CHAPTER N

CORRELATION ENERGY DENSITIES: E PLURIBUS UNUM

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1. Summary and Conclusions

For a given electron density $n(r)$, the correlation energy $E_c$ is unique while the correlation energy density $n(r)\epsilon_c(r)$ is not. Exact correlation energy densities for atoms or molecules have been calculated by Baerends et al [1, 2] and by Huang and Umrigar [3] from two wavefunctions: one for the system at full coupling strength and one for its non-interacting counterpart of the same electron density. Here we argue that this “endpoint” correlation energy density differs in its kinetic-energy component from the conventional correlation energy density, constructed from the correlation hole integrated over coupling constant from zero coupling to full coupling strength. To believe otherwise would require a local version of the adiabatic connection formula or coupling-constant integration [4, 5], which we have not been able to derive.

While many exact correlation energy densities yield the same correlation energy, the conventional one has a special relevance to density functional theory and also has many known properties. We propose a sophisticated hybrid model which predicts the conventional correlation energy density from the conventional potential energy density of correlation. Our model satisfies all known properties,
and differs significantly from the endpoint correlation energy density defined in the previous paragraph.

For the helium atom, we examine correlation energy and correlation potential-energy densities, both exact and approximate. The approximate functionals include the local density approximation [6], two generalized gradient approximations (GGA’s) (Lee-Yang-Parr [7] and Perdew-Burke-Ernzerhof [8]), and two meta-generalized gradient approximations (Colle-Salvetti [9] and Perdew-Kurth-Zupan-Blaha [10, 11]). We suggest that the approximations represent other choices of correlation energy density, which for helium are closer to the conventional than to the endpoint choice for the exact. It has always been known that GGA’s model the system-averaged exchange-correlation hole and energy, not necessarily the conventional local ones.

2. Exact Energy Densities: Conventional vs. Endpoint

Kohn-Sham density functional theory [6, 12, 13] is now the standard model for electronic structure calculations in both condensed matter physics and quantum chemistry. In principle, the exact ground-state energy and density of a many-electron system can be found by solving self-consistent one-electron equations. In practice, the exchange-correlation energy as a functional of the electron density has to be approximated.

Besides its practical utility, density functional theory promises an intuitive, “real-space” insight into the energetics of bonding [12, 14, 15]. This is undoubtedly one of the reasons why Robert G. Parr championed this theory in chemistry many years before it became popular.

One of the simplest questions we can ask is this: How are the total energy and its various components distributed over space? We write

\[ E = \int d^3r \ n(r)\epsilon(r), \]

and examine the energy per unit volume \( n\epsilon \) or the energy per electron \( \epsilon \) at \( r \), where \( n(r) \) is the electron density. In particular, if we can compare the approximate exchange \( (\epsilon_x) \) or correlation \( (\epsilon_c) \) energies to exact ones in simple systems, then we can identify regions of space in which the approximation works or fails. Several recent studies [1, 2, 3] have made such comparisons for correlation in atoms or molecules.

Unfortunately, our simple question does not have a simple answer. The integrated exchange \( (E_x) \) and correlation \( (E_c) \) energies for a given density \( n(r) \) are unique, but \( n(r)\epsilon_x(r) \) and \( n(r)\epsilon_c(r) \) are not. For example, we can add \( \nabla^2F(r) \) to either, where \( F(r) \) vanishes exponentially as \( |r| \to \infty \), without changing the integrated energy. We can also make coordinate transformations [16, 17, 18] which change the energy density but not the energy. Of course, the Kohn-Sham exchange-correlation potential is unique, and can be used to construct an “unam-
ambiguous” energy density [19]. From many different correlation energy densities, we can find one correlation energy: e pluribus unum.

Nevertheless, the starting point for most density functional approximations is the adiabatic connection formula [4, 5]

\[
E_{xc} = \frac{e^2}{2} \int_0^1 d\lambda \int d^3r' n(r') \int d^3r \frac{n^\lambda_{xc}(r, r')}{|r' - r|},
\]

(2)

where \(n^\lambda_{xc}(r, r')\) is the density at \(r'\) of the exchange-correlation hole surrounding an electron at \(r\) in a system with electron density \(n(r)\), electron-electron interaction \(\lambda e^2/|r' - r|\), and external potential \(v_\lambda(r)\). More precisely, if \(\Psi_\lambda\) is the \(N\)-electron ground-state wavefunction of this system, we define the first-order reduced density matrix

\[
\rho^\lambda_1(r, r') = N \sum_{\sigma_1 \cdots \sigma_N} \int d^3r_2 \cdots d^3r_N \Psi_\lambda^*(r, \sigma_1, r_2, \sigma_2, \cdots, r_N, \sigma_N) \\
\Psi_\lambda(r', \sigma_1, r_2, \sigma_2, \cdots, r_N, \sigma_N),
\]

