

Exchange–Correlation Energy Density from Virial Theorem

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Received: January 29, 1998

The virial of the exchange potential in density functional theory yields the exchange energy, but the virial of the correlation potential does not yield the correlation energy. Via the adiabatic connection formula, we define a hypercorrelated potential whose virial is exactly the correlation energy. This exchange–correlation energy density is *uniquely* determined by the exchange–correlation energy functional. We calculate the virial energy density both exactly and within several popular functionals, LDA, PBE, and BLYP, on several atoms. The well-known differences between the potentials generated by these functionals is reflected in this energy density. We speculate on how accurately the correlation energy can be estimated from knowledge of the exact density, and on the construction of an energy density hybrid.

I. Introduction

Kohn–Sham¹ spin density functional theory is a formally exact treatment of electron correlation. For practical calculations of ground-state energies, only the exchange–correlation energy $E_{xc}[\rho_\alpha, \rho_\beta]$ need be approximated as a functional of the spin densities. The local spin density (LSD) approximation E_{xc}^{LSD} has long been the mainstay of solid-state physics calculations,² but recently Kohn–Sham theory has also become extremely popular in quantum chemistry.³ This is due to the improvement in bond energies from use of generalized gradient approximations (GGAs)^{4–9} and hybrid energy functionals,^{10–14} which mix a fraction of exact exchange with GGA exchange–correlation. Typical bond energy errors are about 30 kcal/mol in LSD, 8 kcal/mol within GGA, and only 2–3 kcal/mol in hybrid schemes.¹⁰

However, these functional approximations are designed to reproduce exchange–correlation energies and differences in these energies upon atomization, bond rearrangement, bond stretching, etc. Other properties are not necessarily equally well approximated. In particular, the exchange–correlation *potential* is defined as the functional derivative of the exchange–correlation energy with respect to the spin density $\rho_\sigma(\mathbf{r})$,

$$v_{xc,\sigma}(\mathbf{r}) = \delta E_{xc} / \delta \rho_\sigma(\mathbf{r}) \quad (1)$$

Functionals which yield highly accurate energies often produce potentials which differ markedly from the exact ones.^{15–18}

In Figure 1, we plot the exact and approximate exchange potentials for the He atom within several popular functional approximations, evaluated on the very accurate density used by Umrigar and Gonze.¹⁵ We show only one representative exchange GGA, the Perdew–Burke–Ernzerhof (PBE),⁹ as others (PW91^{7,8,19,20} and Becke 88⁵) look quite similar on this scale. The functional approximations fail to capture^{21,22,16} the correct $-1/r$ behavior at large r and the quadratic behavior at small r . The GGA potentials in fact diverge as $r \rightarrow 0$, some

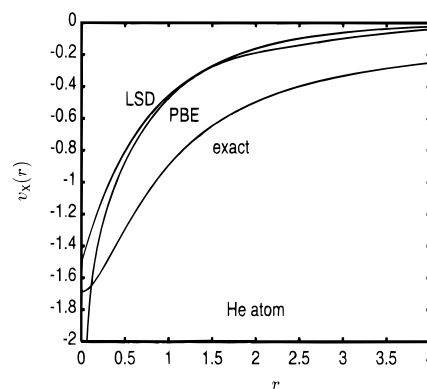


Figure 1. Exchange potential of the He atom (atomic units).

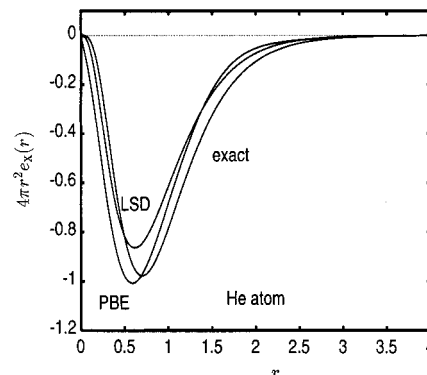


Figure 2. Radial virial exchange energy density for the He atom (atomic units).

have spurious extrema, and overall, look *worse* than their LSD counterparts. So how do they produce better energies?

In the case of exchange, there is a simple answer. Levy and Perdew²³ applied the virial to the interelectron Coulomb repulsion and proved (for finite systems)

$$E_x = - \int d^3r \rho(\mathbf{r}) \mathbf{r} \cdot \nabla v_x(\mathbf{r}) \quad (2)$$

In Figure 2, we plot the radial contribution to this integral. We use the exact density, and the approximate potentials evaluated

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on that density. The approximate curves all look similar to the exact curve, all being negative everywhere. The errors in the approximate potentials near $r = 0$ and as $r \rightarrow \infty$ are hidden by the $4\pi r^3 \rho(r)$ factor in the integrand of eq 2. The LSD curve even mirrors the 10% underestimate of the magnitude of the exchange energy, although the integrated PBE curve contains some “cancellation of errors,” as its error is only about 1%.

