Unambiguous exchange-correlation energy density

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An exact exchange-correlation energy density is constructed using only knowledge of the density dependence of the exchange-correlation energy functional, E_{XC}. The energy density does not depend on the choice of origin, and allows direct comparison between any functional approximation and the exact quantity. The asymptotic behavior of this energy density contains the exact ionization potential. The relative performance of approximation energy functionals is reflected in this energy density, i.e., the local approximation is moderately accurate, generalized gradient approximations work better, while hybrids with exact exchange work best. The intershell spike in atoms is highlighted in this energy density. The energy density can also be calculated for solids, and has implications for many areas of density-functional theory. © *1998 American Institute of Physics.* [S0021-9606(98)30243-3]

I. INTRODUCTION

Density-functional theory is rapidly gaining popularity in quantum chemistry[1] as a relatively inexpensive yet accurate method for finding ground-state energies of electrons. Modern algorithms allow treatment of biologically interesting molecules with near chemical accuracy.[2] The only approximation made in practical ground-state density functional calculations is to the exchange-correlation energy as a functional of the electron density, often written in the form

$$E_{XC}[\rho] = \int d^3r \, e_{XC}[\rho](\mathbf{r}). \qquad (1)$$

where $e_{XC}[\rho](\mathbf{r})$ is called the exchange-correlation energy density. Note that the energy density is ambiguous, as one can always add any quantity whose integral over all space vanishes (e.g., $C\nabla^2\rho$, where C is a constant). Within the local density approximation (LDA), the conventional form is $e_{XC}^{\text{unif}}[\rho(\mathbf{r})]$, the exchange-correlation energy density of a uniform gas,[3,4] while a generalized gradient approximation (GGA) includes a gradient dependence, $e_{XC}^{\text{GGA}}(\rho,\nabla\rho)$. Popular GGA's are Becke-Lee-Yang-Parr (BLYP)[5] and Perdew-Burke-Ernzerhof (PBE)[6] (and its predecessors[7,8]). Hybrids[9,10] of GGA with exact exchange may be written $e_{XC}^{\text{hyb}} = a(e_X - e_{XC}^{\text{GGA}}) + e_{XC}^{\text{GGA}}$, where a is a universal constant, typically about 25%.

There has long been a desire to make comparisons between exact and approximate energy densities. But to make such a comparison meaningful, it must be possible to extract the same quantity from both the exact and approximate theories. Such a definition would have two principal uses. Firstly, for the development of density functionals, comparison of the exact quantity with functional approximations for model systems should tell which regions of space and which features require most effort to improve in the approximate functionals. Secondly, for much larger systems, at the level of accuracy at which a given energy functional can be believed,

the corresponding energy density will give a map of the system, which would show where the significant contributions to the energy density are coming from. In particular, an exchange-correlation energy density could show which regions in space contribute to certain physical properties. In covalent bonds, left–right correlation affects bond energies, and its effect can be seen in the bonding region.[11] Recently, correct treatment of core-valence effects has been identified as important for obtaining accurate energies,[12] and may arise from the intershell region. Contributions to ionization potentials should arise from the valence region, etc.

To understand why previous constructions do *not* meet the above criteria, consider the following definition of an energy density:

$$e_{XC}^{\text{wave fn.}}(\mathbf{r}) = \int d^3r' \, \frac{P(\mathbf{r},\mathbf{r}') - \rho(\mathbf{r})\rho(\mathbf{r}')}{2|\mathbf{r}-\mathbf{r}'|}$$
$$+ \frac{1}{2}\nabla^2\{\gamma(\mathbf{r},\mathbf{r}') - \gamma_s(\mathbf{r},\mathbf{r}')\}|_{\mathbf{r}=\mathbf{r}'}, \qquad (2)$$

where $P(\mathbf{r},\mathbf{r}')$ is the pair density (or diagonal second-order reduced density matrix) and $\gamma(\mathbf{r},\mathbf{r}')$ is the first-order density matrix, with γ_s being its Kohn–Sham counterpart. (We use atomic units, in which $e^2 = \hbar = m_e = 1$, throughout this paper). Integration over all space of Eq. (2) yields

