

# Computation of Covalent and Noncovalent Structural Parameters at Low Computational Cost: the Efficiency of the DH-SVPD Method

Bernardino Tirri,<sup>†</sup> Ilaria Ciofini,<sup>†</sup> Juan Carlos Sancho-García,<sup>‡</sup>  
Éric Brémond,<sup>\*§</sup> Carlo Adamo<sup>\*†¶</sup>

January 24, 2020

## Abstract

DH-SVPD is a tailored atomic basis set originally developed to enhance the domain of applicability of double-hybrid density functionals to large molecular systems in weak interactions. In combination with any density functionals belonging to this approximation, it provides an accurate estimate of noncovalent interaction energies at the cost of a double- $\zeta$  basis set, without adding *a posteriori* an empirical dispersion correction. We show here that the accuracy/cost ratio observed previously for energy properties can be safely extended to the modeling of structural parameters of small- and medium-sized organic molecules. In particular, we demonstrate that in combination with the nonempirical PBE-QIDH double hybrid, DH-SVPD is competitive with very large quadruple- $\zeta$  basis sets when modeling both covalent and noncovalent structural parameters.

---

\*Corresponding authors: [eric.bremond@u-paris.fr](mailto:eric.bremond@u-paris.fr), [carlo.adamo@chimieparistech.psl.eu](mailto:carlo.adamo@chimieparistech.psl.eu)

<sup>†</sup>Chimie ParisTech, PSL Research University, CNRS, Institute of Chemistry for Life and Health Sciences (i-CLeHS), FRE 2027, F-75005 Paris, France.

<sup>‡</sup>Departamento de Química Física, Universidad de Alicante, E-03080 Alicante, Spain.

<sup>§</sup>Université de Paris, ITODYS, UMR CNRS 7086, 15 rue J.-A. de Baïf, F-75013 Paris, France.

<sup>¶</sup>Institut Universitaire de France, 103 Boulevard Saint Michel, F-75005 Paris, France.

# INTRODUCTION

Modern double-hybrid (DH) density functionals<sup>1-3</sup> are considered among the most advanced and accurate approximations to the exchange-correlation energy term within the Kohn-Sham approach to density-functional theory.<sup>4,5</sup> Developed from the middle of the 2000s, their original recipe merges wavefunction- and density-based approaches by mixing a fraction of non-local exact-like exchange (EXX) and second-order perturbation (PT2) correlation with a pure semilocal density-functional approximation (DFA).<sup>6,7</sup> Owing to these ingredients, they peak on the highest rung of the Perdew’s Ladder<sup>8</sup> and become a clean improvement both in terms of sophistication and performance over hybrid and semilocal density functionals.<sup>9</sup> Some variants to the standard definition of a DH were recently developed to solve specific issues. Some of them focus on the orbital-optimization (OO) approach<sup>10</sup> to correct an artificial spin-symmetry breaking occurring in spin unrestricted systems.<sup>11-13</sup> Others are based on the range-separation exchange (RSX) scheme<sup>14</sup> to (partially) cure the self-interaction and delocalization errors<sup>15</sup> (SIE and DE, respectively).<sup>16-19</sup> However, all of them conserve similar features, *i.e.* a fraction of EXX generally larger than 50% and a fraction of PT2 correlation ranging between 10 and 40%, which allow them to reach the chemical accuracy when modeling a large panel of properties ranging from ground-state energies<sup>20</sup> to structures<sup>21</sup> and extending to singlet-singlet vertical excitation energies.<sup>22,23</sup>

Despite their undeniable robustness, DHs remain more computationally demanding than standard density functionals. The computation of their PT2 correlation energy term scales as  $\mathcal{O}(n^5)$ ,  $n$  referring to the size of the basis set. This larger effort in comparison to global hybrids, can however be alleviated under certain conditions<sup>24</sup> by transforming the DHs into their spin-opposite-scaled (SOS) variants.<sup>25-27</sup> The resulting SOS-DHs get a final formal scaling in  $\mathcal{O}(n^4)$ , but in return, strongly loose in performance with respect to weak-interaction properties,<sup>28</sup> one of their main advantage with respect to other classes of density functionals. As a result, it is common practice to couple a SOS-DH with an empirical pairwise dispersion correction<sup>29</sup> to recover the missing correlation effects as an error compensation.<sup>26</sup>

