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Density-corrected DFT explained: Questions and answers

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Abstract

HF-DFT, the practice of evaluating approximate density functionals on Hartree-Fock densities, has long been used in testing density functional approximations. Density-corrected DFT (DC-DFT) is a general theoretical framework for identifying failures of density functional approximations by separating errors in a functional from errors in its self-consistent (SC) density. Most modern DFT calculations yield highly accurate densities, but important characteristic classes of calculation have large density-driven errors, including reaction barrier heights, electron affinities, radicals and anions in solution, dissociation of heterodimers, and even some torsional barriers. Here, the HF density (if not spin-contaminated) usually yields more accurate and consistent energies than those of the SC density. We use the term DC(HF)-DFT to indicate DC-DFT using HF densities only in such cases. A recent comprehensive study (J. Chem. Theory Comput. 2021, 17, 1368–1379) of HF-DFT led to many unfavorable conclusions. A re-analysis using DC-DFT shows that DC(HF)-DFT substantially improves DFT results precisely when SC densities are flawed.

I. Introduction

In any practical Kohn-Sham density functional theory (KS-DFT) calculation, of which there are tens of thousands reported each year, the exchange-correlation (XC) is approximated, and there are literally hundreds of approximations in common use today.[1] In every single case, one can consider the error in the calculation as arising from two different sources: the error in the self-consistent (SC) density and the error in the final evaluation of the total energy.[2] Density-corrected DFT (DC-DFT) is a formal framework for distinguishing these two types of error.[3, 4]

To be clear, in the vast majority of DFT calculations reported, the SC density is an excellent approximation to the exact density, so that the error in the energy is almost entirely due to the functional approximation to the energy. However, in a significant subset of calculations where standard approximations show surprisingly large errors, these errors can be traced to the error in the SC density.[5, 6] In such cases, use of a more accurate density usually reduces the error significantly (typically by a factor of 2 or more). This has been demonstrated for specific classes of problems, such as electron affinities[7], dissociation energy curve of diatomic molecules[5, 8], radical ions in solution[4], σ-hole interaction energies of halogen bonds[6], and spin gaps of transition metal complexes[9].

This observation would be useless if one always needed highly accurate densities to generate these improvements in energies, as such densities would cost at least as much as generating highly accurate energies via, e.g., CCSD(T).[8] However, in practice, when standard semilocal density functionals fail due to density-driven errors, the Hartree-Fock (HF) density is usually sufficient to generate energetic improvements that are comparable to those of the exact density. In various calculations going back to the early 1990's and the rise of DFT for computation in chemistry, there have been applications of this approach, dubbed HF-DFT, mostly for convenience, but no general understanding of when it should be applied.[10, 11, 12, 13, 14, 15, 16] Once codes were reworked to automatically perform self-consistent DFT calculations, which has both formal and practical advantages, it became largely obsolete.

DC-DFT is the theory that explains when HF-DFT should be applied and when it should work. The significance of DC-DFT is that it helps the systematic development of density functional approximation by providing a principle for determining the true error. The exact functional is free of density errors, since both its energy and its functional derivative (which determines the density) are exact. For *any* approximation, the error in the energy has contributions from both the functional and the density. Typical DFT error analysis is based on the total energy error and does not distinguish the source of the error nor determine the accuracy of the functional. According to the principles of DC-DFT, researchers should use just functional errors (or use them together with density-driven errors) to formulate strategies and guidelines for functional correction and development. In the early days of DFT in quantum chemistry, these principles were largely irrelevant, as functionals were rather crude and most calculations had relatively negligible density-driven errors (hence the use of HF-DFT when convenient). With the rise in applications of DFT to many different systems throughout chemistry[17, 18, 19], the characterization of errors for specific properties or systems, and the ever increasing accuracy of modern functionals[1, 20], the importance of the principles of DC-DFT has grown enormously.

DC-DFT is a rigorous theory, separating errors using the exact density. It identifies approximate DFT calculations as abnormal

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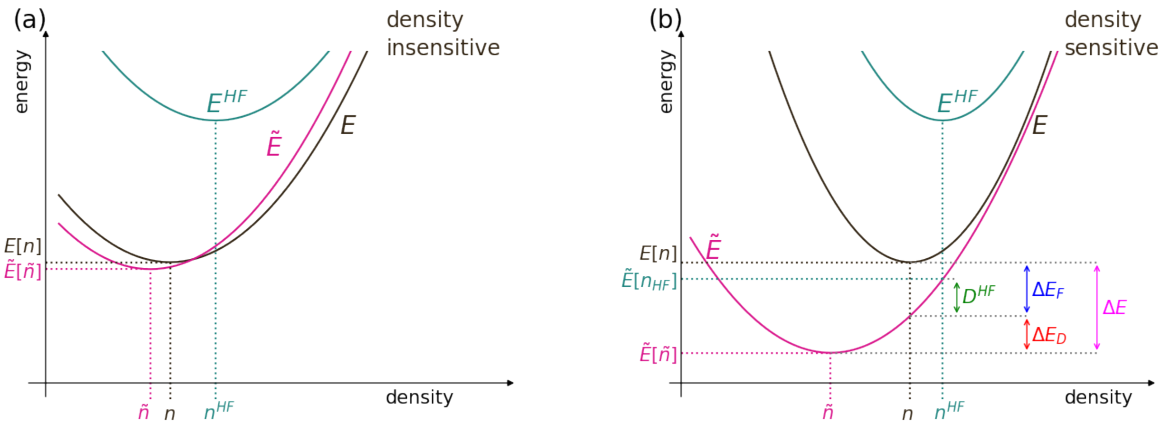

Figure 1: *Cartoon of the exact (black), approximate (magenta, denoted with tilde) and HF energy functionals (green). (a) is the usual case, where accuracy is not much affected by which density is used; (b) is a density-sensitive case, where use of exact (or HF) density significantly reduces error.* $\tilde{E}[n^{HF}]$ *is the approximate energy on the HF density, while* $\tilde{E}[\tilde{n}]$ *is its self-consistent ground-state energy.*

when the density-driven error is signficant. In practice, it is most often applied using the HF density in place of the exact one, and using a simple heuristic like density sensitivity in place of abnormality to decide if the HF density should be used in place of the self-consistent density. We have called that procedure DC(HF)-DFT, meaning density-corrected DFT, using the HF density but only when it is appropriate.

The most immediate application of DC(HF)-DFT is to understand HF-DFT, by producing a recipe stating when it should improve over SC-DFT. Thus, DC(HF)-DFT includes two criteria for when a HF density should be used instead of a SC density. The most important is that the calculation under consideration should be contaminated by a density-driven error. Simple measures that are suitable for many circumstances have evolved.[21] The current criteria is if the energy calculation shows pronounced density sensitivity, i.e., the result changes appreciably when evaluated on two distinct densities. Second, because the HF density is a proxy for the exact density, we avoid its use when it is spin contaminated (note that spin contamination is typically less of a problem for SC-DFT).[22] These criteria are both common sense and understandable in terms of the general theory of DC-DFT.

This paper explains the current state of the art of DC(HF)-DFT, and its relation to HF-DFT (meaning always using HF densities instead of self-consistent ones). In the background section, we give both the general theory of DC-DFT and the history of HF-DFT. The recent work of Jan Martin and co-workers in Ref. [23] was possibly the most comprehensive study of HF-DFT to date (although, as we detailed below, it contained several conceptual confusions and other difficulties). But it did not apply DC(HF)-DFT methodology in its current form. We illustrate with many examples from Ref. [23] data the detailed performance of DC(HF)-DFT.