$$E_{XC} = V_{ee} - U + T - T_S, \qquad (3)$$

where V_{ee} is the interelectronic repulsion, U is the Hartree energy, T is the physical kinetic energy, and T_s is the non-interacting (Kohn–Sham) kinetic energy. This definition has been used to great effect by Baerends, Gritsenko, and co-workers, in density-functional studies of chemical bonding.[11,13–15] To construct $e_{XC}^{\text{wave fn.}}(\mathbf{r})$, they perform an accurate configuration interaction (CI) wave-function calculation, from which they can extract $\rho(\mathbf{r})$, $P(\mathbf{r},\mathbf{r}')$, and $\gamma(\mathbf{r},\mathbf{r}')$. They also construct the Kohn–Sham potential corresponding to this density,[16] producing highly accurate Kohn–Sham orbitals, from which they find γ_s. Other groups have adopted the same definition,[17] and also studied $T_C = T - T_S$, the kinetic contribution to the correlation energy, de-

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fined in this way.[18] These exact energy densities have been calculated for small atoms, and homogeneous and inhomogeneous diatomic molecules.[14,15,19] A slightly different form occurs if one begins from the adiabatic connection formula,[20] which subsumes the kinetic correlation contribution into a coupling-constant integration over the potential contribution

$$e_{XC}^{\text{adia.}}(\mathbf{r}) = \int_0^1 d\lambda \int d^3r' \, \frac{P_\lambda(\mathbf{r},\mathbf{r}') - \rho(\mathbf{r})\rho(\mathbf{r}')}{2|\mathbf{r}-\mathbf{r}'|}, \qquad (4)$$

This is used in the work of Perdew and co-workers[21] and has been calculated for bulk Si by Hood et al.[22]

The difficulty arises if one wishes to compare these energy densities with the conventional ones for approximate functionals, such as $e_{XC}^{\text{LDA}}(\mathbf{r}), e_{XC}^{\text{GGA}}(\mathbf{r}), e_{XC}^{\text{hyb}}(\mathbf{r})$, because the conventional ones are *not* typically approximations to $e_{XC}^{\text{wavefn}}(\mathbf{r})$ in Eq. (2), nor is there any reason to expect that they should be. [A possible exception to this is the energy density of Becke88 exchange, which was designed to reproduce the exchange limit of Eq. (2) at large distances from finite systems.] The conventional forms are simply convenient representations of the approximate functionals, and can be changed by an integration by parts. For example, the original LYP correlation[23] functional contained the Laplacian of the density, but this was removed by an integration by parts to give a simpler form in terms of the gradient alone.[24] These integrations do not alter the resulting energy functional, but can dramatically alter the energy density, as the Laplacian is very sensitive to interesting features in the density.[25] The essential point is that approximations are made to the integrated exchange-correlation *energy*, and generally do not imply that the conventional energy density is an approximation to any specific choice of exact energy density. This point is made strongly in the work of Perdew and co-workers, who argue that in constructing GGA's, only the *system-averaged* exchange-correlation hole is approximated, not its value at each $\mathbf{r}$.[26,27] Specifically, the gradient expansion for exchange produces a Laplacian contribution to the energy density which diverges for a Coulombic interelectron interaction (but which integrates to zero).[28]

II. CONSTRUCTION OF ENERGY DENSITY

A. Virial energy densities

To define energy densities which are *uniquely* determined by the corresponding energy functional, we use the virial theorem[29]

$$E_{XC} + T_C = -\int d^3r \rho(\mathbf{r})\mathbf{r}\cdot\nabla v_{XC}(\mathbf{r}), \qquad (5)$$

where $v_{XC}(\mathbf{r}) = \delta E_{XC}/\delta\rho(\mathbf{r})$ is the exchange-correlation potential. This may be converted into an expression for E_{XC} alone, since[29,30]

$$T_C[\rho] = -E_C[\rho] + \partial E_C[\rho_\gamma]/\partial\gamma|_{\gamma=1}, \qquad (6)$$

where $\rho_\gamma(\mathbf{r}) = \gamma^3\rho(\gamma\mathbf{r})$, Thus Eq. (5) may be rewritten with $E_X[\rho_\gamma] + dE_C[\rho_\gamma]/d\gamma$ on the left, and $v_{XC}[\rho_\gamma]$ on the right. Integrating over γ, we find, at $\gamma=1$

$$e_{XC}^{\text{vir}}[\rho](\mathbf{r}) = -\rho(\mathbf{r})\mathbf{r}\cdot\nabla\widetilde{v}_{XC}[\rho](\mathbf{r}) \qquad (7)$$

where

$$\widetilde{v}_{XC}[\rho](\mathbf{r}) = \int_0^1 \frac{d\gamma}{\gamma} v_{XC}[\rho_\gamma]\left(\frac{\mathbf{r}}{\gamma}\right). \qquad (8)$$

