Unconventional Error Cancellation Explains the Success of Hartree-Fock Density Functional Theory for Barrier Heights

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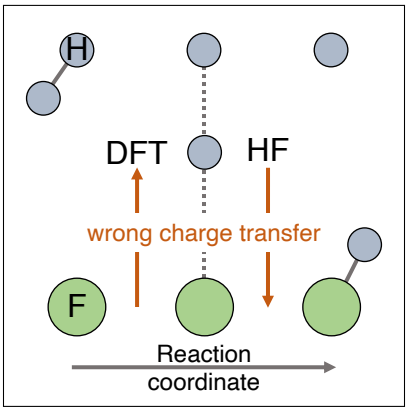
Abstract

Energy barriers, which control the rates of chemical reactions, are seriously underestimated by computationally-efficient semi-local approximations for the exchange-correlation energy. The accuracy of a semi-local density functional approximation is strongly boosted for reaction barrier heights by evaluating that approximation non-self-consistently on Hartree-Fock electron densities, as known for about 30 years. The conventional explanation is that Hartree-Fock theory yields the more accurate density. This article presents a benchmark Kohn-Sham inversion of accurate coupled-cluster densities for the reaction $H_2 + F \rightarrow HHF \rightarrow H + HF$, and finds a strong, understandable cancellation between positive (excessively over-corrected) density-driven and large negative functional-driven errors (expected from stretched radical bonds in the transition state) within this Hartree-Fock density functional theory. This confirms earlier conclusions [*J. Chem. Theory Comput.* **2023**, *19*, 532–543] based on 76 barrier heights and three less reliable, but less expensive, fully-nonlocal density-functional proxies for the exact density.

TOC Graphic



Kohn-Sham density functional theory[1] in principle yields exact ground-state energies and electron densities, while constraint-satisfying approximations to its exchange-correlation energy make useful predictions[2] over a vast materials space. Understanding the successes and failures of such approximations is key to improving them. It has been known for more than thirty years that the computationally efficient semi-local approximations, when implemented self-consistently, severely underestimate the barrier heights to gas-phase chemical reactions,[3–6] and that their accuracy for barriers is strongly boosted by performing a Hartree-Fock (HF) calculation and then replacing the HF exchange energy by the semi-local exchange-correlation energy evaluated on HF densities (and occupied orbitals if needed),[3–6] a procedure known as "Hartree-Fock density functional theory." Early work was done by Scuseria,[3] Bartlett and collaborators,[4,6] and Janesko and Scuseria.[5] More recently, this approach has been systematized by Burke and coworkers as "density-corrected density functional theory",[7–10] and has been shown to improve the average accuracy of other properties of main-group molecules[11] and to remarkably improve the binding energies of water clusters,[12,13] when applied to constraint-satisfying semi-local functionals such as the Perdew-Burke-Ernzerhof generalized gradient approximation (PBE GGA)[14] or the strongly-constrained and appropriately normed (SCAN) meta-GGA.[15] The corresponding (non-self-consistent) Hartree-Fock density functionals are known as PBE@HF and SCAN@HF. More generally, for any density functional approximation (DFA) there is a DFA@HF. While Ref. 7 rigorously defined density-driven error relative to the exact density, more recent work on density corrections has tended for practical reasons to take the HF density as a proxy for the exact density.

For many systems and properties, DFA@HF energy differences can be slightly more or slightly less accurate than those of self-consistent DFA@DFA. For compact neutral atoms and molecules at equilibrium bond lengths (including the water monomer), there is graphical, statistical,[16] and energetic[13] evidence that PBE and especially SCAN densities are modestly more accurate than HF densities. SCAN exchange-correlation potentials for compact

molecules are also reasonably accurate.[17] But for large classes of systems and properties, DFA@HF energy differences are significantly and systematically more accurate than those of DFA@DFA, which we denote as DFA. For some of these systems and properties (dissociation limits of binding energy curves,[18] electron removal energies in small negative ions[19]), the reason is clearly that the more localized HF density yields the correct integer electron numbers on separated subsystems[20] while the too-delocalized DFA density often yields spurious non-integer values.

The conventional explanation for large systematic improvements in energy differences from DFA@DFA to DFA@HF is that in these cases the self-interaction-free Hartree-Fock density is significantly more accurate than the self-consistent density of a semi-local approximation. That explanation is indisputable for many cases, but we now show that a different explanation accounts for the improvements in the barrier heights to chemical reactions and the binding energies of water clusters in going from DFA to DFA@HF.

