Strongly Constrained and Appropriately Normed Semilocal Density Functional

Jianwei Sun,[1,*] Adrienn Ruzsinszky,[1] and John P. Perdew[1,2]
[1]Department of Physics, Temple University, Philadelphia, Pennsylvania 19122, USA
[2]Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122, USA

(Received 12 April 2015; published 14 July 2015)

The ground-state energy, electron density, and related properties of ordinary matter can be computed efficiently when the exchange-correlation energy as a functional of the density is approximated semilocally. We propose the first meta-generalized-gradient approximation (meta-GGA) that is fully constrained, obeying all 17 known exact constraints that a meta-GGA can. It is also exact or nearly exact for a set of "appropriate norms," including rare-gas atoms and nonbonded interactions. This strongly constrained and appropriately normed meta-GGA achieves remarkable accuracy for systems where the exact exchange-correlation hole is localized near its electron, and especially for lattice constants and weak interactions.

DOI: 10.1103/PhysRevLett.115.036402 PACS numbers: 71.15.Mb, 05.30.Fk, 31.15.ej

Over the past 50 years, Kohn-Sham density functional theory [1–3] has become an *ab initio* pillar of condensed matter physics and related sciences. In this theory, the ground-state electron density $n(\vec{r})$ and total energy E for nonrelativistic interacting electrons in a multiplicative external potential can be found exactly by solving self-consistent one-electron equations, given the uncomputable exact universal exchange-correlation energy $E_{xc}[n]$ as a functional of $n = \sum_{i,\sigma}^{occ} |\psi_{i,\sigma}|^2$, with $\psi_{i,\sigma}$ a Kohn-Sham orbital. This xc energy term can be formally expressed as half the Coulomb interaction between every electron and its exchange-correlation hole in a double integral over space [4,5], but in practice its density functional must be approximated. Semilocal functionals approximate it with a single integral and thus are properly size extensive and computationally efficient, especially for large unit cells, high-throughput materials searches, and *ab initio* molecular dynamics simulations.

Many features of the exact functional $E_{xc}[n]$ are known. Nonempirical functionals, constructed to satisfy exact constraints on this density functional [6–9], are reliable over a wide range of systems (e.g., atoms, molecules, solids, and surfaces), including many that are unlike those for which these functionals have been tested and validated. In this Letter, we present a nonempirical semilocal functional that satisfies all known possible exact constraints for the first time, and is appropriately normed on systems for which semilocal functionals can be exact or extremely accurate.

Semilocal approximations can be written as

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

Here $n_\uparrow(\vec{r})$ and $n_\downarrow(\vec{r})$, the electron spin densities, are the only ingredients of the local spin-density approximation (LSDA) [1,10–14]. Spin-density gradients are added in a generalized gradient approximation (GGA) [6,14–19], and the positive orbital kinetic energy densities $\tau_\sigma = \sum_i^{occ}(1/2)|\nabla\psi_{i,\sigma}|^2$ [implicit nonlocal functionals of $n(\vec{r})$] are further added in a meta-GGA [7–9,20,21]. The broad usefulness of nonempirical semilocal functionals is evidenced by the fact that the Perdew-Burke-Ernzerhof (PBE) GGA construction Letter [6] is the 16th most cited scholarly article of all time [22].

The LSDA was based on what we call an "appropriate norm": It was by construction exact for the only set of electron densities for which it could be exact, the electron gas of uniform spin densities (or those that vary slowly over space). LSDA was surprisingly useful even for solid surfaces and atoms or molecules. But the second-order gradient expansion [14,23], which improves upon LSDA in the slowly varying limit, was worse than LSDA for real systems, because LSDA satisfies exact constraints that finite-order gradient expansions do not [4–6,24]. Nonempirical GGAs like PBE [6] and nonempirical meta-GGAs like Tao-Perdew-Staroverov-Scuseria (TPSS) [7] and revised TPSS [8] were constructed to achieve higher accuracy by satisfying more exact constraints, and the H atom was added as an appropriate norm for the meta-GGAs. Unlike the GGAs [18], the meta-GGAs need not choose among incompatible constraints.