We call $\widetilde{v}_C$ the hypercorrelated potential,[31] since it includes $\gamma < 1$, where the system is more correlated than at $\gamma = 1$, the physical value. This result was derived earlier in different form by van Leeuwen and Baerends,[32] and requires that the exchange-correlation energy vanish at $\gamma = 0$, which has been proven.[33]

While the virial energy density of Eq. (7) is solely determined by the density dependence of $E_{XC}[n]$, and therefore, allows comparison between approximate and exact quantities, it has several unappealing features.

Firstly, the virial energy density depends on the choice of origin in Eq. (1). When the origin is shifted, the virial energy density changes shape. In applications to molecules, a large antisymmetric peak appears around nuclei off the origin, whose physical significance is unclear, as its net contribution to the exchange-correlation energy is almost zero.[33]

Secondly, it has a perverse form when applied to extended systems. The factor $\mathbf{r}$ increases without bound as one traverses a solid, i.e., the virial energy density of Eq. (7) is *not* a periodic function of $\mathbf{r}$, even when $\rho(\mathbf{r})$ and $v_{XC}(\mathbf{r})$ are. This leads to an energy density which becomes extremely large at one side of the solid.

Thirdly, within LDA, $\widetilde{v}_{XC}^{\text{unif}}(\mathbf{r}) = \int_0^1 d\gamma v_{XC}^{\text{unif}}[\gamma^3\rho(\mathbf{r})]/\gamma$, where $v_{XC}^{\text{unif}}(\rho) = de_{XC}^{\text{unif}}(\rho)/d\rho$, so that

$$\rho(\mathbf{r})\nabla\widetilde{v}_{XC}^{\text{LDA}}(\mathbf{r}) = v_{XC}^{\text{unif}}(\rho)\nabla\rho/3, \qquad (9)$$

yielding a gradient-dependent LDA virial energy density. Thus in application to a jellium sphere, all the energy density would lie on the surface, even within LDA! Clearly, energy densities with these deficiencies defy simple physical interpretation.

B. Helmholtz construction

In their original work on the virial theorem, Levy and Perdew[29] showed how Eq. (9) recovers the usual LDA energy density, by using

$$\nabla e_{XC}^{\text{unif}}(\rho) = \frac{de_{XC}^{\text{unif}}}{d\rho}\nabla\rho = v_{XC}^{\text{unif}}\nabla\rho. \qquad (10)$$

Thus

$$E_{XC}^{\text{LDA}} = -\tfrac{1}{3}\int d^3r\{\mathbf{r}\cdot\nabla e_{XC}^{\text{unif}}[\rho(\mathbf{r})]\}. \qquad (11)$$

A simple integration by parts then yields

$$E_{XC}^{\text{LDA}} = \int d^3r e_{XC}^{\text{unif}}[\rho(\mathbf{r})], \qquad (12)$$

the conventional form.

We generalize Eq. (11) to the exact exchange-correlation energy functional. Since $\rho\nabla\widetilde{v}_{XC}$ defines a vector field over all space which vanishes rapidly at the boundary, the Helmholtz theorem allows us to write it as a source plus curl contribution:

$$3\rho(\mathbf{r})\nabla\tilde{v}_{XC}(\mathbf{r})=\nabla e_{XC}^{\text{unamb}}(\mathbf{r})+\nabla\times\mathbf{a}_{XC}^{\text{unamb}}(\mathbf{r}). \tag{13}$$