II. BACKGROUND

i. DC-DFT

The core idea of DC-DFT is to separate the energetic error of any SC-DFT calculation into a functional contribution and a density-driven error, where the latter vanishes if an approximate functional is evaluated on the exact density. Writing the total SC-DFT energy error as: $\Delta E = \tilde{E}[\tilde{n}] - E[n]$, where E and n are the exact energy functional and density, and $\tilde{E}$ and $\tilde{n}$ are their approximate counterparts, ΔE is decomposed as:[3, 8, 21]:

$$\Delta E = \underbrace{\tilde{E}[\tilde{n}] - \tilde{E}[n]}_{\Delta E_{\rm D}} + \underbrace{\tilde{E}[n] - E[n]}_{\Delta E_{\rm F}}, \tag{1}$$

where $\Delta E_{\rm F}$ is the functional error and $\Delta E_{\rm D}$ is the density-driven error. Almost all present DFT calculations use the KS scheme[24], in which the functional error is simply the error in the XC approximation, evaluated on the exact density. Moreover, almost all such calculations are for energy differences, so one applies Eq. 1 to each calculation separately, and subtracts.

Most standard XC approximations begin with a semi-local form, including a generalized gradient approximation (GGA). For many molecules and properties of chemical interest, such as dissociations energies, the magnitude of $\Delta E_{\rm D}$ with such functionals is much smaller than that of $\Delta E_{\rm F}$, and can be neglected. On the other hand, in density-sensitive calculations, $|\Delta E_{\rm D}|$ represents a significant fraction of the total error (see the cartoons in Fig. 1 comparing density-sensitive and insensitive calculations). The density-sensitivity of a DFT calculation depends on the system under study, the property being extracted, and the approximate functional.

Generically (but not always), removal of the density-driven error in density-sensitive calculations improves the result substantially. Rigorously, a precise calculation of $\Delta E_{\rm D}$ by Eq. 1 requires highly accurate densities from, e.g., correlated wavefunction calculations. This can only be done for smaller systems. Moreover, the well-known difficulties of performing KS inversions within atom-centered bases limit the precision of such calculations[25, 26], which must be accurate enough to measure the difference in density-driven error between the SC-DFT density and the more accurate one.[8]

By definition, the theory of DC-DFT tells us that, for the vast majority of modern KS-DFT calculations, the SC density is a very good approximation to the exact density. It even provides an extremely meaningful metric of the quality of a density, namely how much of the energy error is due to the density error.[21] Given the formal and practical advantages of SC densities, we should only consider using a different density when the density-driven error is significant.

Finally, we mention that there is extensive theory behind Eq. 1. Ref. [27] shows the functional analysis that can be applied, and derives 79 more equations from Eq. 1. An almost identical analysis applied to geometries in computational chemistry (ranging from force fields to ab initio quantum chemical methods), produces a cornucopia of results.[28] The performance of such methods for molecular geometries typically differs drastically from their energetic performance.

ii. HF-DFT as a DC-DFT procedure

We define HF-DFT as the practice of evaluating an XC approximation on the HF density and orbitals in all cases.[29] For many standard XC approximations, molecules, and properties, when the calculation is density sensitive, HF-DFT yields more accurate results than SC-DFT. For insensitive calculations, this may or may not be true, but it is irrelevant, as the density-driven errors are negligible. Thus the theory of DC-DFT provides criteria for when HF-DFT should yield a better result. The first is that the calculation should be density sensitive. The second is that the HF density should be a good proxy for the exact density, and hence not be, e.g., spin-contaminated or flawed in some other way.

Thus HF-DFT is a *procedure*, whereas DC-DFT is a theoretical framework, and the two terms should not be used interchangeably. We use the acronym DC(HF)-DFT to denote the use of HF-DFT *only* when a calculation is density-sensitive and its HF wavefunction is not spin-contaminated. Unfortunately, this distinction has not always been emphasized in the past. In their paper, Ref. [23] applied the HF-DFT procedure to *every* calculation in the GMTKN55 database[19], which goes against the basic principles of DC-DFT, and provides little or no information about the performance of DC(HF)-DFT.

By the use of the exact $n(\mathbf{r})$, $\Delta E_{\rm D}$ is completely eliminated (Eq. 1), but $n(\mathbf{r})$ is prohibitively expensive in practice. HF densities offer a viable alternative for reducing large density-driven errors. In this way, only for density-sensitive calculations, the $\tilde{E}[n] \approx \tilde{E}[n^{\rm HF}]$ approximation is made. Using $n^{\rm HF}(\mathbf{r})$ in place of SC $\tilde{n}(\mathbf{r})$ to reduce density-driven errors makes sense when:

$$D^{HF} = \left| \tilde{E}[n^{\rm HF}] - \tilde{E}[n] \right| << |\Delta E_{\rm D}|\, . \qquad (2)$$

This condition is sufficient, but is not always neccessary. When HF overlocalizes, HF-DFT can outperform SC-DFT for functionals that delocalize, even if Eq. 2 is not satisfied. From the KS inversion that gives us access to highly accurate densities and KS orbitals for small systems, it has been found that Eq. 2 holds for typical cases when $\Delta E_{\rm D}$ is large.[8] This, in turn, justifies the choice of using $n^{\rm HF}$ in place of n in those calculations. It was also found that, for orbital-dependent XC approximations, the replacement of the KS kinetic energy with the HF kinetic energy also introduces errors that are far smaller than $\Delta E_{\rm D}$.[8]

Since measuring $\Delta E_{\rm D}$ by Eq. 1 requires exact densities, the more practical *density sensitivity* measure has been introduced:[21, 6, 8]

$$\tilde{S} = \left| \tilde{E}[n^{\rm LDA}] - \tilde{E}[n^{\rm HF}] \right|, \qquad (3)$$

where tilde indicates a given functional approximation. This measure requires two non-emprirical densities: HF densities which are typically overlocalized and LDA densities which are typically delocalized. Neither density is too expensive in routine molecular calculations. In this way, $\tilde{S}$ serves as a practical indicator of the density sensitivity of a given reaction and approximate functional. For small molecules, $\tilde{S} > 2$ kcal/mol implies density sensitivity, that the calculation may suffer from a large $\Delta E_{\rm D}$, and for semilocal approximations, HF-DFT will likely improve a functional's performance.[21] Therefore, SC densities should be replaced by HF ones only in density-sensitive calculations. Even in those cases, one has to keep an eye on whether $n^{\rm HF}$ is severely flawed by spin-contamination, as then the use of HF densities (at least those from the spin unrestricted formalism) is not recommended either. There is a need to develop a clever way to deal with the spin contamination issue, but for now, we are converting HF density to SC density for practical reasons. The cutoff of 2 kcal/mol is taken as typical for covalent bonds in small molecules. As molecules grow, the cutoff must grow.[30] For reactions where small energy changes matters like non-covalent interactions, a smaller cutoff is appropriate.

iii. History: HF-DFT before and after DC-DFT

The use of the HF-DFT procedure long predates the analysis of DC-DFT [12, 14, 31]. As far back as the 1970's, Colle and Salvetti developed approximate correlation functionals that were trained and applied to HF densities[32], and led to the LYP functional[33]. Other functionals, such as those of Gordon and Kim[34], and Wilson and Levy[35] were developed in a similar fashion, and these functionals were at the time highly competitive for weak interactions[34, 36] Even the B88 GGA[37] was developed on HF atomic densities. Gill *et al.* used HF-DFT for practical reasons to test the accuracy of GGAs and hybrids without a need to obtain SC densities and orbitals for each of the functionals.[11, 12] Another reason why HF-DFT can be considered more practical than SC-DFT is that the former requires no grids for the XC potential at each self-consistent field (SCF) iteration.[38] In all these cases, we would now say that the authors were assuming (correctly) that the calculations were density-insensitive, and the error was dominated by the error in the XC approximation, regardless of HF versus SC density.

