

Accurate and simple density functional for the electronic exchange energy: Generalized gradient approximation

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The electronic exchange energy as a functional of the density may be approximated as $E_x[n] = A_x \int d^3r n^{4/3} F(s)$, where $s = |\nabla n|/2k_F n$, $k_F = (3\pi^2 n)^{1/3}$, and $F(s) = (1 + 1.296s^2 + 14s^4 + 0.2s^6)^{1/15}$. The basis for this approximation is the gradient expansion of the exchange hole, with real-space cutoffs chosen to guarantee that the hole is negative everywhere and represents a deficit of one electron. Unlike the previously published version of it, this functional is simple enough to be applied routinely in self-consistent calculations for atoms, molecules, and solids. Calculated exchange energies for atoms fall within 1% of Hartree-Fock values. Significant improvements over other simple functionals are also found in the exchange contributions to the valence-shell removal energy of an atom and to the surface energy of jellium within the infinite barrier model.

Kohn-Sham density-functional theory¹ provides an exact-in-principle self-consistent-field description of electronic ground-state energies and densities. In practical applications to atoms, molecules, and solids, the theory is simple, universal, and moderately accurate. Accuracy is currently limited²⁻⁴ by approximations made for the exchange energy as a functional of the density. A simple but accurate approximation for exchange, which might be applied in concert with (for example) the Langreth-Mehl² approximation for correlation, will be introduced here.

The exchange energy for a system of electrons with density $n(\mathbf{r})$ is⁵

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

where $n_x(\mathbf{r}, \mathbf{r} + \mathbf{R})$ is the density at position $\mathbf{r} + \mathbf{R}$ of the exchange hole about an electron at position \mathbf{r} . The exact hole satisfies the conditions

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

$$n_x(\mathbf{r}, \mathbf{r} + \mathbf{R}) \leq 0, \quad (3)$$

$$\int d^3R n_x(\mathbf{r}, \mathbf{r} + \mathbf{R}) = -1. \quad (4)$$

For densities $n(\mathbf{r})$ which vary slowly over space, the ground-state exchange energy constructed from Kohn-Sham orbitals has a gradient expansion⁶⁻⁸

$$E_x[n] = A_x \int d^3r n^{4/3} + C_x \int d^3r |\nabla n|^2 / n^{4/3} + \dots, \quad (5)$$

where $A_x = -\frac{3}{4}(3/\pi)^{1/3}$ and $C_x = -7/[432\pi(3\pi^2)^{1/3}]$ a.u. It is well known⁵ that the local density approximation (LDA), which retains only the first term on the right in Eq. (5), satisfies the exact conditions (2)–(4). In Ref. 4, it was discovered that the gradient expansion approximation (GEA), which retains both the first and second terms, violates conditions (3) and (4). This observation explains the failure of GEA to provide the accurate correction to LDA that might have been expected in atomic calculations. It was also found in Ref. 4 that a cut-off GEA exchange hole, with the cutoffs chosen to satisfy Eqs. (3) and (4), yields an accurate new density functional for the exchange energy. However, this functional was too complicated for

most practical applications; in particular, the functional derivative, needed for self-consistent calculations, could not be evaluated. In this Rapid Communication, the new functional will be simplified, so that it may be used routinely in self-consistent calculations for atoms, molecules, and solids.

In Ref. 4, it was shown that

$$n_x^{\text{GEA}}(\mathbf{r}, \mathbf{r} + \mathbf{R}) = -\frac{1}{2} n(\mathbf{r}) y(\mathbf{r}, \mathbf{R}), \quad (6)$$

where

$$y = J + Lk_F^{-3} \hat{\mathbf{R}} \cdot \nabla k_F^2 + Mk_F^{-6} (\hat{\mathbf{R}} \cdot \nabla k_F^2)^2 + Nk_F^{-6} (\nabla k_F^2)^2 + zLk_F^{-4} (\hat{\mathbf{R}} \cdot \nabla)^2 k_F^2 / 6 - z^2 Jk_F^{-4} \nabla^2 k_F^2 / 48. \quad (7)$$

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

$$J = 72[4 + z^2 - (4 - z^2) \cos z - 4z \sin z] / z^6, \quad (8)$$

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

$$M = 9(-z \cos z + \sin z) / (16z), \quad (10)$$

$$N = 3[8 - (8 - 4z^2) \cos z - (8z - z^3) \sin z] / (16z^4). \quad (11)$$

In Ref. 4, the cutoffs were done directly on y of Eq. (7), which involves first and second derivatives of $n(\mathbf{r})$. Note, however, that the integration over \mathbf{r} in Eq. (1) may be done by parts,⁷ yielding a new expression like Eq. (1), but with $n_x^{\text{GEA}}(\mathbf{r}, \mathbf{r} + \mathbf{R})$ replaced by