In a slightly different context, we point out the well-known difficulty of defining an exchange–correlation energy density that can be used as a test of approximate exchange–correlation energy functionals. A GGA exchange–correlation energy is usually written as an integral over an exchange–correlation energy density:

$$E_{xc}^{GGA} = \int d^3r e_{xc}^{GGA}(\rho_\alpha, \rho_\beta, \nabla\rho_\alpha, \nabla\rho_\beta) \quad (3)$$

with LSD being a special case, using $e_{xc}^{unif}(\rho_\alpha, \rho_\beta)$, the exchange–correlation energy density of a uniform gas.^{24,25} However, adding any quantity which integrates to zero to the energy density does not change the corresponding energy, so that e_{xc} does not have a single unique definition. Thus, there is an infinite number of choices for the energy density of a given energy functional, and use of a given approximate energy functional *does not* imply a specific choice of approximate energy density. To illustrate this essential point, consider the local density approximation for exchange. The energy density is usually written as $e_x^{unif}(\rho(\mathbf{r}))$, but for finite systems, may equally well be written as $-\rho(\mathbf{r})\mathbf{r}\cdot\nabla v_x^{unif}(\rho(\mathbf{r}))$, according to eq 2. Both choices yield $E_x^{LDA}[\rho]$, and use of LDA exchange does not imply either one of them. Similarly, various popular GGAs are derived in different ways, so that the corresponding energy densities may look quite different, while yielding similar energies. There are also several different ways to extract an exact energy density from a wave function calculation, usually based on the exchange–correlation hole.^{26–33} Unfortunately, there is no way to construct these specific energy densities directly from a given approximation to $E_{xc}[\rho_\alpha, \rho_\beta]$, and no reason why these definitions should correspond to a particular choice in eq 3 above. For example, the deviation of the PW91 exchange energy density involves an integration by parts,⁹ so that the standard form for this energy density is *not* the energy density of the exchange hole.

Equation 2 therefore has another important use. Following Engel and Vosko,³⁴ we may define a “virial” exchange energy density,

$$e_x(\mathbf{r}) = -\rho(\mathbf{r})\mathbf{r}\cdot\nabla v_x(\mathbf{r}) \quad (4)$$

such that $E_x = \int d^3r e_x(\mathbf{r})$. The significance of this definition is that the corresponding energy density is *uniquely* determined by $E_x[\rho_\alpha, \rho_\beta]$, via eqs 1 and 2. Thus all functional approximations may be meaningfully compared with the exact curve, as in Figure 2.

The purpose of the current work is to extend these ideas into the murky realm of correlation. This is not as straightforward as might be hoped, as the corresponding virial for the correlation potential is²³

$$E_c + T_c = -\int d^3r \rho(\mathbf{r})\mathbf{r}\cdot\nabla v_c(\mathbf{r}) \quad (5)$$

where T_c is the correlation contribution to the kinetic energy. Thus there is no simple route directly from the correlation potential to the correlation energy.³⁵ However, in section II, we show that, if the correlation potential at all adiabatic coupling constants λ is known, then a hypercorrelated potential may be

constructed whose virial *is* the correlation energy. This may be viewed as a recasting of the line integral formula of van Leeuwen and Baerends³⁶ in terms of the coupling constant, rather than a scaling of the density.

In section 3, we calculate this hypercorrelated potential and its virial energy density for the He atom, within several popular approximations. Unfortunately, we do not compare these curves with the exact virial correlation energy density, because we only have the exact potential at a single value of λ ($\lambda = 1$, the physical value). This drawback can be side-stepped by instead returning to eq 5. This defines a virial energy density for $E_c + T_c$, which *can* be extracted from a wave function calculation, and which can be compared with functional approximations. In fact, as we show, this provides a much tougher test for current functionals.

In the final section, we discuss two underlying motivations behind this study. The first is to achieve the most accurate answer to the question: Given the exact density, how well can we calculate the exact energy?³⁷ For the second note that, as mentioned above, hybrid schemes which mix exact exchange with GGA exchange–correlation have significantly reduced bond energy errors.^{10,38} Recently, these schemes have been (partially) justified by nonempirical procedures, applied to atomization energies.^{12–14} However, these procedures are flawed because they lead to different answers if applied to total energies rather than energy differences.³⁹ A hybrid of the energy density would overcome these flaws. We speculate on the possibility of such a scheme.