However, some pioneering efforts *did* notice that, for some problems where SC-DFT was underperforming, HF-DFT gave systematic improvements. This was most often observed for barrier height calculations, as demonstrated by different authors.[39, 31, 38, 21] We now understand that this entire class of calculation is typically density-sensitive (see below) and DC-DFT tells us why HF-DFT works better here but not, say, for main-group reaction energies. Some of our own earlier works on electron affinities[7, 40, 41] are couched in terms of self-interaction error and were not understood in terms of the general principles of DC-DFT until later.[2, 3] On the other hand, DC-DFT has reignited interest in functionals of the HF density.[42] For example, it has been shown that the large-coupling strength expansion of the Møller-Plesset adiabatic connection is a functional of the HF density.[43, 44, 45] This finding motivated the development of a new class of functionals applied to HF densities, which have been found to be highly accurate for weak interactions.[45]

After DC-DFT was developed[3], explaining the success and validity of HF-DFT results, Sim and co-workers could then identify specific classes of calculations that are prone to density-driven errors, where HF-DFT should (and does) give improved results over SC-DFT. In addition to barrier heights, these include: dissociation of stretched molecules[5], some radical reaction energies[4], electron affinities[41, 40, 7], specific torsional barriers[46], some weak interactions[6], spin gaps of Fe(II) complexes[9], interaction of water clusters[47], etc. The work of Ref. [23] is perhaps the most systematic benchmark of the HF-DFT procedure, but uses nothing from DC-DFT. In the rest of this paper, we shall analyze their results within DC-DFT, the modern theory behind HF-DFT.

III. SPECIFIC EXAMPLES

i. When should HF-DFT give improved results, and when should it not? *HF-DFT works only for density sensitive cases.*

The theory behind DC-DFT shows that correcting the density is relevant only when the self-consistent density is unusually inaccurate. We use density sensitivity as a proxy for this criterion and use a typical number (2 kcal/mol) as a heuristic for small molecules with chemical bonds.

It is not possible to see improvements by simply reporting HF-DFT numbers from large databases. In many classes of calculations, the insensitive cases heavily outnumber the sensitive cases. The gains from using HF densities in sensitive cases can be easily hidden by the many insensitive cases, where it often *worsens* energetics relative to self-consistency.

We illustrate these points with PBE calculations on four specific databases in Fig. 2. The first is the BH76 database of barrier heights. Clearly, HF densities yield better energies when $\tilde{S}$ is above 2 kcal/mol, which is the vast majority of cases in this database. But for the few insensitive cases, we see HF-DFT usually yields worse results. The same pattern is repeated for B30, a database of halogen and other bonding energies. On the other hand, for AL2X6, most are not density-sensitive and HF-DFT worsens the energetics. (The one larger than 2 kcal/mol is still better self-consistently, suggesting a higher threshold is needed here.) Finally, in the DARC data set, no case has a sensitivity greater than 2 kcal/mol and self-consistent calculations are better in almost every case. For this data set, HF-DFT worsens the MAE of SC-DFT by about 1 kcal/mol, but DC(HF)-DFT does not.

These observations illustrate the importance of measuring density errors using energies. The errors of semilocal functionals for both Diels-Alder reactions and barrier heights are both due to *delocalization error*.[49, 50] The density errors are energetically very relevant to barrier height energetics, but irrelevant to Diels-Alder reactions. DC-DFT accounts for this distinction, whereas HF-DFT does not.

ii. Is it easy to spot density-sensitivity? *Not always.*

In Table 1, we show PBE mean absolute errors, in its HF-, DC(HF)-, and SC- versions with and without the D4 dispersion enhancement[52], for three density-sensitive data sets, including and excluding cases where unrestricted HF (UHF) densities are spin-contaminated. For all three datasets, HF-PBE improves over SC-PBE, often substantially. On the other hand, addition of D4 to self-consistent results often worsens them, because the D4 corrections cannot account for poor densities. But D4 corrections on HF densities generally do not worsen them. Situations where Grimme's dispersion enhancement worsens self-consistent results due to large density-driven errors have been already described.[53, 54]

Next, we consider the effect of spin contamination in the UHF calculations. For spin-contaminated cases, DC(HF)-PBE reverts to SC-PBE, simply because we no longer believe the HF density is a better approximation to the exact density. When HF spin-contaminated cases are excluded, the accuracy of DC(HF)-PBE for BH76 is about the same as that of HF-PBE. This indicates that for BH76 even spin-contaminated HF densities lower large PBE density-driven errors. But, for RC21, DC(HF)-PBE improves over HF-PBE and there we can see the benefit of reverting DC(HF)-PBE to SC-PBE when HF is spin-contaminated. In the case of RSE43, the MAE of DC(HF)-PBE is about the same as that of HF-PBE. But when HF spin-contaminated cases are excluded, DC(HF)-PBE worsens HF-PBE. Why is that? It appears that our generic cut-off of 2 kcal/mol for density-sensitive calculations is too large for RSE43, whose averaged absolute energies are several times smaller than those of RC21 and BH76 [19]. When this cut-off is lowered to 1 kcal/mol, the MAE of DC(HF)-PBE for RSE43 (HF spin-contaminated cases excluded) is lowered by 0.5 kcal/mol (see the right panel of Fig. S1). This demonstrates the cutoff of 2 kcal/mol is simply a heuristic aimed at covalent bonds in small molecules, and should be sensibly adjusted in different situations.

iii. Do range-separated hybrids have smaller density-driven errors than their global counterparts? *Yes.*

Ref. [23] found that "range-separated hybrids do not benefit much from HF-DFT as so much HF exchange is already present at a long range." In fact, in an earlier study, we showed that indeed range-separated hybrids (RSHs) suffer much less from density-driven errors than their global counterparts.[53] For example, semilocal DFT caclulations of the WATER27 clusters are prone to large density-driven errors as suggested by their large density sensitivities, which in the case of PBE approaches 30 kcal/mol. Unless this density-driven error is corrected (by, e.g., HF-DFT), dispersion corrections can even worsen the results.[53, 54] In contrast to standard semilocal calculations of the WATER27 clusters, a state-of-the-art RSH developed by Mardirossian and Head-Gordon[20], ωB97M-V, suffers far less from density-driven errors, and its density-sensitivities for WATER27 cluster are about 10 times smaller than those of PBE and 3 times smaller those of B3LYP[53]. Thus DC-DFT explains why such functionals have small density-driven errors.

To further understand density-driven errors in RSHs, consider NaCl. Standard semilocal functionals fail beyond about 5.8 Å, due to incorrect charge transfer, a specific type of delocalization error[56]. We perform calculations for NaCl at 6.4 Å using LC-ωBLYP, which