A forward barrier height is the energy difference between the transition state and the separated reactants, and a reverse barrier height is the energy difference between transition state and products. The higher the barrier height, the slower the reaction. The transition states of chemical reactions are typically stretched radicals. The paradigm stretched radical is stretched H_2^+, where the semi-local functionals evaluated on the exact density can make the total energy severely too negative[21] for reasons discussed in Ref. 22: the exact exchange-correlation hole is shared by two separated density fragments, while its semi-local approximation is not. Thus the DFA error of the barrier height is not necessarily dominated by the error of the DFA density. A more precise language is provided by the analysis of Burke, Sim, and collaborators,[7–10] who write the error of a self-consistent DFA for an energy or energy difference E,

$$\Delta E_{\rm DFA} = E_{\rm DFA}[n_{\rm DFA}] - E_{\rm exact}[n_{\rm exact}] = {\rm FE} + {\rm DE}, \tag{1}$$

as the sum of a functional-driven error

$$\mathrm{FE} = E_{\mathrm{DFA}}[n_{\mathrm{exact}}] - E_{\mathrm{exact}}[n_{\mathrm{exact}}] \tag{2}$$

and a density-driven error

$$\mathrm{DE} = E_{\mathrm{DFA}}[n_{\mathrm{DFA}}] - E_{\mathrm{DFA}}[n_{\mathrm{exact}}]. \tag{3}$$

The exact electron density and exact total energy (but not the separate components of the total energy) are defined in the same way in density functional theory and in traditional quantum chemistry. By the variational principle, DE is negative for a self-consistent DFA. For a DFA@HF calculation, where n_{DFA} is replaced by n_{HF} in Eq. (1), we *define* the analog of Eq. (3) by replacement of n_{DFA} by n_{HF},

$$\mathrm{DE(DFA@HF)} = E_{\mathrm{DFA}}[n_{\mathrm{HF}}] - E_{\mathrm{DFA}}[n_{\mathrm{exact}}], \tag{4}$$

which can then be positive. Equation (2) remains unchanged by the same replacement, and the total error remains equal to FE + DE. With this replacement, Eq. (4) is technically a "density difference"[10] that vanishes when $n_{\mathrm{HF}} = n_{\mathrm{exact}}$, although it was called a "density-driven error of n_{HF} in Ref. 23. When DE(DFA@HF) is positive, the HF density over-corrects the DFA density; when $\mathrm{DE(DFA@HF)} \gg -\mathrm{DE(DFA)}$ it excessively over-corrects the DFA, and use of the HF density cannot be interpreted simply as a density correction to a DFA.

The precise evaluation of Eqs. (2)–(4) would require not only the exact energy $E_{\mathrm{exact}}[n_{\mathrm{exact}}]$ and the exact density $n_{\mathrm{exact}}(\boldsymbol{r})$ (both well approximated in many cases by a coupled-cluster calculation), but also an inversion of the exact density to find the exact Kohn-Sham occupied orbitals for the evaluation of $E_{\mathrm{DFA}}[n_{\mathrm{exact}}]$.[17,23] Accurate implementation of the inversion has been reported for a limited number of polyatomic systems, with few tens of electrons.[24–26] To better understand the errors of the 76 barrier heights in the BH76 test

set,[27–29] Ref. 30 recently applied three fully-nonlocal proxies for the exact functional and density in Eqs. (1)–(4), chosen to satisfy two criteria: (1) accurate self-consistent barrier heights, and (2) nearly correct electron transfers due to nearly-linear variation of the total energy of a separated fragment between adjacent integer electron numbers.[20] (The semi-local approximations bend below the straight-line segment and are too de-localizing,[20,31] while Hartree-Fock bends above and is too localizing.[31]) The proxy functionals were, in order of reliability, the long-range-corrected hybrid LC-ωPBE,[32] a global hybrid of SCAN with 50% exact exchange called SCAN50 or SX-0.5, and the self-interaction corrected SCAN-FLOSIC.[33] All three showed the same pattern: a large negative functional-driven error of PBE and SCAN, largely canceled by a large positive density-driven error when evaluated on the HF density. The estimations of density-driven error (DE) in kcal/mol differed substantially between proxies, leaving some room for doubt. For example, for the forward reaction in Table 1 of this paper, they were (from Table S13 of Ref. 30) -1.3 (PBE@LC-ωPBE), -4.9 (PBE@SCAN50), -6.4 (PBE@SCAN-FLOSIC), although all were significantly different from +11.3 (PBE@HF) from Table 1, which uses an accurate CCSD(T) proxy. The average over the three original proxies, -4.2, was not so different, from -2.2 (PBE) in Table 1.

