

Prescription for the design and selection of density functional approximations: More constraint satisfaction with fewer fits

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We present the case for the nonempirical construction of density functional approximations for the exchange-correlation energy by the traditional method of “constraint satisfaction” without fitting to data sets, and present evidence that this approach has been successful on the first three rungs of “Jacob’s ladder” of density functional approximations (local spin-density approximation or LSD, generalized gradient approximation or GGA, and meta-GGA). We expect that this approach will also prove successful on the fourth and fifth rungs (hyper-GGA and generalized random-phase approximation). In particular, we argue for the theoretical and practical importance of recovering the correct uniform density limit, which many semiempirical functionals fail to do. Among the beyond-LSD functionals now available to users, we recommend the nonempirical Perdew–Burke–Ernzerhof (PBE) GGA and the nonempirical Tao–Perdew–Staroverov–Scuseria (TPSS) meta-GGA, and their one-parameter hybrids with exact exchange. TPSS improvement over PBE is dramatic for atomization energies of molecules and surface energies of solids, and small or moderate for other properties. TPSS is now or soon will be available in standard codes like Gaussian, Turbomole, NWChem, ADF, WIEN, etc. We also discuss old and new ideas to eliminate the self-interaction error that plagues the functionals on the first three rungs of the ladder, bring up other related issues, and close with a list of “do’s and don’t’s” for software developers and users.

I. INTRODUCTION

Kohn–Sham spin density functional theory^{1–4} is now the most widely-used method for electronic structure calculations in condensed matter physics and quantum chemistry, providing useful predictions for atoms, molecules, nanostructures, solids, and solid surfaces. This theory looks (and, more importantly, scales with system size⁵) like a mean-field theory with a self-consistent effective one-electron Schrödinger equation for the Kohn–Sham orbitals, but includes in principle all correlation effects on the ground-state electron density and total energy. Useful extensions of the theory to thermal equilibrium at finite temperature and to excited or time-dependent states have also been made.^{2,3} In principle, only the density functionals for exchange and correlation remain to be approximated. The “due diligence” requirement of good science demands some understanding of what these approximations are and how they are constructed, not only from the developers but also from the users and even the opponents of density functional theory.

We are writing this article for all of these potential readers to express our personal preferences and meta-physical principles for the construction and selection of density functional approximations. We will argue that the traditional nonempirical approach of construction by “constraint satisfaction”^{1,6–9} remains the most convinc-

ing, most universal, and most enduring one, making full use of the many known exact constraints on the density functional for the exchange-correlation energy. In this approach, the density functional approximations are assigned to various rungs of “Jacob’s ladder”,¹⁰ according to the number and kind of their local ingredients. The lowest rung is the local spin density approximation of Kohn and Sham,¹ the second rung is the generalized gradient approximation, and so on. Higher rungs are increasingly more complex. The best nonempirical functional for a given rung is constructed to satisfy as many exact theoretical constraints as possible while providing satisfactory numerical predictions for real systems. Once a rung has been selected, there remains little choice about which constraints to satisfy (but greater freedom in how to satisfy them). Accuracy is expected to increase up the ladder as additional local ingredients enable the satisfactions of additional constraints.

Aside from Coulomb perturbation theory (which fails for metals), the only known alternative to “constraint satisfaction” is “semiempirical fitting”,^{11–15} in which the functionals are fitted to selected data from experiment or from *ab initio* calculations. Of course, the additional ingredients that arise at higher rungs of Jacob’s ladder can also accommodate more fit parameters. Functionals with as many as 21 fit parameters, violating some of the most basic exact constraints, are especially popular in chemistry. Our traditional view that the functionals

should be constructed with few empirical parameters and preferably none is now a minority opinion for which we will present a rationale. We will point to recent developments which show the continuing power of the nonempirical constraint satisfaction approach and discuss possible future developments along the same general direction.

II. IS DENSITY FUNCTIONAL THEORY *AB INITIO*?

Knowing quantum mechanics and Coulomb's law for the electron-electron interaction, we know almost everything we need in principle for the description of atoms, molecules and solids. Numerical studies based upon the correlated many-electron wave function can be *ab initio*, although computationally intractable for large molecules or unit cells. The underlying principles of quantum mechanics and Coulomb's law are accepted as universally valid and basic. This acceptance is itself grounded in experiment, as all good science is.

Starting from these principles, we can derive^{1,16} the Kohn–Sham ground-state density functional theory and prove that the ground-state exchange-correlation energy is a functional of the total electron density $n(\mathbf{r})$ or of the separate up and down spin densities $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$. We can also prove many exact properties (Section VI) of this functional, to constrain our approximation to it. But this functional is known neither exactly nor as a systematic series of approximations converging in every case to the exact answer (the highest expectation of a fully *ab initio* theory).

So is density functional theory *ab initio* or semiempirical? We suggest that it can fall in between as a nonempirical theory when the functionals are constructed by constraint satisfaction without empirical fitting. It is this middle way that is advocated here.

