Description of exchange and correlation in the strongly inhomogeneous electron gas using a nonlocal density functional

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We present exchange-correlation energy densities \( e_{xc} \), total energies \( E_{xc} \), and holes, calculated for strongly inhomogeneous electron gases using the nonlocal weighted density approximation. The results closely resemble variational Monte Carlo simulations performed recently [Phys. Rev. Lett. 87, 036401 (2001)], demonstrating the effectiveness of a nonlocal density functional description.

DOI: 10.1103/PhysRevB.65.193106

PACS number(s): 71.15.Mb, 71.10.Cn

Density functional theory1,2 (DFT) has become a widely accepted method for determining the electronic structure of atoms, molecules, and solids reliably. In DFT many-body electron interactions are captured through the exchange-correlation (XC) functional which is the only unknown quantity. The accuracy of DFT is therefore ultimately governed by the quality of the XC functional and how well it approximates the nonlocal nature of XC interactions. A great deal of understanding has been gained from the local density approximation3 (LDA) in which the XC energy is written solely in terms of the density \( n(r) \),

\[
E_{xc}^{\text{LDA}}[n(r)] = \int n(r) e_{xc}^{\text{LDA}}[n(r)] \, dr. \tag{1}
\]

For many properties the LDA works surprisingly well despite its simplicity. However, the severity of the local approximation inevitably leads to limitations that are now widely known. At the next level is the generalized gradient approximation4 (GGA) which provides a semilocal description of exchange and correlation by including the gradient of the density. The GGA is not a unique functional and there are now many parametrizations; however, it can be written in a general way as

\[
E_{xc}^{\text{GGA}}[n(r)] = \int n(r) e_{xc}^{\text{GGA}}[n(r), \nabla n(r)] \, dr. \tag{2}
\]

Despite the added sophistication, the GGA does not provide a consistent improvement over the LDA in all situations. Also, the GGA does not achieve chemical accuracy—the level at which chemical reactions can be studied. The GGA is not a unique functional and there are now many parametrizations; however, it can be written in a general way as

\[
E_{xc}^{\text{GGA}}[n(r)] = \int n(r) e_{xc}^{\text{GGA}}[n(r), \nabla n(r)] \, dr. \tag{2}
\]

The only approximation made in the WDA is the form of \( g_{xc}(r,r') \) which is only known exactly for a homogeneous electron gas. These approximations can be modeled in a particularly simple fashion in the WDA by writing

\[
g_{xc}(r,r') = G_{WDA}[|r-r'|;\tilde{n}(r)], \tag{5}
\]

where \( G_{WDA} \) is a suitable analytic function. The weighted density parameter \( \tilde{n} \) represents the nonlocality of the system and is obtained at every \( r \) by satisfying the XC sum rule

\[
\int n_{xc}(r,r') \, dr' = -1. \tag{6}
\]

For an XC functional to be universally reliable—that is, be applicable to any electronic system without bias—it must be...
constructed from first principles by satisfying as many exact XC conditions as possible. The WDA includes many basic yet fundamental elements of electron interactions that are not included in other XC functionals. These features include satisfying the sum rule on the XC hole given by relation 6 and the correct $1/(2r)$ limit of the XC energy density as $r \to \infty$. The WDA is, in principle, self-interaction free and it also has a favorable form for the asymptotic limit of the XC potential, decaying as $1/(2r)$ as $r \to \infty$, which differs from the exact result by a factor of 1/2. Another advantage of the WDA is that it has a simple form with a straightforward physical meaning—the XC energy in the WDA is modeled as a Coulomb-type interaction that occurs between the density $n(r)$ and its XC hole $n_{xc}(r,r')$ at the point $r'$, and therefore does not require any explicit information regarding the many electron wave function $\Psi$. However, the choice of model function $G_{WDA}$ is of fundamental importance in the WDA. There exist many functions that fulfill the small number of exact conditions imposed on $G_{WDA}$ and therefore maintain the properties described above. However, we have shown in recent work that the WDA is very sensitive to the choice of the analytic function and that some functions are more physical than others. Specifically, we found a particularly promising model to be that of a simple Gaussian function, and consequently we adopt this model in this work. The function has the following form:

$$G_{WDA}(r-r';\tilde{n}) = C(r') \exp[\frac{|r-r'|}{\lambda(r')}]^2,$$

the parameters $C(r')$ and $\lambda(r')$ being determined at each point in terms of the weighted density parameter $\tilde{n}$. Satisfying the homogeneous gas constraints—that $e_{xc}^{WDA}(\tilde{n})$ equal $e_{xc}^{LDA}(\tilde{n})$ and that the XC sum rule be satisfied for a homogeneous gas of density $\tilde{n}$—gives rise to two expressions that define $C(r')$ and $\lambda(r')$. The particular value of $\tilde{n}$ that is chosen is the one that satisfies the XC sum rule for the actual input density. We have developed an efficient method for calculating the required integrals in the WDA using a periodic representation of the density, the full details of the implementation of which are given in Ref. 12.

