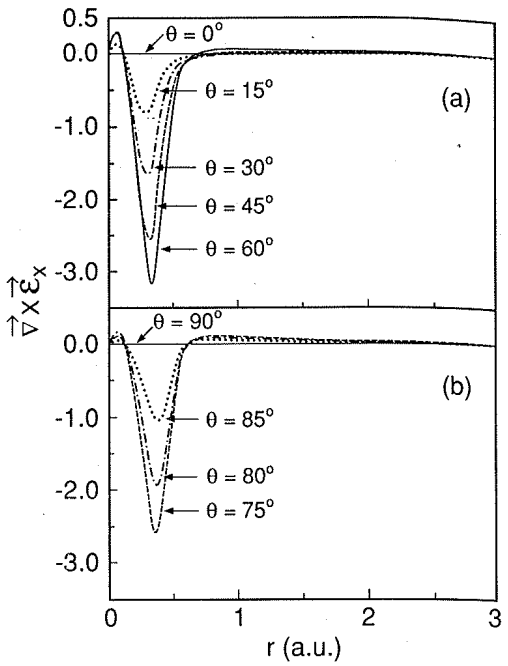

FIG. 2. Variation of the curl of the electric field $\nabla\times\mathcal{E}_x=\hat{\mathbf{i}}_\phi[\nabla\times\mathcal{E}_x(r,\theta)]_\phi$ as a function of the electron position r from the nucleus for different angles θ.

within the atom (see Figs. 1 and 2) and vanishes in *all* directions for $r\gtrsim 2.0$ a.u. It also vanishes at the origin. Thus, in the classically forbidden region and right up to the surface of the atom, the vortex source and thus the solenoidal component of the force field are zero. The total electric field in these regions is thus equivalent to its irrotational component. Therefore, in the classically forbidden region as well as at the origin and in the directions $\theta=0°$ and 90°, the effective exchange potential $W_x^{\text{eff}}(\mathbf{r})$ is equal to the potential $W_x(\mathbf{r})$ due to the Fermi hole charge itself.

What the above analysis, together with the fact that the total Coulomb hole charge is zero, shows is that even for nonsymmetrical-density atoms the work $W_{xc}(\mathbf{r})$ is in fact path independent over substantial regions of configuration space. Furthermore, with a knowledge of the symmetry of a system, specific directions for which this is also the case can be determined. In addition the self-consistent determination of the structure of these atoms is facilitated since the local many-body potential in these regions and directions is then obtained directly from the Fermi-Coulomb hole charge.

As we have seen, the vortex source function $\mathbf{J}_x(\mathbf{r})$ is finite only within the atom. Therefore, the significant question which next needs to be answered is how the irrotational and solenoidal components of the force field compare to each other. This will answer what fraction of the many-body effects is incorporated in the effective Fermi hole charge $\rho_x^{\text{eff}}(\mathbf{r})$ and therefore how accurate the local effective exchange potential $W_x^{\text{eff}}(\mathbf{r})$ is.

The irrotational component $\mathcal{E}_x^I(\mathbf{r})$ of the force field is due to the effective exchange charge distribution, $\rho_x^{\text{eff}}(\mathbf{r})$. The resulting local effective potential $W_x^{\text{eff}}(\mathbf{r})$ must possess the symmetry of the system, and thus the structure

of $\rho_x^{\text{eff}}(\mathbf{r})$ must be similar to that of the electronic density. This is observed to be the case. For a comparison of the structures of the effective charge $\rho_x^{\text{eff}}(\mathbf{r})$ and the density $\rho(\mathbf{r})$ for both a spherically symmetric atom as well as for the present model, we refer the reader to Ref. [4]. We note, however, that in contrast to the Fermi hole charge $\rho_x(\mathbf{r},\mathbf{r}')$, which must be greater than or equal to zero, the effective charge $\rho_x^{\text{eff}}(\mathbf{r})$ can be both positive and negative. Furthermore, its structure delineates the atomic shells just as the radial probability density does.

