

Local and gradient-corrected density functionals: A glance under the hood

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The generalized gradient approximation (GGA) corrects many of the shortcomings of the local spin-density (LSD) approximation. The accuracy of GGA for ground-state properties of molecules is comparable to or better than the accuracy of conventional quantum chemical methods such as second-order Møller-Plesset perturbation theory. By studying various decompositions of the exchange-correlation energy E_{XC} , we show that the real-space decomposition of E_{XC} facilitates the most detailed understanding of how the local spin-density approximation and the Perdew-Wang 1991 GGA work. The real-space decomposition shows that the near universality of the on-top value for the exchange-correlation hole connects the homogeneous electron gas to inhomogeneous systems such as atoms and molecules. The coupling-constant decomposition shows that the exchange-correlation energy at full coupling strength $E_{XC,\lambda=1}$ is approximated more accurately by local and semi-local functionals than is the coupling-constant average E_{XC} . We use this insight both to critique popular hybrid functionals and to extract accurate energies from exact electron densities by using functionals for the exchange-correlation energy at full coupling strength. Finally, we show how a reinterpreted spin density functional theory can be applied to systems with static correlation.

I. DENSITY FUNCTIONALS IN QUANTUM CHEMISTRY

The main goal of quantum chemistry is the reliable prediction of molecular properties [1]. The development of generalized gradient approximations (GGA's) [2–10] has made density functional theory [11–13] a serious competitor to conventional quantum chemistry methods for ground-state properties. The latter methods include Configuration Interaction techniques, Coupled-Cluster methods, and the Møller-Plesset perturbation expansion [14]. They account for electron correlation, but suffer in general from basis set problems. These basis set problems are much less severe in current density functional methods, since (as we show below) the pair density is not expanded in a basis of one-particle functions.

The accuracy of the GGA is usually comparable to conventional quantum chemistry methods, at much lower computational cost. GGA's offer significant improvements in the calculation of molecular properties compared to their ancestor, the local spin-density (LSD) approximation [15]. The local spin-density approximation has not been popular amongst chemists, mainly because of its tendency to overestimate the binding energy of molecules.

In practical electronic structure calculations based on density functional theory [12], a set of independent-particle equations (the Kohn-Sham equations [15]) is solved. These equations require as input an approximation to the exchange-correlation energy E_{XC} as a functional of the electron density. The GGA approximations to E_{XC} depend on both the local spin-density $n_\sigma(\mathbf{r})$ and the gradient of the local spin-density. Among the popular GGA's, the Perdew-

Wang (PW91) [7–10] functional allows the most detailed understanding of how GGA's work and why they work, since this approximation contains no empirical parameter and is constructed from first principles. Results of calculations with this form [9] show that it typically reduces exchange energy errors from 10% in LSD to 1%, and correlation energy errors from 100% to about 10%. PW91 corrects the LSD overestimate of atomization energies for molecules and solids in almost all cases, it enlarges equilibrium bond lengths and lattice spacings, usually correctly, and reduces vibrational frequencies, again usually correctly [10]. PW91 also generally improves activation barriers [16]. For recent results with PW91, see Refs. [17–27].

As indicated above, the exchange-correlation energy E_{XC} as a functional of the electron density is the crucial quantity in Kohn-Sham calculations. In this article we discuss various decompositions of the exchange-correlation energy, and we show which of these decompositions is accurately approximated by LSD and by the PW91 approximation. This analysis makes it possible to understand how and why local and semilocal functionals work even for highly inhomogeneous electron systems, such as atoms and molecules.

