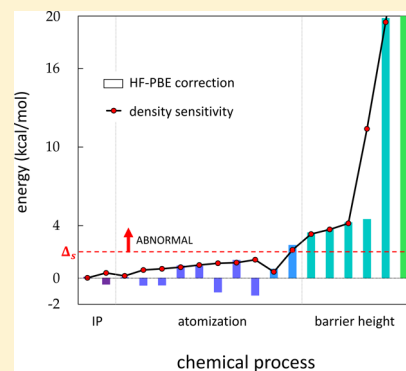


Quantifying Density Errors in DFT

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Supporting Information

ABSTRACT: We argue that any general mathematical measure of density error, no matter how reasonable, is too arbitrary to be of universal use. However, the energy functional itself provides a universal relevant measure of density errors. For the self-consistent density of any Kohn–Sham calculation with an approximate functional, the theory of density-corrected density functional theory (DC-DFT) provides an accurate, practical estimate of this ideal measure. We show how to estimate the significance of the density-driven error even when exact densities are unavailable. In cases with large density errors, the amount of exchange-mixing is often adjusted, but we show that this is unnecessary. Many chemically relevant examples are given.



The Kohn–Sham (KS) approach to density functional theory (DFT) has become very popular, being employed in more than 30 000 scientific papers each year.¹ However, its claim to being first-principles is diluted by the fact that there are literally hundreds of possible exchange–correlation approximations available in most codes.² Over many decades, many researchers have tried studying the self-consistent densities of DFT calculations to gain insight into the quality of approximations.^{3,4} This interest recently intensified with the publication of Medvedev et al.,⁵ which appears to show that the self-consistent densities of recent, empirically parametrized functionals are of poorer quality than those that are more systematically derived by careful comparison with accurate densities of atoms and ions. But their conclusions depend on their choice of how to measure the density error, which was designed to penalize incorrect oscillations in approximate densities. Other reasonable choices lead to other conclusions. Because the density is a function and not a number, the variety of possible error-measures that people can create is endless. We give many alternative measures, some of which produce starkly different rankings. Thus, statements such as “densities became closer to the exact ones” are entirely dependent on the choice of metric and because every researcher can choose their own are of limited value at best.

However, the variational principle provides a natural and unambiguous measure of the accuracy of a density for any system. Moreover, this metric is measured in terms of the resulting energy error. If errors in densities are so small that they have negligible impact on calculated energies, then they surely are not the most important indicator for improving functional approximation. The well-established theory behind density-corrected DFT (DC-DFT) was constructed precisely to measure this error for self-consistent densities from DFT calculations with approximate functionals. Here we show how

this can be done, or at least usefully estimated, even in the absence of the exact density. By measuring density errors via the energy, we find no evidence that empirical functionals yield greater density errors.

Begin with the general idea of measuring errors in densities. Whereas a single number characterizes the error in an approximate energy, the error in an approximate density, $\tilde{n}(\mathbf{r})$, can be quantified in infinitely many ways. For example, an intuitively appealing measure is the simple L2 norm

$$\Delta_{L2}[\tilde{n}] = \int d^3r (\tilde{n}(\mathbf{r}) - n(\mathbf{r}))^2 \quad (1)$$

where $n(\mathbf{r})$ is the exact density, and $N = \int d^3r n(\mathbf{r})$ is the number of electrons. Reference 5 looks at many different functionals (128) on a few very simple systems (14 small closed-shell atoms and ions) and constructs three different measures (a discretized Δ and analogs for gradients and Laplacians) that are combined in several ways to yield some measure of density error. However, the relative ranking strongly depends on the measure.

To understand why such a definition of density error does not suffice, Figure 1 shows the radial density error of three different approximations for the He atom. The exact reference density is from a highly accurate quantum Monte Carlo (QMC) calculation,⁶ and all results are converged to the basis set limit. Because we are only interested in general features, three approximations suffice to make our point. We show the error in the Hartree–Fock (HF) density, that of self-consistent PBE, and that of M11, a relatively recent Minnesota functional.