Language that is now widely used tends to be contradictory and confusing. Some articles distinguish between *ab initio* (wave function-based) and “density functional” calculations, suggesting in a subtle and perhaps unintentional way that density functional theory is semiempirical. Other papers refer to density functional calculations as “first principles” or *ab initio*, but that is a long stretch when the underlying functional has, for example, eight fit parameters like the popular B3LYP,¹⁷ even though these parameters are fixed once for all by a particular fitting to a given data set. (B3LYP has one empirical parameter in its Becke exchange,¹² five in its LYP¹³ correlation, and three more in the hybridization with exact exchange).

A fully *ab initio* density functional approximation would be good for users but uninteresting for developers, as it would leave too little room for creative play. A semiempirical density functional approximation, however, leaves too much room, encouraging an “anything that works” attitude. Many popular functionals including B3LYP are not exact even in the one limit (uniform density) in which they could be. As Wordsworth said,

“Strange fits of passion have I known”.¹⁸ A nonempirical density functional is most interesting from the developer's viewpoint, since its construction requires disciplined imagination and insight (as well as trial and error).

“Semiempirical fitting” leaves unexplained all the data that was fitted. It can make very accurate predictions for systems and properties that are sufficiently similar to those fitted, but can fail badly when the new systems and properties are sufficiently different. In particular, higher-level functionals that are fitted to molecular data can be far less accurate¹⁹ for the bulk and surface properties of simple metals than even the lowest-level functional, the local-spin density approximation. Thus users who want reliable high accuracy for a broad range of systems need a high-level nonempirical functional.

A given rung of Jacob's ladder (Section IV) is too restrictive in form to be exact and must have intrinsic accuracy limits. Thus fitting a given data set too closely can result in “overfitting”. There are two senses in which a semiempirical functional of a given form can be overfitted. The first, which can be avoided by a careful mathematical analysis, involves the introduction of artificial zigs and zags that reduce the fitting error, or the introduction of more parameters than are really justified. For example, the three mixing parameters in the B3PW91²⁰ or B3LYP¹⁷ hybrids can be reduced²¹ to one^{22–25} without a significant overall error increase, and the optimum value of this parameter to predict molecular atomization energies can even be rationalized.²⁴ The second sense is the inevitable bias that arises in the selection of a given fitting set and weights for this set.

One of the authors of this article is old enough to recall the history of the electron-ion pseudopotential in condensed matter physics. The 1960s and 1970s saw the appearance of many realistic semiempirical pseudopotentials. When accurate nonempirical pseudopotentials became available,²⁶ the semiempirical ones quickly and permanently disappeared from the literature. We expect the history of density functional theory to follow a parallel course.

III. WHY THE UNIFORM DENSITY LIMIT IS SACROSANCT

The paradigm density for condensed matter physics is also one of the simplest possible ones, the uniform density in which $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$ are independent of position \mathbf{r} . The periodic valence-electron density in a bulk solid (especially a simple metal) has some resemblance to this uniform density. The earliest and simplest spin-density functional for the exchange-correlation energy was the local spin density (LSD) approximation¹

$$E_{xc}^{\text{LSD}}[n_\uparrow, n_\downarrow] = \int d^3r n \varepsilon_{xc}^{\text{unif}}(n_\uparrow, n_\downarrow), \quad (1)$$

where $\varepsilon_{xc}^{\text{unif}}(n_\uparrow, n_\downarrow)$ is the exchange-correlation energy per particle of an electron gas with uniform spin den-

sities n_\uparrow and n_\downarrow , known accurately from quantum Monte Carlo and other many-electron methods.²⁷ For an accurate parametrization of $\varepsilon_{xc}^{\text{unif}}(n_\uparrow, n_\downarrow)$, see Ref. 28. By construction, Eq. (1) is exact in the one limit in which it can be, the limit of uniform spin densities. This limit is preserved in all nonempirical density functionals, but lost²⁷ in many semiempirical ones which as a result can fail seriously for the bulk and surface properties of simple metals.¹⁹

In our view, if an approximation fails to be essentially exact for the limited class of systems where it can be, it is a self-contradiction and should not underpin any major area of science. The most widely-used functional in quantum chemistry, B3LYP, underestimates the magnitude of the correlation energy of the uniform gas by about 30%²⁷ (as inherited from the 50% underestimation of LYP). In fact, the original three-parameter hybrid proposed by Becke,²⁰ B3PW91, was a semiempirical functional designed to be exact for the uniform electron gas. B3LYP was later favored because of its slightly better performance for a data set of small molecules, although it is now clear that B3PW91 performs better than B3LYP for large organic molecules.²⁹

The local spin density approximation is so accurate for solids that it is still widely used in condensed matter physics. It is less useful for atoms and molecules, which bear less resemblance to a uniform electron gas and are better described by the functionals on higher rungs of Jacob's ladder. But even a practical chemist should respect the uniform density limit, since he or she may someday have to deal with a molecule chemisorbed to the surface of a simple metal.