II. Virial Exchange–Correlation Energy Density

Our construction of a virial relation for the correlation energy begins with the generalization to arbitrary coupling constant of the constrained search definition^{40,41} of the universal functional of Hohenberg and Kohn:⁴²

$$F_\lambda[n] = \min_{\Psi_{\lambda-n}} \langle \Psi_\lambda | \hat{T} + \lambda \hat{V}_{ee} | \Psi_\lambda \rangle \quad (6)$$

where \hat{T} is the kinetic energy operator, \hat{V}_{ee} is the interelectronic Coulomb repulsion operator, and the minimization is over all wave functions yielding the given density $\rho(\mathbf{r})$. The coupling constant λ may be chosen to have any nonnegative value. For $\lambda = 1$, we recover the physical wavefunction and energies, for $\lambda = 0$ we get the Kohn–Sham wave function, in which just the kinetic energy is minimized, while for $\lambda \rightarrow \infty$ we achieve the extreme strong coupling limit, in which just the potential energy is minimized. We can then define the exchange–correlation energy as a function of λ via²³

$$E_{xc}^\lambda = F_\lambda - T_s - \lambda U \quad (7)$$

Note that our definition differs from that of ref 23 by a factor of λ . Then

$$E_{xc}^{\lambda'} = \int_0^{\lambda'} d\lambda \frac{\partial E_{xc}^\lambda}{\partial \lambda} \quad (8)$$

where

$$\frac{\partial E_{xc}^\lambda}{\partial \lambda} = E_{xc,\lambda} = V_{ee,\lambda} - U \quad (9)$$

since the λ -dependence of the wave function in eq 6 does not contribute to the first derivative, by virtue of the variational principle.

Next, we state the virial theorem at arbitrary λ , eqs 3 and 40 of ref 23:

$$E_{xc}^\lambda + T_c^\lambda = - \int d^3r \rho(\mathbf{r}) \mathbf{r} \cdot \nabla v_{xc}^\lambda(\mathbf{r}) \quad (10)$$

where

$$v_{xc}^\lambda = \delta E_{xc}^\lambda / \delta \rho(\mathbf{r}) \quad (11)$$

and $T_c^\lambda = \langle \Psi_\lambda | \hat{T} | \Psi_\lambda \rangle - T_s$ is the kinetic contribution to the correlation energy at coupling constant λ . At $\lambda = 1$, this is eq 5 of the introduction.

However, T_c is simply related to a coupling-constant derivative of the correlation energy (Bass' relation⁴³):

$$T_c^\lambda = E_c^\lambda - \lambda \frac{dE_c^\lambda}{d\lambda} \quad (12)$$

yielding

$$2E_{xc}^\lambda - \lambda \frac{dE_{xc}^\lambda}{d\lambda} = - \int d^3r \rho(\mathbf{r}) \mathbf{r} \cdot \nabla v_{xc}^\lambda(\mathbf{r}) \quad (13)$$

This is a first-order differential equation in λ . Solving by elementary means, we find

$$E_{xc}^\lambda = \lambda^2 \int_{\lambda_c}^\lambda d\lambda' \int d^3r \rho(\mathbf{r}) \mathbf{r} \cdot \nabla v_{xc}^{\lambda'} / \lambda'^3 \quad (14)$$

where λ_c is a constant yet to be determined. Now, $E_{xc,\lambda}$ should tend to a negative constant as $\lambda \rightarrow \infty$,⁴⁴ which implies $\lambda_c = \infty$. Thus we come to a virial for the exchange–correlation energy:

$$E_{xc}^\lambda = - \int d^3r \rho(\mathbf{r}) \mathbf{r} \cdot \nabla \tilde{v}_{xc}^\lambda(\mathbf{r}) \quad (15)$$

where

$$\tilde{v}_{xc}^\lambda = \lambda^2 \int_{\lambda_c}^\lambda \frac{d\lambda'}{\lambda'^3} v_{xc}^{\lambda'} \quad (16)$$

Note that the exchange contribution to this integral contributes in a simple fashion:

$$v_x^\lambda(\mathbf{r}) = \lambda v_x(\mathbf{r}) \quad (17)$$

yielding, correctly,

$$E_x^\lambda = \lambda E_x \quad (18)$$

Note also that at $\lambda = 1$, we have a virial which immediately yields the exchange–correlation energy:

$$E_{xc} = - \int d^3r \rho(\mathbf{r}) \mathbf{r} \cdot \nabla \tilde{v}_{xc}(\mathbf{r}) \quad (19)$$

where

$$\tilde{v}_{xc}(\mathbf{r}) = \int_1^\infty \frac{d\lambda}{\lambda^3} v_{xc}^\lambda(\mathbf{r}) \quad (20)$$