$$\tilde{n}_x^{\text{GEA}}(\mathbf{r}, \mathbf{r} + \mathbf{R}) = -\frac{1}{2} n(\mathbf{r}) \tilde{y}(\mathbf{r}, \mathbf{R}), \quad (12)$$

$$\tilde{y} = J + 4L \hat{\mathbf{R}} \cdot \mathbf{s} / 3 - 16M (\hat{\mathbf{R}} \cdot \mathbf{s})^2 / 27 - 16Ns^2 / 3, \quad (13)$$

where

$$\mathbf{s} = \nabla n / (2k_F n). \quad (14)$$

The quantity \tilde{n}_x^{GEA} is a representation of the exchange hole density in terms of $n(\mathbf{r})$ and its first derivative. Equation (5) is recovered if \tilde{y} is multiplied by a convergence factor⁷ $e^{-\alpha R}$ and if the limit $\alpha \rightarrow 0^+$ is taken after the evaluation of Eq. (1).

In the generalized gradient approximation (GGA) proposed here, the hole is represented by

$$\tilde{n}_x^{\text{GGA}}(\mathbf{r}, \mathbf{r} + \mathbf{R}) = -\frac{1}{2} n(\mathbf{r}) \tilde{y}(\tilde{\mathbf{r}}) \Theta(R_c(\mathbf{r}) - R). \quad (15)$$

The first step function in this equation enforces Eq. (3), and the second involves a cut-off radius R_c chosen to enforce Eq. (4). The GGA clearly takes account of the fact, neglected in the LDA, that the exchange hole in an inhomogeneous system is "off center" with respect to the electron it surrounds. Now Eq. (1) becomes

$$E_x^{\text{GGA}}[n] = A_x \int d^3r n^{4/3} F^{\text{GGA}}(s), \quad (16)$$

where

$$F^{\text{GGA}}(s) = -\frac{(3\pi^2)^{1/3}}{12\pi A_x} \int_0^{z_c} dz z \frac{d\hat{\mathbf{R}}}{4\pi} \tilde{y}\Theta(\tilde{y}). \quad (17)$$

The parameter $z_c = 2k_F R_c$ is determined by the condition

$$\frac{-1}{12\pi} \int_0^{z_c} dz z^2 \int \frac{d\hat{\mathbf{R}}}{4\pi} \tilde{y}\Theta(\tilde{y}) = -1. \quad (18)$$

The angular integration

$$\int \frac{d\hat{\mathbf{R}}}{4\pi} \tilde{y}\Theta(\tilde{y}) = \frac{1}{2} \int_{-1}^1 d\mu (A\mu^2 + B\mu + C) \times \Theta(A\mu^2 + B\mu + C) \quad (19)$$

is performed analytically, and then the z integrations are performed numerically.

Figure 1 displays F^{GGA} as a function of s . A useful analytic fit to the numerical results is

$$F^{\text{GGA}}(s) = (1 + 0.0864s^2/m + bs^4 + cs^6)^m, \quad (20)$$

where $m = \frac{1}{15}$, $b = 14$, and $c = 0.2$. Although the step function cutoffs are too crude to recover

$$F^{\text{GEA}}(s) = 1 + 0.0864s^2 \quad (21)$$

in the limit $s \ll 1$, the parametrization of Eq. (20) has been designed to recover this limit. For plots of $s(\mathbf{r})$ in atoms and at metal surfaces see Ref. 8.

The functional form of Eq. (16) is the simplest one which scales⁹ as an exchange energy:

$$E_x[n_\gamma] = \gamma E_x[n], \quad (22)$$

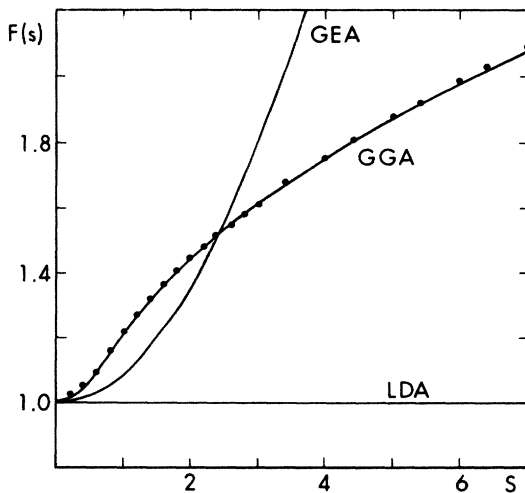


FIG. 1. The LDA, GEA, and GGA versions of the function $F(s)$ of Eq. (16). The dots indicate the numerical GGA of Eqs. (17)–(19), while the solid curve is the analytic fit of Eq. (20).