II. DECOMPOSITIONS OF E_{XC}

The basic formula which serves as the starting point for various decompositions of E_{XC} is [11–13]

$$E_{XC} = \int_0^1 d\lambda \int_0^\infty du \, 2\pi u \int \frac{d\Omega_u}{4\pi} \times \int d^3r \, n(\mathbf{r})n_{XC,\lambda}(\mathbf{r}, \mathbf{r} + \mathbf{u}). \quad (1)$$

The exchange-correlation hole $n_{\text{XC},\lambda}(\mathbf{r}, \mathbf{r} + \mathbf{u})$ at coupling strength λ is given in terms of the pair density $P_\lambda(\mathbf{r}\sigma, (\mathbf{r} + \mathbf{u})\sigma')$ by

$$n(\mathbf{r})[n(\mathbf{r} + \mathbf{u}) + n_{\text{XC},\lambda}(\mathbf{r}, \mathbf{r} + \mathbf{u})] = \sum_{\sigma, \sigma'} P_\lambda(\mathbf{r}\sigma, (\mathbf{r} + \mathbf{u})\sigma'). \quad (2)$$

σ and σ' are the spin variables of the electrons. $P_\lambda(\mathbf{r}\sigma, \mathbf{r}'\sigma')$ (where $\mathbf{r}' = \mathbf{r} + \mathbf{u}$) gives the probability density to find an electron with spin σ at \mathbf{r} and an electron with spin σ' at \mathbf{r}' . The pair density is related to the many-electron wave function $\Psi_\lambda(\mathbf{r}, \sigma, \mathbf{r}', \sigma', \dots, \mathbf{r}_N, \sigma_N)$ by

$$P_\lambda(\mathbf{r}\sigma, \mathbf{r}'\sigma') = N(N-1) \sum_{\sigma_3, \dots, \sigma_N} \int d^3r_3 \dots \int d^3r_N \times \left| \Psi_\lambda(\mathbf{r}, \sigma, \mathbf{r}', \sigma', \dots, \mathbf{r}_N, \sigma_N) \right|^2. \quad (3)$$

Ψ_λ is the ground-state wave function of a system in which the electron-electron repulsion operator is multiplied by λ and the external potential is varied with λ so that the electron density is equal to the physical ground-state density for all values of λ . $\Psi_{\lambda=1}$ is the interacting wavefunction found by traditional correlated methods, while $\Psi_{\lambda=0}$ is the exact exchange wavefunction (which is similar to that of Hartree-Fock [28]). Eqs. 1 and 2 suggest a number of possibilities to decompose E_{XC} by simply permuting the sequence of integrations and summations. The decomposed approximate exchange-correlation energy can then be compared with the corresponding exact quantity.

A. Energy-density decomposition of $E_{\text{XC},\lambda}$

We examine the integrand of the expression

$$E_{\text{XC},\lambda} = \int d^3r n(\mathbf{r}) \epsilon_{\text{XC},\lambda}(\mathbf{r}), \quad (4)$$

where

$$\epsilon_{\text{XC},\lambda}(\mathbf{r}) = \int_0^\infty du 2\pi u \int \frac{d\Omega_u}{4\pi} n_{\text{XC},\lambda}(\mathbf{r}, \mathbf{r} + \mathbf{u}). \quad (5)$$

(E_{XC} is related to $E_{\text{XC},\lambda}$ by $E_{\text{XC}} = \int_0^1 d\lambda E_{\text{XC},\lambda}$). In the local spin-density approximation the energy per particle $\epsilon_{\text{XC},\lambda}(\mathbf{r})$ of an arbitrary inhomogeneous system is approximated by that of a homogeneous electron gas with spin density $n_\sigma(\mathbf{r})$, i.e., $\epsilon_{\text{XC}}(\mathbf{r}) = \epsilon_{\text{XC}}^{\text{unif}}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r}))$. The error in E_{XC} resulting from this approximation is typically about 10%. The energy per particle close to a nucleus is usually overestimated, and that in the tail region of the electron density is underestimated [29]. However, the region close to the nuclei has a small volume and the contribution from the tail region is very small, since the energy per particle

gets weighted by the electron density in Eq. 4. In the valence region of atoms and molecules, $\epsilon_{\text{XC}}^{\text{unif}}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r}))$ shows a semiquantitative agreement with the exact energy per particle. However, the PW91 energy density is not so useful for understanding how the PW91 functional works [30], since the energy density $n\epsilon_{\text{XC},\lambda}^{\text{PW91}}$ has been simplified by an integration by parts, which leaves E_{XC} unchanged but leads to an ill-defined $n(\mathbf{r})\epsilon_{\text{XC},\lambda}^{\text{GGA}}(\mathbf{r})$.

