

Quantum Monte Carlo Analysis of Exchange and Correlation in the Strongly Inhomogeneous Electron Gas

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We use the variational quantum Monte Carlo method to calculate the density-functional exchange-correlation hole n_{xc} , the exchange-correlation energy density e_{xc} , and the total exchange-correlation energy E_{xc} of several strongly inhomogeneous electron gas systems. We compare our results with the local density approximation and the generalized gradient approximation. It is found that the nonlocal contributions to e_{xc} contain an energetically significant component, the magnitude, shape, and sign of which are controlled by the Laplacian of the electron density.

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The Kohn-Sham density-functional theory (DFT) [1] shows that it is possible to calculate the ground-state properties of interacting many-electron systems by solving only one-electron Schrödinger-like equations. The results are exact in principle, but in practice it is necessary to approximate the unknown exchange-correlation (XC) energy functional, $E_{xc}[n]$, which expresses the many-body effects in terms of the electron density $n(\mathbf{r})$. The current popularity of density-functional methods in condensed matter physics, quantum chemistry, and materials science reflects the remarkable success of fairly simple approximate XC energy functionals.

In the local density approximation (LDA), the XC hole $n_{xc}(\mathbf{r}, \mathbf{r}')$ about an electron at \mathbf{r} is approximated by the XC hole of a uniform electron gas of density $n = n(\mathbf{r})$. This works surprisingly well, but not well enough for many chemical and biological applications. The most widely used correction to the LDA is the generalized gradient approximation (GGA) [2–4], in which the effects of inhomogeneity are modeled using the semilocal approximation $E_{xc} \approx \int d\mathbf{r} f(n, |\nabla n|)$, where f is some parametrized nonlinear function of n and ∇n . A common feature of all current GGAs is that their construction is guided by limiting behaviors and sum rules; they are designed to fit various integrated quantities such as total exchange energies of atoms or ionization energies of molecules, but incorporate little or no information about the behavior of local quantities such as $n_{xc}(\mathbf{r}, \mathbf{r}')$ and the exchange-correlation energy density $e_{xc}(\mathbf{r})$ in strongly inhomogeneous systems. This may explain why current GGAs, although better than the LDA in many situations, are not consistently able to deliver the very high accuracy of ~ 0.1 eV required to study, e.g., most chemical reactions. To open a new direction in the search for improved functionals, we use the variational quantum Monte Carlo (VMC) method [5] to calculate n_{xc} and e_{xc} for several strongly inhomogeneous electron gases and analyze the performance of the LDA and the GGA in these systems in detail.

The inhomogeneous electron gases considered all had the same average electron density $n^0 = 3/(4\pi r_s^3)$, where

$r_s = 2a_0$ (approximately the same as for Al). The strong density modulations were one dimensional and periodic, with a roughly sinusoidal profile. Three different modulation wave vectors $q \leq 2.17k_F^0$ were investigated, where k_F^0 is the Fermi wave vector corresponding to n^0 . The strong variation of $n(\mathbf{r})$ on the scale of the inverse local Fermi wave vector $k_F(\mathbf{r})^{-1} = [3\pi^2 n(\mathbf{r})]^{-1/3}$ results in a strikingly nonlocal behavior of n_{xc} that cannot be described by semilocal corrections to the LDA. We show, however, that the LDA errors in e_{xc} have a dominant and energetically significant component, the magnitude, shape, and sign of which are controlled by the semilocal quantity $\nabla^2 n(\mathbf{r})$. Because it depends only on n and $|\nabla n|$, the GGA is unable to correct the LDA errors in E_{xc} resulting from this component adequately, and worsens the LDA in two of our three systems. The relevance of Laplacian terms has been pointed out previously [6], but our calculations provide the first quantitative evidence of their importance in strongly inhomogeneous systems and for e_{xc} .

Our starting point is the adiabatic connection formula [7], which expresses $E_{xc}[n]$ as the volume integral of an XC energy density e_{xc} defined by [8]

$$e_{xc}(\mathbf{r}, [n]) = \frac{1}{2} \int d\mathbf{r}' \frac{n(\mathbf{r})n_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (1)$$

where n_{xc} is the coupling-constant-averaged XC hole. The definition of e_{xc} used in the construction of the GGA differs from ours by an integration by parts that does not affect the integrated E_{xc} . We favor Eq. (1), however, because of its clear physical interpretation and because it aids comparison with the LDA XC energy density, which is constructed from an approximate hole.