Inserting this form into Eq. (7) and integrating over all space, one finds the curl term vanishes, and Eq. (1) is recovered. Thus $e_{XC}^{\text{unamb}}(\mathbf{r})$ defined by Eq. (13) is indeed an energy density. Choosing vanishing boundary conditions at infinity, we find

$$e_{XC}^{\text{unamb}}(\mathbf{r}')=-\frac{3}{4\pi}\int d^3r\,\frac{\nabla\cdot[\rho(\mathbf{r})\nabla\tilde{v}_{XC}(\mathbf{r})]}{|\mathbf{r}-\mathbf{r}'|}. \tag{14}$$

Equations (13) and (14) are the central results of this work. The first is an implicit definition of our exchange-correlation energy density, while Eq. (14) is its explicit solution. All results can be easily generalized to spin-density-functional theory. Note that the same procedure, applied directly to the exchange-correlation potential, yields (three times) the exchange-correlation pressure of Nagy and Parr (Eq. (24) of Ref. 34).

At this point, it is instructive to contrast the unambiguous energy density with earlier choices. Both Eqs. (2) and (4). require knowledge of the reduced density matrices for the system, whereas the the unambiguous energy density requires only knowledge of the density dependence of the energy functional, to first construct the exchange-hypercorrelated potential of Eq. (8), and thus the energy density in Eq. (14). Furthermore, in contrast to Eq. (7), there is no change of shape with origin. This is due to the integration by parts in the derivation of Eq. (14), which removes the explicit origin-dependence in Eq. (7).

III. PROPERTIES OF THE UNAMBIGUOUS ENERGY DENSITY

A. Exact properties

An immediate application of Eq. (14) is as a consistency test between the energy and the potential in either exact or approximate calculations, where it suffers none of the difficulties of the virial expression Eq. (7). This test should be very useful for exact exchange-only calculations, which are now possible for atoms and molecules[35] within the optimized effective potential approach,[36] because E_X can be extracted directly from $v_X(\mathbf{r})$.

When a system is spherically symmetric, Eq. (14) simplifies to

$$e_{XC}^{\text{unamb}}(r')=-3\int_{r'}^{\infty}dr\,\rho(r)\,\frac{d\tilde{v}_{XC}}{dr}. \tag{15}$$

Far from an atom, the density decay is exponential, and determined by the ionization potential, so that

$$e_{XC}^{\text{unamb}}(r)\rightarrow-\frac{3\rho(r)}{2\alpha r^2}\quad r\rightarrow\infty, \tag{16}$$

where $\alpha=\sqrt{2I}$ and I is the ionization potential. For the hydrogen atom, we find

$$e_X^{\text{unamb}}(r)=\frac{3}{\pi}\left\{2[E_1(2r)-E_1(4r)]+\frac{e^{-2r}}{r}\right.$$
$$\left.+e^{-4r}\left[\frac{1}{2}+\frac{1}{r}\right]\right\}, \tag{17}$$

where $E_1(x)=\int_1^{\infty}dt\,\exp(-xt)/t$.

Integrating the unambiguous energy density of Eq. (14) yields

$$E_{XC}=-\frac{3}{4\pi}\int d^3r'\int d^3r\,\frac{\nabla\cdot[\rho(\mathbf{r})\nabla\tilde{v}_{XC}(\mathbf{r})]}{|\mathbf{r}-\mathbf{r}'|}, \tag{18}$$

a form reminiscent of the adiabatic connection formula. However, there are several interesting differences. For example, the integration along coupling-constant (or equivalently, scaling parameter[37]) runs from the physical system to the strongly-correlated (or low-density limit), the reverse of the usual case. This form may inspire new routes for investigating $E_{XC}[\rho]$. For example, functional differentiation yields

$$v_{XC}(\mathbf{r}')=\frac{3}{4\pi}\int d^3r\nabla\cdot\left\{\frac{\nabla\tilde{v}_{XC}(\mathbf{r})}{|\mathbf{r}'-\mathbf{r}|}\right\}$$
$$-\frac{3}{4\pi}\int d^3r\nabla\tilde{f}_{XC}(\mathbf{r}',\mathbf{r})\cdot\int d^3r''\frac{\nabla''n(\mathbf{r}'')}{|\mathbf{r}-\mathbf{r}''|}, \tag{19}$$

where $f_{XC}(\mathbf{r},\mathbf{r}')=\delta v_{XC}(\mathbf{r})/\delta\rho(\mathbf{r}')$ is the exchange-correlation kernel. This equation may be applied to exchange alone, as a test of models[38] for $f_X(\mathbf{r},\mathbf{r}')$, when the exact $v_{XC}(\mathbf{r})$ is known.