Despite early successes [25–27], the TPSS and revTPSS meta-GGAs were less accurate than the PBE GGA for the critical pressures of structural phase transitions of solids [28,29]. This was due to a spurious order-of-limits problem [30,31], which could be removed [9] if τ appeared only in the dimensionless variable

$$\alpha = (\tau - \tau^W)/\tau^{\text{unif}} > 0, \quad (2)$$

where $\tau^W = |\nabla n|^2/8n$ is the single-orbital limit of τ and $\tau^{\text{unif}} = (3/10)(3\pi^2)^{2/3}n^{5/3}$ is the uniform-density limit. α recognizes covalent single ($\alpha = 0$), metallic ($\alpha \approx 1$), and weak ($\alpha \gg 1$) bonds [32] [as does the "electron localization function" [33] $1/(1+\alpha^2)$]. We constructed several interpolations of the exchange energy density [9,34,35] between $\alpha = 0$ and 1, with extrapolation to $\alpha \gg 1$. These abandoned some of the exact constraints satisfied by TPSS and revTPSS. For example, they used a GGA correlation, which is not one-electron self-correlation free. (Note that, in the presence of a paramagnetic current density, meta-GGAs require a gauge correction [36].)

Here we aim to improve the nonempirical meta-GGA by satisfying all known possible exact constraints, including some not satisfied by TPSS and revTPSS. We also add some appropriate norms for which semilocal functionals can be extremely accurate although not exact: rare-gas atoms and nonbonded interactions. Both norms contain information about $0 < \alpha < \infty$, but the latter brings more information about $\alpha \gg 1$. The common feature of all appropriate norms, and a necessary condition for semilocal approximations to be accurate, is that the exact exchange-correlation hole for a considered density remains close to its reference electron. This condition is not satisfied when electrons are shared over stretched bonds, as in stretched $H_2{}^+$. Fully nonlocal functionals, including global [37] and local [38] hybrids with exact exchange or self-interaction corrections [11,39], often start from a good semilocal functional, and can better describe such bonds at increased computational cost.

There is an expected error cancellation between semilocal exchange and semilocal correlation, since the exact exchange-correlation hole is deeper and more localized near the electron than is the exact exchange hole. Localization of the exact exchange hole for a density is thus a sufficient but not a necessary condition for localization of the exact exchange-correlation hole. In closed-shell atoms and nonbonded interactions, but not in bonded molecules or jellium surfaces, even the strongly constrained and appropriately normed (SCAN) exchange energy is accurate.

The exchange energy for any pair of spin densities is negative, and can be found from that for a spin-unpolarized total density via the exact spin-scaling relation [40]. Thus, we only need to construct a meta-GGA for the spin-unpolarized case,

$$E_x[n] = \int d^3r n \epsilon_x^{\mathrm{unif}}(n) F_x(s,\alpha), \tag{3}$$

where $\epsilon_x^{\mathrm{unif}}(n) = -(3/4\pi)(3\pi^2 n)^{1/3}$ is the exchange energy per particle of a uniform electron gas, $F_x(s,\alpha)$ is the exchange enhancement factor, and

$$s = |\nabla n|/[2(3\pi^2)^{1/3} n^{4/3}] \tag{4}$$

is the dimensionless density gradient. By using these dimensionless variables, we satisfy the correct uniform coordinate density-scaling behavior [41].

