Workhorse Semilocal Density Functional for Condensed Matter Physics and Quantum Chemistry

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Semilocal density functionals for the exchange-correlation energy are needed for large electronic systems. The Tao-Perdew-Staroverov-Scuseria (TPSS) meta-generalized gradient approximation (meta-GGA) is semilocal and usefully accurate, but predicts too-long lattice constants. Recent "GGA's for solids" yield good lattice constants but poor atomization energies of molecules. We show that the construction principle for one of them (restoring the density gradient expansion for exchange over a wide range of densities) can be used to construct a "revised TPSS" meta-GGA with accurate lattice constants, surface energies, and atomization energies for ordinary matter.

Kohn-Sham theory [1] is the method of choice to describe large many-electron systems in condensed matter physics (since the 1970s) and quantum chemistry (since the 1990s). In principle, this theory delivers the exact ground-state spin densities $n_\uparrow(\mathbf{r})$, $n_\downarrow(\mathbf{r})$, and energy E for N electrons in external potential $v(\mathbf{r})$, via solution of N self-consistent one-electron Schrödinger equations. In practice, simple and reasonably accurate approximations to the density functional for the exchange-correlation energy are needed. Semilocal approximations (e.g., Refs. [2–4])

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

require only a single integral over real space and so are practical even for large molecules or unit cells. In Eq. (1), $n = n_\uparrow + n_\downarrow$ is the electron density and $\tau_\sigma = \sum_i |\nabla \psi_{i\sigma}|^2/2$ is the positive kinetic energy density; all equations are in atomic units. Semilocal approximations often work because of proper accuracy for a slowly varying density, or because of justified error cancellation between exchange and correlation [5] (requiring a short-ranged xc hole). They can be reasonably accurate for the near-equilibrium and compressed ground-state properties of "ordinary" matter, where neither strong correlation nor long-range van der Waals interaction are important. They can also serve as a base for the computationally more-expensive fully nonlocal approximations needed to describe strongly correlated systems [5] and soft matter [6].

Semilocal functionals should be exact for the uniform electron gas, and should satisfy the spin- and coordinate-scaling properties of the exchange term E_x. The earliest one, the local spin density approximation (LSDA) [1,2], uses only the ingredients $n_\uparrow$, $n_\downarrow$ and predicts reasonable but too-short lattice constants for solids, good surface energies for simple metals (but with substantial error cancellation between exchange and correlation), and molecular atomization energies that are unacceptably high. The nonempirical Perdew-Burke-Ernzerhof (PBE) generalized gradient

approximation (GGA) [3] adds the ingredients $\nabla n_\uparrow$, $\nabla n_\downarrow$, and uses them to recover the gradient expansion for the correlation energy E_c of a slowly varying density, to make the correlation energy scale properly to a constant in the high-density limit, and to satisfy other constraints. The PBE GGA predicts reasonable but too-long lattice constants, surface energies that are better than LSDA for exchange alone and correlation alone but worse for their sum, and improved atomization energies. The nonempirical Tao-Perdew-Staroverov-Scuseria (TPSS) meta-GGA [4] adds the ingredients $\tau_\uparrow$, $\tau_\downarrow$, and uses them to recover the fourth-order gradient expansion for exchange in the slowly varying limit, to make the functional exact for the energy (but not for the potential) of all one-electron ions, to make the exchange potential finite at the nucleus, etc., TPSS predicts lattice constants that are only a little shorter than those of the PBE GGA, good surface energies, and very good atomization energies [4,7]. The bond lengths of stiff molecules are accurate [7] in TPSS. A meta-GGA fitted to molecular data is M06-L [8].

