

Semilocal Density Functionals and Constraint Satisfaction

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We discuss six questions related to the recent “strongly constrained and appropriately normed” (SCAN) meta-generalized gradient approximation (meta-GGA): (1) When and why should a semilocal approximation to the density functional for the exchange-correlation energy be accurate? (2) What is the right dimensionless ingredient for a meta-GGA, and why? (3) In the construction of density functional approximations, should we satisfy more or fewer exact constraints? (4) Is there a tight lower

bound on the exchange energy for all spin-unpolarized densities? (5) Should a semilocal approximation yield any intermediate-range van der Waals interaction? (6) Do semilocal functionals make consistent predictions for the energy differences between different molecules (and thus presumably for reaction and formation energies)? © 2016 Wiley Periodicals, Inc.

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Introduction

Kohn–Sham density functional theory^[1] predicts the ground-state energy and electron density of a many-electron system, such as an atom, molecule, or solid. Exact in principle, the theory requires in practice an approximation to the density functional for the exchange-correlation energy. The SCAN (strongly constrained and appropriately normed) meta-GGA^[2] may be a major step in the non-empirical or constraint-based construction of such approximations. SCAN is the first approximation to satisfy all 17 known exact constraints appropriate to a semilocal functional. It is also fitted to appropriate norms, densities for which a meta-GGA can be expected to be exact or highly accurate. Significantly, the appropriate norms do not include any bonded systems. SCAN has been found to predict accurate structures and energies for diversely-bonded materials (including covalent, metallic, ionic, hydrogen, and van der Waals bonds).^[3] In many cases, SCAN is as or more accurate than a fully nonlocal hybrid functional.^[3] SCAN also predicts the correct ground-state crystal structure, lattice constants, magnetic structure, and even band gap for the “difficult” solid MnO₂.^[4] By itself, SCAN describes the intermediate range van der Waals interaction, which is poorly described in standard GGAs and GGA hybrids. When paired^[5] with the long-range rVV10 nonlocal van der Waals correlation functional, it also accurately describes the interlayer binding energies and lattice constants of 28 layered materials, and the physisorption of a benzene molecule on three coinage-metal surfaces.

SCAN took over 2 years to develop, and its physical ideas were compressed into a fraction of a five-page letter.^[2] Here, we will discuss some of these physical ideas in greater detail.

When and Why Should a Semilocal Density Functional Work?

Semilocal density functionals are of the form

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

Here, the local electron spin densities can be constructed from the occupied Kohn–Sham orbitals

$$n_{\sigma}(\vec{r}) = \sum_{\alpha}^{\text{occup}} |\psi_{\alpha\sigma}(\vec{r})|^2, \quad (2)$$

and are the only ingredients of the local spin density approximation.^[1,6,7] The gradients of the local spin densities are added in a generalized gradient approximation (GGA),^[8,9] and the orbital kinetic energy densities

$$\tau_{\sigma}(\vec{r}) = \sum_{\alpha}^{\text{occup}} |\nabla \psi_{\alpha\sigma}(\vec{r})|^2 / 2 \quad (3)$$

in a meta-GGA.^[2,10] Adding more ingredients makes it possible to satisfy more exact constraints and to fit more appropriate norms. τ_{σ} is a fully nonlocal functional of n_{σ} , but Eq. (1) remains semilocal from the viewpoint of computational efficiency: It requires only a single integration over three-dimensional space of quantities that are available at each position in any Kohn–Sham calculation.

The exchange-correlation energy is an electrostatic interaction between the electron density at each position \vec{r} and the density at position \vec{r}' of the exchange-correlation hole around an electron at \vec{r} .^[11] Only when the exact hole is well-localized around its electron is the semilocal approximation of Eq. (1) expected to be accurate.

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In an atom, the exact hole and its separate exchange and correlation contributions must remain within the density of the atom. So a good semilocal approximation should be accurate for the exchange energy alone and for correlation energy alone in an atom, which is therefore an appropriate norm^[2,12] to which a semilocal functional can be fitted. (Spherical atoms with closed magnetic subshells are especially appropriate, since their noninteracting wavefunctions are unquestionably single Slater determinants.) The same is true of a uniform density or one that varies slowly over space. We regard the fitting of appropriate norms as a normal step in the construction of a nonempirical functional, one that has been present since the advent of the local spin density approximation.