The XC hole n_{xc} is obtained via a coupling-constant integration,

$$\begin{aligned} n(\mathbf{r})n(\mathbf{r}') + n(\mathbf{r})n_{xc}(\mathbf{r}, \mathbf{r}') \\ = \int_0^1 d\lambda \langle \Psi^\lambda | \sum_i \sum_{j(\neq i)} \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) | \Psi^\lambda \rangle, \end{aligned} \quad (2)$$

where Ψ^λ is the antisymmetric ground state of the Hamiltonian $\hat{H}^\lambda = \hat{T} + \lambda \hat{V}_{ee} + \hat{V}^\lambda$ associated with coupling

constant λ . Here \hat{T} and \hat{V}_{ee} are the operators for the kinetic and electron-electron interaction energies, and $\hat{V}^\lambda = \sum V^\lambda(\mathbf{r}_i)$ is the one-electron potential needed to hold the electron density $n^\lambda(\mathbf{r})$ associated with Ψ^λ equal to $n(\mathbf{r})$ for all values of λ between 0 and 1. Our VMC method [9] for calculating n_{xc} and e_{xc} from Eqs. (1) and (2) is a generalization of the scheme used by Hood *et al.* [10]. It amounts to treating *both* Ψ^λ and V^λ variationally and determining the variational parameters by simultaneously minimizing the variance of the local energy [11] and the deviation of n^λ from n [9].

The VMC simulations were performed for a finite spin-unpolarized electron gas in a face-centered cubic simulation cell subject to periodic boundary conditions. The exact interacting ground-state density $n(\mathbf{r})$ was chosen *a priori*, and the constrained minimization scheme was then used to find, at each λ , the exact (within VMC) wave function Ψ^λ and external potential V^λ corresponding to that density [12]. At full coupling ($\lambda = 1$), $V^\lambda(\mathbf{r})$ is the exact external potential of the many-electron system with ground-state density $n(\mathbf{r})$. The input density $n(\mathbf{r})$ was generated by solving, within the LDA, the Kohn-Sham equations for an external potential of the form $V_q \cos(\mathbf{q} \cdot \mathbf{r})$, where V_q was fixed at $2.08\epsilon_F^0$ and ϵ_F^0 is the Fermi energy corresponding to n^0 . The advantages of this procedure are that the input electron density is guaranteed to be noninteracting v -representable and that the Slater determinant of single-particle orbitals is by construction the exact many-body wave function corresponding to $\lambda = 0$. The (density-functional) exchange contributions to e_{xc} , n_{xc} , and E_{xc} , obtained from this Slater determinant, are therefore also exact [9].

We consider potentials with $q = 1.11k_F^0$, $1.55k_F^0$, and $2.17k_F^0$, and cells containing 64, 78, and 69 electrons, respectively. The adiabatic calculations were performed using six equidistant values of λ in the range $[0, 1]$ and with the Slater-Jastrow ansatz given in [9] as our many-body wave function. At each λ , we used a total of 20 variational parameters in Ψ^λ and up to seven coefficients in the plane-wave expansions of n^λ and V^λ . The optimization of the parameters in Ψ^λ and V^λ was performed using 96000 statistically uncorrelated electron configurations. This was sufficient to reduce the root mean square deviation of $n^\lambda(\mathbf{r})$ from $n(\mathbf{r})$ to less than 0.5% of $n(\mathbf{r})$ for all values of λ and all systems. The expectation values were calculated [5] using 10^6 independent configurations of all electrons. Throughout, we used the modified electron-electron interaction described in [13], which virtually eliminates the finite-size errors arising from the long range of the Coulomb potential. The statistical errors were negligible except in n_{xc} in low-density regions, where they were much smaller than the differences between n_{xc} and n_{xc}^{LDA} . The largest systematic errors are caused by the finite size of the system and the approximate nature of Ψ^λ . These errors combine such that, even in a homogeneous electron gas, $e_{xc}^{VMC} \neq e_{xc}^{LDA}$. To circumvent this problem,

we performed additional VMC calculations of the XC energies of finite homogeneous electron gases with $N = 64$ and $r_s = 0.8, 1, 2, 3, 4, 5, 8, \text{ and } 10$. This enabled us to construct a Perdew-Zunger parametrization [14] of the VMC XC energy per electron of a finite uniform electron gas with $N = 64$. By using this parameterization to calculate e_{xc}^{LDA} in all systems studied, we largely eliminated the systematic errors in the calculated differences between e_{xc}^{VMC} and e_{xc}^{LDA} . The same parametrization was also used as input for the evaluation of E_{xc}^{GGA} [2], a procedure that we assume mitigates the errors in $E_{xc}^{GGA} - E_{xc}^{VMC}$.