Can we understand how all the BH76 transition states can have large negative functional-driven errors? Such negative errors arise in the stretched radical H_2^+ (see Fig. 3 of Ref. 22), while large positive functional-driven errors arise in the stretched, symmetry-unbroken singlet or non-radical H_2. All of the BH76 transition states have stretched bonds, with total spins tabulated in Ref. 29. Of 38 forward reactions, 23 involve an odd number of electrons, and their transition states are likely to be stretched radicals. Of the remaining 15, 5 have non-singlet transition states that are also likely to be stretched radicals, and 10 have stretched singlet or non-radical transition states. But none of these 10 dissociate to separated fragments with strong correlation between them. 6 of these 10 do not fragment in either the forward or reverse directions, and the remaining 4 have at most two fragments

in either direction, at least one of which is closed-shell. Thus none of the BH76 transition states appears to be like stretched H_2.

The work of Ref. 30 suggested that this unconventional error cancellation occurs strongly, widely and reliably for barrier heights, but the extent to which the proxies fairly represented the exact functional could still be questioned. Here we will focus on the forward and reverse barrier heights of the BH76 reaction $H_2 + F \rightarrow HHF \rightarrow H + HF$, taking the coupled cluster CCSD(T)/aug-cc-pV5Z [34,35] energies and densities[36] from the PySCF code[37] to be exact. The resulting barrier heights differ by 0.2 kcal/mol or less from the W2-F12 "exact" values in BH76,[29] which aim to reproduce CCSD(T) results in the complete basis-set limit.[38] This work and Ref. 30 together permit a firm conclusion that, for many BH76 barrier heights, the Hartree-Fock density makes a density-driven error that largely cancels the substantial functional-driven error of PBE or SCAN. This article also briefly discusses the possibility of a similar error cancellation in the water clusters, and presents a possible explanation for this unconventional error cancellation in molecules and molecular clusters.

With the help of the accurate coupled cluster method, we can evaluate the total DFA or DFA@HF error of a barrier height from Eq. (1). But finding the separate functional-driven [Eq. (2)] and density-driven [Eq. (3)] errors still requires an accurate determination of the Kohn-Sham orbitals that yield the CCSD(T) density, a challenging inverse problem. For this, we use the partial differential equation constrained optimization method of Refs. 17,25,39. In this method, the inverse problem is formulated as a constrained optimization of the Kohn-Sham exchange-correlation potential $v_{\rm xc}(\boldsymbol{r})$ and solved using a convergent finite-element basis set. Each finite element is a fifth-order Lagrange polynomial in the x, y, and z directions. For open-shell systems, we use a recent extension[40] of the inverse formulation with a spin-dependent exchange-correlation potential. Self-consistent DFA and DFA@HF at the quadruple-zeta level can be found in Ref. 30; we recompute these values at the quintuple-zeta level here. All our density-functional calculations employ the separate up- and down-spin electron densities, not just the total density. The DFA and DFA@HF calculations were

treated as spin-unrestricted for F, H, and the HHF transition state; and as spin-restricted for H_2 and HF. The local spin density approximation (LSDA) uses the parametrization of Ref. 41.

Importantly, none of the functionals predicts a highly spin-contaminated transition state. At the 5ζ level, $\langle \boldsymbol{S}^2 \rangle$ is 0.75 with the exact functional, 0.77 with HF, 0.75 with LSDA and PBE, and 0.76 with SCAN and r^{2}SCAN.