We call \tilde{v}_{xc} the hypercorrelated potential, as it includes contributions from $\lambda > 1$, at which the system is more strongly correlated than at $\lambda = 1$. We define a correlation energy density:

$$e_c(\mathbf{r}) = -\rho(\mathbf{r}) \mathbf{r} \cdot \nabla \tilde{v}_{xc}(\mathbf{r}) \quad (21)$$

such that $E_c = \int d^3r e_c(\mathbf{r})$, and $e_c(\mathbf{r})$ is uniquely determined by $E_c[n]$, via eqs 20, 11, and 7.

This result can be simply related to the line integral of van Leeuwen and Baerends:³⁶

$$E_{xc}[\rho_\gamma] = \int_0^{\gamma'} \frac{d\gamma}{\gamma} \int d^3r v_{xc}[\rho_\gamma] \left(\frac{\mathbf{r}}{\gamma} \right) (3\rho(\mathbf{r}) + \mathbf{r} \cdot \nabla \rho(\mathbf{r})) \quad (22)$$

where

$$\rho_\gamma(\mathbf{r}) = \gamma^3 \rho(\gamma \mathbf{r}) \quad (23)$$

is the uniformly scaled density.⁴⁵ We write $\gamma = 1/\lambda$, and use the fundamental scaling relationship for exchange–correlation:²³

$$E_{xc}^\lambda[\rho] = \lambda^2 E_{xc}[\rho_{1/\lambda}] \quad (24)$$

which shows that changing the coupling constant is simply related to a uniform scaling of the density. Functional differentiation yields

$$v_{xc}^\lambda[\rho](\mathbf{r}) = \lambda^2 v_{xc}[\rho_{1/\lambda}](\lambda \mathbf{r}) \quad (25)$$

Using eq 24 on the left of eq 22 and eq 25 on the right yields

$$E_{xc}^\lambda[n] = \lambda^2 \int_{\lambda'}^\infty \frac{d\lambda'}{\lambda'^3} \int d^3r v_{xc}^{\lambda'}[n](\mathbf{r}) (3\rho(\mathbf{r}) + \mathbf{r} \cdot \nabla \rho(\mathbf{r})) \quad (26)$$

which, when integrated by parts over \mathbf{r} , reproduces eq 15. The scaling relation eq 25 provides an alternative expression for the hypercorrelated potential:

$$\tilde{v}_{xc}[\rho](\mathbf{r}) = \int_0^1 \frac{d\gamma}{\gamma} v_{xc}[\rho_\gamma](\mathbf{r}/\gamma) \quad (27)$$

The earlier work by Engel and Vosko for exchange³⁴ also differed from ours by an integration by parts. We prefer the form of eq 15, in which constants in $v_{xc}(\mathbf{r})$ play no role.

We may also write eq 15 in terms of the potential contribution to $v_{xc}(\mathbf{r})$, defined as

$$v_{xc,\lambda}(\mathbf{r}) = \delta E_{xc,\lambda}[\rho] / \delta \rho(\mathbf{r}) = d v_{xc}^\lambda / d\lambda \quad (28)$$

Writing $v_{xc}^\lambda = \int_0^\lambda d\lambda' v_{xc,\lambda'}$ in the definition of \tilde{v}_{xc}^λ , eq 16, and swapping the order of the λ integrals, produces

$$\tilde{v}_{xc}^\lambda = 1/2 \left(\int_0^\lambda v_{xc,\lambda'} + \lambda^2 \int_\lambda^\infty \frac{d\lambda'}{\lambda'^2} v_{xc,\lambda'} \right) \quad (29)$$

We recognize the first potential on the right-hand side as simply v_{xc}^λ , while we define the second as

$$\bar{v}_{xc}^\lambda = \lambda^2 \int_\lambda^\infty \frac{d\lambda'}{\lambda'^2} v_{xc,\lambda'} \quad (30)$$

Then, at $\lambda = 1$, eq 29 reduces to the simple result

$$\tilde{v}_{xc} = 1/2 (v_{xc} + \bar{v}_{xc}) \quad (31)$$

Moreover, if we take the virial of both sides of this equation, and using eq 5, we find a familiar result⁴⁶

$$E_{xc} = 1/2 ([E_{xc} + T_c] + E_{xc,\lambda=1}) \quad (32)$$

We can also extract an energy density for T_c , by simply subtracting eq 19 from eq 5, to find

$$T_c = \int d^3r t_c(\mathbf{r})$$

$$= - \int d^3r \mathbf{r}(\mathbf{r}) \cdot \nabla(v_c - \tilde{v}_c)(\mathbf{r}) \quad (33)$$