For $\alpha \approx 1$, we construct an approximate PBE-like resummation of the fourth-order gradient expansion (GE4) for exchange [42], valid for slowly varying densities with small s and $\alpha \approx 1$:

$$h_x^1(s,\alpha) = 1 + k_1 - k_1/(1 + x/k_1), \tag{5}$$

with

$$x = \mu_{AK} s^2 [1 + (b_4 s^2/\mu_{AK}) \exp(-|b_4| s^2/\mu_{AK})] + \{b_1 s^2 + b_2(1-\alpha) \exp[-b_3(1-\alpha)^2]\}^2. \tag{6}$$

Here $\mu_{AK} = 10/81$, $b_2 = (5913/405\,000)^{1/2}$, $b_1 = (511/13\,500)/(2b_2)$, $b_3 = 0.5$, and $b_4 = \mu_{AK}^2/k_1 - 1606/18\,225 - b_1^2$. For $\alpha = 0$, we impose the strongly tightened bound $F_x \leq 1.174$ [43], which is satisfied by LSDA ($F_x = 1$) but not by PBE, TPSS, or revTPSS: $F_x(s,\alpha=0) = h_x^0 g_x(s)$, where $h_x^0 = 1.174$ and

$$g_x(s) = 1 - \exp[-a_1 s^{-1/2}]. \tag{7}$$

As in the TPSS and revTPSS meta-GGAs, we fit the exact exchange energy of the hydrogen atom, via $a_1 = 4.9479$. To make the exchange energy per particle scale correctly to a negative constant under nonuniform coordinate scaling to the true two-dimensional limit [44,45] (as it does not in PBE, TPSS, or revTPSS), we make F_x vanish like $s^{-1/2}$ as $s \to \infty$ [43].

Then we interpolate F_x between $\alpha = 0$ and $\alpha \approx 1$, and extrapolate to $\alpha \to \infty$:

$$F_x(s,\alpha) = \{h_x^1(s,\alpha) + f_x(\alpha)[h_x^0 - h_x^1(s,\alpha)]\} g_x(s), \tag{8}$$

$$f_x(\alpha) = \exp[-c_{1x}\alpha/(1-\alpha)]\theta(1-\alpha) - d_x \exp[c_{2x}/(1-\alpha)]\theta(\alpha-1), \tag{9}$$

and $\theta(x)$ is a step function of x. In the spirit of the correction to a different resummed asymptotic series [46], the interpolation or extrapolation gives no correction to our resummed gradient expansion to any power of ∇n in the slowly varying limit. There are three parameters ($c_{1x} = 0.667$, $c_{2x} = 0.8$, $d_x = 1.24$) in the interpolation or extrapolation, and one ($k_1 = 0.065$) in the resummed gradient expansion, determined by the appropriate norms.

Figure 1 shows the SCAN exchange enhancement factor F_x for a spin-unpolarized density as a function of reduced density gradient s for several values of α. Not only does SCAN obey the rigorous bound $F_x \leq 1.174$ for $\alpha = 0$, but it also (and more strongly) obeys the conjectured bound $F_x \leq 1.174$ for *all* α [35,43]. By comparison, the PBE, TPSS, and revTPSS exchange enhancement factors all tend monotonically to the general Lieb-Oxford bound [47] $1.804 = 2.273/2^{1/3}$ as $s \to \infty$ for all α. Thus, SCAN is radically different from those previous semilocal functionals.

By analogy with F_x, we can define an n-dependent $F_{xc} = F_x + F_c$, the enhancement over local exchange due to spin polarization, correlation, and semilocality. The high-density spin-unpolarized limit of F_{xc} is of course F_x of Eq. (3).

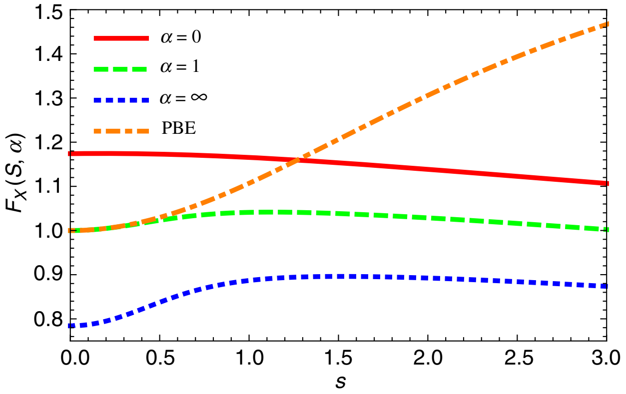

FIG. 1 (color online). The SCAN exchange enhancement factor of Eq. (3) for a spin-unpolarized system, as a function of s (the dimensionless density gradient) for several values of α (the dimensionless deviation from a single orbital shape).