Table 1: Barrier heights (BHs) and their functional-driven errors (FEs), and density-driven errors (DEs) for the reaction H_2 + F $\rightarrow$ HHF $\rightarrow$ H + HF. All units are kcal/mol. (1 Hartree $\approx$ 627.5 kcal/mol; 1 eV $\approx$ 23.06 kcal/mol.) FEs and DEs are computed by taking the CCSD(T)/aug-cc-pV5Z energies and densities as exact. The strong density sensitivity (absolute change of BH from LSDA to LSDA@HF $\gg$ 2 kcal/mol) is often taken as an indicator of the need for HF density correction.[10] However, as BH(DFA) $-$ BH(DFA@CCSD(T)) **is about 1 kcal/mol for SCAN and r^{2}SCAN (see Table S2 of the Supporting Information), this should not be a highly density-sensitive system for the meta-GGAs. The sum of FE and DE yields the total error with reference to the CCSD(T)/aug-cc-pV5Z BH.**

	Forwards			Reverse		
DFA	BH	FE	DE	BH	FE	DE
LSDA	-23.7	-20.7	-4.4	25.4	-3.8	-4.7
LSDA@HF	-5.4	-20.7	13.9	43.2	-3.8	13.1
PBE	-12.6	-11.8	-2.2	24.8	-6.8	-2.3
PBE@HF	0.9	-11.8	11.3	37.6	-6.8	10.5
SCAN	-7.4	-7.8	-1.0	22.0	-10.6	-1.2
SCAN@HF	2.1	-7.8	8.5	30.9	-10.6	7.7
r^{2}SCAN	-6.9	-7.3	-1.0	23.8	-8.9	-1.3
r^{2}SCAN@HF	2.5	-7.3	8.5	32.6	-8.9	7.6
CCSD(T)	1.4	0.0	0.0	33.9	0.0	0.0

Table 1 shows our numerical results. The coupled cluster "exact" barrier heights are much smaller for the forward reaction than for the reverse. The semi-local functionals severely underestimate the barrier heights, but there is overall improvement from LSDA to PBE to SCAN and its more computationally-efficient twin r^{2}SCAN.[42] For these self-consistent DFAs, both FE of Eq. (2) and DE of Eq. (3) are negative, but FE is typically much more negative. From DFA to DFA@HF, the too-delocalized DFA density is replaced by the too-localized

Hartree-Fock density, and DE becomes strongly positive, cancelling most of FE, especially for the more sophisticated SCAN and r^{2}SCAN. This is the same error pattern found for the full BH76 set from the proxy-exact estimates of Ref. 30. By this energetic measure, the Hartree-Fock density for the transition state is actually much less accurate than the self-consistent DFA density. But, as suggested at the end of Ref. 10, there is in principle a DFA that yields the DFA@HF total energy and a self-consistent density expected to be more accurate than the HF density.