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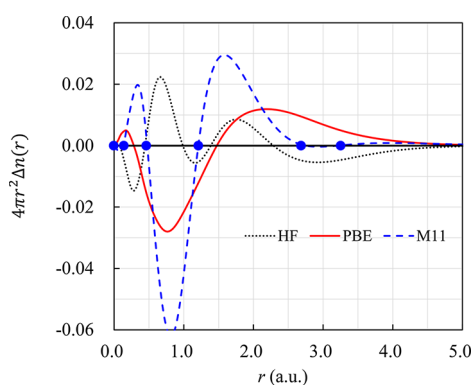


Figure 1. He atomic radial density error for HF (gray dotted), PBE (red solid), and M11 (blue dashed) relative to highly accurate quantum Monte Carlo density. Radii where the M11 density crosses the QMC density are marked with solid dots.

By the measures of ref 5, M11 has substantially worse densities than PBE and even HF, despite providing much better thermochemistry than the latter.

There are infinitely many possible choices of measure. To give an idea of the possible variety, note that the M11 density matches the exact density at 6 radial points. If we define our measure of error as

$$\Delta_{\text{RP}}[\tilde{n}] = \sum_{i=1}^6 (\tilde{n}(r_i) - n(r_i))^2 \quad (2)$$

where the sum is over the crossing points (marked by dots in Figure 1), then M11 has zero error, but all other approximations have finite errors (including PBE and HF in the figure); that is, it beats all 127 other functionals in the study if we apply this strategy to the 14 systems studied. But we could equally as well have taken the PBE crossing points, making it the winner, or indeed *any* of the 128 candidates. Whereas this example may appear facetious, it explicitly demonstrates that the rankings can be arbitrarily reordered. We could even include a 129th, namely, setting $E_{\text{XC}} = 0$ (Hartree approximation), and have it be the best.

One might claim that such measures are unreasonable, whereas using the ingredients of semilocal functional approximations is more reasonable. But the number of such combinations is endless, and other energy components, such as the KS kinetic energy or the Hartree energy, are also used in a KS calculation. In fact, the original approximate DFT, Thomas–Fermi theory, has been rigorously proven to yield relatively exact energies for all systems⁷ despite never producing the correct density pointwise in a certain limit of large particle number. As that limit is approached, the density develops an ever more rapid oscillation (shell structure) that such reasonable measures penalize. The same has been argued for the local density approximation (LDA)⁸ within KS-DFT,⁹ and even the ionization energies of atoms appear to become relatively exact in this limit.¹⁰ In all of these cases, the approximate functional derivatives (potentials) miss the shell structure with corresponding oscillating errors in the densities (figure 4 of ref 10).

There have been many responses and follow-up analyses to ref 5, and we highlight only a few. In a technical comment, Kepp shows that errors in approximate energies and their corresponding approximate density errors (as defined in ref 11) are largely uncorrelated and chemically irrelevant. Brorsen

et al.¹² come to a similar conclusion but specifically study the density accumulation in a bonded region. Wang et al.¹³ argue that with a smaller, more standard basis the recent Minnesota functionals rank more favorably. This is heresy in terms of traditional quantum chemistry, as it argues that an unconverged calculation yields more useful results than a converged one. But because different measures evaluated on different systems yield different rankings, why not this one? In fact, the reply to Kepp’s comment beautifully summarizes the deep intellectual argument for nonempirical functional approximation,¹⁴ and the recent successes of the SCAN meta-GGA confirm its practical significance,¹⁵ but such arguments do not determine a metric. Whereas it is true that when trying to evaluate the quality of an approximate density functional, databases of different systems and properties are often used, some functionals are designed only for molecular problems, whereas others also include materials. All such evaluations require human choices of which systems to include and how to weight the errors, that is, prudent use of statistics. But in the deterministic world of electronic structure, we should not resort to statistics unless we must.

In fact, there is a simple measure of density error that circumvents all of these difficulties. To see this, consider regular quantum mechanics, where the variational principle tells us, for a given system

$$E = \min_{\psi} \langle \psi | \hat{H} | \psi \rangle \quad (3)$$

where \hat{H} is the Hamiltonian, ψ is any allowed normalized trial wave function, and E is the ground-state energy. Thus we naturally say one wave function is better than another, meaning it yields a lower energy. The Hamiltonian itself provides an unambiguous metric for the quality of a wave function for a specific system. The exact wave function is always the winner, and no choices have been made. Of course, a better wave function does not mean better by every measure. Moreover, the error is measured in precisely the units we typically care most about, that is, the energy.

