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Nonlocal approximation to the exchange potential and kinetic energy of an inhomogeneous electron gas

J. A. Alonso and L. A. Girifalco

Department of Metallurgy and Materials Science and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

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A nonlocal approximation to the exchange energy and the exchange potential of an inhomogeneous electron gas is presented that is based on the conservation of the main characteristics of the correct Fermi hole. Tested for atoms, it gives better results than the local-density approximation. A new kinetic-energy functional in the Hartree-Fock approximation is also derived that depends explicitly on the exchange-correlation factor. When our nonlocal approximation is used in it, reasonable results for the kinetic energy of atoms are obtained.

I. INTRODUCTION

The exchange-correlation potential is of major importance in the theory of atoms, molecules, and solids. However, exchange and correlation effects cannot be treated exactly with presently known theories. For free atoms, the Hartree-Fock method can be used to include exchange rigorously, but this method is not practical for complex molecules or solids. Because of this, approximations based on Slater's local-density approximation[1] ($x\alpha$ method,[1] Kohn-Sham[2] local-exchange-correlation method, local-spin-density approximation[3]) have been widely used. These methods provide practical computational schemes and are rather successful. However, exchange and correlation are nonlocal effects, and several recent papers have demonstrated the limitations of the local-density approximation.[4,5] Gradient corrections have been proposed[2,6-8] as systematic improvements of the local-density approximation, but real systems have large density variations, and the accuracy of gradient expansions with a finite number of terms in regions of high gradients is doubtful. The use of gradient corrections failed to improve results in band-structure calculations[9] and was found inadequate in calculations of total energies and electron densities in surface problems.[10,11] It is therefore of interest to pursue nonlocal approximations that are not based on gradient expansions.

The nonlocality of the kinetic energy is closely related to that of exchange and correlation. This is particularly important in energy-density-functional theory.[2,12] The central theorem of that theory states that the ground-state energy of a many-electron system is a universal functional of the electron density.[12] Thus, all ground-state properties can be obtained if the functional is known. The simplest approach to the kinetic-energy functional is the local-density approximation. This can be improved by using a density-gradient expansion,[12] which in practice must be cut off at finite order. These finite gradient expansions have proved useful in the study of atoms,[13] molecules,[14] and solids,[15] but have a well-known defect: the electron distributions obtained by minimizing a functional in which the kinetic energy is given by a finite number of terms in a gradient expansion cannot reproduce density oscillations such as the shell structure of an atom or the Friedel oscillations. Kohn and Sham[2] solved the kinetic-energy problem by deriving a set of one-electron Schrödinger-like equations from the variation of the energy functional, thus making energy-density-functional theory formally identical to Hartree (or Hartree-Fock) theory. However, the kinetic-energy functional is needed if the theory is to be expressed in terms of its fundamental quantity, the electron density, and if it is to be used as a base to improve statistical theories of the Thomas-Fermi type.

The kinetic and exchange-correlation energies are related through joint density matrices or, equivalently, through the exchange-correlation charge density. In this paper, we are primarily concerned with approximating the exchange and kinetic energy by starting with the exchange charge density. Nonlocal approximations to exchange have been proposed[16-18] that avoid gradient expansions, but rely on conserving total exchange charge and satisfying some of the limiting conditions on the exchange charge density. An approximation recently proposed by us[17] and by Gunnarsson *et al.*[18] is based on an expression for the exchange charge density that conserves total exchange charge, satisfies the limiting conditions at the center of and far from the exchange hole, and reduces to the free-electron form for the case of a homogeneous electron gas. This approximation was tested by computing exchange energies and exchange-energy densities in light free atoms. The results showed significant improvements over the local approximation and were closer to the Hartree-Fock results. Because of the large density variations in free atoms, this is quite encouraging, and the approximation should be satisfactory in solids, provided that correlation is also included.

In this paper, we derive the corresponding exchange potential needed in calculations of one-electron properties and compare it to the quantum-number averaged Hartree-Fock exchange potential in the free atoms He, Ne, and in Cu^+. The results show that our approximation is a better representation of the averaged Hartree-Fock exchange potential than either the Slater or Kohn-Sham local-density approximations. We also derive a formula that relates the kinetic and exchange energies in the Hartree-Fock approximation through the correlation factor for exchange. This allows us to translate our exchange approximation to an approximation for the kinetic energy, which was texted for the Ne and He atoms. For He, our result is exact. For Ne, our result is an improvement over the local approximation, but not as dramatic an improvement as for exchange. The reasons for this are discussed.

II. EXCHANGE ENERGY

The Hartree-Fock exchange energy is,[1] in atomic units,

$$E_{x\,\mathrm{HF}} = E_{x\,\mathrm{HF}\uparrow} + E_{x\,\mathrm{HF}\downarrow} = \frac{1}{2}\int [\rho\uparrow(1)U_{x\,\mathrm{HF}\uparrow}(1) + \rho\downarrow(1)U_{x\,\mathrm{HF}\downarrow}(1)]\,dv_1\,, \tag{1}$$

where

$$U_{x\,\mathrm{HF}\uparrow}(1) = -\sum_{i\uparrow,\,j\uparrow} n_i n_j \int u_i^*(1)u_j^*(2)u_j(1)u_i(2)\frac{1}{r_{12}}\,dv_2 \times\left(\sum_{k\uparrow} n_k u_k^*(1)u_k(1)\right)^{-1} \tag{2}$$

with a similar formula for spin down. In these expressions, $\rho\uparrow(1)$ is the density of electrons with spin up at the point $\vec{r}_1$, the u_i are the spin orbitals, and the n_i are the corresponding occupation numbers (zero or one). In terms of the correlation factor $C(1,2)$, Eq. (1) can be written as

$$E_{x\,\mathrm{HF}} = \frac{1}{2}\int \rho\uparrow(1)\left(\int\frac{1}{r_{12}}\,\rho\uparrow(2)C\uparrow(1,2)\,dv_2\right)dv_1 + \frac{1}{2}\int \rho\downarrow(1)\left(\int\frac{1}{r_{12}}\,\rho\downarrow(2)C\downarrow(1,2)\,dv_2\right)dv_1\,, \tag{3}$$

where

$$C\uparrow(1,2) \equiv \frac{\Gamma\uparrow(1,2)}{\rho\uparrow(1)\rho\uparrow(2)} - 1\,. \tag{4}$$

