Jacob's ladder of density functional approximations for the exchange-correlation energy

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Jacob's Ladder of Density Functional Approximations
for the Exchange-Correlation Energy

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Abstract. The ground-state energy and density of a many-electron system are often calculated by Kohn-Sham density functional theory. We describe a ladder of approximations for the exchange-correlation energy as a functional of the electron density. At the lowest rung of this ladder, the contribution to the energy from a volume element of 3-dimensional space is determined by the local density there. Higher rungs or levels incorporate increasingly complex ingredients constructed from the density or the Kohn-Sham orbitals in or around this volume element. We identify which additional exact conditions can be satisfied at each level, and discuss the extent to which the functionals at each level may be constructed without empirical input. We also discuss the research that remains to be done at the exact-exchange level, and present our "dreams of a final theory".

"Jacob left Beer-sheba and went toward Haran. He came to a certain place and stayed there for the night, because the sun had set. Taking one of the stones of the place, he put it under his head and lay down in that place. And he dreamed that there was a ladder set up on the earth, the top of it reaching to heaven; and the angels of God were ascending and descending on it."

<div align="right">Genesis 28.10-12</div>

INTRODUCTION

Kohn-Sham density functional theory [1–5] provides practical estimates for the ground-state energy and electron density of a many-electron system such as an atom, molecule or solid. In particular, it can predict the sizes and shapes of molecules, the crystal structures of solids, and the work required to stretch or break chemical bonds.

The systems of interest typically have Hamiltonians of the form

$$\hat{H} = \sum_{i=1}^{N}\left[-\frac{1}{2}\nabla_i^2 + v(\mathbf{r}_i)\right] + \frac{1}{2}\sum_i\sum_{i\neq j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + V_{nn}\ , \tag{1}$$

where V_{nn} is the electrostatic potential energy of interaction among the nuclei. We use Hartee atomic units with $\hbar = e^2 = m = 1$. The external potential $v(\mathbf{r})$ is usually the electrostatic interaction between electrons and nuclei. The ground-state eigenfunction of $\hat{H}$ is a correlated N-electron wavefunction, a function of 3N arguments whose evaluation and storage is computationally problematical for large systems [2]. Kohn-Sham density functional theory proves that the ground-state spin densities $n_\sigma(\mathbf{r})$ ($\sigma = \uparrow$ or $\downarrow$) and energy E can be found (in principle exactly) by solving instead a self-consistent *one-electron* Schrödinger equation for N orbitals $\psi_{\alpha\sigma}(\mathbf{r})$, each a function of only 3 arguments $\mathbf{r} = (x, y, z)$. The self-consistent orbitals are themselves implicit functionals of $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$.

The Kohn-Sham equations are

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} + v_{xc}^\sigma(\mathbf{r}) \right] \psi_{\alpha\sigma}(\mathbf{r}) = \varepsilon_{\alpha\sigma} \psi_{\alpha\sigma}(\mathbf{r}) \ , \tag{2}$$

$$n(\mathbf{r}) = n_\uparrow(\mathbf{r}) + n_\downarrow(\mathbf{r}) \ , \tag{3}$$

$$n_\sigma(\mathbf{r}) = \sum_\alpha \Theta(\mu - \varepsilon_{\alpha\sigma}) \left| \psi_{\alpha\sigma}(\mathbf{r}) \right|^2 \ , \tag{4}$$

$$E = \sum_\sigma \int d\mathbf{r}\, \tau_\sigma(\mathbf{r}) + \int d\mathbf{r}\, n(\mathbf{r}) v(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} + E_{xc}[n_\uparrow, n_\downarrow] + V_{nn} \ , \tag{5}$$

$$\tau_\sigma(\mathbf{r}) = \sum_\alpha \Theta(\mu - \varepsilon_{\alpha\sigma}) \frac{1}{2} \left| \nabla \psi_{\alpha\sigma}(\mathbf{r}) \right|^2 \ , \tag{6}$$

$$v_{xc}^\sigma(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n_\sigma(\mathbf{r})} \ . \tag{7}$$

In Eqs. (4) and (6), the chemical potential μ is adjusted to make $\int d\mathbf{r}\, n(\mathbf{r}) = N$. The fermion occupation numbers are given by the step function $\Theta(x)$ (0 for $x < 0$, and 1 for $x \geq 0$).

If we neglect the exchange-correlation energy E_{xc} and its functional derivative $\delta E_{xc}/\delta n_\sigma(\mathbf{r})$ (the exchange-correlation potential), these are just the Hartree equations without self-interaction correction. If we neglect the correlation energy E_c in $E_{xc} = E_x + E_c$, but treat the exchange energy E_x exactly, these are the equations of the exchange-only optimized effective potential method [6], a variant of Hartree-Fock theory in which the exchange potential $v_x^\sigma(\mathbf{r}) = \delta E_x/\delta n_\sigma(\mathbf{r})$ is a multiplication operator in position space. The exact exchange energy is

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$$E_x = \int d\mathbf{r}\, n(\mathbf{r})\, \varepsilon_x(\mathbf{r}) \ , \tag{8}$$

$$n(\mathbf{r})\, \varepsilon_x(\mathbf{r}) = -\frac{1}{2} \sum_\sigma \int d\mathbf{r}\,' \frac{|\rho_\sigma(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \ , \tag{9}$$

where

$$\rho_\sigma(\mathbf{r}, \mathbf{r}') = \sum_\alpha \Theta(\mu - \varepsilon_{\alpha\sigma}) \psi_{\alpha\sigma}^*(\mathbf{r}) \psi_{\alpha\sigma}(\mathbf{r}') \tag{10}$$

is the Kohn-Sham one particle density matrix.

