Accurate Density Functional with Correct Formal Properties: A Step Beyond the Generalized Gradient Approximation

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We approximate the exchange-correlation energy of density functional theory as a controlled extrapolation from the slowly varying limit. While generalized gradient approximations (GGA's) require only the local density and its first gradient as input, our meta-GGA also requires the orbital kinetic energy density. Its exchange energy component recovers the fourth-order gradient expansion, while its correlation energy is free of self-interaction error. Molecular atomization energies and metal surface energies are significantly improved over GGA, while lattice constants are little changed. [S0031-9007(99)08696-2]

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Density functional theory [1,2] is a popular tool for electronic structure calculations of ground-state properties in atoms, molecules, and solids. In this theory, only the exchange-correlation energy $E_{xc} = E_x + E_c$ as a functional of the electron density $n(\mathbf{r}) = n_\uparrow + n_\downarrow$ must be approximated. Despite its simplicity, the local spin density (LSD) approximation [1,2]

$$E_{xc}^{\mathrm{LSD}}[n_\uparrow, n_\downarrow] = \int d^3r\, n(\mathbf{r})\epsilon_{xc}^{\mathrm{unif}}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r}))\,, \qquad (1)$$

is still widely used in solid-state physics. More recently, generalized gradient approximations (GGA's) [3–5],

$$E_{xc}^{\mathrm{GGA}}[n_\uparrow, n_\downarrow] = \int d^3r\, n\epsilon_{xc}^{\mathrm{GGA}}(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow)\,, \qquad (2)$$

have made a strong advance into the realm of quantum chemistry. However, the goal of constructing a universal functional with chemical accuracy (atomization energy errors of order 1 kcal/mole = 0.0434 eV) remains elusive.

One way to go beyond the restricted GGA form of Eq. (2) is to construct a fully nonlocal density functional, as we have proposed in recent work [6]. A more practical way is to construct "meta–generalized gradient approximations" (MGGA's) which expand the arguments of the integrand of Eq. (2) to include additional semilocal information, e.g., the Laplacian $\nabla^2 n_\sigma$ or the kinetic energy density of the occupied Kohn-Sham orbitals,

$$\tau_\sigma(\mathbf{r}) = \frac{1}{2}\sum_{\alpha}^{\mathrm{occup}} |\nabla\psi_{\alpha\sigma}(\mathbf{r})|^2, \qquad (3)$$

where $\sigma = \uparrow, \downarrow$ and $n_\sigma = \sum_\alpha |\psi_{\alpha\sigma}|^2$. Although τ_σ is a nonlocal functional of the density, it is accessible in every calculation. Early meta-GGA's [7,8] preceded most GGA's. Meta-GGA's are computationally efficient and can achieve order-N scaling with unit-cell size.

Meta-GGA's can also achieve high accuracy, as demonstrated by recent constructions [9–11] based upon fits to chemical data. However, semiempirical constructions are unsatisfactory in two ways: (1) The density functional should derive from quantum mechanics, without the need for 10 or 20 fit parameters. (2) Semiempirical functionals typically fail for the uniform electron gas—the one limit in which the GGA and meta-GGA forms can be exact—and more generally for solids. Universal functionals must be based on universal principles.

To construct a meta-GGA, we follow the philosophy of Perdew, Burke, and Ernzerhof (PBE) [5], who constructed a GGA by preserving and extending the correct formal properties of LSD. If everything right is kept and nothing wrong is added, the resulting functional can never be less accurate than LSD, unless by accident. For molecules, the PBE GGA reduces the LSD overbinding and greatly improves atomization energies. It gives realistic binding-energy curves for rare-gas dimers, where other GGA's fail [12,13]. In solid-state physics, it improves lattice constants and magnetic properties of many metals, and pressures for phase transitions [14]. However, the PBE GGA does not always improve upon LSD lattice constants and can even predict less accurate ones as in Ge. Moreover, surface exchange energies are significantly underestimated by this and other GGA's.

In this Letter, we construct a new functional for the exchange-correlation energy which retains the good formal properties of the PBE GGA while adding others. This new functional makes predictions which significantly improve upon those of PBE. The price for this general improvement (which seems unreachable within the GGA form) is the addition of another local variable, the kinetic energy density $\tau = \tau_\uparrow + \tau_\downarrow$, which for $n_\uparrow = n_\downarrow$ has the second-order gradient expansion [15]

$$\tau^{\mathrm{GEA}} = \frac{3}{10}(3\pi^2)^{2/3} n^{5/3} + \frac{1}{72}\frac{|\nabla n|^2}{n} + \frac{1}{6}\nabla^2 n. \quad (4)$$

Becke has argued that τ is a natural ingredient of both the exchange energy [16] and the correlation energy [11]. For compatibility, these two should be approximated together in the same way.