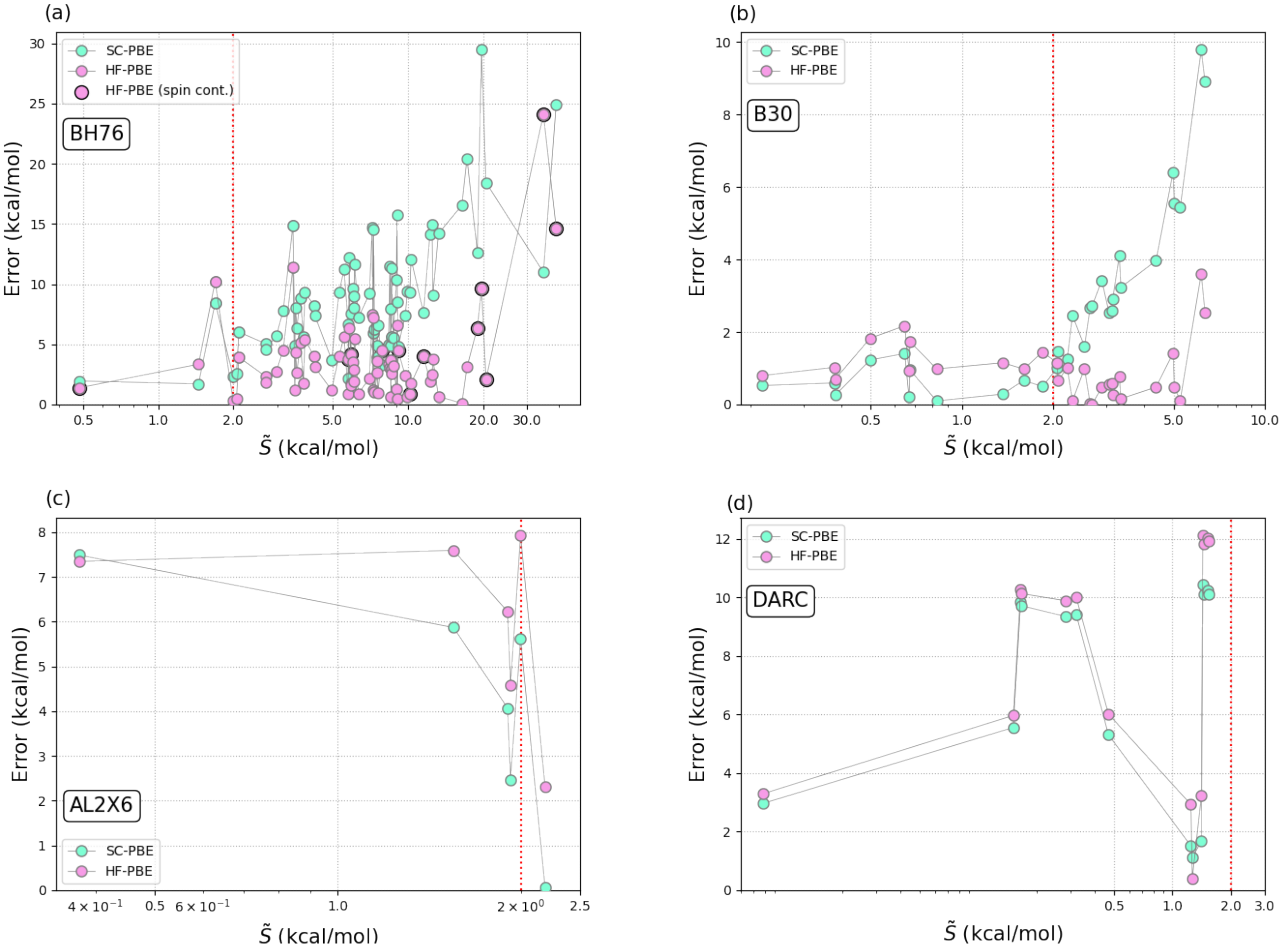

Figure 2: *Importance of density sensitivity: Self-consistent and HF absolute errors versus density-sensitivity [Eq. 3] for PBE on the (a) BH76[19] dataset, containing 76 hydrogen and non-hydrogen transfer reaction barrier heights (spin contaminated cases are marked as black marker edge color), (b) B30[48] dataset, containing 30 halogen, chalcogen and pnictogen bonding energies, (c) AL2X6[19, 49] dataset, containing 6 dimerization energies of alane derivatives, and (d) DARC[19, 49] dataset, containing 14 Diels-Alder reaction energies.*

employs ωB88 exchange at short distances and HF exchange at long distances. We calculate ΔE_{D} for the atomization energy of this system as a function of the range-separation parameter, ω, by using accurate density from CCSD as done in Ref. [8]. The results are shown in Fig. 3. The inset shows the intrinsic atomic orbital (IAO)[55] population of the Na atom as a function of ω and the dotted horizontal lines represents accurate IAO from CCSD (calculated via inverted KS orbitals[8]). The CCSD and HF's IAOs are virtually indistinguishable. If $\omega = 0.2$ for example, the turnover distance to full exchange is sufficiently large that significant density-driven errors would occur, just as in global hybrids. But already at $\omega = 0.4$, the default value used in LC-ωBLYP [57], ΔE_{D} and the deviation of the IAO charge from the reference are small.

iv. Can one see that the HF density is more accurate than the self-consistent density by studying density plots? *Typically, it is hopeless.*

There is a long history of studying density differences and density error plots in DFT, in both physics and chemistry, with the aim of improving approximations. Comparison is not only related to the difference between HF and self-consistent DFT approximations, but also for the density of other methods such as MPn and CASSCF.[58] Very little insight can be gained for improving functionals from such plots, due to the complexities of the relation between densities and potentials, as well as that between potentials and energy functionals. Because most good XC energy approximations yield good densities in most calculations, despite their very poor approximate potentials, it is very difficult to trace the effects of a good energy approximation in the (often) tiny differences in densities. Even in cases where we know a better density is yielding better energetics, it is often not possible to say which aspects are relevant. (See Fig. 4 of Ref. [9].)

The clearest case is that of small anions. For atomic anions, the

		$\tilde{S}_{avg}$	SC	HF	SC-D4	HF-D4	DC(HF)	DC(HF)-D4
BH76	all	8.0	8.8	3.9	9.3	4.0	4.4	4.7
	w/o 12 spinc	6.6	8.5	3.3	8.9	3.6	3.3	3.5
RC21	all	9.2	5.4	4.6	6.9	4.0	4.3	4.1
	w/o 9 spinc	11.3	6.8	4.8	8.5	3.8	4.8	3.8
RSE43	all	3.7	3.1	2.0	3.0	2.0	2.0	1.9
	w/o 8 spinc	2.0	2.9	1.0	2.8	0.9	1.5	1.5

Table 1: *PBE mean absolute errors (MAE) on three datasets (BH76, RC21, and RSE43) self-consistently, with the HF density, and DC(HF). $\tilde{S}_{avg}$ is the averaged density sensitivity for each dataset. The deviation of HF's $\langle S^2 \rangle$ by more than 10% from the ideal value the criterion for spin-contamination [51]. For all 3 datasets, MAE/Root-mean-squared-displacement of absolute errors (RMSD) values of SC-PBE becomes (5.8/4.9 kcal/mol) to (5.7/4.3) when eliminating the spin-contaminated cases while HF-PBE becomes (3.1/3.6) to (2.4/2.5). The D4 parameters uses the same parameter as PBE-D4 of Ref. [52]. See Table S2 for other RMSD information.*

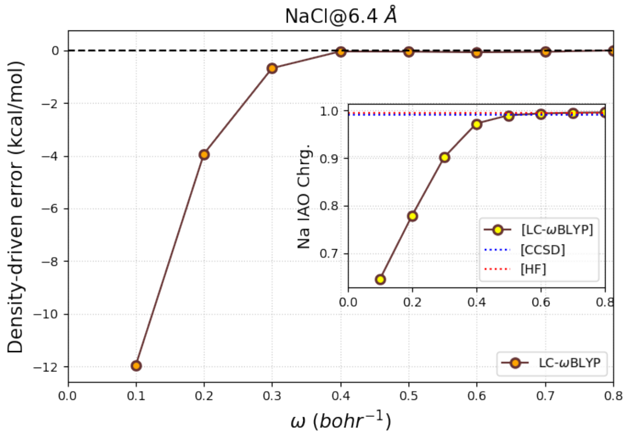

Figure 3: *Density-driven error (ΔE_D) for atomization energy of NaCl at 6.4 Å bond length from LC-ωBLYP with respect to ω (the range-separation parameter). Accurate CCSD/def2-QZVPPD density and orbitals are obtained from a Kohn-Sham inversion as in Ref. [8]. The inset shows the intrinsic atomic orbitals (IAO) population of the Na atom [55].*

true self-consistent density with semilocal functionals is typically one with about 0.3 electrons escaping to infinity, and $Z + 0.7$ electrons bound to the nucleus. In that case, the error in the density is glaringly obvious, even to the eye (see Fig. 2 of Ref. [3]). But for a complicated molecular reaction in which a small energy difference is being calculated (such as a barrier height of the type we have already studied), the difference in such differences is typically both small and subtle and tremendously difficult to interpret.

In Fig. 4, we illustrate this with two density difference plots, being differences between HF and PBE densities. These differences tend to be invisible on the scale of the densities themselves (without labels, could one guess which density is HF and which is PBE?) and the differences display many changes of sign. The upper panel (c) is for the reactants, the lower for the transition state geometry. How can one tell that one case is density sensitive, and the other not? But the extreme right-hand panel tells us that there is a significant energetic difference between the two different densities when calculating the reaction barrier, and indeed the density sensitivity of the PBE barrier is higher than 2 kcal/mol (4.9 kcal/mol and 9.1 kcal/mol for forward and backward each). Moreover, PBE evaluated on the SC density predicts that the forward reactions has no barrier, whereas the PBE barrier calculated from the HF density is highly accurate. Again, this is something that one would not be able to deduce by comparing the (d) and (e) density plots.