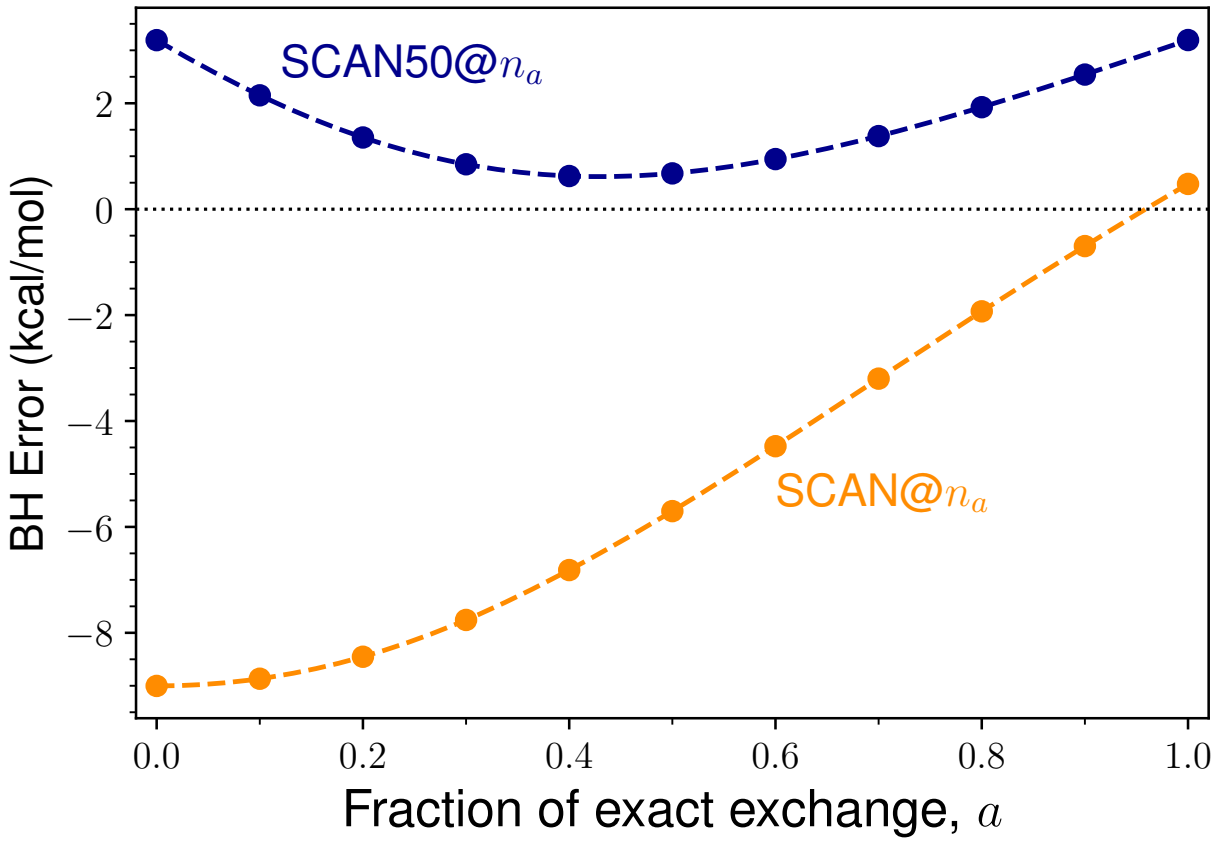


Figure 1: Error of the forward energy barrier height for the reaction $H_2 + F \rightarrow HHF \rightarrow H + HF$ from SCAN (green) and proxy-exact SCAN50 (black), evaluated on a density n_a that interpolates between the self-consistent SCAN density at $a = 0$ and the HF density at $a = 1$. That density is found self-consistently from the exchange-correlation functional of Eq. (5).

Hartree-Fock DFT is a successful density correction to a DFA like SCAN when FE is small in magnitude and DE(DFA) is large, as in the dissociation limits of molecular binding energy curves or the electron affinities of atoms or small molecules, because in these cases

the too-delocalized DFA density is qualitatively wrong while the too-localized HF density is qualitatively right. In the barrier heights problem, however, DE(DFA) is much smaller in magnitude than FE, so that a true density correction would leave most of the total error uncorrected. To understand what actually happens for the barrier heights, imagine a density n_a computed self-consistently from a linear interpolation of the exchange-correlation energy

$$E_{\rm xc}([n];a) = E_{\rm xc}^{\rm DFA}[n] + a(E_{\rm x}^{\rm HF}[n] - E_{\rm xc}^{\rm DFA}[n]) \quad (0 \le a \le 1). \tag{5}$$

This $E_{\rm xc}([n];a)$ functional interpolates between the DFA ($a = 0$) and HF ($a = 1$) functionals. The error in the barrier height is due to a small density variation around a minimizing density n_a, for which $E_{\rm DFA}[n_a] \approx E_{\rm DFA}[n_{\rm DFA}] + C_{\rm DFA}a^2$, and $C_{\rm DFA} > 0$, as we now show.

Figure 1 plots the forward barrier height errors of SCAN and SCAN50 when evaluated on n_a, as a function of a. The error in the SCAN50@n_a barrier height minimizes at 0.6 kcal/mol for $a \approx 0.43$ (by spline interpolation). Taking SCAN50 as a proxy for the *exact energy functional only*, then the density which is closest to the exact one lies roughly in the range $0.3 \lesssim a \lesssim 0.5$. Let $a = a_{\rm best}$ be that value of a for which $n_{a_{\rm best}} \approx n_{\rm exact}$ is closest to the exact density. Under the simplifying assumptions that DE(DFA@n_a) is linear in a^2, and that $E_{\rm DFA}[n_{a_{\rm best}}] = E_{\rm DFA}[n_{\rm exact}]$,

$$\text{DE(DFA)} \approx -C_{\rm DFA}a_{\rm best}^2, \tag{6}$$

$$\text{DE(DFA@HF)} \approx C_{\rm DFA}(1 - a_{\rm best}^2) \tag{7}$$

consistent with the signs and relative magnitudes of these two DEs in Table 1. In particular, the SCAN data in Table 1 suggest $C_{\rm SCAN} \approx 9.5$ kcal/mol and $a_{\rm best} \approx 0.32$ for the forward reaction, and $C_{\rm SCAN} \approx 8.9$ kcal/mol and $a_{\rm best} \approx 0.37$ for the reverse reaction.