For the purpose of describing cohesion among atoms, neither the Hartree approximation (which neglects E_{xc}) nor the Hartree-Fock approximation (which neglects the correlation energy E_c) can compete with even the simplest density functional approximation for E_{xc} (see Table 1). The exchange-correlation energy is "nature's glue" [7], without which cohesion would be far weaker than it really is.

A formally-exact expression for $E_{xc}[n_\uparrow, n_\downarrow]$ is the double integral [8–10]

$$E_{xc} = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}\,' n(\mathbf{r}) \frac{\bar{n}_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} = E_x + E_c \ . \tag{11}$$

We introduce a coupling constant α which varies from $\alpha = 1$ for the real interacting system to $\alpha = 0$ for the Kohn-Sham noninteracting system. Then

$$\bar{n}_{xc}(\mathbf{r}, \mathbf{r}') = \int_0^1 d\alpha\, n_{xc}^\alpha(\mathbf{r}, \mathbf{r}') = n_x(\mathbf{r}, \mathbf{r}') + \bar{n}_c(\mathbf{r}, \mathbf{r}') \tag{12}$$

is the average over the coupling constant α of the density at $\mathbf{r}'$ of the exchange-correlation hole about an electron at $\mathbf{r}$:

$$n_{xc}^\alpha(\mathbf{r}, \mathbf{r}') = \frac{< \Psi_\alpha | \hat{n}(\mathbf{r})\, \hat{n}(\mathbf{r}') | \Psi_\alpha >}{n(\mathbf{r})} - \delta(\mathbf{r} - \mathbf{r}') \ , \tag{13}$$

and $n_x(\mathbf{r}, \mathbf{r}') = n_{xc}^{\alpha=0}(\mathbf{r}, \mathbf{r}')$ is the exchange hole. Here Ψ_α is the ground-state wavefunction for a system with the same spin densities $n_\sigma(\mathbf{r}) = < \Psi_\alpha | \hat{n}_\sigma(\mathbf{r}) | \Psi_\alpha >$ as the real system but with the electron-electron interaction reduced by the factor α (and with the external potential adjusted from $v(\mathbf{r})$ to $v_\alpha(\mathbf{r})$). Because of electron number conservation, the Pauli exclusion principle, and Coulomb repulsion, each electron digs a hole around itself, and the hole density satisfies the sum rule

$$\int d\mathbf{r}\,' n_{xc}^\alpha(\mathbf{r}, \mathbf{r}') = -1 \ . \tag{14}$$

Eqs. (11) - (13), which require correlated wavefunctions Ψ_α, have conceptual but not practical utility. The real usefulness of density functional theory arises from the possibility of making simple but accurate approximations for the functional $E_{xc}[n_\uparrow, n_\downarrow]$, and of refining these approximations. For a compilation of approximations, see the Website http://www.centrcn.umontreal.ca/~casida.

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Here we shall discuss a hierarchy of density functional approximations for E_{xc}, stretching from the simplest to the most sophisticated. Let us write
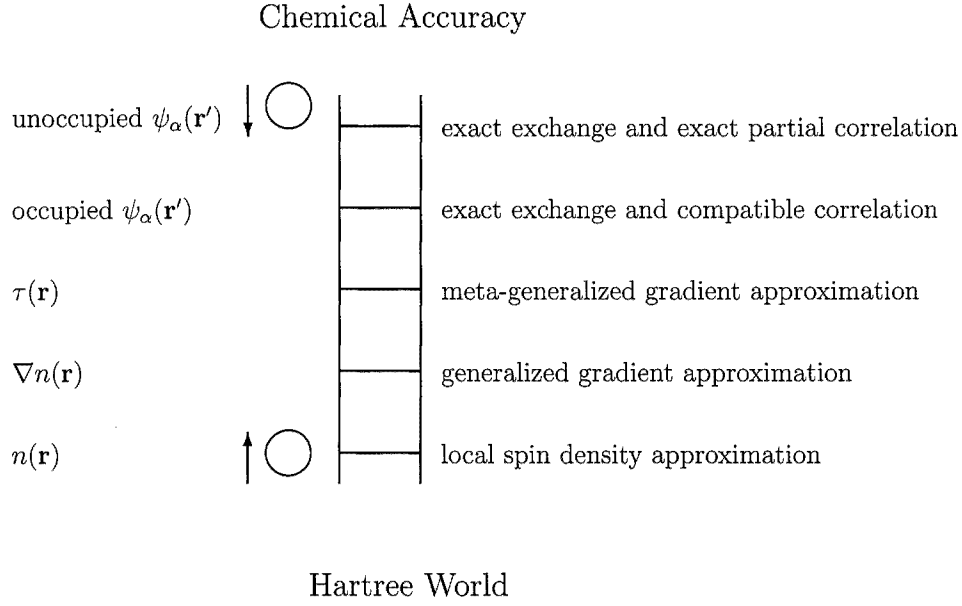
$$E_{xc}[n_\uparrow, n_\downarrow] = \int d\mathbf{r}\, n(\mathbf{r})\, \varepsilon_{xc}([n_\uparrow, n_\downarrow]; \mathbf{r}) \quad , \tag{15}$$

where the integrand $n\varepsilon_{xc}$ is an exchange-correlation energy density, and ε_{xc} is an exchange-correlation energy per electron. Our hierarchy is ordered by the use of increasingly complex ingredients to construct $\varepsilon_{xc}([n_\uparrow, n_\downarrow]; \mathbf{r})$. At the lowest level, we use the local densities $n_\uparrow(\mathbf{r})$, $n_\downarrow(\mathbf{r})$. At the next level, we add the density gradients $\nabla n_\uparrow(\mathbf{r})$ and $\nabla n_\downarrow(\mathbf{r})$. Still more ingredients, including those constructed from the Kohn-Sham orbitals $\psi_{\alpha\sigma}$ in or around the volume element $d\mathbf{r}$, are added at higher levels. Each added ingredient makes it possible to satisfy additional exact or nearly-exact formal properties of $E_{xc}[n_\uparrow, n_\downarrow]$, and we shall also discuss which conditions can be satisfied at each level. The higher levels are typically (but not uniformly) more accurate and more computationally demanding than the lower ones. At each level, we follow a reductionist agenda: to derive the density functional from the principles of quantum mechanics by satisfying as many exact conditions as we can, and to rely as little as possible upon fitting to experimental data. At the lower and higher levels of our hierarchy (but not at the intermediate ones), we have constructed the functionals without empirical fitting (although of course with an eye on the agreement between theory and experiment).

