of B3LYP), they were irrelevant. But in the modern era of vast databases that include weak interactions, stretched bonds, etc., these errors are sometimes as big as (or larger than) the differences between functional errors.[17, 20] However, the common practice of direct comparison with accurate energies conflates both errors and cannot distinguish the two. Recent advances in machine learning of density functionals target the density as well as the energy, and likely succeed because both errors are simultaneously minimized.[24]

The cure for this difficulty is simple: where relevant, empirical schemes should be trained on purely functional errors, i.e., the functional error of a parameterized approximation to the energy should be optimized against accurate energy databases, rather than the self-consistent error. For calculations that are not density-sensitive, the differences are so small as to make this irrelevant. But for those that are, this procedure isolates the self-consistency error, and avoids the corruption of the optimization process, and allows density-sensitive cases to be included, even for training.

The current paper demonstrates the dangers of ignoring this distinction when optimizing parameters in empirical functionals. We first create a totally artificial problem that highlights the difficulties, especially when one uses a semilocal approximation for the self-consistent density, but a more accurate form for the energy. In this case, we show how the exact functional is missed by the standard procedure. Next, we take the D3 correction of Grimme and co-workers,[25] and show how, if complexes with large density-driven errors are naively included, the results become noticeably worse. On the other hand, the use of DC-DFT allows previous good results to be retained, and the more difficult complexes to be included. Lastly, we apply our method to double-hybrids, producing a combination that competes with similar functionals, but also works when density-driven errors become strong.

For the purposes of this paper, we write a 4-parameter double-hybrid functional ($DH4p$) as:

$$E_{\rm XC}^{\rm DH4p} = E_{\rm X}^{\rm Slater} + a(E_{\rm X}^{\rm HF} - E_{\rm X}^{\rm Slater}) + b(E_{\rm X}^{\rm GGA} - E_{\rm X}^{\rm Slater}) + cE_{\rm C}^{\rm GGA} + dE_{\rm C}^{\rm ab-initio}, \quad (2)$$

where E_X^{Slater} is the local density approximation for exchange, $E_{\rm X}^{HF}$ is the HF exchange, $\tilde{E}_{\rm X}^{GGA}$ and $\tilde{E}_{\rm C}^{GGA}$ denote the approximate GGA exchange and correlation energy, respectively, and $E_{\rm C}^{ab-initio}$ is the correlation energy from an $ab-initio$ calculation such as MP2. The standard procedure then is to run self-consistent calculations of Eq. 2 without the ab-initio correlation, but evaluate energies with the full DH expression on the orbitals.[21, 26, 27] The parameters are then chosen to minimize errors for specific molecular data sets. As we show, this assumes that density-driven differences between this and doing the entire procedure self-consistently are negligible.

Often, highly-accurate densities required in Eq. 1 are too expensive to calculate. A practical measure of density sensitivity is given by:[19, 20, 23]

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

where tilde indicates a given functional approximation. Given the HF tendency to overlocalize, and the LDA tendency to delocalize, and that both are non-empirical, $\tilde{S}$ is a practical guide to the density sensitivity of a given reaction and approximate functional. For small molecules, $\tilde{S} > 2$ kcal/mol implies density sensitivity and suggests DC-DFT will improve a functional's performance. In such cases, usually the HF density is sufficient to produce improved energies (HF-DFT).