(3)

and the pair density

\[
\rho^\lambda_2(r, r') = N(N - 1) \sum_{\sigma_1 \cdots \sigma_N} \int d^3r_3 \cdots d^3r_N |\Psi_\lambda(r, \sigma_1, r', \sigma_2, r_3, \sigma_3, \cdots, r_N, \sigma_N)|^2.
\]

(4)

Then

\[
\rho^\lambda_2(r, r') = n(r)n(r') + n^\lambda_{xc}(r, r').
\]

(5)

By definition, \(n^\lambda_{xc} = n + n^\lambda_0\) where

\[
n^\lambda_{xc=0}(r, r') = n_x(r, r')
\]

(6)

is the exchange hole, which can be evaluated from the Slater determinant \(\Psi_0\).

We can then define “conventional” energies per electron

\[
\epsilon^\text{conv}_x(r) = \frac{e^2}{2} \int d^3r' n_x(r, r')
\]

(7)

\[
\epsilon^\text{conv}_c(r) = \frac{e^2}{2} \int_0^1 d\lambda \int d^3r' n^\lambda_c(r, r')
\]

\[
= \nu^\text{conv}_c(r) + \tau^\text{conv}_c(r),
\]

(8)

where

\[
\nu^\text{conv}_c(r) = \frac{e^2}{2} \int d^3r' n^\lambda_{xc=1}(r, r')
\]

(9)
is the conventional potential energy of correlation and $\tau_c^{\text{conv}}(r)$ is the conventional kinetic energy of correlation per electron. The exchange and correlation holes obey well-known sum rules [4, 5, 20]:

$$n_x(r, r') \leq 0,$$

(10)

$$\int d^3r' \ n_x(r, r') = -1,$$

(11)

$$\int d^3r' \ n^\lambda_c(r, r') = 0.$$

(12)

These equations provide important constraints on the conventional energy densities of Eqs. (7)-(9). Unconventional energy densities can have holes which do not satisfy Eqs. (11) and (12) at each $r$, but only in the system average over $n(r)$ [16, 17, 18].

In the high-density or weakly-interacting limit, where $\lambda e^2/|r' - r|$ can be treated as a weak perturbation, we find that $n^\lambda_c(r, r')$ is linear in $\lambda$ and thus that

$$\epsilon_c^{\text{conv}}(r) \rightarrow \frac{1}{2} \epsilon_c^{\text{conv}}(r) \quad \text{(high-density limit)}$$

(13)

from Eqs. (8) and (9). In the low-density or strongly-interacting limit, $n^\lambda_c(r, r')$ becomes independent of $\lambda$ and thus

$$\epsilon_c^{\text{conv}}(r) \rightarrow \nu_c^{\text{conv}}(r) \quad \text{(low-density limit)}.$$

(14)

The conventional energy densities in an atom have known asymptotics. Gunnarsson, Jonson and Lundqvist [21] showed that

$$\lim_{r \to \infty} \epsilon_x^{\text{conv}}(r) = -\frac{e^2}{2r},$$

(15)

$$\lim_{r \to \infty} \epsilon_c^{\text{conv}}(r) = 0.$$

(16)

More recently, March et al [22] derived cusp conditions at a nucleus of charge $Z$:

$$\frac{d}{dr}(n_x^{\text{conv}})|_{r=0} = -\frac{2Z}{a_0}(n_x^{\text{conv}})|_{r=0},$$

(17)

$$\frac{d}{dr}(n_c^{\text{conv}})|_{r=0} = -\frac{2Z}{a_0}(n_c^{\text{conv}})|_{r=0},$$

(18)

where $a_0 = \hbar^2/me^2$. Since the density $n(r)$ obeys a similar cusp condition, we conclude that $\epsilon_x^{\text{conv}}(r)$ and $\epsilon_c^{\text{conv}}(r)$ are cuspless.
It is straightforward to evaluate the exact $\epsilon_x^{\text{conv}}(r)$ of Eq. (7) from the Slater determinant $\Psi_0$, and results have been reported for atoms, molecules, and surfaces [2, 16, 23, 24, 25, 26].