The meta-GGA for exchange must satisfy the spin-scaling relation [17]

$$E_x[n_\uparrow, n_\downarrow] = \frac{1}{2}E_x[2n_\uparrow] + \frac{1}{2}E_x[2n_\downarrow], \quad (5)$$

the uniform density-scaling relation [18]

$$E_x[n_\lambda] = \lambda E_x[n], \quad (6)$$

where $n_\lambda(\mathbf{r}) = \lambda^3 n(\lambda \mathbf{r})$, and the Lieb-Oxford lower bound [19]

$$E_x[n_\uparrow, n_\downarrow] \geq E_{xc}[n_\uparrow, n_\downarrow] \geq -1.679 \int d^3r\, n^{4/3}. \quad (7)$$

We write the meta-GGA for a spin-unpolarized density n as

$$E_x^{\mathrm{MGGA}}[n] = \int d^3r\, n \epsilon_x^{\mathrm{unif}}(n) F_x(n, \nabla n, \tau), \quad (8)$$

where $\epsilon_x^{\mathrm{unif}}(n) = -\frac{3}{4\pi}(3\pi^2 n)^{1/3}$ is the exchange energy per particle of the uniform electron gas. The enhancement factor F_x for a slowly varying density has the fourth-order gradient expansion of Svendsen and von Barth [20]

$$F_x = 1 + \frac{10}{81}p + \frac{146}{2025}q^2 - \frac{73}{405}qp + Dp^2 + O(\nabla^6), \quad (9)$$

where

$$p = |\nabla n|^2/[4(3\pi^2)^{2/3} n^{8/3}]. \quad (10)$$

is the square of the reduced density gradient, and

$$q = \nabla^2 n/[4(3\pi^2)^{2/3} n^{5/3}] \quad (11)$$

is the reduced Laplacian of the density. While the first two gradient coefficients in Eq. (9) are known exactly, the third has an uncertainty of 20% [20] and the fourth (D) is unknown.

We define a new variable

$$\tilde{q} = 3\tau/[2(3\pi^2)^{2/3} n^{5/3}] - 9/20 - p/12, \quad (12)$$

which by Eq. (4) reduces to q in the slowly varying limit but remains finite at a nucleus where q diverges. A simple enhancement factor, which scales like Eq. (6) and reduces to Eq. (9) in the slowly varying limit, is

$$F_x(p, \tilde{q}) = 1 + \kappa - \kappa/(1 + x/\kappa), \quad (13)$$

a form similar to that of Ref. [5] but with

$$x = \frac{10}{81}p + \frac{146}{2025}\tilde{q}^2 - \frac{73}{405}\tilde{q}p + \left[D + \frac{1}{\kappa}\left(\frac{10}{81}\right)^2\right]p^2, \quad (14)$$

a new inhomogeneity parameter which replaces $0.21\,951 p$. $\kappa = 0.804$ is the largest value which ensures that the Lieb-Oxford bound of Eq. (7) is satisfied for all possible densities. We estimate $D = 0.113$ by minimizing the mean absolute error in the atomization energies of the molecules from Ref. [5] (Table I). This estimate of D, which makes $x \geq 0$ (hence $F_x \geq 1$), is also supported by studies of the surface exchange energy for slowly varying density profiles [21].

Unlike this meta-GGA (but like other GGA's [4]), the PBE GGA does not recover the correct gradient expansion for exchange even to second order in ∇. Its coefficient for the term linear in p in the enhancement factor is larger than the correct value $10/81$ [22] by a factor of 1.778. This choice was made in Ref. [5] to recover the LSD linear response of the uniform electron gas, because the second-order gradient expansion is a less satisfactory approximation to this response. The meta-GGA recovers the exact linear response function $\gamma_x(k)$ up to fourth order in $k/2k_F$, where k_F is the Fermi wave vector. The combined (exchange plus correlation) linear response function $\gamma_{xc}(k)$ in meta-GGA is in good agreement [21] with nearly exact results for $0 \leq k/2k_F \lesssim 1.5$.

TABLE I. Atomization energies (in kcal/mole). All functionals evaluated on GGA densities at experimental geometries. Zero-point vibration removed from experimental energies [5]. The GGA is PBE [5], and the LSD is the local part of PBE. The Gaussian basis sets are of triple-zeta quality, with p and d polarization functions for H and d and f polarization functions for first- and second-row atoms.