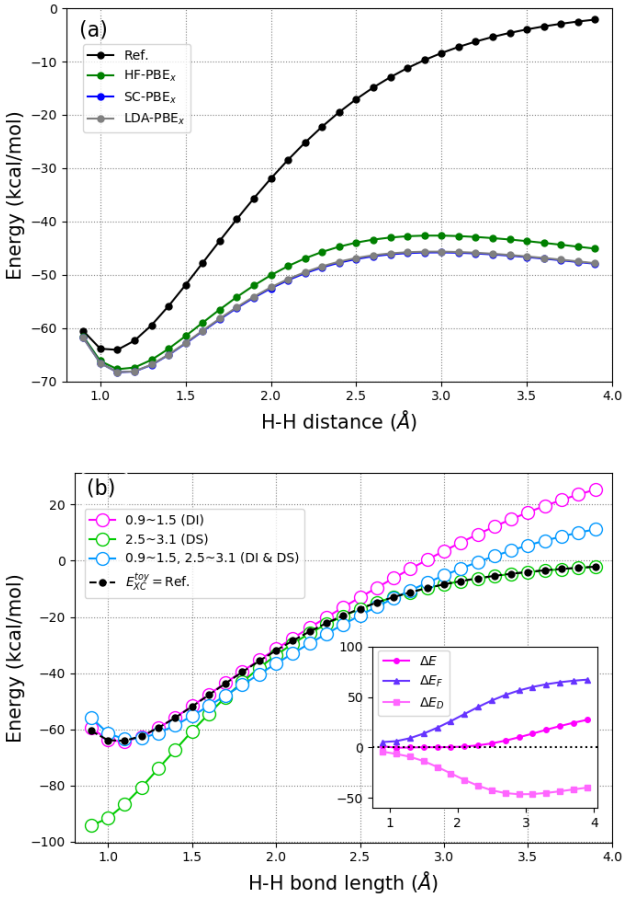

Figure 2: *Potential energy surface (PES) of H_2^+ from: (a) exactly (black), self-consistent $PBE_{\rm X}$ (blue) and $PBE_{\rm X}$ on the exact (HF) density (green) and on the LDA density (grey); (b) the toy functional of Eq. 2 with $c = d = 0$ and no HF in the self-consistent density, with the a and b parameters optimized in different regions: (magenta) the density-insensitive (DI) region (0.9Å-1.5Å), (green) the density-sensitive (DS) region (2.5Å-3.1Å), (blue) combination of both DS and DI regions. The inset shows ΔE decomposition for the toy functional trained on the DI region. See also Figures S1, S2, and Table S3.*

Illustration: Missing the exact solution for one electron– In this section, we illustrate the dangers of ignoring the distinction between density-driven and functional errors in a simple,

toy model: A simplified hybrid applied to the elementary case of H_2^+ as a function of bond length, which is a paradigm of self-interaction error, or more generally, delocalization error.[28, 29] Standard semilocal approximations yield long-recognized catastrophic errors as the bond is stretched, missing entirely the dissociation limit (see Fig 2).[29] A HF calculation trivially gets this exactly right, since it is exact for (fully spin-polarized) one-electron systems.

We apply the double-hybrid philosophy to our H_2^+ molecule, using different separations to generate data sets. Because this is a one-electron system, we simplify the general DH form to just exchange, setting $c = d = 0$ in Eq. 2, and use PBE[30] as an example GGA. Figure 2(a) shows the exact binding curve (black) easily found by HF, and two other curves of the PBE_X evaluated either self-consistently (blue) or on the HF density (green). The largely irrelevant difference between blue and green curves show that this is a true functional error, not a density-driven one. Even on the exact density, PBE_X fails very badly as the bond is stretched. However, the difference in the two curves becomes greater than 2 kcal/mol at about 1.5Å, showing a density sensitivity (the curve with LDA density is indistinguishable from the self-consistent curve) in this problem. (Standard HF-DFT produces accurate curves for heteronuclear diatomics, not homonuclear ones.[16, 17])

Now, to mimic the DH procedure, we perform self-consistent calculations without the HF contribution (since it yields the exact answer in this case), but evaluate the energy with it included. Figure 2(b) shows the results of training in the density-sensitive (stretched, DS) and density-insensitive (near equilibrium, DI) region of the binding curve. In each case, the optimal parameterization yields accurate energies on the training data, but fails badly outside the training range. Even a combination of both equilibrium and stretched data does not help much.

How can this be happening? Obviously, if we set $a = 1$ and $b = 0$ in Eq. 2, we get HF, and so produce the exact answer. But, because the self-consistent calculation uses only a GGA form, which has an unbalanced self-interaction error as the bond is stretched, the exact result is never found. To illustrate the issue, we use Eq. 1 to partition the error for the functional trained near equilibrium, showing $\Delta E_{\rm D}$ and $\Delta E_{\rm F}$ in the inset of Figure 2(b). The optimal parameters (which are nonsensical, see Table S3 of the supporting information) keep the total error to a minimum in the training region by having $\Delta E_{\rm D}$ and $\Delta E_{\rm F}$ be about equal and opposite. Outside the training region, this artificial cancellation of errors fails badly. Obviously, we trivially solve this toy problem if we always train on the HF density instead of the self-consistent GGA density.