In a multicenter system like a molecule, the exact exchange hole can delocalize over the available centers. But the exact exchange-correlation hole tends in every system to be deeper and more localized around its electron than the exact exchange hole.^[11,13] In other words, there is an error cancellation between semilocal exchange and semilocal correlation.^[2,11,12] This is why

semilocal functionals often work well for exchange and correlation in molecules near equilibrium bond lengths.

But this error cancellation is always imperfect at best, so molecules are *not* appropriate norms for a semilocal functional. We regard semilocal functionals fitted to molecules as empirical. Indeed there are well known cases where the exact hole is completely delocalized, and no error cancellation can occur, such as the one-electron molecule ion H_2^+ stretched to infinite bond length, for which no semilocal functional can be expected to be accurate. The transition states for chemical reactions are also typically stretched radicals with delocalized exact exchange-correlation holes. Only fully nonlocal functionals can be accurate for such systems.

From the same viewpoint, the appropriate constraints^[3] for a semilocal functional are those exact constraints that can be satisfied by a model exchange-correlation hole that is well localized around its electron.^[11] Inappropriate constraints include asymptotic exchange and correlation potentials that are experienced by an electron that wanders far outside the electron density distribution, leaving its exact hole behind.

We define a nonempirical functional as one constructed to satisfy appropriate constraints and appropriate norms. The first nonempirical density functional for the exchange-correlation energy was the local density approximation. It was constructed to satisfy an appropriate norm, the electron gas of uniform density, before it was realized that it also satisfied appropriate constraints. Subsequent nonempirical functionals have added more appropriate norms and appropriate constraints.

What Is the Right Dimensionless Ingredient for a Meta-GGA, and Why?

The orbital kinetic energy density τ is a natural ingredient of a semilocal density functional because it is needed to recognize one- and two-electron ground-state densities and thus to satisfy the exact constraints specific to those densities. It also appears in the second derivative of the exact exchange hole density at the position of the electron.^[14]

Our experience of recent years^[2,15–17] suggests that the right dimensionless ingredient for a meta-GGA in a spin-unpolarized system is

$$\alpha = (\tau - \tau_W) / \tau_{\text{unif}}, \quad (4)$$

where $\tau_W = |\nabla n|^2 / (8n)$ is the ground-state one- and two-electron density limit of τ and $\tau_{\text{unif}} = (3/10)(3\pi^2)^{2/3} n^{5/3}$ is its uniform-density limit. This quantity can recognize and deliver an appropriately different GGA description for covalent single bonds ($\alpha \approx 0$), metallic bonds ($\alpha \approx 1$), and van der Waals bonds ($\alpha \gg 1$).^[18] Indeed the “electron localization function”^[19] is $1/(1+\alpha^2)$. If the ground state has a non-zero current density, then Eq. (4) must be modified in a known way.^[20]

Since τ_W is also the orbital kinetic energy density for ground-state bosons, $\tau - \tau_W$ can be identified as the specifically fermionic contribution to τ , and many good reasons why it should appear in a meta-GGA are summarized in Ref. [21]. Here, we will add one more: The fourth-order gradient expansion of the exchange energy can be expressed in terms of α plus GGA ingredients.^[22]

Many of the known exact constraints cluster around $\alpha=0$ or 1. Thus in SCAN^[2] and its precursors^[15–17] we interpolate the integrand of Eq. (1) between $\alpha=0$ and 1, and extrapolate it to $\alpha \gg 1$.

Should We Satisfy More or Fewer Exact Constraints?

The first nonempirical density functional was the local spin density approximation.^[1,6] Early tests in condensed matter physics showed that it was unexpectedly accurate for real systems, including those that did not resemble a uniform electron gas. The search for an explanation led to the discovery that this approximation satisfied “hidden” exact constraints on the exchange-correlation hole^[11,23] and energy.^[24] Early GGAs^[8,9] and later functionals were constructed explicitly to satisfy those and other exact constraints.

There is also an empirical school of density functional construction, which fits to datasets of reference energies, typically for molecules. While the exact constraints are the guiding lights of the nonempirical school, they can be barriers to getting an optimal fit in the empirical school. This situation led to the following interesting observation by Peverati and Truhlar in 2014: “Are there prospects for further improvement? It is always hard to make predictions, ‘especially about the future’; however, we believe that there will be further improvement. This may involve breaking some of the constraints that we are already following right now or – less likely as it seems to us – adding new constraints.”^[25]

As we will see in the next section, a new constraint has led to further improvement. (Besides that new constraint, however, SCAN was also constructed^[2] to satisfy several older constraints that had been largely ignored in earlier density functional constructions.) We believe that nonempirical semilocal functionals based on appropriate constraints and appropriate norms will prove to be more widely useful, more reliable, and more predictive than empirical ones.

