

## Quantum-Mechanical Interpretation of the Exchange-Correlation Potential of Kohn-Sham Density-Functional Theory

Manoj K. Harbola and Virahat Sahni

*Department of Physics, Brooklyn College of the City University of New York, Brooklyn, New York 11210, and  
The Graduate School and University Center of the City University of New York,  
33 West 42nd Street, New York, New York 10036*

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We interpret the exchange-correlation potential of Kohn-Sham density-functional theory to be the work required to move an electron against the electric field of its Fermi-Coulomb hole charge distribution. We substantiate this interpretation in the exchange-only approximation by proving the satisfaction of a necessary condition as well as by application to few-electron atomic and many-electron metallic surface systems. This interpretation also provides insights into the exact Slater exchange potential.

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In this Letter we provide a physical interpretation for the exchange-correlation potential  $\mu_{xc}(\mathbf{r})$  of Hohenberg-Kohn-Sham<sup>1,2</sup> density-functional theory. At present this potential is known only in terms of its mathematical definition as the functional derivative of the exchange-correlation energy functional. Initially we develop the interpretation from a physical viewpoint based on the tenets of electrodynamic theory. We then substantiate the physics by proving the satisfaction of a necessary condition. The understanding of the physical origin of this potential also provides insights into the exact Slater<sup>3</sup> exchange potential.

As a consequence of the proof of the Kohn-Sham<sup>2</sup> theorem via the variational principle for the energy, the potential  $\mu_{xc}(\mathbf{r})$  is derived to be the functional derivative  $\delta E_{xc}[\rho]/\delta\rho$  of the exchange-correlation energy functional  $E_{xc}[\rho]$  of the density  $\rho(\mathbf{r})$ . The profundity of Kohn-Sham<sup>2</sup> theory lies in the fact that the potential  $\mu_{xc}(\mathbf{r})$  in which all the many-body effects are incorporated is *local*. However, although for systems with a large number of electrons, this potential can be thought of as the exchange-correlation contribution to the chemical potential, and there is at present no physical understanding of what this potential means. On the other hand, the exchange-correlation energy functional  $E_{xc}[\rho]$  does have an interpretation. In any interacting electronic system each electron is surrounded by its Fermi-Coulomb (exchange-correlation) hole charge distribution. This charge is equal in magnitude but opposite in sign to that of the electron. Thus, the exchange-correlation energy may be thought<sup>4,5</sup> of as the interaction energy between an electron at  $\mathbf{r}$  and its Fermi-Coulomb hole charge density  $\rho_{xc}(\mathbf{r},\mathbf{r}')$  at  $\mathbf{r}'$ , and consequently written as

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

Based on this definition of  $E_{xc}[\rho]$ , the exchange-correlation potential must be the work done to bring an electron to  $\mathbf{r}$  in the electric field produced by its Fermi-Coulomb hole charge density. A similar interpretation exists for the Hartree electrostatic potential  $V_{es}(\mathbf{r})$ .

Mathematically,<sup>2</sup> this potential is the functional derivative of the electrostatic energy functional  $E_{es}[\rho]$  given as

$$E_{es}[\rho] = \int v(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}', \quad (2)$$

where  $v(\mathbf{r})$  is the external potential seen by the electrons. Thus, the electrostatic potential is

$$V_{es}(\mathbf{r}) = \frac{\delta E_{es}[\rho]}{\delta\rho(\mathbf{r})} = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'. \quad (3)$$

The physical interpretation of this potential is that it is the work done in moving an electron from infinity up to its final position against the field of the total (electronic plus nuclear) charge distribution. However, because of the functional dependence of  $\rho_{xc}(\mathbf{r},\mathbf{r}')$  on  $\rho(\mathbf{r})$ , the functional derivative of  $E_{xc}[\rho]$  of Eq. (1) is not  $\int d\mathbf{r}' \rho_{xc}(\mathbf{r},\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$ . Furthermore, since this functional dependence is unknown, the functional derivative cannot be obtained. To account for the dependence of  $\rho_{xc}$  on  $\rho$  in calculating the exchange-correlation potential, the electric field due to the Fermi-Coulomb charge distribution, which according to Coulomb's law is

$$\mathcal{E}_{xc}(\mathbf{r}) = \int \frac{\rho_{xc}(\mathbf{r},\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}', \quad (4)$$

must first be determined. The corresponding potential which is the work done in bringing an electron from  $\infty$  to  $\mathbf{r}$  against the force of this field is then

$$W_{xc}(\mathbf{r}) = - \int_{\infty}^{\mathbf{r}} \mathcal{E}_{xc} \cdot d\mathbf{l}. \quad (5)$$

