Climbing the Density Functional Ladder: Nonempirical Meta–Generalized Gradient Approximation Designed for Molecules and Solids

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The electron density, its gradient, and the Kohn-Sham orbital kinetic energy density are the local ingredients of a meta–generalized gradient approximation (meta-GGA). We construct a meta-GGA density functional for the exchange-correlation energy that satisfies exact constraints without empirical parameters. The exchange and correlation terms respect two paradigms: one- or two-electron densities and slowly varying densities, and so describe both molecules and solids with high accuracy, as shown by extensive numerical tests. This functional completes the third rung of "Jacob's ladder" of approximations, above the local spin density and GGA rungs.

Kohn-Sham spin-density functional theory [1] reduces the many-electron ground-state problem to a self-consistent noninteracting electron form that is exact in principle for the density and energy, requiring in practice an approximation for the exchange-correlation (xc) energy functional $E_{xc}[n_\uparrow, n_\downarrow]$. No other method achieves comparable accuracy at the same cost. The exact functional is universal; its approximations should be usefully accurate for both molecules and solids, and thus for intermediate cases (clusters, biological molecules) or combinations (chemisorption and catalysis on a solid surface). The paradigm densities of quantum chemistry (hydrogen atom and electron pair bond) and condensed matter physics (uniform electron gas) thus deserve special respect. Semiempirical functionals can fail outside their fitting sets [2,3]; those fitted only to molecules can be unsuitable for solids. Alternatively, functionals can be constructed to satisfy exact constraints on $E_{xc}[n_\uparrow, n_\downarrow]$. Nonempirical functionals are not fitted to actual or computer experiments for real systems, but are validated by such data.

The first three rungs of "Jacob's ladder" [4] of approximations can be summarized by the formula

$$E_{xc}[n_\uparrow, n_\downarrow] = \int d^3r\, n \epsilon_{xc}(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow, \tau_\uparrow, \tau_\downarrow), \quad (1)$$

where $n(\mathbf{r}) = n_\uparrow(\mathbf{r}) + n_\downarrow(\mathbf{r})$ is the total density, and

$$\tau_\sigma(\mathbf{r}) = \sum_i^{occup} \frac{1}{2} |\nabla \psi_{i\sigma}(\mathbf{r})|^2 \quad (2)$$

is the kinetic energy density for the occupied Kohn-Sham orbitals $\psi_{i\sigma}(\mathbf{r})$, which are nonlocal functionals of the density $n_\sigma(\mathbf{r})$. (We use atomic units where $\hbar = m = e^2 = 1$.) The first rung, found by dropping the ∇n_σ and τ_σ dependences in Eq. (1), is the local spin density (LSD)

approximation [1,5], exact for the uniform electron gas and often usefully accurate for solids. The second rung, found by dropping only the τ_σ dependence in Eq. (1), is the generalized gradient approximation (GGA) [6–8] (useful for molecules as well). The Perdew-Burke-Ernzerhof (PBE) GGA has two nonempirical derivations based on exact properties of the xc hole [7] and energy [8].

The third rung of the ladder, the meta-GGA, makes use of all the ingredients shown in Eq. (1). The kinetic energy density $\tau_\sigma(\mathbf{r})$ recognizes [9] when $n_\sigma(\mathbf{r})$ has one-electron character by the condition $\tau_\sigma(\mathbf{r}) = \tau_\sigma^W(\mathbf{r})$, where $\tau_\sigma^W(\mathbf{r}) = |\nabla n_\sigma|^2/8n_\sigma$ is the von Weizsäcker kinetic energy density for real orbitals. Moreover, Eq. (1) can be correct to fourth order in ∇ for a slowly varying density [10]. However, prior meta-GGAs [2,10,11] have been at least partly empirical, and have not taken full advantage of $\tau_\sigma(\mathbf{r})$. The aim of this work is to construct a reliable nonempirical meta-GGA to complete the third rung of Jacob's ladder.