B. Real-space decomposition of $E_{\text{XC},\lambda}$

The real-space decomposition of the $E_{\text{XC},\lambda}$, which is defined by

$$E_{\text{XC},\lambda} = N \int_0^\infty du 2\pi u \langle n_{\text{XC},\lambda}(u) \rangle \quad (6)$$

where the system- and spherically averaged hole is

$$\langle n_{\text{XC},\lambda}(u) \rangle = \int \frac{d\Omega_u}{4\pi} \frac{1}{N} \int d^3r n(\mathbf{r}) n_{\text{XC},\lambda}(\mathbf{r}, \mathbf{r} + \mathbf{u}), \quad (7)$$

offers the most detailed insight into the LSD and PW91 functionals. In fact the PW91 exchange-correlation functional is based on a model for the system-averaged exchange-correlation hole $\int d^3r n(\mathbf{r}) n_{\text{XC},\lambda}(\mathbf{r}, \mathbf{r} + \mathbf{u})/N$. Detailed studies [31] of $\langle n_{\text{XC},\lambda}(u) \rangle$ have shown that even the LSD approximation to this quantity is remarkably accurate. Many exact conditions on the exact $\langle n_{\text{XC},\lambda}(u) \rangle$, such as the normalization condition $\int_0^\infty du 4\pi u^2 \langle n_{\text{XC},\lambda}(u) \rangle = -1$, are satisfied by LSD, since the LSD exchange-correlation hole is the hole of a possible physical system. The normalization condition on the hole together with the on-top ($u = 0$) value for $n_{\text{XC},\lambda}(\mathbf{r}, \mathbf{r} + \mathbf{u})$ set the scale for the exchange-correlation hole and therefore the scale for $\langle n_{\text{XC},\lambda}(u) \rangle$ and $E_{\text{XC},\lambda}$. Thus the on-top value of $n_{\text{XC},\lambda}(\mathbf{r}, \mathbf{r} + \mathbf{u})$ plays a crucial role in density functional theory. Investigations [32] on a number of systems show that the on-top value of the hole as a function of the local density is almost universal among Coulomb systems. Thus the LSD approximation to this quantity is very accurate, especially in the valence and tail regions of the electron density [32]. As a consequence, any approximate density functional should reproduce the correct LSD on-top value of the exchange-correlation hole in the limit of slowly varying electron densities. The PW91 functional has the LSD on-top value built in. It is based on a systematic expansion of the exchange-correlation hole in terms of the local density and the gradient of the local density. This gradient expansion approximation (GEA) to second order in ∇n improves the description of the hole at intermediate u values, but its spurious large- u behavior [33] violates a number of important constraints on the exact hole, such as the normalization condition. By restoring these conditions via the real-space cutoff procedure [8], we obtain the PW91 model for the exchange-correlation hole. Since the r integration

in Eq. 7 involves an integration by parts which changes the local hole $n_{\text{XC},\lambda}(\mathbf{r}, \mathbf{r} + \mathbf{u})$, only the system-averaged hole is a well-defined quantity in the PW91 construction. Detailed studies [29,31] of the spherical- and system-averaged hole for molecules and atoms show that the PW91 approximation to this quantity significantly improves the LSD model. Other popular GGA's [5,6] do not provide models of the exchange-correlation hole and thus do not allow a detailed analysis of correlation effects on molecular bond formation.