In Fig. 1 we show snapshots of the deformation of n_{xc}^{VMC} around an electron moving in the $q = 1.11k_F^0$ system along a line parallel to \mathbf{q} , the direction of maximum inhomogeneity, from a density maximum towards the tail of $n(\mathbf{r})$. The XC hole is plotted as a function of \mathbf{r}' around a fixed electron at \mathbf{r} , with \mathbf{r}' ranging in a plane parallel to \mathbf{q} . Also shown is the corresponding LDA hole n_{xc}^{LDA} [7]. At the density maximum (not shown), both n_{xc}^{VMC} and n_{xc}^{LDA} are centered at the electron. However, unlike n_{xc}^{LDA} , which is always spherically symmetric, n_{xc}^{VMC} is contracted in the direction of the inhomogeneity. As the electron moves away from the density maximum to a point on the slope (top panel), the nonlocal nature of n_{xc}^{VMC} becomes manifest. While n_{xc}^{LDA} is still centered at the electron and is rather diffuse, n_{xc}^{VMC} lags behind near the density maximum and is much more compact. The nonlocal behavior of n_{xc}^{VMC} becomes remarkable at the density minimum. Here n_{xc}^{VMC} has two large nonlocal minima, each centered at a density maximum ~ 2.80 a.u.

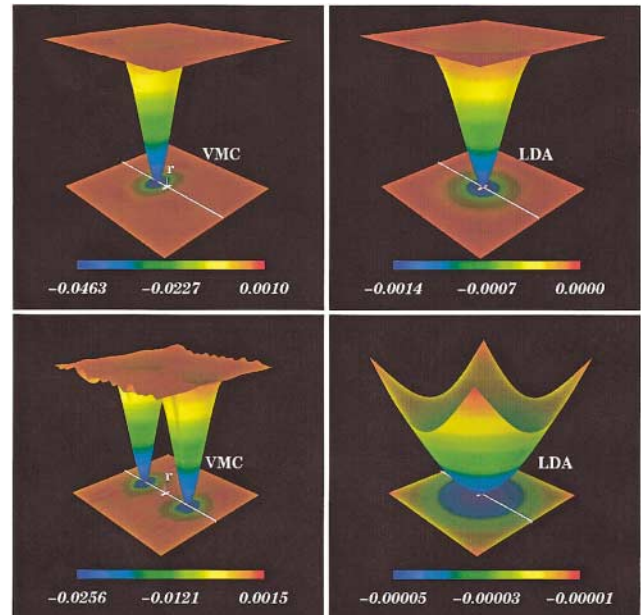


FIG. 1 (color). The VMC and LDA $n_{xc}(\mathbf{r}, \mathbf{r}')$ for the $q = 1.11k_F^0$ system plotted around an electron fixed at \mathbf{r} (indicated in the figure), with \mathbf{r}' ranging in a plane parallel to \mathbf{q} ; (top) electron on the slope; (bottom) electron at a density minimum. The solid line shows the direction parallel to \mathbf{q} (see Fig. 2 for the profile of the electron density along this line).

away from the electron (the small fluctuations of n_{xc}^{VMC} at this point are statistical errors). The LDA hole, by contrast, is spread over the whole system in order to satisfy the sum rule [7]: $\int d\mathbf{r}' n_{xc}^{LDA}(\mathbf{r}, \mathbf{r}') = -1$. This striking nonlocality of n_{xc}^{VMC} also occurs in the other two systems we considered, and similar nonlocal behavior has previously been observed for the exchange plus Coulomb hole of the hydrogen molecule [15]. Clearly, semilocal corrections are unable to significantly improve the LDA description of the XC hole in our systems, and fully nonlocal approximations are required. We found, however, that, despite the strong nonlocality of n_{xc}^{VMC} , the LDA errors in e_{xc}^{VMC} can be described in terms of a semilocal quantity, the Laplacian of the electron density.