We may also apply the Helmholtz construction to find the curl term defined by Eq. (13)

$$\mathbf{a}_{XC}^{\text{unamb}}(\mathbf{r}')=\frac{3}{4\pi}\int d^3r\,\frac{\nabla\rho(\mathbf{r})\times\nabla\tilde{v}_{XC}(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}, \tag{20}$$

which vanishes whenever $\nabla\rho$ and $\nabla\tilde{v}_{XC}$ are parallel everywhere, such as in a spherically symmetric system.

Note that our requirements for an energy density still do not uniquely determine $e_{XC}(\mathbf{r})$. One could add, e.g., $\nabla^2\{v_{XC}^{\text{unif}}[\rho(\mathbf{r})]-v_{XC}(\mathbf{r})\}$ to Eq. (14), and still have an energy density determined solely by the density dependence of the energy functional, and reducing to $e_{XC}^{\text{unif}}[\rho(\mathbf{r})]$ in LDA.

B. Approximate functionals

Since the right-hand-side of Eq. (14) is given in terms of the (scaled) potential and the density, $e_{XC}^{\text{unamb}}(\mathbf{r})$ is solely determined by the density dependence of $E_{XC}[\rho]$. Thus, given any approximation $E_{XC}^{\text{approx}}[\rho]$, one can (fairly easily) deduce the corresponding approximate $e_{XC}^{\text{unamb}}[\rho](\mathbf{r})$ via Eqs. (8) and (14). In particular, use of Eq. (9) shows that $e_{XC}(\mathbf{r})\rightarrow e_{XC}^{\text{unif}}[\rho(\mathbf{r})]$ when $E_{XC}\rightarrow E_{XC}^{\text{LDA}}$. Thus we expect $e_{XC}^{\text{unif}}[\rho(\mathbf{r})]$ to be a moderately accurate, extremely reliable approximation to $e_{XC}(\mathbf{r})$, just as E_{XC}^{LDA} is to E_{XC}. Furthermore, differences between $e_{XC}^{\text{unif}}[\rho(\mathbf{r})]$ and $e_{XC}^{\text{unamb}}(\mathbf{r})$ will highlight the limitations of LDA.

Note that a GGA energy functional depending only on the density and its gradient at a point

$$E_{XC}^{\text{GGA}}=\int d^3r\,e_{XC}^{\text{GGA}}[\rho(\mathbf{r}),\nabla\rho(\mathbf{r})], \tag{21}$$

when inserted into Eq. (14), produces an unambiguous energy density which includes several higher order gradients. Thus the unambiguous energy density differs from the con-
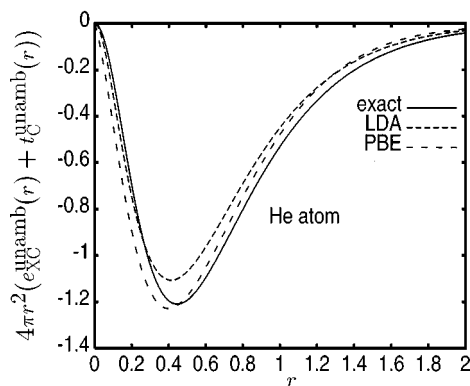
FIG. 1. Radial unambiguous exchange-correlation plus kinetic-correlation energy density for the He atom (atomic units).

TABLE I. Energy components in hartrees for several atoms, evaluated on exact densities (Ref. 46).

	Energy	Exact	LSD	PBE	BLYP
He	$E_{XC}+T_C$	-1.030	-0.928	-1.017	-1.035
Ne	$E_{XC}+T_C$	-12.15	-11.27	-12.09	-12.22
Ne	E_{XC}	-12.48	-11.76	-12.40	-12.51

sities. Strictly speaking, the virial theorem applies only to self-consistent calculations. However, the difference between the energy evaluated directly from the density and from the virial theorem applied to that density are so small that it has no effect on the digits reported in Table I. The small magnitude of $|E_C+T_C|$ reflects the insensitivity[47] of E_C to coordinate scaling in Eq. (6).