Some of the intermediate and higher levels of the hierarchy (in particular, some of these making use of exact exchange) are still incomplete, and for these we discuss possibilities for further research. In the final section of the paper, we suggest a way in which our reductionist approach might be complemented by the alternative empiricist approach to density functional construction, and present our "dreams of a final theory".

Our hierarchy of density approximations is a kind of ladder (Fig. 1) lifted up to the goal of "chemical accuracy", the accuracy needed to predict the rates of chemical reactions (energy errors of the order of 1 kcal/mol= 0.0434 eV). Each rung incorporates the design elements of the lower rungs, and more. When we climb to a higher rung, we do not kick away the lower rungs, which retain their value and importance. The accuracy and sophistication of the higher rungs is complemented by the simplicity and transparency of the lower ones. Users are free to choose the rungs appropriate to their accuracy requirements and computational resources. Users could help developers by reporting their results not only at the chosen level but at all lower ones, for comparison.

Although for simplicity we show and discuss only five rungs of Jacob's ladder, other rungs might be added for explicit fully-nonlocal functionals of the density [11], for self-interaction corrections [12], etc.

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Chemical Accuracy

unoccupied $\psi_\alpha(\mathbf{r}')$ exact exchange and exact partial correlation

occupied $\psi_\alpha(\mathbf{r}')$ exact exchange and compatible correlation

$\tau(\mathbf{r})$ meta-generalized gradient approximation

$\nabla n(\mathbf{r})$ generalized gradient approximation

$n(\mathbf{r})$ local spin density approximation

Hartree World

FIGURE 1. Jacob's ladder of density functional approximations. Any resemblance to the Tower of Babel is purely coincidental. Also shown are angels in the spherical approximation, ascending and descending. Users are free to choose the rungs appropriate to their accuracy requirements and computational resources. However, at present their safety can be guaranteed only on the two lowest rungs.

LOCAL SPIN DENSITY APPROXIMATION

The mother of all approximations is the local spin density (LSD) approximation of Kohn and Sham [1]:

$$E_{xc}^{LSD}[n_\uparrow, n_\downarrow] = \int d\mathbf{r}\, n(\mathbf{r})\, \varepsilon_{xc}^{unif}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})) \ , \tag{16}$$

where $\varepsilon_{xc}^{unif}(n_\uparrow, n_\downarrow)$ is the exchange-correlation energy per particle of an electron gas with uniform spin densities $n_\uparrow$ and $n_\downarrow$. $\varepsilon_{xc}^{unif}(n_\uparrow, n_\downarrow)$ is accurately known [13,14] and parametrized [12,15,16]. The exchange contribution to LSD is the Xα ($\alpha = 2/3$) energy [17].

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By construction, Eq. (16) is exact for spin densities $n_\sigma(\mathbf{r})$ that vary slowly over space. The approximation is also manifestly size-consistent, i.e., it predicts that the total energy of a collection of well-separated densities is the sum of the separate energies [18]. Failures of size-consistency can pose problems for certain quantum chemical methods.

LSD proved to be a surprisingly accurate approximation for solids and solid surfaces, including those with rapid density variations. Eventually it was realized that this fact is a consequence of exact properties which LSD inherits from the uniform electron gas, a possible many-electron system with an external potential $v(\mathbf{r})$.

First of all, the LSD exchange-correlation hole satisfies the sum rule of Eq. (14), which helps to hold the LSD energy to realistic values [8–10]. In fact, the spherical LSD hole, $\bar{n}_{xc}^{LSD}(\mathbf{r}, u) = \bar{n}_{xc}^{unif}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r}); u)$ where $u = |\mathbf{r}' - \mathbf{r}|$, is a fair model for the spherical average $n_{xc}(\mathbf{r}, u)$ of the true hole around its electron in an atom or molecule , and the energy integral

$$\varepsilon_{xc} = \frac{1}{2} \int_0^\infty du\, 4\pi\, u^2\, \bar{n}_{xc}(\mathbf{r}, u) \frac{1}{u} \tag{17}$$

is usefully constrained by the sum rule

$$\int_0^\infty du\, 4\pi\, u^2\, \bar{n}_{xc}(\mathbf{r}, u) = -1 \ . \tag{18}$$

The LSD exchange hole satisfies the exact negativity constraint [19]

$$n_x(\mathbf{r}, u) \leq 0 \ . \tag{19}$$

The LSD hole also satisfies the exact cusp condition [20]

$$\left. \frac{d}{du} n_{xc}^\alpha(\mathbf{r}, u) \right|_{u=0} = \alpha\, [n(\mathbf{r}) + n_{xc}^\alpha(\mathbf{r}, u = 0)] \ . \tag{20}$$

Although the LSD "on-top" hole density $n_{xc}^\alpha(\mathbf{r}, u = 0)$ is not exact [21] for all α, it is exact at $\alpha = 0$ and accurate for all α in a "normal" system [20]. Because the exact on-top exchange hole density $n_x(\mathbf{r}, u = 0) = n_{xc}^{\alpha=0}(\mathbf{r}, u = 0)$ is fixed by the local spin densities $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$ [22], it is given exactly by LSD; this is the reason why in practice one needs to construct the energy from the spin densities for an open-shell system in a spin-independent external potential, even though the formal theory says that in this case only the total density $n = n_\uparrow + n_\downarrow$ is needed in principle [1]. Moreover, in some systems spurious spin polarization can simulate strong correlation [23].