In Figs. 3, 4, and 5 we compare the magnitudes $|\mathcal{E}_x^I(q)|$ and $|\mathcal{E}_x^S(q)|$ of the irrotational and solenoidal components of the force field as a function of the radial distance r for the different angles $\theta=0°$, 30°, and 60°, respectively. In Fig. 3, which corresponds to $\theta=0°$, there is only the irrotational component $|\mathcal{E}_x^I(q)|$ since in this direction the vortex source vanishes. This force field increases from a small value in the deep interior to a maximum within the K shell of the atom. The structure of the field clearly delineates between the atomic shells, with its value in the L shell being much smaller. In the figure the function $r^2|\mathcal{E}_x^I(q)|$ is also plotted as the dashed line. From this graph it is evident that the force field decays asymptotically as $1/r^2$ in the $\theta=0°$ direction. Consequently the asymptotic structure of the effective potential $W_x^{\text{eff}}(\mathbf{r})$ in this direction must be $-1/r$. Figures 4 and 5 correspond to $\theta=30°$ and 60° for which the vortex source is finite (see Fig. 2), so that there is a solenoidal component $|\mathcal{E}_x^S(q)|$ of the field in these directions. Observe that the solenoidal component is negligible in the deep interior of the atom. It reaches a maximum at approximately the same electron position as that of the irrotational component. However, this maximum in $|\mathcal{E}_x^S(q)|$ is *two orders* of magnitude smaller than that of $|\mathcal{E}_x^I(q)|$. The solenoidal component vanishes for $r \gtrsim 2.0$, as expected since the vortex source function vanishes in this region. These figures thus indicate that the effective exchange potential $W_x^{\text{eff}}(\mathbf{r})$ is accurate throughout space. The structure of the irrotational component in the $\theta=30°$ and 60° directions is similar to that for $\theta=0°$, once again delineating between the shells and decaying asymptotically as $1/r^2$. Thus, as is the case for spherically symmetric atoms, the effective potential $W_x^{\text{eff}}(\mathbf{r})$ for open shell atoms must decay asymptotically as $-1/r$ in all directions. This is because the asymptotic structure of $W_x^{\text{eff}}(\mathbf{r})$ is due

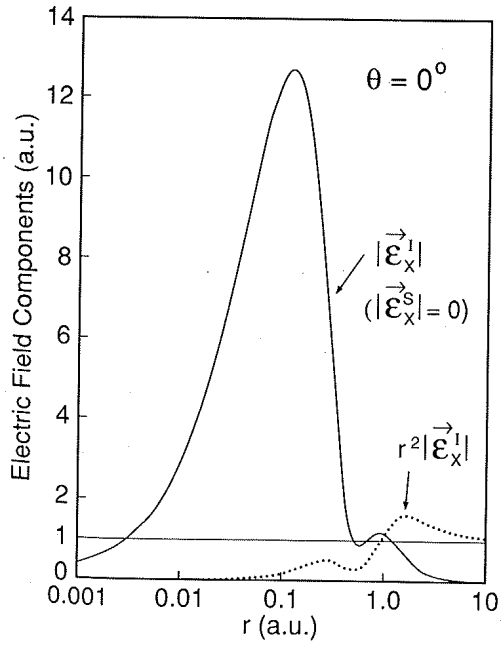

FIG. 3. The magnitudes of the irrotational $|\mathcal{E}_x^I(r,\theta)|$ and solenoidal $|\mathcal{E}_x^S(r,\theta)|$ components of the electric field $\mathcal{E}_x(\mathbf{r})$ as a function of electron position r for $\theta=0°$. The function $r^2|\mathcal{E}_x^I(r,\theta)|$ is also plotted as the dashed line.