In fact, the relatively poor LSD atomization energies have led to an undervaluation of LSD in chemistry. LSD gives remarkably accurate bond lengths,²⁹ and the errors of its atomization energies can be dramatically reduced by introducing one empirical parameter to represent the energy of each free atom.³⁰ For chemistry without free atoms, LSD is not such a bad starting point.

IV. JACOB'S LADDER OF DENSITY FUNCTIONAL APPROXIMATIONS

Although many generalizations of the LSD of Eq. (1) were proposed, the first practical one was the generalized gradient approximation (GGA)^{7,9,12,13,31–35}

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

which introduces the density gradients $\nabla n_\uparrow(\mathbf{r})$ and $\nabla n_\downarrow(\mathbf{r})$ as additional local ingredients or arguments of $\varepsilon_{xc}^{\text{GGA}}$. While LSD is the first, GGA is the second rung of Jacob's ladder.

The original motivation for Eq. (2) was the second-

order gradient expansion (GEA)

$$E_{xc}^{\text{GEA}}[n_\uparrow, n_\downarrow] = \int d^3r \left[n \varepsilon_{xc}^{\text{unif}}(n_\uparrow, n_\downarrow) + \sum_{\sigma, \sigma'} C_{xc}^{\sigma\sigma'}(n_\uparrow, n_\downarrow) \frac{\nabla n_\sigma \cdot \nabla n_{\sigma'}}{n_\sigma^{2/3} n_{\sigma'}^{2/3}} \right], \quad (3)$$

an expression valid for slowly-varying densities. The coefficients $C_{xc}^{\sigma\sigma'}$ were derived in the hope that Eq. (3) would improve upon LSD for real solids and even for molecules, but this hope was disappointed. Langreth and Perdew⁶ identified the root of the problem, which was also the key to the development of new functionals by the method of constraint satisfaction as defined in the Introduction.

The exact exchange-correlation energy can be expressed by the adiabatic connection or coupling constant integration^{36,37}

$$E_{xc}[n_\uparrow, n_\downarrow] = \frac{1}{2} \int d^3r n(\mathbf{r}) \int d^3r' \int_0^1 d\lambda \frac{n_{xc}^\lambda([n_\uparrow, n_\downarrow]; \mathbf{r}, \mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|}. \quad (4)$$

We consider a series of systems having the same ground-state density $n(\mathbf{r})$, different electron-electron repulsions $\lambda/|\mathbf{r}' - \mathbf{r}|$ (where the coupling constant falls in the range $0 \leq \lambda \leq 1$), and corresponding external potentials $v_\lambda(\mathbf{r})$. The real system has $\lambda = 1$ and the Kohn-Sham non-interacting system has $\lambda = 0$. In Eq.(4), $n_{xc}^\lambda([n_\uparrow, n_\downarrow]; \mathbf{r}, \mathbf{r}')$ is the density at \mathbf{r}' of the exchange-correlation hole surrounding an electron at \mathbf{r} :

$$n_{xc}^\lambda = n_x + n_c^\lambda, \quad (5)$$

where the exchange hole density n_x is independent of λ . Note that n_{xc}^λ can be found from the correlated wave function for a given λ . The exact exchange-correlation hole has the following key properties:^{8,36,37}

$$\int d^3r' n_x(\mathbf{r}, \mathbf{r}') = -1, \quad (6)$$

$$\int d^3r' n_c^\lambda(\mathbf{r}, \mathbf{r}') = 0, \quad (7)$$

$$n_x(\mathbf{r}, \mathbf{r}') \leq 0. \quad (8)$$

The LSD hole, being the hole of a possible physical system (the uniform electron gas), satisfies Eqs. (6)–(8), which constrain Eq. (4) to reasonable values. The LSD “on-top” hole density $n_{xc}^{\lambda, \text{LSD}}(\mathbf{r}, \mathbf{r}')$ is also nearly exact.³⁸ However, the GEA hole, being only the expansion of a hole to second order in ∇ , has a spurious large $|\mathbf{r}' - \mathbf{r}|$ behavior that violates Eqs. (6)–(8). Simple cutoffs that restore some or all of these constraints led to the first GGAs, which markedly improved the calculated total and atomization energies of molecules.

