Role of the Exchange–Correlation Energy: Nature’s Glue

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ABSTRACT: In the Kohn–Sham density functional theory of ground-state electronic structure, only the exchange–correlation energy $E_{xc}$ must be approximated. Although $E_{xc}$ is not typically a large component of the total energy, it is the principal ingredient of the glue that binds atoms together to form molecules and solids. To illustrate this fact, we present self-consistent results for atomization energies of molecules and for surface energies and work functions of jellium, calculated within the “Hartree” approximation, which neglects $E_{xc}$. The Hartree world displays weak bonding between atoms, low or negative surface energies, and work functions that are close to zero. Other aspects of the Hartree world can be deduced from known size–effect relationships. The mechanism behind the glue role of exchange and correlation is the suppression of Hartree charge fluctuations. © 2000 John Wiley & Sons, Inc. Int J Quant Chem 77: 814–818, 2000

Key words: Hartree approximation; density functional theory; exchange–correlation energy; jellium surface energy; bonding

Introduction

Kohn–Sham density functional theory [1–3] is the most widely used method to find the ground-state electronic structure of atoms, molecules, and solids. In this theory, the density of electrons of spin $\sigma$,

$$n_{\sigma}(r) = \sum_{a} \theta(\mu - \varepsilon_{a\sigma}) |\psi_{a\sigma}(r)|^2,$$

is constructed from orbitals that solve the self-consistent one-electron Schrödinger equation

$$\left( -\frac{1}{2} \nabla^2 + v(r) + \int d^3r' \frac{n(r')}{|r-r'|} + v_{xc}^a(r) \right) \psi_{a\sigma}(r) = \epsilon_{a\sigma} \psi_{a\sigma}(r).$$

In Eq. (2), $v(r)$ is the external potential, and $n(r) = n_{\uparrow}(r) + n_{\downarrow}(r)$. The total energy is

$$E = \sum_{a\sigma} \theta(\mu - \varepsilon_{a\sigma}) \int d^3r \frac{1}{2} \nabla |\psi_{a\sigma}(r)|^2 + \int d^3r n(r)v(r) + \frac{1}{2} \int d^3r \int d^3r' \frac{n(r)n(r')}{|r-r'|} + E_{xc}[n_{\uparrow}, n_{\downarrow}] + E_{nn},$$

where $E_{nn}$ is the Coulomb repulsion of the nuclei.

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The exchange–correlation energy \( E_{\text{xc}} \) in Eq. (3) accounts for three distinct physical effects: The exchange energy \( E_x \leq 0 \) corrects the spurious self-interaction of one electron with itself and also contains the effects of the Pauli exclusion principle. The correlation energy \( E_c = E_{\text{xc}} - E_x \leq 0 \) accounts for the effects of Coulomb correlation upon the many-electron wave function. The exchange–correlation potential in Eq. (2) is the functional derivative

\[
v_{\text{xc}}^0(r) = \frac{\delta E_{\text{xc}}}{\delta n(r)}. \tag{4}
\]

Apart from the practical need to approximate the functional dependence of \( E_{\text{xc}} \) upon the spin densities \( n_1(r) \) and \( n_{\uparrow}(r) \), Kohn–Sham theory is exact for \( n_1, n_{\uparrow}, \) and \( E \). While it tends to be a relatively small part of the total energy of Eq. (3), especially for the heavier elements, \( E_{\text{xc}} \) plays an extremely important role in physics and chemistry: It is the major ingredient of the “glue” that binds atoms together to form molecules and solids.

The purpose of this short article is to stress the importance of \( E_{\text{xc}} \) by showing what the world would be like in the “Hartree” approximation, which neglects both \( E_{\text{xc}} \) and \( v_{\text{xc}}^0(r) \). This is not the approximation originally proposed by Hartree [4], which includes an orbital-dependent self-interaction correction for both \( E_{\text{xc}} \) and \( v_{\text{xc}}^0(r) \), except as discussed in the Appendix. The Hartree approximation can be simplified even further by making the Thomas–Fermi approximation [5, 6] in which the orbital kinetic energy of Eq. (3) is replaced by its local spin density approximation:

\[
T_s^{\text{TF}}[n_1, n_{\uparrow}] = \frac{1}{2} T_s^{\text{TF}}[2n_1] + \frac{1}{2} T_s^{\text{TF}}[2n_{\uparrow}], \tag{5}
\]

\[
T_s^{\text{TF}}[n] = \frac{3}{10} (3\pi^2)^{2/3} \int d^3 r n^{5/3}(r). \tag{6}
\]