Finally, although all our formulas were presented as functionals of the density, they may easily be generalized to spin-density functionals, using

$$E_{xc} + T_c = - \int d^3r \sum_{\sigma=\alpha,\beta} [\rho_{\sigma}(\mathbf{r}) \mathbf{r} \cdot \nabla v_{xc,\sigma}(\mathbf{r})] \quad (34)$$

III. Functional Approximations

Energies relevant to this study are given in Table 1. All were calculated on the highly accurate densities of Umrigar, and most of these energies appear in his work with others.^{15,18} Elsewhere, we will present calculations for the Hooke's atom for several different frequencies.⁴⁷ Note that, in powers of the coupling constant, E_x is the first order in λ , E_c and T_c are second order, while $E_c + T_c$ is third order.⁴⁵ Hence the diminishing magnitudes of the energies. Note also some trends in the GGA energies. The PBE simplification of PW91 is typically not as accurate as PW91 for total correlation energies of atoms and molecules, due to slight differences with PW91 in the core.⁴⁸ Furthermore, while LYP is always slightly better than PW91 for E_c , LYP always underestimates T_c , sometimes significantly. This implies that LYP contains stronger static correlation than PW91, which may mimic the static correlation in atomization energies,⁴⁹ where LYP produces noticeably better results.

Before we look in detail at the correlation potentials and energy densities, we first reconsider the exchange case, as detailed in Figures 1 and 2. In particular, we note the failure of the Becke exchange GGA to reproduce the asymptotic behavior of the exchange potential as $r \rightarrow \infty$, namely $-1/r$. This GGA was designed to yield a correct energy density, but not the virial energy density discussed here. If the functional had been designed to yield the correct potential, then it would also have gotten the correct virial energy density.³⁴ For all figures, the PW91 potentials (not shown) are almost identical to the PBE potentials, except for the small oscillations which were removed in the derivation of PBE.⁹ However, in the energy densities, these oscillations lead to wild peaks and valleys, whose net effect on the area under the curve is negligible.

Next we turn to correlation. In Figure 3, we plot both the exact correlation potential and the functional approximations to it. We now include also the Lee–Yang–Parr correlation potential (LYP).⁶ We find that none of the functionals produce potentials which look like the exact one, which becomes positive at large r and tends to a finite negative value as $r \rightarrow 0$. The LSD curve is everywhere negative. The GGA curves all have positive divergences at $r = 0$, and become negative for most values of r . It has even been pointed out that the GGA potentials would look better upside down.¹⁵ We return to this point below.

To construct the hypercorrelated potential, we extract the coupling-constant dependence of the potential via eq 25. Any program to find the potential within a given functional approximation can be modified to scale the density and calculate v_c^λ . (A little care must be taken in the strongly correlated limit ($\lambda \rightarrow \infty$) where, e.g., $v_c^{\text{LSD}\lambda} \sim O(\lambda^{3/2})$.) Integration of this potential as a function of λ according to eq 31 then yields \tilde{v}_c . Unfortunately, we do not plot an exact curve here, as the λ -dependence of the correlation potential has not yet been calculated. While exact correlation potentials can be found from the exact density for any finite system,^{21,50–54,15,55,22} calculation of the exact λ -dependence is only now becoming practical.³²

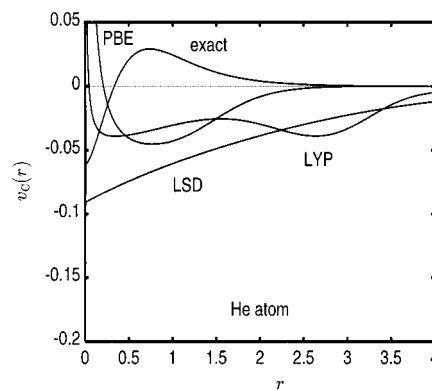


Figure 3. Correlation potential for the He atom (atomic units).

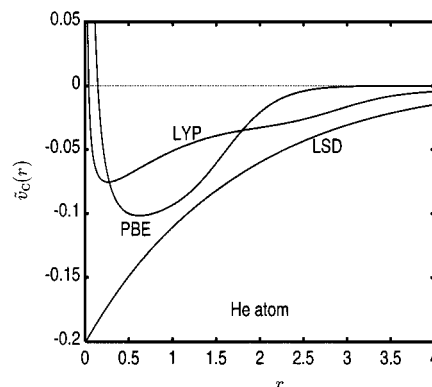


Figure 4. Hypercorrelated potential, \tilde{v}_c of eq 20, for the He atom (atomic units).