Our recommended nonempirical GGA is that of Perdew, Burke and Ernzerhof (PBE).⁹ It has two different derivations, one (which it shares with its PW91 twin,³⁴ the first completely nonempirical GGA) based

upon satisfying the constraints (6)–(8) on the system-averaged hole,³⁵ and the other based upon satisfying constraints on the exchange-correlation energy itself.⁹ Revisions^{39–41} of PBE satisfy only the second set of constraints, not the first, and so are less convincing. These revisions typically work better than PBE for the atomization energies of molecules (their target property), but worse than PBE for molecular bond lengths^{42,43} and for lattice constants and surface energies of solids.¹⁹

Adding the next natural set of local ingredients produces the meta-GGA^{8,14,44–48} or third rung of Jacob’s ladder:

$$E_{xc}^{\text{MGGA}}[n_{\uparrow}, n_{\downarrow}] = \int d^3r n \quad (9)$$

$$\times \varepsilon_{xc}^{\text{MGGA}}(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}, \nabla^2 n_{\uparrow}, \nabla^2 n_{\downarrow}, \tau_{\uparrow}, \tau_{\downarrow}).$$

The Laplacians $\nabla^2 n_{\sigma}(\mathbf{r})$ seem like the more natural next step, since they appear in the fourth-order gradient expansion, but the Kohn–Sham orbital kinetic energy densities,

$$\tau_{\sigma}(\mathbf{r}) = \frac{1}{2} \sum_i^{\text{occ.}} |\nabla \phi_{i\sigma}(\mathbf{r})|^2, \quad (10)$$

which appear in the Taylor expansion of the exchange hole density about $|\mathbf{r}' - \mathbf{r}| = 0$, are also (implicit) functionals of the density and permit the satisfaction of more constraints (Section VI) than the Laplacians do. They carry the same information in the limit of a slowly-varying density, since⁴⁹

$$\tau_{\sigma}^{\text{GEA}} = \tau_{\sigma}^{\text{unif}} + \frac{1}{72} \frac{|\nabla n_{\sigma}|^2}{n_{\sigma}} + \frac{1}{6} \nabla^2 n_{\sigma}, \quad (11)$$

where $\tau_{\sigma}^{\text{unif}} = \frac{3}{10} (6\pi^2)^{2/3} n_{\sigma}^{5/3}$.

The only nonempirical meta-GGA for exchange and correlation is that of Tao, Perdew, Staroverov and Scuseria (TPSS),⁴⁸ which utilizes only τ_{\uparrow} and τ_{\downarrow} without $\nabla^2 n_{\uparrow}$ and $\nabla^2 n_{\downarrow}$. It is constructed by satisfying only constraints on the exchange-correlation energy, but we can probably “reverse-engineer” TPSS exchange and correlation holes⁵⁰ satisfying the hole constraints of Eqs. (6)–(8). Extensive numerical tests^{29,51–58} of TPSS suggest that the nonempirical “constraint satisfaction” approach continues to work on the meta-GGA level, producing a functional that is fully competitive with semiempirical ones. Compared to PBE, TPSS greatly improves atomization energies for molecules and surface energies for solids.

LSD is a local and GGA is a semi-local functional of the density. Meta-GGA is a semi-local functional of the density and the occupied orbitals, which are readily available in any Kohn–Sham-like calculation. Semi-local functionals are expected to work best when the exact exchange-correlation hole is well-localized around its electron, as it is in slowly-varying and in compact (e.g., spherical) electron densities.

Higher rungs of Jacob’s ladder necessarily introduce a more computationally challenging nonlocal functional of

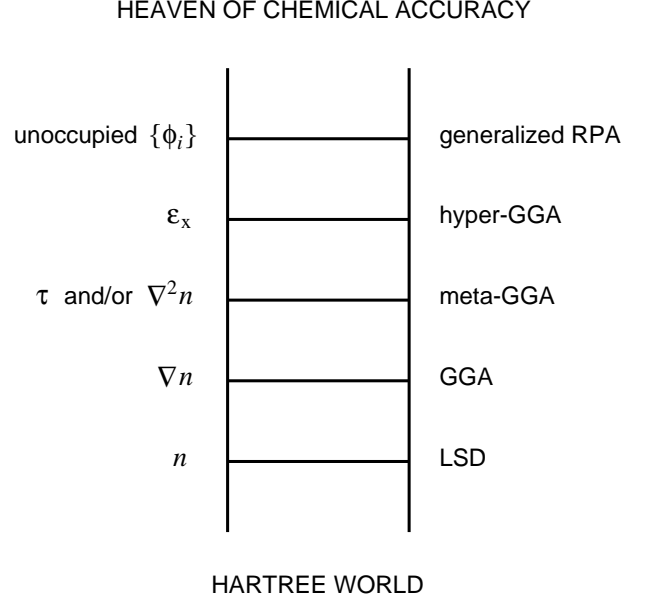


FIG. 1: Jacob’s ladder of density functional approximations to the exchange-correlation energy.

the orbitals. The fourth rung adds as a local ingredient the exact exchange energy density

$$\varepsilon_{x\sigma}(\mathbf{r}) = \frac{1}{2} \int d^3r' \frac{n_{\sigma}^{\sigma}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} \quad (12)$$

$$= -\frac{1}{2n_{\sigma}(\mathbf{r})} \int d^3r' \frac{|\sum_i^{\text{occ.}} \phi_{i\sigma}^*(\mathbf{r}) \phi_{i\sigma}(\mathbf{r}')|^2}{|\mathbf{r}' - \mathbf{r}|},$$

or any quantity such as the exact exchange energy that can be found from it. The hyper-GGA^{10,59} is then

$$E_{xc}^{\text{HGGA}}[n_{\uparrow}, n_{\downarrow}] = \int d^3r n \quad (13)$$

$$\times \varepsilon_{xc}^{\text{HGGA}}(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}, \tau_{\uparrow}, \tau_{\downarrow}, \varepsilon_{x\uparrow}, \varepsilon_{x\downarrow}).$$