$\Gamma\uparrow(1,2)$ is the spin-dependent second-order density matrix.[19-21]

In the local-density approximation, it is assumed that

$$\rho\uparrow(2) = \rho\uparrow(1)\,, \tag{5a}$$

$$C\uparrow(1,2) = C_{\rho\uparrow(1)}(1,2)\,, \tag{5b}$$

where $C_{\rho\uparrow(1)}$ is the correlation factor for a homogeneous electron gas of density $\rho\uparrow(1)$, given by[22]

$$C_{\rho\uparrow(1)}(1,2) = -\frac{9}{2}\left(\frac{\sin y - y\cos y}{y^3}\right)^2, \tag{6}$$

$$y = r_{12}[3\pi^2\rho\uparrow(1)]^{1/3}\,. \tag{7}$$

Inserting Eqs. (5)–(7) into Eq. (3) gives the local approximation to the exchange energy as

$$E_{x\,\mathrm{L}} = -\frac{3}{4}\left(\frac{6}{\pi}\right)^{1/3}\int \{[\rho\uparrow(1)]^{4/3} + [\rho\downarrow(1)]^{4/3}\}\,dv_1\,. \tag{8}$$

The authors[17] and Gunnarsson *et al.*[18] have recently proposed that the exchange energy be approximated by retaining $\rho\uparrow(2)$ in Eq. (3) [i.e., rejecting assumption (5a)] and using, for $C\uparrow(1,2)$ the functional form of the correlation factor for the homogeneous gas, but replacing the density by an average density determined by the conservation of exchange charge. That is, we choose the correlation factor to be

$$C_{\tilde{\rho}\uparrow(1)}(1,2) = -\frac{9}{2}\left(\frac{\sin\tilde{y} - \tilde{y}\cos\tilde{y}}{\tilde{y}^3}\right)^2, \tag{9}$$

where

$$\tilde{y} = r_{12}[3\pi^2\tilde{\rho}\uparrow(1)]^{1/3} \tag{10}$$

and $\tilde{\rho}\uparrow(1)$ is determined by

$$\int \rho\uparrow(2)C_{\tilde{\rho}\uparrow(1)}(1,2)\,dv_2 = -1\,. \tag{11}$$

Using (9) in (3) gives a nonlocal approximation to the exchange energy:

$$E_{x\,\mathrm{NL}} = \frac{1}{2}\int \rho\uparrow(1)\left[\int\frac{\rho\uparrow(2)}{r_{12}}\,C_{\tilde{\rho}\uparrow(1)}(1,2)\,dv_2\right]dv_1 + \frac{1}{2}\int \rho\downarrow(1)\left[\int\frac{\rho\downarrow(2)}{r_{12}}\,C_{\tilde{\rho}\downarrow(1)}(1,2)\,dv_2\right]dv_1\,. \tag{12}$$

Comparing this to Eq. (1), we get a nonlocal approximation to $U_{x\,\mathrm{HF}}$:

$$U_{x\,\mathrm{NL}\uparrow}(1) = \int \rho\uparrow(2)C_{\tilde{\rho}\uparrow(1)}(1,2)r_{12}^{-1}\,dv_2\,. \tag{13}$$

For the nonspin polarized case (as in Ref. 17),

$$\rho\uparrow(1) = \rho\downarrow(1) = \tfrac{1}{2}\rho(1)\,, \tag{14a}$$

$$U_{x\,\mathrm{HF}\uparrow}(1) = U_{x\,\mathrm{HF}\downarrow}(1)\,, \tag{14b}$$

and Eq. (1) becomes

$$E_{x\,\mathrm{HF}}=\frac{1}{2}\int\rho(1)\left(\int\rho(2)C(1,2)r_{12}^{-1}\,dv_2\right)dv_1, \qquad (15)$$

where

$$C(1,2)=2\Gamma(1,2)/\rho(1)\rho(2)-1. \qquad (16)$$

[Note that the factor of 2 appears in (16) but not in (4).]

For the non-spin-polarized case, Eq. (12) reduces to

$$E_{x\,\mathrm{NL}}=\frac{1}{2}\int\rho(1)\left[\int\rho(2)C_{\tilde{\rho}(1)}(1,2)r_{12}^{-1}\,dv_2\right]dv_1. \qquad (17)$$

Equation (17) was tested for free atoms[17,18] using Hartree-Fock electron densities, and the results showed a great improvement over the local-density approximation.[23-25] This was the result of a detailed improvement of the exchange-energy density over all regions of the atom.

III. EXCHANGE POTENTIAL

The Hartree-Fock exchange potential is,[1] for the ith electron,

$$V_{x\,\mathrm{HF}\,i}(1)=-\frac{\sum_j n_j\int u_i^*(1)u_j^*(2)u_j(1)u_i(2)r_{12}^{-1}\,dv_2}{u_i^*(1)u_i(1)}. \qquad (18)$$

In the sum on j, only terms with the same spin as that of electron i give a nonzero contribution. To simplify (18), Slater[1] replaced it by an average potential defined by

$$[V_{x\,\mathrm{HF}\,i\uparrow}(1)]_{\mathrm{av}}=-\sum_{i\uparrow,j\uparrow}n_i n_j\int u_i^*(1)u_j^*(2)u_j(1)u_i(2)r_{12}^{-1}\,dv_2\left(\sum_l n_l u_l^*(1)u_l(1)\right)^{-1}. \qquad (19)$$