Our starting point is the Perdew-Kurth-Zupan-Blaha (PKZB) meta-GGA [10], which by design yields the correct exchange and correlation energies through second order in ∇ for a slowly varying density, and the correct correlation energy for any one-electron density. PKZB has one empirical parameter (fitted to atomization energies) in its exchange part, and has demonstrated unexpected successes and failures including (i) an accurate strong-interaction limit for the correlation energy of a spin-unpolarized nonuniform density [12], (ii) accurate surface [2,10] and atomization [2,10,13] energies, (iii) poor equilibrium bond lengths [13], and (iv) poor description of hydrogen-bonded complexes [14]. While PKZB correlation requires only minor technical improvements, PKZB exchange (the root of the bond-length errors) needs to take into account both paradigm densities. Since it is impossible within the meta-GGA form to

achieve the exact exchange energy for an arbitrary one- or two-electron density (i.e., the fully nonlocal self-interaction correction to the Hartree energy), we shall instead require that the meta-GGA exchange potential be finite at the nucleus for ground-state one- and two-electron densities, an exact constraint satisfied by LSD but lost in GGA [6]. This is the key idea of our construction. Because the PKZB meta-GGA is explained in detail in Ref. [10], we focus here on the added features of our proposed meta-GGA functional which will be referred to as "TPSS" (from the authors' initials).

We begin with the exchange energy. Because of the exact spin-scaling relation [10] $E_x[n_\uparrow, n_\downarrow] = E_x[2n_\uparrow]/2 + E_x[2n_\downarrow]/2$, where $E_x[n] \equiv E_x[n/2, n/2]$, we need consider only the spin-unpolarized case. Using the uniform density scaling constraint [Eq. (6) of Ref. [10]], the meta-GGA (MGGA) can be written as

$$E_x^{\text{MGGA}}[n] = \int d^3r \, n \epsilon_x^{\text{unif}}(n) F_x(p, z), \qquad (3)$$

where $\epsilon_x^{\text{unif}}(n) = -\frac{3}{4\pi}(3\pi^2 n)^{1/3}$ is the exchange energy per particle of a uniform electron gas. The enhancement factor F_x (which equals 1 in LSD) is a function of two dimensionless inhomogeneity parameters

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

and $z = \tau^W/\tau \le 1$, where $\tau = \sum_\sigma \tau_\sigma$ and $\tau^W = \frac{1}{8}|\nabla n|^2/n$. To ensure the Lieb-Oxford bound [Eq. (7) of Ref. [10]], we choose

$$F_x = 1 + \kappa - \kappa/(1 + x/\kappa), \qquad (5)$$

where $\kappa = 0.804$ and $x(p, z) \ge 0$ will be defined later. (A tighter bound [15] would make $\kappa = 0.758$.)

For a density that varies slowly over space, F_x should recover the fourth-order gradient expansion of Svendsen and von Barth [16],

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

where $q = \nabla^2 n/[4(3\pi^2)^{2/3} n^{5/3}]$ is the reduced Laplacian. In PKZB, the gradient coefficient D is an empirical parameter equal to 0.113, but in TPSS we set $D = 0$, the best numerical estimate for this coefficient [16]. The second-order gradient expansion for τ [Eq. (4) of Ref. [10]] makes it possible to recover Eq. (6) from a Taylor expansion of $F_x(p, z)$. Note, in particular, that

$$\tilde{q}_b = (9/20)(\alpha - 1)/[1 + b\alpha(\alpha - 1)]^{1/2} + 2p/3, \quad (7)$$

an inhomogeneity parameter constructed from p and z, tends to the reduced Laplacian q in the slowly varying limit. In Eq. (7),

$$\alpha = (\tau - \tau^W)/\tau^{\text{unif}} = (5p/3)(z^{-1} - 1) \ge 0, \qquad (8)$$

where $\tau^{\text{unif}} = \frac{3}{10}(3\pi^2)^{2/3} n^{5/3}$ is the uniform-gas kinetic

energy density. When the parameter b in Eq. (7) is set to zero, $\tilde{q}_b$ reduces to the dimensionless variable $\tilde{q}$ defined in Eq. (12) of Ref. [10]; b will be defined later.