TABLE 1: Energy Components in hartrees for Several Atoms, Evaluated on Exact Densities^{15,18}

energy	exact	LSD	PW91	PBE	BLYP
He					
E_x	-1.025	-0.883	-1.016	-1.013	-1.025
E_c	-0.042	-0.112	-0.046	-0.042	-0.044
T_c	0.037	0.068	0.038	0.038	0.034
$E_c + T_c$	-0.005	-0.044	-0.008	-0.004	-0.010
Be					
E_x	-2.674	-2.321	-2.654	-2.645	-2.667
E_c	-0.096	-0.225	-0.095	-0.086	-0.096
T_c	0.073	0.139	0.074	0.072	0.062
$E_c + T_c$	-0.023	-0.086	-0.021	-0.014	-0.034
Ne					
E_x	-12.085	-11.021	-12.102	-12.054	-12.125
E_c	-0.393	-0.742	-0.381	-0.350	-0.383
T_c	0.328	0.495	0.312	0.305	0.285
$E_c + T_c$	-0.065	-0.247	-0.069	-0.044	-0.099

In Figure 4, we plot the hypercorrelated potentials and note the similarities to Figure 3. The effect of hypercorrelation is clear. Many of the features visible in the curves become more pronounced. Interestingly, the PBE and LYP curves become more similar.

From the curves in Figure 4, we construct the corresponding radial virial energy densities, $-4\pi r^3 \rho(r)(d\tilde{v}_c/dr)$, and plot them in Figure 5. The net area between these curves and the axis yields the correlation energy, within a given functional approximation. In principle, we should use the self-consistent densities calculated within each functional approximation in order for the virial theorem to apply. In practice, we have used the exact density everywhere, and have noticed no difference between, for example, E_c and the virial of the hypercorrelated potential, to the number of digits quoted in Table 1.

First note the greater structure of the GGA curves relative to

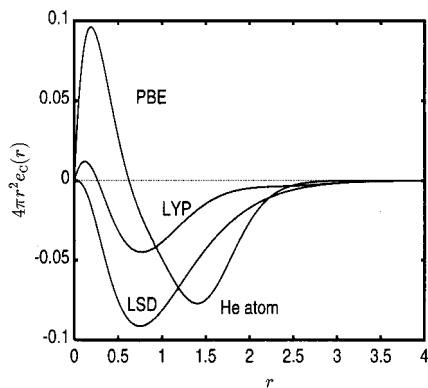


Figure 5. Radial virial correlation energy density, extracted from the hypercorrelated potential, for the He atom (atomic units).

that of LSD. Each of the GGA correlation potentials contains at least one extremum at a finite value of r , in common with the exact curve. This implies a zero in the corresponding energy density and so a change in sign of that density. There is therefore a large cancellation of errors within the correlation energy integral for the GGAs. Presumably, the exact curve shares this feature (for further evidence, see below). But the LSD correlation potential is monotonic, so that the LSD energy density has no cancellation of errors. This is another view of the characteristic LSD overestimate of the correlation energy.

We can derive a simple expression for the virial exchange–correlation energy density in the special case of the local approximation. If we write

$$E_{xc}^{\text{LSD}}[\rho] = \int d^3r e_{xc}^{\text{unif}}(\rho(\mathbf{r})) \quad (35)$$

where $e_{xc}^{\text{unif}}(n)$ is the accurately known^{24,56,57} exchange–correlation energy density of a uniform gas. Taking the functional derivative, we find

$$v_{xc}^{\text{LSD}}(\mathbf{r}) = d(e_{xc}^{\text{unif}})/d\rho \quad (36)$$

The virial energy density is given by eq 19. Using eq 25 to rewrite it in terms of the scaled density, we find

$$e_{xc}^{\text{LSD}} = -\rho(\mathbf{r})\mathbf{r} \cdot \nabla \int_1^\infty \frac{d\lambda}{\lambda} v_{xc}^{\text{LSD}}(\rho(\mathbf{r})/\lambda^3) \quad (37)$$

Writing $\tilde{n} = n/\lambda^3$, we find

$$\begin{aligned} e_{xc}^{\text{LSD}} &= -1/3 \rho(\mathbf{r})\mathbf{r} \cdot \nabla \int_0^{\rho(\mathbf{r})} \frac{d\tilde{\rho}}{\tilde{\rho}} v_{xc}^{\text{LSD}}(\tilde{\rho}) \\ &= -1/3 (\mathbf{r} \cdot \nabla \rho) v_{xc}(\rho) \end{aligned} \quad (38)$$

This simple result is only true for a local functional. The LSD virial energy density depends on both the local density and its gradient. We also used it as a check on our λ -integrations, calculating the LSD potential from either eq 20 or eq 38.