This potential still poses great practical difficulties for computations in complex systems, so Slater further simplified it by using the local-density approximation:

$$V_{x\,\mathrm{L}\uparrow}(1)=-3[(3/4\pi)\rho\uparrow(1)]^{1/3}. \qquad (20)$$

We note that the right-hand sides of Eqs. (2) and (19) are the same. Therefore, Eq. (13) gives our nonlocal approximation to the average exchange potential, i.e.,

$$V_{x\,\mathrm{NL}\uparrow}(1)=\int\rho\uparrow(2)C_{\tilde{\rho}\uparrow(1)}(1,2)r_{12}^{-1}\,dv_2 \qquad (21)$$

or, in the non-spin-polarized case

$$V_{x\,\mathrm{NL}}(1)=\int\rho(2)C_{\tilde{\rho}(1)}(1,2)r_{12}^{-1}\,dv_2. \qquad (22)$$

IV. NONLOCAL APPROXIMATION TO EXCHANGE POTENTIAL IN ENERGY-DENSITY-FUNCTIONAL THEORY

In the energy density functional theory,[2,12] the exchange potential is given by

$$V_{x\,\mathrm{DF}}(\vec{r})=\frac{\delta E_x[\rho]}{\delta\rho(\vec{r})}, \qquad (23)$$

where $E_x[\rho]$ is the exchange-energy functional. We start with $E_{x\,\mathrm{NL}}$ of Eq. (17) and calculate its variation corresponding to the variation in the electron density. This gives

$$\delta E_{x\,\mathrm{NL}}[\rho]=\frac{1}{2}\int\int r_{12}^{-1}\rho(1)\rho(2)\,\delta C_{\tilde{\rho}(1)}(1,2)\,dv_1dv_2+\frac{1}{2}\int\int r_{12}^{-1}\rho(1)\,\delta\rho(2)[C_{\tilde{\rho}(2)}(1,2)+C_{\tilde{\rho}(1)}(1,2)]\,dv_1\,dv_2. \qquad (24)$$

Because of the form of $C_{\tilde{\rho}(1)}(1,2)$ [see Eqs. (9) and (10)], we have

$$\delta C_{\tilde{\rho}(1)}(1,2)=\frac{\delta C_{\tilde{\rho}(1)}(1,2)}{\delta\tilde{\rho}(1)}\,\delta\tilde{\rho}(1). \qquad (25)$$

Since $\tilde{\rho}(1)$ is a functional of the electron density,

$$\delta\tilde{\rho}(1)=\int\frac{\delta\tilde{\rho}(1)}{\delta\rho(3)}\,\delta\rho(3)\,dv_3. \qquad (26)$$

To obtain $\delta\tilde{\rho}(1)/\delta\rho(3)$, we use the exchange charge conservation condition of Eq. (11). Setting the variation of Eq. (11) equal to zero gives

$$\frac{\delta\tilde{\rho}(1)}{\delta\rho(3)}=-C_{\tilde{\rho}(1)}(1,3)\left(\int\rho(1')\frac{\delta C_{\tilde{\rho}(1)}(1,1')}{\delta\tilde{\rho}(1)}\,dv_{1'}\right)^{-1}. \qquad (27)$$

Using Eqs. (25)–(27) in (24), and relabeling indices, we get the following approximation to (23):

$$V_{x\,\mathrm{DF\,NL}}=\frac{1}{2}\int r_{12}^{-1}\rho(2)[C_{\tilde{\rho}(1)}(1,2)+C_{\tilde{\rho}(2)}(1,2)]\,dv_2$$
$$-\frac{1}{2}\int\rho(2)C_{\tilde{\rho}(2)}(1,2)B(1,2)\,dv_2, \qquad (28)$$

where

$$B(1,2)=\int r_{13}^{-1}\rho(3)\,\frac{\delta C_{\tilde{\rho}(2)}(2,3)}{\delta\tilde{\rho}(2)}\,dv_3 \times\left(\int\rho(3)\,\frac{\delta C_{\tilde{\rho}(2)}(2,3)}{\delta\tilde{\rho}(2)}\,dv_3\right)^{-1}. \tag{29}$$

The variational derivative in (29) is a known, well-behaved function of $\tilde{\rho}$, so the potential of Eq. (28) can be calculated once the electron density is known. However, the computation is tedious, and is not as practical as that for the potentials defined by Eqs. (21) and (22).

The difference between $V_{x\,\mathrm{NL}}$ of Eq. (22) and $V_{x\,\mathrm{DF\,NL}}$ of Eq. (28) has the same origin as the difference between the Kohn-Sham[2] and the Slater[1] local potentials. In order to obtain the approximate exchange potential from the exact exchange energy of Eq. (1), two steps are taken here as well as in the Kohn-Sham or Slater methods: one is variational in nature and the other is an approximation. In Slater's method the variation is taken first and leads to the exact Hartree-Fock potential, $V_{x\,\mathrm{HF}}$ of Eq. (18). The local approximation is then made in passing from $V_{x\,\mathrm{HF}}$ to the $V_{x\,\mathrm{L}}$ of Eq. (20). By contrast, in the Kohn-Sham method the order is reversed: first, the exchange energy functional is written in the local approximation as in Eq. (8) and then the variational derivative is taken. The two steps mentioned do not commute and the result is that the Kohn-Sham and the Slater potentials differ by a multiplicative constant.

Our work is completely parallel to this, except that we are dealing with a nonlocal approximation. Nevertheless, the difference between the two final potentials is not just a constant but is more complicated. If we regard $V_{x\,\mathrm{NL}}$ and $V_{x\,\mathrm{DF\,NL}}$ as approximations to the exact $V_{x\,\mathrm{HF}}$ of Eq. (18), then it is not easy to say which of the two will give better results because $V_{x\,\mathrm{NL}}$ and $V_{x\,\mathrm{DF\,NL}}$ are both quantum-number-independent approximations to $V_{x\,\mathrm{HF}}$, which does depend on quantum number and the kind of average potential that $V_{x\,\mathrm{NL}}$ and $V_{x\,\mathrm{DF\,NL}}$ represent is not the same [see Ref. (2) for the local case]. In the local approximation, the Kohn-Sham potential leads to better eigenfunctions, while the Slater potential leads to better eigenvalues and a compromise is obtained with the empirical $x\alpha$ potential. Aside from these points, it is computationally easier to use $V_{x\,\mathrm{NL}}$ than $V_{x\,\mathrm{DF\,NL}}$.