Second, the LSD exchange energy respects the exact spin-scaling relation [24]

$$E_x[n_\uparrow, n_\downarrow] = \frac{1}{2} E_x[2n_\uparrow] + \frac{1}{2} E_x[2n_\downarrow] \ , \tag{21}$$

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where $E_x[n] = E_x[\frac{n}{2}, \frac{n}{2}]$, and an exact uniform-density-scaling relation [25]: If

$$n(\mathbf{r}) \rightarrow n_\gamma(\mathbf{r}) \equiv \gamma^3 n(\gamma \, \mathbf{r}) \ , \tag{22}$$

then

$$E_x[n] \rightarrow E_x[n_\gamma] = \gamma E_x[n] \ . \tag{23}$$

And the LSD correlation energy scales properly in the low-density limit [26] :

$$E_c[n_\gamma] \rightarrow \gamma E_c[n] \quad \text{as} \quad \gamma \rightarrow 0 \ . \tag{24}$$

Third, LSD obeys the Lieb-Oxford lower bound [26–28]

$$0 \geq E_x[n_\uparrow, n_\downarrow] \geq E_{xc}[n_\uparrow, n_\downarrow] \geq -1.679 \int \mathrm{d}\mathbf{r} \, n^{4/3}(\mathbf{r}) \ . \tag{25}$$

(A slightly closer lower bound has been derived recently [29].)

Fourth, LSD gives a good description of the linear response of the density of a uniform electron gas to a weak static perturbing potential, for typical valence densities in metals [30].

Finally, we observe that LSD is almost always a better approximation for E_{xc} than it is for E_x or E_c separately. The exchange energy and the correlation energy have opposing nonlocalities which tend to cancel when both are approximated in the same way, as they are in LSD. It is no surprise that E_{xc} is more local than E_x: $\bar{n}_{xc}(\mathbf{r}, u)$ is deeper at $u \sim 0$ than is $n_x(\mathbf{r}, u)$ and thus by the sum rule (14) more short-ranged in u. Only a short-ranged hole can be described by the local density at $\mathbf{r}$.

GENERALIZED GRADIENT APPROXIMATION

LSD has been a standard approximation in solid state physics since the early 1970's, but was never popular with the majority of quantum chemists. Jones and Gunnarsson [3] and others demonstrated that LSD yields reasonable molecular geometries and vibration frequencies, but can strongly overestimate atomization energies (Table 1). The atomization energy errors were greatly reduced (Table 1) by the generalized gradient approximation (GGA) [19,28,31–38]

$$E_{xc}^{GGA}[n_\uparrow, n_\downarrow] = \int \mathrm{d}\mathbf{r} \, n(\mathbf{r}) \, \varepsilon_{xc}^{GGA}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r}), \nabla n_\uparrow(\mathbf{r}), \nabla n_\downarrow(\mathbf{r})) \ , \tag{26}$$

leading to the adoption of GGA as a standard quantum-chemical method in the 1990's.

For spin densities that vary slowly over space, the leading correction to LSD yields the second-order gradient correction approximation (GE2) [1]. Because of the spin-scaling relation (21) for the exchange energy, we only need

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$$E_x^{GE2}[n] = \int \mathrm{d}\mathbf{r} \left[n\,\varepsilon_x^{unif}(n) + C_x \frac{|\nabla n|^2}{n^{4/3}} \right] \ , \tag{27}$$

where C_x is a negative constant [39,40]. After some simplification [41] of the spin-dependence [42], the correlation energy is

$$E_c^{GE2}[n_\uparrow, n_\downarrow] = \int \mathrm{d}\mathbf{r} \left[n\,\varepsilon_x^{unif}(n_\uparrow, n_\downarrow) + \phi(\zeta)\,C_c(n) \frac{|\nabla n|^2}{n^{4/3}} \right] \ , \tag{28}$$

where $\zeta = (n_\uparrow - n_\downarrow)/n$, $\phi(\zeta) = \left[(1+\zeta)^{2/3} + (1-\zeta)^{2/3} \right]/2$, and $C_c(n)$ is a weak function of the density which tends in the high-density limit to the positive constant $C_c(\infty) = 4.235 \times 10^{-3}$ [31,43,44]. Henceforth, we take $C_c(n) = C_c(\infty)$.

For realistic densities, GE2 provides a serious overcorrection to LSD. For example, the correlation energies of atoms, which are too negative by about 100 % in LSD, are improperly positive in GE2 [31]. The fact that GE2 is worse than LSD for realistic densities demonstrates the importance of exact constraints other than the slowly-varying limit. Clearly we need a generalization of the gradient expansion which will reduce to Eqs. (27) and (28) *only* for small density gradients.

Langreth and Perdew [44] examined the second-order gradient expansion of the correlation hole and found that it violates the exact sum rule

$$\int_0^\infty \mathrm{d}u\, 4\pi\, u^2\, \bar{n}_c(\mathbf{r}, u) = 0 \ . \tag{29}$$

Later Perdew [19] found that the gradient expansion of the exchange hole density is not everywhere negative, in violation of Eq. (19). Cutoffs [28,45] of the spurious large-u contributions can be made to restore the exact properties of the holes, and the resulting numerically-defined GGA can be parametrized to satisfy exact conditions. This is a nonempirical construction. Moreover, the parametrization of Perdew, Burke, and Ernzerhof (PBE) [38] does not introduce any parameters (other than those in LSD) which are not fundamental constants.