Ref. [23] comments: "What is the effect of the HF density here really? We attempted to create a difference density plot between HF-PBE and PBE for the water dimer, but nothing of note is easily visible." This is typically the case, but only emphasizes the importance of the DC(HF)-DFT energtic criteria for the accuracy of densities. In Ref. [21], handmade measures of errors in the density are too arbitrary to be of universal use.

DC-DFT builds an energetic criterion for measuring errors in approximate densities:

$$\Delta E^{ideal}[\tilde{n}] = E[\tilde{n}] - E[n], \tag{4}$$

which is always a single nonegative energy and provides an unambiguous measure for all systems and approximate densities. In general, obtaining $\Delta E^{ideal}[\tilde{n}]$ is expensive as computing $E[\tilde{n}]$ requires the inversion of a many-body problem and becomes more difficult than computing $E[n]$ itself. $\Delta E^{ideal}[\tilde{n}]$ is typically very close to $\Delta E_{\rm D}$[27], which although still expensive can be computed for more systems to gain insights into the density errors. For larger systems, where computing $\Delta E_{\rm D}$ becomes intractable, the sensitivity quantity of Eq. 3 designed to signal large density-driven errors can be used instead.

v. Can double hybrids benefit from HF-DFT? *Yes, if DC-DFT is applied very carefully.*

By generalizing their findings for standard hybrids, Ref. [23] concluded that HF-DFT is not beneficial for double hybrids (DHs) as these use large percentages of the HF exchange (typically $\geq 1/2$). We agree with Ref. [23] that it is reasonable to expect that the higher the exact percentage in a *global* hybrid is, the smaller DC-DFT correction is made by the use of HF densities. However, one has to be careful with the generalization of this statement to DHs given that the MP2-like energy expression evaluated on the KS orbitals is often very different from the same energy expression evaluated on the HF orbitals.[59] For that reason, the accuracy of standard DHs deteriorates when HF orbitals are used and so does the accuracy of HF-DHs when applied to the DFT orbitals (this is illustrated in Fig. S4 of Ref. [53]). At a more formal level, the adiabatic connection formalism that underpins the construction of

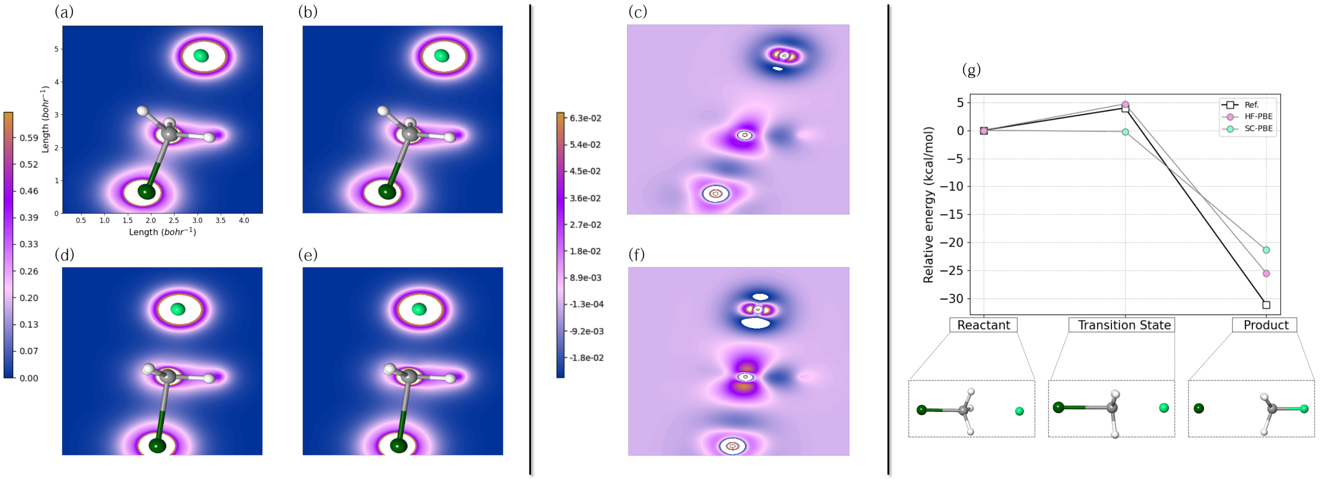

Figure 4: *Density plots for $CH_3Cl+F^- \rightarrow FCH_3+Cl^-$ (electrons per $bohr^3$): (a) and (b) are the PBE and HF densities for CH_3Cl+F^-, (d) and (e) are their analogs for the transition state geometries, and (e) and (f) are density differences. There is no way to deduce which method gives less density error or which geometry is more density sensitve by just looking at the real space density plot. But the reaction pathway plot in (g) shows that the HF density does better than the SC density, which was predictable from the large S values for both forward (4.9 kcal/mol) and backward (9.1 kcal/mol) barrier height.*

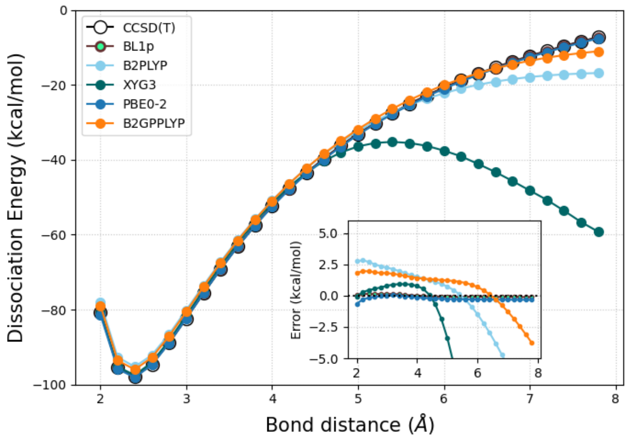

Figure 5: *Dissociation energy curve for NaCl with various approaches: standard DHs (B2PLYP, XYG3, PBE0-2, B2GPPLYP), HF-DH (BL1p) and CCSD(T) as a reference. def2-QZVPPD basis set is used in all calculations. Errors relative to CCSD(T) are shown in the inset.*

the recently proposed HF-DHs[43, 45, 60] is different from the usual DFT adiabatic connection used to rationalize and build standard DHs[61, 62].

Finally, we have recently developed 'BL1p', a single-parameter HF-DH trained and applied to HF densities. Using principles of DC-DFT in its design, BL1p fixes the problems of conventional DHs when applied to prototypical calculations suffering from large density-driven errors.[53] In Fig. 5, we show the NaCl dissociation as a prototypical case where density-driven errors are large, where the standard DHs fail at large distances, despite containing large amounts of the exact exchange but BL1p does not. Despite the claims of Ref. [23], DC-DFT had already provided improvements in DHs[53].

vi. Does HF-DFT work better than self-consistent DFT for electron affinities? *Yes, because standard calculations are unconverged, as demonstrated by their positive HOMO energies.*

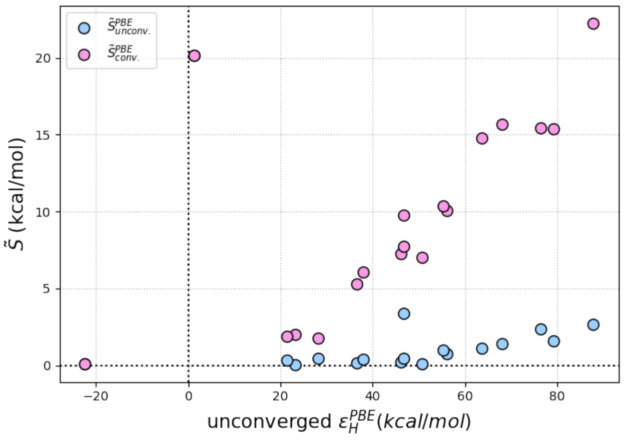

Figure 6: *Relationship between unconverged HOMO energy (ϵ_H^{PBE}) of the anion and density sensitivity $\tilde{S}^{PBE}$ for the electron affinities. ϵ_H^{PBE} energies are mostly positive as calculated from a finite basis set (if a loss of a fraction of an electron is enabled in the calculations ϵ_H^{PBE} would hit 0). The results are taken from Table 2, and include both converged (HOMO ≈ 0.000 a.u.) and unconverged $\tilde{S}$ values.*

