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Improved local density approximation to the exchange and kinetic energy functionals for atomic systems

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Abstract. Through the derivation of a bound to the gradient correction for the exchange energy, a new local density (LD) approximation to the exchange energy density functional and an analogous LD form for the kinetic energy density functional are proposed. Both these gradient-free functionals valid for spherically symmetric electron densities, yield excellent results for exchange and kinetic energies, using Hartree–Fock atomic densities.

1. Introduction

Density functional theory (March and Deb 1987, Parr and Yang 1989, Kryachko and Ludena 1990) has established itself as a highly versatile tool for the study of electronic structure of atoms, molecules and solids. In this theory, the energy of an N -electron system characterized by an external potential $v(r)$, is expressed as a unique functional $E[\rho]$ of its electron density $\rho(r)$, namely

$$E[\rho] = \int dr v(r)\rho(r) + \frac{1}{2} \iint dr dr' \rho(r)\rho(r')/|r-r'| + G[\rho] \quad (1)$$

where $G[\rho]$ is a universal functional of density and consists of contributions from kinetic and exchange–correlation energies, the exact forms of which are not known. This is the reason for the important and continuing search for good approximations to these functionals, which are necessary for practical calculations.

The simplest approximation to the kinetic energy (κE) functional is the Thomas–Fermi (TF) result (see March 1957) (atomic units are used throughout)

$$T_0[\rho] = C_k \int dr \rho(r)^{5/3} \quad C_k = \frac{3}{10}(3\pi^2)^{2/3} \quad (2)$$

while the exchange energy (χE) is given by the Dirac (1930) expression

$$E_x^{\text{LDA}}[\rho] = -C_x \int dr \rho(r)^{4/3} \quad C_x = \frac{3}{4}(3/\pi)^{1/3}. \quad (3)$$

Equations (2) and (3), derived from homogeneous electron gas results, form the basis

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of the local density approximation (LDA) to the $\kappa\epsilon$ and $\chi\epsilon$ functionals of inhomogeneous many-electron systems and provide the leading terms in improved versions of these functionals through gradient expansions. The correction term of second order in density gradient for the $\kappa\epsilon$ functional first proposed by von Weizsacker (1935) and subsequently modified by a multiplicative $\frac{1}{2}$ factor (see Chattaraj and Deb 1984 for a review), is given by

$$T_2[\rho] = \frac{1}{2} \int d\mathbf{r} |\nabla \rho(\mathbf{r})|^2 / \rho(\mathbf{r}). \quad (4)$$

Analogous correction for the $\chi\epsilon$ (see Herman *et al* 1969) functional is given by

$$E_x^{(2)}[\rho] = -D_x \int d\mathbf{r} |\nabla \rho(\mathbf{r})|^2 / \rho(\mathbf{r})^{4/3} \quad (5)$$

where D_x is an empirical constant, different values of which have been suggested by different authors (Kleinman 1984). Although with a suitable choice of D_x and using Hartree-Fock (HF) densities, $E_x^{\text{LDA}}[\rho] + E_x^{(2)}[\rho]$ yield good estimates of the $\chi\epsilon$ s of atomic systems, the major drawback of this functional is that the exchange potential obtained from the functional derivative $\delta E_x^{(2)}[\rho] / \delta \rho$ diverges at large distances where the density approaches zero.

Becke (1986a) has recently proposed on empirical grounds, the $\chi\epsilon$ functional

$$E_x = E_x^{\text{LDA}}[\rho] - \beta \int d\mathbf{r} \{ |\nabla \rho(\mathbf{r})|^2 / \rho(\mathbf{r})^{4/3} \} [1 + \gamma |\nabla \rho(\mathbf{r})|^2 / \rho(\mathbf{r})^{8/3}]^{-1} \quad (6)$$

which does not lead to asymptotic divergence in the corresponding exchange potential. Also, the numerical results obtained from this expression with a suitable choice of values for the parameters β and γ are much closer to the HF values. Further improvements have been attempted by Becke (1986b), but here we restrict our discussion to the simpler expression given by equation (6). There are also other procedures involving gradient terms, e.g. the real space cut-off for the exchange hole (Perdew 1985) and a new phase space route (Ghosh and Parr 1986) leading to good predictions for the $\chi\epsilon$ s.