V. KINETIC ENERGY AND THE CORRELATION FACTOR

The kinetic energy of a many-electron system is (in atomic units)

$$E_K=-\frac{1}{2}\int\nabla_1^2\Gamma(1'|1)\,|_{\vec{r}_1=\vec{r}_1'}\,dv_1, \tag{30}$$

where $\Gamma(1'|1)\equiv\Gamma(\vec{r}_1'|\vec{r}_1)$ is the joint density matrix.[19-21] In Hartree-Fock theory, the joint density matrix and the two-particle density matrix $\Gamma(1,2)$ are related by

$$\Gamma_F(1|2)\Gamma_F(2|1)=2\rho(1)\rho(2)-4\Gamma_F(1,2). \tag{31}$$

Using Eq. (16), this gives

$$\Gamma_F(1|2)\Gamma_F(2|1)=-2C(1,2)\rho(1)\rho(2). \tag{32}$$

We now assume that

$$\Gamma_F(1|2)=\Gamma_F(2|1) \tag{33}$$

(This assumption is not completely general, but is correct for instance for atoms with filled shells and for the homogeneous electron gas.) Combining (32) and (33) gives

$$\Gamma_F(1|2)=A_F(1,2)[\rho(1)\rho(2)]^{1/2}, \tag{34}$$

where

$$A_F(1,2)\equiv[-2C(1,2)]^{1/2}. \tag{35}$$

Taking the Laplacian of (34) gives

$$\nabla_1^2\Gamma_F(1|2)=[\rho(1)\rho(2)]^{1/2}\nabla_1^2A_F(1,2)-\tfrac{1}{4}A_F(1,2)\rho(1)^{-3/2}\rho(2)^{1/2}\,|\nabla\rho(1)|^2+\tfrac{1}{2}A_F(1,2)\rho(1)^{-1/2}\rho(2)^{1/2}\nabla^2\rho(1) +\rho(1)^{-1/2}\rho(2)^{1/2}\nabla_1A_F(1,2)\cdot\nabla\rho(1). \tag{36}$$

If we define a kinetic-energy density $e_K(1)\equiv e_K(\vec{r}_1)$ by

$$E_K=\int e_K(1)\,dv_1, \tag{37}$$

then using Eqs. (30) and (36), we get

$$e_K(1)=-\tfrac{1}{2}\rho(1)\nabla_1^2A_F(1,2)\,|_{\vec{r}_1=\vec{r}_2}+\tfrac{1}{8}A_F(1,1)[|\nabla\rho(1)|^2/\rho(1)]-\tfrac{1}{4}A_F(1,1)\nabla^2\rho(1)-\tfrac{1}{2}\nabla_1A_F(1,2)\,|_{\vec{r}_1=\vec{r}_2}\cdot\nabla\rho(1). \tag{38}$$

In the Hartree-Fock approximation, $A_F(1,1)=1$ exactly, so that

$$e_K(1)=-\tfrac{1}{2}\rho(1)\nabla_1^2A_F(1,2)\,|_{\vec{r}_1=\vec{r}_2}+\tfrac{1}{8}[|\nabla\rho(1)|^2/\rho(1)]-\tfrac{1}{4}\nabla^2\rho(1)-\tfrac{1}{2}\nabla_1A_F(1,2)\,|_{\vec{r}_1=\vec{r}_2}\cdot\nabla\rho(1). \tag{39}$$

This is a formally exact expression [subject to condition (33)] for the Hartree-Fock kinetic energy, which displays the close relation between the kinetic and exchange energies through the correlation factor. Thus, approximations for exchange that are based on approximating the correlation factor can be translated to approximations in the kinetic energy. However, the kinetic energy depends on the derivatives of the correlation factor whereas the exchange energy depends on integrals of the correlation factor. We therefore would expect that the kinetic energy is more sensitive than the exchange energy to the details of approximate correlation factors.

The simplest approximation to (39) is obtained by using the local-density expression [Eq. (6)] for the correlation factor [and therefore for $A_F(1,2)$, through Eq. (35)]. Equation (39) then gives the following approximation to the kinetic energy

$$e_{K\,\mathrm{L}}=\tfrac{3}{10}(3\pi^2)^{2/3}\rho^{5/3}+\tfrac{1}{8}(|\nabla\rho|^2/\rho)-\tfrac{1}{4}\nabla^2\rho. \tag{40}$$

The first term in (40) is the usual kinetic-energy density of a homogeneous electron gas, and the second term is identical with the gradient correction of Weizsäcker.[26] However, it must be stressed that Eq. (39) is not a gradient expansion. The second and third terms in (39) [and thus the last two terms in (40)] are exact. Improvements on the correlation factor will change the first term in (40), but not the others.

In density gradient expansion theory of the kinetic energy, there has been some controversy as to whether the correct coefficient for the $|\nabla\rho|^2/\rho$ term should be $\frac{1}{8}$, or $\frac{1}{72}$ as derived by Kompaneets and Pavlovskii[27] and by Kirzhnits.[28] Jones and Young[29,30] have shown that each coefficient is valid for different types of density variations. In our method, this controversy does not arise.