The variational principle also applies to DFT. For a given system, determined by its one-body potential $v(\mathbf{r})$, there is a well-defined, exact ground-state energy, E_v , and density, $n(\mathbf{r})$. (For simplicity, we limit ourselves to nondegenerate, spin-unpolarized cases.) An ideal metric for the error in an approximate density \tilde{n} is

$$\Delta E^{\text{id}}[\tilde{n}] = E[\tilde{n}] - E[n] \quad (4)$$

where $E[n]$ is the exact total energy functional for a given system. This is never negative and, if it is much smaller than the corresponding energy error in the approximate functional that produced $\tilde{n}(\mathbf{r})$, would tell you that such density errors are unimportant. In principle, this provides an unambiguous relevant measure for all systems and approximate densities. (Of course, for specific properties of practical interest, one might use a different measure, such as the density at a nucleus for NMR shifts.)

Unfortunately, evaluating $E[\tilde{n}]$ requires the inversion of a many-body problem, which is more difficult than solving the original problem exactly and has been achieved in only a few model cases.¹⁶ However, in the special case of a self-consistent density from an approximate KS-DFT calculation, we have an excellent proxy for $\Delta E^{\text{id}}[\tilde{n}]$, from the well-established theory of DC-DFT. The true error in an XC approximation, \tilde{E}_{XC} , on any given density is

$$\Delta E_F[n] = \tilde{E}_{\text{XC}}[n] - E_{\text{XC}}[n] = \Delta E_{\text{XC}}[n] \quad (5)$$

called the functional error. The density-driven error is defined as the difference between this and the total energy error

$$\Delta E_D = \Delta E - \Delta E_{\text{XC}}[n] = \tilde{E}[\tilde{n}] - \tilde{E}[n] \quad (6)$$

where \tilde{E} is the total energy functional when \tilde{E}_{XC} is used. As illustrated in Figure 2, if the approximate functional has the

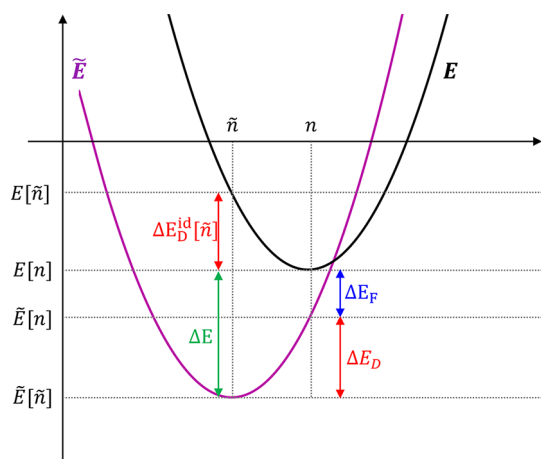


Figure 2. Cartoon of the exact (black) and approximate (purple, denoted with tilde) energy functionals. The minima are marked as n and \tilde{n} , respectively. Our ΔE_D mimics the ideal (but practically uncomputable) ΔE_D^{id} , the energy error of the exact functional due to evaluation on \tilde{n} instead of n . The calculation shown is abnormal (if \tilde{n} is brought much closer to n , then the red errors become much smaller than the blue, and the system is normal).

same curvature as the exact one and the densities are sufficiently close, then $\Delta E_D \approx -\Delta E^{\text{id}}[\tilde{n}]$. Practically, we can evaluate ΔE_D once we know the exact density and energy without needing $E[\tilde{n}]$. Of all of the 30 000+ DFT calculations published each year,¹ in any case where the exact energy and density are known, the DFT errors can be decomposed in this way.

Examination of the ratio of the magnitudes of the functional- and density-driven errors has shown that in the vast majority of KS calculations, including all of those of ref 5, the error reported in the energy is dominated by the functional error.¹⁷ Such calculations are labeled *normal* in DC-DFT, and the density-driven error is a small fraction of the total and so is irrelevant to the energy error. But in several important classes of DFT calculations with standard functionals (electron affinities, reaction barriers, stretched heteronuclear bonds,

and ions and radicals in solution, for example), density-driven errors are significant. These are labeled *abnormal*, and errors decrease significantly if exact densities are used instead of self-consistent ones.^{18–20} In practice, it is rarely straightforward (or inexpensive) to generate highly accurate densities (and hybrid functionals also require KS orbitals). In practice, for molecules, HF densities usually suffice because they do not suffer from self-interaction (or delocalization) error as semilocal approximations do. With a simple script²¹ and at no additional computational cost, an HF-DFT calculation (i.e., DFT energy on HF density) can be run and yields substantially improved energetics.