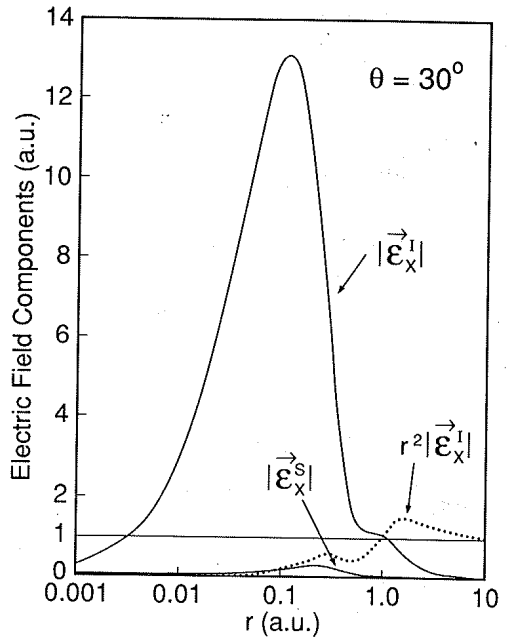

FIG. 4. Same as Fig. 3 with the exception that this figure is plotted for $\theta=30°$.

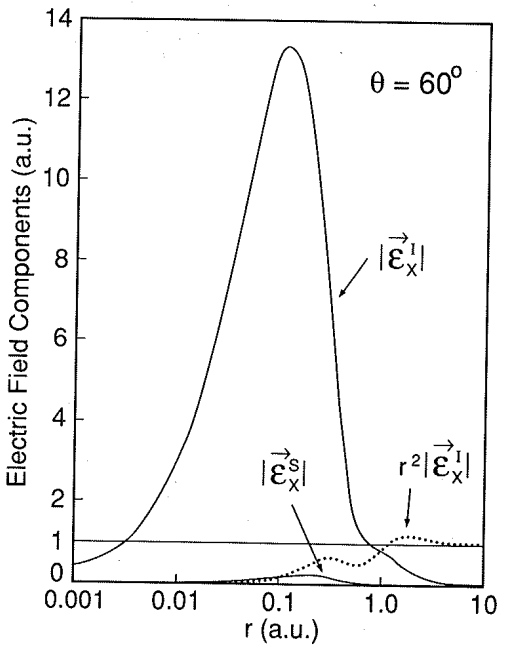

FIG. 5. Same as Fig. 3 with the exception that this figure is plotted for $\theta=60°$.

to the unit positive charge contained in $\rho_x^{\text{eff}}(\mathbf{r})$. Equivalently, since the vortex source vanishes in the classically forbidden region, the asymptotic structure of $W_x^{\text{eff}}(\mathbf{r})$ is the same as that of $W_x(\mathbf{r})$ which in turn arises from the unit positive charge of the Fermi hole $\rho_x(\mathbf{r},\mathbf{r}')$.

It is also evident from the plots of $r^2|\mathcal{E}_x^I(q)|$ in Figs. 3–5 that the total electric field $\mathcal{E}_x(\mathbf{r})$ approaches the $1/r^2$ asymptotic limit at different rates in different directions. This is to be expected due to the nonspherical nature of the density. However, the different asymptotic decay rates of the force field, and consequently of the potential $W_x(\mathbf{r})$, can be explained more rigorously by a study of the center of mass $\langle \mathbf{r}' \rangle$ of the Fermi hole for these electron positions. Since for the orbitals assumed, the Fermi hole has azimuthal symmetry, the center of mass always lies along the z' ($\theta=0°$) axis irrespective of the coordinates (r,θ) of the electron. In Fig. 6 we plot $\langle \mathbf{r}' \rangle$ as a function of the radial electron distance r for $\theta=0°$, 30°, 60°, and 90°. Observe that as for spherically symmetric atoms [2], the Fermi hole is centered behind the nucleus for small electron positions. The center of mass then follows the electron within the atom. For asymptotic positions of the electron, the center of mass approaches a constant value which lies between 0 and 0.5 a.u. for $90° \le \theta \le 0°$ since the $\lim_{r\to\infty}\langle \mathbf{r}' \rangle \sim \cos\theta/[1+\cos^2\theta]$. That the center of mass approaches a constant can also be seen by plotting the Fermi hole for asymptotic positions of the electron. For these electron positions the changes in the structure of the Fermi hole are negligible and the charge has stabilized. In Fig. 7 we plot the cross sections of the Fermi hole in the $\theta'=0$ plane for asymptotic electron positions at $r=20$ a.u. and $\theta=0°$, 30°, 60°, and 90°. From the figure it is evident that with the exception of the $\theta=90°$ direction for which the Fermi hole is symmetric about the nucleus at the origin, the center of mass in other directions cannot be located at the nucleus. Thus, together with the fact that the total charge of the Fermi hole is unity, the different asymptotic values of its center of mass in different directions explains why the electric field decays towards $1/r^2$ with different