The cutoff procedure seems to work more naturally for correlation than for exchange. For the correlation energy, the cutoff procedure recovers Eq. (28) in the slowly-varying limit, as does the PBE parametrization of it. Both the cutoff procedure and the PBE parametrization satisfy the condition $E_c \le 0$, and also the high-density limit for uniform scaling [46,47]

$$E_c[n_\gamma] \to \text{constant as} \quad \gamma \to \infty \tag{30}$$

(while LSD yields a $\ln \gamma$ term in this limit). For particles with Coulomb interactions, the high-density limit is also the weak-interaction limit.

For exchange, the cutoff procedure does not recover the form of Eq. (27) for small gradients, but can still be represented fairly well [45] by this form with the choice $C_x = -C_c(\infty)$, which has the advantage that it preserves the good LSD description of the linear response [48] of a uniform electron gas at metallic densities. So far as

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we know, *every* good formal property of LSD is preserved by the PBE GGA. The approximate cancellation between the nonlocalities of exchange and correlation is manifest in the PBE GGA (see Fig. 1 of Ref. [38]).

There are also exact *nonuniform* density scaling conditions [47], which are important in the limit where a three-dimensional density is collapsed to a true two- or one-dimensional density [49,50]. These conditions are satisfied by the PBE GGA for correlation, but not for exchange – another indication that the cutoff construction works better for the former than for the latter.

META-GENERALIZED GRADIENT APPROXIMATION

The Kohn-Sham kinetic energy densities $\tau_\sigma(\mathbf{r})$ of Eq. (6) are implicit functionals of the spin densities $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$, like the Kohn-Sham orbitals from which they are constructed. From several points of view [51–56], $\tau_\uparrow(\mathbf{r})$ and $\tau_\downarrow(\mathbf{r})$ are natural ingredients of E_{xc}. Thus, beyond the GGA lies the meta-generalized gradient approximation (MGGA):

$$E_{xc}^{MGGA}[n_\uparrow, n_\downarrow] = \int d\mathbf{r}\, n\, \varepsilon_{xc}^{MGGA}(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow, \tau_\uparrow, \tau_\downarrow) \ . \tag{31}$$

MGGA's [57–61] can also make use of the Laplacians $\nabla^2 n_\uparrow$ and $\nabla^2 n_\downarrow$, but we shall not consider this possibility here.

The meta-GGA level is the highest level of our hierarchy which avoids full non-locality, e.g., the computationally-demanding requirement for a second integral:

$$\varepsilon_{xc}^{nonlocal}(\mathbf{r}) = \int d\mathbf{r}'\, f(\mathbf{r}, \mathbf{r}') \ . \tag{32}$$

LSD, which constructs $\varepsilon_{xc}(\mathbf{r})$ from $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$, is a *local* functional of the density, since it requires only the density at $\mathbf{r}$. GGA is a *semi-local* functional of the density, since it requires the density in an infinitesimal neighborhood around $\mathbf{r}$. Meta-GGA is a fully nonlocal functional of the density, but a semilocal functional of the orbitals; thus in a Kohn-Sham calculation it is not computationally much more demanding than GGA.

By adding $\tau_\uparrow(\mathbf{r})$ and $\tau_\downarrow(\mathbf{r})$ to our ingredients list, we can test [54] to see if a point $\mathbf{r}$ lies in a one-electron region of space, where ε_c should vanish [12]: A one-electron region has only one of the two spin densities (say, $n_\sigma(\mathbf{r})$) nonzero, and also has

$$\tau_\sigma(\mathbf{r}) = \frac{1}{8} \frac{|\nabla n_\sigma(\mathbf{r})|^2}{n_\sigma(\mathbf{r})} \qquad \text{(one electron)} \ . \tag{33}$$

Thus we can construct a self-correlation-free meta-GGA [57–61], satisfying the exact condition [12]

$$E_c[n, 0] = 0 \qquad \text{(one electron)} \tag{34}$$

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for any density such that $\int d\mathbf{r}\, n(\mathbf{r}) = 1$.

Perdew, Kurth, Zupan, and Blaha (PKZB) [59] started from the PBE GGA and constructed from it a meta-GGA satisfying Eq. (34). They also observed that, for a slowly-varying density with $n_\uparrow = n_\downarrow = n/2$, $\tau = \tau_\uparrow + \tau_\downarrow$ has the second-order gradient expansion

$$\tau^{GE2} = \frac{3}{10}(3\pi^2)^{2/3} n^{5/3} + \frac{1}{72}\frac{|\nabla n|^2}{n} + \frac{1}{6}\nabla^2 n \ . \tag{35}$$

From this fact, they developed a meta-GGA for exchange which for a slowly-varying density has the fourth-order gradient expansion

$$E_x^{GE4}[n] = \int d\mathbf{r} \left[n\, \varepsilon_x^{unif}(n) + C_x \frac{|\nabla n|^2}{n^{4/3}} + \alpha_x \frac{|\nabla^2 n|^2}{n^2} + \beta_x \frac{|\nabla n|^2 \nabla^2 n}{n^3} + \gamma_x \frac{|\nabla n|^4}{n^4} \right] \ , \tag{36}$$

with the correct gradient coefficients $C_x = -2.382 \times 10^{-3}$ [40], $\alpha_x = -3.633 \times 10^{-5}$, [62], and $\beta_x = 9.083 \times 10^{-5}$ [63]. (Recall that even C_x was not correct in the PBE GGA). The unknown gradient coefficient γ_x introduces a free parameter which was fixed by fitting the atomization energies of 20 small molecules (Table 1).

The good GGA linear response of the density of a uniform electron gas at metallic densities is not destroyed by MGGA [64], nor are the correct formal properties.

Table 1 shows that MGGA atomization energies are more accurate than those of GGA [59,65]. Metal surface energies also seem to be more accurate [66]. Lattice constants for solids are mostly improved [61], but bond lengths of molecules can be worsened [65], especially for hydrogen bonds [67].