To illustrate our assertions, begin with simple one- and two-electron calculations, where highly accurate densities are available, so that density-driven errors can be precisely calculated. We choose an energy error standard of $\Delta_s = 2$ kcal/mol, as we do not expect our approximations to achieve that accuracy, and so we regard errors smaller than Δ_s as not meaningful. In Table 1, we show energy errors for the humble H atom. All approximations in the table have errors below Δ_s . We also see that the true and density-driven errors are also below threshold. Ironically, the nonempirical PBE has almost exactly zero error in this case, but our decomposition shows that this is accidental, as the functional and density-driven errors cancel almost perfectly.

Turn next to He^+ . The density-driven errors are unchanged (as the shape of the density barely changes), but the greater dominance of exchange unbalances PBE, which is then improved upon by PBE0. Next, consider He, where now errors are noticeably bigger. Most have reasonable density errors (except MN15), and all errors are dominated by the XC error. But chemistry concerns energy differences, so at the bottom of Table 1 we give the ionization potential (IP) of He and the electron affinity (EA) of H. We apply exactly the same formulas to energy differences as we have used for total energies. All He ionization potential calculations have small density errors, and the error in the ionization potential is dominated by the XC error: These are all normal calculations.

Next, we consider a paradigm of *abnormality*, namely, the hydrogen anion. Its density errors are shown in Figure 3. Note the scale is larger than Figure 1, and some errors do not oscillate. With many semilocal approximations, a self-consistent solution leads to ~ 0.35 electrons escaping the system. (The HOMO is then at 0, unlike in calculations where the anion is bound artificially by the basis and the HOMO is positive.¹⁷) It is not the scale of the density errors that determines abnormality but their effect on the calculated energy. Thus H, He^+ , and He are generically *normal* systems

Table 1. Errors (kcal/mol) in DFT Approximations for One- and Two-Electron Systems^a

system	error											
	PBE			PBE0			M06			MN15		
	ΔE	ΔE_F	ΔE_D	ΔE	ΔE_F	ΔE_D	ΔE	ΔE_F	ΔE_D	ΔE	ΔE_F	ΔE_D
H	0.0	0.4	−0.4	−0.8	−0.7	−0.2	−0.1	0.3	−0.4	0.3	2.0	−1.7
He^+	3.9	4.3	−0.4	2.0	2.3	−0.2	0.2	0.6	−0.3	−3.8	−2.0	−1.8
He	6.8	7.5	−0.7	5.4	7.5	−2.1	−4.1	−1.8	−2.3	−11.0	−7.1	−3.9
H^-	−6.5	−1.1	−5.4	−1.4	4.3	−5.7	−1.9	4.0	−5.9	−2.1	2.8	−5.0
He (IP)	−2.9	−3.2	0.3	−3.3	−5.2	1.9	4.3	2.3	2.0	7.2	5.1	2.1
H (EA)	6.5	1.5	5.0	0.6	−5.0	5.5	1.8	−3.7	5.5	2.4	−0.8	3.3

^aTwo-electron systems are calculated with CASSCF density as for the reference and compared with reference QMC energies.

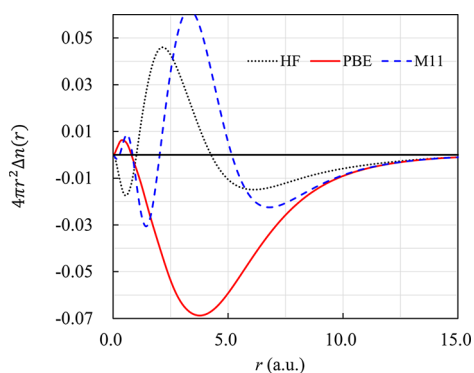


Figure 3. H^- radial density errors for the same approximations as in Figure 1.