Meta-GGA is not computationally much more expensive than LSDA or GGA, once a self-consistent program (e.g., Refs. [7,9]) has been written. For molecules containing transition-metal atoms, TPSS is only 30% slower [9] than the PBE GGA. By respecting the paradigms of both condensed matter physics and quantum chemistry, the TPSS meta-GGA was intended to be a workhorse semilocal functional for both, and, in particular, for molecules bonded to or reacting on solid surfaces. Perhaps due to its lattice-constant errors, TPSS has not been so widely adopted. Because of the sensitivity of many solid state properties (magnetism, ferroelectricity [10], bulk modulus, etc.) to lattice constant, recent years have seen instead the emergence of "GGA's for solids" [e.g., the Armiento-Mattsson 2005 (AM05) GGA [11] and the modified PBE GGA for solids, PBEsol [12]] which typically predict good lattice constants and surface energies, but rather poor atomization energies.

The construction principle for the PBEsol GGA for solids [12] was to restore the second-order gradient expansion for exchange over a wide range of densities. Here we will show that this principle can be imposed to make a revised TPSS (revTPSS) meta-GGA that preserves all the correct constraints of TPSS, keeps its good surface and atomization energies, but yields lattice constants as good as those of the GGA's for solids. We hope that revTPSS can become the workhorse functional that TPSS was intended to be.

We begin with the semilocal exchange energy of a spin-unpolarized density [4]:

$$E_x^{\text{sl}}[n] = \int d^3 r n \epsilon_x^{\text{unif}}(n) F_x(p, z). \tag{2}$$

Here $\epsilon_x^{\text{unif}}(n) = -3(3\pi^2 n)^{1/3}/4\pi$ is the exchange energy per electron of a uniform gas of density n, $p = s^2$ is the square of the reduced density gradient $s = |\nabla n|/[2(3\pi^2 n)^{1/3} n]$, and $z = \tau^W/\tau$ where $\tau^W = |\nabla n|^2/8n$ is the von Weizsäcker kinetic energy density and $\tau = \tau_\uparrow + \tau_\downarrow$. The exchange enhancement factor F_x is 1 in LSDA, and otherwise $1 + \kappa - \kappa/(1 + x/\kappa)$, where $\kappa = 0.804$. For a slowly varying density, x is small and of order ∇^2, making $F_x \approx 1 + x$. In GGA, $x = \mu p$, where $\mu = 0.21951$ in the PBE GGA and $10/81 = 0.12346$ in the PBEsol GGA. In meta-GGA, x depends upon z as well as p, and only its slowly varying asymptote is $(10/81)p$, but the large-p asymptote of F_x, $1 + \kappa - \kappa^2/\mu p$, is independent of z. As in Ref. [4], we introduce $\alpha = (\tau - \tau^W)/\tau^{\text{unif}} = (5p/3)(z^{-1} - 1)$, where $\tau^{\text{unif}} = n(3/10)(3\pi^2 n)^{2/3}$ is the orbital kinetic energy density of the uniform gas. Any one- or two-electron density has $z = 1$ or $\alpha = 0$, while a slowly varying density has small $z \approx 5p/3$ and $\alpha \approx 1$.