A nonlocal approximation to the kinetic-energy density is now readily obtained from our nonlocal approximation to exchange. Using Eq. (9) in Eqs. (35) and (39) gives

$$e_{K\,\mathrm{NL}}=\tfrac{3}{10}(3\pi^2)^{2/3}\tilde{\rho}^{2/3}\rho+\tfrac{1}{8}(|\nabla\rho|^2/\rho)-\tfrac{1}{4}\nabla^2\rho. \tag{41}$$

Our method for the kinetic energy is similar to that of March and Young,[31] who worked directly with the joint density matrix. They also found the Weizsäcker term as part of an exact kinetic-energy density, and that it is the first (nongradient) term that is subject to approximations. In their method, they approximate the joint density matrix by

$$\Gamma(\vec{r}_1\,|\,\vec{r}_2)=[J(\vec{r}_1)J(\vec{r}_2)]^{1/2}\Gamma_0(\vec{R}_1\,|\,\vec{R}_2), \tag{42}$$

where Γ_0 is a known joint density matrix (e.g., for the homogeneous electron gas) and J is the Jacobian of the transformation

$$\begin{aligned}\vec{R}_1&=\vec{R}(\vec{r}_1),\\ \vec{R}_2&=\vec{R}(\vec{r}_2).\end{aligned} \tag{43}$$

Our method, however, corresponds to the transformation of the form

$$\rho^{1/3}r_{12}\to\tilde{\rho}^{1/3}r_{12}. \tag{44}$$

Since $\tilde{\rho}$ is determined as a kind of average over the exchange hole, (42) is not sufficiently general to cover our case.

VI. VIRIAL THEOREM

The nonlocal approximation for the exchange and kinetic energies proposed here satisfies the virial theorem. To prove this, it is only necessary to show[19] that if all distances are multiplied by a scaling factor η, so that the density scales as

$$\rho_\eta=\eta^3\rho(\eta\vec{r}) \tag{45}$$

then the kinetic and potential energies scale as

$$(E_K)_\eta=\eta^2(E_K)_{\eta=1} \tag{46}$$

$$(E_P)_\eta=\eta(E_P)_{\eta=1}\,. \tag{47}$$

Since the argument of the correlation factor we use is a product of the cube root of a density and a distance, it is easy to show that the exchange energy (17) scales as Eq. (47), and that the kinetic energy, using Eq. (41), scales as Eq. (46). This shows that our approximation satisfied the virial theorem.

In fact, any approximation based on this correlation factor will satisfy the virial theorem, if its arguments are the products of a distance and the cube root of an electron density. However, this must be the case, since Eq. (39) is exact, and the only way the kinetic energy can scale properly is for the arguments of A to be dimensionless.

VII. NUMERICAL RESULTS FOR THE EXCHANGE POTENTIAL

To compare the $V_{x\,\mathrm{NL}}$ with $V_{x\,\mathrm{L}}$ and $(V_{x\,\mathrm{HF}})_{\mathrm{av}}$ we performed model calculations for the He and Ne atoms, and for Cu$^+$, using Hartree-Fock densities.[32] The results for $(V_{x\,\mathrm{HF}})_{\mathrm{av}}$ are taken from Kim and Gordon[24] for Ne and from Hartree[33] for Cu. The different potentials are plotted in Fig. 1–5. The Kohn-Sham local potential $V_{x\,\mathrm{KS}}$, which is two-thirds of $V_{x\,\mathrm{L}}$ is also plotted. (The potential of the $X\alpha$ method is intermediate between $V_{x\,\mathrm{L}}$ and $V_{x\,\mathrm{KS}}$). The figures show that $V_{x\,\mathrm{NL}}$ gives the best approximation to $(V_{x\,\mathrm{HF}})_{\mathrm{av}}$, though it must be recognozed that $V_{x\,\mathrm{KS}}$ was not derived as an approximation to $(V_{x\,\mathrm{HF}})_{\mathrm{av}}$. Note that $V_{x\,\mathrm{NL}}$ is slightly smoother and slightly more negative than $(V_{x\,\mathrm{HF}})_{\mathrm{av}}$. The NL approximation for He is exact and has been

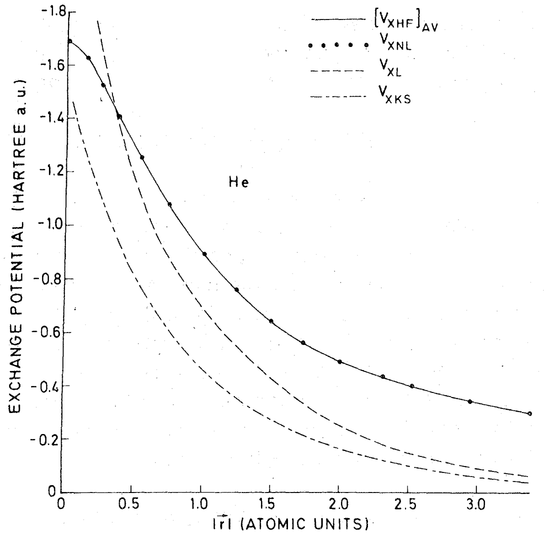

FIG. 1. Comparison of exchange potentials in He.

commented elsewhere.[17,18]

The kind of results to be expected if $V_{x\,\mathrm{NL}}$ is used in self-consistent field calculations can be anticipated from the work of Garrett and Mullins,[34] who used $(V_{x\,\mathrm{HF}})_{\mathrm{av}}$ in self-consistent calculations for Cu^+, Ne, and Ar, and found a significant improvement over the use of $V_{x\,\mathrm{L}}$. Since $V_{x\,\mathrm{NL}}$ is a good approximation to $(V_{x\,\mathrm{HF}})_{\mathrm{av}}$, its use should result in a similar improvement. This is particularly important for solids, in which the use of $(V_{x\,\mathrm{HF}})_{\mathrm{av}}$ is not practical. There is some indication that $V_{x\,\mathrm{NL}}$ can give even better results than $(V_{x\,\mathrm{HF}})_{\mathrm{av}}$ since, as recently pointed out by Gopinathan,[35] both the $X\alpha$ method and $V_{x\,\mathrm{L}}$ give eigenvalues greater than the exact Hartree-Fock eigenvalues. This is a result of the fact that these exchange potentials are insufficiently negative. However, the work of Garrett and Mullins[34] shows that $(V_{x\,\mathrm{HF}})_{\mathrm{av}}$ suffers the same defect, but to a lesser degree. Since $V_{x\,\mathrm{NL}}$ is slightly more negative than $(V_{x\,\mathrm{HF}})_{\mathrm{av}}$ it should lower the computed eigenvalues, and the results will be improved, unless there is too large a correction from this source.

