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Brief Reports

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Density-functional exchange-energy approximation with correct asymptotic behavior

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Current gradient-corrected density-functional approximations for the exchange energies of atomic and molecular systems fail to reproduce the correct $1/r$ asymptotic behavior of the exchange-energy density. Here we report a gradient-corrected exchange-energy functional with the proper asymptotic limit. Our functional, containing only one parameter, fits the exact Hartree-Fock exchange energies of a wide variety of atomic systems with remarkable accuracy, surpassing the performance of previous functionals containing two parameters or more.

It is well-known that the Hartree-Fock exchange energy of an inhomogeneous many-electron system can be reasonably approximated by the so-called *local-density* approximation (LDA) which, in atomic units, is given by

$$E_X^{\mathrm{LDA}} = -C_X \sum_\sigma \int \rho_\sigma^{4/3} d^3\mathbf{r} \ , \tag{1a}$$

$$C_X = \frac{3}{2}\left[\frac{3}{4\pi}\right]^{1/3} , \tag{1b}$$

where σ denotes either "up" or "down" electron spin, and where the integrand is essentially the volume exchange-energy density of a *uniform* spin-polarized electron gas of spin density ρ_σ. The LDA typically underestimates the exchange energies of atomic and molecular systems by roughly 10%, and corrections for the obvious nonuniformity of atomic and molecular densities have a long history. Corrections depending on local density *gradients* have been derived by Sham,[1] among others,[2] and have also been proposed in a purely empirical context by Herman, Van Dyke, and Ortenburger.[3] Nonlocal corrections of other types, such as the weighted density scheme of Gunnarsson and Jones,[4] have also been proposed, but gradient-type corrections have received most attention due to their great simplicity.

The *lowest-order* gradient correction (LGC) to the local-density approximation is uniquely determined by dimensional analysis, and is given by

$$E_X^{\mathrm{LGC}} = E_X^{\mathrm{LDA}} - \beta \sum_\sigma \int \frac{(\nabla\rho_\sigma)^2}{\rho_\sigma^{4/3}} d^3\mathbf{r} \ , \tag{2}$$

where β is a constant. This LGC functional (named "$X\alpha\beta$" by Herman *et al.*[3]) has, however, well-known and severe deficiencies. First of all, the corresponding exchange *potential* diverges asymptotically in atomic and molecular systems and thus requires *ad hoc* adjustment in practical applications. Secondly, the value of the constant β is a matter of considerable confusion, to which we shall return in later paragraphs.

Motivated by the first of these problems, we have introduced the following "modified" gradient-corrected exchange-energy functional on semiempirical grounds:[5]

$$E_X^{\mathrm{SE}} = E_X^{\mathrm{LDA}} - \beta \sum_\sigma \int \rho_\sigma^{4/3} \frac{x_\sigma^2}{(1+\gamma x_\sigma^2)} d^3\mathbf{r} \ , \tag{3}$$

where SE denotes semiempirical, and where x_σ is the dimensionless ratio

$$x_\sigma = \frac{|\nabla\rho_\sigma|}{\rho_\sigma^{4/3}} \tag{4}$$

and β and γ are parameters. This functional, named $X\alpha\beta\gamma$ in Ref. 5, is determined by the reasonable criteria that (1) dimensional consistency is satisfied, (2) the LGC functional is obtained in the case of small density gradients, and (3) the exchange *potential* is well behaved in the large-gradient (i.e., large-x_σ) limit. Note that the large-x_σ limit corresponds to the asymptotic exponential tail of an atomic or molecular charge distribution.

The functional of Eq. (3) is certainly not the only conceivable such functional, but is probably the simplest. If parameters β and γ are chosen on the basis of a least-squares fit to selected atomic data, we find that the SE functional approximates a wide range of atomic Hartree-Fock exchange energies extremely well.[5] Moreover, we find that the SE functional, in combination with appropriate approximations for antiparallel spin correlations, yields molecular dissociation energies in remarkably good agreement with experiment.[5] This exciting observation has therefore been applied to a variety of problems in transition-metal chemistry by Ziegler *et al.*[6]

Nevertheless, the somewhat arbitrary choice of large-gradient behavior in Eq. (3) leaves much to be desired. Perdew[7] and Becke[8] have presented improved theoretical models with large-x_σ limits close to that of Eq. (3), and other researchers[9,10] have proposed still other gradient correction terms. Therefore, the optimum form of the large-x_σ limit is, unfortunately, ambiguous at the present time.

However, the *exact* asymptotic behavior of the exchange-energy density of any finite many-electron system is known, and is given by

$$\lim_{r\to\infty} U_X^\sigma = -\frac{1}{r} , \tag{5}$$

where U_X^σ is the Coulomb potential of the *exchange charge* or *Fermi hole* density $\rho_X^\sigma(\mathbf{r},\mathbf{r}')$ at reference point $\mathbf{r}$ (see Ref. 11), and is related to the total exchange energy by

$$E_X = \tfrac{1}{2}\sum_\sigma \int \rho_\sigma U_X^\sigma d^3\mathbf{r} . \tag{6}$$

This result reflects the fact that, for reference points very far from a finite system, the Fermi hole remains "attached" to the system. Given also that the Fermi hole contains exactly one electron, Eq. (5) is obvious. A very recent discussion of this result has been provided by March.[12]