It is almost as straightforward to evaluate the exact $\nu^{\text{conv}}(r)$ from Eq. (9) using the exact $\Psi_0$ and $\Psi_1$. But $\epsilon^{\text{conv}}(r)$ of Eq. (8) appears to require $\Psi_\lambda$ for all $\lambda$ between 0 and 1 (and has been evaluated in that way for some model or real solids [27, 28] and for the valence electrons of the silicon atom [29]).

From the fact that [4, 5]

$$E_c = V_c + T_c = \langle \psi_1 | \hat{H} | \psi_1 \rangle - \langle \psi_0 | \hat{H} | \psi_0 \rangle,$$  

(19)

we can of course define an easily-calculated endpoint correlation energy density,

$$\epsilon_c^{\text{endpt}}(r) = \nu^{\text{conv}}(r) + \tau_L^{\text{Lap}}(r),$$  

(20)

where the kinetic energy of correlation arises from

$$n(r)\tau_L^{\text{Lap}}(r) = -\frac{\hbar^2}{2m} \frac{\partial}{\partial r} \cdot \frac{\partial}{\partial r'} [\rho_1^{\lambda=1}(r,r') - \rho_1^{\lambda=0}(r,r')] |_{r'=r},$$  

(21)

as Huang and Umrigar [3] have done. Or we could define

$$n(r)\tau_L^{\text{grad}}(r) = -\frac{\hbar^2}{2m} \frac{\partial}{\partial r} \rho_1^{\lambda=1}(r,r') - \rho_1^{\lambda=0}(r,r')] |_{r'=r},$$  

(22)

as used by Baerends et al [1, 2]. In fact, according to Refs. 2 and 3,

$$\tau_L^{\text{Lap}}(r) = \tau_L^{\text{grad}}(r).$$  

(23)

Eq. (20) is an appealing choice for an exact correlation energy density, but probably

$$\tau_L^{\text{conv}}(r) \neq \tau_L^{\text{Lap}}(r), \quad \epsilon^{\text{conv}}(r) \neq \epsilon^{\text{endpt}}(r),$$  

(24)

as suspected in Refs. 1-3. So far as we can see, there is no simple local version of the adiabatic connection [4, 5]; the final integration over $r$ in Eq. (2) is needed to eliminate a mess of correction terms. Moreover, Fig. 1 of Ref. 1 or Fig. 3 of Ref. 3 for the He atom suggests that, while $\nu^{\text{conv}}(r)$ may be cuspless, $\tau_L^{\text{endpt}}(r)$ and $\epsilon^{\text{endpt}}(r)$ show pronounced cusps at the nucleus, where $\epsilon^{\text{conv}}(r)$ should show none [22]. Neither figure comes close to satisfying Eq. (13), contrary to our expectation for a weakly-interacting system like the helium atom.

3. Sophisticated Hybrid Model for the Conventional Correlation Energy Density

From the myriad of exact correlation energy densities, the conventional one of Eq. (8) stands out for its relevance to density functional theory and for its known properties: semper e pluribus unum.
Figure 1: Two exact local correlation energies per electron $\varepsilon_c(r)$ for the He atom ($< r > = 0.93$ bohr) compared to the exact conventional potential energy of correlation per electron $\nu^{\text{conv}}_c(r)$ from Refs. 3 and 31. $\varepsilon^{\text{endpt}}_c$ of Eq. (20) was calculated in Ref. 3. $\varepsilon^{\text{conv}}_c$ is our hybrid model of Eq. (25) for the conventional correlation energy per electron. $r$ is the radial distance from the nucleus.

As a model for $\varepsilon^{\text{conv}}_c(r)$, we propose a hybrid of wavefunction and density-functional theory:

$$\varepsilon^{\text{conv}}_c(r) = \nu^{\text{conv}}_c(r) \left[ 1 + C \frac{\tau^{PBE}_c(r)}{\nu^{PBE}_c(r)} \right],$$

(25)

$$C = \frac{T_c}{\int d^3 r n(r) \nu^{\text{conv}}_c(r) \frac{\tau^{PBE}_c(r)}{\nu^{PBE}_c(r)}},$$

(26)

where $\nu^{PBE}_c(r)$ and $\tau^{PBE}_c(r) = \varepsilon^{PBE}_c(r) - \nu^{PBE}_c(r)$ are the PBE GGA energies per electron from sections 4 and 5, and $\nu^{\text{conv}}_c(r)$ is the exact conventional potential energy of correlation per electron. Eq. (25) clearly integrates to the exact $E_c$. It satisfies Eq. (13) in the high-density limit (where $\tau^{PBE}_c/\nu^{PBE}_c \to -\frac{1}{2}$), and Eq. (14) in the low-density limit (where $\tau^{PBE}_c/\nu^{PBE}_c \to 0$, and C remains of order 1). It satisfies the cusp condition of Eq. (18), and is exact in two more limits: for a uniform density (where $\tau^{PBE}_c/\nu^{PBE}_c$ is exact) and for a one-electron density (where $\nu^{\text{conv}}_c = 0$).