FIG. 1. The difference $\Delta e_{xc} = e_{xc}^{LDA} - e_{xc}^{WDA}$ along the direction of inhomogeneity for (a) $q = 1.12 k_F^0$ and (b) $q = 1.56 k_F^0$ systems. Shown in (c) and (d) are the corresponding density (solid line) and Laplacian of the density (dotted line) for these systems. Distances are given in terms of the Fermi wavelength $\lambda_f^0 = 2\pi/k_F^0$. 

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In the same manner as Nekovee et al. we study three model systems with strong density inhomogeneity, obtained by applying an external potential with the form
\[ v_{\text{ext}} \sim r^5 v_q \cos (\mathbf{q} \cdot \mathbf{r}) \]
to an electron gas along one of the three dimensions. To be consistent with the VMC calculations we determine the densities from self-consistent Kohn-Sham calculations using the LDA. This procedure gives rise to density profiles that are approximately sinusoidal in one direction, with the modulation controlled by the amplitude \( v_q \) and the size of the wave vector \( q \). All three systems have the same average density \( n^0 = 3/4 \pi r_s^3 \), with density parameter \( r_s = 2a_0 \), and we use cubic cells containing \( N = 48, 60, \) and 52 electrons. The sizes of the cells are designed such that they admit two, three, and four cycles of the cosine potential within the length of each cell. The densities therefore contain two, three, and four peaks, respectively, in the direction of inhomogeneity. With the predefined number of electrons, \( N \), this corresponds to wave vectors of size \( 1.12k_F, 1.56k_F, \) and \( 2.18k_F \), where \( k_F = (3 \pi^2 n^0)^{1/3} \) is the Fermi wave vector associated with the average density \( n^0 \). For all three systems we use \( v_q = 2.08e_F \) where \( e_F \) is the Fermi energy corresponding to \( n^0 \). The values of \( q \) and \( v_q \) used here lead to strong variations in the density on the scale of the local Fermi wavelength \( \lambda_F = 2 \pi / k_F \).

The WDA XC energy expression is written in terms of a particular XC hole, and so the XC energy density \( e_{\text{xc}}^{\text{WDA}} \) is well defined in the WDA. The VMC method utilizes the same expression for \( E_{\text{xc}}^{\text{VMC}} \); consequently, \( e_{\text{xc}}^{\text{WDA}} \) can be directly compared with \( e_{\text{xc}}^{\text{VMC}} \). While this is also true for the LDA [although the LDA can be simplified to give Eq. (1)], this is not feasible within the GGA since it is possible to add a function that modifies the integrand of Eq. (2) and yet integrates to zero, thereby leaving \( E_{\text{xc}}^{\text{GGA}} \) unchanged.14 For the purpose of comparing with VMC data, we define \( e_{\text{xc}}^{\text{LDA}} \) as being the integrand of expression (1) and \( e_{\text{xc}}^{\text{WDA}} \) as
\[
e_{\text{xc}}^{\text{WDA}}[\rho](\mathbf{r}, \mathbf{r}') = \frac{1}{2} \rho(\mathbf{r}) \int \frac{n(\mathbf{r}') G^{\text{WDA}}[\rho(\mathbf{r} - \mathbf{r}'); \rho]}{[\mathbf{r} - \mathbf{r}']} d\mathbf{r}'.
\]
For the LDA results we use the Perdew-Zunger15 parametrization of the Ceperely-Alder data16 for the correlation energy. Nekovee et al. in their work use the VMC method to reparametrize the Perdew-Zunger form of the LDA in order to eliminate both finite-size errors and the approximation introduced by the ground-state wave function \( \Psi^k \) in the VMC

<table>
<thead>
<tr>
<th>( q/k_F )</th>
<th>( E_{\text{xc}}^{\text{WDA}}/N )</th>
<th>( \Delta E_{\text{xc}}^{\text{LDA}}/N )</th>
<th>( \Delta E_{\text{xc}}^{\text{GGA}}/N )</th>
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<tr>
<td>1.12</td>
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<td>2.18</td>
<td>-0.2874</td>
<td>-0.0096</td>
<td>-0.0160</td>
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![FIG. 2. The exchange-correlation hole \( n_{\text{xc}}(\mathbf{r}, \mathbf{r}') \), calculated using the WDA when the reference electron is located at (a) a density maximum and (b) a density minimum, for the \( q = 1.12k_F \) system. At the density minimum the electron (not shown) is situated in the center of the plane, equidistant from the XC hole minima. Shown in (c) is the LDA XC hole calculated at the density minimum, which remains centered on the electron.](image-url)
calculations. This procedure was also carried out for the homogeneous gas constants in the GGA. Consequently this may lead to slight differences in \( E_{xc}^{\text{LDA}} \) and \( E_{xc}^{\text{GGA}} \) calculated in this work. For the GGA results we use the form developed by Perdew, Burke, and Ernzerhof\(^{17}\) (PBE).

