

Density Functional Theory with Correct Long-Range Asymptotic Behavior

Roi Baer^{1,*} and Daniel Neuhauser^{2,†}

¹*Department of Physical Chemistry and the Lise Meitner Minerva-Center for Computational Quantum Chemistry, the Hebrew University of Jerusalem, Jerusalem 91904 Israel*

²*Department of Chemistry and Biochemistry, University of California at Los Angeles, Los Angeles, California 90095, USA*
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We derive an exact representation of the exchange-correlation energy within density functional theory (DFT) which spawns a class of approximations leading to correct long-range asymptotic behavior. Using a simple approximation, we develop an electronic structure theory that combines a new local correlation energy (based on Monte Carlo calculations applied to the homogeneous electron gas) and a combination of local and explicit long-ranged exchange. The theory is applied to several first-row atoms and diatomic molecules where encouraging results are obtained: good description of the chemical bond at the same time allowing for bound anions, reasonably accurate affinity energies, and correct polarizability of an elongated hydrogen chain. Further stringent tests of DFT are passed, concerning ionization potential and charge distribution under large bias.

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Density functional theory (DFT) [1,2] is an in-principle exact approach to molecular electronic structure furnishing a starting point for useful approximations. The local density (LDA) [2] and local spin-density (LSDA) approximations form surprisingly well-balanced, robust, and reasonably accurate theories for ground-state properties of molecules, solids, and even metals [3–5]. The generalized gradient approximation (GGA) [6,7] improves accuracy further and in finite systems hybrid functional approximations (HFA) [8,9] are often even more powerful. Despite their great success, present functionals often fail to account for anions and processes involving long-range charge transfer. For example, the polarizability of elongated molecules is strongly exaggerated [10]. These problems are associated with the existence of self-interaction in the local functionals [11–15], leading to spurious asymptotic form of the exchange-correlation (XC) potentials derived from them [13,16].

A particularly useful method for self-interaction correction (SIC) was suggested by Perdew and Zunger [13] (PZ), and has been successfully applied to anions and computation of electron affinities [17]. Recently, a systematic study of this method was performed [18]. The theoretical difficulties were overcome by the optimized effective potential (OEP) [19], further developed in a form that can be applied to systems beyond atoms [20,21]. SIC and OEP predict correct polarizability and electron affinity where LSDA/GGA fail [21].

One well-known “type” of electronic-structure theory not having the problem of self-interaction is the Hartree-Fock theory (HFT). In HFT, the interplay between exchange and Hartree terms results in exact self-interaction removal. HFT, however, is not sufficiently accurate because it neglects the correlation energy. The simple approach, adding an LSDA correlation energy functional to the explicit orbital exchange of HFT, is unsatisfactory

because the exact exchange disrupts a delicate cancellation of errors existing in LSDA [3].

This Letter describes a new approach to self-interaction correction and long-range behavior of DFT approximations. We derive a new exact representation of the correlation energy that endorses approximations with correct asymptotic behavior. A simple approximation using this theory is then shown to yield a new useful functional, exhibiting good description of chemical bonds while allowing for stable anions and correct polarizability of elongated molecules. The new functional is better suited for use in confined systems, where the homogeneous electron gas (HEG) correlation energy is usually too large by about 100%. An account of the theory, followed by a demonstration on a few representative systems, is given below.

We consider a system of N electrons, with the Hamiltonian $\hat{H} = \hat{T} + \hat{V} + \hat{U}$ where $\hat{T} = \sum_{i=1}^N (-\frac{1}{2}\nabla_i^2)$ is the kinetic energy (we use atomic units, $e^2/4\pi\epsilon_0 = \hbar = \mu_e = 1$) $\hat{V} = \sum_{i=1}^N v(\hat{\mathbf{r}}_i)$ the external potential, and $\hat{U} = \frac{1}{2} \times \sum_{i \neq j=1}^N u(\hat{r}_{ij})$ (where $\hat{r}_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$) is the interaction, with $u(r)$:

$$u(r) = \frac{1}{r}. \quad (1)$$

In DFT, all expectation values are functionals of the ground-state density $n(\mathbf{r})$. The energy functional [2]

$$E_{v,N}[n] = T_s[n] + V[n] + E_H[n] + E_{XC}[n] \quad (2)$$

is the basic functional since by minimizing it one maps the interacting electrons onto noninteracting fermions obtaining the ground-state density and energy. In Eq. (2), $T_s[n]$ is the noninteracting kinetic energy, $V[n] = \int v(\mathbf{r})n(\mathbf{r})d^3r$,

$$E_H[n] = \frac{1}{2} \int n(\mathbf{r})n(\mathbf{r}')u(|\mathbf{r} - \mathbf{r}'|)d^3rd^3r' \quad (3)$$

is the Hartree energy, and

$$E_{\text{XC}}[n] = T[n] - T_s[n] + U[n] - E_H[n] \quad (4)$$

is the exchange-correlation energy (XCE), where $T[n]$ is the kinetic energy and $U[n]$ the electron-electron repulsion energy functionals.

The XCE is of course practically impossible to determine exactly. Yet we can express it using a straightforward extension of the adiabatic-connection theorem [22–24]. For this, we consider a family of N particle systems continuously parameterized by $0 \leq \gamma < \infty$, all having the same ground-state density n but in each the particles interact via a different descreened two-body interaction:

$$u_\gamma(r) = \frac{1 - e^{-\gamma r}}{r}. \quad (5)$$

For large interparticle distances $\gamma r \gg 1$, the particles of system γ repel just like electrons, but at short distances the repulsion is moderated and nonsingular. Each system γ has a unique ground-state wave function Ψ_γ (assuming v representability). The system with $\gamma = \infty$ is the original Coulomb interacting system, having the wave function Ψ_∞ . The system with $\gamma = 0$ corresponds to noninteracting particles with Ψ_0 a Slater determinant of N spin orbitals. The adiabatic-connection theorem states

$$E_{\text{XC}}[n] = \int_0^\infty \langle \Psi_{\gamma'} | \hat{W}_{\gamma'} | \Psi_{\gamma'} \rangle d\gamma' - E_H[n], \quad (6)$$

where $\hat{W}_\gamma = \frac{1}{2} \sum_{i \neq j} w_\gamma(\hat{r}_{ij})$, $w_\gamma(r) = e^{-\gamma r}$.

Evaluating the XCE, Eq. (6) is again impossible. Yet, a simple approximation already leads to a meaningful theory: assume that, in Eq. (6), Ψ_γ is replaced by Ψ_0 . Under this approximation, the integral can be performed and yields the HFT exchange energy. The next simple approximation is to assume $\Psi_{\gamma'} = \Psi_0$ for $\gamma' < \gamma$ and $\Psi_{\gamma'} = \Psi_\infty$ for $\gamma' > \gamma$, for some $0 < \gamma < \infty$, giving

$$\int_0^\infty \langle \Psi_{\gamma'} | \hat{W}_{\gamma'} | \Psi_{\gamma'} \rangle d\gamma' \approx \langle \Psi_0 | \hat{U}_\gamma | \Psi_0 \rangle + \langle \Psi_\infty | \hat{Y}_\gamma | \Psi_\infty \rangle, \quad (7)$$

where $\hat{U}_\gamma = \frac{1}{2} \sum_{i \neq j} u_\gamma(\hat{r}_{ij})$ and $\hat{Y}_\gamma = \frac{1}{2} \sum_{i \neq j} y_\gamma(\hat{r}_{ij})$, with $y_\gamma(r) = e^{-\gamma r}/r$ the Yukawa potential. The first term on the right in Eq. (7) is simply a HFT potential energy $\langle \Psi_0 | \hat{U}_\gamma | \Psi_0 \rangle \equiv E_H^\gamma[n] + K_X^\gamma[n]$ for the interaction $u_\gamma(r)$, where $E_H^\gamma[n]$ is defined by Eq. (3) with the Coulomb potential $u(r)$ replaced by the descreened potential $u_\gamma(r)$ and