It has long been known[34] that semilocal functionals fail to bind an additional electron to neutral atoms when a fully converged

	Electron Affinity (kcal/mol)				ϵ_H (kcal/mol)			
	PBE		B3LYP					
name	SC	DC	SC	DC	PBE	B3LYP	HF	exact
CH	3.9	3.1	-1.2	-2.3	56.1	37.5	-47.4	-27.9
CH_2	0.5	-0.5	-0.8	-1.3	55.2	37.3	-31.7	-13.4
CH_3	-2.4	-3.4	-5.1	-5.7	63.6	45.2	-18.8	-1.2
NH	-0.3	-1.8	-3.0	-4.1	79.3	57.8	-9.3	-8.3
NH_2	-0.8	-2.0	-4.2	-5.1	68.0	46.4	-29.2	-16.8
OH	4.1	0.8	-1.0	-3.0	46.7	22.3	-68.7	-41.7
SiH	0.5	0.2	-4.0	-4.8	36.6	25.6	-34.0	-29.3
SiH_2	2.4	1.8	-1.6	-2.6	37.9	27.0	-30.4	-25.1
SiH_3	-0.7	-0.6	-2.4	-2.1	23.1	8.3	-43.5	-31.4
PH	-3.1	-3.2	-3.9	-3.8	50.6	35.1	-18.5	-23.5
PH_2	-3.7	-3.3	-5.2	-4.8	46.1	30.8	-24.7	-28.8
HS	-0.5	-0.7	-2.5	-2.5	21.3	3.9	-59.7	-54.2
O_2	-0.1	-2.4	0.2	-1.1	76.4	47.7	-56.9	-9.5
NO	3.0	0.3	3.6	1.6	87.8	57.1	-59.8	0.2
PO	1.3	0.8	0.0	-0.8	46.7	28.7	-47.8	-24.9
S_2	-2.4	-2.0	-2.0	-1.6	28.2	10.4	-52.9	-38.0
Cl_2	4.6	4.5	7.6	7.1	-22.4	-45.9	-106.8	-54.7
MAE	2.0 (1.5)	1.9 (1.3)	2.8 (2.0)	3.2 (1.8)				
MAE*	2.9 (2.2)	1.8 (1.6)	2.1 (2.0)	2.0 (1.7)				

Table 2: *Electron affinity errors and anion HOMO energies for the G21EA dataset, omitting CN due to large spin-contamination in HF. Errors relative to GMTKN95 reference, and exact HOMO is negative of electron affinity. MAE is the mean absolute error with RMSD values in paraenthesis. All results use def2-QZVPPD basis set, except the last line, which are summary statistics using aug-cc-pVQZ.*

self-consistent solution is found. This is because the approximate KS potential (evaluated on the exact density) is far too shallow and becomes positive not far from the nucleus and stays that way until extremely far away (about 15 Å). This feature that makes it possible to extract accurate anion energies with reasonable standard atom-centered basis, because such basis cannot represent the regions distant from the nucleus. Thus such calculations yield a useful representation of the density, but at the price of having a positive HOMO, a definitive sign of an unconverged result. Such calculations are formally unjustified, as pointed out by Rösch and Trickey.[63] In a fully numerical calculation, one finds that the minimizing density loses about 0.3 electron to the continuum, and only binds about 1.7 electrons (for H^-). Thus the truly converged self-consistent solution[64] is extremely density sensitive (perhaps the most visible example we know of) and properly converged calculations have large density-driven errors.

Nonetheless, the trick of using a reasonable atomic basis does yield a reasonable density, despite formally being a meta-stable state, and thus accurate energetics. In fact, many electron affinities (EA) calculated in this way are more accurate than the corresponding ionization potentials. Ref. [23] finds that HF-DFT "appears to do more harm than good" when electron-affinities are calculated, and indeed the numbers are comparable. But DC-DFT provides formally more solid ground for calculating electron affinities than the standard DFT approximations with limited basis sets.[7, 40]

Consider what happens when we try to add an extra electron to the hydrogen atom within the PBE functional. First, we do the calculation in a large atomic basis. For the electron affinity of the hydrogen atom, PBE/aug-cc-pV6Z yields an error that is less than 1 kcal/mol (see Table S1 for numerical details). Moreover, the density sensitivity of this calculation is about 1 kcal/mol, which is less than our sensitivity threshold. This consideration would naively indicate that there is no need to invoke HF-DFT. But the positive HOMO of PBE reminds us that H^- is artificially bound by a finite atom-centered basis set despite its large size (aug-cc-pV6Z). The results for both electron affinity and $\tilde{S}$ are unconverged. If, instead, we converge the PBE calculation of H^- by enabling fractional occupations until the HOMO energy hits zero (as done in Ref. [21]), things change dramatically. About 0.37 of an electron is lost confirming that the converged PBE calculation does not even bind H^-. Moreover, the converged $\tilde{S}$ becomes 8 kcal/mol, showing that the calculation is in fact extremely density-sensitive.

We now repeat this test for the G21EA dataset and compare converged (a fraction of charge enabled until the HOMO hits zero) vs. unconverged (anions bound only by a finite basis) $\tilde{S}$ of PBE. These are shown in Figure 6 as a function of the HOMO energies of the anions (these are mostly positive as calculated from a finite basis set). First we note that the two sensitivities are identical in only one case (Cl_2), where self-consistent PBE gives a negative HOMO energy and therefore a bound anion. In all other cases, the unconverged calculations severely underestimate $\tilde{S}$. Furthermore, Fig. 6 also shows a clear correlation between the HOMO energy of the anion and $\tilde{S}$ of EA. In nearly all cases, the converged $\tilde{S}$ is above our 2 kcal/mol threshold. Thus DC-DFT invokes HF-DFT for calculations of the affinities given that HF HOMOs of the anions are bound and properly converged PBE calculations in nearly all cases give unbound anions.

What about the numbers? Basis-set bound DFT calculations give reasonable accuracies for the electron affinities. Table 2 shows electron affinity errors of PBE and B3LYP and their HF-DFT counterparts, and the corresponding anion HOMO energies. The MAEs of DC-DFT and basis-set bound (unconverged) DFT are comparable. But note that the RMSD values are noticeably smaller for DC-DFT, showing a smaller variance and less outliers. Moreover, if the smaller aug-cc-pVQZ basis set is used instead, as it often is in practice, many results shift by amounts comparable to these errors (see Table S3). Finally, we note that these molecules form the G21EA data set, with CN excluded as its HF wavefunction is heavily spin contaminated, so DC-DFT simply reverts to SC-DFT for that case. If, however, restricted open-shell HF (ROHF) is used instead of UHF for the CN molecule, the error of HF-PBE is greatly reduced. We currently use UHF as a default in our HF-DFT calculations of open-shell systems and we will further investigate the usability of ROHF-DFT[65] in the future.

vii. Is slow grid convergence as much a problem for HF-SCAN as it is for SCAN? *Yes, it can be.*

Ref. [23] have shown the HF-SCAN displays an excellent performance for the GMTKN55 database and gets beaten only by few modern and highly parameterized functionals. The painfully slow convergence of SC-SCAN calculations is well known, and even for simple atomization energies SCAN is difficult to converge within the available grid sizes in many standard quantum-chemical codes.[66] In the case of HF-SCAN, the orbitals are taken from a HF calculation so grids are only needed for the final energy evaluation and not for the whole SCF procedure. For that reason, one would assume that the grid convergence is less of a problem for HF-SCAN. Nevertheless, as shown in Fig. S4 for the G21IP dataset, HF-SCAN is also not converging within the grid sizes available in the quantum-chemical package ORCA. The r^{2}SCAN functional is designed to fix the grid convergence issues of SCAN, and as shown in Fig. S4, the HF-r^{2}SCAN results converge even within smaller ORCA grids. At the same time, the accuracy of HF-SCAN is comparable to HF-r^{2}SCAN (see, e.g., Fig. S4 illustrating this for the G21IP dataset). These difficulties are overcome by using extremely large grids in Qchem, showing that HF-SCAN can yield highly accurate MB-pol potentials for water simulations.[67]

viii. What are the current limitations of DC-DFT and where else can it be applied?