In the TPSS meta-GGA, x of the previous paragraph is given by Eq. (10) of Ref. [4]. For $\alpha \approx 1$ we can make the meta-GGA F_x more like that of the PBEsol GGA through two changes: (1) Change a term in x from $cz^2 p/(1 + z^2)^2$ to $cz^3 p/(1 + z^2)^2$, which shifts this term (whose coefficient c is much larger than a typical gradient coefficient) from 6th to 8th order in the gradient expansion. All TPSS exchange constraints remain satisfied, without any change in the coefficients c, e, and μ. F_x is unchanged for $\alpha = 0$, and at large s for all α, but is reduced at smaller s for $\alpha = 1$. The energy is raised more for a molecule (which has more regions of small s) than for the component atoms. (2) Now change μ from its TPSS (and PBE) value 0.21951 toward its PBEsol value $10/81$, letting c and e adjust accordingly to satisfy all TPSS constraints. Figure 1 shows a good emulation of the PBEsol GGA by $\mu = 0.14$, $c = 2.35204$, and $e = 2.1677$, over the range of physical importance $0 < s < 3$, and especially for $s < 1$ where the second-order gradient expansion for exchange is valid [12,13]. Reducing μ reduces F_x at large s, raising the energy more for the component atoms (which have more regions of large s) than for the molecule. The net effect of these two changes is to decrease atomization energies slightly, on average, and to increase surface energies.
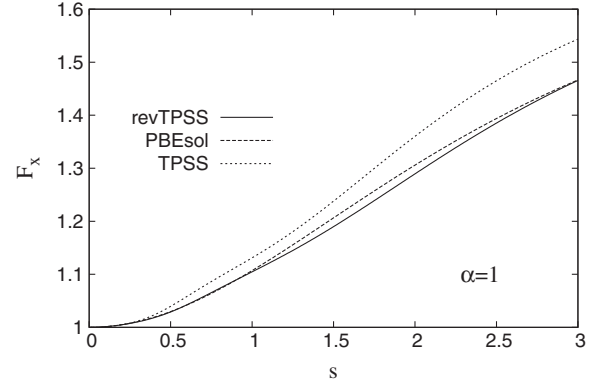

FIG. 1. Exchange enhancement factor vs reduced density gradient for the PBEsol GGA and for two meta-GGAs at $\alpha = 1$. The slowly varying limit is $\alpha \approx 1$ and $s \approx 0$. By construction, revTPSS is closer to the PBEsol GGA than TPSS is.

While the exact exchange energy is unique, the exact exchange energy density is not. The conventional choice based on the Fock integral of the Kohn-Sham orbitals is just the $\lambda = 1$ member of a one-parameter ($0.5 \leq \lambda \leq 1$) family of exact exchange energy densities, based upon a simple coordinate transformation [14], which all agree for uniform densities but not for nonuniform ones. All have the same system-averaged exchange hole [15]. Figure 2 for the hydrogen atom shows that the choice $\lambda = 0.893$ closely matches the revTPSS energy density of Eq. (2). Thus revTPSS has two reference systems in which it reproduces an exact exchange-correlation energy density: the uniform gas (a paradigm for condensed matter) and the one-electron atom or ion (a paradigm for quantum chemistry). (The same statement is true of TPSS [16].) Kohn and Mattsson [17] proposed supplementing the uniform gas reference system by one in which the density decays evanescently, but their second reference system was the Airy gas and not the hydrogen atom. AM05 [11] exchange was constructed in part by fitting the conventional exchange energy density of the Airy gas [18]. Knowing the exact exchange energy density in the revTPSS or TPSS
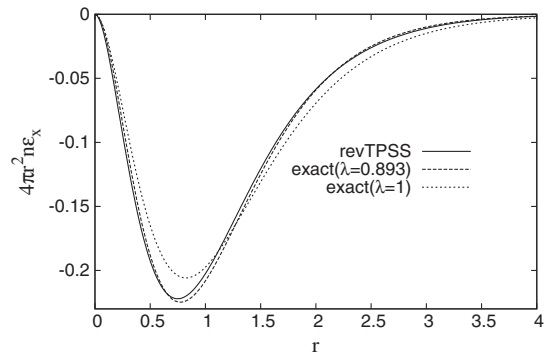

FIG. 2. Radial exchange energy density for the hydrogen atom. The revTPSS curve is from a spin-scaled Eq. (2). Two λ-dependent exact exchange energy densities are also shown; the conventional one is $\lambda = 1$.

gauge may be useful for the construction of hyper-GGA's [5,16].