The resulting DHs corrected empirically for dispersion interactions are among the best performing DFT-like approaches.<sup>20</sup> Several energy benchmark tests show that the coupling

is particularly optimal by considering semiempirical DHs, *i.e.* DHs whose parameters are trained to reproduce reference energy databases. It remains however questionable when it enrolls nonempirical DHs since it often leads to overbinding situations when the size of the weakly interacting systems is not large enough.<sup>30</sup> To overcome these limitations and while keeping homogeneous performances independently of the system-size, we recently proposed an alternative to empirical dispersion corrections based on the use of a tailored atomic basis set.<sup>31</sup>

Like second-order Møller-Plesset (MP2) perturbation theory, DHs exhibit a larger binding behavior in weakly interacting systems when using smaller basis set (*i.e.* double- versus quadruple- $\zeta$  or larger, respectively).<sup>32</sup> From this observation, we specifically developed the so-called DH-SVPD,<sup>31</sup> a double- $\zeta$  basis set derived under the Varandas' constraint<sup>33</sup> and which takes advantage of an error compensation between the basis set incompleteness and superposition errors (BSIE and BSSE, respectively). In association with a DH, the DH-SVPD basis set allows the recovery of both energy and structural features of dispersion interactions in small to large systems<sup>31,34</sup> at the reduced computational cost of a modest double- $\zeta$  split-valence basis set.

We propose here to go further and evaluate the performance of the association between a DH density functional and the tailored DH-SVPD basis set to model intramolecular structural parameters of organic molecules. Structure optimizations are indeed often performed in small basis set due to the increasing computational time caused by the successive evaluations of energy and gradient up to the fulfillment of convergence criteria. Furthermore, we want to verify that the observed improvement on both structural and energy features in weakly interacting molecules is not done at the expense of a basic property, such as molecular geometry.<sup>9,35</sup>

Our benchmarking investigation focuses on the CCse and B3se databases of accurate structural parameters introduced some years ago by Barone and co-workers.<sup>36-39</sup> The former gathers a collection of 21 small organic molecules whose reference covalent structural parameters are derived from a mixed coupled-cluster singles and doubles plus perturbative triples [CCSD(T)], and experimental protocol. The latter is an extension to the former containing 26 extra medium-sized organic molecules but derived using a lower (B3LYP) level of the-

ory. To illustrate the performance of the DH-SVPD basis set on weakly interacting systems, we also include to the previous collection of data, the formamide dimer whose structural parameters were recently derived<sup>37</sup> and whose representation is provided in Figure 1.

# COMPUTATIONAL DETAILS

All the computations were performed with the Revision B.01 of the Gaussian'16 software using a tight threshold as a convergence criteria for energy and structure optimization in addition to an ultrafine integration grid.<sup>40</sup> The performance of the tailored DH-SVPD double- $\zeta$  basis set were benchmarked versus the CCse and B3se databases,<sup>38,39</sup> in addition to the formamide dimer.<sup>37</sup> They were compared with those obtained with 4 Ahlrichs double- to quadruple- $\zeta$  basis sets (*i.e.*, def2-SVP, def2-SVPD, def2-TZVPP and def2-QZVPP),<sup>41</sup> plus the aug-cc-pVTZ Dunning augmented triple- $\zeta$  basis set.<sup>42</sup> Since DH-SVPD is developed for the first-row atoms, we restricted our benchmarking investigation to subsets of the above-mentioned datasets containing 17 and 38 reference structures, respectively, that is to say a total of 217 references covalent bond lengths. More details are provided in Figures S1 and S2 of the Supporting Information.

The impact of the coupling between the density functional and the basis set on the structure optimization property was evaluated by testing 10 different exchange-correlation approximations. We select 3 of them from the 06' edition of the Minnesota family which mix different percentage of EXX, *i.e.* M06-L (EXX = 0%),<sup>43</sup> M06 (27%)<sup>44</sup> and M06-2X (54%).<sup>44</sup> We complete this list with other commonly used DHs: PBE0-DH (EXX = 50%, PT2 =  $\sim$ 12%),<sup>45</sup> B2-PLYP (53%, 27%),<sup>7</sup> mPW2-PLYP (55%, 25%),<sup>46</sup> PBE-QIDH<sup>47</sup> (EXX =  $\sim$ 69%, PT2 =  $\sim$ 33%) and extend it with 3 extra DHs coupled with empirical dispersion corrections: DSD-PBEP86-D3(bj) (EXX = 69%, PT2<sub>SS</sub> = 22%, PT2<sub>OS</sub> = 52%),<sup>48</sup> B2-PLYP-D<sup>49</sup> and B2-PLYP-D3(bj).<sup>50</sup>