Figures 4 and 5 suffer noticeably from the lack of an exact curve to compare the density functional approximations with. This is because, although our definition of the virial correlation energy density is uniquely determined by the correlation energy functional, one needs to know that functional different coupling constants, or equivalently, for scaled densities. A traditional wavefunction calculation only produces $\Psi_{\lambda=1}$. Thus we cannot calculate the exact curve to make the comparison with. Until recently, the full λ -dependence was known only for the uniform gas. Now the λ -dependence of the exchange–correlation energy

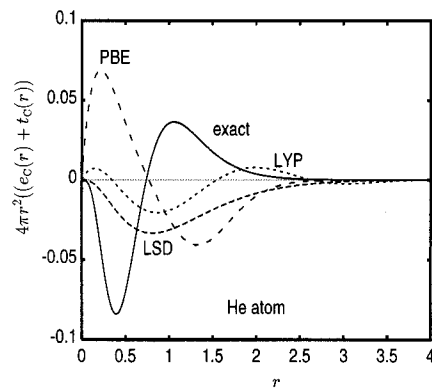


Figure 6. Radial virial correlation plus kinetic-correlation energy density, extracted from the correlation potential, for the He atom (atomic units).

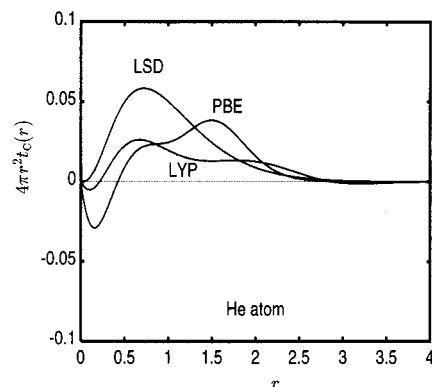


Figure 7. Radial virial kinetic-correlation energy density for the He atom (atomic units).

for the He and Be series has been accurately calculated using a standard configuration interaction program,⁵⁸ for the Hooke's atom using approximate density scaling, and quantum Monte Carlo calculations have been performed on Si and sinusoidally varying potentials.³²

However, we can avoid this difficulty by returning to eq 5. Here we have a correlation virial energy density which *can* be found from $\Psi_{\lambda=1}$, but integrates up to $E_c + T_c$, rather than E_c itself. Since this quantity is much less accurately predicted by density functionals, this produces a more stringent test than the virial for E_c . In Figure 6, we plot the radial energy density for the exact curve and the approximate ones. The transformation from Figure 5 to Figure 6 is similar to that from Figure 3 to Figure 4 in reverse. The strength of the features is weakened. Most importantly, the exact and GGA curves have almost perfect cancellation between their positive and negative contributions, yielding very similar energies. But, just as in the case for the potential, the GGA energy densities differ markedly from the exact ones point-by-point.

Again we see the resolution of the paradox of the apparently worse GGA potential curve, but better GGA energy. The small oscillation in the PBE correlation potential curve around $r = 1.0$ in Figure 3 leads to a change in sign of its energy density, producing a large cancellation of errors in the integral. The smoother, better looking LSD potential has no such feature. Since $E_c + T_c$ is a very small number, this cancellation is vital and is included in GGA, but missed by LSD, leading to an error which is almost 10 times larger (see Table 1).

Finally, we plot the correlation contribution to the kinetic energy density of eq 33 in Figure 7. We see the significant difference between the overestimate of LDA due its monotonicity, just as for E_c in Figure 5. However, we also see a large

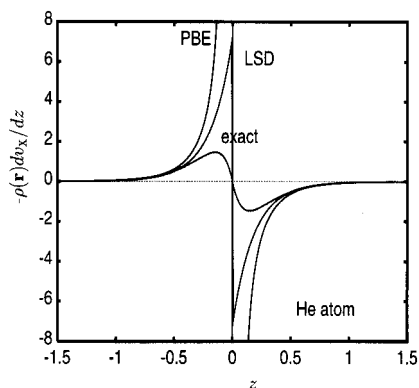


Figure 8. Change in He atom virial exchange energy density when origin is shifted by 1 (atomic units).

difference between the PBE and LYP curves, leading to the underestimate of T_c by LYP mentioned earlier. These curves can be compared to Figure 1a of ref 59, but there the exact $t_c(r)$ is defined in terms of the difference in kinetic energy density of the physical and Kohn–Sham wave functions, and the approximate $t_c(r)$ extracted by scaling the traditional correlation energy density of eq 3, rather than using the virial definition of eq 33.

