

Unambiguous Exchange–Correlation Energy Density for Hooke’s Atom

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ABSTRACT: Recently, we used Helmholtz’s theorem to construct an unambiguous exchange–correlation energy density for use in density functional theory. This energy density requires only knowledge of the density dependence of the exchange–correlation energy functional, E_{XC} , for its calculation. We calculate this energy density for Hooke’s atom in three different regimes: the high-density (or weakly correlated) limit; a moderate density, comparable to that of the He atom; and a low density, in which the system is strongly correlated. We compare the exact unambiguous energy density with approximate energy densities found from approximate energy functionals. The exchange–correlation energy can be deduced directly from the density in the highly correlated limit and a new formula for the high-density limit of the correlation energy is given. © 1998 John Wiley & Sons, Inc. *Int J Quant Chem* 70: 583–589, 1998

Introduction

A principal aim of quantum chemistry is the calculation of ground-state electronic properties in an accurate and reliable fashion [1]. Traditional approaches based on the wave function have recently been complimented by those of density functional theory [2]. Density functional calculations are typically much less expensive computationally and so become the method of choice for larger systems [3]. This advance has been made

possible by the increase in accuracy of generalized gradient approximations (GGAs) [4–9] (and hybrids of GGAs with exact exchange [10–14]) over the local density approximation (LDA).

The only quantity which must be approximated in a Kohn–Sham spin-density functional calculation [15] is the exchange–correlation energy as a functional of the spin densities, $E_{XC}[\rho_\alpha, \rho_\beta]$, since its functional derivative, $v_{XC\sigma}(\mathbf{r}) = \delta E_{XC} / \delta \rho_\sigma(\mathbf{r})$, is the only unknown in the Kohn–Sham equations. There are several popular approximations to E_{XC} , including LDA, GGA, and hybrids. These approximations can be tested by calculation of the properties of the system, such as total energies, ionization potentials, binding energies, bond lengths, vibrational frequencies, and transition-state barriers and

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by comparing them either with more accurate calculations or with experiment [16, 17]. However, all these properties are determined entirely by E_{XC} , evaluated on different densities, which is a quantity integrated over the system. To better understand how these approximate functionals work, one would like to examine quantities *other* than just E_{XC} . If your energy in a given calculation comes out poorly, where will you look to find out why?

A simple choice might be to study the spin densities themselves. However, many approximate calculations (Hartree–Fock, LDA, GGA, etc.) yield very similar spin densities [18], so it is not easy to study an approximate density to determine the error in the corresponding energy functional approximation. Furthermore, for stretched H_2 , some approximate functionals can have quite incorrect spin densities, while still yielding accurate total energies [19, 20]. Thus, the relation between the self-consistent spin densities and the total energy may be too subtle to easily learn about one from the other.

Another feature which has been studied is the exchange–correlation hole surrounding an electron in the system [4, 6, 21–24]. One can consider the LDA and GGA energy functionals as models for the exact system-averaged exchange correlation hole. Certain aspects of the exact hole are well approximated in LDA [25], because the LDA energy functional replaces the hole by that of another system: the uniform electron gas. Thus, various sum-rules and nonpositivity conditions are shared by the exact hole and its local approximation [26]. This reasoning was extended by Perdew and coworkers to construct a sequence of GGAs (PW86 [4, 5], PW91 [6], and PBE [7]) in which the gradient expansion for the hole was corrected to include these good features. However, only the system and spherical average of these holes is accurately reproduced [24, 26] and, even then, the complications of calculating these approximate holes mean that few systems have been tested. (On the other hand, the potential in LDA arises from an unspherical charge distribution [27].) Similar remarks are true for the LYP correlation functional [9], which is based on the Colle–Salvetti approximations to the pair correlation function [28, 29].