C. Spin-decomposition of $E_{\text{XC},\lambda}$

Another decomposition of the exchange-correlation hole and therefore of the exchange-correlation energy distinguishes between electrons with parallel and anti-parallel spins:

$$E_{\text{XC},\lambda} = E_{\text{XC},\lambda}^{\uparrow\uparrow} + E_{\text{XC},\lambda}^{\downarrow\downarrow} + E_{\text{XC},\lambda}^{\uparrow\downarrow}, \quad (8)$$

where

$$E_{\text{XC},\lambda}^{\sigma,\sigma} = \frac{1}{2} \int d^3r \int d^3r' \frac{P_\lambda(\mathbf{r}\sigma, \mathbf{r}'\sigma) - n_\sigma(\mathbf{r})n_\sigma(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|},$$

$$E_{\text{XC},\lambda}^{\uparrow\downarrow} = \int d^3r \int d^3r' \frac{P_\lambda(\mathbf{r}\uparrow, \mathbf{r}'\downarrow) - n_\uparrow(\mathbf{r})n_\downarrow(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (9)$$

The Pauli principle prevents two parallel-spin electrons from coming close to each other, i.e., $P(\mathbf{r}\sigma, \mathbf{r}\sigma) = 0$. Electron-electron repulsion cannot deepen the corresponding hole at $u = 0$, so the spatial extent of the hole is not significantly reduced. Note that the deeper the hole at $u = 0$, the shorter-ranged it must be to satisfy the normalization condition. On the other hand, the on-top value of the exchange-correlation hole for two electrons with antiparallel-spin orientation is significantly lowered by electron-electron repulsion, and the normalization therefore assures that the spatial extent of the hole gets reduced by correlation. Local and semilocal approximations work best if the exchange-correlation hole is confined to a small region of space around the reference electron. In this case the information about the local density and the gradient of the density is sufficient to capture the important features of the exchange-correlation hole. Thus it is not surprising that local and semilocal functionals work better for the correlation energy between antiparallel-spin electron than they do for the correlation energy between parallel-spin electrons [29]. However, attempts to construct a hybrid scheme which uses a GGA for antiparallel-spin correlation and wave function methods for parallel-spin correlation are of limited use [29], since the correlation effects between parallel-spin electrons are as difficult to describe within a finite basis set approach as are correlation effects between antiparallel-spin electrons.

Finally we note that the approximate GGA for antiparallel-spin [34] predicts $E_{\text{C}}^{\downarrow\downarrow} + E_{\text{C}}^{\uparrow\uparrow}$ to be 20% of the total correlation energy of Ne , in good agreement with sophisticated wave function calculations which give a value [29] of 24%.

D. Coupling-constant decomposition of E_{XC}

The kinetic correlation energy contribution T_{c} to the total energy need not be explicitly approximated as a functional of the electron density. T_{c} is implicitly accounted for in E_{XC} of Eq. 1 via the coupling-constant integration over the λ -dependent exchange-correlation hole [35]. This coupling-constant integration leads to another decomposition of the exchange-correlation energy:

$$E_{\text{XC}} = \int_0^1 d\lambda E_{\text{XC},\lambda}, \quad (10)$$

where

$$E_{\text{XC},\lambda} = \int_0^\infty du 2\pi u \int \frac{d\Omega_u}{4\pi} \int d^3r n(\mathbf{r}) n_{\text{XC},\lambda}(\mathbf{r}, \mathbf{r} + \mathbf{u}). \quad (11)$$

This decomposition has become a popular tool in density functional theory [36–38]. For $\lambda = 0$, the electrons are not Coulomb-correlated, so $E_{\text{XC},\lambda=0} = E_{\text{X}}$ accounts for the self-interaction correction and for the Pauli exclusion principle. Compared to the hole at finite values of λ , the hole at $\lambda = 0$ is shallower and therefore more long-ranged. At full coupling-strength ($\lambda = 1$), $E_{\text{XC},\lambda=1} = E_{\text{XC}} - T_{\text{C}}$. Electrons close to the reference electron get pushed away at small u -values and pile up at large u -values, making the hole deeper at $u = 0$ and more short-ranged. Local and semilocal approximations usually work best for small u . Thus they are least suitable for $\lambda = 0$ (the exchange-only limit). These expectations about the range of the hole are confirmed by a study [31] of the λ -dependent exchange-correlation hole, and are probably true for all systems.