For realistic densities, the amount by which the GGA fails to satisfy Eq. (34) is small. But in the low-density ($n \to n_\gamma$ and $\gamma \to 0$) or strong-interaction limit, the self-correlation errors of both GGA and LSD are severe, producing an exaggerated instability against the formation of symmetry-breaking charge-density waves [68,69]. Meta-GGA, which is self-correlation free, should provide a much better description of this limit [70].

For the explicit density functionals LSD and GGA, it is straightforward to find the functional derivative of Eq. (7) and so perform self-consistent calculations. For the implicit density functionals (meta-GGA and all higher levels), the functional derivative can still be constructed, but only by a complicated process of averaging over the orbitals [6,71–73] to construct an optimized effective potential. In our initial tests at these higher levels, we can [74] and do avoid this averaging process by using LSD or GGA densities and orbitals. However, we expect that this averaging process would produce much more realistic exchange-correlation potentials, especially at the levels above meta-GGA.

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EXACT EXCHANGE AND COMPATIBLE CORRELATION

The exact exchange energy, Eqs. (8)-(10), is manifestly a fully nonlocal functional of the Kohn-Sham orbitals, in the sense of Eq. (32).

Becke [75,76] noticed that the lower limit of the coupling-constant integral (12) must mix some exact exchange into E_{xc}, and suggested hybrid density functionals of the form

$$E_{xc}^{hybrid} = E_{xc}^{GGA} + a\left(E_x^{exact} - E_x^{GGA}\right) \; , \tag{37}$$

where $a \approx 1/4$ was found by fitting the atomization energies. (There were also two other mixing parameters which are unimportant in the context of this discussion.) Subsequent work has explained [77–79] why $a = 1/4$ is nearly optimal, and excellent results have been found from this choice [80,81].

However, to satisfy the correct high-density scaling limit [25]

$$E_{xc}[n_\gamma]/E_x^{exact}[n_\gamma] \to 1 \qquad \text{as} \qquad \gamma \to \infty \; , \tag{38}$$

one needs to use 100% (not 25%) of exact exchange *and* a correlation energy functional satisfying Eq. (30). Exact exchange satisfies the self-interaction-free property [12]

$$E_x[n,0] + \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} = 0 \qquad \text{(one electron)} \tag{39}$$

for any one-electron density $n(\mathbf{r})$. Possible benefits of exact exchange [82–84] include improvements in derivative discontinuities [71,85] and a more accurate exchange-correlation potential, essential for a correct description of linear and nonlinear polarizabilities of large systems [86,87] as well as time-dependent and excited-state phenomena [88]. In particular, exact exchange yields the correct limit [12,71,85]

$$v_{xc}(\mathbf{r}) \to -\frac{1}{|\mathbf{r}|} + \text{constant as } |\mathbf{r}| \to \infty \tag{40}$$

for a finite system. Exact exchange is also expected to be important for sp and sd transfer energies [3] and core-valence interactions [89] in atoms.

To use exact exchange in this sense, we need a correlation energy functional which is compatible with it, in a way to be explained below. So far, the only compatible correlation energy functionals are the complicated ones that employ exact partial correlation. First we shall discuss three simpler choices; the first one fails in an instructive way, while the others are currently under study.

11

Exact Exchange and Meta-GGA Correlation

Exact exchange plus meta-GGA correlation (XXMC)

$$E_{xc}^{XXMC}[n_\uparrow, n_\downarrow] = E_x^{exact}[n_\uparrow, n_\downarrow] + E_c^{MGGA}[n_\uparrow, n_\downarrow] \tag{41}$$

satisfies every known exact condition, and works well for atoms, but fails badly for molecules (Table 1).

How can anything so right be so wrong? The answer is that the XXMC functional of Eq. (41) is unbalanced, treating exchange as a fully nonlocal functional of the orbitals and correlation as a semi-local one. In a molecule, the exact exchange hole around an electron on one atom can have a long-ranged component reaching into the other atom, which is nearly canceled by a compensating long-range component of the exact correlation hole. The semi-local meta-GGA for E_c cannot produce the required long-range component.

We suspect that a correlation energy functional compatible with exact exchange must be at least a nonlocal functional of the occupied Kohn-Sham orbitals, and we discuss two such functionals below.

Hyper-GGA

A hyper-GGA (HGGA) uses exact exchange, i.e.,

$$\varepsilon_x^{HGGA}(\mathbf{r}) = \varepsilon_x^{exact}(\mathbf{r}) \ , \tag{42}$$

and constructs $\varepsilon_c^{HGGA}(\mathbf{r})$ from the meta-GGA ingredients plus $\varepsilon_x(\mathbf{r})$ [90]. A possible form is

$$\varepsilon_c^{HGGA} = \varepsilon_c^{MGGA} + \left(\varepsilon_x^{MGGA} - \varepsilon_x^{exact}\right)\left[1 - e^{-\nu\left(\frac{\varepsilon_c^{MGGA}}{\varepsilon_x^{MGGA}}\right)}\right] \ , \tag{43}$$

where ν is a large positive number. In an exchange-dominated region of space, where $\varepsilon_c^{MGGA}/\varepsilon_x^{MGGA} \ll 1$, we find $\varepsilon_{xc}^{HGGA} \approx \varepsilon_x^{exact} + \varepsilon_c^{MGGA}$. Otherwise, we find $\varepsilon_{xc}^{HGGA} \approx \varepsilon_{xc}^{MGGA}$. HGGA has most of the correct formal properties of the XXMC functional of the previous section, but its correlation part is more compatible with exact exchange.