It is well known that the local exchange potentials behave incorrectly at large distances from the nucleus in atoms. As shown in the figures, this is not the case for $V_{x\,\mathrm{NL}}$.

$V_{x\,\mathrm{NL}}$ is a spatially nonlocal potential, but it is the same for all electrons, since it does not depend on quantum number. The use of quantum-state-averaged potentials has been criticized by Overhauser,[36] and some quantum-number-dependent approximate potentials have been proposed.[34,37,38] However, these are not very practical in solid-state calculations. What is needed

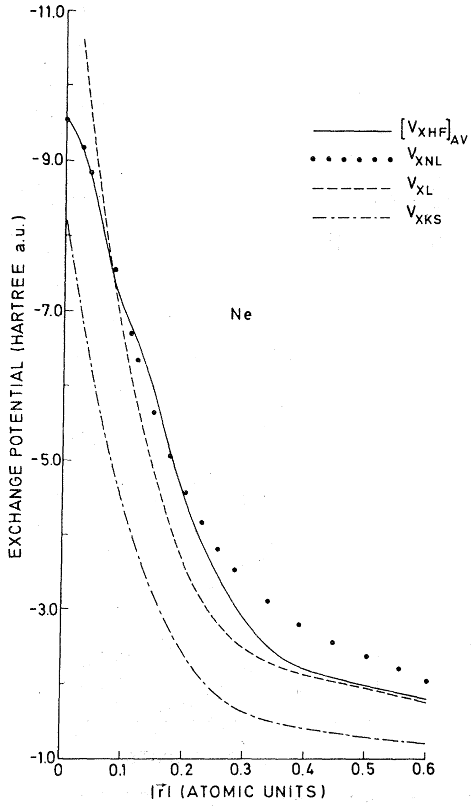

FIG. 2. Comparison of exchange potentials in Ne.

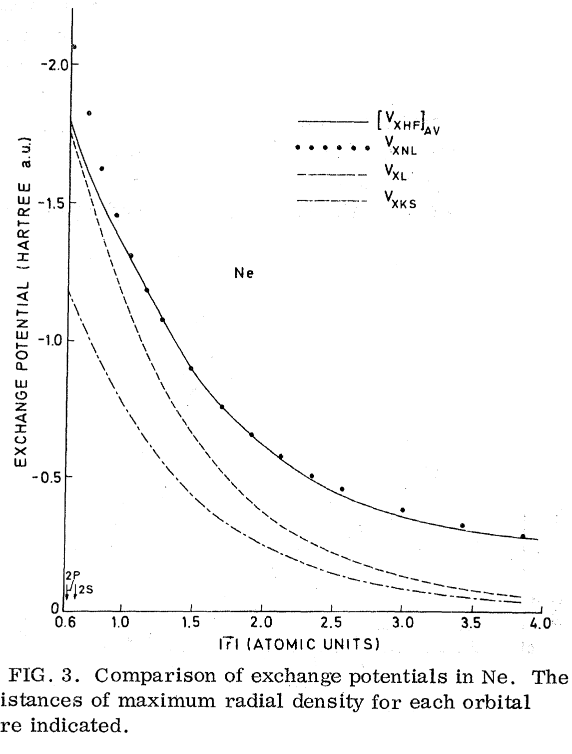

FIG. 3. Comparison of exchange potentials in Ne. The distances of maximum radial density for each orbital are indicated.

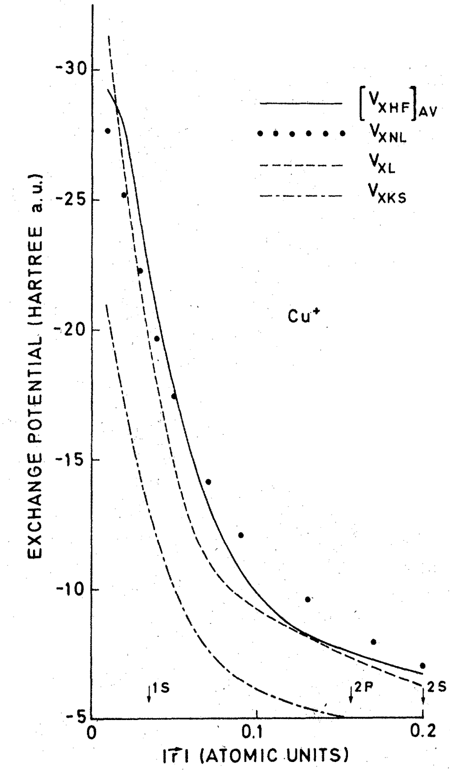

FIG. 4. Comparison of exchange potentials in Cu^+. The distances of maximum radial density for each orbital are indicated.

and practical at present is a scheme formally similar to the one-electron Hartree equations, but with exchange and correlation included via effective potentials. The approximation we propose provides such a potential for exchange that is an improvement over the local approximation, and is computationally practical.

For solid-state calculations, the introduction of correlation is essential. Nonlocal exchange-correlation energies and potentials can be similarly derived in analogy with Eq. (17) by setting

$$E_{xc}=\frac{1}{2}\int dv_1\rho(1)\int dv_2\frac{1}{r_{12}}\,\rho(2)C^{xc}_{\tilde{\rho}(1)}(1,2), \qquad (48)$$

where $C^{xc}_{\tilde{\rho}(1)}(1,2)$ is the pair distribution function of a homogeneous electron gas (with both exchange and correlation considered) and the density parameter $\tilde{\rho}(1)$ is determined by the sum rule stating that the exchange-correlation density $\rho(2)C^{xc}_{\tilde{\rho}(1)}(1,2)$ integrates to -1. The major difficulty is that the pair distribution function of a homogeneous electron gas with both exchange and correlation included is not exactly known and different theories give different pair distribution functions.[39]

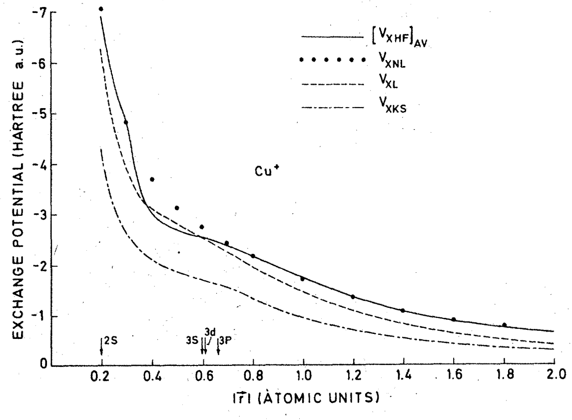

FIG. 5. Same as in Fig. 4.