DFT-D3 for weak interactions– The D3 empirical correction of Grimme and co-workers has become a standard technique for improving the accuracy of DFT approximations when applied to noncovalent interactions.[25, 31] While most such calculations are density insensitive, DFT calculations of specific types of noncovalent interactions, such as halogen bonds, are seriously plagued by density-driven error, which can be larger than the D3 correction itself.[20]

	[SC]		[HF]	
opt. data set	DI	DS	DI	DS
without opt.	2.24	3.05	2.51	5.72
$D3_{\rm orig}$	0.31	5.52	0.25	1.79
12DB	0.36	4.50	0.26	1.72
DS-12DB	1.27	1.89	0.40	1.28
DI-12DB	0.29	5.31	0.24	1.91

Table 1: *Mean absolute errors (kcal/mol) of B3LYP and modifications on density-insensitive (DI) and density-sensitive (DS) test cases (columns) versus optimization on various databases (rows), with self-consistent (SC) densities on left and HF densities on right. $D3_{\rm orig}$ denotes the original Grimme data set, 12DB is our large (360 values) mixed data set, DI-12DB are its 276 DI cases, and DS-12DB its 46 DS cases.*

DC-DFT fixes this problem by replacing the SC density with the HF density, on which semilocal functionals yield more accurate energies in such cases.[20] This procedure is HF-DFT, and it represents the simplest form of DC-DFT.[14, 19, 20, 22] It was recently shown that use of the HF density in place of the exact density introduces much smaller errors than the improvements made by HF-DFT.[23] (As an aside, this does not imply that the pointwise accuracy of the underlying HF density is better than that of SC-DFT densities.[19])

The example of Ref. [20] was an extreme case. Here we study the effects of density-driven errors of SC-DFT-D3 calculations of weak interactions when they are more subtle. We use 12 data sets (7 from the original D3 parameterization [25]) of noncovalent interactions (320 data points in total, see Table S1, S4, and S5 of the supporting information).[32] The data points are classified as DS or DI based on their PBE sensitivity, $S^{\rm PBE}$ (see Eq. 3 and Figure S3). Only 46 are DS, and these are mostly from B30[33] and WATER27[32], with only one such data point present in the data set used for the training of the original D3 parameters.

In Table 1, we demonstrate the importance of accounting for density-driven errors when optimizing parameters for D3 corrections. The first two numbers in the 2nd column show the dramatic reduction in error in the B3LYP functional when the original D3 correction is made, on the density-insensitive cases. The next entry shows that when we optimize over our much expanded database, the errors for DI cases are only slightly worse. But if we optimize specifically over our DS cases (4th entry), this greatly worsens results on our DI test cases.

Moving over one column, we find results when tested on the DS cases. Now the original D3 parameterization yields a large (greater than 5 kcal/mol) error, demonstrating that density-sensitivity creates large errors. Even when optimized for DS cases, the error remains about 1.9 kcal/mol.

In the next column, we report the DI test results, but using HF densities instead of SC densities. We see that in all cases

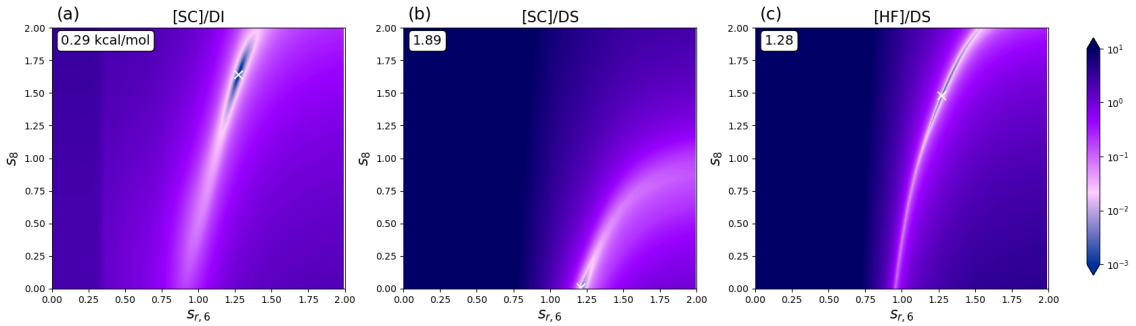

Figure 3: *Mean absolute error (MAE) of B3LYP as a function of dispersion parameters[25], for various densities and test sets: (a) self-consistent (SC) density on density-insensitive (DI) cases, (b) SC density for density-sensitive (DS) cases, and (c) HF density for DS cases. The global minima are marked as X.*

of interest, the results are (slightly) improved, but for the DS optimized parameters, greatly improved (a factor of 3), showing that the differences in optimized parameters are much smaller when HF densities are used. This is shown in Figure 3, which shows the variation of the error with parameters. Figure 3(a) shows the usual case (SC densities on DI cases). Figure 3(b) is SC densities on DS cases, showing a total different landscape. Figure 3(c) is HF densities on DS cases, showing about the same landscape as (a). The position of the minimum (marked by an X) is about the same for (a) and (c), but very different in (b).

Finally, the fourth column of Table 1 shows results on the DS cases using HF densities. While overall, these are much less accurate than the DI cases (by about a factor of 5), they are much better than those of column 2, which uses SC densities (See also Table S6 and Figure S4).

