

Accurate Density Functional for the Energy: Real-Space Cutoff of the Gradient Expansion for the Exchange Hole

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The density-gradient expansion of the fermion exchange hole is analyzed in real space. Unlike the local-density approximation, the second-order gradient-expansion approximation is found to violate two important properties of the exact hole: The exact hole is negative everywhere, and represents a deficit of one electron. Imposition of these exact constraints leads to an accurate new density functional for the exchange energy. Residual errors in the exchange energy for atoms are about 1% of this quantity. The new functional approximation may be generalized to include correlation.

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Kohn-Sham density-functional theory¹ is the foundation of many modern electronic structure calculations, especially those for solids. In principle, the exact ground-state energy E and electron density $n(\mathbf{r})$ may be found from a self-consistent-field calculation in which $v_{xc}(\mathbf{r}) = \delta E_{xc} / \delta n(\mathbf{r})$ plays the role of the exchange-correlation potential. The exchange-correlation energy has a gradient expansion

$$E_{xc}[n] = \int d^3r A_{xc}(n)n^{4/3} + \int d^3r C_{xc}(n) |\nabla n|^2 / n^{4/3} + \dots, \quad (1)$$

which is asymptotically valid for densities that vary slowly over space. The local-density approximation (LDA), which retains only the leading term in Eq. (1), often permits useful predictions of electron densities, binding and bonding energies, atomic positions, and vibration frequencies, etc. However, the LDA also makes some disturbing errors: Total energies for atoms are much less realistic than those of the Hartree-Fock approximation.² Transfer energies between s and p , or between s and d , orbitals are often poorly described.³ Dissociation energies are usually accurate for s -bonded molecules, but are as much as 0.09 hartree too large⁴ in sp -bonded molecules like O_2 . Recently, Jones and Gunnarsson⁵ have identified errors in the LDA exchange energy as the major source of these discrepancies. Although a number of improvements upon LDA have been suggested,^{2,6-8} the goal of chemical accuracy has remained elusive.

For realistic electron densities, the second-order gradient-expansion approximation (GEA), which retains the first two terms of Eq. (1), is something of a disaster.⁸ The grossest errors of this approximation arise from the gradient contribution to the correlation energy, and may be purged by the method of wave-vector analysis.^{7,9} Indeed, with the advent of the Langreth-Mehl approximation⁷ for correlation, it is still the exchange energy which is the largest remaining source of error in the density-functional theory. This Letter presents a *real-space* analysis of the gradient expansion for the exchange energy, and a new density-functional approximation for exchange based upon this analysis. The new scheme is readily generalized to include correlation.

The "exchange energy" is, of course, a Fock integral constructed either from Hartree-Fock orbitals [belonging to a nonlocal effective potential $V(\mathbf{r}, \mathbf{r}')$] or from Kohn-

Sham orbitals [belonging to a local $V(\mathbf{r})$]. Although the numerical difference is often small, the conceptual difference is important. Since the Hartree-Fock exchange energy has no density-gradient expansion,¹⁰ it is the Kohn-Sham exchange energy which will be discussed here.

The exact exchange energy as a functional of the density $n(\mathbf{r})$ is defined in the following way¹¹: Given the density $n(\mathbf{r})$, find that effective potential $V(\mathbf{r})$ which generates it via the equations $[-\frac{1}{2}\nabla^2 + V(\mathbf{r})]\psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$ and $n(\mathbf{r}) = \sum_i \theta(\mu - \epsilon_i) |\psi_i(\mathbf{r})|^2$. [The step function $\theta(x)$ equals 1 for $x > 0$, and 0 for $x < 0$.] The Kohn-Sham or noninteracting density matrix is

$$\rho(\mathbf{r}, \mathbf{r} + \mathbf{R}) = \sum_i \theta(\mu - \epsilon_i) \psi_i^*(\mathbf{r} + \mathbf{R}) \psi_i(\mathbf{r}). \quad (2)$$

The density at point $\mathbf{r} + \mathbf{R}$ of the exchange hole about an electron at point \mathbf{r} is

$$n_x(\mathbf{r}, \mathbf{r} + \mathbf{R}) = -\frac{1}{2} |\rho(\mathbf{r}, \mathbf{r} + \mathbf{R})|^2 / n(\mathbf{r}). \quad (3)$$

The hole satisfies the conditions

$$n_x(\mathbf{r}, \mathbf{r}) = -n(\mathbf{r})/2, \quad (4)$$

$$n_x(\mathbf{r}, \mathbf{r} + \mathbf{R}) \leq 0, \quad (5)$$

$$\int d^3R n_x(\mathbf{r}, \mathbf{r} + \mathbf{R}) = -1. \quad (6)$$

The exchange energy is

$$E_x[n] = \int d^3r e_x([n]; \mathbf{r}), \quad (7)$$

where

$$e_x([n]; \mathbf{r}) = \frac{1}{2} n(\mathbf{r}) \int d^3R n_x(\mathbf{r}, \mathbf{r} + \mathbf{R}) / R \quad (8)$$

is the exchange-energy density.