with semilocal DFT, whereas atomic anions are generically *abnormal*.^{22,23}

A crucial practical point is if abnormality in a system can be detected without access to the exact density. (If the exact $n(\mathbf{r})$ was always needed, then there could be no practical benefit for larger systems.) The many successes of HF-DFT^{20,24} show that for almost all abnormal calculations the use of the HF density instead of the exact density yields an excellent estimate of the density-driven error, yielding a very practical scheme for correcting those errors. (The only exceptions are due to spin contamination of the HF calculation¹⁹ or the ultra abnormal paradigm, H^- .¹⁷) We thus use this in our analysis of nontrivial abnormal systems. Initial DC-DFT work showed that when the KS gap in a self-consistent semilocal DFT calculation becomes unusually small, there is likely to be a substantial density-driven error.¹⁷ This is true for all cases listed above. However, this leaves open the question of “how small is small enough?”; that

Table 2. Classification of Normal (N) versus Abnormal (A) Calculations ($S > 2$ kcal/mol)^a

system	N vs A ^a	S_1	\bar{S}_3	\bar{S}_4	\bar{N}^c	\bar{S}_K	DFT errors ^b							
							PBE	[HF]	B3LYP	[HF]	M06	[HF]	MN15	[HF]
Atomization Energy														
HCl	N	0.2	0.3	0.1	0.1	0.4	0.5	0.4	1.8	1.7	0.6	-0.1	-1.0	-1.7
LiH	N	0.6	0.5	0.4	0.1	0.4	4.8	5.3	-0.2	0.1	0.1	0.5	-5.6	-6.7
NaCl	N	0.7	0.6	0.4	0.2	0.9	3.2	3.7	4.9	4.8	-6.8	-4.4	-2.7	-1.5
CH ₂ (³ B ₁)	N	0.8	1.4	1.1	0.3	1.2	-2.1	-1.2	0.1	1.6	0.1	1.5	4.3	3.3
CH	N	1.0	1.2	0.9	0.1	1.0	-1.2	-0.2	-1.8	-0.9	-0.6	0.2	1.8	1.9
CH ₂	N	1.1	1.2	0.9	0.1	1.0	3.3	4.4	1.2	2.1	-0.2	0.8	3.9	1.4
NH	N	1.2	1.8	1.2	0.2	2.0	-5.9	-4.5	-5.5	-4.1	0.1	2.8	1.0	2.0
CH ₄	N	1.4	1.6	1.1	0.1	1.6	0.9	2.2	-0.2	1.0	2.0	4.0	3.3	-0.7
Reaction Energy														
HCl + CH ₃ → CH ₄ + Cl	N	0.5	0.6	0.2	0.2	0.7	1.8	2.3	-0.6	-0.3	-0.1	0.8	1.7	1.2
Ionization Energy														
C ₂ H ₂	N	0.0	0.1	0.1	0.0	0.1	2.1	2.0	2.0	2.0	5.7	6.0	2.6	2.2
He	N	0.4	0.5	0.3	0.3	0.3	2.6	3.1	-8.4	-7.9	0.6	-0.1	-1.0	-1.7
Double Ionization Energy														
Ne ⁶⁺ /Ne ⁸⁺	N	0.4	0.8	0.3	0.2	0.6	-21	-22	-14	-15	-66	-67	-37	-44
B ⁺ /B ³⁺	N	0.5	0.7	0.4	0.2	0.6	-3.9	-4.6	3.5	3.0	-21	-21	-16	-18
N ³⁺ /N ⁵⁺	N	0.5	0.7	0.4	0.2	0.6	-11	-11	-2.0	-2.5	-38	-38	-24	-28
O ⁴⁺ /O ⁶⁺	N	0.4	0.7	0.3	0.2	0.6	-14	-15	-5.7	-6.2	-47	-47	-28	-33
Electron Affinity														
H	A	8.5	10	5.8	0.7	6.7	6.7	-1.6	4.6	3.3	2.0	-2.6	2.6	1.3
Reaction Barrier Height														
H + HF → HF + H	A	3.4	3.9	2.9	0.2	3.7	-15	-11	-11	-7.7	-1.5	2.9	-5.0	-2.6
CH ₄ + Cl → HCl + CH ₃	A	3.7	4.1	2.9	0.2	3.2	-7.8	-4.1	-1.1	1.5	-0.6	2.0	0.3	5.6
HCl + CH ₃ → CH ₄ + Cl	A	4.2	4.7	3.1	0.2	3.9	-6.0	-1.8	-1.7	1.2	-0.7	2.7	2.0	6.7
H + N ₂ O → OH + N ₂	A	11	13	9.9	0.1	12	-8.0	3.5	-6.6	2.8	0.3	11	-2.3	7.0
OH + N ₂ → H + N ₂ O	A	20	21	16	0.7	18	-29	-9.2	-8.8	5.9	-10	5.3	-6.2	7.4
Dissociation of Stretched Molecule														
H ₂ ⁺ (at 5.0 Å)	A	2.8	2.3	2.5	0.1	2.1	-50	-47	-41	-39	-41	-39	-36	-35
NaCl (at 6.0 Å)	A	14	13	10	2.0	8.2	-10	3.5	-3.7	4.2	-13	-9.6	-4.1	-5.2
NaCl (at 10.0 Å)	A	28	28	23	2.0	20	-24	3.9	-15	4.5	-21	-9.4	-9.4	-5.3
Radical Reaction Energy														
NH ₂ + H → NH ₃	N	0.5	0.7	0.3	0.2	0.8	-0.8	-0.1	-0.6	-0.1	0.4	1.6	2.5	4.7
NHCH ₃ + H → NH ₂ CH ₃	A	2.1	2.8	1.4	0.4	2.0	-3.8	-1.3	-2.7	-1.1	-1.1	0.8	0.5	3.7
H + N ₂ O → OH + N ₂	A	8.1	8.3	6.3	0.5	6.1	-21	-13	-2.2	3.2	-10	-6.1	-3.8	0.4
High- and Low-Spin Energy Difference														
[Fe(NCH) ₆] ²⁺	A	44	43	28	3.4	32	48	3.7	24	2.2	14	-11	24	-2.0