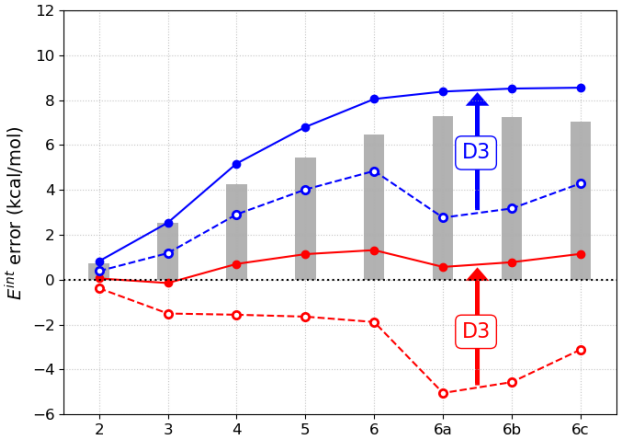

Figure 4: *PBE binding energy error for small water clusters, $E^{\rm int} = nE_{\rm H_2O} - E_{\rm (H_2O)_n}$ $(n = 2 \sim 6)$, in WATER27 data set. Blue denotes self-consistent, while red is for the HF density; dashed is without dispersion correction, while solid denotes with D3 (revised is similar to original). The gray bar shows the density-sensitivity of Eq. 3.*

Most of the DS noncovalent complexes used in the training

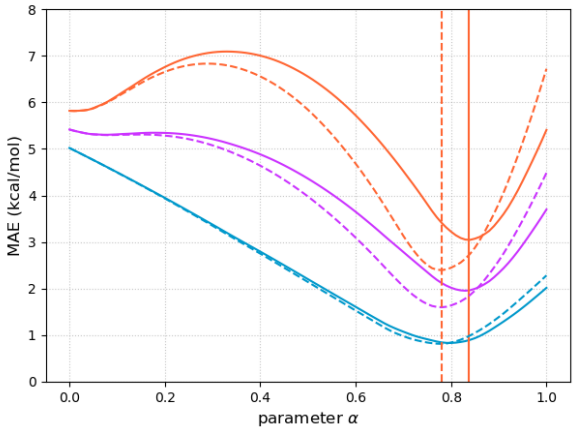

Figure 5: *Mean absolute errors for the training data set (orange), test (blue), and all (purple) of HF-DHs as a function of α, with MP2 (solid) and CC2 (dashed) correlation. Vertical lines are at the optimal α values.*

set in Table 1 belong to the B30 and WATER27 data sets. In Figure 4, we compare errors of SC-PBE and HF-PBE, with and without the (rev)D3 correction, for binding energies of water clusters of the WATER27 data set. The DFT calculations of these binding energies are highly DS, as shown by the large values for $S^{\rm PBE}$ shown in Figure 4. We see that DC-DFT corrections are larger than D3 here, and that D3 on self-consistent densities actually corrects in the wrong direction. HF-DFT-D3 reduces errors for the largest clusters from about 8 kcal/mol to less than 1 kcal/mol.

Double-hybrids– The energy functional of widely popular DHs (e.g. Eq. 2) is typically evaluated on the hybrid density and orbitals found in a self-consistent calculation that neglects the $E_C^{ab-initio}$ term.[21, 26] We test the DH idea with only one empirical parameter:[26]

$$E_{\rm XC}^{\rm DH1p} = E_{\rm XC}^{\rm GGA} + \alpha(E_{\rm X}^{\rm HF} - E_{\rm X}^{\rm GGA}) + \alpha^2(E_{\rm C}^{\rm ab-initio} - E_{\rm C}^{\rm GGA}) \quad (4)$$