The popular hybrid schemes [36–38] can be viewed as attempts to exploit this observation. We consider only hybrid schemes which recover the slowly-varying electron gas limit. In such a scheme, the coupling-constant integral is replaced by the weighted sum of the integrands at the endpoints of the coupling-constant integration and the density functional approximation to the exchange energy $E_{\text{XC},\lambda=0}$ is replaced by the Hartree-Fock exchange energy [29,38]. In formulas,

$$E_{\text{XC}} = aE_{\text{X}}^{\text{HF}} + (1 - a)E_{\text{X}}^{\text{GGA}} + E_{\text{C}}^{\text{GGA}}. \quad (12)$$

The parameter a is usually adjusted to minimize the root-mean-square errors of various molecular properties. However, it has been demonstrated [32,29] that the parameter a is far from universal for molecular systems. This can be seen by considering the stretched H_2 molecule: The restricted Hartree-Fock hole is always distributed equally over both H -atoms, whereas the exact hole and its GGA model are localized on the H atom at which the reference electron is located. Thus no finite amount of exact exchange should contribute to E_{XC} in the limit of infinite stretching.

E. Exchange-correlation potential

It has been shown [39,40] that the PW91 approximation to the exchange-correlation potential $v_{XC} = \delta E_{XC}[n]/\delta n$, which appears in the Kohn-Sham Hamiltonian, deviates considerably from the exact potential, especially in the core and tail regions of atoms. However, we have argued that approximate local and semilocal density functionals give good approximations only to system-averaged quantities such as the system-averaged exchange-correlation hole. It is therefore more appropriate to study quantities which involve system-averages of the exchange-correlation potential v_{XC} and its components v_X and v_C , rather than the potential itself. The virial theorem shows that [41]

$$E_X = - \int d^3r n(\mathbf{r}) \mathbf{r} \cdot \nabla v_X(\mathbf{r}) \quad (13)$$

and

$$E_C + T_C = - \int d^3r n(\mathbf{r}) \mathbf{r} \cdot \nabla v_C(\mathbf{r}). \quad (14)$$

In this system average, the region close to the nuclei and the tail region of the electron density, where v_{XC} is not well approximated by PW91, get little weight. Due to error cancellation within the integral of Eqs. 14, the system-averaged quantities are far better approximated by PW91 than by LSD [31].

F. Exchange-correlation energies from exact densities

An approach which makes use of the improvement in accuracy of the LSD and GGA approximations at full coupling strength ($\lambda = 1$) relative to the coupling-constant average can be formulated based on knowledge of the exact density $n(\mathbf{r})$ corresponding to a known external potential $v(\mathbf{r})$ [42]. Several methods are known for calculating the exact Kohn-Sham potential $v_s(\mathbf{r})$ from a given electron density [43–47]. The exact exchange-correlation potential can then be obtained according to

$$v_{XC}(\mathbf{r}) = v_s(\mathbf{r}) - v(\mathbf{r}) - \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (15)$$

The virial relations Eqs. 13 and 14 show that the virial of the exchange-correlation potential is given by the sum of $T_C + E_{XC}$. Since $E_{XC,\lambda=1} = E_{XC} - T_C$, we obtain the exact relation

$$E_{XC} = \frac{1}{2}[E_{XC,\lambda=1} - \int d^3r n(\mathbf{r}) \mathbf{r} \cdot \nabla v_{XC}(\mathbf{r})]. \quad (16)$$

$E_{XC,\lambda=1}$ on the right hand side of this equation will now be replaced by its local or semilocal approximation, a replacement typically involving less error than the functional

approximation of E_{XC} . As shown in Table 1, the resulting expressions for E_{XC} give a significant improvement compared to the local and semi-local approximations of E_{XC} itself.