Why is the unconventional error cancellation between FE(DFA) and DE(DFA@HF) so good for barrier heights? Such a reliable effect is unlikely to be accidental. Taking SCAN50 to be a proxy for the exact functional's barrier height energy, the FE of SCAN, computed

as the difference between the barrier-height errors in SCAN@n_a and SCAN50@n_a in Fig. 1, strongly decreases in magnitude as a approaches 1, the HF limit. The physical reason for this could be that SCAN and other semi-local functions become more accurate for a given density as that density becomes more localized and more HF-like. Over the range $0 < a < 1$, SCAN varies much more strongly than proxy-exact SCAN50.

Table 2: Binding energies (BEs), functional-driven errors (FEs), and density-driven errors (DEs) for the water dimer, using the aug-cc-pVQZ basis set.[35] In the CCSD(T) columns, FEs and DEs are computed by taking the CCSD(T) density to be n_{exact} in Eqs. (2)–(4). In the r^{2}SCAN50 columns, FEs and DEs are computed using the self-consistent densities of the 50% global hybrid of r^{2}SCAN, r^{2}SCAN50, as a proxy[30] for the exact density n_{exact} in Eqs. (2)–(4). In all cases, we take the self-consistent CCSD(T) binding energy to be $E_{\text{exact}}[n_{\text{exact}}]$. All values are in kcal/mol.

		FE		DE	
DFA	BE	CCSD(T)	r^{2}SCAN50	CCSD(T)	r^{2}SCAN50
LSDA	-8.1	-2.6	-2.5	-0.4	-0.4
LSDA@HF	-6.9	-2.6	-2.5	0.7	0.7
PBE	-5.2	0.1	0.1	-0.2	-0.2
PBE@HF	-4.4	0.1	0.1	0.6	0.6
SCAN	-5.4	-0.1	-0.1	-0.2	-0.1
SCAN@HF	-4.7	-0.1	-0.1	0.4	0.5
r^{2}SCAN	-5.1	0.2	0.1	-0.2	-0.1
r^{2}SCAN@HF	-4.5	0.2	0.1	0.4	0.5
r^{2}SCAN50	-4.8				
CCSD(T)	-5.1				

Finally we turn to the (negative-definite) binding energy of a water cluster $(H_2O)_n$, defined as the energy of the bound cluster minus the energies of its n separated H_2O monomers (at their optimized geometries). SCAN is accurate for the relative energies of different hydrogen-bond networks, and even for the binding energy of the water dimer $(H_2O)_2$, but overestimates the binding of larger water clusters, reaching an error of about -20 kcal/mol for $(H_2O)_{20}$ clusters. However, SCAN@HF reaches almost coupled-cluster accuracy for the binding energies of the larger water clusters.[12,13] Kohn-Sham inversion of a coupled cluster density for a large water cluster is computationally prohibitive at present, but we have done this for the water dimer in Table 2. While LSDA overbinds the water dimer by -3

kcal/mol, PBE, SCAN and especially r^{2}SCAN overbind by only a few tenths of a kcal/mol, in comparison to CCSD(T). DFA@HF is more accurate than DFA for LSDA but not for PBE or SCAN. Nevertheless, we still find that DFA@HF turns a small negative density-driven error of DFA into a substantially larger positive density-driven error. In the larger water clusters, there might again be a cancellation in DFA@HF between negative FE and positive DE. Table 2 also shows that the r^{2}SCAN 50% global hybrid is a good proxy for the exact or CCSD(T) density, yielding almost the same FEs and DEs. However, as its parent meta-GGA r^{2}SCAN makes essentially zero FE for the water dimer, admixture of exact exchange to correct errors in the r^{2}SCAN density introduces a more substantial FE to the r^{2}SCAN50 BE. Composite methods like HF-r^{2}SCAN-DC4[43] (with a long-range dispersion correction) might be general-purpose practical solutions to this apparent catch-22.

Table S1 of the Supporting Information shows that our Kohn-Sham inversion is sufficiently accurate for our study. Letting PBE-inv denote the density obtained from Kohn-Sham inversion of the PBE density, the barrier heights from PBE@PBE and PBE@PBE-inv agree within 0.4 kcal/mol. There is a small but noticeable difference, $\sim$ 2 kcal/mol between DFA@HF and DFA@HF-inv (the Hartree-Fock density obtained from Kohn-Sham inversion). This is associated with the difference in the Hartree-Fock and Kohn-Sham orbitals.