Semiempirical hyper-GGAs include the widely-used global hybrid functionals like B3LYP, B3PW91 or PBE0^{22,23} that mix a fixed fraction of exact exchange with GGA exchange, and the local hybrids.⁶⁰ Although the global hybrid functionals can be remarkably accurate for molecules and strongly inhomogeneous solids, they are theoretically less than ideal because they do not satisfy any exact constraints that GGAs do not satisfy. We are working on nonempirical hyper-GGAs that use 100% of exact exchange with a compatible fully-nonlocal correlation.⁵⁹

The fifth and final rung of Jacob’s ladder utilizes *all* of the Kohn–Sham orbitals, unoccupied as well as occupied. At this level the adiabatic connection of Eq. (4) leads to generalizations^{61–64} of the random phase approximation (RPA) that obviate the need for electron gas data (in fact, generating this data), and also account for the long-range van der Waals attraction between non-overlapped

electron densities. These generalizations are still based upon constraint satisfaction, but at a higher level.

Figure 1 shows Jacob’s ladder rising (half dream and half reality) from the Hartree world of unrealistically weak or missing bonding in five steps to the heaven of chemical accuracy. Note that it is not only the higher rungs that have value. The lower rungs may be less accurate, but they are also simpler to understand and they require less programming and computation time.

In our own nonempirical constructions, we try to follow a conservative “don’t re-invent the wheel” approach. Thus, our functionals resemble Chinese boxes or Russian dolls: LSD is inside the PBE GGA, PBE GGA is inside the TPSS meta-GGA, and TPSS meta-GGA will probably be inside our hyper-GGA.

From the nonempirical viewpoint, LSD and GGA are controlled *extrapolations* from the slowly-varying limit, while meta-GGA and hyper-GGA are controlled *interpolations* between the limits of slowly-varying and compact one- or two-electron densities (the paradigm densities for condensed matter physics and quantum chemistry, respectively). The remaining constraints “control” the extrapolation or interpolation. We believe that the first three rungs are essentially completed by the LSD, PBE and TPSS functionals respectively. We encourage users to report and compare their results for all three of these functionals. Nonempirical functionals on the fourth and fifth rungs remain to be developed or adequately tested. Although the hybrid functionals on the fourth rung are semiempirical, we can also recommend the PBE0,^{22,23} ω PBEh,⁶⁵ and TPSSH²⁹ hybrids, which satisfy many exact constraints and have at most one fit parameter.

V. IS EXACT EXCHANGE NEEDED?

The use of a fraction of exact exchange was introduced²⁰ into density functional approximations to improve the calculated atomization energies of molecules, at a significant computational cost. It was later shown¹⁴ that flexible functional forms involving the kinetic energy density (VSXC¹⁴) were capable of yielding similar and even better thermochemistry without exact exchange. However, this was achieved at the cost of empirical parametrization. Now that accurate atomization energies are predicted by a nonempirical density functional *without* exact exchange (TPSS), do we still need exact exchange in chemistry?

It seems that we do need exact exchange, or perhaps self-interaction correction (Section VII), to describe situations in which the exact exchange-correlation hole has a long-range component that cannot be captured by semi-local approximations like LSD, GGA, or meta-GGA. The simplest example is stretched H_2^+ (a highly noncompact one-electron density), but less extreme and more practical examples are moderately stretched molecules⁵² and the transition state of a chemical reaction. The forward and reverse energy barriers tend to be seriously under-

estimated in LSD. These errors are typically reduced by about a factor of two in the PBE GGA or the TPSS meta-GGA, but the remaining error is still far too large for chemical kinetics.^{57,58} The progression from LSD to PBE GGA to TPSS meta-GGA seems to show a consistent and continuing reduction of error only for reactions that do not involve a free H atom or H_2 molecule. The hybrid functionals that admix exact exchange, such as PBE0, achieve a significant further reduction of the error, but are still far from satisfactory. It appears that self-interaction correction can significantly improve energy barriers.⁶⁶ Perhaps a nonempirical hyper-GGA or an improved self-interaction correction will solve this problem, and will also improve the description of molecules containing transition-metal atoms where again TPSS makes only a small improvement⁵⁵ over PBE.

Because inclusion of exact exchange implies moving up Jacob’s ladder, we expect hybrid and hyper-GGA functionals to provide better description for solids as well. Direct evaluation of exact exchange for solids with metallic character remains prohibitively expensive, but the recently developed screened Coulomb potential method⁶⁵ for hybrid functionals overcomes this obstacle with only a slight loss of precision.