Homonuclear dimers: As a form of DC-DFT, HF-DFT is meant to reduce only density-driven errors and not functional errors. In cases where DFT errors are large even when an approximate functional is evaluated on the exact density, HF-DFT cannot help. While HF-DFT substantially reduces the errors of DFT in stretched heterodimers, this is not the case for homodimers. For example, upon stretching H_2^+ or He_2^+, the standard DFT methods have large self-interaction errors, only a tiny fraction of which is density-driven.[53] HF-DFT also cannot help stretching H_2[3], the case where standard DFT methods have large static correlation error[59].

Transition metals: DC(HF)-DFT has been mostly applied to main-group chemistry, but it also can be greatly useful in the transition-metal chemistry (see, e.g., Ref. [9] for the calculations of spin gaps of Fe(II) complexes). Further study on the usefulness of HF-DFT for the transition-metal chemsitry is warranted.[30]

Materials and surface science calculations: Different forms of DC-DFT have been also used to analyse the errors of DFT for surface science applications. The cases where more accurate densities improves the results of semilocal functionals drastically improves the adsorption description of CO on metallic surfaces have been identified.[68] In other cases, such as the challenging barrier height for attaching O_2 to the Al(111) surface, GGAs benefit little from more accurate densities.[69] This implies that the accuracy of their density is satisfactory at the GGA level and evaluating a hybrid functional on those GGA densities gives results similar to fully SC-hybrid calculations, but at a fraction of the cost.[69] Similar cost reduction strategies have been applied to semiconductor calculations.[70] In future years, where and how DC-DFT can be useful in surface and material science needs to be further explored.

Forces: Despite being a non-SCF scheme, the calculation of the analytical gradients for HF-DFT is just slightly more involved than those of SC-DFT. This has been demonstrated by Bartlett and co-workers[38, 71]. The more recent Pyxdh code[72] is written based on the PYSCF package[73] and with little modifications can be used for HF-DFT geometry optmizations. Besides earlier calculations of barrier heights by using HF-DFT optmized transition states[38] and exploration of radical potential energy surfaces[4], the performance of HF-DFT for molecular structures relative to their SC-DFT counterparts is yet to be systematically explored. This is another topic that we will cover in the future, and recently developed unambigious measures for assessing the quality of approximate molecular structures should prove useful.[28]

IV. CONCLUSIONS

We hope this short work explains and clarifies many of the basic issues behind density-corrected DFT. Most important among these are (a) that there exist many situations where the energy error in a DFT calculation has a significant density-driven contribution, (b) that blind application of HF-DFT (using DFT approximations on HF densities) is not DC-DFT and most (if not all) of the benefits of DC-DFT are lost in the details of large databases, but (c) careful application of the principles of DC-DFT shows that DC-(HF)-DFT, as a practical scheme, almost always works for density-sensitive cases.

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V. SUPPORTING INFORMATION

CCSD	17.3
HF-PBE	15.6
PBE (un-conv.)	16.6
PBE (conv.)	23.9
S^{PBE} (un-conv.)	1.1
S^{PBE} (conv.)	8.4

Table S1: *Electron affinity information of hydrogen atom. CCSD/aug-cc-pV6Z is used as a reference. For standard PBE functional, 0.37 electrons are unbound and denoted as un-converged. For converged cases, where electrons are omitted to match HOMO equals 0, denoted as converged.*

		$\tilde{S}_{avg.}$	SC	HF	DC(HF)	SC-D4	HF-D4	DC(HF)-D4
BH76	12 spinc	8.0	8.8 (5.0)	3.9 (3.7)	4.4 (5.0)	9.3 (5.1)	4.0 (3.7)	4.7 (5.1)
	w/o spinc	6.6	8.5 (3.8)	3.3 (2.6)	3.3 (2.4)	8.9 (3.9)	3.6 (2.7)	3.5 (2.6)
RC21	9 spinc	9.2	5.4 (3.2)	4.6 (3.5)	4.3 (3.1)	6.9 (3.7)	4.0 (2.7)	4.1 (2.9)
	w/o spinc	11.3	6.8 (2.8)	4.8 (3.2)	4.8 (3.2)	8.5 (2.9)	3.8 (2.4)	3.8 (2.4)
RSE43	8 spinc	3.7	3.1 (1.4)	2.0 (3.3)	2.0 (1.7)	3.0 (1.4)	2.0 (3.4)	1.9 (1.6)
	w/o spinc	2.0	2.9 (1.2)	1.0 (0.8)	1.5 (1.1)	2.8 (1.2)	0.9 (0.7)	1.5 (1.0)

Table S2: *PBE mean absolute errors (MAE, kcal/mol) on three datasets (BH76, RC21, and RSE43) self-consistently, with the HF density, and DC(HF). Root-mean-squared-displacement of absolute errors (RMSD) values are noted in the parenthesis.* $\tilde{S}_{avg.}$ *is the averaged density sensitivity (kcal/mol) for the given dataset. The deviation of HF's* $\langle S^2 \rangle$ *by more than 10% from the ideal* $\langle S^2 \rangle$ *value is taken as a criterion for spin-contamination [51]. The D4 parameters uses the same parameter as PBE-D4 of Ref. [52].*

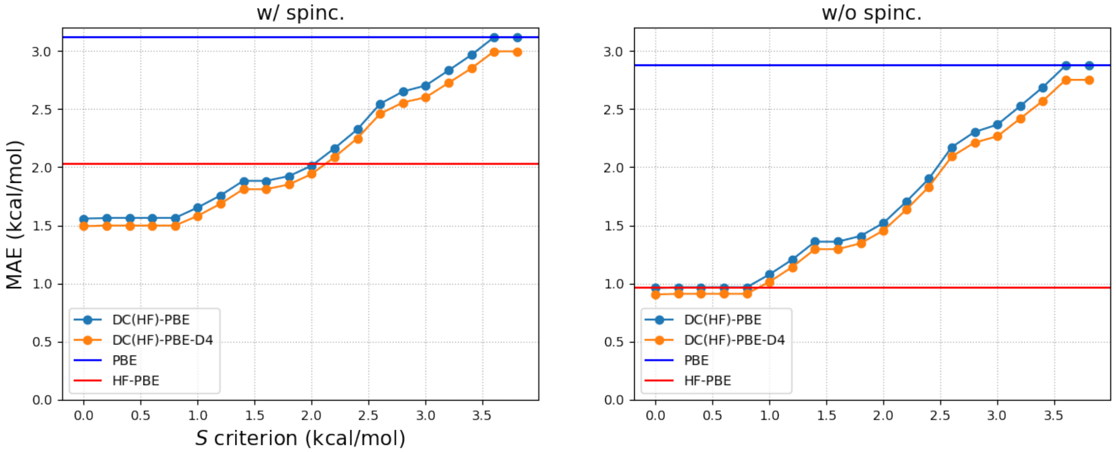

Figure S1: *MAE of RSE43 dataset with respect to the* $\tilde{S}$ *value cut-off criterion for DC(HF)-PBE. DC(HF)-PBE is SC-PBE for spin-contaminated cases and below the* $\tilde{S}$ *cut-off criterion value (the x-axis of the plots) and HF-PBE otherwise. The l.h.s. panel is the MAE of all cases in RSE43 and the r.h.s. panel is the MAE of non-spin-contaminated cases.*