where $n_\gamma(\mathbf{r}) = \gamma^3 n(\gamma\mathbf{r})$ is a scaled density. The local density approximation is $F^{\text{LDA}}(s) = 1$. The Langreth-Mehl² $f = 0.15$ (LM) approximation for exchange, based upon a cutoff of the GEA in wave-vector space, is

$$F^{\text{LM}}(s) = 1 + 1.521(0.0864s^2). \quad (23)$$

Recently, Becke¹⁰ and Macdonald and Vosko¹¹ have proposed versions of $F(s)$ fitted to exact-exchange results for atoms. An interesting approximation to the exchange functional, which does not have the form of Eq. (16), has been presented recently by Ghosh and Parr.¹²

The exchange potential, for use in self-consistent calculations, is the functional derivative

$$\frac{\delta E_x}{\delta n(\mathbf{r})} = A_x n^{1/3} \left[\frac{4}{3} F - ts^{-1} \frac{dF}{ds} - \left(u - \frac{4}{3} s^3 \right) \frac{d}{ds} \left(s^{-1} \frac{dF}{ds} \right) \right], \quad (24)$$

where

$$t = (2k_F)^{-2} n^{-1} \nabla^2 n$$

and

$$u = (2k_F)^{-3} n^{-2} \times \nabla n \cdot \nabla |\nabla n|.$$

The functional derivative diverges as $|\mathbf{r}| \rightarrow \infty$ in the GEA and LM approximations, but tends to zero in this limit in the GGA.

From a density functional $E_x[n]$, one constructs a spin-density functional

$$E_x[n_\uparrow, n_\downarrow] = \frac{1}{2} E_x[2n_\uparrow] + \frac{1}{2} E_x[2n_\downarrow], \quad (25)$$

$$\frac{\delta E_x[n_\uparrow, n_\downarrow]}{\delta n_\sigma(\mathbf{r})} = \frac{\delta E_x[n]}{\delta n(\mathbf{r})} \bigg|_{n(\mathbf{r}) = 2n_\sigma(\mathbf{r})}. \quad (26)$$

It is the spin-density functionals which will be tested in this Rapid Communication.

Table I displays LDA, GEA, LM, GGA, and exact-exchange energies of spherically symmetric atoms. Hartree-Fock densities¹³ have been used in each case. The greatest relative errors are 14% for LDA, 6% for GEA, 3% for LM, and 1% for GGA. The absolute error for the GGA exchange energy is several times smaller than the correlation energy (except in H , where the correlation energy is zero).

Table II displays the exchange-energy contribution (ΔE_x) to the valence-shell removal energy, a quantity of greater chemical and physical relevance than the total exchange en-

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

Atom	LSD	GEA	LM	GGA	Exact
H	-0.268	-0.294	-0.308	-0.311	-0.3125
He	-0.884	-0.970	-1.015	-1.033	-1.026
Li	-1.538	-1.675	-1.747	-1.789	-1.781
Be	-2.31	-2.50	-2.60	-2.68	-2.67
Ne	-11.03	-11.55	-11.82	-12.22	-12.11
Ar	-27.86	-28.86	-29.39	-30.29	-30.18
Zn	-65.63	-67.36	-68.25	-69.93	-69.7
Kr	-88.6	-90.7	-91.8	-93.8	-93.9
Xe	-170.6	-173.9	-175.6	-178.6	-179.1

TABLE II. Exchange contributions ΔE_x (in a.u.) to the valence-shell removal energies of atoms with nonrelativistic Hartree-Fock densities.

Atom	Shell	LSD	GEA	LM	GGA	Exact
Li	(2s) ¹	0.117	0.116	0.116	0.133	0.129
Be	(2s) ²	0.36	0.35	0.35	0.40	0.39
Ne	(2p) ⁶	4.40	4.40	4.40	4.57	4.51
Zn	(4s) ²	0.35	0.33	0.31	0.39	0.39
Zn ²⁺	(3d) ¹⁰	10.85	10.79	10.76	10.90	10.89

ergy. For this property, the GEA and LM approximations are somewhat *less* accurate than LDA, while GGA is apparently *more* accurate.

Table III presents the exchange contribution to the surface energy of jellium within the infinite barrier model.⁸ For the extremely inhomogeneous density of this rather unphysical model, no simple density functional is very accurate, but GGA is more accurate than the others.

In future work, GGA will be applied to nonspherical

TABLE III. Exchange contribution σ_x (in units of $\bar{k}_F^3 \times 10^{-3}$ a.u.) to the surface energy of jellium (bulk density $\bar{k}_F^3/3\pi^2$) in the infinite barrier model. (Strictly, the Langreth-Mehl approximation for exchange should not be applied to such an extended system.)

LDA	GEA	LM	GGA	Exact
0.894	-0.316	-0.946	0.322	0.576

atoms, molecules, and more realistic metal surfaces. The results of self-consistent calculations for atoms will also be reported then. For now, it may be said that GGA leads to a significant improvement over LDA in the density moment $\langle r^{-1} \rangle$, but the improvement over LDA in the moment $\langle r^2 \rangle$ is small and perhaps not significant. The self-consistent valence electron density in an atom is still somewhat too diffuse.

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