This is the *local* effective exchange-correlation potential seen by the electrons. The understanding of this interpretation lies in the physics. The structure of the Fermi-Coulomb hole of an electron in an inhomogeneous electron gas is *dynamic* and changes as a function of electron position. This is a consequence of the dependence of the hole on the electronic density. Thus, in contrast to the electrostatic potential  $V_{es}(\mathbf{r})$ , which is due to a *static* charge distribution, the exchange-correlation potential is due to a charge distribution that depends on the

position of the test charge, and therefore must be determined in the manner described above.

Although the interpretation given to the local potential incorporating all the many-body effects has been arrived at on physical grounds, it is nonetheless rigorous since the analysis is based on fundamental precepts of both electrodynamic and density-functional theory. However, in order to explicitly relate this physical interpretation to density-functional theory, we next prove that the work done satisfies a necessary condition for it to be the functional derivative.

For our proof we work within the exchange-only<sup>6</sup> approximation of density-functional theory. In this approximation only Pauli correlations between the electrons are assumed in the wave function. Although the density dependence of the corresponding Fermi hole (or exchange charge density) is unknown, the hole can be defined precisely in terms of the electronic wave functions. For an electron with wave function  $\psi(\mathbf{r})$  at  $\mathbf{r}$ , the Fermi hole  $\rho_x(\mathbf{r}, \mathbf{r}')$  at  $\mathbf{r}'$  is defined<sup>3</sup> as

$$\rho_x(\mathbf{r}, \mathbf{r}') = |\gamma(\mathbf{r}, \mathbf{r}')|^2 / 2\rho(\mathbf{r}), \quad (6)$$

where the single-particle density matrix  $\gamma(\mathbf{r}, \mathbf{r}') = \sum_i \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}')$  satisfies the condition  $\gamma(\mathbf{r}, \mathbf{r}') = \gamma^*(\mathbf{r}', \mathbf{r})$ . The total charge of the Fermi hole is also equal in magnitude and opposite in sign to that of the electron. As an electron is removed from within a system such as an atom, molecule, or a metal, its Fermi hole distribution *changes* substantially as a function of electron position. In atoms<sup>7-9</sup> and molecules this changing charge distribution is *localized* about the system, whereas in metals<sup>9,10</sup> it is *delocalized* and spread throughout the crystal.

Now employing the virial theorem, Levy and Perdew<sup>11</sup> have proved that the exchange-energy functional  $E_x[\rho]$  may also be written as

$$E_x[\rho] = - \int \rho(\mathbf{r}) \mathbf{r} \cdot \nabla \mu_x(\mathbf{r}) d\mathbf{r}, \quad (7)$$

where  $\mu_x$  is the functional derivative  $\delta E_x[\rho] / \delta \rho(\mathbf{r})$ . This expression for the exchange energy is valid for arbitrary density  $\rho(\mathbf{r})$ . Replacing  $\mu_x$  in Eq. (7) by  $W_x$ , where  $W_x$  is the work done in the electric field  $\mathcal{E}_x$  of the Fermi hole, and noting that  $\mathcal{E}_x(\mathbf{r}) = -\nabla W_x(\mathbf{r})$ , we have on substituting for  $\mathcal{E}_x$  and  $\rho_x(\mathbf{r}, \mathbf{r}')$  from Eqs. (4) and (6) that

$$E_x[\rho] = \frac{1}{2} \iint |\gamma(\mathbf{r}, \mathbf{r}')|^2 \frac{\mathbf{r} \cdot (\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} d\mathbf{r} d\mathbf{r}'. \quad (8)$$