## RESULTS AND DISCUSSION

Figure 2 reports the performance of the DH-SVPD basis set in association with the nonempirical PBE-QIDH double-hybrid density functional to model CH, CC, CN, CO, NH and OH bond lengths, and compares it with those obtained with the def2-SVP, def2-SVPD, def2-TZVPP, def2-QZVPP Ahlrichs and aug-cc-pVTZ Dunning basis sets. At first glance, the statistics derived from both CCse and B3se datasets are homogeneous, independently on the basis set. The mean absolute deviations (MADs) derived from both datasets are indeed in close agreement. The only exception are the absolute deviations calculated with respect to the CN bonds which differ because of the poor performance of PBE-QIDH with respect to aziridine, a molecule only included in B3se.

Going further into details, Figure 2 shows that the covalent structural parameters smoothly converge with the size of the basis set. Already, a triple- $\zeta$  basis set augmented or not with diffuse functions (def2-TZVPP or aug-cc-pVTZ, respectively) provides MADs in close agreement with the very large def2-QZVPP quadruple- $\zeta$  basis set. As an example, the MADs for the CH, CC, CN and CO bond lengths gathered in the CCse dataset are calculated to be 0.001, 0.006, 0.005 and 0.009 Å, respectively, with def2-TZVPP while they are estimated to 0.002, 0.007, 0.007 and 0.010 Å, respectively, at def2-QZVPP level of theory. A deviation not larger than 0.002 Å is therefore observed between the two levels of theory.

The DH-SVPD tailored double- $\zeta$  basis set slips from this convergence trend and provides here the best performance with deviations calculated to 0.004, 0.003, 0.002, 0.006, 0.002 and 0.004 Å for the CH, CC, CN, CO, NH and OH bond lengths, respectively, for the CCse benchmark set (Figure 2). In comparison, the original def2-SVPD basis set exhibits poorer performances determined as 0.008, 0.003, 0.003, 0.007, 0.002 and 0.001 Å, respectively. DH-SVPD tends indeed to shorten the covalent bond lengths. As a result, CH bonds, which are systematically modeled as too long with def2-SVPD, are better estimated with DH-SVPD. However, OH bonds, which are correctly predicted with def2-SVPD, are tends to be too shorten with DH-SVPD. As found for energy properties,<sup>31,34</sup> the error balance ruled by the association between a DH density functional and the DH-SVPD basis set results here in an increase of the binding behavior from a structural point of view.

On the formamide dimer case of study (Figure 2), the latter conclusion regarding covalent bonds is confirmed and can be also extended to the H-bond assuring the noncovalent binding of the system. Indeed, DH-SVPD models the  $r(\text{O}\cdots\text{H}_{\text{cis}})$  bond length as 1.816 Å (the reference being 1.836 Å, Figure 1) while def2-SVPD and def2-QZVPP predicts them as 1.817 and 1.823 Å. As a conclusion, the tailored DH-SVPD basis set in association with PBE-QIDH systematically shortens covalent and noncovalent bond lengths.

To confirm the trend obtained with PBE-QIDH, we compare it with the performance of 9 other popular density functionals belonging to the semilocal, hybrid and double-hybrid approximations and gathering different fraction of EXX and PT2 correlation (Figure 3). Concerning the 53 covalent bond lengths gathered into the CCse dataset, we observe a non-uniform influence of the basis set size with respect to the density functional (Figure 3). If a triple- $\zeta$  augmented or not with diffuse functions unanimously provides converged results, DH-SVPD can be view either as a compromise in between the double- and triple- $\zeta$  level of theory or as a real improvement with respect to all the investigated basis sets. Indeed, the combination of DH-SVPD with semilocal and hybrid density functionals provides a real improvement with respect to the original def2-SVPD basis set. The mean signed deviation (MSD) for M06-L, M06 and M06-2X are about 0.003, 0.002 and 0.002 Å, respectively, at DH-SVPD level and 0.005, 0.005 and 0.005 Å, respectively, at def2-SVPD level. The same trend is observed for the MAD of the B3se dataset (see Figures S3 to S5 within the Supporting Information). Results of an average quality are found for semiempirical DHs. DH-SVPD provides a slight improvement with respect to def2-SVPD and does not reach the performance obtained with def2-TZVPP. As an example, with B2-PLYP, the MSD is calculated as 0.008, 0.006 and 0.001 Å for def2-SVPD, DH-SVPD and def2-TZVPP, respectively. The addition of a pairwise dispersion correction does not significantly influence that much the deviations, the MSD change being lower than 0.001 Å for B2-PLYP-D and B2-PLYP-D3(bj). The real improvement with respect to other basis sets observed is found for the PBE0-DH and PBE-QIDH nonempirical DHs. Their MSD are part of those of the best approaches and are evaluated to less than 0.001 Å for the former and 0.001 Å for the latter. This association allows thus to obtain reliable results at the computational prize of a double- $\zeta$  basis set.