Such comparisons as mentioned in the previous paragraph suffer from the need for detailed knowledge of the construction of a given approximation. But an approximation might not carry with it a derivation which suggests such a comparison. For

a practical calculation, all one really needs is an approximate spin-density functional for E_{XC} . This naturally suggests study of $v_{XC\sigma}(\mathbf{r})$ itself. For the exact case, one needs only a highly accurate density, as several methods now exist for then solving for the Kohn–Sham potential and orbitals [30–34] and so deducing the exchange–correlation contribution to the potential. Thus, comparison of approximate and exact potentials could be hoped to yield insight into how approximate functionals work.

Unfortunately [18, 35, 36], potentials corresponding to accurate functionals do not look much like the exact potentials. Thus, the study of potentials appears to provide little guidance for the construction of approximate energy functionals. There are several ways to rationalize how these potentials can look so poor:

First, focusing on correlation alone ignores a wealth of experience in functional approximations, in which the exchange and correlation errors cancel. This can be understood simply in terms of the specific effects which occur for pure exchange [12], which are not captured by LDA and GGA, but which wash out when the Coulomb interaction between electrons is included.

Next, as discussed above, system-averaging is important in studying the behavior of density functionals [37]. Many properties of approximate functionals are incorrect in, for example, the asymptotic limit far from a finite system [38], but these have little effect on the total energy or even on energy differences involving only valence electrons.

Furthermore, approximate functionals which incorporate only the density and its gradient cannot have any derivative discontinuities with respect to particle number, which are known to occur in the exact functional [39–42]. These discontinuities lead to constants in the potential which are missed by approximate functionals and so can make the corresponding potentials look poorer.

An alternative to studying the exchange–correlation potential might be provided by the exchange–correlation energy density, that is, a function of \mathbf{r} which, when integrated over all space, yields the exchange–correlation energy. Unfortunately, such a requirement does not uniquely specify which among an infinite number of choices, as the addition of any function whose integral over all space vanishes will produce another energy density. In fact, several choices have been suggested in the past. A popular one, especially for

chemical purposes, is that of Baerends and Gritsenko [43], who defined their energy density in terms of the potential contribution to the exchange-correlation hole, plus the difference of the kinetic energy density from the interacting and noninteracting density matrices. While this energy density can be extracted from an accurate wavefunction calculation, there is no reason why any of the conventional approximate energy densities, used to define the integrated energy, should look much like this one. Indeed, the LYP functional [9] has been integrated by parts in order to remove inconvenient Laplacian terms [44]. Similar arguments apply to the definition in terms of the coupling-constant integrated exchange-correlation hole [26].

Similarly, the work of Harbola and Sahni [45, 46] and others [47] has led to an energy density in terms of potential and kinetic exchange-correlation fields. But the construction of, for example, the potential fields, is based on the exchange-correlation hole (at full coupling strength), which is modeled only in some GGAs. Comparisons of these energy densities with exact ones can only be made with those GGAs which provide a model for this hole [46].

The remainder of this article is devoted to the construction of an unambiguous exchange-correlation energy density, that is, one which is solely determined by the density dependence of E_{XC} . The full details of the construction are given elsewhere [49], but a pedagogical derivation is given here. Results on the Hooke's atom (two electrons in an external oscillator potential) are presented for three cases: moderate correlation, strong correlation, and weak correlation. Atomic units ($e^2 = \hbar = m_e = 1$) are used throughout.

Construction of Unambiguous Energy Density

In this section, we review the construction of the unambiguous energy density. For simplicity, we restrict ourselves to density functionals, but all results are easily generalized to spin-density functionals.