VI. SHORT SUMMARY OF KNOWN EXACT CONSTRAINTS ON $E_{xc}[n_\uparrow, n_\downarrow]$

Here we will summarize some of the major known exact constraints on $E_{xc}[n_\uparrow, n_\downarrow]$ and discuss whether or not they are satisfied by approximate functionals. Size-consistency is of course a basic constraint, but one that is always satisfied by semi-local functionals. (Making the functional depend upon an integrated property like $N = \int d^3r n(\mathbf{r})$ can however violate size-consistency.)

For the exchange energy, the spin-scaling relation⁶⁷

$$E_x[n_\uparrow, n_\downarrow] = \frac{1}{2}E_x[2n_\uparrow] + \frac{1}{2}E_x[2n_\downarrow] \quad (14)$$

(where $E_x[n] \equiv E_x[n/2, n/2]$) and the uniform-density scaling relation⁶⁸

$$E_x[n_\gamma] = \gamma E_x[n] \quad (15)$$

[where $n_\gamma(\mathbf{r}) = \gamma^3 n(\gamma\mathbf{r})$] are satisfied by all the density functionals we know, whether nonempirical or semiempirical, as is the upper bound $E_x[n_\uparrow, n_\downarrow] \leq 0$.

The Lieb–Oxford lower bound^{69,70} (expressed in terms of a local density approximation)

$$E_x[n_\uparrow, n_\downarrow] \geq E_{xc}[n_\uparrow, n_\downarrow] \geq 2.273 E_x^{\text{LSD}}[n/2, n/2] \quad (16)$$

for all possible spin densities is satisfied by LSD and by the PBE GGA and TPSS meta-GGA. Most semiempirical functionals can violate this bound for possible but unrealistic densities. The bound is nonetheless important, and its satisfaction for all densities has implications for real densities.

The correlation energy scales in the high-density limit to a constant, as shown by Levy:⁷¹

$$\lim_{\gamma \rightarrow \infty} E_c[n_\gamma] = \text{const.} \quad (17)$$

This condition is violated by LSD and by many semiempirical functionals, but satisfied by PBE GGA and TPSS meta-GGA. In the low-density limit under uniform scaling ($\gamma \rightarrow 0$), correlation scales like exchange; within LSD, PBE GGA and TPSS meta-GGA, the spin-density functionals $E_{xc}[n_\uparrow, n_\downarrow]$ properly become density functionals $E_{xc}[n]$ in this limit.

For a uniform electron gas,^{27,28} LSD, PBE GGA, and TPSS meta-GGA are all exact by construction, while many semiempirical functionals are not. The nonempirical functionals also have gradient expansions like Eq. (3) in the limit of slowly-varying densities. In LSD, the gradient coefficients are all zero. PBE GGA and TPSS meta-GGA have correct second-order gradient coefficients for correlation.⁶ The TPSS meta-GGA has correct gradient coefficients for exchange through fourth order in ∇ .^{72,73} LSD, PBE GGA, and TPSS meta-GGA all have a reasonable linear response⁵⁴ for the uniform electron gas, although this is achieved in PBE GGA by using a second-order gradient coefficient for exchange that is too big by a factor of 1.778.

For any one-electron density $n_1(\mathbf{r})$, we know that⁷⁴

$$\begin{aligned} E_x[n_1, 0] &= -U[n_1] \\ &= -\frac{1}{2} \int d^3r \int d^3r' \frac{n_1(\mathbf{r})n_1(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|}, \end{aligned} \quad (18)$$

$$E_c[n_1, 0] = 0. \quad (19)$$

In other words, the exchange energy of a fully spin-polarized one-electron system is a self-interaction correction to the Hartree-energy, and the correlation energy for such a system vanishes. Because the right hand side of Eq. (18) is a fully nonlocal functional of the density, this constraint cannot be satisfied on the first three rungs of Jacob's ladder, although it can be satisfied on the fourth rung by hyper-GGAs that use full exact exchange. Eq. (19) cannot be satisfied on the first two rungs, but is satisfied by the TPSS meta-GGA on the third rung.

The exact exchange potential, $v_{xc\sigma}(\mathbf{r}) = \delta E_{xc} / \delta n_\sigma(\mathbf{r})$, at the nuclear cusp of the electron density is finite.⁷⁵ This condition, satisfied by LSD, is necessarily lost in GGA, but is restored in the TPSS meta-GGA. The region around the nucleus is one in which the density is dominated by a single orbital shape and the reduced density gradient $s = |\nabla n| / 2(3\pi^2)^{1/3} n^{4/3}$ is small; these conditions can also hold simultaneously near the centers of chemical bonds.

As a consequence of Eqs. (15) and (17), the high-density ($\gamma \rightarrow \infty$) limit of $E_{xc}[n_\uparrow, n_\downarrow]$ is the exact exchange energy $E_x[n_\uparrow, n_\downarrow]$. This condition can be satisfied on the fourth rung of Jacob's ladder by hyper-GGAs that use full exact exchange. And so for that matter will *any* constraint on the exchange energy.