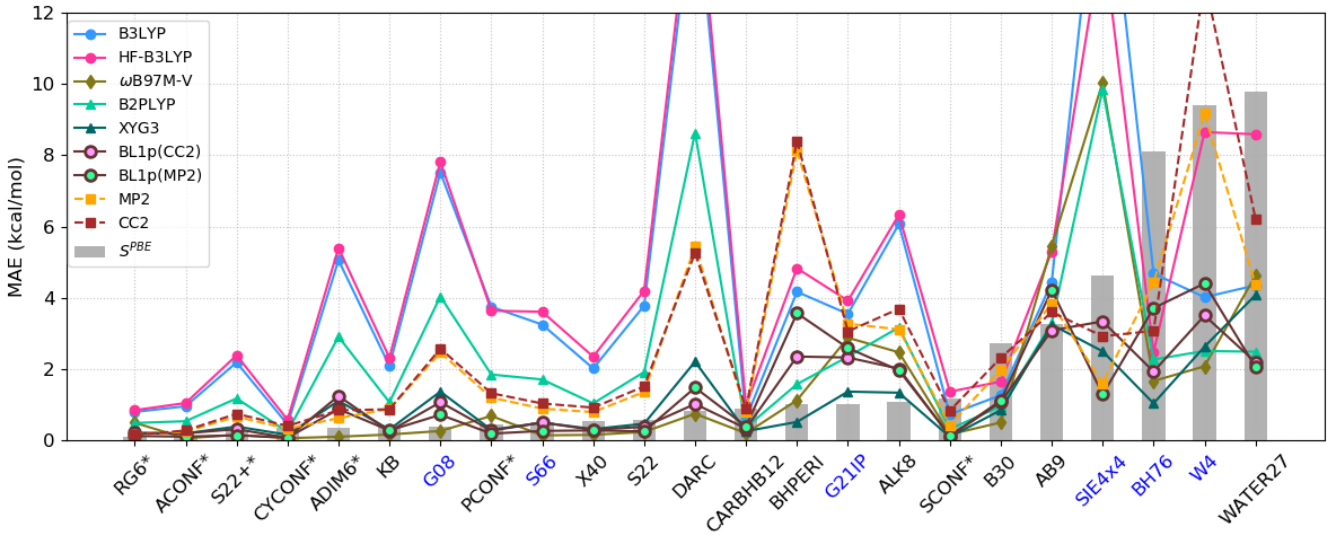

Figure 6: *MAEs for several methods on many databases: BL1p with CC2 and MP2, other double-hybrids (B2PLYP and XYG3), B3LYP on SC and HF densities, a range-separated meta-GGA hybrid (ωB97M-V), and MP2 and CC2. Blue data sets were used to optimize α in BL1P (Eq. 4). For details, see Table S8.*

as suggested by Sharkas *et al.* based on *adiabatic connection* arguments.[26] To construct a family of HF-DHs based on Eq. 4, we use combinations of: (i) B88 exchange[1] with LYP correlation;[2] (ii) PBE exchange and correlation.[30] (iii) E_C^{MP2} (MP2 correlation)[34] and (iv) E_C^{CC2} (CC2 correlation).[35] This gives us in total 4 distinct one-parameter (1p) HF-DHs: (i) BL1p(MP2); (ii) BL1p(CC2); (iii) PP1p(MP2); (iv) PP1p(CC2), where L denotes LYP and P denotes PBE. We show BL1p results in the main paper, while very similar PP1p values are given in supporting information. Also, see Figure S5 to compare 1DH-BLYP (BL1p[SC]) of Ref. [26] and BL1p[HF].

Our training set consists of the W4, BH76, SIE4x4, G21IP, S66, and G08 molecular databases[32] to optimize the α parameter (Eq. 4) for each of the four HF-DHs, as shown in Figure 5. The training set was chosen to represent a variety of chemical systems and includes both weak and strong interactions. At $\alpha = 0$, HF-DHs reduce to HF-GGA, whereas at $\alpha = 1$, they reduce to CC2 or MP2. The optimal HF-DHs have α parameters ranging from 0.72 to 0.84 (see Table S7) and the MAE is several kcal/mol smaller than those at either $\alpha = 0$ and $\alpha = 1$. BL1p with CC2 is slightly better than MP2, but costs more to compute.

In Figure 6, we compare the performance of BL1P(MP2) and BL1P(CC2) with the standard DHs (B2PLYP[21] and XYG3[36]) and also with the range-separated functional (ωB97M-V[37]), which we detail in the SI. Both BL1P(MP2) and BL1P(CC2) (containing just one empirical parameter) yield an accuracy that is competitive with the standard DHs for all databases, not only for those used in the training. Results for PP1p are comparable to BL1p and given in Table S9 and S10 of the supporting information.

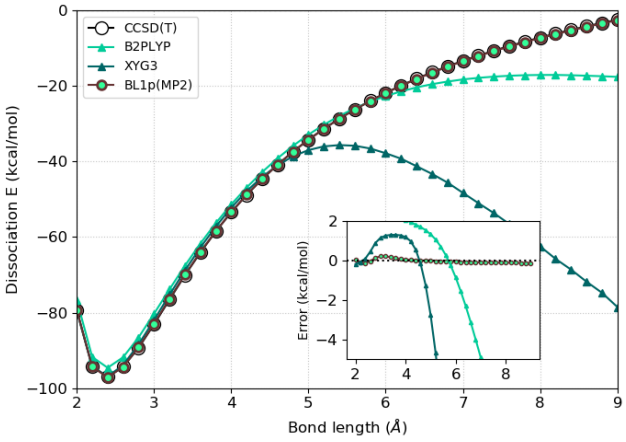

Figure 7: *Dissociation curve of NaCl: BL1p(MP2) works well compared to CCSD(T) while other double-hybrid functionals fail after 5∼6 Å. Such failures are explained in Ref. [16]. Note that aug-cc-pVTZ basis set is used.*