The density-gradient expansion for the exchange energy

was proposed on dimensional grounds by Herman, Ortenburger, and Van Dyke,¹² and the first *a priori* calculation of the coefficient C_x in Eq. (1) was made by Sham.¹³ Gross and Dreizler¹⁴ have derived the second-order expansion from the Kirzhnits operator-algebra formalism. Equations (18) and (19) of Gross and Dreizler may be combined to yield the gradient expansion of the density matrix. The gradient expansion (GEA) of the exchange hole then follows from Eq. (3):

$$n_x(\mathbf{r}, \mathbf{r} + \mathbf{R}) \approx -\frac{1}{2}n(\mathbf{r})y(\mathbf{r}, \mathbf{R}), \quad (9)$$

$$y = J + Lk_F^{-3}\hat{\mathbf{R}} \cdot \nabla k_F^2 + (z^2J - 4zL)k_F^{-6}(\nabla k_F^2)^2/192 + Mk_F^{-6}(\hat{\mathbf{R}} \cdot \nabla k_F^2)^2 - z^2Jk_F^{-4}\nabla^2 k_F^2/48 + zLk_F^{-4}(\hat{\mathbf{R}} \cdot \nabla)^2 k_F^2/6, \quad (10)$$

where $\hat{\mathbf{R}} = \mathbf{R}/R$, $k_F = [3\pi^2 n(\mathbf{r})]^{1/3}$, and

$$J = 74(4 - 4\cos z - 4z\sin z + z^2 + z^2\cos z)/z^6, \quad (11)$$

$$L = 9(2 - 2\cos z - z\sin z)/z^3, \quad (12)$$

$$M = 9(\sin z - z\cos z)/16z, \quad (13)$$

with $z = 2k_F R$. Equation (9) is new, although it follows rather directly from the equations of Ref. 14. At large R the gradient terms in Eq. (9) display undamped oscillations proportional to $\cos(2k_F R)$, so that the integrals in Eqs. (6) and (8) are undefined. Nevertheless, partial integration over \mathbf{r} yields¹⁴ the exchange energy in the form of Eq. (1), with $A_x(n) = 0.73856$ and $C_x(n) = -0.001667$ a.u., the *a priori* values of Sham.¹³

It should be mentioned here that these results are obtained by replacing the Coulomb interaction $1/R$ in Eq. (8) by the screened interaction $\exp(-\alpha R)/R$, and then taking the limit $\alpha \rightarrow 0$ at the end of the calculation. This procedure can be justified for any *finite* system: When α^{-1} is much bigger than the size of the system, there can be no significant difference between $1/R$ and $\exp(-\alpha R)/R$. (Kleinman,¹⁵ who worked with a $1/R$ interaction in an infinite system, derived a gradient coefficient C_x which is $\frac{8}{7}$ of Sham's coefficient, and attributed the difference to a peculiarity of the $\alpha \rightarrow 0$ limit.)

The LDA exchange hole [which retains only the first term on the right-hand side of Eq. (10)] obeys the exact conditions of Eqs. (4)–(6). Gunnarsson and Lundqvist¹⁶ have emphasized that satisfaction of Eq. (6) is a major reason for the success of LDA outside its domain of formal validity, while Connolly¹⁷ and Harris¹⁸ have made similar claims for Eq. (4). The comparable importance of Eq. (5) is asserted here. Now the GEA of Eq. (9) obeys Eq. (4) but *not* Eqs. (5) and (6). This observation suggests the following extension of the GEA:

$$n_x(\mathbf{r}, \mathbf{r} + \mathbf{R}) \approx -\frac{1}{2}n(\mathbf{r})y\theta(y)\theta(R_c(\mathbf{r}) - R). \quad (14)$$

The first step function in Eq. (14) forces the satisfaction of Eq. (5), while the second involves a cutoff radius $R_c(\mathbf{r})$ which is chosen to satisfy Eq. (6). The angular integrations over the direction $\hat{\mathbf{R}}$ in Eqs. (6) and (8) are performed analytically, leaving only the radial integrations

TABLE I. Exchange energies E_x (in hartrees) of atoms with nonrelativistic Hartree-Fock densities.