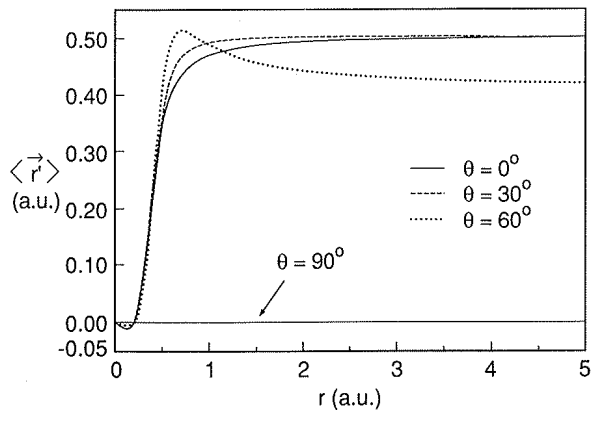

FIG. 6. The center of mass $\langle \mathbf{r}' \rangle$ of the Fermi hole as a function of the radial electron distance r for different directions $\theta=0°$, 30°, 60°, and 90°. Due to the azimuthal symmetry of the Fermi hole, its center of mass lies along the z' axis irrespective of the coordinates (r,θ) of the electron.

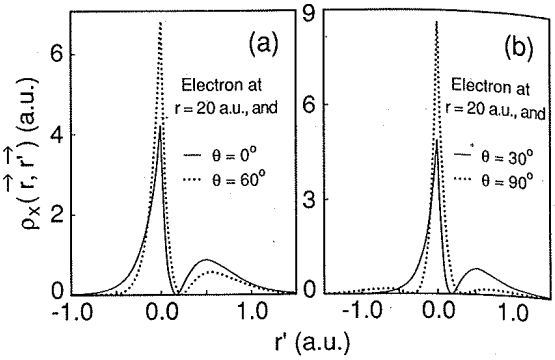

FIG. 7. Cross sections of the Fermi hole $\rho_x(\mathbf{r},\mathbf{r}')$ in the $\theta'=0°$ plane as a function of r' for different electron positions at $r=20$ a.u. and $\theta=0°$, 30°, 60°, and 90°. The nucleus is at the origin.

decay rates in these directions. For wave functions more accurate than hydrogenic functions, the center of mass would either decay to zero or to a smaller constant value closer to the nucleus. Consequently so would the electric field and potential achieve their asymptotic structures closer to the surface of the atom.

For electron positions in the deep interior of the atom (see Figs. 3–5), the magnitude of the irrotational component $|\mathcal{E}_x^I|$ though small is finite. This is the case even at $r=0.001$ a.u. Thus, even at this electron position, the effective potential $W_x^{\text{eff}}(\mathbf{r})$ must have a small though finite slope. However, for an electron at the origin, the Fermi hole charge is spherically symmetric. As such the solenoidal as well as the irrotational components and therefore the total electric field itself vanishes for this electron position. Thus, at the origin, the effective poten-