Returning to our starting point, stretched NaCl is a prototypical case where self-consistent hybrids and GGAs are contaminated by large density errors.[16] These errors are typical of semilocal functionals for dissociating heterodimers.[38, 39] HF densities fix this problem, and HF-DFT is able to dissociate heterodimers correctly.[16] From Figure 7, in contrast to a standard DHs (B2PLYP and XYG3 shown here) that fail at large bond lengths, our HF-DHs dissociate NaCl correctly (See also Figure S6 and S7). In the the supporting information, we show other examples (e.g. bonding energies of π-complexes in Figure S8) where the HF-DHs developed here outperform their conventional counterparts.

Concluding remarks– We have shown the dangers of ignoring density-driven errors in the construction of empirical approximations. In our simple H_2^+ example, a parameterized semilocal functional trained on a specific H_2^+ binding curve region fails in all other regions. Moreover, high accuracy in the training region results from an enforced error cancellation between the density-driven and functional error (Eq. 1), which fails outside this region. We showed standard DFT with empirical D3 corrections breaks down when applied to *density-sensitive* noncovalent systems, but is fixed by using the HF density. Finally, we found that greater accuracy and reliability could be achieved with simple 1-parameter double-hybrids, once they are trained and applied to HF densities. As always, we stress that our use of HF densities does not imply that they are point-wise more accurate than self-consistent densities. HF densities simply yield more accurate energetics when a reaction is density sensitive.

Our main goal is not to introduce a new empirical XC functional, but to warn of the contamination due to ΔE_{D} in fitting procedures and to show how minimizing ΔE_{F} improves the performance of empirical functionals. Our selection of training sets has not been carefully scrutinized or designed for optimal performance for general use. Nevertheless, our 1-parameter double-hybrids trained on HF densities outperform the standard approximations for most of the GMTKN55 database considered here. While it is beyond the scope of this work, technical advances in optimization details should further improve statistical accuracy. In summary, we recommend that all empirical functionals be trained on HF densities to reduce density-driven errors and so choose the best energy functional. Moreover, for any density-sensitive systems, they should be applied to HF densities (unless these are extremely flawed, such as severe spin-contamination.) With the use of HF densities where applicable, the dangers of contamination by errors in the density can be avoided with minimal extra effort.

Computational Details

All HF, DFT, and HF-DFT calculations have been performed with the TURBOMOLE v7.0.2.[40] The following functionals have been used in DFT and HF-DFT calculations: LDA (SVWN[41, 42]), GGA (PBE[30], BLYP[1, 2]), mGGA (TPSS[43]), hybrids (B3LYP[4], PBE0[44], M06, M06-2X[45], B2PLYP[21], XYG3[36], and ωB97M-V[37]. The scripts for performing HF-DFT energy calculations are available.[46] Unless otherwise stated, the def2-QZVP basis set has been used. All molecular geometries and multiplicities have been taken from Ref. [32]. Further computational details can be found in the supporting information.

Data availability

The authors declare that the data supporting the findings of this study are available within the paper and its supplementary information files.

Supplementary Information

- Data set description
- Optimized parameters and mean absolute error for H_2^+, revD3, and HF-DHs
- HF-DHs for Na-Cl potential energy curve, π-π interaction, and AE6 data set

acknowledgement

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References

[1] Axel D Becke. Density-functional exchange-energy approximation with correct asymptotic behavior. *Physical Review A*, 38(6):3098–3100, 1988.

[2] Chengteh Lee, Weitao Yang, and Robert G Parr. Development of the colle-salvetti correlation-energy formula into a functional of the electron density. *Physical Review B*, 37(2):785–789, 1988.

[3] Axel D Becke. Density-functional thermochemistry. iii. the role of exact exchange. *Journal of Chemical Physics*, 98(7):5648–5652, 1993.

[4] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch. Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields. *The Journal of Physical Chemistry*, 98(45):11623–11627, 1994.

[5] Haoyu S Yu, Shaohong L Li, and Donald G Truhlar. Perspective: Kohn-sham density functional theory descending a staircase. *Journal of Chemical Physics*, 145(13):130901, 2016.