In the opposite direction, the Hartree approximation can be refined by a sequence of approximations for \( E_{\text{xc}} \). The simplest is the local spin density (LSD) approximation [1]:

\[
E_{\text{xc}}^{\text{LSD}}[n_1, n_{\uparrow}] = \int d^3 r n(r) \epsilon_{\text{xc}}(n_1(r), n_{\uparrow}(r)), \tag{7}
\]

where \( \epsilon_{\text{xc}}(n_1, n_{\uparrow}) \) is the exchange–correlation energy per particle for an electron gas with uniform spin densities \( n_1 \) and \( n_{\uparrow} \). Next, in order of sophistication, is the generalized gradient approximation (GGA) [7],

\[
E_{\text{xc}}^{\text{GGA}}[n_1, n_{\uparrow}] = \int d^3 r f(n_1, n_{\uparrow}, \nabla n_1, \nabla n_{\uparrow}). \tag{8}
\]

The “meta-GGA” [8] makes use of additional local information, such as the Laplacian \( \nabla^2 n_\sigma \) or the kinetic energy density that appears in the first term of Eq. (3). These approximations are potentially exact for an electron gas of uniform or slowly varying density, and those functionals that are constructed nonempirically are typically exact or nearly exact in this limit. Near the upper level of sophistication is an approach [9] that treats exchange exactly, long-range correlation in the random-phase approximation (RPA), and the short-range correction to RPA in GGA.

### Atomization Energies, Surface Energies, and Work Functions

The atomization energy of a molecule is the minimum total energy that must be added to break the molecule into separate atoms. Table I shows the atomization energies of seven typical molecules, calculated in various approximations and compared to experiment. All calculations have been performed at the observed equilibrium geometries, and the contribution from zero-point vibration has been removed from the experimental atomization energies [7]. These calculations have been done self-consistently with the CADPAC [10] program, using a Gaussian basis set of triple-zeta quality that includes \( p \) and \( d \) polarization functions for hydrogen and \( d \) and \( f \) polarization functions for the first-row elements.

By Teller’s theorem [11], atoms do not bind to form molecules within the Thomas–Fermi approximation. The Hartree approximation, which neglects \( E_{\text{xc}} \) and the unrestricted Hartree–Fock approximation, which neglects \( E_{\text{xc}} \), produce binding, but it

#### Table I

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( \Delta_{\text{Hartree}} )</th>
<th>( \Delta_{\text{UHF}} )</th>
<th>( \Delta_{\text{LSD}} )</th>
<th>( \Delta_{\text{GGA}} )</th>
<th>( \Delta_{\text{expt}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)</td>
<td>57</td>
<td>84</td>
<td>113</td>
<td>105</td>
<td>109</td>
</tr>
<tr>
<td>N(_2)</td>
<td>112</td>
<td>115</td>
<td>267</td>
<td>243</td>
<td>229</td>
</tr>
<tr>
<td>O(_2)</td>
<td>35</td>
<td>33</td>
<td>175</td>
<td>144</td>
<td>121</td>
</tr>
<tr>
<td>F(_2)</td>
<td>2</td>
<td>–37</td>
<td>78</td>
<td>53</td>
<td>39</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>94</td>
<td>201</td>
<td>337</td>
<td>302</td>
<td>297</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>76</td>
<td>155</td>
<td>267</td>
<td>234</td>
<td>232</td>
</tr>
<tr>
<td>HF</td>
<td>50</td>
<td>97</td>
<td>162</td>
<td>142</td>
<td>141</td>
</tr>
</tbody>
</table>

\( ^a \)UHF is unrestricted Hartree–Fock. Experimental values were taken from [7] (1 kcal/mol = 1.594 \times 10^{-3} hartrees.)
is far weaker than in reality. LSD overbinds, and GGA reduces but does not entirely eliminate this overbinding tendency.

