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Exchange and exchange-correlation functionals based on the gradient correction of the electron gas

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We demonstrate that the functional form of the Padé approximant of the second-order density gradient correction of Rasolt and Geldart [Phys. Rev. Lett. **35**, 1234 (1975)] for the inhomogeneous electron gas yields excellent results when applied to atoms. The gradient correction employed by us uses the $\frac{10}{7}$ factor as suggested by Kleinman and Lee [Phys. Rev. B **37**, 4634 (1988)] with the constants of Rasolt and Geldart replaced by an empirically derived set, based upon numerical fits of the exchange and exchange-correlation energies of the atoms He through Ar. The resulting fitted nonlocal gradient corrections were then used in the minimization of the Kohn-Sham functional to solve for the exchange-only and exchange-correlation total energies. The resulting standard deviations in the calculated total energies were 0.0043 for exchange only and 0.0014 for exchange correlation.

The search for good exchange-correlation energy density functionals is a major challenge in density-functional theory [1–3] (DFT). Although there has been success in this area, much work still remains before we can accurately describe atomic and molecular systems. A popular and widely used approximation is the local-density approximation (LDA). However, the LDA functional suffers some serious problems when applied to real systems of interest [1,4]. Nonlocal corrections have been proposed, but many, such as the formal gradient expansion [1,5–7], provide only a modest improvement in the calculated results and introduce unwanted singularities in the potential.

The orbital-density description of density-functional theory is given by Kohn-Sham theory. For atoms we may write

$$E[\{\phi_i\}]=T_s[\{\phi_i\}]+J[\rho]+E_{\mathrm{xc}}[\rho]+V_{\mathrm{NE}}[\rho]\ , \tag{1}$$

where T_s is the kinetic energy of a noninteracting system,

$$J[\rho]=\tfrac{1}{2}\int\int\frac{\rho(1)\rho(2)}{r_{12}}d\tau_2 d\tau_1 \tag{2}$$

is the Coulomb energy, E_{xc} is the unknown exchange-correlation energy density functional,

$$V_{\mathrm{NE}}=-Z\int\frac{\rho}{r}d\tau \tag{3}$$

is the nuclear-electron attraction energy (Z being the nuclear charge of the atom), and ρ is the electron density. Minimizing $E[\{\phi_i\}]$ with respect to variations in the ϕ_i, subject to the constraints $\rho=\sum_i^N\phi_i^2$ and $\langle\phi_i|\phi_i\rangle=1$, one arrives at the following Euler-Lagrange equation:

$$-\frac{1}{2}\frac{\nabla^2\phi_i}{\phi_i}+\frac{\delta E_{\mathrm{xc}}}{\delta\rho}+\frac{\delta J}{\delta\rho}-\frac{Z}{r}=\varepsilon_i\ . \tag{4}$$

Rasolt and Geldart [8–11] have provided a form for the unknown E_{xc} that contains nonlocal corrections to the LDA functional. To derive their nonlocal correction to E_{xc}, they summed up all possible second-order exchange and correlation diagrams in the random-phase approximation and also incorporated higher-order contributions in an average sense. Their expression, truncated to second order, is

$$E_{\mathrm{xc}}=E_{\mathrm{xc}}^{\mathrm{LDA}}+\int B_{\mathrm{xc}}\left[\frac{\nabla\rho}{\rho^{2/3}}\right]^2 d\tau\ , \tag{5}$$

where B_{xc} is represented by the Padé approximant

$$B_{\mathrm{xc}}(\rho)=-1\times10^{-3}c_1\frac{1+c_2r_s+c_3r_s^2}{1+c_4r_s+c_5r_s^2+c_6r_s^3} \tag{6}$$

and $r_s=(3/4\pi\rho)^{1/3}$. The constants c_i, as obtained by Rasolt and Geldart [8–11], are given in the first column of Table I. This form has proven quite successful when applied to systems other than atoms and molecules [11]. Recently, Kleinman [12–14] has argued that to preserve the high-density limit, Eq. (5) should be modified such that the nonlocal correction is premultiplied by the factor $\frac{10}{7}$. We too find (at least empirically) that it is appropriate for atoms and have used it in all the calculations presented below.