Since  $|\gamma(\mathbf{r}, \mathbf{r}')|^2 = |\gamma(\mathbf{r}', \mathbf{r})|^2$ , Eq. (8) may be rewritten by interchanging  $\mathbf{r}$  and  $\mathbf{r}'$  as

$$E_x[\rho] = - \frac{1}{2} \iint |\gamma(\mathbf{r}, \mathbf{r}')|^2 \frac{\mathbf{r}' \cdot (\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} d\mathbf{r} d\mathbf{r}'. \quad (9)$$

Adding Eqs. (8) and (9) and dividing by 2 gives

$$E_x[\rho] = \frac{1}{4} \iint \frac{|\gamma(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}', \quad (10)$$

which is Eq. (1) in the exchange-only case. Thus, the work  $W_x$  satisfies the necessary condition for it to be the functional derivative of the exchange-energy functional  $E_x[\rho]$ . This also shows that  $W_x$  is consistent with the virial theorem.

The proof of the equivalence of the work done to the functional derivative requires in addition a sufficiency criterion since there might exist several functions which when substituted for  $\mu_x$  in Eq. (7) lead to the exact exchange energy. However, it is equally important that these functions be derivable from fundamental physical considerations. On the basis of the fact that the work  $W_x$  is so derived, as well as by the agreement with the tenets of density-functional theory of the results of application to few- and many-electron nonuniform systems as discussed below, we conjecture that it is the functional derivative.

Although the above proof has been given for exchange-only theory, we believe the necessary condition to also be satisfied by the potential  $W_C$  derived from the Coulomb hole. Our conjecture is based on the arguments that though the physical origins of the Fermi and Coulomb holes are different, their charge distributions are similar in that they are both dynamic as a function of electron position. It is this property of the charge distributions that is intrinsic to the construction of the corresponding potentials via the laws of electrodynamic theory, and consequently both potentials should satisfy similar identities and conditions.

Thus far, the principal approach to the application of Kohn-Sham theory has been via approximate energy functionals  $E_{xc}[\rho]$  and their functional derivatives. However, as a consequence of the above interpretation and proof, the local exchange-correlation potential can now be determined *directly* from the Fermi-Coulomb hole. Therefore, the differential equation to be solved for the determination of the properties of an interacting electronic system within the context of density-functional theory is

$$\left[ -\frac{1}{2} \nabla^2 + V_{es}(\mathbf{r}) + W_{xc}(\mathbf{r}) \right] \Psi_i(\mathbf{r}) = \epsilon_i \Psi_i(\mathbf{r}), \quad (11)$$

or with  $W_{xc} = W_x + W_C$ , and with  $\rho(\mathbf{r}) = \sum_i |\Psi_i(\mathbf{r})|^2$ .

It is thus evident that the fundamental property of an interacting Fermion system in which all the many-body effects are incorporated is the Fermi-Coulomb hole charge distribution. A knowledge of the Fermi-Coulomb hole leads not only to the exchange-correlation energy  $E_{xc}$  but via the local potential  $W_{xc}$  to the ionization energy<sup>12</sup>  $-\epsilon_{\max}$ . Approximate forms of this distribution must reproduce,<sup>9</sup> at least qualitatively, the correct dynamics of the exact hole for both the energy and ionization potential to be obtained accurately. However, the fact that an approximate Fermi-Coulomb hole may have the same spherical average as the exact hole, thereby leading to the same exchange-correlation energy, does not imply that the corresponding work done will be the

same. The potential  $W_{xc}$  depends explicitly on the Fermi-Coulomb hole structure and not on any such average.

