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First-order gradient correction for the exchange-energy density functional for atoms

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Summary. Spurred by earlier discoveries by Deb and others that a first-order correction in the kinetic energy functional leads to an improved kinetic energy, a first-order gradient term is studied as a component of the gradient-corrected functional for atomic exchange energy. This term is shown to improve the local density approximation to the exchange energy more than does the usual second-order gradient correction. The imperative of systematically deriving this gradient correction is discussed but not resolved.

Key words: Atomic exchange energy – Gradient-corrected functional – Kinetic energy functional – First-order gradient correction

1 Introduction

The exact energy functional $E[\varrho]$ of density functional theory remains unknown, although much progress has been made both in the theory itself and in its computational implementation [1]. Many studies have been directed toward finding improved approximations to various components of $E[\varrho]$: the kinetic energy $T[\varrho]$, the exchange energy $K[\varrho]$, and the exchange-correlation energy $E_{xc}[\varrho]$ of the Kohn–Sham method. We are here concerned with $K[\varrho]$.

For a uniform electron gas, the exchange energy is well known to be given by the Dirac formula:

$$K[\varrho] = 2^{1/3}\alpha \sum_{\sigma} \int \varrho_{\sigma}^{4/3}\, d\vec{r}, \tag{1}$$

where the $\varrho_\sigma = \varrho_\uparrow$ or $\varrho_\downarrow$ are spin densities and $\alpha = (3/4)(3/\pi)^{1/3} = 0.7386$. Without modification this formula gives poor results for atoms. Atoms are not uniform systems, and atoms do not possess translational symmetry.

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Aside from the adjustment of α to give Slater's famous X_α method [2], most suggestions for correcting Eq. (1) involve gradient corrections for nonuniformity and produce formulas containing integrals of $\nabla\varrho$ and its powers. Foremost among these is the formal gradient expansion [3], but there are also arguments based on wave-vector analysis [4], exchange hole behavior [5], or mainly empirical considerations [6, 7]. A formula due to Becke [7] currently has wide currency. All of these formulations involve even powers of $\nabla\varrho$ only, as a consequence of the translational invariance of the uniform reference system. There is a similar history of gradient corrections to the Thomas–Fermi kinetic energy functional [1].

The question arises, for atoms, could there occur in the kinetic energy functional terms of the form:

$$\int \frac{\vec{r}\cdot\nabla\varrho}{r^2}\,d\vec{r} \equiv -\int \frac{\varrho}{r^2}\,d\vec{r}. \tag{2}$$

For a system with translational symmetry, such terms can not enter. However, for a system with spherical symmetry such terms might well enter. A hint of this is contained in an old paper by Langer [8] who pointed out that the difference between the quantum-mechanical $l(l+1)$ and the classical $(l+1/2)^2$ corresponded to a kinetic energy increment acting like $1/r^2$. Later, Kemister and Nordholm [9] introduced just such a term in a one dimensional statistical model for atoms that treated the coordinate r statistically, and coordinates θ and ϕ quantum-mechanically. And then Deb and coworkers explicitly showed that addition of such a kinetic-energy term in the three dimensional Thomas–Fermi model gave good results [10, 11]. A corresponding term in the exchange would take the form:

$$\int \frac{\vec{r}\cdot\nabla\varrho}{r^2\varrho^{1/3}}\,d\vec{r} \equiv -\tfrac{3}{2}\int \frac{\varrho^{2/3}}{r^2}\,d\vec{r}. \tag{3}$$

In this paper we study this term as a component in an approximate exchange functional.

2 New first-order correction

We write:

$$K[\varrho] = 2^{1/3}\alpha \sum_\sigma \int \varrho_\sigma^{r/3}\,d\vec{r} + F_x[\varrho_\uparrow, \varrho_\downarrow, \nabla\varrho_\uparrow, \nabla\varrho_\downarrow, \ldots], \tag{4}$$

where $F_x[\varrho_\uparrow, \varrho_\downarrow, \nabla\varrho_\uparrow, \nabla\varrho_\downarrow, \ldots]$ is an appropriate functional. We have:

$$F_x[\varrho_\uparrow, \varrho_\downarrow, 0, 0, \ldots] = 0, \tag{5}$$

which is automatically true for a homogeneous electron gas. That is to say, F_x is the inhomogeneous component of the exchange energy. A simple F_x is:

$$F_x[\varrho_\uparrow, \varrho_\downarrow, \nabla\varrho_\uparrow, \nabla\varrho_\downarrow, \ldots] = 2^{-1/3}\beta \sum_\sigma \int \frac{(\nabla\varrho_\sigma)^2}{\varrho_\sigma^{4/3}}\,d\vec{r}. \tag{6}$$