We note the general features of these curves. First, the LDA curve is less negative than the exact curve for most values of $\mathbf{r}$, reflecting its typical underestimate of the exchange-correlation energy. Next, GGA (here choosing PBE as a representative example) significantly improves on LDA, especially in the region of greatest weight, although still having a small error of changing sign.

Next we look in more detail. Figure 2 shows the error made by functional approximations to the unambiguous energy density for He. All functionals demonstrate a cancellation of errors in the integral, but this cancellation is poorest for LDA, leading to a significantly greater error in the energy. We note also that BLYP appears noticeably worse than PBE. This is due to the lack of kinetic correlation in BLYP, so that there is less successful cancellation between $e_C(\mathbf{r})$ and $-t_C(\mathbf{r})$. BLYP would probably outperform PBE in a comparison of $e_C(\mathbf{r})$ alone, just as it does for the integrated energy (see Table I). Finally, note how hybridizing the GGA with exact exchange (in this case, we chose a 25% mixture with PBE) significantly reduces the error in the unambiguous energy density.

The same overall features are found for Be and Ne. However, these atoms also exhibit some shell structure, which provides a much keener test of the energy density. Figure 3 is analogous to Fig. 1, but zooms in on the shell structure region in Ne. Here we see clearly the improvement of PBE over BLYP, and both over LDA.

ventional one used for these functionals, as will be illustrated below. One can also show that there is no GGA whose unambiguous energy density as given by Eq. (14) depends only on the density and its gradient at $\mathbf{r}$.

As mentioned above, the Becke 88 exchange functional was customized to reproduce the exchange limit of Eq. (2) at large distances from finite systems. It is well-known that the resulting asymptotic potential is incorrect. If, on the other hand, the *potential* had been fitted, then the unambiguous energy density would also be correct. This philosophy was followed by Engel and Vosko,[39] so that their exchange GGA reproduces the correct unambiguous exchange energy density at large distances.

These arguments apply equally to correlation. GGA's constructed to fit the potential[40,41] will fit the unambiguous energy density as well. In this regard, fitting the unambiguous energy density has the advantage of automatically fitting the integrated energy. Note that questions concerning constants in the potential[42–45] do not arise here, as Eq. (14) depends only on the gradient of the potential.

IV. CALCULATIONS OF UNAMBIGUOUS ENERGY DENSITY

A. Finite systems

Exact calculation of the unambiguous energy density is complicated by the need to scale the density to find the hypercorrelated potential. This makes it difficult to compare with the results of wave function calculations, which yield v_{XC} only at $\gamma=1$. This problem may be side stepped, by applying Eq. (14) directly to v_{XC} itself, yielding, from Eq. (5)

$$e_{XC}^{\text{unamb}}(\mathbf{r})+t_C^{\text{unamb}}(\mathbf{r})=-\frac{3}{4\pi}\int d^3r\,\frac{\nabla\cdot[\rho(\mathbf{r})\nabla v_{XC}(\mathbf{r})]}{|\mathbf{r}-\mathbf{r}'|},$$

(22)

which integrates to $E_{XC}+T_C$. The kinetic contribution can be calculated from accurate wave functions, by constructing the Kohn–Sham kinetic energy from the density, as discussed above. In Fig. 1, we plot the radial unambiguous energy density for $E_{XC}+T_C$ for the He atom, both exactly and within several typical approximations. All calculations were performed by applying approximate functionals to exact den-
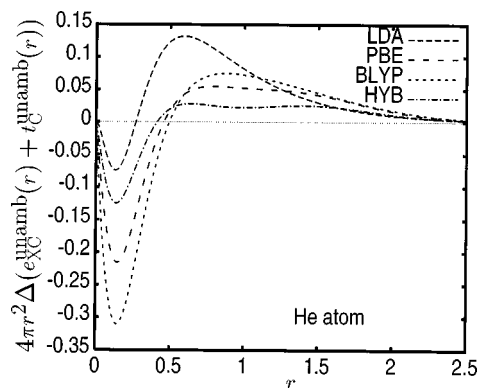

FIG. 2. Error in radial unambiguous exchange-correlation plus kinetic-correlation energy density for the He atom (atomic units).