The correlation energy is similarly constructed as an interpolation between $\alpha = 0$ and $\alpha \approx 1$, and an extrapolation to $\alpha \to \infty$. The $\alpha \approx 1$ limit uses a PBE-like expression that recovers the second-order gradient expansion for correlation in the slowly varying limit [14]. The $\alpha = 0$ limit shares the same formula with the $\alpha \approx 1$ limit, with its local part designed just for one- and two-electron systems [48]. The $\alpha = 0$ limit makes the correlation energy vanish for any (fully spin-polarized) one-electron density. In the spin-unpolarized case, it satisfies the two-electron version of the Lieb-Oxford bound [47,48], $F_{xc} \leq 1.67$ and fits the exchange-correlation energy of the He atom. The SCAN correlation energy is by construction nonpositive. It properly scales to a finite negative value per electron under uniform density scaling to the high-density limit [44], and to zero like the exchange energy in the low-density limit. Its correlation energy per electron is properly finite (but improperly zero) under nonuniform density scaling to the true two-dimensional limit [44,45]. The interpolation has three parameters, to be determined by the appropriate norms. All detailed formulas, and a list of all 17 exact constraints plus our appropriate norms, are given in the Supplemental Material [49]. An important practical feature of our exchange-correlation enhancement factor F_{xc} is that, as functions of s, curves for different α do not cross one another strongly (see, e.g., Fig. 1). In our experience, this condition is needed to achieve self-consistent solutions by the approach of Neumann, Nobes, and Handy [56].

By recovering GE4, plus the second-order gradient expansion for correlation, we also recover a nearly exact linear response for a uniform density [57]. Finally, we are able to satisfy the rigorous general Lieb-Oxford bound $F_{xc} \leq 2.215$, as tightened by Chan and Handy [58]. This bound is approached only in the low-density limit, where our F_{xc} properly shows a weak dependence [7,12] on relative spin polarization.

Now there are seven parameters (c_{1x}, c_{2x}, d_x, k_1, c_{1c}, c_{2c}, d_c) which are determined by fitting to (1) the large-Z asymptotic coefficients [17,59] for the exchange energies of neutral rare-gas atoms [15] of atomic number Z,

$$\lim_{Z\to\infty} E_x(Z) = E_x^{\text{LDA}} + \gamma_{x1} Z + \gamma_{x2} Z^{2/3}, \qquad (10)$$

(2) the large-Z asymptotic coefficient of the correlation energy of neutral rare-gas atoms [60],

$$\lim_{Z\to\infty} E_c(Z) = E_c^{\text{LDA}} + \gamma_{c1} Z, \qquad (11)$$

identified as a key exact constraint for functional approximation [60], (3) the binding energy curve of compressed Ar_2 [61] [with a mean absolute error (MAE) less than 1 kcal/mol for $R = 1.6$, 1.8. and 2.0 Å, bond lengths much smaller than the equilibrium bond length 3.76 Å], as a paradigm of nonbonded interaction (with Kr, another rare-gas atom, as the united-atom limit), and (4) the jellium surface exchange-correlation energy [18,62] at bulk density parameters $r_s = 2$, 3, 4, and 6 bohr, within the "range of the possible" set by two recent quantum Monte Carlo calculations [63,64] and a kernel-corrected random phase approximation calculation [64]. Note that the exact exchange and correlation holes in the jellium surface have long-range parts that cancel one another perfectly [65,66]. [In Eqs. (10) and (11), we have found the reference coefficients $\gamma_{x1} = -0.2259$, $\gamma_{x2} = 0.2551$, $\gamma_{c1} = 0.0388$ by extrapolating accurate energies for Ne, Ar, Kr, and Xe.]