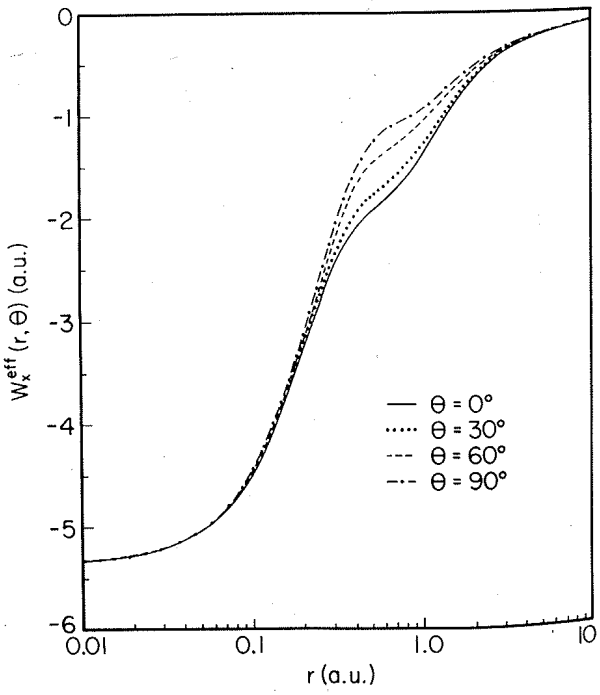

FIG. 8. Variation of the path-independent local effective exchange potential $W_x^{\text{eff}}(r,\theta)$ as a function of the radial distance r for different angles θ.

tial $W_x^{\text{eff}}(\mathbf{r})$ is equivalent to the potential $W_x(\mathbf{r})$ and its slope there, as for spherically symmetric atoms, is zero.

Finally, for completeness we repeat [4] in Fig. 8 the variation of the path-independent local effective exchange potential $W_x^{\text{eff}}(r,\theta)$ as a function of the radial distance r for different angles θ. The potentials increase monotonically throughout space so that the work done to remove an electron in all directions is always positive. The potentials in each direction also clearly delineate between the K and L shells, there being a distinct change in the structure of the potentials in the intershell region. As expected from our discussion of the asymptotic structure of the electric field, the effective exchange potentials decay to $-1/r$ at different rates in the different directions. By $r=10$ a.u. the potentials are all exact to two decimal places. It is also evident from the figure that in the deep interior of the atom, the differences between the potentials in the different directions is negligible and that they all approach the same value at the origin. Also observe that the slope of these potentials diminishes as the origin is approached and that the slopes are virtually zero even at $r=0.01$ a.u.

IV. CONCLUSIONS

From our analysis of the work formalism as applied to a degenerate ground state of the carbon atom in the Pauli-correlated approximation, we have learned the following.

The vector vortex source function $\mathbf{J}_x(\mathbf{r})$ for the solenoidal component $\mathcal{E}_x^S(\mathbf{r})$ of the electric field $\mathcal{E}_x(\mathbf{r})$ due to the Fermi hole charge $\rho_x(\mathbf{r},\mathbf{r}')$ is finite only within the atom. This follows from the fact that for such finite systems the Fermi hole charge is localized in the atom about the nucleus. The vector source function vanishes in the classically forbidden region and along certain axes of symmetry. As such, the effective exchange potential $W_x^{\text{eff}}(\mathbf{r})$ in these regions and directions is equal to $W_x(\mathbf{r})$, the work done in the force field of the Fermi hole charge. Therefore, over the substantial fraction of configuration space corresponding to these electron positions, the work $W_x(\mathbf{r})$ is path independent. Furthermore, the self-consistent determination of the local exchange potential in the classically forbidden region and along these specific symmetry directions is facilitated since its structure for those electron positions can then be determined directly from the Fermi hole $\rho_x(\mathbf{r},\mathbf{r}')$ itself rather than via the effective charge $\rho_x^{\text{eff}}(\mathbf{r})$.

Although the solenoidal component $\mathcal{E}_x^S(\mathbf{r})$ of the force field is finite within the atom, it is *two orders* of magnitude smaller than the irrotational component $\mathcal{E}_x^I(\mathbf{r})$. This means that essentially all the many-body effects are incorporated in the effective Fermi hole charge $\rho_x^{\text{eff}}(\mathbf{r})$. Therefore, the potential $W_x^{\text{eff}}(\mathbf{r})$ is an accurate representation of the local exchange potential acting upon the electrons within the atom, and will consequently lead to accurate ground-state energies. Furthermore, the fact that the difference in the potential $W_x^{\text{eff}}(\mathbf{r})$ in the different directions is small except for the intershell region explains why the central-field model of atoms is so accurate.