VIII. NUMERICAL RESULTS FOR KINETIC ENERGY

We computed the kinetic energy of the atoms He and Ne from Hartree-Fock electron densities using Eqs. (40) and (41) and compared the results to those using the density gradient expansion[13] and to exact results from Hartree-Fock theory. The total energies are shown in Table I. The first point to note is that for He our nonlocal approximation agrees exactly with the Hartree-Fock result. The reason for this is that there are only two electrons in He, and the only value of $\tilde{\rho}$ that satisfies the charge conservation condition [see Eq. (11)] is $\tilde{\rho}=0$, corresponding to a correlation factor equal to $-\frac{1}{2}$ everywhere, the exact result. Thus, the exchange hole is infinitely wide, and the kinetic energy is given by just the gradient terms in (41).

The results using Eq. (40) are quite poor, as expected, since this equation is just the Weizsäcker approximation (the term in $\nabla^2\rho$ gives no contribution to the total energy), and Jones and Young[29] have shown that the density variations in atoms are not in the region where the Weizsäcker approximation is valid. In our theory, the results show that

TABLE I. Kinetic energy in free atoms (in a.u.). The last three lines are from Wang *et al.* (Ref. 13) paper and give the results for the gradient expansion. T_0 is the local term. T_2 is the second-order term and T_4 is the fourth-order term.

	He	Ne
Exact HF$^{(32)}$	2.86	128.6
Eq. (40)	5.42	208.4
Eq. (41)	2.86	133.7
T_0	2.56	117.8
T_0+T_2	2.88	127.8
$T_0+T_2+T_4$	2.96	129.7

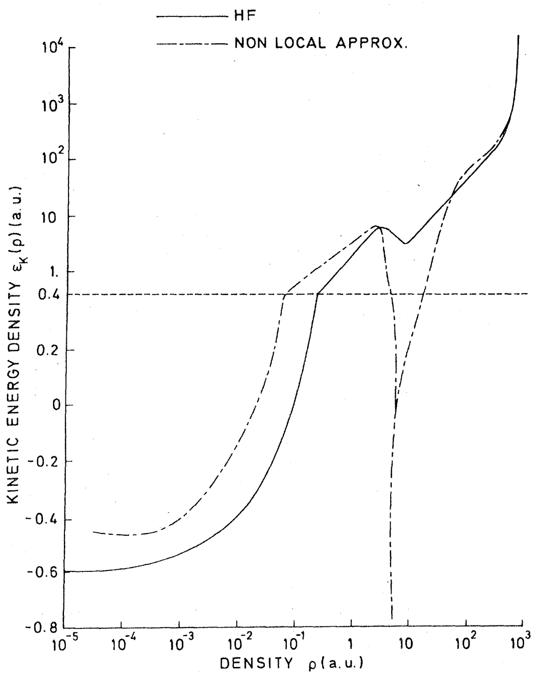

FIG. 6. Kinetic-energy density for Ne. The HF results are taken from Kim and Gordon (Ref. 24). The nonlocal approximation corresponds to Eq. (41).

the local approximation to the correlation factor is poor in free atoms. Equation (41) gives a much better result, the error for Ne being only 4%. Table I also includes the results of Wang *et al.*[13] using a gradient expansion including fourth-order gradient terms. Their results for Ne are quite good, but it is not clear what the effect of including higher-order terms would be (in fact, as seen in the table, the inclusion of fourth-order term fails to improve results). Nevertheless, our approximation to the correlation factor is inadequate for computation of the kinetic energy in atoms, relative to a fourth-order gradient expansion. The reason for this can be seen in the plot of the kinetic-energy density in Ne shown in Fig. 6 (see Ref. 40 for an analysis of the kinetic-energy density corresponding to the gradient expansion, in atoms). Our method shows a large deviation from the Hartree-Fock kinetic-energy density in the region where shell structure exists. Since $\tilde{\rho}$ is obtained by sampling the electron density over the exchange hole, and since the exchange hole is large relative to the scale of the shell structure, the effect of these density variations is smeared out, and leads to serious error in the region. It is clear that the correlation factor must be known with greater accuracy to treat better the kinetic energy.

IX. CONCLUSION

The method used in this paper is a promising alternative to the density gradient expansion methods of treating exchange-correlation and kinetic energy in inhomogeneous systems. It is based on approximations to the correlation factor in density matrix theory (or, equivalently, on approximations to the exchange-correlation charge or to the joint density matrix). Its physical basis can best be understood in terms of the exchange-correlation charge density, which is approximated in such a way as to preserve its major features. A rather simple modification of the correlation factor for the homogeneous electron gas is used which conserves the total exchange charge, gives the proper depth of the exchange hole, vanishes at large distances from the center of the hole, and reduces to the homogeneous gas form when the electron density is constant. Furthermore, the correlation factor contains an average density that depends on the entire electron density distribution and is therefore nonlocal. The exchange potential derived from this approximation was tested in He, Ne, and Cu^+ and was found to be an excellent approximation to the quantum-number-averaged HF exchange potential, and it is a significant improvement over the local-density approximation. This is an encouraging result for the theory of solids, since the heterogeneity of the electron density is less in solids than in atoms. The use of our potential in solid-state calculations would be only a little more complex than using a local potential and much less difficult than the Hartree-Fock method. For solids, nevertheless, it is essential to introduce correlation effects. Though this is a very difficult task (the problem is not yet completely solved even for the homogeneous electron gas), the lines along with the knowledge of exchange-correlation effects can be used to derive nonlocal exchange-correlation approximations in inhomogeneous systems were indicated.