We begin with the virial theorem [50]:

$$2T = \langle \Psi | \sum_{i=1}^N \mathbf{r}_i \cdot \nabla_i V(\mathbf{r}_1, \dots, \mathbf{r}_N) | \Psi \rangle, \quad (1)$$

where T is the kinetic energy; Ψ , the ground-state many-body wave function; N , the number of electrons; and V , the potential energy. This may easily be derived by uniformly scaling the coordinates of the wave function [51]. We apply this theorem to both the physical system and the noninteracting Kohn-Sham system. In the former case, $V = V_{ee} + V_{ext}$, where V_{ee} is the electron-electron Coulomb repulsion and V_{ext} is the external potential. This yields

$$2T = -V_{ee} + \int d^3r \rho(\mathbf{r}) \mathbf{r} \cdot \nabla v_{ext}(\mathbf{r}), \quad (2)$$

since V_{ee} is homogeneous of degree -1 in the coordinates. Similarly, for the noninteracting Kohn-Sham system,

$$\begin{aligned} 2T_S &= \int d^3r \rho(\mathbf{r}) \mathbf{r} \cdot \nabla v_s(\mathbf{r}) \\ &= \int d^3r \rho(\mathbf{r}) \mathbf{r} \cdot \nabla (v_{ext}(\mathbf{r}) + v_{XC}(\mathbf{r})) - U, \end{aligned} \quad (3)$$

where $v_s(\mathbf{r})$ is the Kohn-Sham potential and U is the Hartree energy. Subtraction of Eq. (3) from Eq. (2) yields

$$2(T - T_S) + V_{ee} - U = - \int d^3r \rho(\mathbf{r}) \mathbf{r} \cdot \nabla v_{XC}(\mathbf{r}). \quad (4)$$

The second term on the left can be identified as the potential contribution to E_{XC} , so that the addition of one factor of $T_C = T - T_S$, the kinetic contribution, yields E_{XC} . Thus,

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

This powerful result was proven for the exact functional by Levy and Perdew [51].

The integrand of Eq. (5) is an energy density which is unambiguously determined by the density dependence of the exchange-correlation energy functional, via the potential, its derivative. Unfortunately,

1. It is an energy density not for exchange-correlation, but for exchange-correlation plus kinetic-correlation.
2. Its value depends on the choice of origin. If the origin is shifted, the energy density changes (see Fig. 8 of [52]).

3. This energy density does not reduce to the familiar $e_{XC}^{unif}(\rho(\mathbf{r}))$, the energy density of a uniform gas, when v_{XC}^{LDA} is inserted on the right.

The first of these shortcomings was easily solved, using the adiabatic connection formula of density functional theory [53]. A coupling-constant λ is introduced to multiply the electron–electron repulsion and is varied while keeping the density fixed. All quantities can then be considered functions of λ . In particular, Bass’ relation [54] relates T_C to E_C^λ , via

$$T_C^\lambda = E_C^\lambda - \lambda \frac{dE_C^\lambda}{d\lambda}. \quad (6)$$

Using this on the generalization of Eq. (5) to arbitrary λ , we found [49] a virial for the exchange–correlation energy itself:

$$E_{XC} = - \int d^3r \rho(\mathbf{r}) \mathbf{r} \cdot \nabla \tilde{v}_{XC}(\mathbf{r}), \quad (7)$$

where

$$\tilde{v}_{XC}(\mathbf{r}) = \int_1^\infty \frac{d\lambda}{\lambda^3} v_{XC}^\lambda(\mathbf{r}) \quad (8)$$

is called the exchange–hypercorrelated potential, as it includes contributions from $\lambda > 1$, at which the system is more strongly correlated than at $\lambda = 1$. This potential can also be written as [55]

$$\tilde{v}_{XC}[\rho](\mathbf{r}) = \int_0^1 \frac{d\gamma}{\gamma} v_{XC}[\rho_\gamma](\mathbf{r}/\gamma), \quad (9)$$

where

$$\rho_\gamma(\mathbf{r}) = \gamma^3 \rho(\gamma \mathbf{r}) \quad (10)$$

is a uniformly scaled density. Thus, the integrand on the right of Eq. (7) forms an unambiguous exchange–correlation energy density, as it is completely determined by the density dependence of E_{XC} itself, via its potential, evaluated on scaled densities. In particular, it is very straightforward to modify any approximate functional to calculate $\tilde{v}_{XC}(\mathbf{r})$ instead of $v_{XC}(\mathbf{r})$ simply by scaling the density arguments, according to Eq. (9).