On the  $r(\text{O}\cdots\text{H}_{\text{cis}})$  H-bond length of the formamide dimer example (Figure 3), the

DH-SVPD basis set illustrates well its ability to reinforce the binding behavior of weakly interacting systems by shortening weak bond lengths. In association with semiempirical DHs, DH-SVPD tends to improve the modeling of H-bond lengths with respect to larger basis sets since this type of density functionals are recognized to lack from dispersion interactions. The deviations are particularly small when the semiempirical DH is coupled with a pairwise dispersion correction like for B2-PLYP-D, B2-PLYP-D3(bj) and DSD-PBEP86-D3(bj). The error compensation between BSIE and BSSE is well illustrated by the results obtained. In association with a nonempirical DH like PBE0-DH or PBE-QIDH, the DH-SVPD tailored basis set emphasizes however the already excellent binding behavior of the dimer and thus overshoots the H-bond lengths. The diverging behavior observed between empirical and nonempirical DHs is related to the semilocal approximation used by construction in the DH, the PBE<sup>51</sup> exchange density functional capturing better dispersion forces than other semilocal approximation.<sup>30,52</sup>



## CONCLUSIONS

In this research article, we showed the ability of the coupling of the tailored and cost-effective DH-SVPD basis set with a DH density functional to model covalent structural parameters of small- and medium-sized organic molecules. In particular, the results obtained for the nonempirical PBE-QIDH density functional are competitive with those found when using a very large basis set (quadruple- $\zeta$ ). Since the DH-SVPD basis set provides an accurate estimation of weak noncovalent interaction energies, the resulting level of theory allows the accurate modeling of both covalent and noncovalent structural parameters at a reasonable computational cost. These results further increase the possibility of applying DHs by enhancing their accuracy/cost ratio. At the same time, they strengthen the theoretical background of nonempirical DHs since they prove that the pairing with empirical dispersion corrections can be avoided by the use of tailored basis set.

## **ACKNOWLEDGMENTS**

E.B. thanks ANR (Agence Nationale de la Recherche) and CGI (Commissariat à l'Investissement d'Avenir) for their financial support of this work through Labex SEAM (Science and Engineering for Advanced Materials and devices) ANR-10-LABX-096, ANR-18-IDEX-0001. The authors acknowledge the GENCI-CINES for HPC resources (Projects A0040810359 and A0060810359). C. A. and I. C. acknowledge ANR (grand E-Storic) for financial support.