^aIn all cases, classification agrees with previous observations of abnormality. ^bCCSD(T) value was used for the reference value to evaluate the DFT errors. Note that the basis set information is classified in the Computational Details section. ^cKepp's \bar{N} function should be >1 kcal/mol for abnormal systems, but often it is not.

is, it does not provide a clear quantitative answer and also does not use only energies of ground-state calculations.

The answer lies in measuring the sensitivity of the energy to different densities. In recent work extending HF-DFT to the energy differences between spin states of Fe(II) complexes, “rainbow” plots take a range of different functionals of different classes and show the energy of every functional on every self-consistent density.²⁴ The spread in such a plot indicates the sensitivity to the density: If there is more variation with density than there is with functional choice, then the system is abnormal. Kepp took four popular approximations of different kinds and estimated the degree of normality in a calculation²⁵ by averaging over their evaluation on each other’s self-consistent densities. But this misses a key element in DC-DFT: separation of accuracy of densities and energies. For example, the HF density yields much improved energetics with semilocal DFT energies, but the HF energy is so poor it is rarely used. Thus Kepp’s scheme does not include pure HF densities.

To detect abnormality, we should measure the sensitivity of a functional to the density. So we evaluate two extreme nonempirical densities: HF and LDA. For any approximate functional, define

$$S(\tilde{E}_{XC}) = |\tilde{E}[n^{LDA}] - \tilde{E}[n^{HF}]| \quad (7)$$

If $S > \Delta_c$, our 2 kcal/mol cutoff, then this suggests abnormality, which, in turn, implies a density-driven error that would be cured by using HF densities (for molecules). Moreover, S approximates the density-driven error (see eq 6) if the LDA density is close to the self-consistent density and the HF density is close to the exact one. In principle, the abnormality of a DFT calculation depends on the approximate functional used, the system, and the energy difference being calculated. However, abnormal calculations with standard semilocal approximations are often much improved by use of HF densities. We calculate \bar{S}_m , an average over m approximate XC functionals. Here we chose S_1 as using just PBE but \bar{S}_3 averaging over LDA, PBE, and BLYP (i.e., generalized gradient approximation (GGA) level) and \bar{S}_4 as averaging over PBE, PBE0, BLYP, and B3LYP, that is, semilocal and hybrid level. Table 2 shows results for many different chemical processes. Whereas there is some spread in the different measures, there is great consistency: Whenever the density sensitivity is >2 kcal/mol, the system is abnormal at the semilocal/hybrid level. Atomization energies, standard reaction energies, and ionization energies are all normal. In such cases, use of the HF density barely changes the result and may not improve it. In normal calculations, there is no reason to think the HF density is more accurate than the self-consistent DFT density (and many reasons to think it is not⁴). All entries for the systems of ref 5 indicate their normality, and their density-driven errors are very small.