Is There a Tight Lower Bound on the Exchange Energy of Any Spin-Unpolarized Density?

The PBE GGA^[9] was constructed to satisfy a rigorous^[26] but not necessarily tight bound on the exchange energy of any spin-unpolarized density in terms of the local density approximation (LDA) exchange energy:

$$E_x[n] / E_x^{\text{LDA}}[n] \leq 1.804 \quad (5)$$

Recently it has been shown^[27] that, for spin-unpolarized two-electron densities,

$$E_x[n] / E_x^{\text{LDA}}[n] \leq 1.174. \quad (6)$$

The LDA of course satisfies this constraint, but earlier GGAs and meta-GGAs all violate it for certain possible densities.^[27] Since SCAN can recognize two-electron densities, this rigorous and tight bound was imposed in the construction^[2] of SCAN. Unexpectedly, SCAN turned out to satisfy Eq. (6) for *all* spin-unpolarized densities. Could Eq. (6) be proved for *all* spin-unpolarized densities?

If so, it would not be the first time that an approximation in DFT has suggested an exact result. The Perdew–Zunger self-interaction correction,^[28] while approximate, suggested the exact density functional theory of open systems with fractional particle number.^[29]

Should a Semilocal Functional Yield Any Intermediate-Range van der Waals Bonding?

Semilocal density functional approximations obviously cannot yield any long-range or asymptotic van der Waals interaction: Where there is no density overlap between two objects, there can be no exchange-correlation-driven interaction at the

Table 1. Error statistics of molecular and atomic energies (to be precise: enthalpies of formation) by the method of atomic equivalents (DATEF).^[36]

Method	RMSE(303)	RMSE(592)	extreme(-)	extreme(+)
G3	1.9 ¹	4.7 ⁵	60	47
LSDA	7.5	7.5	33	23
PBE	4.9	5.2	23	23
B3LYP	4.7 ⁵	5.4 ⁹	24	23
M06-L	4.1 ²	4.7 ¹⁴	26	20
SCAN	3.8	4.2	21	18

The considered molecules have six or fewer non-hydrogen atoms. Smaller numbers are everywhere better in this table. RMSE means root mean square error. The 303 set consists of 303 species, mostly molecular, some free atom, with experimental error specified as $< 3\text{kJ/mol} = 0.72\text{ kcal/mol} = 1.1\text{ mHartree}$. The 592 species set includes the 303, plus further well-characterized molecules and all of the 15 elements occurring in the molecules as free atoms. The superscript shows the number of calculations that did not converge, as explained in the text; these are not included in the statistics. This number is an indicator for nonrobustness of the method. As RMSE is the estimator for the sigma of a Gaussian distribution, one expects to find one species with about ± 3 sigma error deviation for the 592 set. All methods show \pm extreme errors clearly larger than 3 sigma. Large numbers here are indicative of lesser reliability of a method.

semilocal level. But there is often significant density overlap at the equilibrium bond length.

The local density approximation typically *overestimates* van der Waals bonding around the equilibrium bond length. Some GGAs like Becke 1988^[30] yield no such bonding, while others like PBE typically yield an underestimated van der Waals bond. SCAN however realistically binds many such complexes.^[2,3]

It has been argued that semilocal functionals should yield no van der Waals bonding. The strongest argument for this claim is that the van der Waals bond in exact quantum mechanics arises from correlation, while in semilocal functionals it arises from the exchange functional.^[5,31] But, as stated in Section 1, multicenter systems typically show a strong error cancellation between semilocal exchange and semilocal correlation. In covalent bonds, semilocal exchange provides the important static or long-range correlation.

Do Semilocal Functionals Make Consistent Predictions of the Energy Differences Between Molecules?

The atomization energies of molecules are an important but possibly misleading test of density functionals in chemistry. Molecules are multicentered, while atoms are single-centered. Most molecules are closed-shell and spin-unpolarized while most atoms are open-shell and spin-polarized. Atoms often have a multiplet structure. Typical chemical reaction and formation energies, which are of greater chemical interest than atomization energies, involve energy differences among molecules or solids, with no atom. Nevertheless, standard compilations of experimental heats of formation are often used as atomization-energy tests for electronic structure methods, as explained in the next paragraph.