## References

1. E. Brémond, I. Ciofini, J. C. Sancho-García, and C. Adamo, *Acc. Chem. Res.* **49**, 1503 (2016), URL <http://dx.doi.org/10.1021/acs.accounts.6b00232>.
2. L. Goerigk and S. Grimme, *WIREs Comput. Mol. Sci.* **4**, 576 (2014), ISSN 1759-0884, URL <http://dx.doi.org/10.1002/wcms.1193>.
3. J. C. Sancho-Garcia and C. Adamo, *Phys. Chem. Chem. Phys.* **15**, 14581 (2013), URL <http://dx.doi.org/10.1039/C3CP50907A>.
4. W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965), URL <https://link.aps.org/doi/10.1103/PhysRev.140.A1133>.
5. P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964), URL <https://link.aps.org/doi/10.1103/PhysRev.136.B864>.
6. Y. Zhao, B. J. Lynch, and D. G. Truhlar, *J. Phys. Chem. A* **108**, 4786 (2004), URL <http://pubs.acs.org/doi/abs/10.1021/jp049253v>.
7. S. Grimme, *J. Chem. Phys.* **124**, 034108 (2006), URL <http://scitation.aip.org/content/aip/journal/jcp/124/3/10.1063/1.2148954>.
8. J. P. Perdew, A. Ruzsinszky, L. A. Constantin, J. Sun, and G. I. Csonka, *J. Chem. Theory Comput.* **5**, 902 (2009), URL <http://pubs.acs.org/doi/abs/10.1021/ct800531s>.
9. E. Brémond, M. Savarese, A. J. Pérez-Jiménez, J. C. Sancho-García, and C. Adamo, *J. Phys. Chem. Lett.* **6**, 3540 (2015), URL <http://dx.doi.org/10.1021/acs.jpcllett.5b01581>.
10. R. C. Lochan and M. Head-Gordon, *J. Chem. Phys.* **126**, 164101 (2007), URL <https://doi.org/10.1063/1.2718952>.
11. A. Najibi and L. Goerigk, *J. Phys. Chem. A* **122**, 5610 (2018), URL <https://doi.org/10.1021/acs.jpca.8b04058>.

12. J. C. Sancho-García, A. J. Pérez-Jiménez, M. Savarese, E. Brémond, and C. Adamo, *J. Phys. Chem. A* **120**, 1756 (2016), URL <https://doi.org/10.1021/acs.jpca.6b00994>.
13. R. Peverati and M. Head-Gordon, *J. Chem. Phys.* **139**, 024110 (2013), URL <https://doi.org/10.1063/1.4812689>.
14. A. Savin, in *Recent Developments and Applications of Modern Density Functional Theory*, edited by J. M. Seminario (Elsevier, Amsterdam, 1996), pp. 327–357.
15. A. J. Cohen, P. Mori-Sánchez, and W. Yang, *Science* **321**, 792 (2008), URL <http://www.sciencemag.org/content/321/5890/792.abstract>.
16. É. Brémond, Á. J. Pérez-Jiménez, J. C. Sancho-García, and C. Adamo, *J. Chem. Phys.* **150**, 201102 (2019), URL <https://doi.org/10.1063/1.5097164>.
17. C. Kalai and J. Toulouse, *J. Chem. Phys.* **148**, 164105 (2018).
18. É. Brémond, M. Savarese, Á. J. Pérez-Jiménez, J. C. Sancho-García, and C. Adamo, *J. Chem. Theory Comput.* **14**, 4052 (2018), URL <https://doi.org/10.1021/acs.jctc.8b00261>.
19. J.-D. Chai and M. Head-Gordon, *J. Chem. Phys.* **131**, 174105 (2009), URL <https://doi.org/10.1063/1.3244209>.
20. L. Goerigk, A. Hansen, C. Bauer, S. Ehrlich, A. Najibi, and S. Grimme, *Phys. Chem. Chem. Phys.* **19**, 32184 (2017), URL <http://dx.doi.org/10.1039/C7CP04913G>.
21. E. Brémond, M. Savarese, N. Q. Su, A. J. Pérez-Jiménez, X. Xu, J. C. Sancho-García, and C. Adamo, *J. Chem. Theory Comput.* **12**, 459 (2016), URL <http://dx.doi.org/10.1021/acs.jctc.5b01144>.
22. E. Brémond, M. Savarese, A. J. Pérez-Jiménez, J. C. Sancho-García, and C. Adamo, *J. Chem. Theory Comput.* **13**, 5539 (2017), URL <http://dx.doi.org/10.1021/acs.jctc.7b00627>.
23. T. Schwabe and L. Goerigk, *J. Chem. Theory Comput.* **13**, 4307 (2017), URL <https://doi.org/10.1021/acs.jctc.7b00386>.