$$E_X^\gamma[n] = \frac{1}{2} \int |P[n](\mathbf{r}, \mathbf{r}')|^2 u_\gamma(|\mathbf{r} - \mathbf{r}'|) d^3r d^3r' \quad (8)$$

is the corresponding exchange energy. In Eq. (8) $P[n](\mathbf{r}, \mathbf{r}')$ is the density matrix of noninteracting electrons having density n . From Eqs. (4), (6), and (7), the error, i.e., the difference between the exact and approximate XCE, is

$$\Delta E_{\text{XC}}^\gamma = [T(n) + \langle \Psi_\infty | \hat{U}_\gamma | \Psi_\infty \rangle - [T_s(n) + \langle \Psi_0 | \hat{U}_\gamma | \Psi_0 \rangle]]. \quad (9)$$

We now study two limits of this approximation. For $\gamma = 0$, $U_\gamma = 0$ so the error is $\Delta E_{\text{XC}}^{\gamma=0} = T[n] - T_s[n]$, a manifestly *non-negative* quantity [4], while, for $\gamma \rightarrow \infty$, $U_\gamma \rightarrow U$ and so $\Delta E_{\text{XC}}^\gamma \rightarrow E_C$, where E_C is the correlation energy, a manifestly *nonpositive* quantity. Thus, assuming continuity, we conclude that there must always exist $0 < \gamma < \infty$ (in general depending on the density) for which $\Delta E_{\text{XC}}^\gamma = 0$, i.e., the approximation (7) is *exact*. This allows us to assert that the energy functional can be accurately written as

$$E_{v,N}[n] = T_s[n] + V[n] + E_H[n] + E_X^\gamma[n] + E_{\text{XC}}^\gamma[n], \quad (10)$$

where

$$E_{\text{XC}}^\gamma[n] = \langle \Psi_\infty | \hat{Y}_\gamma | \Psi_\infty \rangle - \frac{1}{2} \int n(\mathbf{r})n(\mathbf{r}')y_\gamma(|\mathbf{r} - \mathbf{r}'|)d^3r d^3r'. \quad (11)$$

The sum of the last two terms in Eq. (10) is an exact representation of the XC energy and constitutes a starting point for approximations, concentrating on simplified forms for the functionals $\gamma[n]$ and $E_{\text{XC}}^\gamma[n]$. The important feature is that this approach allows to naturally introduce the explicit exchange functional $E_X^\gamma[n]$. This functional produces a potential which at large distances ($r\gamma \gg 1$) corrects the spurious self-interaction in the Hartree-potential derived from $E_H[n]$. Thus, $E_X^\gamma[n]$ heals the ailments of local and generalized gradient density approximations associated with the spurious long-range self-interaction.

Let us now make the simplest and perhaps crudest approximation: assume γ is *completely independent* of n . We show that this leads to a useful molecular electronic-structure theory. For definiteness, we further assume $\gamma = 1a_0^{-1}$ (future optimization of this value is likely to improve results). Additionally, the energy of Eq. (11) is approximated as a local-density functional:

$$E_{\text{XC}}^\gamma[n] \approx \int \varepsilon_{\text{XC}}^\gamma(n(\mathbf{r}))n(\mathbf{r})d^3r, \quad (12)$$

where $\varepsilon_{\text{XC}}^\gamma(n)$ is the XCE per particle of Eq. (11) for a HEG. For convenience, we write this function as

$$\varepsilon_{\text{XC}}^\gamma(n) = \varepsilon_X^\gamma(n) + \varepsilon_C^\gamma(n), \quad (13)$$

where $\varepsilon_X^\gamma(n)$ is the analytical local screened exchange in a HEG given in [25]. The function $\varepsilon_C^\gamma(n)$ was evaluated numerically for the HEG using the shifted-contour auxiliary field Monte Carlo (SCAFMC) method [26,27], performed with plane waves. In this preliminary account we made no attempt to fully converge to the infinite cell size limit and the statistical error is estimated to be $\sim 10\%$. A more rigorous calculation and a full account of the details will be published elsewhere. We calculated $\varepsilon_C^\gamma(n)$ (with $\gamma = 1a_0^{-1}$) at several densities given by $r_s = 1, 2, 3, 5, 10, 20$. For convenience of application, the results are expressed in terms of the ratio $\eta = \varepsilon_C^\gamma/\varepsilon_C^{\text{LDA}}$ where $\varepsilon_C^{\text{LDA}}$ is the (usual) full

correlation energy for the HEG (parametrized in any DFT code).