In Fig. 1 we present plots of \( \Delta e_{xc} = e_{xc}^{\text{LDA}} - e_{xc}^{\text{WDA}} \), along the direction of inhomogeneity, as well as the corresponding density and Laplacian of the density \( \nabla^2 n(r) \) for the \( q = 1.12 k^b_F \) and \( q = 1.56 k^b_F \) systems. It is clear that \( \Delta e_{xc} \) bears a close relation to \( \nabla^2 n(r) \), which is consistent with the VMC findings.\(^8\) Although the densities used here are different, the magnitudes of the deviations produced by the WDA are also in very good agreement with the VMC results.

Shown in Table I is the WDA total XC energy per electron, \( E_{xc}^{\text{WDA}}/N \), along with the difference relative to the LDA, \( \Delta E_{xc}^{\text{LDA}}/N = (E_{xc}^{\text{LDA}} - E_{xc}^{\text{WDA}})/N \), and the GGA, \( \Delta E_{xc}^{\text{GGA}}/N = (E_{xc}^{\text{GGA}} - E_{xc}^{\text{WDA}})/N \), for all three systems. For both the LDA and GGA, the deviations are positive for the \( q = 1.12 k^b_F \) system. As the wave vector and hence the degree of inhomogeneity increase, \( \Delta E_{xc}^{\text{LDA}}/N \) and \( \Delta E_{xc}^{\text{GGA}}/N \) become negative, with the LDA providing closer agreement with the WDA in both cases. Again, it is not possible to compare our WDA values directly with the VMC results since we are using different densities; nevertheless, exactly the same trends are observed for the VMC total XC energy relative to the LDA and the GGA given in Table I of Ref. 8.

Shown in Fig. 2 is the WDA XC hole \( n_{xc}(r, r') \) associated with a reference electron situated at \( a \) a density maximum and \( b \) a density minimum for the \( q = 1.12 k^b_F \) system. The WDA XC hole is obtained by fixing the reference electron at \( r \) and determining \( \tilde{n} \) at each point \( r' \) within the plane parallel to \( q \). This determines \( C(r', \tilde{n}) \), and \( \lambda(r') \) and these are then used to construct \( n_{xc}(r, r') \) at each point in the plane. When the electron is at a density maximum the XC hole is centered directly at the site of the electron and is contracted in the direction of inhomogeneity. As the electron moves toward the density minimum the XC hole trails behind the electron, which remains centered at the density maximum and still contracted in the direction of \( q \). Around the density minimum, the XC hole becomes highly nonlocal as it develops two minima due to the peaks in the density either side of the electron. This is shown in Fig. 2(b) where the electron is located in the center of the plane, equidistant from the XC hole minima. The same variations in the XC hole between high and low densities are observed for the two other systems. The nonlocal features exhibited by the WDA are in contrast to the LDA, where XC holes are always spherically symmetric and centered on the electron. This is illustrated in Fig. 2(c) for an electron at a density minimum. The XC holes produced by the WDA exhibits the same nonlocal features as the VMC calculations.

By examining systems that are strongly inhomogeneous we have shown that the WDA, together with a very simple model for the pair-correlation function, can yield values for \( e_{xc} \) that are in close agreement with the variational Monte Carlo method. This also leads to a successful determination of total XC energies by the WDA, as demonstrated by the similar trends in \( \xi_{xc} \) with the VMC data. The difference in \( e_{xc} \) for the LDA relative to the WDA (and VMC method) is strikingly linked to \( \nabla^2 n(r) \) for the systems studied here. It is therefore reasonable to assume that including \( \nabla^2 n(r) \) in semilocal XC functionals may provide an important contribution to the correction of LDA XC energies. However, we find that these Laplacian-type errors only occur for systems that are sufficiently inhomogeneous. When the value of \( v_q \) is reduced so that the systems become more slowly varying, we find that \( \Delta e_{xc} \) does not resemble \( \nabla^2 n(r) \).\(^{18}\) Consequently, the inclusion of \( \nabla^2 n(r) \) may only improve semilocal XC functionals in strongly inhomogeneous regimes.

We are encouraged by the similarities between the WDA and VMC results. The WDA provides XC energies and holes at a level comparable to the VMC method, and yet is only moderately more expensive than the GGA compared with quantum Monte Carlo techniques. The WDA is also simple, physically intuitive, and easy to develop, since modifying the functional form only involves changing the model function \( C^{\text{WDA}} \). We therefore expect the WDA to play an increasingly important role in XC functional development in the future.

P.P.R. thanks M. Nekovee for discussions and acknowledges the EPSRC for funding.

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