24. Y. Jung, Y. Shao, and M. Head-Gordon, *J. Comput. Chem.* **28**, 1953 (2007), ISSN 1096-987X, URL <http://dx.doi.org/10.1002/jcc.20590>.
25. É. Brémond, M. Savarese, J. C. Sancho-García, Á. J. Pérez-Jiménez, and C. Adamo, *J. Chem. Phys.* **144**, 124104 (2016), URL <https://aip.scitation.org/doi/abs/10.1063/1.4944465>.
26. S. Kozuch, D. Gruzman, and J. M. L. Martin, *J. Phys. Chem. C* **114**, 20801 (2010), URL <http://pubs.acs.org/doi/abs/10.1021/jp1070852>.
27. Y. Jung, R. C. Lochan, A. D. Dutoi, and M. Head-Gordon, *J. Chem. Phys.* **121**, 9793 (2004), URL <http://scitation.aip.org/content/aip/journal/jcp/121/20/10.1063/1.1809602>.
28. R. C. Lochan, Y. Jung, and M. Head-Gordon, *J. Phys. Chem. A* **109**, 7598 (2005), URL <http://dx.doi.org/10.1021/jp0514426>.
29. S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, *J. Chem. Phys.* **132**, 154104 (2010), URL <http://scitation.aip.org/content/aip/journal/jcp/132/15/10.1063/1.3382344>.
30. D. Bousquet, E. Brémond, J. C. Sancho-García, I. Ciofini, and C. Adamo, *Theor. Chem. Acc.* **134**, 1602 (2014), ISSN 1432-2234, URL <https://doi.org/10.1007/s00214-014-1602-6>.
31. J. S. García, É. Brémond, M. Campetella, I. Ciofini, and C. Adamo, *J. Chem. Theory Comput.* **15**, 2944 (2019), URL <https://doi.org/10.1021/acs.jctc.8b01203>.
32. L. A. Burns, M. S. Marshall, and C. D. Sherrill, *J. Chem. Theory Comput.* **10**, 49 (2014), URL <https://doi.org/10.1021/ct400149j>.
33. A. Varandas, *Chem. Phys. Lett.* **69**, 222 (1980), ISSN 0009-2614, URL <http://www.sciencedirect.com/science/article/pii/0009261480850500>.
34. É. Brémond, I. Ciofini, J. C. Sancho-García, and C. Adamo, *J. Phys. Chem. A* **123**, 10040 (2019), URL <https://doi.org/10.1021/acs.jpca.9b06536>.

35. É. Brémond, M. Savarese, C. Adamo, and D. Jacquemin, *J. Chem. Theory Comput.* **14**, 3715 (2018), URL <https://doi.org/10.1021/acs.jctc.8b00311>.
36. C. Puzzarini, *Int. J. Quantum Chem.* **116**, 1513 (2016), URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/qua.25202>.
37. S. Alessandrini and C. Puzzarini, *J. Phys. Chem. A* **120**, 5257 (2016), URL <https://doi.org/10.1021/acs.jpca.6b01130>.
38. E. Penocchio, M. Piccardo, and V. Barone, *J. Chem. Theory Comput.* **11**, 4689 (2015), URL <https://doi.org/10.1021/acs.jctc.5b00622>.
39. M. Piccardo, E. Penocchio, C. Puzzarini, M. Biczysko, and V. Barone, *J. Phys. Chem. A* **119**, 2058 (2015), URL <http://dx.doi.org/10.1021/jp511432m>.
40. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, et al., *Gaussian~16 Revision B.01* (2016), gaussian Inc. Wallingford CT.
41. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.* **7**, 3297 (2005), URL <http://dx.doi.org/10.1039/B508541A>.
42. T. H. Dunning, K. A. Peterson, and D. E. Woon, in *Encyclopedia of Computational Chemistry* (John Wiley & Sons, Ltd, 2002), ISBN 9780470845011, URL <http://dx.doi.org/10.1002/0470845015.cca053>.
43. Y. Zhao and D. G. Truhlar, *J. Chem. Phys.* **125**, 194101 (2006), URL <https://dx.doi.org/10.1063/1.2370993>.
44. Y. Zhao, N. E. Schultz, and D. G. Truhlar, *Theor. Chem. Acc.* **120**, 215 (2008), URL <https://dx.doi.org/10.1007/s00214-007-0310-x>.
45. E. Brémond and C. Adamo, *J. Chem. Phys.* **135**, 024106 (2011), URL <http://scitation.aip.org/content/aip/journal/jcp/135/2/10.1063/1.3604569>.
46. T. Schwabe and S. Grimme, *Phys. Chem. Chem. Phys.* **8**, 4398 (2006), URL <http://dx.doi.org/10.1039/B608478H>.