However, we must now confront the non-uniqueness of the energy density $n(\mathbf{r})\varepsilon_{xc}(\mathbf{r})$: the integrated energy E_{xc} is unchanged by the addition to the integrand of any function that integrates to zero. If and *only* if ε_x^{MGGA} corresponds to the same choice of energy density as ε_x^{exact}, then E_c^{HGGA} has the same correct second-order gradient expansion as E_c^{MGGA}. Studies of the exchange energy density are underway [90–95]. If necessary, we could replace $\varepsilon_x^{MGGA} - \varepsilon_x^{exact}$ in Eq. (43) by the difference between Burke's unambiguous energy densities [95] for MGGA and exact exchange.

12

Correlation Factor Model

In the correlation factor model (CFM) [96,97], ε_{xc} is found from Eq. (17) with

$$\bar{n}_{xc}^{CFM}(\mathbf{r}, u) = K_{xc}(\mathbf{r}, u)\, n_x^{exact}(\mathbf{r}, u) \ . \tag{44}$$

The correlation factor K_{xc} should be chosen to satisfy the sum rule of Eq. (18), to retain the good LSD on-top value and cusp, and to recover the correct exchange-correlation hole in the uniform density limit [98–101]. So long as $K_{xc} \to 0$ as $u \to \infty$ (as it does for the uniform electron gas), CFM correlation has a chance to be compatible with exact exchange.

Details remain to worked out. CFM is not computationally simple, because of its need for the spherical average of the exact exchange hole and because of the requirement to satisfy Eq. (18) at every point $\mathbf{r}$ in space.

EXACT EXCHANGE AND EXACT PARTIAL CORRELATION

We can write Eqs. (11)-(13) as

$$E_{xc}[n_\uparrow, n_\downarrow] = \int_0^1 d\alpha\, W_\alpha[n_\uparrow, n_\downarrow] \ . \tag{45}$$

For fixed spin-densities $n_\uparrow$ and $n_\downarrow$, the integrand W_α has a perturbation expansion [102,103]

$$W_\alpha[n_\uparrow, n_\downarrow] = E_x[n_\uparrow, n_\downarrow] + 2E_c^{GL2}[n_\uparrow, n_\downarrow]\,\alpha + \dots \ , \tag{46}$$

where E_c^{GL2} is the Görling-Levy second-order correlation energy. For atoms and molecules, E_c^{GL2} has been evaluated by several authors [73,77]. The explicit expression is

$$E_c^{GL2} = -\sum_{\nu=1}^{\infty} \frac{|\langle \Psi_0|\hat{V}_{ee} - \hat{V}_H - \hat{V}_x|\Psi_0^\nu\rangle|^2}{E_o^\nu - E_0} \ . \tag{47}$$

Here Ψ_0^ν is the ν-th exited state (Slater determinant) of the Kohn-Sham non-interacting N-particle Hamiltonian $\hat{H}_{KS}$ (with ground state Ψ_0), i.e., $\hat{H}_{KS}\Psi_0^\nu = E_0^\nu\Psi_o^\nu$; $\hat{V}_{ee} = \frac{1}{2}\sum_i\sum_{i\neq j}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}$ is the electron-electron repulsion, $\hat{V}_H = \sum_{i=1}^N \int d\mathbf{r}'\frac{n(\mathbf{r}')}{|\mathbf{r}'-\mathbf{r}_i|}$, and $\hat{V}_x = \sum_{i=1}^N v_x(\mathbf{r}_i)$. For other perturbation approaches, see Refs. [44] and [104–106].

The individual terms of Eq. (46) are nonlocal functionals of *all* the Kohn-Sham orbitals, unoccupied as well as occupied. Exact partial correlation evaluates one or more terms, or an infinite sub-series, from this series. We shall mention two approaches which have already been tested to some extent.

13

Interaction Strength Interpolation

Eq. (46) is the weak-interaction ($\alpha \to 0$) limit of density functional theory. The strong-interaction ($\alpha \to \infty$) limit is also known [107–109]:

$$W_\alpha[n] = W_\infty[n] + W'_\infty[n]\alpha^{-1/2} + \ldots \; , \tag{48}$$

where only the total density $n = n_\uparrow + n_\downarrow$ is needed. Rather accurate explicit density functional approximations for $W_\infty[n]$ and $W'_\infty[n]$ exist [70,109].

Seidl, Perdew and Kurth [109,110] proposed an interaction strength interpolation (ISI) between these two limits, and used it to find accurate atomization energies for molecules (Table 1). They also estimated the radius of convergence of density functional perturbation theory, finding it typically close to the physical value $\alpha = 1$.

The ISI correlation energy functional is clearly compatible with exact exchange. It yields the exact correlation energy in the high-density ($\gamma \to \infty$) limit, and also that for an ion of fixed electron number in the limit of infinite nuclear charge [111].

Random Phase Approximation Plus Corrections

In the uniform electron gas, and presumably in any bulk metal, the second-order correlation energy per electron (E_c^{GL2}/N) diverges, and sensible results from Eq. (46) can only be found by formally summing an infinite sub-series of terms, as in the density functional version [44] of the random phase approximation (RPA). More generally, formal summation is needed outside the radius of convergence of Eq. (46).

RPA (using Kohn-Sham and not Hartree orbitals) is believed to treat long-range correlation exactly, and thus to be compatible with exact exchange. RPA also gives most of the van der Waals interaction [112–114] between two well-separated densities, an interaction missed by lower levels of our hierarchy.

However, RPA is poor for short-range correlation. Short-range correlation can be incorporated into RPA-like equations through a local field factor [115,116], or added on via an explicit density functional.

Recently a GGA has been constructed for the short-range correlation energy correction to RPA [117], using the same cutoff procedure that earlier provided a GGA for the total correlation energy. This GGA short-range correction is a large part of the total correlation energy, but a surprisingly small part of iso-electronic energy changes such as the atomization energies of molecules. That fact suggests that a corrected RPA could achieve chemical accuracy for molecules. Early studies [118] (which may not be completely converged with respect to basis sets) suggest that the corrected RPA is at least as accurate as GGA for exchange and correlation.