For a two-electron ground-state density, $z = 1$ ($\alpha = 0$) and the meta-GGA reduces to GGA form with an enhancement factor $\tilde{F}_x(s) = F_x(p = s^2, z = 1)$. The corresponding exchange potential $\tilde{v}_x(\mathbf{r}) = \delta \tilde{E}_x/\delta n(\mathbf{r})$ has a $\nabla^2 n$ term which diverges at a nucleus unless its coefficient, proportional to $d\tilde{F}_x/ds$ [Eq. (24) of Ref. [6]], vanishes there. Since, for a two-electron exponential density, s at a nucleus is 0.376, we eliminate this spurious divergence (see Fig. 1 of Ref. [17]) by requiring that

$$d\tilde{F}_x/ds|_{s=0.376} = 0. \qquad (9)$$

All of the above exact constraints imposed on the TPSS meta-GGA, beyond those imposed on the PBE GGA [7,8], concern small dimensionless density derivatives. We have no reason to modify the large-p behavior of the PBE enhancement factor $F_x \sim 1 + \kappa - \kappa^2/(\mu p)$ ($p \to \infty$), where $\mu = 0.21951$. Thus we retain this large-p limit, which can describe weak binding [18].

To satisfy all of the above conditions, we choose x of Eq. (5) to be

$$x = \left\{ \left[\frac{10}{81} + c\frac{z^2}{(1 + z^2)^2} \right] p + \frac{146}{2025}\tilde{q}_b^2 \right.$$
$$- \frac{73}{405}\tilde{q}_b\sqrt{\frac{1}{2}\left(\frac{3}{5}z\right)^2 + \frac{1}{2}p^2} + \frac{1}{\kappa}\left(\frac{10}{81}\right)^2 p^2$$
$$\left. + 2\sqrt{e}\frac{10}{81}\left(\frac{3}{5}z\right)^2 + e\mu p^3 \right\}/(1 + \sqrt{e}p)^2, \qquad (10)$$

where the constants $c = 1.59096$ and $e = 1.537$ are chosen to enforce Eq. (9) and to yield the correct exchange energy (-0.3125 hartree) for the exact ground-state density of the hydrogen atom. The form of Eq. (10), which is not uniquely constrained, is chosen to make F_x smooth and monotonic as a function of s for $0 \le \alpha \le 1$. Finally, the parameter $b = 0.40$ in Eq. (7) is chosen to have the smallest value that preserves F_x as a monotonically increasing function of s even for fixed $\alpha \gg 1$; this is done for esthetic reasons, since $b = 0$ produces nearly the same results in our molecular tests.

Figure 1 shows that TPSS has a strong but local exchange enhancement at small s for $\alpha = 0$. In contrast, PKZB has $F_x \approx 1$ in the small-s region (see the $r_s = 0$ curves for $\alpha = 0$ and 1 in Figs. 1 and 2 of Ref. [2]), while the PBE GGA F_x is altogether independent of α.

We turn now to correlation, making minor refinements (independent of TPSS exchange) to PKZB [10]:

$$E_c^{\text{MGGA}}[n_\uparrow, n_\downarrow] = \int d^3r \, n \epsilon_c^{\text{revPKZB}}$$
$$\times [1 + d\epsilon_c^{\text{revPKZB}}(\tau^W/\tau)^3], \qquad (11)$$
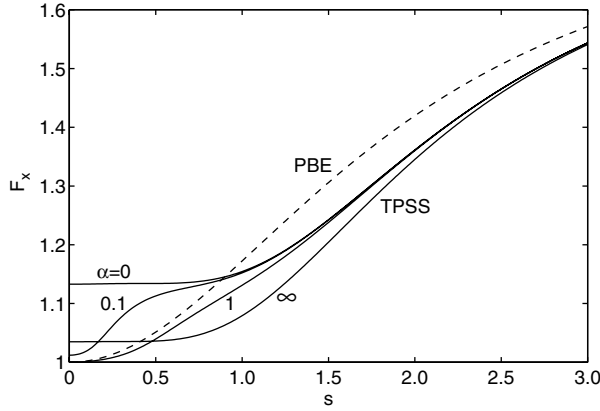
FIG. 1. TPSS and PBE exchange enhancement factors as functions of the reduced gradient s of Eq. (4). The TPSS plots (solid lines) are drawn for four different values of α of Eq. (8). Ground-state two-electron densities have $\alpha = 0$; slowly varying densities have $\alpha \approx 1$ and $s \ll 1$.