TABLE I. Exchange-correlation energies in Hartrees for several atoms [42] We compare exact values with those of LSD and PW91, and with improvements thereof (marked by a prime) using Eq. (16). Unless otherwise indicated, the exact values are from Ref. [48], while the approximate functionals are evaluated on the Hartree-Fock densities of Ref. [49].

atom	exact	LSD	LSD'	PW91	PW91'
H ^a	-0.312	-0.290	-0.307	-0.314	-0.316
H ^{- a,b}	-0.423	-0.409	-0.420	-0.425	-0.422
He	-1.068	-0.997	-1.048	-1.063	-1.066
Li	-1.827	-1.689	-1.786	-1.821	-1.829
Be ^{++ b}	-2.321	-2.107	-2.243	-2.298	-2.312
Ne ^{8+ b}	-6.073	-5.376	-5.776	-5.989	-6.036
Be	-2.772	-2.536	-2.686	-2.739	-2.755
Be ^a	-2.772	-2.545	-2.691	-2.748	-2.760
N	-6.78	-6.32	-6.61	-6.77	-6.78
Ne ^c	-12.48	-11.78	-12.20	-12.50	-12.47

^aApproximate functionals evaluated on exact densities.

^bExact results from Ref. [39].

^cExact results from Ref. [43].

G. Static correlation in density functional theory

In the context of density functional theory, systems which show only dynamical correlation effects are called normal systems [50,51]. For small values of the coupling-constant λ , normal systems are well described by a single Slater determinant, and the on-top value of the hole is well reproduced by LSD and PW91. Systems with static correlation, such as H_2 stretched beyond the Coulson-Fisher point, are called abnormal systems. The exact wavefunction of stretched H_2 (with bond length $R \rightarrow \infty$) does not reduce to a single determinant as $\lambda \rightarrow 0$. Instead, it remains a Heitler-London type wavefunction, keeping one electron localized on each atom. But in a restricted single-determinant approximation, the electrons cannot localize on individual atoms. As a consequence, the on-top value of the exchange-correlation hole that results from a restricted calculation (Hartree-Fock, LSD, or GGA) is quite incorrect. To see this, note first that for a single Slater determinant, the on-top pair density is simply $P(\mathbf{r}, \mathbf{r}) = 2n_\uparrow(\mathbf{r})n_\downarrow(\mathbf{r})$. In a restricted calculation, in which $n_\uparrow(\mathbf{r}) = n_\downarrow(\mathbf{r}) = n(\mathbf{r})/2$, we find $P_{\lambda=1}(\mathbf{r}, \mathbf{r}) = P_{\lambda=1}^{\text{unif}}(n(\mathbf{r})/2, n(\mathbf{r})/2; u=0)$, instead of the correct result, $P_{\lambda=1}(\mathbf{r}, \mathbf{r}) = 0$ for all \mathbf{r} . A cure for

this problem is provided by an alternative interpretation of spin-density functional theory [50,51]. In this alternative interpretation, the quantities predicted are not the individual spin-densities $n_{\uparrow}(\mathbf{r})$ and $n_{\downarrow}(\mathbf{r})$, but the total density $n(\mathbf{r}) = n_{\uparrow} + n_{\downarrow}$ and the full coupling strength on-top pair density $P_{\lambda=1}(\mathbf{r}, \mathbf{r}) = P_{\lambda=1}^{\text{unif}}(n_{\uparrow}, n_{\downarrow}; u = 0)$. In abnormal systems, the spin symmetry can then be broken with impunity. In the stretched H_2 molecule, an electron with up-spin localizes on one hydrogen atom and an electron with down-spin localizes on the other. The spin-density in such an unrestricted calculation is obviously no longer accurately reproduced, but the total density is. Furthermore, $P_{\lambda=1}(\mathbf{r}, \mathbf{r}) = P_{\lambda=0}(\mathbf{r}, \mathbf{r})$ correctly vanishes for all values of \mathbf{r} , since either $n_{\uparrow}(\mathbf{r})$ or $n_{\downarrow}(\mathbf{r})$ is zero everywhere. This behavior of the on-top value of the pair density ensures that the unrestricted Kohn-Sham calculation gives an accurate dissociation energy.

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