There are also known constraints for non-uniform density scaling,⁷⁶ whether two-dimensional $n_\gamma^{xy}(x, y, z) = \gamma^2 n(\gamma x, \gamma y, z)$ or one-dimensional $n_\gamma^x(x, y, z) = \gamma n(\gamma x, y, z)$, which in the limit $\gamma \rightarrow \infty$ can produce a crossover from a three- to a one- or two-dimensional electron density, respectively.⁷⁷

Except in the one-electron and high-density limits, the most long-ranged parts of the exact exchange and correlation holes tend to cancel,⁷⁸ making $E_{xc}[n_\uparrow, n_\downarrow]$ less strongly nonlocal than $E_x[n_\uparrow, n_\downarrow]$. Thus it is unacceptable to combine exact exchange with meta-GGA correlation. Exact exchange can only be combined with a fully nonlocal correlation, constructed on the fourth or fifth rungs of the ladder.

VII. SELF-INTERACTION CORRECTION OF SEMI-LOCAL FUNCTIONALS, AND HOW TO IMPROVE IT

The semi-local density functionals on the first three rungs of Jacob's ladder violate Eq. (18) and those on the first two rungs also violate Eq. (19). Simple functionals that work well for many-electron systems cannot be exact for one-electron systems. This problem was evident long ago within LSD, and led Perdew and Zunger⁷⁴ to propose a self-interaction correction (SIC) to LSD or any other density functional approximation (DFA):

$$\begin{aligned} E_{xc}^{\text{SIC-DFA}}[n_\uparrow, n_\downarrow] &= E_{xc}^{\text{DFA}}[n_\uparrow, n_\downarrow] \\ &\quad - \sum_{i\sigma}^{\text{occ.}} (U[\tilde{n}_{i\sigma}] + E_{xc}^{\text{DFA}}[\tilde{n}_{i\sigma}, 0]), \end{aligned} \quad (20)$$

where $\tilde{n}_{i\sigma}(\mathbf{r}) = |\tilde{\phi}_{i\sigma}(\mathbf{r})|^2$ is the density of an occupied orbital (in general, not a Kohn-Sham orbital but some more localized orbital constructed to minimize the self-interaction corrected energy). The SIC of Eq. (20) properly vanishes when the original density functional approximation is exact. This feature seems to be absent from a recently proposed alternative self-interaction correction to the one-electron potential.^{79,80}

The Perdew-Zunger SIC has a long history of striking successes and failures.⁸¹⁻⁸³ It appears that elimination of self-interaction error is often important, but that Eq. (20) is not necessarily the best way to achieve this. In chemical applications, for example, the GGA seems to need only about 40%⁸⁴ of the self-interaction correction presented in Eq. (20) (although a simple scaling by 0.4 produces a functional that is no longer exact for one-electron densities). The results of SIC calculations of reaction barriers show us that a scaling factor of 0.5-0.7 is needed, depending on the reaction type and functional.^{66,85} A systematic thermochemical study⁸⁶ shows that the Perdew-Zunger SIC indeed overcorrects beyond-LSD functionals.

There are also formal problems with Eq. (20). If we find localized orbitals for a uniform density, our SIC functional will no longer be exact in the uniform or slowly-varying density limit. But if we find delocalized orbitals

for a uniform density, then Eq. (20) will produce a “false surface energy”⁸¹ for any finite jellium system.

An alternative self-interaction correction⁸⁷ that avoids these formal difficulties while scaling down the self-interaction correction for many-electron densities is found by introducing an effective orbital density at \mathbf{r}' for an electron of spin σ at \mathbf{r} , i.e.,

$$n_{\mathbf{r}\sigma}(\mathbf{r}') \equiv -n_{\mathbf{x}}^{\sigma}(\mathbf{r}, \mathbf{r}'), \quad (21)$$

where $n_{\mathbf{x}}^{\sigma}(\mathbf{r}, \mathbf{r}')$ is the exact exchange hole density, and noting that $0 \leq \tau_{\sigma}^W/\tau_{\sigma} \leq 1$, where τ_{σ} is defined by Eq. (10) and $\tau_{\sigma}^W = |\nabla n_{\sigma}|^2/8n_{\sigma}$ is the von Weizsäcker kinetic energy density:

$$E_{\text{xc}}^{\text{SIC-DFA}}[n_{\uparrow}, n_{\downarrow}] = E_{\text{xc}}^{\text{DFA}}[n_{\uparrow}, n_{\downarrow}] - \sum_{\sigma} \int d^3r \left(\frac{\tau_{\sigma}^W}{\tau_{\sigma}} \right)^k n_{\sigma}(\mathbf{r}) \{U[n_{\mathbf{r}\sigma}] + E_{\text{xc}}^{\text{DFA}}[n_{\mathbf{r}\sigma}, 0]\}, \quad (22)$$