In Fig. 2 we show $e_{xc}^{LDA} - e_{xc}^{VMC}$ for two of the strongly inhomogeneous systems studied, where e_{xc}^{LDA} is calculated using the exact ground-state density $n(\mathbf{r})$. (The very similar graph for the third system has been omitted to save space.) The results are plotted along a line parallel to \mathbf{q} (we call this direction y). Also shown are $n(\mathbf{r})$ and $\nabla^2 n(\mathbf{r})$ plotted along the same line. It is apparent that the shape, magnitude, and sign of the LDA errors in e_{xc} closely follow the shape, magnitude, and sign of $\nabla^2 n(\mathbf{r})$. The LDA errors in e_{xc} are large and negative in regions where $\nabla^2 n(\mathbf{r})$ is large and negative (around density maxima), and large and positive in regions where $\nabla^2 n(\mathbf{r})$ is large and positive. The GGA XC energy density is not defined via Eq. (1) and is not shown here [16]. The VMC values of the integrated E_{xc} are shown in Table I, along with the differences $\Delta E_{xc}^{LDA} = E_{xc}^{LDA} - E_{xc}^{VMC}$ and $\Delta E_{xc}^{GGA} = E_{xc}^{GGA} - E_{xc}^{VMC}$ (the version of the GGA used here is due to Perdew, Burke, and Ernzerhof [2]). The LDA errors in E_{xc} reflect the profound effect of the Laplacian errors in e_{xc} and change sign from positive (for the

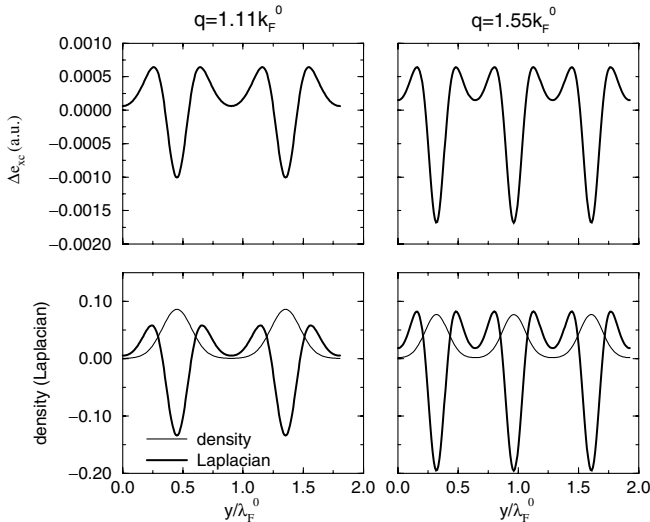


FIG. 2. The upper graphs show $e_{xc}^{LDA} - e_{xc}^{VMC}$ along a direction parallel to \mathbf{q} for two different strongly inhomogeneous systems. The lower graphs show the corresponding electron densities (light lines) and Laplacians (heavy lines). Distances are in units of the Fermi wavelength $\lambda_F^0 = 2\pi/k_F^0$.

$q = 1.11k_F^0$ system) to negative (for the two other systems) as q increases and the negative contributions to Δe_{xc} , which occur where $\nabla^2 n(\mathbf{r}) < 0$, become dominant. The GGA corrections are by construction *always* negative [2–4]; they improve E_{xc}^{LDA} for the $q = 1.11k_F$ system but worsen it for the two other systems. We note that GGA corrections also worsen the LDA in quasi-two-dimensional electron gases [17], a shortcoming shared by the recently proposed meta-GGA (MGGA) [18]. Although our systems are not quasi two dimensional [19], we believe that a similar semilocal effect lies behind the failure of the GGA in both cases, namely, an increasing negative contribution to the LDA errors in e_{xc} originating from the strongly negative Laplacian around the peak of $n(\mathbf{r})$. Similar errors are known to occur near the nuclei in molecules, but are overcompensated by positive errors in the bonding and outer regions [20]. We note that, since $\nabla^2 n(\mathbf{r})$ integrates to zero, an energy-density correction proportional to $\nabla^2 n(\mathbf{r})$ would not improve E_{xc}^{LDA} . As shown below, however, the dependence on $\nabla^2 n$ observed here is nonlinear.