IV. Uniqueness and Application to Molecules

The virial of the hypercorrelated potential yields the exact exchange–correlation energy, thereby defining an exchange–correlation energy density which is uniquely determined by the exchange–correlation energy functional. However, this choice of energy density is itself by no means unique. A simple way to see this is to change the origin in eq 19. The exchange–correlation energy does not change, since

$$\int d^3r \rho(\mathbf{r}) \nabla \tilde{v}_{xc}(\mathbf{r}) = 0 \quad (39)$$

but the corresponding energy density does. To illustrate this, imagine shifting the origin one atomic unit along the z -axis, away from the nuclear center. Then, for example, the exchange energy density of eq 4 changes by an amount

$$\Delta e_x(\mathbf{r}) = -\rho(\mathbf{r}) \frac{dv_x}{dz}(\mathbf{r}) \quad (40)$$

This quantity is plotted for the He atom along the z -axis in Figure 8. It integrates to zero, but has a pronounced structure as a function of \mathbf{r} . This will be particularly important when calculating these energy densities for molecules. If the origin is chosen on one nucleus, the contribution at another nucleus will pick up a term similar to that of Figure 8, but which will be slightly asymmetric, due to the bonding. Thus this contribution cannot be ignored, as it does not integrate to zero.

This illustrates an important point in the interpretation of the energy densities defined in this work. It is unclear what physical significance should be attributed to the value of these energy densities at a point in the system. They are highly nonfocal functionals of the density, as evinced by the differences between the exact curves and the LDA curves. Thus they do not yield chemical insight into the nature of bond formation^{27–30} nor are they close to “local”.³¹ On the other hand, one can choose *any* origin for the purposes described here (i.e., comparison between approximate and exact functionals).

V. Conclusions

We have shown how to construct a correlation energy density which is uniquely determined by the correlation potential (as a

function of coupling constant) and therefore by the correlation energy functional itself. We find that neither the local density approximation nor any popular GGA approximate this energy density point-by-point.

We can apply this study to the question of how well the ground-state energy can be estimated, *given* the exact density, without recourse to solving an interacting problem. For the spin-unpolarized two-electron problem, the answer is that E can be deduced exactly. We write $E = \epsilon + E_1$, where ϵ is the Kohn–Sham eigenvalue, deducible from the decay of the density,⁶⁰ while E_1 is the ground-state energy of the remaining one-electron ion. More generally, both the exchange and correlation potentials can be found exactly from the density.⁶¹ Thus if one can deduce the hypercorrelated potential from the correlation potential, then the problem is solved. We are currently working on schemes to estimate the hypercorrelated potential. Note that even an exact solution to this problem does not provide an exact ground-state energy functional, since use of the virial theorem renders the energy nonvariational.

This might also be extended to estimating the hypercorrelated potential from the exchange potential alone, as might be found in an optimized effective potential calculation (OEP) using, for example, the KLI approximation.⁶² This suggests the possibility of an exchange–correlation energy density hybrid of exact exchange with GGA exchange–correlation. Recently, the hybrid idea, which reduces atomization energy errors by a factor of 2–3, has been derived in a parameter-free fashion.^{12–14} Unfortunately, these schemes are all applied to the energy difference between atoms and molecules, rather than on the energies themselves, so losing the uniqueness of the definition of the total energy.⁶³ However, any scheme which mixed energy densities on a pointwise basis would not suffer from such a defect, by construction. This was the original motivation behind the current work. Unfortunately, since the current functionals do not produce energy densities similar to the exact quantities, it is difficult to see how to implement such a hybrid scheme, which would be of the form

$$e_{xc}^{\text{hyb}}(\mathbf{r}) = a(\mathbf{r})[e_x(\mathbf{r}) - e_x^{\text{GGA}}(\mathbf{r})] + e_{xc}^{\text{GGA}}(\mathbf{r}) \quad (41)$$

where $a(\mathbf{r})$ would be determined by some nonempirical recipe. In the case of atomization energies, the errors in the GGA functionals are of definite sign and nature⁴⁹ and can be understood in terms of general chemical arguments.⁶³ Thus they can be repaired by hybrid recipes which account for them.^{12,14} For the energy density, we are still searching for an understanding of these errors,⁶⁴ without which it is unclear how best to proceed.

Acknowledgment. We thank Cyrus Umrigar for providing us with highly accurate densities and potentials and John Perdew and Mel Levy for useful discussions. This work was supported by an award from Research Corporation.

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