To understand the density errors of DFA or DFA@HF, $E_{\rm DFA}[n]$ must be used, as in Eqs. (3) and (4), but there are many other ways to measure density errors that can lead to different conclusions about the relative accuracies of the DFA and HF densities. For the neutral water dimer, Ref. 13 set up a plane perpendicular to the bond axis, such that a coupled cluster calculation put exactly 10 electrons on each side, and found electron transfer errors of opposite sign for semi-local DFAs and for HF. Ref. 30 found the same behavior for several transition states. The errors were small in magnitude, and smaller for HF than for a few DFAs. In the cases studied here, $E_{\rm DFA}[n_{\rm HF}] - E_{\rm DFA}[n_{\rm exact}]$ is strongly positive, but that does not rule out $E_{\rm exact}[n_{\rm HF}] - E_{\rm exact}[n_{\rm DFA}]$ being negative; the HF density could be better than the DFA density in the sense of the exact density functional variational principle. That

said, Fig. S1 of the Supplemental Material shows an independent measure by which the density error of H...H...F decreases from Hartree-Fock to SCAN to CCSD(T).

In summary, we have shown that DFA@HF works for the barrier heights to chemical reactions, and have suggested that it works for the binding energies of larger water clusters, not because the Hartree-Fock density is more accurate than the self-consistent DFA density but because the Hartree-Fock density creates a positive and excessive over-correction of the DFA density-driven error that cancels much of the negative functional-driven error. The large functional-driven error for barrier heights was estimated first in Ref. 30, and has been refined and confirmed here. It is clear from Refs. 7–10 and from Eqs. (1)–(3) that, when the functional-driven error of a DFA is large and its density-driven error is small in comparison, a true density correction cannot lead to high accuracy. Future work will employ proxy-exact functionals to test this hypothesis for larger water clusters. Clearly, improved functionals will need the right amount of fully nonlocal density dependence, in both the exchange-correlation energy and the exchange-correlation potential. Self-interaction corrections[30,44] to DFAs, while needing improvement for some properties, appear for barrier heights to get the right answer for the right reason, by significantly reducing both functional- and density-driven errors.

Besides density-corrected density functional theory, there is a second evolution from HF-DFT which is less relevant to our work but also interesting. Bartlett and collaborators[45,46] have proposed a correlated orbital theory and associated QTP functionals in which the orbital energy eigenvalues yield accurate vertical ionization energies from all the occupied states (a condition they infer from adiabatic time-dependent density functional theory). In their work, the (generalized) Kohn-Sham potential, and not the density, takes center stage. As an example, they start with a four-parameter range-separated hybrid functional, then adjust the parameters in the functional (and thus in its potential) to give a best fit of the energy eigenvalues to the five vertical ionization energies of the water molecule.[45] The same parameters produce good vertical ionization energies and other properties in other systems,

with low many-electron self-interaction error. This approach should not be applied to the semi-local functionals considered here, for which all parameters satisfy other constraints and for which the orbital energy eigenvalues are strongly contaminated by self-interaction error. It could however be a way to improve one-electron self-interaction corrections to the semi-local functionals.

The conclusions of Ref. 30 (cancellation of functional- and density-driven errors) for the BH76 barrier heights in Hartree-Fock density functional theory were based upon three (hybrid or self-interaction-corrected) proxies for the exact densities, and have been confirmed here for the $H_2 + F \rightarrow H + HF$ barriers, and their accurate Kohn-Sham inversions. A confirmation for the full BH76 set, using a more efficient but perhaps less accurate approach (orbital optimized MP2), has been made recently in Ref. 47. Reference[48] provides recent confirmation of our findings, with an interesting analysis of barrier-height errors with and without a self-interaction correction. The higher accuracy of GGA, meta-GGA, and hybrid functional densities over the Hartree-Fock density was demonstrated for isolated atoms[16] and for the dipole moments of molecules at equilibrium.[49]

For the barrier heights to chemical reactions, as for the binding energies of equilibrium molecules, the density-driven errors of self-consistent DFA calculations are small, as the variational principle applied to Eq. (3) would suggest, but the functional-driven errors of the barrier heights are large in magnitude, as in Table 1.

Supporting Information

Numerical validation of the Kohn-Sham inversion; single-point total energies with respect to basis set size; complete basis set extrapolation; molecular geometries; analysis of density errors of HF, SCAN, and CCSD(T) relative to Brueckner coupled-cluster doubles (CCD) density

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