where

$$U[n_{\mathbf{r}\sigma}] = \frac{1}{2} \int d^3r' \int d^3r'' \frac{n_{\mathbf{r}\sigma}(\mathbf{r}')n_{\mathbf{r}\sigma}(\mathbf{r}'')}{|\mathbf{r}'' - \mathbf{r}'|} \quad (23)$$

and $E_{\text{xc}}^{\text{DFA}}[n_{\mathbf{r}\sigma}, 0]$ involves integration over \mathbf{r}' . For any one-electron density of spin σ , $\tau_{\sigma}^W/\tau_{\sigma} = 1$ and $n_{\mathbf{r}\sigma}(\mathbf{r}') = n_{\sigma}(\mathbf{r}') = n(\mathbf{r}')$. To preserve the correct slowly-varying limit requires $k \geq 3$ when the DFA is the TPSS meta-GGA. Within TPSS, the correlation contribution to Eq. (22) vanishes. We must have $k \geq 2$ for the PBE GGA and $k \geq 1$ for LSD.

Because $n_{\mathbf{r}\sigma}(\mathbf{r}')$ of Eq. (21), $n_{\sigma}(\mathbf{r})$, and $\tau_{\sigma}(\mathbf{r})$ are invariant under a unitary transformation of the occupied orbitals, no localizing transformation is needed in the implementation of the SIC-DFA of Eq. (22). Moreover, the effective one-electron Hamiltonian (with a non-multiplicative potential) for Eq. (22) is self-adjoint and its canonical orbitals are orthonormal. Although Eq. (22) may not be easy to implement, it has these interesting and promising formal properties in common with the meta- and hyper-GGAs.

Why think about a self-interaction correction to the meta-GGA when the hyper-GGA will be exact for any one-electron density? One answer is that the Perdew-Zunger SIC of Eq. (20) provides a nearly correct description of fractional particle number in a many-electron open system,⁸⁸ and this good description is not guaranteed in the hyper-GGA, which could thereby fail (like LSD, GGA and meta-GGA) to describe charge transfer correctly.

VIII. OTHER ISSUES

A good density functional for the exchange-correlation energy should produce a realistic integrated energy and a realistic electron density. There is no reason to expect it to produce any given energy density, since the energy density is neither physical nor unique, although it can be

useful for other purposes.^{89–91} Energy density may be an issue for local hybrids⁶⁰ and hyper-GGAs.^{10,59}

There is also no reason to expect the Kohn–Sham determinant to display all the symmetries of the true wave function. Symmetry breaking in the spin densities is more disturbing,⁹² but often has a simple physical interpretation.⁹³ Nor does a good density functional need to produce the spin resolution of the correlation energy into $\uparrow\uparrow$, $\downarrow\downarrow$, and $\uparrow\downarrow$ contributions. In fact, a widely-used spin resolution is incorrect⁹⁴ in the uniform-density limit.

An interesting recent development is the appearance of tractable nonlocal density functionals that include the long-range van der Waals interaction.⁹⁵ It remains to be seen if those functionals can be merged with the various functionals on the first four rungs of Jacob’s ladder.

We also note in passing that the orbitals that minimize the meta-GGA energy belong to a self-adjoint but non-multiplicative effective one-electron Hamiltonian. However, it seems to make little energetic difference if one uses instead a multiplicative optimized effective potential^{96,97} or even the PBE GGA potential. At the same time, proper inclusion of exact exchange into the Kohn–Sham scheme via a multiplicative potential greatly improves the accuracy of single-particle spectra⁹⁸ and is expected to be important for time-dependent and excited-state applications.

IX. CONCLUSIONS

We have argued that density functional approximations should be constructed nonempirically via the satisfaction of known exact constraints (valid for all densities or for a large class of them), and that the uniform density limit in particular is a logically required constraint. We realize that this nonempirical construction is a slow and uncertain process, and that for certain systems and properties the users will want to employ semiempirical or fitted functionals. In such cases, we recommend functionals that are correct for the uniform electron gas and contain few fitted parameters, such as the PBE0 or TPSSH hybrids. Even then, we believe that results should also be reported for the nonempirical functionals like LSD, PBE GGA, and TPSS meta-GGA, as a measure of how much we really understand and what remains to be understood.

We close with some general “do’s and don’t’s”. Software developers should take care to program and document density functionals correctly, and to update their codes with significant new functionals. Superseded functionals (in the sense that PW86^{32,33} and PW91³⁴ are superseded by PBE⁹) should be allowed to retire gradually. Users should not randomly mix and match functionals, but should use exchange and correlation pieces designed to work together, with their designer-recommended local parts. They should not shop indiscriminately for the functional that “works best”. Users should always say which functional they used, with its proper name and literature reference, and why they chose it. Statements

like “we used density functional theory” or “we used the generalized gradient approximation” are almost useless to a reader or listener who wants to reproduce the results.

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