Molecule	ΔE^{LSD}	ΔE^{GGA}	ΔE^{MGGA}	ΔE^{expt}
H_2	113.3	104.6	114.5	109.5
LiH	61.1	53.5	58.4	57.8
CH_4	462.6	419.8	421.1	419.3
NH_3	337.3	301.7	298.8	297.4
OH	124.2	109.8	107.8	106.4
H_2O	266.6	234.2	230.1	232.2
HF	162.3	142.0	138.7	140.8
Li_2	23.8	19.9	22.5	24.4
LiF	156.1	138.6	128.0	138.9
Be_2	12.8	9.8	4.5	3.0
C_2H_2	460.3	414.9	401.2	405.4
C_2H_4	632.7	571.5	561.5	562.6
HCN	360.8	326.1	311.8	311.9
CO	298.9	268.8	256.0	259.3
N_2	266.9	243.2	229.2	228.5
NO	198.4	171.9	158.5	152.9
O_2	174.9	143.7	131.4	120.5
F_2	78.2	53.4	43.2	38.5
P_2	143.0	121.1	117.8	117.3
Cl_2	82.9	65.1	59.4	58.0
Mean abs. error	31.69	7.85	3.06	···

Our meta-GGA correlation energy functional retains the correct formal properties of PBE GGA correlation, such as the correct slowly varying limit and the finite limit for $E_c[n_\lambda]$ under uniform scaling as the scale parameter $\lambda \to \infty$. We also require that the correlation energy be self-interaction free, i.e., vanish for a spin-polarized one-electron density. We use the form

$$E_c^{\mathrm{MGGA}}[n_\uparrow, n_\downarrow] = \int d^3r \left\{ n\epsilon_c^{\mathrm{GGA}}(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow) \left[1 + C\left(\frac{\sum_\sigma \tau_\sigma^W}{\sum_\sigma \tau_\sigma} \right)^2 \right] - (1 + C) \sum_\sigma \left(\frac{\tau_\sigma^W}{\tau_\sigma} \right)^2 n_\sigma \epsilon_c^{\mathrm{GGA}}(n_\sigma, 0, \nabla n_\sigma, 0) \right\}, \tag{15}$$

where $\epsilon_c^{\mathrm{GGA}} = \epsilon_c^{\mathrm{unif}} + H$ is the PBE GGA correlation energy per electron [5]. Here

$$\tau_\sigma^W = \frac{1}{8} \frac{|\nabla n_\sigma|^2}{n_\sigma}, \tag{16}$$

the Weizsäcker kinetic energy density, is exact for a one-electron system. Thus Eq. (15) vanishes for any one-electron density, for any value of the parameter C. Becke [11] and others [9,23] have used τ_σ and τ_σ^W to construct self-interaction-free correlation energy functionals. We have shifted the self-interaction correction to fourth order in ∇, where it has no effect on the correct second-order gradient coefficient in $\epsilon_c^{\mathrm{GGA}}$.

Just as our self-interaction correction has no effect on a system of slowly varying density, it should have none on the surface energy of an extended solid. The choice $C = 0.53$ gives surface correlation energies for jellium (with bulk density parameter r_s, $2 \leq r_s \leq 6$ bohr) in close agreement with those of PBE GGA; atomic correlation energies also agree, but less precisely. For the Hartree-Fock density of the He atom, the MGGA energies in hartrees are $E_x[n] = -1.020$, $E_c[n] = -0.047$, and $\lim_{\lambda\to\infty} E_c[n_\lambda] = -0.054$.

By making the correlation energy self-interaction free, we achieve proper uniform scaling behavior for all one-electron densities. This improvement seems to carry over to many-electron systems. Under uniform scaling to the low-density or strongly interacting limit ($\lambda \to 0$), $E_c[n_\lambda]$ scales to $\lambda W_c[n]$. For the density $n(\mathbf{r})$ of the helium atom, $W_c[n]$ in hartrees is -0.84 (LSD), -0.68 (PBE GGA), -0.48 (MGGA), and -0.48 (exact [24]).

Unlike the PBE GGA, our meta-GGA [Eqs. (3), (5), (8), (13), and (15)] has fitted parameters (C, D), but far fewer than other recent functionals. Comparison with other functionals will be made elsewhere.