[6] Narbe Mardirossian and Martin Head-Gordon. Thirty years of density functional theory in computational chemistry: an overview and extensive assessment of 200 density functionals. *Molecular Physics*, 115(19):2315–2372, 2017.

[7] Michael G Medvedev, Ivan S Bushmarinov, Jianwei Sun, John P Perdew, and Konstantin A Lyssenko. Density functional theory is straying from the path toward the exact functional. *Science*, 355(6320):49–52, 2017.

[8] Enrico Clementi and Subhas J Chakravorty. A comparative study of density functional models to estimate molecular atomization energies. *Journal of Chemical Physics*, 93(4):2591–2602, 1990.

[9] Nevin Oliphant and Rodney J Bartlett. A systematic comparison of molecular properties obtained using hartree–fock, a hybrid hartree–fock density-functional-theory, and coupled-cluster methods. *Journal of Chemical Physics*, 100(9):6550–6561, 1994.

[10] Benjamin G Janesko and Gustavo E Scuseria. Hartree–fock orbitals significantly improve the reaction barrier heights predicted by semilocal density functionals. *Journal of Chemical Physics*, 128(24):244112, 2008.

[11] David RB Brittain, Ching Yeh Lin, Andrew TB Gilbert, Ekaterina I Izgorodina, Peter MW Gill, and Michelle L Coote. The role of exchange in systematic dft errors for some organic reactions. *Physical Chemistry Chemical Physics*, 11(8):1138–1142, 2009.

[12] Min-Cheol Kim, Eunji Sim, and Kieron Burke. Communication: Avoiding unbound anions in density functional calculations. *Journal of Chemical Physics*, 134(17):171103, 2011.

[13] Prakash Verma, Ajith Perera, and Rodney J. Bartlett. Increasing the applicability of dft i: Non-variational correlation corrections from hartree-fock dft for predicting transition states. *Chemical Physics Letters*, 524:10 – 15, 2012.

[14] Min-Cheol Kim, Eunji Sim, and Kieron Burke. Understanding and reducing errors in density functional calculations. *Physical Review Letters*, 111(7):073003, 2013.

[15] Min-Cheol Kim, Eunji Sim, and Kieron Burke. Ions in solution: Density corrected density functional theory (dc-dft). *Journal of Chemical Physics*, 140(18):18A528, 2014.

[16] Min-Cheol Kim, Hansol Park, Suyeon Son, Eunji Sim, and Kieron Burke. Improved dft potential energy surfaces via improved densities. *The Journal of Physical Chemistry Letters*, 6(19):3802–3807, 2015.

[17] Adam Wasserman, Jonathan Nafziger, Kaili Jiang, Min-Cheol Kim, Eunji Sim, and Kieron Burke. The importance of being self-consistent. *Annual Review of Physical Chemistry*, 68(1):555–581, 2017.

[18] Suhwan Song, Min-Cheol Kim, Eunji Sim, Anouar Benali, Olle Heinonen, and Kieron Burke. Benchmarks and reliable dft results for spin gaps of small ligand fe (ii) complexes. *Journal of Chemical Theory and Computation*, 14(5):2304–2311, 2018.

[19] Eunji Sim, Suhwan Song, and Kieron Burke. Quantifying density errors in dft. *The Journal of Physical Chemistry Letters*, 9(22):6385–6392, 2018.

[20] Yeil Kim, Suhwan Song, Eunji Sim, and Kieron Burke. Halogen and chalcogen binding dominated by density-driven errors. *The Journal of Physical Chemistry Letters*, 10(2):295–301, 2018.

[21] Stefan Grimme. Semiempirical hybrid density functional with perturbative second-order correlation. *Journal of Chemical Physics*, 124(3):034108, 2006.

[22] Stefan Vuckovic, Suhwan Song, John Kozlowski, Eunji Sim, and Kieron Burke. Density functional analysis: The theory of density-corrected dft. *Journal of Chemical Theory and Computation*, 15(12):6636–6646, 2019.

[23] Seungsoo Nam, Suhwan Song, Eunji Sim, and Kieron Burke. Measuring density-driven errors using Kohn-Sham inversion. *arXiv e-prints*, page arXiv:2004.11595, April 2020.

[24] Ryo Nagai, Ryosuke Akashi, and Osamu Sugino. Completing density functional theory by machine learning hidden messages from molecules. *npj Computational Materials*, 6(1):1–8, 2020.

[25] Stefan Grimme, Jens Antony, Stephan Ehrlich, and Helge Krieg. A consistent and accurate ab initio parametrization of density functional dispersion correction (dft-d) for the 94 elements h-pu. *Journal of Chemical Physics*, 132(15):154104, 2010.