Figure 1 compares $\varepsilon^{\text{conv}}_c$ of Eq. (25) to $\varepsilon^{\text{endpt}}_c$ of Eq. (20) and to $\nu^{\text{conv}}_c$ for the He atom, where $\varepsilon^{\text{endpt}}_c$ and $\nu^{\text{conv}}_c$ are from Refs. 3 and 31. For the helium atom, we find $C = 0.983$. It appears to us that $\varepsilon^{\text{conv}}_c$ is a very plausible representation.
Table 1: Correlation energies $E_c$, correlation potential energies $V_c$ and correlation kinetic energies $T_c$ for the helium atom (hartrees). Exact values from Refs. 3 and 32.

<table>
<thead>
<tr>
<th>method</th>
<th>$E_c$</th>
<th>$V_c$</th>
<th>$T_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA</td>
<td>-0.1125</td>
<td>-0.1806</td>
<td>0.0681</td>
</tr>
<tr>
<td>LYP</td>
<td>-0.0438</td>
<td>-0.0775</td>
<td>0.0337</td>
</tr>
<tr>
<td>CS</td>
<td>-0.0416</td>
<td>-0.0760</td>
<td>0.0344</td>
</tr>
<tr>
<td>PBE</td>
<td>-0.0420</td>
<td>-0.0794</td>
<td>0.0374</td>
</tr>
<tr>
<td>PKZB</td>
<td>-0.0473</td>
<td>-0.0868</td>
<td>0.0395</td>
</tr>
<tr>
<td>exact</td>
<td>-0.0421</td>
<td>-0.0788</td>
<td>0.0366</td>
</tr>
</tbody>
</table>

of the conventional correlation energy per electron.

4. Approximate Correlation Energy Densities

Density functional approximations for the correlation energy naturally take the form

$$E_{c}^{\text{approx}} = \int d^3r \ n(r)\epsilon_{c}^{\text{approx}}(r). \quad (27)$$

$\epsilon_{c}^{\text{approx}}(r)$ could be, but need not be, an approximation to either $\epsilon_{c}^{\text{conv}}(r)$ or $\epsilon_{c}^{\text{endpt}}(r)$. Even approximations that are based upon Eq. (2) typically make an integration by parts over $r$, and so need not agree with $\epsilon_{c}^{\text{conv}}(r)$.

As an example, let us consider the helium atom. In our own calculations, we will use an analytic Hartree-Fock electron density [30]; it would be better to use a correlated density, but our results would change little if we did. We have used this electron density to evaluate various approximate correlation energies $\epsilon_{c}^{\text{approx}}(r)$ for comparison with the model conventional $\epsilon_{c}^{\text{conv}}$ of Eq. (25).

Figure 2 shows this comparison for the local density approximation (LDA), the Colle-Salvetti (CS) meta-generalized gradient approximation (meta-GGA), and the Lee-Yang-Parr (LYP) approximation to CS. LYP faithfully reproduces CS, including its divergence of $\epsilon_{c}^{\text{approx}}(r)$ at the nucleus due to the divergence of its $\nabla^2n$ term [7]. The $\nabla^2n$ term in LYP is commonly eliminated via integration by parts, but here we are using the original LYP model for the correlation energy density.

Figure 3 shows the same comparison, but for the Perdew-Kurth-Zupan-Blaha (PKZB) meta-GGA and the Perdew-Burke-Ernzerhof (PBE) GGA. These two approximations (which reduce to LDA for a slowly-varying $n(r)$) give similar correlation energy densities. They have no divergence at the nucleus, but they do show a cusp of $\epsilon_{c}^{\text{approx}}(r)$ there.
Figure 2: Local correlation energy per electron $\epsilon_c(r)$ in the helium atom. Our hybrid model of Eq. (25) for the exact conventional $\epsilon_c(r)$ ("conv" exact) is compared to $\epsilon_c^{\text{approx}}(r)$ of the local density approximation, the Colle-Salvetti [9] functional, and the Lee-Yang-Parr [7] functional. $r$ is the radial distance from the nucleus.