The exchange-correlation energy density is a unique functional of the electron density. Provided that the electron density has a convergent Taylor expansion about the point \mathbf{r} , it can therefore be written as $e_{xc}(\mathbf{r}, [n]) = e_{xc}[\mathbf{r}, n(\mathbf{r}), \nabla_i n(\mathbf{r}), \nabla_i \nabla_j n(\mathbf{r}), \dots]$. The GGA may be viewed as an attempt to approximate this mapping by a nonlinear function of $n(\mathbf{r})$ and $\nabla_i n(\mathbf{r})$ only. In the case of the exchange energy (although not, unfortunately, the correlation energy), a uniform scaling argument [21] shows that $e_x = F_x(s, l, \dots)e_x^{LDA}$, where e_x is the exact (density-functional) exchange-energy density obtained from $\Psi^{\lambda=0}$ [9], F_x is an enhancement factor, e_x^{LDA} is the exchange-energy density within the LDA, and $s = |\nabla n|/[2k_F(\mathbf{r})n(\mathbf{r})]$ and $l = \nabla^2 n/[4k_F^2(\mathbf{r})n(\mathbf{r})]$ are a dimensionless gradient and a dimensionless Laplacian, respectively. Figures 3a and 3b are scatter plots comparing the values of F_x at different points in space with the values of s and l at those points. Because $n(\mathbf{r})$ appears in the denominator of l and s , the maximum absolute values of l and s occur where the electron density is smallest and are largest for the $q = 1.11k_F$ system.

The two-valued nature of Fig. 3a arises because the mapping from s to position is two-valued in our systems. For example, s is zero at both the minimum and the maximum of the density, where the required corrections to the LDA exchange hole are completely different, as can be inferred from Fig. 1 [22]. In sharp contrast, Fig. 3b shows

TABLE I. Exchange-correlation energies (Hartrees per electron) and the LDA and GGA errors in this quantity for different values of the wave vector \mathbf{q} . The statistical errors in E_{xc}^{VMC} are indicated.

q/k_F^0	E_{xc}^{VMC}	ΔE_{xc}^{LDA}	ΔE_{xc}^{GGA}
1.11	-0.3289 ± 0.001	+0.0042	+0.0001
1.55	-0.3127 ± 0.001	-0.0005	-0.0074
2.17	-0.2882 ± 0.001	-0.0066	-0.0140

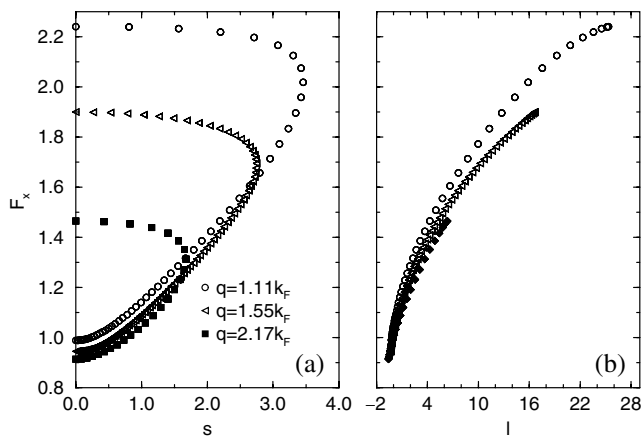


FIG. 3. The left panel (a) plots values of the exact exchange enhancement factor F_x against values of the reduced density gradient for three strongly inhomogeneous systems. The right panel (b) plots values of the exact exchange enhancement against values of the reduced density Laplacian.

that F_x is a simple and almost unique function of l , with the physically different regions around the maximum and the minimum of the density corresponding to regions of negative and positive Laplacian, respectively. This suggests that the inclusion of Laplacian terms may allow the construction of simpler and more accurate approximate functionals. Springborg and Dahl recently reached a similar conclusion [23] based on their studies of the exchange-energy densities of closed shell atoms, although their definition of e_x differs from ours. In most gradient expansions, the Laplacian terms allowed by symmetry are transformed into $|\nabla n(\mathbf{r})|^2$ terms via an integration by parts. This is possible only when the dependence on l is linear, however, which is not the case here, as can be seen from Fig. 3b. Furthermore, the integration by parts destroys the physical interpretation in terms of the XC hole and so hinders further progress. We note that there is a one-to-one relationship between position and l in each of our systems, and so an enhancement factor of the form $F_x(l)$ might not be as universal as Fig. 3b suggests. However, the consistent results obtained for all three systems, the energetic significance of the Laplacian terms, and the strong similarities between the form of the Laplacian and the LDA errors in e_{xc} (see Fig. 2) give us confidence in the physical importance of the Laplacian in describing inhomogeneity corrections to the LDA.

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