We use a simple form to fit the SCAFMC results:

$$\eta(r_s) \equiv \frac{\varepsilon_C^{\gamma=1}(n)}{\varepsilon_C^{\text{LDA}}(n)} = \frac{A}{C_0 + C_1 r_s + r_s^2}, \quad (14)$$

finding $A = 3.4602$, $C_0 = 3.2$, $C_1 = -0.9$, as shown in Fig. 1. For almost all densities, except the very high density regime, η is smaller than 1, decaying to zero as $r_s \rightarrow \infty$. Thus, ε_C^γ is smaller than $\varepsilon_C^{\text{LDA}}$ as we know it should be for confined systems. It is interesting that SCAFMC results show that η is somewhat greater than 1 in the high-density limit. This has to be further checked by increasing the accuracy of the SCAFMC calculation, a feat left for future investigations. For the purpose of demonstration, we used the ratio η also for the spin-polarized correlation energy.

The functional of Eq. (10) contains a long-range portion of explicit exchange $E_X^\gamma[n]$, and a complementary local-density exchange and correlation functionals based on $\varepsilon_X^\gamma(n)$ and $\varepsilon_C^\gamma(n)$. In principle, a KS application of the functional requires an OEP approach [19]. To circumvent this complication, we minimized the energy E_v as a functional of orbitals instead of the density. Since both approaches are variational they are known to yield very similar occupied orbitals and energies [19]. We now show this functional furnishes balanced molecular electronic structure: it has built-in correct long-range behavior and good description of the chemical bond. We performed several calculations done with a plane-wave code, using norm-conserving pseudopotentials [28] and a LDA parametrization of the HEG correlation energy [29]. All results are fully self-consistent and converged with respect to cell size and grid spacing.

We first discuss the computed polarizability of linear chains of hydrogen atoms [10], shown in Fig. 2, using LDA, HFT, and the new functional. The HFT results are known to be similar to accurate wave function methods

[21], and the new functional gives essentially identical results to HFT, in contrast to LSDA which greatly overestimates polarizability. Chemical bonds and atomic electron affinities are reasonably well described by the new functional as shown for several examples in Table I, compared with experiments. Comparing to LSDA, it is seen that atomization energies are greatly improved; vibrational frequencies have comparable errors but bond lengths are worse. Atomic electron affinities are reproduced well with the maximal error of 0.34 eV for F. An additional test is in the equality of ε_H and IP; the former is the energy of the highest occupied level and IP is the ionization potential [16]. For the atoms considered in Table I, LSDA yields a poor result $(\text{IP}/\varepsilon_H)_{\text{LDA}} \approx 1.8$, while the new functional yields a good value, $(\text{IP}/\varepsilon_H)_{\gamma=1} \approx 1.05$. Another stringent test for DFT is the ‘‘derivative discontinuity’’ property: a weakly coupled molecule or atom must have an *integer* number of electrons [12]. We checked this by considering two distant hydrogen atoms under a bias v_{bias} . LSDA erroneously shows a continuous charge transfer between the atoms as v_{bias} is increased. The new functional describes the correct physics: when $v_{\text{bias}} < \text{IP} + \text{EA}$ no charge is transferred while a complete electron is transferred otherwise.

Summarizing, we developed an exact representation of the XC energy, constructing a new approximate functional exhibiting correct long-range behavior. The function $v_\gamma(r)$ [Eq. (5)] is not fundamental: any interaction that smoothly turns off the Coulomb potential ‘‘from the inside out’’ leads to a similar theory. Recently, the form $\text{erf}(\gamma r)$ was used [30] in an exchange-only method. Related approaches to ours [31,32] also separated the interaction to long-range and short-range parts but for different purposes.