For the fully correlated case when both Pauli and Coulomb correlations are considered, we know that the Coulomb hole charge $\rho_c(\mathbf{r},\mathbf{r}')$, and therefore the effective Coulomb hole $\rho_c^{\text{eff}}(\mathbf{r})$ are localized about the nucleus of the atom with total charge zero. Thus asymptotically the effective correlation potential $W_c^{\text{eff}}(\mathbf{r})$ vanishes and the effective exchange-correlation potential $W_{\text{xc}}^{\text{eff}}(\mathbf{r})$ reduces to that of $W_x^{\text{eff}}(\mathbf{r})$. As noted above, the effective potential $W_x^{\text{eff}}(\mathbf{r})$ in turn is equivalent to the potential $W_x(\mathbf{r})$ in the classically forbidden region since there the vortex source $\mathbf{J}_x(\mathbf{r})$ vanishes. Thus, as is the case for closed-shell atoms, the structure of the local exchange-correlation potential for open-shell atoms in the region near and outside the surface of the atom is also *exactly* known and given by $W_x(\mathbf{r})$. In the truly asymptotic region $W_x(\mathbf{r})=-1/r$ in *all* directions. The highest occupied eigenvalue of the differential equation when only Pauli correlations are considered, Eq. (21), should therefore be a good approximation to the ionization potential and electron affinity of atoms and also give rise to accurate transition energies and polarizabilities.

For an electron at the nucleus, the Fermi-Coulomb hole charge is spherically symmetric. The vortex source, therefore, vanishes, and the effective potential $W_{\text{xc}}^{\text{eff}}(\mathbf{r})$ there is equal to $W_{\text{xc}}(\mathbf{r})$. Thus the unique value of the potential at the origin can also be determined directly from the Fermi-Coulomb hole charge. Since the electric field $\mathcal{E}_{\text{xc}}(\mathbf{r})$ is also zero at this electron position, the effective potential $W_{\text{xc}}^{\text{eff}}(\mathbf{r})$ in the different directions all approach this unique value at the origin with diminishing slope, with the slope finally vanishing at that position.

Finally, as we have seen, even with the choice of hydrogenic orbitals the solenoidal component of the force field is negligible in comparison to the irrotational component. For self-consistently determined orbitals for which the distortion of the electron density from sphericity is expected to be far less pronounced, the solenoidal component will be still smaller. As a consequence, the effective exchange potential $W_x^{\text{eff}}(\mathbf{r})$ will be more accurate since essentially all the many-body correlation effects would then have been accounted for in the determination of its structure. A self-consistent solution within the Pauli-correlated approximation with the true electron-nucleus external potential would also answer whether there even exists a solenoidal component of the force field, and therefore whether the potential $W_x(\mathbf{r})$ for such nonsymmetrical-density systems is in fact path-independent throughout space.

ACKNOWLEDGMENTS

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APPENDIX

In this appendix we give the analytical and integral expressions for the various properties discussed in the text as derived for the hydrogenic orbitals [Eq. (22)] assumed.

To simplify the expressions we define $q\equiv(r,\theta)$, $q'\equiv(r',\theta')$, $z=r\cos\theta$, $z'=r'\cos\theta'$, $p=1-3r$, and $p'=1-3r'$. The functions $f_1(r,r')$ and $f_2(q,q')$ up to $f_5(q,q')$ are defined as

$$f_1(r,r')=e^{-3r'}p-e^{-3r}p' ,$$

$$f_2(q,q')=e^{-3r}z'-e^{-3r'}z ,$$

$$f_3(q,q')=z'p-zp' ,$$

$$f_4(q,q')=z-z'+3z[\hat{\mathbf{i}}_r\cdot(\mathbf{r}-\mathbf{r}')] ,$$

$$f_5(q,q')=z-z'+3r(\sin\theta)[\hat{\mathbf{i}}_\theta\cdot(\mathbf{r}-\mathbf{r}')] .$$