Our calculations to construct and test the SCAN meta-GGA are described next: For the rare-gas atoms, we use accurate Hartree-Fock orbitals [67]. For jellium surfaces, LDA orbitals are used. Our other calculations are self-consistent. For the Ar_2 binding energy curve, we use the GAUSSIAN code [68] with triple-, quadruple-, and quintuple-zeta basis sets, extrapolated to the complete basis-set limit. For other molecules, we use the $6\text{-}311++G\ (3df, 3pd)$ basis set. For weak interactions in the S22 set [69], we use the counterpoise correction to reduce the basis-set superposition error. For solids, we use the VASP code [70] with converged plane wave basis sets and k-space meshes.

Table I shows the relative errors of SCAN for E_x, E_c, and E_{xc} for the rare-gas atoms, in comparison to accurate reference values [15,35,71,72]. The errors in E_x are less than 0.5%, but error cancellation with the much smaller E_c leads to errors in E_{xc} less than 0.1%. This confirms that rare-gas atoms are an appropriate norm. The relative errors of E_x for compressed Ar_2 are 0.26%, about the same as for a single Ar atom.

Table II shows the error statistics of SCAN and other semilocal functionals for molecules and solids.

For the G3 set [73] of 223 molecules, including some large organic ones, the error is by construction almost minus the error of the atomization energy. For this set, SCAN is much more accurate than the GGAs PBE and especially PBEsol [18], and about as accurate as the meta-GGAs TPSS [7] and M06 L [20]. However, M06 L has 35

TABLE I. Relative errors (%) of SCAN for the exchange, correlation, and exchange-correlation energies of the rare-gas atoms.

	Ne	Ar	Kr	Xe
E_x	0.46	0.25	0.19	0.07
E_c	−11.80	−4.49	−5.07	−3.36
E_{xc}	0.07	0.14	0.09	0.01

TABLE II. Mean error (ME) and mean absolute error (MAE) of SCAN and other semilocal functionals for the G3 set of molecules [73], the BH76 set of chemical barrier heights [74], the S22 set of weakly bonded complexes [69], and the LC20 set of solid lattice constants [75]. For the G3-1 subset of small molecules, the SCAN MAE is 3.2 kcal/mol. $G3^{HC}$ is a subset of 46 G3 hydrocarbons, to which we have applied empirical corrections for the C atom as described in the text to show how consistently SCAN describes molecules. For all data sets, zero-point vibration effects have been removed from the reference experimental values. The LSDA results for G3 are from Ref. [25]. Becke-Lee-Yang-Parr (BLYP) [15,76], PBEsol [18], and PBE [6] are GGAs; SCAN, TPSS [7], and M06 L [20] are meta GGAs. We could not locate BLYP in VASP, but Ref. [77] suggests that its LC20 MAE may be more than twice that of PBE. (1 kcal/mol = 0.0434 eV.)

	$G\ 3^{HC}$ (kcal/mol)		G3 (kcal/mol)		BH76 (kcal/mol)		S22 (kcal/mol)		LC20(Å)	
	ME	MAE	ME	MAE	ME	MAE	ME	MAE	ME	MAE
LSDA	−5.6	13.0	−83.7	83.7	−15.2	15.4	2.3	2.3	−0.081	0.081
BLYP	1.8	6.2	3.8	9.5	−7.9	7.9	−8.7	8.8		
PBEsol	−4.1	6.5	−58.7	58.8	−11.5	11.5	−1.3	1.8	−0.012	0.036
PBE	−2.1	6.6	−21.7	22.2	−9.1	9.2	−2.8	2.8	0.051	0.059
TPSS	1.9	3.8	−5.2	5.8	−8.6	8.7	−3.7	3.7	0.035	0.043
M06 L	−0.2	4.6	−1.6	5.2	−3.9	4.1	−0.9	0.9	0.015	0.069
SCAN	−0.8	2.7	−4.6	5.7	−7.7	7.7	−0.7	0.9	0.007	0.016