For example, consider the formation energy of the molecule CO. This is the total ground-state energy of CO minus the sum of

the energy per C atom in its standard-state (solid graphite) and the energy per O atom in its standard state (the molecule O₂). Although all these energies can be computed in DFT, at least for molecules and crystalline solids, the solid-state calculation is not doable by wavefunction methods. Thus in chemistry it is standard to add and subtract the sum of the energies of the free C and O atoms, reformulating the formation energy as minus the difference between the atomization energy of the CO molecule and the sum of the atomization energies per atom for solid graphite (taken from experiment) and the atomization energy per atom of the molecule O₂ (also taken from experiment). Then, neglecting experimental error, the error in the computed formation energy of a molecule is minus the error in its atomization energy. That standard chemistry approach is the one to be refined by the method of the next paragraph.

Dewar and Storch^[32] pointed out that statistics on how well theoretical molecular energies track experimental molecular energies^[2,32–37] are a better predictor for the accuracy of theoretical chemical reaction energies than are the popular atomization energy statistics. The method of Ref. [32] requires introducing elemental energies as fit parameters. These have subsequently often been called “atomic equivalents.” A side bonus of this method, as opposed to the atomization method, is that errors can be assigned to theoretical free atom values. Here, we follow this approach as described in more detail in Ref. [36]. Methods like B3LYP, which look very good in the atomization statistics, do so by hitting small free atom errors for the frequently occurring atoms according to the present method. Conversely, the local spin density approximation (LSDA) looks bad in atomization statistics because its errors for atoms are inconsistent with its errors for molecules.

From the results in Table 1 on error statistics of molecular energies, based on the CCCBDB database,^[38] it is obvious that there is systematic progress in density functional approximations from LSDA (with Perdew–Wang correlation) to good meta-GGAs. The more computationally intensive but popular hybrid functional B3LYP^[39,40] does not perform better than the two included meta-GGA approximations, M06-L^[41] and SCAN.^[2] The number of missing calculations, as shown in the superscripts, indicates issues with robustness of the B3LYP and M06-L calculations. The composite quantum chemistry calculations of G3 type display small errors for the tight experimental-error subset. For the larger set, the G3 RMSE is not better than that of the meta-GGAs. The largest G3 errors hint at a lesser reliability for this method when applied to a wider set of compounds. In any case solids are not accessible with G3. Conversely, SCAN tests well for solids too.^[2,4] It appears to be a significant fact that the SCAN functional least exceeds the Gaussian expectations for its extreme deviations. It should thus offer the most reliable predictions for thermochemistry (excluding barrier heights) among the methods in Table 1.

The calculations in Table 1, other than those using the G3 method, were done with the code DMol³ using DNP basis sets and standard grids as defined in Ref. [42], the same methodology as used in Ref. [36]. It was found that larger basis sets and grids did not change the statistics of Table 1 appreciably. The entries for the G3 method in Table 1 were obtained from a statistical analysis

of data in Ref. [38]. For the DMol³ calculations using B3LYP and M06-L, there are some cases that are difficult to converge self-consistently. The most common reason for this problem is level crossing which occurs in the SCF iterations. In certain cases, it is found that the SCF solution obeying Fermi occupation involves accidentally degenerate orbital levels with fractional occupation of more than one HOMO orbital. Even if such a solution can be found, it may be deemed unacceptable for a gas phase molecule. In the case of the G3 method, we do not know the reasons why its authors^[38] did not show G3 results for all molecules, while they showed results for all molecules from other methods.

Conclusions

The first nonempirical semilocal density functional (LSDA^[1]) for the exchange-correlation energy was fitted to the uniform electron gas, and later found to satisfy hidden constraints.^[11,23,24] Early explicit constraints on the energy functional were derived by Mel Levy (e.g., Ref. [24]). The idea of “appropriate” norms and constraints was there almost from the beginning, although the word “appropriate” appears only recently.^[2,3] Reference 12 is an early identification of atoms as appropriate norms. Nonempirical semilocal functionals have been repeatedly improved by the satisfaction of additional appropriate norms and appropriate constraints, leading to the SCAN meta-GGA.^[2]

We believe that SCAN will be useful throughout materials science and chemistry, providing a computationally efficient and usually accurate and reliable approximation. Of course, like all semilocal functionals, SCAN must fail when electrons are shared over stretched bonds. That can happen when a system is out of equilibrium, or when its equilibrium results from a competition between stretched (e.g., *d*) and compressed (e.g., *sp*) bonds. In that case, full nonlocality (as in a self-interaction correction^[25]) is needed.

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