The $\kappa\epsilon$ functional ($T_0 + T_2$) does not suffer from any asymptotic divergence problem. It yields good results when evaluated with atomic HF density, although the $\kappa\epsilon$ density at the nuclear site remains finite. Corrections involving first power of the density gradient have also been suggested by Haq *et al* (1984), yielding better local and global estimates of the $\kappa\epsilon$. Very recently Lee *et al* (1991) have obtained a modified form for the $\kappa\epsilon$ functional in the spirit of Becke's correction (Becke 1988) for the $\chi\epsilon$. The relationship between the $\kappa\epsilon$ and $\chi\epsilon$ has been considered earlier by Deb and Ghosh (1983), and more recently by March and Santamaria (1991). However, all these functional forms for the $\kappa\epsilon$ and $\chi\epsilon$ involve corrections to the LDA results through density gradient terms. Corrections involving the number of electrons have also been proposed recently by Samanta and Ghosh (1991).

The purpose of the present work is to suggest new gradient-free functional forms for these two energy quantities which are local functionals of the electron density. The corresponding functional derivatives appearing in the Euler-Lagrange equation for density calculation would therefore be free from gradients or integrals, thereby reducing the effort in solving the equation (Deb and Chattaraj 1988, 1992).

2. A new local density functional for the exchange energy

We first derive a new bound to the gradient term for the exchange energy given by equation (5). Consider the inequality (Hardy *et al* 1934)

$$J[y] \equiv \int_0^\infty dr [4(dy/dr)^2 - y^2/r^2] > 0 \quad (7)$$

valid for any arbitrary function $y(r)$ satisfying the condition $y(0)=0$. For the choice $y(r)=r\rho(r)^{1/3}$, where $\rho(r)$ represents the spherically symmetric electron density of an atomic system, inequality (7) can be written as

$$\int_0^\infty dr [(4/9)r^2|\nabla\rho|^2/\rho^{4/3} + 3\rho^{2/3} + 4r(d/dr)\rho^{2/3}] > 0. \quad (7a)$$

Since $r(d/dr)\rho^{2/3} = (d/dr)(r\rho^{2/3}) - \rho^{2/3}$ and $\rho(r) \rightarrow 0$ as $r \rightarrow \infty$, one has $\int_0^\infty dr r(d/dr)\rho^{2/3} = -\int_0^\infty dr \rho^{2/3}$, which can be used to simplify equation (7a) to obtain the inequality

$$\int dr |\nabla\rho|^2/\rho^{4/3} > (9/4) \int dr \rho^{2/3}/r^2. \quad (8)$$

The gradient term for the xE given by equation (5) is thus bounded by the relation

$$-E_x^{(2)}[\rho] > (9D_x/4) \int dr \rho^{2/3}/r^2 \quad (9)$$

where the numerical coefficient $(9D_x/4)$ may be taken as $\frac{1}{120}$ corresponding to the choice of $D_x = 0.003\ 69$. We replace this second gradient term in xE by a term proportional to the right-hand side of equation (9), i.e.

$$E_x^{(2)}[\rho] = -\beta \int dr \rho^{2/3}/r^2 \quad (10)$$

and thus obtain the gradient-free xE density functional

$$E_x = E_x^{\text{LDA}}[\rho] - \beta \int dr \rho^{2/3}/r^2 \quad (11)$$

with the parameter β to be determined empirically by matching the calculated xEs with the corresponding HF values for atoms.

While equation (11) provides a new LDA result for the xE, the corresponding exchange potential, like its original counterpart (i.e. equation (5)), is not free from asymptotic divergence. We therefore propose to have an LDA equivalent of Becke's modified xE functional given by equation (6). For this purpose, we view the approximation introduced through equation (10) as the replacement of the integrand of equation (5), i.e. $(|\nabla\rho|^2/\rho^{4/3})$ locally by $(\alpha\rho^{2/3}/r^2)$ with α as a proportionality constant. We then propose a similar replacement in the integrand of equation (6) to eliminate the gradient terms and obtain the gradient-free representation of the xE functional given by

$$E_x[\rho] = E_x^{\text{LDA}} - \beta \int dr \{ \rho^{4/3} \} / \{ 1 + r^2 \rho^{2/3} / \alpha_x \} \quad (12)$$

where the parameters β and α_x are to be determined empirically. The exchange potential corresponding to this functional does not show asymptotic divergence. At $r \rightarrow 0$ or ∞ , the energy densities of the two terms on the right-hand side of equation (12) are identical. This prompts us to assume β to be replaceable by C_x defined in equation (3). This leaves only one parameter α_x to be determined empirically so as to obtain good predictions of the xEs.