Furthermore, the asymptotic behavior of the spin density ρ_σ is also known,[13] and is given by

$$\lim_{r\to\infty} \rho_\sigma = e^{-a_\sigma r} , \tag{7}$$

where a_σ is a constant related to the ionization potential of the system. In view of this known asymptotic density dependence, we propose a new gradient-corrected exchange-energy functional that reproduces the exact asymptotic behavior of Eqs. (5) and (6):

$$E_X = E_X^{\mathrm{LDA}} - \beta \sum_\sigma \int \rho_\sigma^{4/3} \frac{x_\sigma^2}{(1+6\beta x_\sigma \sinh^{-1} x_\sigma)} d^3\mathbf{r} , \tag{8}$$

where β is a constant. It is easily verified that this functional generates the asymptotic potential of Eq. (5) under substitution of the asymptotic spin density of Eq. (7). Furthermore, this new exchange-energy functional reduces to the LGC expression in the limit of small density gradients, and, thanks to the antisymmetry of the function $\sinh^{-1}x_\sigma$, is expressible as a Taylor series in *even* powers of x_σ (and hence even powers of $|\nabla\rho_\sigma|$) as required of any analytically well-behaved functional.

Notice, also, that our functional contains only *one* parameter β because the coefficient of $x_\sigma \sinh^{-1} x_\sigma$ is fixed by Eq. (5). Considering that the previous functionals of Ref. 5 and Refs. 7–10 contain at least *two* parameters, this is a further desirable feature of the present work.

TABLE I. Exchange-energy fit (a.u.).

	Exact	LDA[a]	PW[b]
He	−1.026	−0.884	−1.025
Ne	−12.11	−11.03	−12.14
Ar	−30.19	−27.86	−30.15
Kr	−93.89	−88.62	−93.87
Xe	−179.2	−170.6	−179.0
Rn	−387.5	−373.0	−387.5

[a]LDA: local-density approximation, Eq. (1).
[b]Present work: Eq. (8) with best-fit $\beta=0.0042$ a.u.

Parameter β may be easily determined by a least-squares fit to exact atomic Hartree-Fock data. Specifically, we have determined the value of β which best fits the exchange energies of the six noble gas atoms helium through radon. The required Hartree-Fock densities are obtained from the wave functions of Ref. 14. We find a best-fit value, to two significant figures, of $\beta=0.0042$ a.u., which yields a rms relative deviation from the exact exchange energies of only 0.11%. Results are presented in Table I. The present *one*-parameter functional fits atomic Hartree-Fock exchange energies better than either of our previous *two*-parameter functionals of Refs. 5 or 8.

In Tables II and III further exchange energies are presented for atoms hydrogen through argon in Table II and the first transition series in Table III. The value $\beta=0.0042$ a.u. is used throughout, and in open-shell cases the input Hartree-Fock densities are spherically averaged. The agreement between the present density-functional results and the exact exchange energies is excellent.

The value $\beta=0.0042$ a.u. found in our least-squares fit is consistent with previous empirical studies[3,5,8] and the

TABLE II. Atomic exchange energies (a.u.).

	Exact	LDA[a]	PW[b]
H	−0.313	−0.268	−0.310
He	−1.026	−0.884	−1.025
Li	−1.781	−1.538	−1.775
Be	−2.667	−2.312	−2.658
B	−3.744	−3.272	−3.728
C	−5.045	−4.459	−5.032
N	−6.596	−5.893	−6.589
O	−8.174	−7.342	−8.169
F	−10.00	−9.052	−10.02
Ne	−12.11	−11.03	−12.14
Na	−14.02	−12.79	−14.03
Mg	−15.99	−14.61	−16.00
Al	−18.07	−16.53	−18.06
Si	−20.28	−18.59	−20.27
P	−22.64	−20.79	−22.62
S	−25.00	−23.00	−24.98
Cl	−27.51	−25.35	−27.49
Ar	−30.19	−27.86	−30.15

[a]LDA: Eq. (1).
[b]Present work: Eq. (8) with $\beta=0.0042$ a.u.

TABLE III. Exchange energies. $3d$ transition series (a.u.).

	Exact	LDA[a]	PW[b]
Sc	−38.03	−35.28	−38.03
Ti	−41.04	−38.14	−41.05
V	−44.20	−41.15	−44.22
Cr	−47.76	−44.64	−47.87
Mn	−50.98	−47.66	−51.06
Fe	−54.38	−50.93	−54.48
Co	−57.97	−54.36	−58.08
Ni	−61.68	−57.95	−61.84
Cu	−65.79	−62.00	−66.06
Zn	−69.64	−65.64	−69.86

[a]LDA: Eq. (1).
[b]Present Work: Eq. (8) with $\beta=0.0042$ a.u.

observation of a high-Z *asymptote* of order $\beta=0.004$ a.u. in atomic systems.[5] Sham,[1] however, and many others,[2] have derived a β value roughly three times smaller than the present value on the basis of a wave-vector analysis of the nonuniform electron gas. Though Sham's β is undoubtedly appropriate in slowly varying *infinite* systems,[15] Langreth and Mehl[16] have suggested that the usual wave-vector analysis may be problematic in systems of *finite* extent. As our interests are restricted to atomic and molecular applications only, we make no attempt to incorporate the Sham value of β into our functionals as other authors have done.[7,9,10]

To summarize, then, we have found a gradient-corrected density-functional exchange-energy approximation with large-gradient behavior that correctly reproduces the exact asymptotic potential of Eq. (5) in finite systems. This is the first reported exchange-energy functional of the *gradient* type to possess this feature, though *weighted density* approximations have also been proposed with proper asymptotic dependence.[4] Our *one-parameter* functional fits the Hartree-Fock exchange energies of the six noble gas atoms, helium through radon, with a rms deviation of only 0.11%. This work significantly advances the semiempirical search initiated in Ref. 5 for an optimal gradient-corrected exchange-energy functional for application to quantum chemical problems (see, for example, Ref. 6).

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