Atom	LDA	GEA	Eq. (14)	Exact
He	-0.884	-0.970	-1.033	-1.026
Ne	-11.03	-11.55	-12.24	-12.11
Ar	-27.86	-28.86	-30.36	-30.18
Kr	-88.6	-90.7	-94.5	-93.9
Xe	-170.6	-173.9	-180.5	-179.1

over R to be performed numerically. For slowly varying densities, the new approximation of Eq. (14) properly reduces to the GEA of Eq. (9). Significantly, it is found that the truncated exchange hole in an atom always encompasses the nucleus.

Table I displays the exchange energies of atoms with analytic Hartree-Fock densities.¹⁹ The "exact" exchange energy was constructed by subtraction of the classical electrostatic energy from the Hartree-Fock potential energy.¹⁹ In principle, this procedure is not quite correct because the orbitals being employed in Eq. (2) are Hartree-Fock and not Kohn-Sham orbitals; in practice, the numerical difference is almost negligible, as evidenced by comparison with the exact Kohn-Sham exchange energies in Table II of Ref. 11.

Table I shows that the LDA underestimates the magnitude of the exchange energy by about 10%, and the GEA corrects only about one third to one half of this error. However, the new density-functional approximation of Eq. (14) corrects essentially all of the LDA error in atoms. Remaining errors in the exchange energy are about 1% (i.e., about one third of the correlation energy²). Numerical studies also show that, without the factor $\theta(y)$ in Eq. (14), no improvement over GEA would be obtained. Table II compares various nonlocal density functionals for the exchange energy of the neon atom, and indicates the improved accuracy of the presence approximation.

One of the original motivations for this work came from Table II of Ref. 11. That table showed that, while the local-density approximation makes comparable percent errors for the exchange energy E_x and the noninteracting kinetic energy T_s in atoms, the gradient-expansion approximation makes 5% errors in E_x and only 1% errors in T_s . It is therefore gratifying that, with the imposition of the constraints of Eqs. (5) and (6) upon the gradient-expansion approximation, 1% errors are obtained for *both* E_x and T_s . [The kinetic energy density, defined as $-\frac{1}{2}\nabla_{\mathbf{R}}^2\rho(\mathbf{r}, \mathbf{r} + \mathbf{R})$ evaluated at $R=0$, is unaffected by the real-space cutoff procedure.]

Table III shows the exchange-energy contribution, $\Delta E_x = E_x(\text{ion}) - E_x(\text{atom})$, to the valence-shell removal

TABLE II. Exchange energy E_x (in hartrees) of the neon atom from approximate nonlocal functionals.

LDA	-11.03
GEA	-11.55
Average density ^a	-12.54
Average density shell ^a	-12.28
Weighted density ^a	-12.80
Weighted density shell ^a	-12.44
Self-interaction correction ^b	-12.41
Langreth-Mehl ($f=0.15$) ^c	-11.76
Eq. (14)	-12.24
Exact	-12.11

^aReference 3.^cReference 7.^bReference 2.

energies of several atoms. Again, analytic Hartree-Fock densities¹⁹ have been employed. The most remarkable thing about Table III is the good accuracy of *all three* density-functional approximations for the valence-shell removal energies in the exchange-only treatment.

More challenging and chemically relevant tests of the new functional approximation, such as the *sp* and *sd* transfer energies in atoms and the dissociation energies in molecules, will require calculations for non-spherical densities. Recently, however, Jones and Gunnarsson⁵ have suggested that calculations with accurate density func-

TABLE III. Exchange-energy contribution ΔE_x (in hartrees) to the valence-shell removal energies of atoms.

Atom	Shell	LDA	GEA	Eq. (14)	Exact
Be	(2s) ²	0.356	0.353	0.413	0.390
Ne	(2p) ⁶	4.40	4.40	4.55	4.51
Zn	(3d) ¹⁰ (4s) ²	11.2	11.1	11.4	11.3

tions and *spherically averaged* densities should adequately describe the *sd* transfer energies in atoms. Table IV shows the exchange-energy contribution to the *sd* energy in the scandium atom, and indicates that Eq. (14) corrects most of the error of the local-density approximation for this quantity.