Figure 3: Same as Fig. 2, but for the Perdew-Kurth-Zupan-Blaha [10, 11] and Perdew-Burke-Ernzerhof [8] functionals.
Overall, there is no better than modest agreement between $\epsilon_{c}^{\text{approx}}(r)$ and $\epsilon_{c}^{\text{"conv"}}(r)$, although (with the exception of LDA) there is good agreement between $E_{c}^{\text{approx}}$ and $E_{c}^{\text{exact}}$, as shown in Table 1.

5. Approximate Correlation Potential-Energy Densities

It is known [33, 34, 35] that

$$n_{c}^{\lambda=1}(r, r') = [1 - a_{0} \frac{\partial}{\partial a_{0}}] \int_{0}^{1} d\lambda n_{c}^{\lambda}(r, r'),$$

where $a_{0} = \hbar^{2}/me^{2}$ is the Bohr radius. It follows at once from Eqs. (8) and (9) that

$$\nu_{c}^{\text{"conv"}}(r) = e^{2}[1 - a_{0} \frac{\partial}{\partial a_{0}}] \left( \frac{\epsilon_{c}^{\text{"conv"}}(r)}{e^{2}} \right).$$

Within LDA, GGA, or meta-GGA, we can write

$$\epsilon_{c}^{\text{approx}} = -\frac{3e^{2}}{4\pi}(3\pi^{2}n)^{1/3}F_{c}^{\text{approx}}(r_{s}, s_{1}, \cdots),$$

where

$$r_{s}(r) = a_{0}^{-1} \left( \frac{3}{4\pi n(r)} \right)^{1/3}$$

and $s_{1}(r) \cdots$ are dimensionless variables that do not depend upon $a_{0}$ (such as $s = |\nabla n|/2k_{F}n$ where $k_{F} = (3\pi^{2}n)^{1/3}$). Then we define [36, 37]

$$\nu_{c}^{\text{approx}}(r) = -\frac{3e^{2}}{4\pi}(3\pi^{2}n)^{1/3}[1 + r_{s} \frac{\partial}{\partial r_{s}}]F_{c}^{\text{approx}}(r_{s}, s_{1}, \cdots).$$

Even if $\epsilon_{c}^{\text{approx}}$ does not correspond to $\epsilon_{c}^{\text{"conv"}}$, $\nu_{c}^{\text{approx}}$ still yields $V_{c}^{\text{approx}}$.

In Figs. 4 and 5, we compare $\nu_{c}^{\text{approx}}(r)$ for He in LDA, CS, LYP, PBE, and PKZB against the exact conventional $\nu_{c}^{\text{"conv"}}(r)$ [3, 31]. Again, there is no better than modest agreement in $\nu_{c}(r)$ to match the good agreement between $V_{c}^{\text{approx}}$ and $V_{c}^{\text{exact}}$ in Table 1.

It appears to us that the approximations are not trying to reproduce $\nu_{c}^{\text{"conv"}}(r)$ but some other choice of correlation potential energy per electron. However, for the PKZB and PBE approximations this other choice is not too different from the conventional $\nu_{c}^{\text{"conv"}}(r)$. The difference and that of Figs. 2 and 3 presumably arise from the integration by parts over $r$ of a $\nabla^{2}n$ term in the second-order gradient expansion of the correlation hole at an early stage of the derivation [38] of the PBE correlation energy functional. It has always been stressed that GGA’s model the system averages

$$< n_{xc}(u) >= \frac{1}{N} \int d^{3}r n(r) n_{xc}^{\text{"conv"}}(r, r + u),$$

(33)
Figure 4: Local potential energy of correlation per electron $\nu_c(r)$ in the helium atom. The exact conventional correlation potential-energy density from Refs. 3 and 31, $\nu_{c^{\text{conv}}}(r)$ of Eq. (9), is compared to $\nu_{c^{\text{approx}}}(r)$ from Eq. (32) in the local density, CS and LYP approximations. $r$ is the radial distance from the nucleus.

Figure 5: Same as Fig. 4, but for the PKZB and PBE approximations.
\[ E_{xc} = \int d^3r \ n(r) \epsilon_{xc}^{conv}(r), \quad (34) \]

and not necessarily the conventional local quantities.

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References