Having improved TPSS exchange, we now refine TPSS correlation. The PBE GGA and TPSS [through its ingredient $\epsilon_c^{\mathrm{PBE}}(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow)$] use a correlation gradient coefficient $\beta = 0.066\,725$ derived in the high-density limit by Ma and Brueckner [19]. Langreth and Vosko [20] have derived a more correct value about 17% bigger, but the difference comes from a long-range contribution to the gradient expansion of the correlation hole that would be cut off by our underlying real-space cutoff construction [21] of the PBE GGA. We do not in any case need to restore the correct gradient coefficient for correlation, since for real densities the second-order gradient expansion for the correlation energy is never even close to being valid [12,13]. However, Hu and Langreth [22] have derived the density dependence of the Ma-Brueckner β beyond the random phase approximation, which *is* relevant to our cutoff construction and which we have fitted roughly (Fig. 3) by

$$\beta(r_s) = 0.066725(1 + 0.1r_s)/(1 + 0.1778r_s), \quad (3)$$

where $n = 3/(4\pi r_s^3)$. Equation (3) is designed so that, for $r_s \to \infty$, the second-order gradient terms for exchange and correlation cancel by innocuous assumption. The reduction of β with r_s increases atomization energies slightly, on average, and decreases surface energies. Aside from our use of Eq. (3), we keep the form of TPSS correlation unchanged, satisfying the TPSS constraints with

$$C(\zeta, 0) = 0.59 + 0.9269\zeta^2 + 0.6225\zeta^4 + 2.1540\zeta^6, \quad (4)$$

which replaces Eq. (13) of Ref. [4].

We turn now to the results, which are summarized briefly in Table I (in terms of the mean error or ME and the mean absolute error or MAE, or their relative analogs MRE and MARE) and in full detail (along with figures for revTPSS F_x and F_{xc}) in Ref. [23]. Table I shows the error statistics of several density functionals for the lattice constants of 21 solids, in comparison with experimental values corrected to a static lattice, calculated as in Ref. [24] using
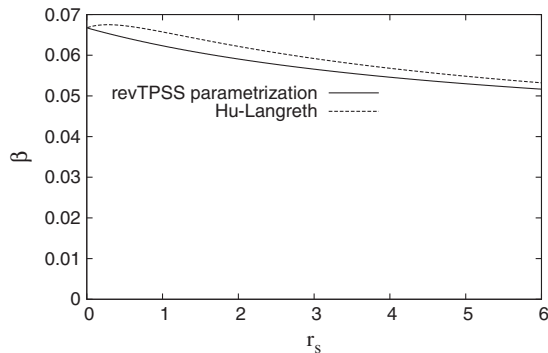

FIG. 3. Finite-range contribution to the gradient coefficient for correlation, as a function of density parameter r_s, from Ref. [22] and from Eq. (3).

the BAND [25] code. The 21 solids include 11 metals (Li, Na, Ca, Sr, Ba, Al, Pb, Cu, Rh, Pd, Ag) and 10 nonmetals (C diamond, Si, SiC, Ge, GaAs, NaCl, NaF, LiCl, LiF, MgO). Our test set is the same as that of Ref. [24], except that we have here omitted the three softest solids (K, Rb, Cs), for which the revTPSS lattice constants are about 0.10–0.15 Å too long. K, Rb, and Cs have bulk moduli (4 to 2 GPa [24]) close to those of the rare-gas solids Xe, Kr, and Ar [26] (and less than 1% of that of diamond), and so could be classified as "soft matter" where the long-range van der Waals interaction between large ion cores can significantly shrink the lattice constant; we plan to investigate this in future work. Table I shows that revTPSS performs about as well (and actually better) than the "GGA's for solids," the PBEsol GGA and the AM05 GGA. Larger data sets [27] show error statistics similar to ours for the functionals that preceded revTPSS. After the lattice constants, Table I reports some cohesive energy results for solids.

Table I also shows the error statistics for the exchange- and exchange-correlation surface energies for jellium, computed as in Ref. [12], in comparison to the exact exchange and nearly exact revTPSS exchange-correlation values for bulk densities with $r_s = 2$, 3, 4, and 6. Again, revTPSS performs well. Its very accurate surface exchange energies reflect [12,13] its correct recovery of the gradient expansion for exchange.