[26] Kamal Sharkas, Julien Toulouse, and Andreas Savin. Double-hybrid density-functional theory made rigorous. *Journal of Chemical Physics*, 134(6):064113, 2011.

[27] Jan ML Martin and Golokesh Santra. Empirical Double-Hybrid Density Functional Theory: A âĂŸThird WayâĂŹin Between WFT and DFT. *Israel Journal of Chemistry*, 60:1–19, 2019.

[28] Aron J. Cohen, Paula Mori-Sánchez, and Weitao Yang. Insights into current limitations of density functional theory. *Science*, 321(5890):792–794, 2008.

[29] Aron J Cohen, Paula Mori-Sánchez, and Weitao Yang. Challenges for density functional theory. *Chemical Reviews*, 112(1):289–320, 2011.

[30] John P Perdew, Kieron Burke, and Matthias Ernzerhof. Generalized gradient approximation made simple. *Physical Review Letters*, 77(18):3865, 1996.

[31] Eike Caldeweyher, Sebastian Ehlert, Andreas Hansen, Hagen Neugebauer, Sebastian Spicher, Christoph Bannwarth, and Stefan Grimme. A generally applicable atomic-charge dependent london dispersion correction. *Journal of Chemical Physics*, 150(15):154122, 2019.

[32] Lars Goerigk, Andreas Hansen, Christoph Bauer, Stephan Ehrlich, Asim Najibi, and Stefan Grimme. A look at the density functional theory zoo with the advanced gmtkn55 database for general main group thermochemistry, kinetics and noncovalent interactions. *Physical Chemistry Chemical Physics*, 19(48):32184–32215, 2017.

[33] Antonio Bauza, Ibon Alkorta, Antonio Frontera, and Jose Elguero. On the reliability of pure and hybrid dft methods for the evaluation of halogen, chalcogen, and pnicogen bonds involving anionic and neutral electron donors. *Journal of Chemical Theory and Computation*, 9(11):5201–5210, 2013.

[34] Chr. Møller and M. S. Plesset. Note on an approximation treatment for many-electron systems. *Physical Review*, 46(7):618–622, October 1934.

[35] Ove Christiansen, Henrik Koch, and Poul Jørgensen. The second-order approximate coupled cluster singles and doubles model cc2. *Chemical Physics Letters*, 243(5-6):409–418, 1995.

[36] Ying Zhang, Xin Xu, and William A Goddard. Doubly hybrid density functional for accurate descriptions of nonbond interactions, thermochemistry, and thermochemical kinetics. *Proceedings of the National Academy of Sciences*, 106(13):4963–4968, 2009.

[37] Narbe Mardirossian and Martin Head-Gordon. ω b97m-v: A combinatorially optimized, range-separated hybrid, meta-gga density functional with vv10 nonlocal correlation. *Journal of Chemical Physics*, 144(21):214110, 2016.

[38] Oleg V Gritsenko and Evert Jan Baerends. Effect of molecular dissociation on the exchange-correlation kohn-sham potential. *Physical Review A*, 54(3):1957, 1996.

[39] Sara Giarrusso, Stefan Vuckovic, and Paola Gori-Giorgi. Response potential in the strong-interaction limit of dft: Analysis and comparison with the coupling-constant average. *Journal of Chemical Theory and Computation*, 9(11):3137–3142, 2018.

[40] TURBOMOLE V7.0 2015, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from `http://www.turbomole.com`.

[41] Paul AM Dirac. Note on exchange phenomena in the thomas atom. In *Mathematical Proceedings of the Cambridge Philosophical Society*, volume 26, pages 376–385. Cambridge University Press, 1930.

[42] Seymour H Vosko, Leslie Wilk, and Marwan Nusair. Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. *Canadian Journal of Physics*, 58(8):1200–1211, 1980.

[43] Jianmin Tao, John P Perdew, Viktor N Staroverov, and Gustavo E Scuseria. Climbing the density functional ladder: Nonempirical meta–generalized gradient approximation designed for molecules and solids. *Physical Review Letters*, 91(14):146401, 2003.

[44] Kieron Burke, Matthias Ernzerhof, and John P Perdew. The adiabatic connection method: a non-empirical hybrid. *Chemical Physics Letters*, 265:115–120, 1997.

[45] Yan Zhao and Donald G Truhlar. The m06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four m06-class functionals and 12 other functionals. *Theoretical Chemistry Accounts*, 120(1-3):215–241, 2008.

[46] `http://tccl.yonsei.ac.kr/mediawiki/index.php/DC-DFT`.