The surface energy of a solid is the energy per unit area needed to cleave a macroscopic surface. The simplest model of a solid is jellium, in which the surface energy of jellium, calculated self-consistently as in the work of Lang and Kohn [12, 13]. The negative surface energies at small electron density profile at the jellium surface. Table II shows the surface energy of jellium, calculated self-consistently as in the work of Lang and Kohn [12, 13]. The negative surface energies at small electron density profile at the jellium surface. Table II shows the surface energy of jellium, calculated self-consistently as in the work of Lang and Kohn [12, 13]. The negative surface energies at small electron density profile at the jellium surface. Table II shows that the work function, which is the energy needed to remove an electron through the surface, is close to zero in the Hartree approximation and seriously too low.

But the Hartree surface energies, like those [13] of the Thomas–Fermi approximation, are all negative and seriously too low.

The work function [12, 16] is the minimum energy needed to remove an electron through the surface. Table II shows that the work function, which is identically zero [13] in the Thomas–Fermi approximation, is close to zero in the Hartree approximation but realistic in LDA and GGA. These self-consistent Hartree results are prefigured in a variational calculation [17] with a simple analytic model for the electron density profile at the jellium surface.

Hartree electron densities are too diffuse, making the electrostatic dipole moment at the jellium surface,

\[
D = 4\pi \int_{-\infty}^{\infty} dx \frac{x(n(x) - \bar{n}(x))}{x},
\]

(10)
too large. And the Hartree approximation contains no driving force for magnetism or spin polarization, other than an external magnetic field or an odd electron number.

The too-low Hartree atomization energies of Ta of Table I, and the too-low Hartree surface energies of Table II, are related by the formulas of the following section.

### Size–Effect Relationships

The size–effect formulas presented here are approximate relationships between the properties of a macroscopic solid metal and the properties of a finite spherical cluster of radius \( R \). The smallest cluster is the atom, whose volume \( 4\pi R^3/3 = z/\bar{n} \) is assumed to be the volume per atom of the bulk solid. (Here \( z \) is the valence and \( \bar{n} \) the average valence electron density.) These formulas will help to describe the Hartree world in the next section.

The energy required to create the positively curved surface of a spherical cluster is [18]

\[
\sigma 4\pi R^2 + \gamma 2\pi R,
\]

(11)
and the energy to create the negatively curved surface of a vacancy is [18]

\[
\sigma 4\pi R^2 - \gamma 2\pi R,
\]

(12)
where \( \sigma \) is the surface energy and \( \gamma \) the curvature energy [15, 18]. The cohesive energy (atomization energy per atom of the solid) is estimated by applying Eq. (11) to a single atom.

The first ionization energy \( I \) and electron affinity \( A \) of a cluster are [19, 20]

\[
I = W + \left( \frac{1}{2} + c \right)/(R + \delta),
\]

(13)
\[
A = W + \left( -\frac{1}{2} + c \right)/(R + \delta),
\]

(14)
where \( W \) is the bulk work function; \( c \) and \( \delta \) are small, material-dependent parameters [20]. These equations may also be applied to a single atom.

### Conclusions: The Hartree World

It is sometimes suggested that Kohn–Sham theory works because the exchange–correlation energy, which must be approximated, is small. This statement is only partially true. In fact, the Hartree
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These two pictures are very different. In particular, a small finite volume fragment of the system has no charge fluctuation in the first picture, and a strong charge fluctuation [23] in the second picture. Random clusters of electrons have high electrostatic energy. To reconcile the two pictures, start with the second one (classical ideal gas of finite electrons) and imagine that each electron is divided into \( m \geq 2 \) equal parts, with no change in the charge density. The electrostatic energy remains as in (A1), the root-mean-square number fluctuation [23] in a fixed volume element increases by \( \sqrt{m} \), but the charge fluctuation decreases by \( \sqrt{m} / m \), and tends to zero as \( m \to \infty \). In the latter limit, the two pictures become the same.

In the second picture, exchange and correlation reduce the Hartree charge fluctuations [23, 24] at fixed electron charge, and so lower the energy. This lowering is greater when the electrons are brought closer together, explaining the glue role of exchange and correlation.

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