The *electronic density* has azimuthal symmetry so that

$$\rho(\mathbf{r})=\rho(q)=\frac{432}{\pi}e^{-6r}A(q) ,$$

where

$$A(q)=e^{-6r}+\tfrac{1}{8}(p^2+9z^2) .$$

The *Fermi hole* is independent of the azimuthal angles ϕ and ϕ' so that

$$\rho_x(q,q')=\frac{216}{\pi}e^{-6r'}\frac{B^2(q,q')}{A(q)} ,$$

where

$$B(q,q')=e^{-3(r+r')}+\tfrac{1}{8}(pp'+9zz') .$$

The *gradient of the Fermi hole*

$$\nabla\rho_x(q,q')=\hat{\mathbf{i}}_r\frac{\partial\rho_x}{\partial r}+\hat{\mathbf{i}}_\theta\frac{1}{r}\frac{\partial\rho_x}{\partial\theta} ,$$

where

$$\frac{\partial\rho_x}{\partial r}=\frac{486B}{\pi A^2}e^{-6r'}[re^{-3r}f_1+e^{-3r}(1+3r)f_2\cos\theta+\tfrac{1}{8}f_3\cos\theta] ,$$

$$\frac{1}{r}\frac{\partial\rho_x}{\partial\theta}=-\frac{486B}{\pi A^2}e^{-6r'}[e^{-3r}f_2\sin\theta+\tfrac{1}{8}pf_3\sin\theta] .$$

The *electric field* due to the Fermi hole [see Eq. (5)] has azimuthal symmetry and does not have an azimuthal component. Thus

$$\mathcal{E}_x(q)=\hat{\mathbf{i}}_r\mathcal{E}_{x,r}(q)+\hat{\mathbf{i}}_\theta\mathcal{E}_{x,\theta}(q)$$
$$=\hat{\mathbf{i}}_r\int\rho_x(q,q')\frac{\hat{\mathbf{i}}_r\cdot(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}d\mathbf{r}'+\hat{\mathbf{i}}_\theta\int\rho_x(q,q')\frac{\hat{\mathbf{i}}_\theta\cdot(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}d\mathbf{r}' .$$

The *curl of the electric field* also has azimuthal symmetry but only an azimuthal component:

$$\nabla\times\mathcal{E}_x(\mathbf{r})=\hat{\mathbf{i}}_\phi[\nabla\times\mathcal{E}_x(q)]_\phi$$
$$=\hat{\mathbf{i}}_\phi\left\{\hat{\mathbf{i}}_\phi\cdot\int\frac{\nabla\rho_x(q,q')\times(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}d\mathbf{r}'\right\}$$
$$=\int\frac{[\hat{\mathbf{i}}_\theta\cdot(\mathbf{r}-\mathbf{r}')]\frac{\partial\rho_x}{\partial r}-[\hat{\mathbf{i}}_r\cdot(\mathbf{r}-\mathbf{r}')]\frac{1}{r}\frac{\partial\rho_x}{\partial\theta}}{|\mathbf{r}-\mathbf{r}'|^3}d\mathbf{r}' .$$

The *vortex source function* [see Eq. (18)] is then

$$\mathbf{J}_x(q)=\hat{\mathbf{i}}_\phi J_{x,\phi}(q)=\hat{\mathbf{i}}_\phi[\nabla\times\mathcal{E}_x(q)]_\phi/4\pi .$$

The *effective exchange charge* [see Eq. (14)] is

$$\rho_x^{\text{eff}}(q)=\frac{\rho(q)}{2}+\frac{243}{2\pi^2A^2}\int\frac{Be^{-6r'}}{|\mathbf{r}-\mathbf{r}'|^3}[\{\hat{\mathbf{i}}_r\cdot(\mathbf{r}-\mathbf{r}')\}re^{-3r}f_1+e^{-3r}f_2f_4+\tfrac{1}{8}f_3f_5]d\mathbf{r}' .$$