If a spin-density-functional approximation to the exchange energy is desired, it can be found from the exact relationship

$$E_x[n_\uparrow, n_\downarrow] = \frac{1}{2} E_x[2n_\uparrow] + \frac{1}{2} E_x[2n_\downarrow]. \quad (15)$$

The spin-density-functional version of Eq. (14) was in fact used in Table IV. If accuracy greater than that of Eq. (14) is desired, it may perhaps be found by imposing the exact constraint

$$n_s(\mathbf{r}, \mathbf{r} + \mathbf{R}) \geq -n(\mathbf{r} + \mathbf{R}). \quad (16)$$

The natural extension of Eq. (14) to satisfy Eq. (16) is

$$n_x(\mathbf{r}, \mathbf{r} + \mathbf{R}) \approx \left[-\frac{1}{2} n(\mathbf{r}) y \theta(y) \theta(n(\mathbf{r} + \mathbf{R}) - \frac{1}{2} n(\mathbf{r}) y) - n(\mathbf{r} + \mathbf{R}) \theta\left(\frac{1}{2} n(\mathbf{r}) y - n(\mathbf{r} + \mathbf{R})\right) \right] \theta(R_c(\mathbf{r}) - R). \quad (17)$$

The alternative new functional approximation of Eq. (17) satisfies the same theoretical constraints as the weighted-density approximation,⁶ and additionally reduces to the gradient expansion in the slowly varying limit. Equation (17) should be no harder to implement than the weighted approximation.

It remains to test the new functional approximations of Eqs. (14) and (17) for a wide range of systems, to construct the functional derivatives $\delta E_x / \delta n(\mathbf{r})$ for use in self-consistent calculations, and to include correlation. In physical systems, the neglected correlation energy is of course important, especially for the description of bonding in molecules and cohesion in solids. Equation (14) for the exchange energy may be teamed with the Langreth-

Mehl approximation⁷ for the correlation energy. (The Langreth-Mehl approximation has been tested for both atoms⁷ and molecules²⁰; the spin-density-functional version is now available.²¹) Table V shows exchange-correlation energies for several atoms calculated in this way.

The approximations of Eqs. (14) and (17) may also be generalized directly to include correlation, since the exact exchange-correlation hole $n_{xc}(\mathbf{r}, \mathbf{r} + \mathbf{R})$ also obeys Eqs. (6) and (16). The real-space cutoff procedure for exchange *and* correlation may be more accurate than that for exchange alone, since correlation digs a deeper, more compact hole around each electron. [This is the reason why

TABLE IV. Exchange-energy contribution ΔE_x (in hartrees) to the *sd* transfer energy in the scandium atom. The quantity shown is

$$E_x[(4s\uparrow)(4s\downarrow)(3d\uparrow)] - E_x[(4s\uparrow)(3d\uparrow)^3].$$

The approximations have been made spin dependent via Eq. (15). The inputs have been taken to be *spherically averaged* Hartree-Fock spin densities $n_\uparrow(r)$ and $n_\downarrow(r)$.

Atom	LDA	GEA	Eq. (14)	Exact
Sc	0.191	0.199	0.167	0.160

TABLE V. Exchange-correlation energies E_{xc} (in hartrees) of atoms with nonrelativistic Hartree-Fock densities. Present: Eq. (14) for exchange plus Langreth-Mehl approximation ($f=0.15$) for correlation.

Atom	LDA ^a	Present ^b	Exact ^a
He	-0.994	-1.086	-1.066
Ne	-11.74	-12.65	-12.49
Ar	-29.27	-31.16	-30.91

^aCorrelation energies from Ref. 2.^bCorrelation energies from Ref. 7.

the LDA is a better approximation for exchange-correlation (Table V) than it is for exchange alone (Table I).] All that is lacking at present is the gradient expansion for the correlation hole, i.e., the analog of Eq. (9). In fact, the real-space cutoff of the gradient expansion for the correlation hole at large R is very much like the Langreth-Perdew-Mehl wave-vector cutoff of the gradient expansion for the correlation energy at small k .^{7,9} This wave-vector-cutoff procedure does not greatly improve the exchange energy, however, because the anomalous large- R behavior of the GEA energy hole is associated not with the $k \rightarrow 0$ limit but with distributional singularities⁹ at $k = 2k_F$ in the wave-vector analysis of the GEA exchange energy.

In summary, the error in the density-gradient expansion for the exchange energy $E_x[n]$ has been explained and substantially expunged. The prospect of density-functional calculations with chemical accuracy no longer seems so remote.

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