To overcome the second two difficulties, we generalized an argument of Levy and Perdew [51], which they used to show that the virial theorem was satisfied by LDA for a slowly varying electron gas. This generalization amounts to making the

following exact identification:

$$3\rho(\mathbf{r}) \nabla \tilde{v}_{XC}(\mathbf{r}) = \nabla e_{XC}(\mathbf{r}) + \nabla \times \mathbf{a}_{XC}(\mathbf{r}). \quad (11)$$

Insertion of Eq. (11) into Eq. (7), followed by an integration by parts, shows that the \mathbf{a}_{XC} term does not contribute to the energy, while the e_{XC} term is our unambiguous energy density. By use of the Helmholtz theorem of vector calculus, we can write an integral form for e_{XC} :

$$e_{XC}(\mathbf{r}') = \frac{3}{4\pi} \int d^3r \rho(\mathbf{r}) \nabla \tilde{v}_{XC}(\mathbf{r}) \cdot \nabla \frac{1}{|\mathbf{r} - \mathbf{r}'|}. \quad (12)$$

This is an exact energy density that depends solely on the density dependence of the exchange–correlation energy functional. Thus, unambiguous comparisons of exact and approximate results can be made. Furthermore, if E_{XC}^{LDA} is used on the right, $e_{XC}^{unif}(\rho(\mathbf{r}))$ comes out on the left. Thus, all plots of $e_{XC}^{unif}(\rho(\mathbf{r}))$ can be interpreted as approximate plots of the exact unambiguous $e_{XC}(\mathbf{r})$.

The right-hand side of Eq. (12) contains the exchange–hypercorrelated potential, that is, the potential integrated over coupling constants greater than 1, as defined in Eq. (8). This is necessary to produce the exchange–correlation energy density on the left. Alternatively, if $v_{XC} = v_{XC}^{\lambda=1}$ is inserted on the right, an energy density $e_{XC}(\mathbf{r}) + t_C(\mathbf{r})$ emerges on the left, as can be seen from Eq. (5). For any approximate functional, it is straightforward to calculate either quantity. However, for the *exact* functional, we only have $v_{XC}(\mathbf{r})$ for a few model systems, where the exact density was evaluated by a highly accurate wave-function calculation and v_{XC} calculated from it. Thus, for purposes of comparison, it is more convenient to study $e_{XC} + t_C$. Ongoing studies of the adiabatic connection should allow construction of \tilde{v}_{XC} in the future. We anticipate little difference in the qualitative features of the comparison, as the hypercorrelated potential is a smooth distortion of the correlated potential (see Fig. 6 of [56]).

Results

To illustrate this energy density, we calculate it for several values of the spring constant in Hooke’s atom, which consists of two electrons in an external oscillator potential [57, 58]. This model has been used to study many density functional properties [36, 59, 60].

MODERATE CORRELATION

We begin with a moderately correlated example, $\omega = 1/2$, in which $E_C/E_X \sim 7\%$ and $T_C/|E_C| \sim 75\%$. In Figure 1, we plot the radial unambiguous exchange-correlation plus kinetic-correlation energy density, both exactly and within several functional approximations. We see that, indeed, the LDA curve underestimates the exact one almost everywhere, while the GGA curves reduce the maximum error significantly. The best GGA curve in this case is BLYP (but see real atoms in [49]). Note that the decay of this energy density at large distances is given in [49] and depends on the ionization potential and is not captured by any present-day approximate functionals.

STRONG CORRELATION

Next, we consider the highly correlated (or low-density) limit. We choose $\omega = 10^{-4}$, at which value the density is very close to semiclassical, that is, a Gaussian centered on the classical electrostatic equilibrium position [58]. At the maximum, $\rho \sim 10^{-8}$ or $r_s \sim 270$. Values for the components of the energy are given in Table I, from which we see that $E_C/E_X \sim 40\%$ and $T_C/|E_C| \sim 4\%$. Thus, correlation has become comparable to exchange and is almost entirely static. In this extreme regime, we do not expect too much from our approximate functionals, and Figure 2 shows that the GGA corrections to the LSD energy density do not show

TABLE I
Energy components in milliHartrees for two extreme values of ω , evaluated on the exact densities.