A formula for the kinetic energy in terms of the correlation factor was derived which explicitly displays the relationship between kinetic energy and exchange, and provides a basis for nonlocal approximations without using gradient expansions. Translating our approximation for exchange to the kinetic energy gives a nonlocal expression that reproduces the Hartree-Fock kinetic energy in Ne to within 4%, and is exact for He. Examination of the kinetic-energy density shows that the major source of error in our kinetic-energy formula arises from the regions of very rapidly varying electron density corresponding to atomic shell structure. It is clear that the correlation factor must be known with more accuracy to compute the kinetic energy.

It is interesting to note that the method satisfies the virial theorem. Also, the exchange part of the effective potential of energy-density-functional theory is readily approximated using our method, but the result is rather complex and does not have computational simplicity.

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[1] J. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1974), Vol. 4.

[2] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

[3] O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B 13, 4274 (1976) and reference herein.

[4] H. Shore, J. Rose, and E. Zaremba, Phys. Rev. B 15, 2858 (1977).

[5] N. Elyashar and D. Koelling, Phys. Rev. B 15, 3620 (1977).

[6] F. Herman, J. P. Van Dyke, and I. B. Ortenburger, Phys. Rev. Lett. 22, 807 (1969) and Int. J. Quantum Chem. 35, 827 (1969).

[7] L. Kleinman, Phys. Rev. B 10, 2221 (1974).

[8] M. Rasolt and D. Geldart, Phys. Rev. Lett. 35, 1234 (1975).

[9] A. M. Boring, Phys. Rev. B 3, 3093 (1971).

[10] J. Wang and M. Rasolt, Phys. Rev. B 13, 5330 (1976).

[11] J. Perdew, D. Langreth, and V. Sanhi, Phys. Rev. Lett. 38, 1030 (1977).

[12] P. Hohenberg and W. Kohn, Phys. Rev. B 13, 864 (1964).

[13] W. Wang, R. Parr, D. Murphy, and G. Henderson, Chem. Phys. Lett. 43, 409 (1976).

[14] See for instance P. Gombás, Acta Phys. Acad. Sci. Hung. 9, 461 (1959); J. Goodisman, Phys. Rev. A 3, 1819 (1971); C. Shih and Y. Uang, Bull. Am. Phys. Soc. 21, 1301 (1976).

[15] See for instance J. Alonso and E. Santos, J. Phys. Chem. Solids 38, 307 (1977); J. Alonso and L. Girifalco, *ibid.* 38, 869 (1977); N. Lang, Solid State Phys. 28, 225 (1973).

[16] O. Gunnarsson, M. Jonson, and B. Lundqvist, Phys. Lett. A 59, 177 (1976).

[17] J. A. Alonso and L. A. Girifalco, Solid State Commun. 24, 135 (1977).

[18] O. Gunnarsson, M. Jonson, and B. Lundqvist, Solid State Commun. 24, 765 (1977).

[19] P. O. Löwdin, *Advances in Chemical Physics*, edited by I. Prigogine (Interscience, New York, 1959), Vol. II, p. 207.

[20] H. Brooks, Nuovo Cimento Suppl. 7, 165 (1958).

[21] R. McWeeny and B. Sutcliffe, *Methods of Molecular Quantum Chemistry* (Academic, London, 1969).

[22] F. Seitz, *Modern Theory of Solids* (McGraw-Hill, New York, 1940).

[23] In Ref. 17 we claimed for the exchange energy in the nonlocal approximation, errors of −1.2% (He) and 1.8% (Ne) as compared with the −14.9% (He and −12.15% (Ne) in the local approximation. These were based on the HF values given by Kim and Gordon (Ref. 24). More recent computations (Refs. 18 and 25) give better values for the HF exchange energy, and the resulting errors are 0% (He), 5.7% (Ne) in the nonlocal approximation and −13.8% (He), −8.9% (Ne) in the local approximation (for other light atoms (Ref. 18) the nonlocal approximation displays errors in between those for He and Ne). Although the results for Ne do not show as great an improvement as we claimed in Ref. 17, we believe that the test determines the validity of the nonlocal approximation is the improvement of the energy density, as was shown in Ref. 17.

[24] Y. S. Kim and R. Gordon, J. Chem. Phys. 60, 1842 (1974).

[25] C. Shih, Phys. Rev. A 14, 919 (1976).

[26] C. F. Weizsäcker, Z. Phys. 96, 431 (1935).

[27] A. Kompaneets and E. Pavlovskii, Soviet Phys.-JETP 4, 328 (1957).

[28] D. Kirzhnits, *Field Theoretical Methods in Many-body Systems* (Pergamon, New York, 1967).

[29] W. Jones and W. Young, J. Phys. C 4, 1322 (1971).

[30] W. Jones, Phys. Lett. A 34, 351 (1971).

[31] N. March and W. Young, Proc. Phys. Soc. London 72, 182 (1958). See also A. Müller, R. Baltin, and P. Schroth, Phys. Lett. A 32, 515 (1970) and P. Gombas, *ibid.* 28, 585 (1969).

[32] E. Clementi and C. Roetti, At. Data Nucl. Data Tables 14, 177 (1974).

[33] D. Hartree, Phys. Rev. 109, 840 (1958).

[34] W. Garrett and L. Mullins, J. Chem. Phys. 48, 4140 (1968).

[35] M. Gopinathan, Phys. Rev. A 15, 2135 (1977).

[36] A. W. Overhauser, Phys. Rev. B 2, 874 (1970).

[37] D. Liberman, Phys. Rev. 171, 1 (1968).

[38] J. Slater, T. Wilson, and J. Wood, Phys. Rev. 179, 28 (1969).

[39] P. Vashishta and K. S. Singwi, Phys. Rev. B 6, 875 (1972).

[40] J. Alonso and L. A. Girifalco, Chem. Phys. Lett. 53, 190 (1978).