We note that the method of RPA plus corrections has already been applied [66,117] to calculate the surface energy of the uniform electron gas, where it gives answers in close agreement with other sophisticated density functional methods such as meta-GGA exchange-correlation.

14

DREAMS OF A FINAL THEORY

Our approach to density functional construction is a reductionist one. It may be ambitious to try to "reduce" all of density functional theory to quantum mechanics, but this ambition is much more modest than, say, the attempt to reduce all of biology to physics.

There is an alternative empiricist school of density functional construction [58,119,120] which has made many valuable contributions. The idea here is to guess a functional form depending upon several (up to 20) parameters, and then to fit these parameters to a data set of accurate energies, energy differences or geometries. Typically atoms and molecules, but not solids, are included in the data set. For example, accurate experimental data for a variety of molecules were compiled by Pople and co-workers [121]. The guessed functional forms typically incorporate some exact constraints, but often overlook the uniform-gas or second-order gradient expansion limits.

In a recent study [61], several reductionist and empiricist functionals were compared in calculations of the properties of atoms, molecules, and solids. While the empiricist functionals were sometimes more accurate for atoms and molecules, the kind of system for which they are constructed, they gave rather bad results for solids. The reductionist functionals were more universal and more uniform in performance. The uniform-gas and second-order gradient expansion limits, which are of little importance for atoms and molecules, are definitely needed for solids. We claim that the distinction between quantum chemistry and solid state physics is an arbitrary one, and that there are many real systems which represent natural bridges between these two disciplines.

Some empirical functionals combine all of the ingredients from our hierarchy (except exact partial correlation). A recent study by Chan and Handy [120] suggests that no real improvement in the fit is achieved by making use of the kinetic energy density or mixing in some exact exchange energy. However, we stress that these ingredients *are* necessary if simple functionals are to satisfy the known exact constraints on $E_{xc}[n_\uparrow, n_\downarrow]$.

There is a way in which empiricism might complement reductionism. It is not clear that we can know in advance all the exact or approximate conditions on the functional $E_{xc}[n_\uparrow, n_\downarrow]$ that must be satisfied to constrain it adequately. There might be "emergent" or "pre-emergent" conditions that we cannot anticipate. But, if we impose all the conditions that we know on the form of the functional before fitting to a data set, we might see new conditions "emerge" from the fit.

We do not yet have a perfect ladder of density functional approximations, but like Jacob we have a dream of one. The perfect ladder would be constructed nonempirically, and would satisfy at each level all exact constraints appropriate to that level and lower ones.

The principle of balance or compatibility requires that an exchange energy functional at a given level be paired with a correlation energy functional at the same level. For example, we have seen how (and why) exact exchange should not be

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paired with meta-GGA correlation, even though this combination is nonempirical and respects essentially all known exact constraints. However, the constraints themselves do not have to be satisfied in a balanced way. For example, the correct second-order gradient coefficient for correlation is appropriate to the GGA level, but that for exchange may be only appropriate to the meta-GGA level.

We believe that the ladder is now complete at its two lowest levels. The higher levels are under active construction and testing.

Molecule	XX	LSD	GGA	MGGA	XXMC	ISI	exper.
H_2	84.0	113.2	104.6	114.5	112.7	107.3	109.5
LiH	33.9	61.0	53.5	58.4	57.7	58.8	57.8
CH_4	327.2	462.3	419.8	421.1	429.3	423.4	419.3
NH_3	199.5	337.3	301.7	298.8	288.8	300.9	297.4
OH	67.3	124.1	109.8	107.8	98.2	108.6	106.4
H_2O	154.6	266.5	234.2	230.1	215.0	235.7	232.2
HF	96.1	162.2	142.0	138.7	125.5	143.7	140.8
Li_2	3.5	23.9	19.9	22.5	20.8	22.5	24.4
LiF	86.8	156.1	138.6	128.0	111.3	142.7	138.9
Be_2	-11.0	12.8	9.8	4.5	-5.2	5.7	3.0
C_2H_2	290.6	460.3	414.9	401.2	384.4	-	405.4
C_2H_4	423.9	632.6	571.5	561.5	558.6	-	562.6
HCN	194.5	361.0	326.1	311.8	273.5	-	311.9
CO	169.2	299.1	268.8	256.0	218.2	265.9	259.3
N_2	110.2	267.4	243.2	229.2	175.3	234.6	228.5
NO	45.6	198.7	171.9	158.5	99.0	157.9	152.9
O_2	24.9	175.0	143.9	131.4	67.2	123.6	120.5
F_2	-43.3	78.2	53.4	43.2	-21.8	34.0	38.5
P_2	31.8	143.8	121.1	117.8	83.4	-	117.3
Cl_2	15.5	83.0	65.1	59.4	40.9	-	58.0
m.a.e.	74.0	31.7	7.9	3.1	23.9	3.5	-

TABLE 1. Atomization energies of 20 small molecules, in kcal/mol. (1 kcal/mol = 0.0434 eV.) The mean experimental atomization energy is 189.2 kcal/mol. The calculations are performed for non-vibrating molecules, so the contribution from the zero-point vibration has been removed from the experimental energies. All functionals were evaluated on GGA densities and energies at experimental geometries, and all symmetries were allowed to break. The last row shows the mean absolute error. The functionals tested are exact exchange and no correlation (XX), the local spin density (LSD) and generalized gradient approximations (GGA) [38], the meta-GGA (MGGA) [59], exact exchange plus meta-GGA correlation (XXMC), and the interaction strength interpolation (ISI) [109]. (sources: [61] and [109]).

ACKNOWLEDGMENTS

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