Since the coefficients c_i were obtained from properties of electron densities that are far removed from those as-

TABLE I. Coefficients for the Padé approximant representation of B_{xc}. Atomic units are used throughout.

	Rasolt-Geldart[a]	E_{xc} fit[b]	E_{x} fit[c]
c_1	2.568	2.568	2.568
c_2	9.0599	−5.9845	8.6847
c_3	2.877×10^{-3}	10.8527	−1.7976
c_4	8.723	−2.0801	7.7764
c_5	0.472	−9.3206	−1.6990
c_6	7.389×10^{-2}	27.9143	0.1710

[a] Taken from References [8–11].

[b] The standard error of the nonlinear least-squares fit was 0.0012.

[c] The standard error of the nonlinear least-squares fit was 0.0034.

sociated with atoms and molecules, we decided to see how well the functional form of Eqs. (5) and (6) fared when applied to atomic systems. We therefore used Eqs. (5) and (6), with the coefficients of Rasolt and Geldart but with the $\frac{10}{7}$ factor included, to approximate E_{xc} in Eq. (4) and then solved for the ground-state energies of the atoms He through Ar. We found that the calculated energies have a standard deviation of 0.58, when compared to the correct energies. These correct energies are taken as the sum of the Hartree-Fock energy [15,16] E^{HF} plus the known correlation energy [17,18] E_{c}; see the second column of Table II. In these calculations we used the Gunnarsson-Lundqvist [19] parametrization of $E_{\text{xc}}^{\text{LDA}}$. The resulting total energies are given in the fourth column of Table II. This is a slight improvement over just using $E_{\text{xc}}=E_{\text{xc}}^{\text{LDA}}$, which has a standard deviation of 0.75. For comparison, we list the E^{LDA} total energies in the fifth column of Table II. We note that using the c_i of Rasolt and Geldart [8–11], without the $\frac{10}{7}$ factor, a much smaller standard error is obtained, namely, 0.19. Since the nonlocal correction as defined by Eqs. (5) and (6) produced improved energies, we believed that its functional form was suitable for atoms and that by changing the c_i, we could obtain even better results. A new set of c_i $(i=2,\ldots,6)$ was obtained by performing nonlinear least-squares fits of Eqs. (5) and (6) to $E_{\text{x}}^{\text{HF}}+E_{\text{c}}$, where E_{x}^{HF} is the Hartree-Fock exchange energy [15,16]. We used Hartree-Fock densities [15,16] to evaluate E_{xc} and minimized the sum of squares,

$$\sum_i \left[1-\frac{E_{\text{xc}}[\rho_{\text{HF}}]}{E_{\text{x}}^{\text{HF}}+E_{\text{c}}} \right]^2 . \tag{7}$$

The resulting c_i are given in the second column of Table I. The standard error of this fit was 0.0012, showing that we have an exceedingly good fit. However, this good fit, in itself, does not guarantee that solutions of the Kohn-Sham equation will yield good results. Using this set of coefficients in Eqs. (6) and (5), we solved the Kohn-Sham equation, Eq. (4). The standard deviation of the resulting total energies was 0.0014, showing that we have an exceedingly good approximation to E_{xc}. We list the resulting total energies in the third column of Table II. Energy difference calculated ionization potentials, as well as transition state ionization potentials, are also very good. This is to be expected, since the total energies are well reproduced. Earlier we stated that the $\frac{10}{7}$ factor was also appropriate for atoms. We came to this conclusion by looking at a six-term nonlinear least-squares fit, i.e., we let c_1 vary. The resulting standard error was essentially the same as that of the five-term fit and the fitted value of c_1 was close to the value 2.568 times $\frac{10}{7}$. This suggests that the five-term fit with the $\frac{10}{7}$ factor is appropriate. Although we do not give the results, the fitted six-term c_i gave slightly poorer total energies when the Kohn-Sham equation was solved.

In spite of the fact that scaling arguments would prevent the nonlocal gradient correction of Rasolt and

TABLE II. Ground-state total energies, in atomic units, of the atoms of He through Ar.