47. E. Brémond, J. C. Sancho-García, A. J. Pérez-Jiménez, and C. Adamo, *J. Chem. Phys.* **141**, 031101 (2014), URL <http://scitation.aip.org/content/aip/journal/jcp/141/3/10.1063/1.4890314>.
48. S. Kozuch and J. M. L. Martin, *J. Comput. Chem.* **34**, 2327 (2013), ISSN 1096-987X, URL <http://dx.doi.org/10.1002/jcc.23391>.
49. T. Schwabe and S. Grimme, *Phys. Chem. Chem. Phys.* **9**, 3397 (2007), URL <http://dx.doi.org/10.1039/B704725H>.
50. L. Goerigk and S. Grimme, *J. Chem. Theory Comput.* **7**, 291 (2011), URL <http://pubs.acs.org/doi/abs/10.1021/ct100466k>.
51. J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996), URL <http://link.aps.org/doi/10.1103/PhysRevLett.77.3865>.
52. F. O. Kannemann and A. D. Becke, *J. Chem. Theory Comput.* **5**, 719 (2009), URL <https://doi.org/10.1021/ct800522r>.

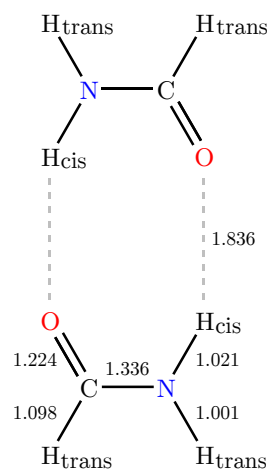


Figure 1: Molecular structure and reference bond lengths ( $\text{\AA}$ ) of the formamide dimer (from Ref. 37).



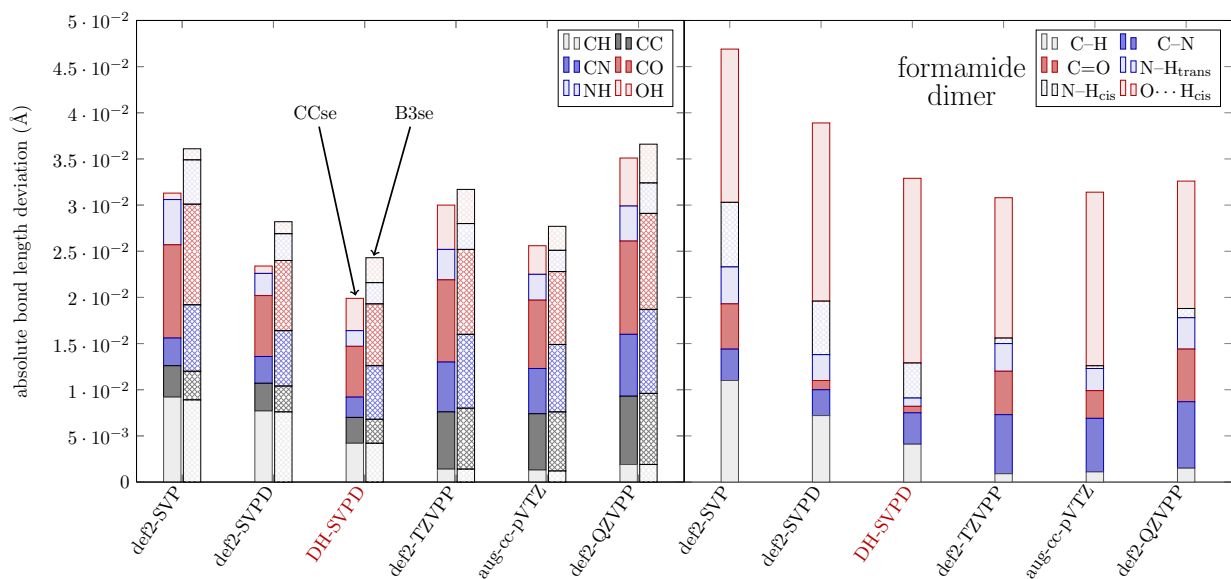


Figure 2: (left) Mean absolute deviations ( $\text{\AA}$ ) computed with the PBE-QIDH double hybrid and different basis sets taking as reference the 53 (164) CCSD(T) (B3LYP) equilibrium bond length references gathered into the CCse (B3se) databases.<sup>38,39</sup> (right) Absolute bond length deviations ( $\text{\AA}$ ) computed with the PBE-QIDH double hybrid and a selection of basis sets versus the 6 intra- and inter-molecular equilibrium CCSD(T) reference parameters of the formamide dimer.<sup>37</sup>