Component	Exact	LSD	PBE	BLYP
$\omega = 10^{-4}$				
E_X	-3.00	-2.90	-3.40	-3.54
E_C	-1.24	-2.29	-1.67	-0.55
T_C	0.05	0.20	0.17	0.003
$E_C + T_C$	-1.19	-2.09	-1.50	-0.55
$\omega = 100$				
E_X	-7,923	-6,773	-7585	-7717
E_C	-49	-221	-77	-29
T_C	48	164	72	33
$E_C + T_C$	-0.9	-57	-4	5

Values for $\omega = 1/2$ and 0.00189 are in [56].

a pointwise improvement. In fact, in this regime, the exact energy density appears more similar to LSD than above.

An important question was raised by Morrison and Parr [48], which can be stated as follows: Given the exact density of some $N > 1$ electronic problem, can you find the exact ground-state energy without solving an $N > 1$ problem? Recently, we pointed out that the answer is yes when $N = 2$ for spin-unpolarized systems [56], since the asymptotic decay of the density determines the ionization potential, so that one is left with a

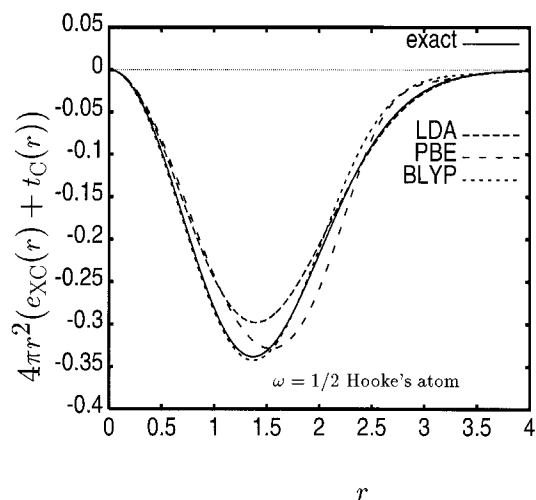


FIGURE 1. Radial unambiguous exchange-correlation plus kinetic-correlation energy density for $\omega = 1/2$ Hooke's atom (atomic units).

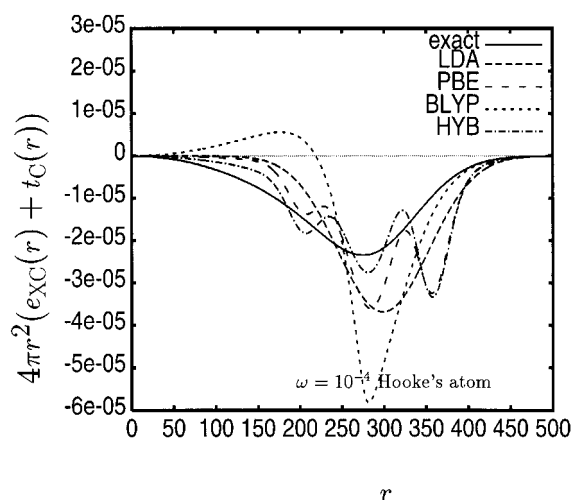


FIGURE 2. Radial unambiguous exchange-correlation plus kinetic-correlation energy density for $\omega = 10^{-4}$ Hooke's atom (atomic units).

one-electron problem to solve. Here, we point out that it is also true in the extreme high-correlation (or low-density) limit, since $T_C \rightarrow 0$, so that the virial of the exchange–correlation potential yields the exchange–correlation energy.