empirical parameters fitted to atomization energies and other chemical data. TPSS has no such empirical parameter, but its complicated form was developed when atomization energies were a gold standard, and may have been indirectly biased by that. (The form of TPSS was complicated by its use of a second dimensionless ingredient built from τ [9,31,32], $z = \tau^W/\tau > 0$.)

There is little statistical correlation [78] between the error that a functional makes for atomization energies and its error for reaction energies. (1) Most atoms that bind into molecules or solids are open shell and at least partly spin polarized, while most molecules and solids are spin unpolarized. (2) Most chemical reaction energies and all heats of formation from the standard states of the elements, when calculated *ab initio*, do not involve free atoms. It is most important that the functionals should predict energy differences among molecules and solids at fixed atomic composition [79,80], e.g., $2H_2O \rightarrow 2H_2 + O_2$. We have verified that SCAN is much better than TPSS or PBE for the energy differences between the diamond and beta-tin structures of solid Si under pressure, and we will test SCAN for other structural phase transformations and for the heats of formation of molecules and solids in future work.

To see that SCAN may give a more consistent description of molecular energies than other semilocal functionals, we define the $G3^{HC}$ set of 46 hydrocarbon molecules. For each tested functional, we subtract from the energy of the partly spin-polarized C atom the average over $G3^{HC}$ of the functional's error per C atom. After this correction, the MAE is much smaller for SCAN than for any other tested functional.

The BH76 set [74] comprises 76 barrier heights for chemical reactions (of order 0–50 kcal/mol). The barrier arises at a transition state with long, weak bonds, and full nonlocality can improve it substantially. Nevertheless, SCAN gives better barrier heights than any functional in Table II except the meta-GGA M06 L, which was partly fitted to barrier heights.

S22 [69] is a set of 22 weak interaction energies (hydrogen and van der Waals bonds, with equilibrium binding energies from about 0 to 20 kcal/mol) between closed-shell complexes. For these energies, SCAN is much better than other functionals (and competes with M06 L, which was fitted in part to weak interactions). We believe that this success is related to our appropriate norming. (Of course, no semilocal functional can capture the long-range part of the van der Waals interaction, but SCAN captures much of the intermediate-range part, as M06 L does.)

LC20 [75] is a set of 20 lattice constants of solids (from 3.451 to 6.042 Å). For this set, SCAN is far more accurate than any other functional in Table II. Far less accurate is M06 L, which was fitted to molecular data. We expected SCAN to be accurate for lattice constants: Fuchs and Scheffler [81] established that lattice-constant errors arise from the region of core-valence overlap [9].

In summary, we have constructed the first meta-GGA that satisfies all known possible exact constraints (about 6 for exchange, 6 for correlation, and 5 for the sum of the two [49]). But there are still infinitely many ways to satisfy these constraints. Thus, we have also satisfied appropriate norms, for which our SCAN meta-GGA can be extremely accurate: the energies of rare-gas atoms and nonbonded interactions. We have not fitted to any real bonded system. Thus, we regard our functional as a nonempirical one that can be reliably applied to a wide range of problems unlike those to which it was normed.

Table II suggests that SCAN is a major improvement over PBE (and much more so over LSDA), at nearly the same computational cost. In future work, we will further explore the possibilities and limitations of SCAN, which we suspect are close to those of the semilocal form, Eq. (1).

This work was supported by NSF under Grant No. DMR-1305135 (J. P. P., J. S., and A. R.). We thank the Center for Computational Science (Tulane) for computer time.

[*] Corresponding author.
jianweisun791012@gmail.com

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