FIG. 3. Radial unambiguous exchange-correlation plus kinetic-correlation energy density, for the Ne atom (atomic units).
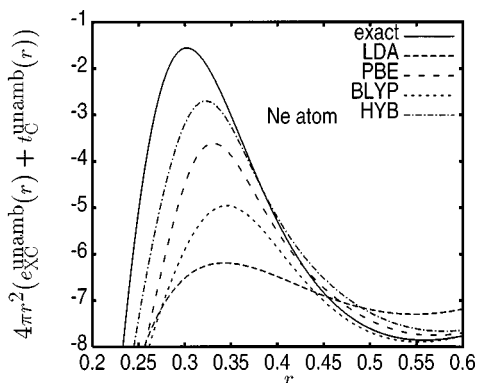

FIG. 5. Error in radial unambiguous exchange-correlation plus kinetic-correlation energy density, for the Ne atom (atomic units).

To demonstrate that these qualitative effects also occur in $e_{XC}^{unamb}(\mathbf{r})$, we repeat Fig. 3, but plotting $e_{XC}^{unamb}(\mathbf{r})$, in Fig. 4. We have also plotted the conventional GGA energy densities, and see that these curves are far less effective in showing the shell structure. The Helmholtz construction depends on the Laplacian and higher-order gradients of the density, whereas the conventional definitions do not.

Lastly, in Fig. 5, we show the outer electron region in Ne. This figure shows how much the hybrid improves upon the GGA in these chemically important regions. Interestingly, the GGA's do *worse* than LDA here.

Note that the unambiguous energy density partially resolves an important question raised about the potentials of GGA and other approximate functionals. It is well-known that many GGA's, while producing very accurate energies, can yield potentials which look quite different from the corresponding exact quantities.[40,48] In Fig. 6, we plot the correlation plus kinetic correlation energy per electron

$$\epsilon_C^{unamb}(\mathbf{r}) + \tau_C^{unamb}(\mathbf{r}) = [e_C^{unamb}(\mathbf{r}) + t_C^{unamb}(\mathbf{r})]/\rho(\mathbf{r}), \tag{23}$$

for the He atom. Comparison with Fig. 3 of Ref. 17 shows that this Helmholtz construction yields an energy per electron quite similar $e_{XC}^{wave\ fn}$, which was used there. The figure shows that many of the poor qualities of the potential occur also in this correlation energy per particle: GGA's diverge at

the nucleus,[40] decay too rapidly, and sometimes even appear to be upside down. However, contrast this figure with all the preceding figures. This comparison shows the importance of studying quantities whose integral yields the energy, as that shows which errors are significant. For example, constants in the potential do not contribute to the unambiguous energy density, small r behavior is unimportant because of phase space factors, while asymptotic behavior is unimportant because of the density-weighting factor.[21,49] Thus the potentials of GGA's are not as poor as they appear, because they lead to good unambiguous energy densities.

It has also been argued that local and semilocal functionals can yield accurate system-averaged quantities such as energies and system-averaged exchange-correlation holes, but not point-wise quantities such as the potential, since these continuous approximations cannot capture the derivative discontinuity of the exact functional.[45] Note that our expression Eq. (14) *contains* a system-average in the integration over the second variable, so that even when potentials look poor, the energy densities look good.

B. Extended systems

For solids, Eq. (14) has interesting consequences. From Eq. (13), we can determine $e_{XC}^{unamb}(\mathbf{r})$ everywhere within a unit cell, but only up to a constant. We may write
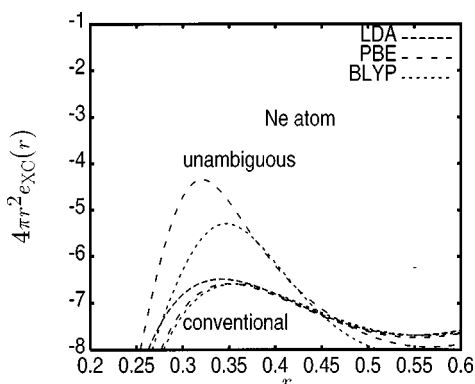