WEAK CORRELATION

Finally, we consider the weakly correlated (or high-density) limit, by studying $\omega = 100$. Now, $E_C/E_x \sim 0.5\%$, while $T_C/|E_C| \sim 98\%$. In this limit, it becomes appropriate to separate correlation from exchange, since Görling–Levy perturbation theory applies [61]. In Figure 3, we plot the radial unambiguous correlation plus kinetic correlation energy densities and their functional approximations. We now see a true limitation of LDA, in that its energy density does not change sign, so that there is no cancellation in the integral. The exact curve integrates to zero in the $\omega \rightarrow \infty$ limit. The GGAs do better, and this is reflected in their energies, although the BLYP curve does not follow the shape of the exact curve. Figure 3 also highlights an undesirable feature of the new energy density. The integrated quantity vanishes, so should not the integrand vanish also? It would be preferable if the energy density never changed sign (as, indeed, the uniform gas energy density does not), since then the allocation of energy densities throughout the system would be cumulative, and one could more

easily define averages over the distribution. Since the prescription described here does not uniquely specify the choice of energy density, the question of whether such a variation can be found remains open.

The high-density limit also raises a slight conundrum: Using Levy scaling [62], one finds $v_C^\lambda \approx \lambda^2 v_C^{(2)}$, in the high-density limit, where $v_C^{(2)}$ is the finite correlation potential when the density is scaled to the high-density limit, that is, $v_C^{(2)}(\mathbf{r}) = \lim_{\gamma \rightarrow \infty} v_C[\rho_\gamma](\gamma \mathbf{r})$. Insertion of this λ -dependence directly into Eq. (12) would cause the hypercorrelated potential to diverge everywhere. In reality, this does not happen, because $E_C \rightarrow -\text{constant}$, even in the low-density limit. This implies that $v_C^\lambda \approx O(\lambda)$ as $\lambda \rightarrow \infty$, and this change in behavior always occurs for some $\lambda \sim O(r_s)$ for any real system, making the integral converge. Thus, the high-density limit cannot be taken *before* the coupling-constant integration.

This raises an interesting point about Eq. (12) in the high-density limit, since it yields the correlation energy in terms of an integral which stretches down to the low-density (highly correlated) limit. For two-electron systems, one may show that the virial theorem becomes

$$E_C^{(2)} = -\frac{1}{2} \int d^3r \rho(\mathbf{r}) \mathbf{r} \cdot \nabla \int_1^\infty \frac{d\lambda}{\lambda^2} \frac{\delta V_{ee}^\lambda}{\delta \rho(\mathbf{r})}, \quad (13)$$

where V_{ee}^λ is the expectation value of the interelectronic Coulomb repulsion evaluated on the wave function at coupling-constant λ , and $E_C^{(2)} = \lim_{\gamma \rightarrow \infty} E_C[\rho_\gamma]$. One may, of course, apply the Helmholtz construction to this expression also to yield an origin-independent energy density as in Eq. (12).

Conclusions

To summarize, we have presented a new tool for the exploration of density functionals. The unambiguous energy density provides several interesting advantages over earlier constructions, and preliminary calculations of this energy density are promising [49].

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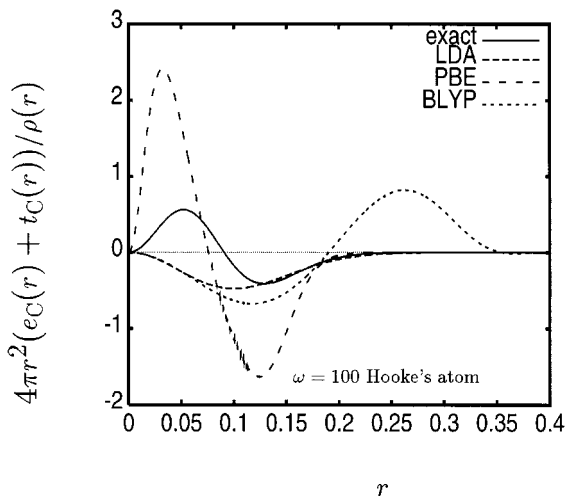


FIGURE 3. Radial unambiguous exchange–correlation plus kinetic–correlation energy density for $\omega = 100$ Hooke’s atom (atomic units).

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