But transition-state barriers,^{26–28} spin energy differences of Fe(II) complexes,²⁴ dissociation of stretched molecules,¹⁹ and some (but not all) radical reaction energies¹⁸ are abnormal. In almost every abnormal case, the use of an HF density in place of the self-consistent density improves the energetics, often substantially. This is an illustration of the greater accuracy of the HF density in such cases by our measure. Because of averaging only self-consistent densities, Kepp’s measure, precisely as given in ref 25, is too insensitive to indicate many abnormal cases (although altering the cutoff might

improve its performance). However, S_K , using Kepp’s functionals but on LDA versus HF densities, does work.

To illustrate the use of our measure in the present context, we consider the broad range of processes covered by Table 2. Those labeled “normal” have density errors that are irrelevant by our measure: They do not matter to the accuracy of predicted energies. But our abnormal systems are, by definition, those in which the density error is relevant. In Figure 4, we plot the density-driven errors of several

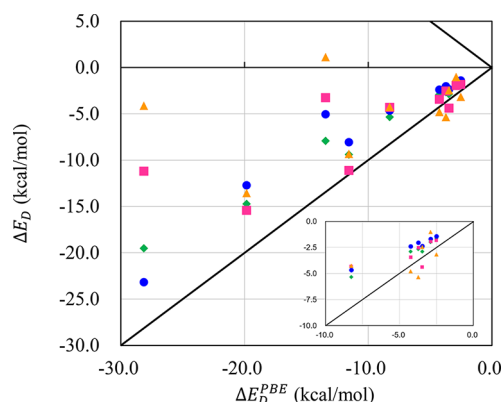


Figure 4. Comparison of density-driven errors (calculated with HF densities as the reference) for abnormal systems of different functionals against PBE in Table 2. B3LYP is labeled as green diamond, PBE0 as blue dot, M06 as pink square box, and MN15 as orange triangle. All points between diagonals (solid black lines) have density-driven errors smaller than those of PBE. The electron affinity of H^- has been excluded.

functionals against the density-driven error of PBE for all abnormal processes in Table 2. Even in these extreme cases, we see no clear evidence of particularly large density errors for specific classes of functionals. Moreover, the mean absolute error (MAE) of these approximations over the abnormal systems is 9.1 (kcal/mol) for PBE, 6.1 for PBE0, 5.4 for B3LYP, 5.3 for M06, and 4.7 for MN15, again with no obvious pattern. (The inset suggests that for abnormal calculations with density-driven errors <10 kcal/mol, the empirical functionals may be trading density-driven errors against functional errors, as one might expect from fitting data.)

Our last topic concerns the amount of exchange mixing in a global hybrid functional

$$E_{\text{hyb}}[n] = a(E_X^{\text{HF}}[n] - E_X^{\text{GGA}}[n]) + E_{\text{XC}}^{\text{GGA}}[n] \quad (8)$$

Becke introduced the idea, and the B3LYP functional uses $a = 0.20$.²⁹ Using arguments from perturbation theory, Perdew et al. argued^{30–32} $a = 1/4$, the value used in PBE0.³³ A crucial aspect of such hybrids is that the amount of exchange mixing is fixed in the functional, and not system-dependent, to retain size-consistency. Moreover, large values of a typically yield highly inaccurate ground-state energetics (almost as bad as HF). On the contrary, for many properties related to orbital eigenvalues, orbital-dependent functionals are more accurate. The hybrid HSE06 often yields better gaps for semiconductors within generalized KS calculations, and this can be crucial when studying localized impurity levels.³⁴ Recent papers often adjust a to improve the positions of orbital energies. However, such adjustments will destroy the quality (and generality) of the ground-state energy functional and, worse still, create non-size-consistent schemes with ambiguities in even the definition

of the ground-state energy. Thus there is a parameter dilemma: Increasing a often improves response properties but destroys the accuracy of ground-state energetics and even the rigor of the calculation.