This expression was first employed in its spin-unpolarized form by Herman et al. [3] in the so-called $X_{\alpha\beta}$ self-consistent scheme. The β value was determined in two ways, atom by atom: (1) optimize β by minimizing the total self-consistent $X_{\alpha\beta}$ energy with respect to the value of β, or (2) fit the calculated Hartree–Fock (HF) energy to get the β value.

For atoms we now propose considering an additional first-order gradient correction to the exchange. Namely, we set:

$$F_x[\varrho_\uparrow, \varrho_\downarrow, \nabla\varrho_\uparrow, \nabla\varrho_\downarrow, \ldots] = 2^{-1/3} \sum_\sigma \int \left[-\gamma \frac{\vec{r} \cdot \nabla\varrho_\sigma}{r^2 \varrho_\sigma^{1/3}} + \beta \frac{(\nabla\varrho_\sigma)^2}{\varrho_\sigma^{4/3}} \right] d\vec{r}, \tag{7}$$

where β and γ are parameters to be determined.

We note in passing that the first-order gradient correction is a lower bound to the second-order correction in systems with spherical symmetry. From the inequality [12]:

$$\int_0^\infty \left[4 \left(\frac{df(r)}{dr} \right)^2 - \left(\frac{f(r)}{r} \right)^2 \right] dr \geqslant 0 \tag{8}$$

for all $f(r)$ with $f(\infty) = f(0) = 0$, we obtain the derived bound by letting $f(r) = r\varrho^{1/3}$:

$$\int \frac{(\nabla\varrho)^2}{\varrho^{4/3}} d\vec{r} \geqslant -4 \int \frac{\vec{r} \cdot \nabla\varrho}{r^2 \varrho^{1/3}} d\vec{r}. \tag{9}$$

Now we have:

$$K[\varrho] = \sum_\sigma \int \left[2^{1/3} \lambda \varrho_\sigma^{4/3} - 2^{-1/3} \gamma \frac{\vec{r} \cdot \nabla\varrho_\sigma}{r^2 \varrho_\sigma^{1/3}} + 2^{-1/3} \beta \frac{(\nabla\varrho_\sigma)^2}{\varrho_\sigma^{4/3}} \right] d\vec{r}, \tag{10}$$

where λ is a parameter. If $\lambda = \alpha$ the first term will be the Dirac exchange energy. The corresponding exchange potential is:

$$\frac{\delta K}{\delta\varrho_\sigma} = -\frac{4}{3(2^{1/3})} \lambda \varrho_\sigma^{1/3} - 2^{-1/3} \gamma \frac{1}{r^2 \varrho_\sigma^{1/3}} - 2^{-1/3} \beta \left[\frac{4(\nabla\varrho_\sigma)^2}{3\varrho_\sigma^{7/3}} - \frac{2\nabla^2\varrho_\sigma}{\varrho_\sigma^{4/3}} \right]. \tag{11}$$

This potential can be used in Kohn–Sham self-consistent calculations, though a modification must be made. The potential is divergent for both large r and small r. By introducing multiplicative factors as Herman et al. [3] have done, we can remove these divergences.

3 Calculations

One can determine the parameters λ, β, and γ by minimizing the Kohn–Sham total energy with respect to the parameters or by requiring Kohn–Sham total energy to equal the corresponding Hartree–Fock total energy using the potential given by Eq. (11) with divergences removed. We will not do these things here. What we do, instead, is to fit the parameters so that the exchange energy given by Eq. (10) is as close to the corresponding Hartree–Fock exchange energy as possible. We use Hartree–Fock densities throughout [16].

Results are summarized in Table 1. We have employed several ways to determine the parameters λ, β, and γ. The first- and the second-order gradient terms can be considered to be corrections to the Dirac exchange energy. In this case we fix λ value at 0.7386, the Dirac value, and optimize either β, or γ, or both. We can also optimize the λ value. Optimized values of parameters with corresponding averaged residues are given in Table 1. Optimization is carried out over all neutral atoms with nuclear charge $Z = 2-54$ and 86. The quantities underlined in Table 1 are not optimized but are held fixed at the indicated values.