Within density-functional theory, the prescription for solution of *any* inhomogeneous electron-gas system whether it be atomic, molecular, or surface system is now known *exactly* in the exchange-only approximation<sup>6</sup> [ $W_C=0$  in Eq. (11)]. Furthermore, since the potential is local, the self-consistent solution of these equations is considerably less complex numerically than those of Hartree-Fock theory. For the fully correlated electron gas, approximate forms of the Coulomb or Fermi-Coulomb holes such as those within the random-phase approximation must be employed. Now since both the Fermi-Coulomb and Fermi hole charge distributions integrate to unity, the total Coulomb hole charge is zero. Thus, asymptotically, the work  $W_C$  done in removing an electron from the field of this charge distribution must vanish. The asymptotic structure of the exchange-correlation potential for the fully correlated nonuniform system is therefore that of  $W_x$  alone, and thus also known exactly. The more accurate the representation of the Coulomb hole, the more accurate will be the results for the ground-state energy, ionization potential, and other properties. However, approximating the Coulomb hole charge density implies that the energy is no longer a rigorous upper bound, because the rigor of the Hohenberg-Kohn theorem proof is lost if the correlation energy functional is approximated. Finally, we note, that since the Fermi-Coulomb holes for electrons in their ground and excited states are different, the corresponding potentials will be too, and therefore the formalism is not restricted to being only a ground-state theory.

The physical interpretation of the many-body potential also leads to insights into the *exact* Slater<sup>3</sup> potential. Within the exchange-only formalism, Slater too had suggested that all the electrons could be treated as if they moved in the same local effective potential. The *ad hoc* potential proposed by him was

$$V_x^{\text{Slater}}(\mathbf{r}) = \int \frac{\rho_x(r, r')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (12)$$

This potential is not the functional derivative of the exchange-energy functional  $E_x[\rho]$  as written in Eq. (1) in terms of the Fermi hole. Furthermore, as pointed out by Kohn and Sham,<sup>2</sup> the Slater potential for the homogeneous electron gas corresponds to the average value of the electronic energy which is a factor of  $\frac{3}{2}$  greater than the Kohn-Sham potential which is the energy value at the Fermi level. However, the physical reason why the Slater potential is incorrect is that the Fermi hole is a dynamic<sup>8-10</sup> charge distribution. As a consequence, the correct local effective exchange potential is the work done on the electron in the electric field due to the Fermi hole. The Slater potential would be correct only if the Fermi hole were static.

In the literature it is assumed that the Kohn-Sham po-

tentials for atoms in the exchange-only approximation<sup>6</sup> are those derived by the optimized-potential method (OPM) of Talman and co-workers.<sup>13</sup> The OPM is a numerical scheme that determines variationally a central local potential which minimizes the expectation value of the Hartree-Fock Hamiltonian. The result of the variation is a complex linear integral equation for the local exchange potential. In order to determine whether these are the Kohn-Sham potentials, we have calculated the local potential  $W_x$  for atoms with the corresponding Fermi hole and electric field determined using the self-consistent Talman orbitals.<sup>13</sup> In Fig. 1 we compare the OPM and  $W_x$  potentials for the argon atom.

A study of the graph shows that in the deep interior of the atom up to and including the *K* shell, which is the region from which the principal contribution<sup>9</sup> to the exchange energy arises, the  $W_x$  and OPM curves are essentially equivalent. They are also indistinguishable in the *L* and *M* shell regions. (The values of the OPM and  $W_x$  potentials at the nucleus, for example, are  $-28.1297$  and  $-27.3940$  Ry, respectively. The corresponding value for the Slater potential is  $-35.6533$  Ry.)

Asymptotically far from the nucleus, both the  $W_x$  and OPM curves fall off as  $-1/r$ . Talman and Shadwick<sup>13</sup> have proved mathematically that the linear integral equations of the OPM lead to this asymptotic structure. That this must be the asymptotic structure of  $W_x$  is evident from the fact that the Fermi hole has a total charge of unity which is localized about the nucleus of the atom. Furthermore, for asymptotic positions of the electron the Fermi hole stabilizes,<sup>8</sup> i.e., it is static, with its center of mass at the nucleus. In this asymptotic region the structure of  $W_x$  and the Slater potential are thus, also the