Here we show how HF-DFT avoids this dilemma because the amount of mixing mostly affects the quality of the density, not the energy. In Figure 5, we see that for a typical abnormal

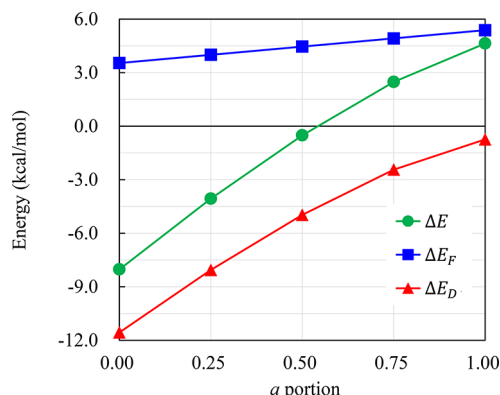


Figure 5. Density-driven and functional errors for a -PBE calculation of abnormal reaction barrier $\text{H} + \text{N}_2\text{O} \rightarrow \text{OH} + \text{N}_2$ as a function of amount of exact exchange mixing (calculated with HF densities as the reference).

calculation (a reaction barrier) the total energy error is very sensitive to a because the density-driven error is. But the functional error barely changes with a .

We close with some discussion of context. The fact that the exact functional recovers the exact energy and density tells us nothing about the accuracy of approximate functionals for either the energy or the density. The concept of accuracy of approximations requires a quantitative measure of error. For any given system, an approximate functional makes an error in the ground-state energy, but no single number can characterize all errors in the density. The choices of ref 5, while eminently reasonable, are arbitrary, and any subsequent ranking of approximations can be reordered with different choices. In the most extreme case, any approximation can be made the best.

The energy functional itself provides a natural universal measure of density error, which is easily estimated if a density is the result of an approximate KS calculation. Moreover, it has led to the concept of abnormal DFT calculations, that is, those in which the density error contributes significantly to the calculated energy and where results can often be improved by using a “better” density. In many (but not all) abnormal molecular calculations, the HF density suffices, yielding the extremely trivial trick of performing HF-DFT calculations. We note that HF-DFT is not a panacea, as it gives up the use of self-consistency. Apart from the practical difficulties of dealing with the failure of the Hellmann–Feynman²⁸ theorem, and whereas HF-DFT often improves energetics by a factor of two or three for well-founded reasons, it does not apply to all delocalization errors and can never replace the need to get both energy and density accurately from a single functional. The work of Bartlett and coworkers, called *ab initio* DFT, yields accurate XC potentials and hence densities while retaining self-consistency.³⁵ Similarly, the work of Yang and coworkers to develop locally scaled corrections that restore the linearity of the energy with particle number produces

approximate functionals that solve these problems self-consistently.³⁶

COMPUTATION DETAILS

All HF, DFT (SVWN,^{37,38} PBE,³⁹ B3LYP,⁴⁰ PBE0,³¹ M06,⁴¹ M11,⁴² MN15⁴³), HF-DFT, and CCSD(T) results were performed with Gaussian16 package.⁴⁴ Dunning’s augmented correlation-consistent quintuple zeta basis set (aug-cc-pV5Z) was used for the calculations in Table 1.^{45,46} For Table 2, the aug-cc-pVTZ basis set^{47,48} was used for almost all calculations, whereas Ahlrichs’ newer redefinition quadruple- ζ (def2-QZVP) basis set⁴⁹ was used for the dissociation of stretched molecules for the comparison with the previous work.¹⁹ To perform every calculation at its given orientation, molecular symmetry within the calculation was not considered. Molecular geometry data were from the G2 database set⁵⁰ for the atomization energy and ionization energy, whereas molecular reaction geometries were from Zhao et al.^{51,52} The high- and low-spin $[\text{Fe}(\text{NCH})_6]^{2+}$ geometries were from ref 24. For the radical reaction energies, B3LYP/aug-cc-pVTZ was used for the geometry optimization. Because the hydrogen anion of Tables 1 and 2 has the positive HOMO problem, SVWN, PBE, B3LYP, PBE0, and M06 calculations were performed with the TURBOMOLE package⁵³ for calculating the fractional occupation within unrestricted KS scheme. For the energy convergence criteria, SCF = tight option for the Gaussian16, whereas scfconv = 8 and denconv = 1.0d-8 were used for TURBOMOLE. To calculate errors in Table 1, DFT exchange-correlation energies for two-electron systems were calculated on the CASSCF density from 60 active spaces and 2 active electrons⁵⁴ and compared with QMC energies.⁶

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcllett.8b02855.

Table S1. Raw data of Table 2 (PDF)

XYZ coordinates of molecules in Table 2 and Table S1 (TXT)

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Notes

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