$$\epsilon_c^{\text{revPKZB}} = \epsilon_c^{\text{PBE}}(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow)[1 + C(\zeta, \xi)(\tau^W/\tau)^2]$$
$$- [1 + C(\zeta, \xi)](\tau^W/\tau)^2 \sum_\sigma \frac{n_\sigma}{n} \tilde{\epsilon}_c. \quad (12)$$

The basic ingredient here is $\epsilon_c^{\text{PBE}}(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow)$ [8] which already has the correct second-order gradient expansion, scales properly under uniform density scaling to the high- and low-density (weak- and strong-interaction) limits, is nonpositive, and vanishes as $p \rightarrow \infty$. The quantity $\tilde{\epsilon}_c$ could be $\epsilon_c^{\text{PBE}}(n_\sigma, 0, \nabla n_\sigma, 0)$ as in PKZB, but to ensure the exact constraint $E_c \leq 0$ for all possible densities we take $\tilde{\epsilon}_c = \max[\epsilon_c^{\text{PBE}}(n_\sigma, 0, \nabla n_\sigma, 0), \epsilon_c^{\text{PBE}}(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow)]$. The switch is almost seamless in the rare cases where it occurs such as the Li atom (see Fig. 2 of Ref. [17]), and would probably not occur at all for a perfectly designed GGA. Note also that $\tau^W = |\nabla n|^2/8n$ was spin resolved in PKZB.

For any $C(\zeta, \xi)$, E_c^{MGGA} of Eq. (11) properly vanishes for a one-electron density [for which $\tau = \tau^W$ and $\zeta \equiv (n_\uparrow - n_\downarrow)/n = \pm 1$]. Since a self-interaction correction should not change the energy of delocalized electrons, we set $C(0, 0) = 0.53$ (as in PKZB) and $d = 2.8$ hartree^{-1}. This choice leaves the surface correlation energy of jellium unchanged from its PBE GGA values over the range of valence-electron bulk densities.

By properly eliminating the self-correlation error for spin-unpolarized ($\zeta = 0$) densities, the PKZB and TPSS approximations yield correct correlation energies for atomic densities (with $\zeta = 0$) even in the strong-interaction limit [12], where LSD and GGA fail badly. In this limit, electrons are kept apart by Coulomb repulsion, so they ''forget'' that they are fermions and the exchange-correlation energy E_{xc} for a given density $n(\mathbf{r})$ becomes independent of the relative spin polarization ζ (as it almost does in LSD and PBE GGA). To achieve this independence over the range $0 \leq |\zeta| \leq 0.7$ for Gaussian

one-electron and other densities of uniform ζ requires

$$C(\zeta, 0) = 0.53 + 0.87\zeta^2 + 0.50\zeta^4 + 2.26\zeta^6. \quad (13)$$

In a monovalent atom such as Li, a self-interaction correction should zero out the correlation energy density in the valence region without creating any additional correlation energy density in the core-valence overlap region (a PKZB error, see Fig. 2 of Ref. [17]). We achieve this with

$$C(\zeta, \xi) = \frac{C(\zeta, 0)}{\{1 + \xi^2[(1 + \zeta)^{-4/3} + (1 - \zeta)^{-4/3}]/2\}^4}, \quad (14)$$

where $\xi = |\nabla \zeta|/2(3\pi^2 n)^{1/3}$ is large in the overlap region. (ξ also appears in Ref. [19]). For a spin-unpolarized density, setting $d = 0$ in Eq. (11) recovers PKZB.

Finally, we have made extensive numerical tests of the TPSS meta-GGA for atoms, molecules, solids, and jellium surfaces. Total energies of atoms are exceptionally accurate, but we focus in Table I on energy differences and related properties of greater chemical and physical interest. In Table I, we also report LSD, PBE GGA, PKZB meta-GGA, and PBE0 hybrid [20] results for comparison. Details of our study, and comparisons with other functionals, will be presented in later publications [17].