In Table I, we present the error statistics for the six atomization energies (SiH$_4$, SiO, S$_2$, C$_3$H$_4$, C$_2$H$_2$O$_2$, C$_4$H$_4$) of the small representative AE6 [28] set and the 223 enthalpies of formation of the G3 [29] set, computed self-consistently using a modified Gaussian code [30]. Note that, by construction, the error of the enthalpy of formation is nearly equal and opposite to that of the atomization energy. The revTPSS values are good, and even a little better on average than the TPSS values. For the 47 G3 pure hydrocarbons, the MAE drops from 5.9 (TPSS) to 3.1 (revTPSS) kcal/mol.

Finally, as a check on hydrogen bonds, we have applied revTPSS to the W6 set [31] of dissociation energies of six small water clusters (four dimers, two trimers). The revTPSS error statistics (ME $= -1.0$ kcal/mol, MAE $= 1.0$ kcal/mol) are only slightly worse than those of TPSS (ME $= -0.9$ kcal/mol, MAE $= 0.9$ kcal/mol), but not as good as those of the PBE GGA (ME $= -0.0$ kcal/mol, MAE $= 0.3$ kcal/mol). In the original TPSS, μ was set to the PBE value 0.219 51 out of concern for the hydrogen bonds. Note that the inclusion of long-range van der Waals interaction could at least reduce the revTPSS error statistics for the W6 set.

Stereoelectronic effects on the energies of hydrocarbons are actually better described [32] by the PBEsol GGA than by the PBE GGA or TPSS. We plan to test revTPSS for these problems.

In summary, we have shown that the PBEsol idea [12], restoring the second-order gradient expansion for ex-

TABLE I. Error statistics for various density functionals. (0.5292 Å = 1 bohr; 1 kcal/mol = 0.0434 eV = 0.001 59 hartree.) The exact jellium surface exchange-correlation energy is still imprecisely known. We have taken it to be the revTPSS value, although it could instead be the TPSS value as in Ref. [12]. The non-revTPSS lattice constants are from Ref. [24]. Most non-revTPSS surface energies and atomization energies are from Ref. [12]. The non-revTPSS enthalpies of formation are from Ref. [7].

	LSDA	PBE GGA	TPSS	AM05 GGA	PBEsol GGA	revTPSS
			Lattice constants (Å) of 21 solids			
ME	−0.079	0.054	0.033	0.014	−0.010	0.011
MAE	0.079	0.065	0.047	0.039	0.038	0.036
			Cohesive energies of 9 nontransition metals and 6 insulators (eV/atom)			
ME	0.32	−0.10	⋯	⋯	0.11	0.03
MAE	0.32	0.11	⋯	⋯	0.14	0.09
			Jellium surface exchange energies (%) for r_s = 2, 3, 4, 6			
MRE	45.8	−20.9	−11.9	28.8	2.9	−1.0
MARE	45.8	20.9	11.9	28.8	2.9	2.2
			Jellium surface exchange-correlation energies (%) for r_s = 2, 3, 4, 6			
MRE	−2.9	−5.6	−0.8	0.6	−0.4	0.0
MARE	2.9	5.6	0.9	0.9	1.2	0.0
			Atomization energies (kcal/mol) of the 6 AE6 molecules $(6 − 311 + G(3df, 2p))$			
ME	77.4	12.4	4.1	38.7	35.9	3.3
MAE	77.4	15.5	5.9	38.7	35.9	5.9
			Enthalpies of formation (kcal/mol) of the 223 G3 molecules $(6 − 311 + G(3df, 2p))$			
ME	−121.9	−21.7	−5.1	⋯	⋯	−3.6
MAE	121.9	22.2	5.7	⋯	⋯	4.8

change over a wide range of densities, can be applied to the TPSS meta-GGA [4], leading to a revised version (revTPSS) with good lattice constants, surface energies, and atomization energies. revTPSS could well become a workhorse semilocal density functional for the ordinary matter of condensed matter physics and quantum chemistry, as well as a base for the construction of fully nonlocal approximate functionals.

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