As with the electric field, its *irrotational component* [see Eq. (15)] has azimuthal symmetry and only radial (r) and θ components:

$$\mathcal{E}_x^I(q)=\hat{\mathbf{i}}_r\mathcal{E}_{x,r}^I(q)+\hat{\mathbf{i}}_\theta\mathcal{E}_{x,\theta}^I(q)$$
$$=\hat{\mathbf{i}}_r\int\rho_x^{\text{eff}}(q')\frac{\hat{\mathbf{i}}_r\cdot(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}d\mathbf{r}'+\hat{\mathbf{i}}_\theta\int\rho_x^{\text{eff}}(q')\frac{\hat{\mathbf{i}}_\theta\cdot(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}d\mathbf{r}' .$$

The *solenoidal component of the electric field* [see Eq. (20)] only has azimuthal symmetry and only r and θ components:

$$\mathcal{E}_x^S(q)=\hat{\mathbf{i}}_r\mathcal{E}_{x,r}^S(q)+\hat{\mathbf{i}}_\theta\mathcal{E}_{x,\theta}^S(q) ,$$

where

$$\mathcal{E}_{x,r}^S(q)=\int\frac{\left[[\hat{\mathbf{i}}_{\theta'}\cdot(\mathbf{r}'-\mathbf{r}'')]\frac{\partial\rho_x(q',q'')}{\partial r'}-[\hat{\mathbf{i}}_{r'}\cdot(\mathbf{r}'-\mathbf{r}'')]\frac{1}{r'}\frac{\partial\rho_x(q',q'')}{\partial\theta'}\right]}{4\pi|\mathbf{r}-\mathbf{r}'|^3|\mathbf{r}'-\mathbf{r}''|^3}\{(\hat{\mathbf{i}}_\theta\cdot\hat{\mathbf{i}}_{\phi'})[\hat{\mathbf{i}}_\phi\cdot(\mathbf{r}-\mathbf{r}')]-(\hat{\mathbf{i}}_\phi\cdot\hat{\mathbf{i}}_{\phi'})[\hat{\mathbf{i}}_\theta\cdot(\mathbf{r}-\mathbf{r}')]\}d\mathbf{r}'d\mathbf{r}''$$

and

$$\mathcal{E}_{x,\theta}^S(q)=\int\frac{\left[[\hat{\mathbf{i}}_{\theta'}\cdot(\mathbf{r}'-\mathbf{r}'')]\frac{\partial\rho_x(q',q'')}{\partial r'}-[\hat{\mathbf{i}}_{r'}\cdot(\mathbf{r}'-\mathbf{r}'')]\frac{1}{r'}\frac{\partial\rho_x(q',q'')}{\partial\theta'}\right]}{4\pi|\mathbf{r}-\mathbf{r}'|^3|\mathbf{r}'-\mathbf{r}''|^3}\{(\hat{\mathbf{i}}_\phi\cdot\hat{\mathbf{i}}_{\phi'})[\hat{\mathbf{i}}_r\cdot(\mathbf{r}-\mathbf{r}')]-(\hat{\mathbf{i}}_r\cdot\hat{\mathbf{i}}_{\phi'})[\hat{\mathbf{i}}_\phi\cdot(\mathbf{r}-\mathbf{r}')]\}d\mathbf{r}'d\mathbf{r}'' .$$

The local *effective exchange potential* [see Eq. (12)] is

$$W_x^{\text{eff}}(q)=\frac{1}{2}\int\frac{\rho(q')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'+\frac{243}{2\pi^2}\int\frac{B(q',q'')e^{-6r''}}{A^2(q')|\mathbf{r}-\mathbf{r}'||\mathbf{r}'-\mathbf{r}''|^3}\{[\hat{\mathbf{i}}_{r'}\cdot(\mathbf{r}'-\mathbf{r}'')]r'e^{-3r'}f_1(r',r'')+e^{-3r'}f_2(q',q'')f_4(q',q'')$$
$$+\tfrac{1}{8}f_3(q',q'')f_5(q',q'')\}d\mathbf{r}'d\mathbf{r}'' .$$

The six-dimensional integrals for the irrotational and solenoidal components of the electric field and that for the effective exchange potential are performed by the Monte Carlo method [8].

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