Except for the jellium surface [2], all our calculations are performed self-consistently (although post-PBE results would be similar) by the method for τ-dependent functionals described in Ref. [21] using a developmental version of the Gaussian program [22]. Alternatively, a meta-GGA Kohn-Sham potential could be found by the optimized effective potential method [23]. All molecular calculations use the large 6-311+ +G(3df, 3pd) Gaussian basis set. Performance of the functionals for molecular binding properties is assessed by computing atomization energies for the 148 molecules (built up from atoms with $Z \leq 17$) of the G2 test set [24]. For organic molecules larger than those in this set, TPSS is much more accurate [17,25] than PKZB. We also studied the ten hydrogen-bonded complexes of Ref. [14], reporting the errors with respect to Møller-Plesset (MP2) predictions (which agree with experimental values where available), and 18 solids (Li, Na, K, Al, C, Si, SiC, Ge, GaAs, NaCl, NaF, LiCl, LiF, MgO, Cu, Rh, Pd, Ag in their normal crystal structures) calculated with various basis sets.

Table I shows that the TPSS meta-GGA gives generally excellent results for a wide range of systems and properties, correcting overestimated PKZB bond lengths in molecules, hydrogen-bonded complexes, and ionic solids. We attribute this good performance to the satisfaction of additional exact constraints on $E_{\text{xc}}[n_\uparrow, n_\downarrow]$, especially the key constraint of Eq. (9). Note also that PBE0 [20] results are comparable to TPSS, but TPSS has a practical advantage, since hybrid functionals are not easily evaluated for solids. More generally, exact exchange is inaccessible or too slow in many codes.

TABLE I. Statistical summary of the errors of five density functionals for various properties of molecules, solids, and surfaces. 1 kcal/mol $= 0.0434$ eV $= 0.001\,59$ hartree. For jellium, $r_s = (3/4\pi n)^{1/3}$ characterizes bulk density.

Property (units)	Test set	Mean value of property	Mean absolute errors					Mean error of TPSS
			LSD	PBE	PBE0	PKZB	TPSS	
Atomization energy ΣD_0 (kcal/mol)	G2 (148 mols.)	478	83.8	17.1	5.1	4.4	6.2	5.4
Ionization potential (eV)	G2 (86 species)	10.9	0.22	0.22	0.20	0.29	0.23	-0.11
Electron affinity (eV)	G2 (58 species)	1.4	0.26	0.12	0.17	0.14	0.14	-0.01
Bond length r_e (Å)	96 molecules	1.56	0.013	0.016	0.010	0.027	0.014	0.014
Harmonic frequency ω_e (cm^{-1})	82 diatomics	1430	48.9	42.0	43.6	51.7	30.4	-18.7
H-bond dissoc. energy D_0 (kcal/mol)	10 complexes	13.4	5.8	1.0	0.7	2.9	0.6	0.2
H-bond lengths r_e (Å)	11 H-bonds	2.06	0.147	0.043	0.032	0.179	0.021	0.021
H-bond angles (deg)	13 angles	111	4.0	2.6	1.8	3.5	2.0	2.0
Lattice constant (Å)	18 solids	4.47	0.069	0.057	. . .	0.078	0.040	0.039
Bulk modulus (GPa)	18 solids	116	15.1	7.6	. . .	7.8	8.2	-0.5
XC surface energy (erg/cm^2)	$r_s = 2, 4, 6$	1245	22	55	39	5	13	-10

The atomization energy of a molecule can be regarded as the extra surface energy of the separated atoms. Meta-GGAs are sophisticated enough to reduce the too-large LSD atomization energies and increase the too-small LSD jellium surface energies, while GGAs reduce both.

While LSD and PBE GGA are controlled extrapolations from the slowly varying limit, TPSS meta-GGA is more like a controlled interpolation between slowly varying and one- or two-electron limits. Our functionals are nested like Chinese boxes: LSD is inside PBE GGA, and PBE GGA is inside TPSS meta-GGA. In a future work, we will carry TPSS forward into the fourth rung of Jacob's ladder, where an exact-exchange ingredient is employed in a global hybrid [9] like PBE0, a local hybrid [26], or a hyper-GGA [4]. A hyper-GGA is exact for any one-electron density, and for any density scaled uniformly to the high-density limit.

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