FIG. 4. Functional approximations to the radial unambiguous exchange-correlation energy density, for the Ne atom (atomic units) and the corresponding conventional energy densities.
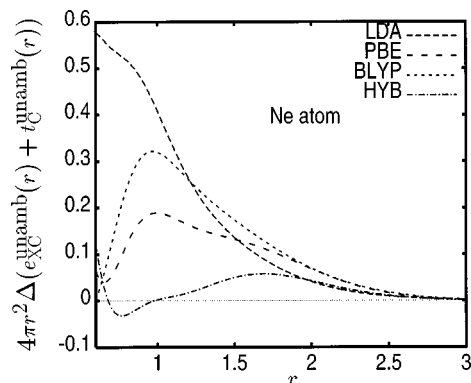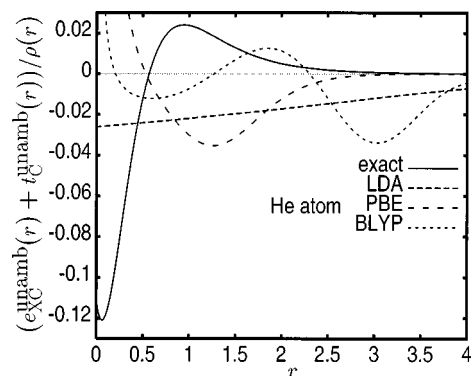

FIG. 6. Unambiguous exchange-correlation plus kinetic-correlation energy per electron for the He atom (atomic units).

$$E_{XC}^{\text{cell}} = \int_{\text{cell}} d^3 r \left[e_{XC}^{\text{unamb}}(\mathbf{r}) - e_{XC}^{\text{unamb}}(\mathbf{r}_0) \right] + V_{\text{cell}} e_{XC}^{\text{unamb}}(\mathbf{r}_0),$$

(24)

where $\mathbf{r}_0$ is some point within the cell, and V_{cell} is the volume of the cell. Then $e_{XC}^{\text{unamb}}(\mathbf{r}_0)$ is determined by the condition that $e_{XC}^{\text{unamb}}(\mathbf{r})$ vanishes *outside* the system, i.e., via Eq. (14) applied to a solid with a surface. This point is best illustrated in the case of a jellium sphere. Then the value of e_{XC}^{unamb} within the interior is determined by integrating Eq. (15) through the surface. Thus $e_{XC}^{\text{unamb}}(\mathbf{r}_0)$ is a purely bulk property, but one which can be calculated by an integral through the surface and must, therefore, be independent of the surface profile. Jellium sphere calculations within LDA and GGA confirm this point. Note that this effect does *not* signify any extreme nonlocality in the functional, as the bulk value is independent of the surface profile. The effect occurs even within LDA, and so may be considered as an artifact of the Helmholtz construction of the energy density.

V. CONCLUSIONS AND IMPLICATIONS

Equation (14) gives a new formula for the exchange-correlation energy of density-functional theory. In particular, it defines an energy density which is solely determined by the density dependence of the exchange-correlation energy functional. Thus it allows for unambiguous comparison of approximate and exact energy densities.

Many interesting properties in density-functional theory can be reconsidered in the light of Eq. (14), to examine their consequences for the energy density. For example, how near-sighted is this energy density, in the sense of how much is it affected by far away changes in the density?[50] A qualitative answer is that, since LDA provides a rough approximation, and the LDA energy density is completely near-sighted, the exact energy density is hoped to be quite near-sighted also. (Note, however, that functional differentiation of the energy with respect to the density will partially undo some of the system average, so that approximate functionals may not provide a good guide for the behavior of the exact quantity here.) Another example: LDA and GGA do not contain dispersive forces, because of their dependence solely on the density and its gradient at each point. Yet the exact energy density must contain these forces, so differences between these approximations and the exact quantity must become vital for this effect. Exploration of these and other questions is ongoing,[51] but beyond the scope of the present work.

The universal nature of Eq. (14) should allow the density and gradient analysis of exchange-correlation energies and their differences[52] to be performed in an unambiguous fashion.

The need for integration through a surface might limit the usefulness of this energy density as a consistency check for bulk calculations[22,53] of properties of solids. However, even without this feature, the energy density can be calculated from knowledge of its gradient and the energy itself, so that plots of the energy density can be made from calculations on a single cell in an infinite periodic system. For surface calculations, the independence of the bulk energy density on the surface profile should provide a check on calculations of surface electronic structure.

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