Future work is needed. Monte Carlo calculations will be extended, seeking a spin-polarized $\varepsilon_C^\gamma(n)$. It is important to optimize γ or try new forms of $\gamma[n]$. Applications await, computing molecular response, excitations, especially for

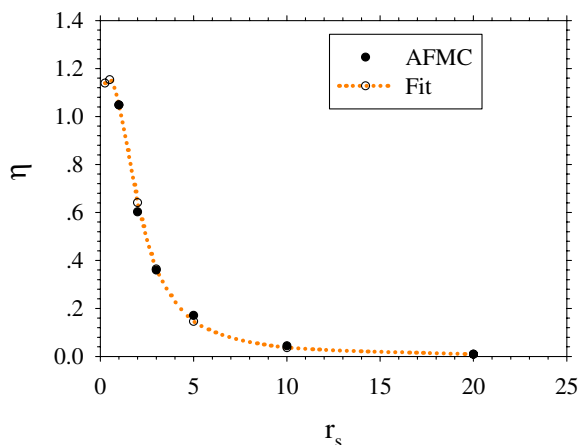


FIG. 1 (color online). The ratio $\eta = \varepsilon_C^\gamma / \varepsilon_C^{\text{LDA}}$ as a function of r_s for $\gamma = 1a_0^{-1}$. Shown are the AFMC results (filled dots) and the analytical fit (dotted curve and empty circles).

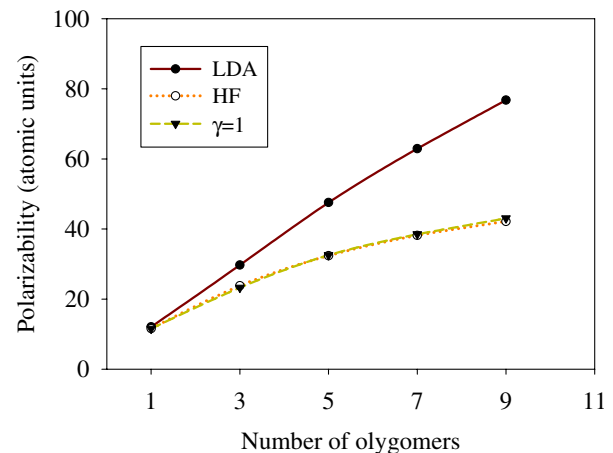


FIG. 2 (color online). Polarizability of a linear hydrogen chain, as a function of its length, calculated with LDA, HFT, and the present functional.

TABLE I. Atomization energy, bond length, and vibrational frequency, and atomic affinity energy, comparing experimental data to the $\gamma = 1$ approximation and the LSDA.

Atom (X)		kcal/mol ΔE ($X2$)		Angstrom R_e ($X2$)		cm^{-1} ω_e ($X2$)		eV EA (X)	
C	Expt.	145	[36]	1.242		1855	[37]	1.26	[38]
	$\gamma = 1$	132		1.27		1810		1.33	
	LSDA	169		1.25		1770			
N	Expt.	225	[39]	1.098	[37]	2358	[37]	Unstable	
	$\gamma = 1$	223		1.06		2540		Unstable	
	LSDA	256		1.089		2520			
O	Expt.	118	[39]	1.208	[37]	1580	[37]	1.46	[38]
	$\gamma = 1$	122		1.14		1640		1.50	
	LSDA	167		1.20		1590			
F	Expt.	37	[39]	1.412	[37]	916	[37]	3.40	[38]
	$\gamma = 1$	35		1.330		1200		3.73	
	LSDA	75		1.390		1000			

Rydberg states using time-dependent DFT. In molecular conductance [33] self-repulsion removal is important, as they are for metallic surfaces [34] and strong lasers [35].

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*Electronic address: roi.baer@huji.ac.il

†Electronic address: dxn@chem.ucla.edu

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