The xE functional of equation (12) can easily be generalized to the spin-polarized case and the resulting expression is given by

$$E_x[\rho_\alpha, \rho_\beta] = -2^{1/3} C_x \sum_{\sigma} \int dr \rho_{\sigma}^{4/3} - 2^{1/3} C_x \sum_{\sigma} \int dr \rho_{\sigma}^{4/3} / \{1 + r^2 (2\rho_{\sigma})^{2/3} / \alpha_x\} \quad (13)$$

where the summations are over spin σ , with ρ_{σ} denoting the density for an electron of spin σ .

3. A new local density functional for the kinetic energy

The KE functional that we propose is based on modification of the first-gradient expression of Haq *et al* (1984), which for a spherically symmetric density can be written as

$$T[\rho] = T_0[\rho] + C \int dr \rho / r^2 \quad (14)$$

where C is an empirical constant. Although this functional yields good predictions of the total KE with HF density for atoms, the corresponding functional derivative is highly singular at the origin, requiring a cut-off to be used in density calculations. We therefore propose the following modified expression of this functional:

$$T[\rho] = T_0[\rho] + \beta \int dr \{ \rho^{4/3} / r \} / \{ 1 + r \rho^{1/3} / \alpha_k \} \quad (15)$$

obtained by multiplying the integrand of the last term in equation (14) by a suitable function of r and ρ so that the resulting functional derivative has the correct behaviour (r^{-1} singularity) at the origin. This empirical modification is in the same spirit as that of Becke's modification of the gradient exchange term of equation (5), leading to equation (6) which avoids asymptotic divergence.

The spin-polarized generalization of equation (15) is given by

$$T[\rho_\alpha, \rho_\beta] = 2^{2/3} C_k \sum_{\sigma} \int dr \rho_{\sigma}^{5/3} + 2^{2/3} \beta \sum_{\sigma} \int dr \{ \rho_{\sigma}^{4/3} / r \} / \{ 1 + r (2\rho_{\sigma})^{1/3} / \alpha_k \}. \quad (16)$$

The parameter β is assumed to be C_x as in the exchange functional and α_k is to be determined empirically by comparing with HF results. Thus, the gradient-free corrections for both xE and KE incorporate C_x .

4. Results and discussion

The xE and KE functionals proposed here have been evaluated by using the HF densities of Clementi and Roetti (1974) for a number of open- and closed-shell atoms, with the

Table 1. Calculated exchange energies (au) of atomic systems. AV, using spin-averaged density; SP, using spin-polarized density; B, Becke.

Atom	HF ^a	$E_x(\text{AV})^b$	$E_x(\text{SP})^c$	$E_x(\text{B}_1)^d$	$E_x(\text{B}_2)^e$
He	1.026	1.026	1.026	1.027	1.024
Li	1.781	1.758	1.775	1.780	1.774
Be	2.667	2.657	2.657	2.669	2.659
B	3.744	3.714	3.727	3.744	3.732
C	5.045	4.973	5.031	5.050	5.037
N	6.596	6.447	6.587	6.608	6.594
O	8.174	8.106	8.168	8.192	8.179
F	10.00	10.00	10.02	10.04	10.03
Ne	12.11	12.14	12.14	12.16	12.15
Na	14.02	14.02	14.03	14.06	14.05
Mg	15.99	16.00	16.00	16.03	16.02
Al	18.07	18.06	18.07	18.10	18.09
Si	20.28	20.23	20.27	20.30	20.29
P	22.64	22.53	22.62	22.65	22.64
S	25.00	24.94	24.98	25.01	25.00
Cl	27.51	27.48	27.49	27.52	27.51
Ar	30.19	30.15	30.15	30.18	30.18
Kr	93.89	93.94	93.94	93.82	—
Xe	179.2	179.2	179.2	178.9	—

^a Exact (HF) exchange energies from Becke (1986a).^b Exchange energies calculated from equation (12) with $\beta = C_x$ and $\alpha_x = 0.0244$.^c Exchange energies calculated from equation (13) with $\beta = C_x$ and $\alpha_x = 0.0244$.^d Exchange energies calculated from equation (6); results from Becke (1986a).^e Exchange energies calculated from modified equation (6); results from Becke (1986b).