Table 1. The best coefficients in Eq. (10) determined by minimizing sum of fractional error squared of Eq. (10) relative to exact Hartree–Fock exchange energy for neutral atoms from He through Rn [a]

Case	A (LDA)	B	C	D	E	F	G	H
α	$\underline{0.7386}$	$\underline{0.7386}$	$\underline{0.7386}$	$\underline{0.7386}$	0.7939	0.7541	0.7438	0.7381
β	$\underline{0.0}$	0.00351	$\underline{0.0}$	−0.00145	$\underline{0.0}$	0.00269	$\underline{0.0}$	−0.00156
γ	$\underline{0.0}$	$\underline{0.0}$	0.01324	0.01866	$\underline{0.0}$	$\underline{0.0}$	0.01216	0.01915
R [b]	$5.53E-3$	$9.23E-5$	$9.33E-6$	$1.63E-6$	$6.91E-4$	$1.10E-5$	$2.88E-6$	$1.62E-6$

[a] Numbers underlined held fixed at indicated values during optimization procedures

[b] Average fitting residues as defined in the text

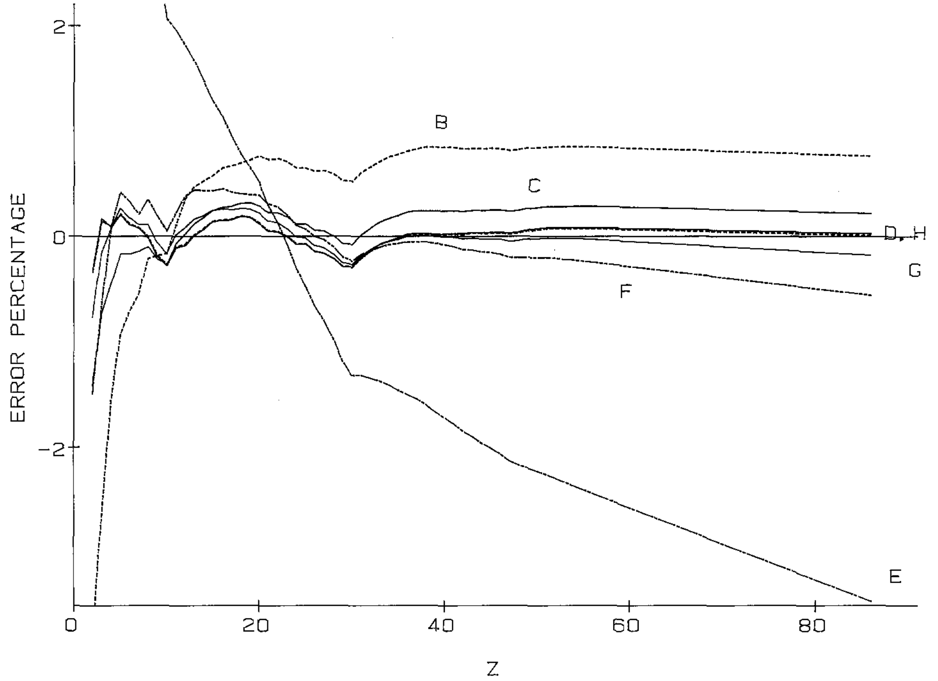

Fig. 1. Error percentages of exchange energies calculated from Eq. (10) vs. atomic number Z. Parameters given in Table 1. The LDA case, which has an error percentage of about 10, is excluded. The zero line is the Hartree–Fock curve

For example, in case B, β was optimized with fixed λ and γ. Note that the hydrogen atom is not included. The average residue, which is the quantity being minimized in the optimization process, is the average of fractional errors squared, over all the atoms. The error percentage is relative to the Hartree–Fock values. The error percentages are plotted in Fig. 1 with the LDA cases excluded. The improvement of any of these gradient-corrected formulas over the LDA, which has an average error of about 10 per cent, is evident.