Since the meta-GGA exchange-correlation energy depends explicitly on the occupied Kohn-Sham orbitals, the corresponding exchange-correlation potential can be found by the optimized potential method [25,26]. However, in this paper we evaluate meta-GGA energies with orbitals and densities from self-consistent LSD or GGA calculations for surfaces and for molecules and solids, respectively. Experience with other functionals suggests that results obtained this way will be very close to those of fully self-consistent meta-GGA calculations.

Table I shows the atomization energies of 20 small molecules calculated [27] with different functionals. The meta-GGA functional performs remarkably well; it reduces the mean absolute error to 3 kcal/mole, more than a factor of 2 better than the PBE GGA and a factor of 10 better than LSD. The PBE GGA overbinding of multiply bonded molecules is strongly reduced, without degrading the quality of the results for singly bonded molecules. The largest errors occur for O_2 with almost 11 kcal/mole overbinding, and for LiF which is underbound by almost the same amount. For atomization energies, meta-GGA accuracy is comparable to that achieved more expensively by mixing GGA with exact exchange [28].

Table II shows surface exchange and correlation energies for jellium. The meta-GGA gives surface exchange energies σ_x closer to exact values [29] than either LSD (which overestimates) or PBE GGA (which underestimates). The combined MGGA $\sigma_{xc} = \sigma_x + \sigma_c$ is close to estimates of the exact σ_{xc} [6] which treat exchange and long-range correlation within the random phase approximation (RPA) [29], and short-range correlation (the correction to RPA) within LSD.

The general improvement we have achieved over PBE GGA seems to be a consequence of the more general meta-GGA form. Attempts to revise PBE within the GGA form

TABLE II. Exchange and correlation contributions to surface energies (in erg/cm^2) for jellium, using self-consistent LSD densities. Exact surface exchange energies were provided by Pitarke and Eguiluz [29].

r_s	$\sigma_x^{\mathrm{exact}}$	σ_x^{LSD}	σ_x^{GGA}	σ_x^{MGGA}	σ_c^{LSD}	σ_c^{GGA}	σ_c^{MGGA}
2.00	2624	3037	2438	2578	317	827	824
2.07	2296	2674	2127	2252	287	754	750
2.30	1521	1809	1395	1484	210	567	564
2.66	854	1051	770	825	137	382	380
3.00	526	669	468	505	95	275	274
3.28	364	477	318	346	72	215	214
4.00	157	222	128	142	39	124	124
5.00	57	92	40	47	19	67	66
6.00	22	43	12	15	10	40	40

TABLE III. Lattice constants (in Å) for some solids studied in Ref. [32], from scalar-relativistic all-electron full-potential linearized augmented plane wave calculations [33] without zero-point anharmonic expansion. GGA densities used for all but the LSD calculations.

Solid	a^{LSD}	a^{GGA}	a^{MGGA}	a^{expt}
Na	4.05	4.20	4.31	4.23
NaCl	5.47	5.70	5.82	5.64
Al	3.98	4.05	4.02	4.05
Si	5.40	5.47	5.46	5.43
Ge	5.63	5.78	5.73	5.66
GaAs	5.61	5.76	5.72	5.65
Cu	3.52	3.63	3.60	3.60
W	3.14	3.18	3.17	3.16
Mean abs. error	0.078	0.051	0.059	⋯

[30] achieve limited improvement in atomization energies, but worsen the surface energies. Even for atomization energies, the "revised PBE" GGA improves results for the multiply bonded molecules at the cost of worsening them for the singly bonded ones [31].

The meta-GGA distinguishes between different limiting regions of space: (i) iso-orbital regions, such as density tails in atoms and single bonds in molecules, where the density is dominated by one orbital or several of the same shape, making $\tau \approx \tau^W$, and (ii) regions of strong orbital overlap, such as intershell regions in atoms or valence regions in metals, where $\tau \gg \tau^W$. (By the Cauchy-Schwarz inequality, $\tau \geq \tau^W$.)

Convincing evidence [32] indicates that the core-valence intershell region is the main source for the errors of LSD and GGA lattice constants of solids. In this region, the reduced Laplacian of Eq. (11) is rather large ($q \approx 2$). Table III shows that meta-GGA lattice constants [33] do not consistently improve upon those of GGA. In NaCl, neglect of long-range van der Waals attraction may be a second source of error.

Some say that "there is no systematic way to construct density functional approximations." But there are more or less systematic ways, and the approach taken in Ref. [5] and here is one of the former. As LSD is embedded in GGA, so GGA is embedded in meta-GGA. While real electron densities are seldom close to the slowly varying limit, this limit still provides an important global constraint on the density functional.

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