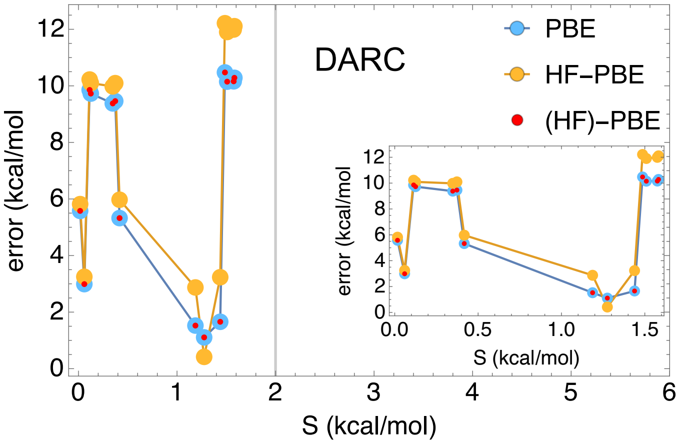

Figure S2: *Same as Fig. 2, but for the DARC dataset.*

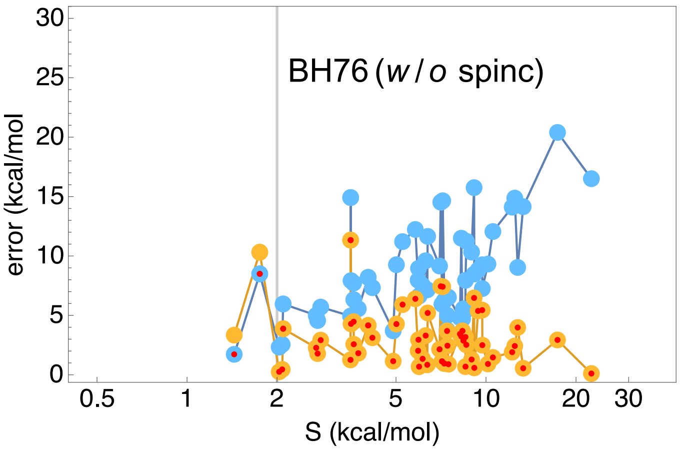

Figure S3: *Same as Fig. 2, but with spin-contaminated cases excluded.*

	Electron Affinity (kcal/mol)				ϵ_H (kcal/mol)			
	PBE		B3LYP					
name	SC	DC	SC	DC	PBE	B3LYP	HF	exact
CCH	7.5	5.5	1.5	-0.2	44.0	28.4	-49.3	-27.9
CH_2	3.6	1.8	1.8	0.8	44.5	29.5	-33.5	-13.4
CH_3	1.6	-0.2	-1.8	-2.8	48.7	34.0	-22.1	-1.2
NH	4.7	1.4	1.2	-1.2	64.3	46.7	1.0	-8.3
NH_2	2.6	0.7	-1.5	-2.6	57.0	38.2	-31.3	-16.8
OH	3.6	0.8	-1.2	-3.0	49.1	23.7	-68.6	-41.7
SiH	2.8	2.2	-1.9	-2.9	28.7	18.9	-35.7	-29.3
SiH_2	4.0	3.2	-0.2	-1.3	32.1	22.4	-30.4	-25.1
SiH_3	-0.2	-0.1	-1.9	-1.6	20.4	6.3	-44.2	-31.4
PH	1.0	0.6	-0.1	-0.3	38.0	24.4	-21.3	-23.5
PH_2	-0.2	0.0	-2.0	-1.8	35.1	21.4	-28.7	-28.8
HS	-0.6	-0.7	-2.5	-2.4	22.0	4.3	-59.7	-54.2
O_2	-0.2	-2.3	0.2	-1.0	77.7	48.1	-57.0	-9.5
NO	6.2	1.4	5.5	2.6	75.9	50.7	-60.2	0.2
CN	-2.8	17.3	1.6	19.1	0.0	-27.1	-120.9	-89.5
PO	3.8	2.6	1.9	0.8	39.2	23.5	-48.7	-24.9
S_2	-2.0	-1.5	-1.5	-1.1	28.5	10.4	-53.0	-38.0
Cl_2	5.4	5.2	8.4	7.9	-22.5	-46.0	-106.8	-54.7
MAE	2.9 (2.1)	2.6 (3.9)	2.0 (1.9)	3.0 (4.2)				
MAE*	2.9 (2.2)	1.8 (1.6)	2.1 (2.0)	2.0 (1.7)				

Table S3: *Same as the Table 2 but with aug-cc-pvqz basis set. Electron affinity errors for the G21EA dataset relative to GMTKN55 reference. HOMO energies (kcal/mol) for anions (ϵ_H). The exact value is the -EA of the reference energy. MAE is the mean absolute error of all electrons affinities while MAE* is the MAE without CN. RMSD values are given in the paraenthesis. CN is omitted due to large spin-contamination. See text for details.*

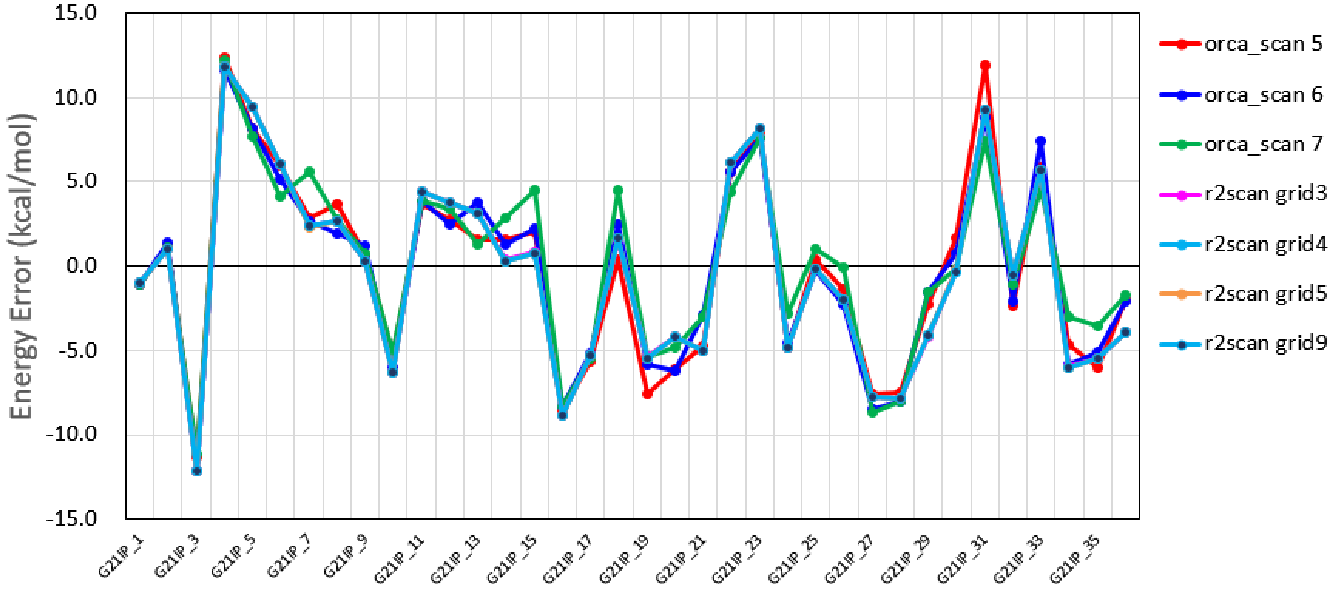

Figure S4: *G21IP reaction energy errors for SCAN and r2SCAN with various grid levels. SCAN shows a grid convergency issue (calculated by ORCA pacakge). Note that all r2SCAN results are very similar (almost no changes).*