Atom	$-E^{\text{exact}}$[a]	$-E^{\text{xc-fit}}$[b]	$-E^{\text{RG}}$[c]	$-E^{\text{LDA}}$[d]	$-E^{\text{x-fit}}$[e]	$-E^{\text{HF}}$[f]
He	2.9042	2.9054	3.0317	2.8601	2.8642	2.8617
Li	7.4781	7.4772	7.6473	7.3704	7.4349	7.4327
Be	14.6675	14.6745	14.8911	14.4966	14.5888	14.5730
B	24.6538	24.6536	24.9158	24.4097	24.5338	24.5291
C	37.8163	37.8152	38.1305	37.5095	37.6575	37.6597
N	54.4812	54.4941	54.8681	54.1287	54.2970	54.2962
O	75.0271	75.0234	75.4597	74.5979	74.7845	74.7692
F	99.741	99.736	100.235	99.247	99.450	99.409
Ne	128.937	128.964	129.522	128.403	128.623	128.547
Na	162.257	162.268	162.862	161.624	161.903	161.859
Mg	200.058	200.075	200.705	199.340	199.637	199.615
Al	242.357	242.365	243.028	241.533	241.867	241.877
Si	289.356	289.365	290.063	288.435	288.799	288.835
P	341.202	341.232	341.967	340.202	340.595	340.649
S	398.113	398.120	398.895	396.993	397.414	397.479
Cl	460.196	460.186	461.005	458.963	459.411	459.482
Ar	527.605	527.586	528.452	526.267	526.743	526.818

[a] The exact energies are taken as the sum of the Hartree-Fock values (Refs. [15] and [16]) and known correlation energies (Refs. [17] and [18]).

[b] Total energies calculated using the E_{xc} fitted coefficients in Eqs. (5) and (6).

[c] Total energies calculated using the Rasolt and Geldart (Refs. [8–11]) coefficients in Eqs. (5) and (6) with the $\frac{10}{7}$ factor included.

[d] Total energies calculated using the LDA approximation to E_{xc}.

[e] Exchange-only total energies calculated using the E_{x} fitted coefficients.

[f] Hartree-Fock total energies (Refs. [15] and [16]).

Geldart [8–11] from being considered as an exchange-only correction, we decided to see if the functional form would be adequate for exchange-only calculations. Writing the exchange energy,

$$E_x = E_x^{\text{Dirac}} + \tfrac{10}{7} \int B_x \left[\frac{\nabla \rho}{\rho^{2/3}} \right]^2 d\tau \ , \tag{8}$$

where the E_x^{Dirac} is the Dirac [20] local approximation for the exchange energy. Assuming that the form of $B_x(\rho)$ was given by Eq. (6), we determined a set of c_i by performing nonlinear least-squares fits of the Hartree-Fock exchange energies. The resulting coefficients are given in the third column of Table I. The standard error of this fit was 0.0034—not as good as the exchange-correlation fit, but still quite good. Solving the Kohn-Sham equation produced exchange-only total energies that had a standard deviation of 0.0043 when compared to exact Hartree-Fock energies. These exchange-only total energies are listed in the sixth column of Table II. For comparison, we list the Hartree-Fock energies in the last column of this table. These numerical results show that the Rasolt and Geldart [8–11] nonlocal correction can also be used to improve exchange-only calculations. As with the exchange-correlation fits, we found that a six-term fit was not any better than a five-term fit with the $\frac{10}{7}$ factor modifying the Rasolt and Geldart [8–11] value of c_1.

We have shown from numerically calculated atomic total energies that the nonlocal gradient correction of Rasolt and Geldart [8–11], with suitably modified coefficients, is an excellent choice for the exchange-correlation and the exchange-only energy density functionals. We wish to emphasize that these modified coefficients are not based upon any fundamental many-body calculations, but that they are empirically derived. We are not aware of any previous approximate $E_{xc}[\rho]$ that has produced as good total energies, when used in the solution of the Kohn-Sham equation. Although this nonlocal correction has led to excellent total energies, its functional derivative suffers from not having the correct long-range or short-range behavior. This is not serious when it comes to the energy and its components, but the singularity at the nucleus destroys the cusp and the incorrect long-range behavior produces a density that does have the correct exponential falloff far from the nucleus. Hopefully, by modifying the current nonlocal gradient functional, we can maintain the current excellent results while removing the unwanted long- and short-range behaviors of the potential.

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