empirical values $\alpha_x = 0.0244$ and $\alpha_k = 0.043$. Table 1 compares our calculated values of x_E s with the exact (HF) results and those of Becke (1986a, b). The agreement is very good. Our k_E results reported in table 2 also agree very well with the HF values. A major objective of this work has been to find a good LD prescription for the x_E , which can be used in Kohn–Sham type calculations as well as TF-type direct density procedures (Deb and Chattaraj 1988, 1992). For this purpose, we have included results obtained from the expression involving total density (equation (12)) and also its spin-polarized generalization (equation (13)). Analogously, for the k_E , we have the results corresponding to equations (15) and (16). In all cases, the spin-polarized results seem to be in better agreement with the HF values.

Since the inequality derived in equation (8) is new, we also calculated the ratio $(\int dr |\nabla \rho|^2 / \rho^{4/3}) / (\int dr \rho^{2/3} / r^2)$ for several atoms. The results 4.27, 3.65, 3.51, 3.31 and 3.24 for the atoms He, Ne, Ar, Kr and Xe respectively indicate that the ratio is higher than $\frac{9}{4}$, the limit set by equation (8) and approaches this limit as Z increases.

The numerical results of table 1 reveal that the present LDA form for the exchange is comparable in accuracy to that of Becke's gradient expression for x_E . However our LD form is much easier to evaluate than the gradient forms. Thus, for atomic systems, our x_E density functional can be a promising alternative to Becke's exchange (Becke 1986a). It should however be noted that the present LD forms are applicable to systems with decaying electron density and are not expected to yield the uniform electron gas result (the first term of equations (12) or (13)) as a limiting condition.

Furthermore, the LD form for k_E leads to a non-differential Euler–Lagrange equation for the calculation of density (Deb and Chattaraj 1988, 1992). Since the derivative

Table 2. Calculated kinetic energies of atomic systems. FG, first gradient.

Atom	HF ^a	T(AV) ^b	T(SP) ^c	T(FG) ^d	T(FGSP) ^e
He	2.862	2.852	2.852	2.860	2.860
Li	7.433	7.416	7.437	7.435	7.456
Be	14.573	14.537	14.537	14.569	14.569
B	24.529	24.261	24.304	24.306	24.350
C	37.688	37.057	37.326	37.116	37.385
N	54.401	53.384	54.234	53.456	54.305
O	74.810	73.564	74.035	73.646	74.117
F	99.410	98.245	98.391	98.333	98.479
Ne	128.55	128.04	128.04	128.13	128.13
Na	161.86	161.42	161.44	161.51	161.53
Mg	199.61	199.28	199.28	199.36	199.36
Al	241.87	241.54	241.56	241.62	241.64
Si	288.85	288.48	288.57	288.54	288.64
P	340.71	340.28	340.58	340.33	340.62
S	397.51	397.07	397.22	397.09	397.24
Cl	459.47	459.07	459.12	459.07	459.11
Ar	526.81	526.57	526.57	526.54	526.54
Kr	2752.0	2750.9	2750.9	2749.1	2749.1
Xe	7232.0	7233.4	7233.4	7227.0	7227.0

^a Hartree-Fock kinetic energies from Clementi and Roetti (1974).^b Kinetic energies calculated from equation (15) with $\beta = C_x$ and $\alpha_k = 0.043$.^c Kinetic energies calculated from equation (16) with $\beta = C_x$ and $\alpha_k = 0.043$.^d Kinetic energies calculated from equation (14) with $C = \frac{1}{40}$. See also Haq *et al* (1984).^e Kinetic energies calculated from spin-polarized version of equation (14) with $C = \frac{1}{40}$.

of the present KE density functional has the correct singularity at the nucleus, it would eliminate a serious drawback of the TF theory, namely infinite density at the nucleus. Imposition of the finite density constraint has earlier resulted (Ghosh and Parr 1987) in a significant improvement of the TF results and the present work can be used to satisfy this condition rather easily. Even with this constraint, improved TF-type calculations on neutral atoms, monopositive and mononegative ions have yielded very encouraging results (Deb and Chattaraj 1988). It may be emphasized that while columns 3, 5 and 4, 6 in table 2 are quite comparable, the present LD functionals do not have extra singularities at the origin.

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