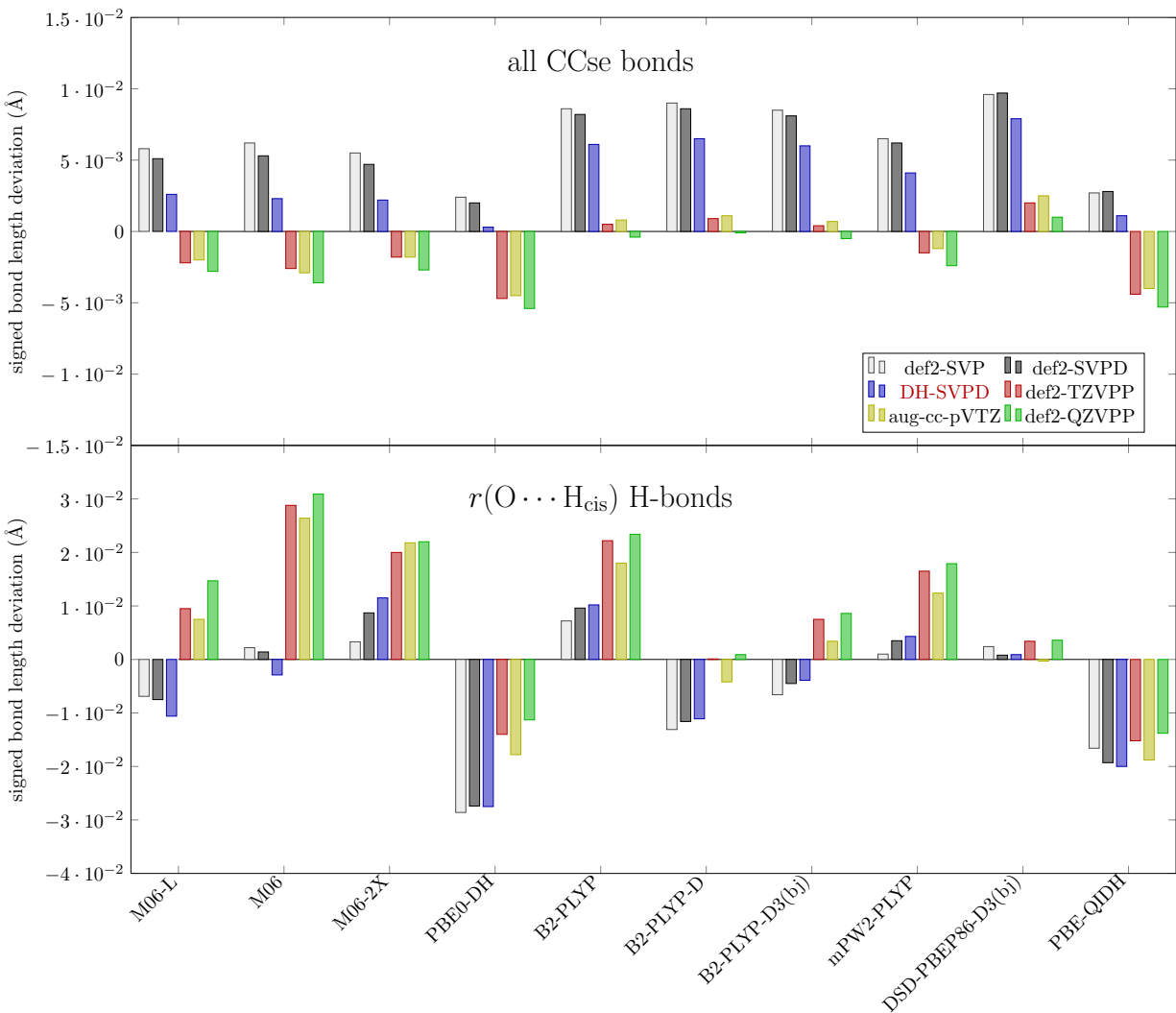


Figure 3: (top) Mean signed deviations ( $\text{\AA}$ ) computed over a selection density functionals and basis sets versus the 53 CCSD(T) equilibrium bond length references gathered into the CCse database.<sup>38,39</sup> (down) Signed bond length deviations ( $\text{\AA}$ ) computed over a selection density functionals and basis sets versus the H-bond CCSD(T) equilibrium reference distance of the formamide dimer.<sup>37</sup>