Note that the first-order-gradient-only functional gives better results than the second-order-gradient-only functional for both fixed and optimized λ. Another fact of interest is that the optimized λ value is essentially the same as the

Table 2. Exchange energies for noble gas atoms: LDA, Second-order-only gradient correction (B), First-order-only gradient correction (C), full optimization of Eq. (10) (H), Langreth–Mehl (LM), Perdew–Wang (GGA), Becke, and Exact HF (Exact)

Atom	LDA	B [a]	C [a]	H [a]	LM [b]	GGA [c]	Becke [d]	Exact
He	0.884	1.065	1.040	1.029	1.015	1.033	1.025	1.026
Ne	11.03	12.13	12.14	12.14	11.82	12.22	12.14	12.11
Ar	27.86	29.97	30.09	30.13	29.39	30.29	30.15	30.19
Kr	88.62	93.09	93.64	93.83	91.8	93.8	93.87	93.89
Xe	170.6	177.6	178.6	178.9	175.6	178.6	179.0	179.2
Rn	373.0	384.6	386.7	387.4			387.5	387.5

[a] From Eq. (10) with parameters as given in Table 1

[b] Langreth–Mehl values from Refs. [4] and [5]

[c] Perdew and Wang values from Ref. [5]

[d] Becke values from Ref. [7]

conventional Dirac value if all λ, β, and γ are optimized (Case H in Table 1). This demonstrates that the Dirac term is the natural leading term in the exchange energy. Given in Table 2 are exchange energies of Case A (LDA), B (second-order-gradient-only), C (first-order-gradient-only), and H (full optimization of λ, β, and γ) for noble gas atoms along with corresponding results of other sophisticated gradient corrections. We see that the first-order-gradient-only exchange energies are almost as good as Becke's and Perdew and Wang's corrected values and better than Langreth and Mehl's. In our calculations we use the spherically averaged Hartree–Fock spin-density of the true ground-state configuration determined from a spin-polarized modification of the Fischer numerical Hartree–Fock program [13].

The value of β in case F differs from values in Ref. [3] for two reasons. First, our calculations are spin-polarized, while those in Ref. [3] are not. Second, as described above the values in Ref. [3] were obtained by quite different methods.

4 Discussion

The superiority of the first-order-gradient-only exchange energy functional over the second-order-gradient-only one demonstrates the desirability of the inclusion of a first-order gradient correction to the exchange energy functional for atoms. The presence of the first-order gradient correction term in both kinetic and exchange energy functional would be a manifestation of the relationship between the kinetic and the exchange energy functionals [14–17]. As a matter of fact we find that the "conjointness" between kinetic and exchange energies discovered earlier [17] is satisfied by the first-order-gradient-only functionals. With this conjointness we expect that the first-order correction to exchange energy reflects the angular dependence of the exchange energy. The angular dependence of the corresponding term in the kinetic energy functional was discussed by Langer [8], Kemister and Nordholm [9], and Deb and coworkers [10, 11].

It is possible to write accurate or approximate density functionals in such a way that some components of them are symmetry-dependent. That is, there may be components that dominate for one symmetry, vanish for another. For example, nonuniform contributions completely disappear for a uniform system. The first-order gradient terms in Eqs. (2) and (3) are symmetry-dependent functionals with spherical symmetry elements built-in. A preliminary study of noninteracting electrons in a one-dimensional quantum well shows that the symmetry-dependent component of the kinetic energy in fact dominates when we take the low density limit [18]. This confirms that a symmetry-adapted approximation would be here preferable.

Note that we generally lose some required properties of the exact energy functional whenever we make an approximation in the functional. The exact energy functional is universal, but approximations used in deriving approximate functionals need not be universal. Indeed, it may be expected for different approximations to work differently for different kinds of systems. For example, the LDA functional works well for solids, badly for atomic systems. Thus we do not expect the first-order gradient correction of the present paper to be appropriate for other than spherically symmetric systems.

A universal functional as defined by Levy's constrained search method [19] is a complicated functional of three-dimensional functions defined through manipulation of $3N$-dimensional functions. This functional is defined point by point (that is, there is one definition for each density). A simple universal functional form for this functional may never be found even though it exists. Fortunately, systematic approximation of this functional is possible. What we have illustrated in this paper is a way to approximate the exchange functional by including symmetry elements in the functional. In principle, symmetry-adapted functionals can be constructed from the constrained search method. Symmetric density comes from symmetric wavefunctions. So we imagine searching over all wavefunctions of a certain symmetry only. We first construct the point-by-point functional for all densities of a certain symmetry. We then find a functional form which best fits this point-by-point functional. It is easier to find an approximate functional representing a smaller domain of densities of interest than one representing the whole density space. Such a symmetry-adapted functional may be quite reliable in its applicable domain.

The first-order corrections to both kinetic and exchange energy functionals appear to merit more study.

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