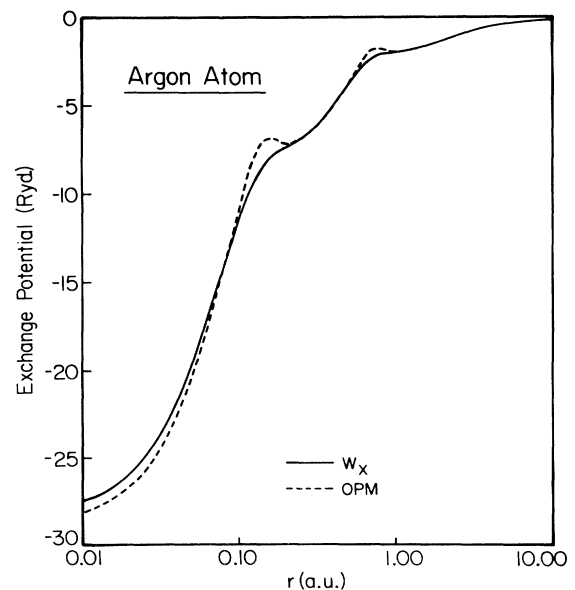


FIG. 1. The variation of  $W_x$  and the OPM central potential for the argon atom.

same.

As indicated earlier, the asymptotic structure of  $W_x$  is also the structure for the fully correlated systems, and in atoms<sup>14</sup> and molecules the Coulomb hole is also localized and must stabilize for asymptotic electron positions. This is consistent with detailed derivations<sup>15,16</sup> for atoms which show that  $\mu_{xc} \sim -1/r - \alpha/2r^4$  as  $r \rightarrow \infty$ , where  $\alpha$  is the polarizability of the positive ion, and where the leading term is due to exchange effects alone.

It is only in the intershell regions that the OPM and  $W_x$  curves differ, the former exhibiting bumps which are absent in the latter. The fact that the slope of  $W_x$  is positive throughout, however, means that work must always be done on the electron against the attractive force of the Fermi hole in order to remove it from the atom. The negative slope of the OPM curves, on the other hand, implies that the electron is being pushed out by the exchange charge distribution in this region of the atom. It is thus clear that although very close, the Talman potentials (or any other local potentials which exhibit such bumps in atoms) are not the true Kohn-Sham potentials. In exchange-only density-functional theory,<sup>6</sup> the potential is determined from that single determinant which minimizes the fully interacting Hamiltonian and which simultaneously is constrained to be the ground state of a noninteracting Hamiltonian with this local potential. Although the Talman orbitals minimize the expectation value of the Hartree-Fock Hamiltonian, they do not satisfy the latter constraint. This is reflected in the fact that the exchange energies determined by these orbitals and potentials from Eqs. (1) and (7) differ. For the argon atom, the exchange energies as obtained by these different expressions are  $-60.32$  and  $-59.94$  Ry, respectively. Substitution of the work  $W_x$  as calculated by the Talman orbitals in Eq. (7), however, leads to the value of  $-60.32$  Ry as must be the case.

Finally, we make the following observation with regard to the popular local-density approximation<sup>2</sup> for the exchange-correlation energy from which the functional derivative is easily obtained in terms of the density. In this approximation the Fermi-Coulomb charge is always centered and symmetric about the electron, and consequently the work done vanishes for all electron positions. Thus, the approximation, though exact for the uniform electron gas, is weakly founded for nonuniform systems.

We have recently obtained the self-consistent solution of the  $W_x$  equation for a few light atoms. These results as well as those for other elements of the periodic table will be presented elsewhere.<sup>17</sup> We are also studying the structure of the  $W_x$  potential at metallic surfaces using physically realistic wave functions.<sup>18</sup> Results for this

case indicate that with reference to the vacuum level, the potential  $W_x$  (in units of  $3k_F/2\pi$ , where  $k_F$  is the Fermi momentum) approaches a value of  $-0.67$  in the bulk metal as it must according to Kohn-Sham theory. The corresponding value in the Slater theory is  $-1.00$ . The fact that our results for both few- and many-electron systems are entirely consistent with the tenets of density-functional theory further supports our contention that  $W_x$  and  $W_{xc}$  are the exchange-only and fully correlated system Kohn-Sham potentials.

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