

Is There Still Room for Parameter Free Double Hybrids? Performances of PBE0-DH and B2PLYP over Extended Benchmark Sets

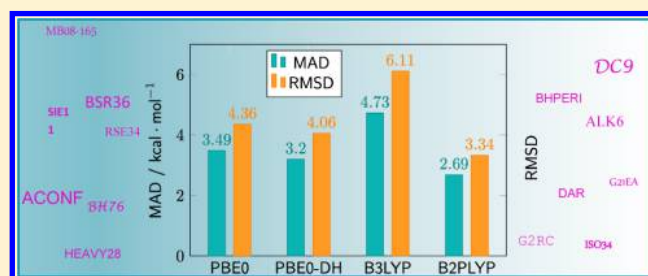
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ABSTRACT: The performances of two double hybrids, namely B2PLYP and PBE0-DH, are tested over the large GMNKT30 benchmark and compared with the results obtained with the related global hybrids, B3LYP and PBE0 with the aim of defining if there is still room for the development on nonparametrized functionals at DH level. Beyond the intrinsic interest in figures, these functionals' pairs are chosen as representative of the parametrized (B2PLYP/B3LYP) and parameter-free (PBE0-DH/PBE0) approaches to density functional theory. The obtained results show that the behavior of the double hybrids in general parallel the performances of the corresponding global hybrids, thus showing that either using a parametrized or using a nonparameterized approach to design new double hybrids, the performances are generally ameliorated with respect to the corresponding global hybrids. Nevertheless, the accuracy of B2PLYP is still higher than that of PBE0-DH, especially for thermochemistry. Albeit a link between performances and functional physics is difficult to extricate, it could be argued that this last result is not surprising since both B3LYP and B2PLYP are tuned on this last property.



1. INTRODUCTION

The development of new exchange correlation functionals is one of the main challenges in Density Functional Theory (DFT). Not surprisingly, in order to obtain accurate and relevant models for the description of chemical reactivity and properties, especially of molecular systems, an extremely large number of functionals have been developed during the past decade.

Following the Perdew classification,¹ functionals are nowadays classed as a function of their degree of nonlocality, which is actually an effective way of organizing the very diverse existing DF approximations (DFAs). The lowest rung in the Perdew's ladder is actually represented by the local density approximation (LDA) while the two highest rungs correspond to functionals including a dependence on both occupied and unoccupied orbitals, respectively. Moving from a lower to a higher rung in this ladder is supposed to yield results that are more and more accurate. In particular, at the level of the global or range separated hybrid functionals, for which the dependence only on the occupied orbitals is introduced by the presence of a—constant or variable—mix of Kohn–Sham (KS) exchange–correlation contribution and Hartree–Fock (HF) exchange,² very good performances on reactivity, structure, and properties can be already obtained, as clearly stressed by literature over the past few decades.

More recently, a new class of functionals, including the correlation energy as a perturbation term computed at Moller–Plesset (MP2) level,^{3,4} was developed. In such a way, the dependency on virtual orbitals is included into the energy functional but not in the potential so that, strictly speaking, such functionals do not belong to the last rung of Perdew's ladder, as usually admitted. Truhlar⁵ defined first this new class of functionals as double hybrid (DH), and this approach was largely further developed by Grimme, the author of the B2PLYP model.^{6,7} According to Grimme, the general expression for this DH functional is

$$E_{xc}^{DH} = a_x E_x^{HF} + (1 - a_x) E_x^B + (1 - a_c) E_c^{LYP} + a_c E_c^{MP2} \quad (1)$$

where E_x^{HF} represents the HF-like exchange contribution, E_x^B the Becke exchange part,⁸ E_c^{LYP} the Lee–Yang–Parr correlation,⁹ and E_c^{MP2} the correlation perturbative term computed using second-order Moller–Plesset (MP2) approach. The two empirical parameters present in this formulation ($a_x = 0.53$ and $a_c = 0.27$) were determined by a fitting procedure in order to minimize the error on the G2 set including the experimental heat of formation of 148 organic molecules.⁶ Along with B2PLYP, an entire family of double hybrids was generated

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Table 1. Sets Considered in This Work Together with the Number of Reactions (nr) and the Average Reference Energies (ΔE , in kcal/mol)

set	description of the set	nr	ΔE	section ^a
MB08-165	decomposition energies of artificial molecules	165	117.2	decomposition and atomization energies
W4-08	atomization energies of small molecules	99	237.5	
W4-08woMR	W4-08 without multireference cases	83	261.5	
BSR36	bond separation reactions of saturated hydrocarbons	36	16.7	
G21IP	adiabatic ionization potentials	36	250.8	adiabatic processes
G21EA	adiabatic electron affinities	25	33.6	
PA	adiabatic proton affinities	12	174.9	
BHPERI	barrier heights of pericyclic reactions	26	19.4	barriers heights and reaction energies
BH76	barrier heights of hydrogen transfer, heavy atom transfer, nucleophilic substitution, unimolecular, and association reactions	76	18.5	
BH76RC	reaction energies of the BH76 set	30	21.5	
O3ADD6	reaction energies, barrier heights, and association energies for addition of O ₃ to C ₂ H ₄ and C ₂ H ₂	6	22.7	
G2RC	reaction energies of selected G2/97 systems	25	50.6	
DARC	reaction energies of Diels–Alder reactions	14	32.2	
RSE34	radical stabilization energies	43	7.5	
NBPRC	oligomerizations and H ₂ fragmentations of NH ₃ /BH ₃ systems; H ₂ activation reactions with PH ₃ /BH ₃ systems	12	27.3	
ALK6	fragmentation and dissociation reactions of alkaline and alkaline-cation-benzene complexes	6	44.6	
AL2X	dimerization energies of AlX ₃ compounds	7	33.9	
ACONF	relative energies of alkane conformers	15	1.8	
SCONF	relative energies of sugar conformers	17	4.9	
CYCONF	relative energies of cysteine conformers	10	2.1	
ISO34	isomerization energies of small and medium-sized organic molecules	34	14.3	
ADIM6	interaction energies of <i>n</i> -alkane dimers	6	3.3	dispersion and non covalent interactions
S22	binding energies of noncovalently bound dimers	22	7.3	
HEAVY28	noncovalent interaction energies between heavy element hydrides	28	1.3	
RG6	interaction energies of rare gas dimers	6	0.46	
SIE11	self-interaction error related problems	11	34.0	self-interaction error
DC9	nine difficult cases for DFT	9	35.7	nine difficult cases for DFT

^aRefers to section of this present paper.

following the same semiempirical philosophy, such as, for instance Martin's B2K-PLYP¹⁰ or the B2GP-PLYP¹¹ functionals. Xu and collaborators, following a different approach, formulated the XYG3 functional that makes use of the standard B3LYP functional to generate density¹² and orbitals to be used to compute the double hybrid energy. Indeed, it is worth stressing that the hybrid (ex. B3LYP) and corresponding double hybrid (ex. B2PLYP) functional do not necessarily contain the same percentage of HF-like exchange. Even the so-developed DH functionals allowed obtaining an improvement of many properties, they clearly include a number of fitted, thus empirical, parameters (usually two). The newer and better performing functionals developed by Martin (such as DSD-BLYP¹³ or DSD-PBEB86¹⁴ for instance) or the latest Grimme's PWPB95,¹⁵ further ameliorate the parent DH properties by inclusion of spin component or spin-opposite scaling, respectively, of the MP2 contribution and empirical dispersion corrections. As a matter of fact the same authors have clearly underlined that London dispersion, when properly included, substantially enhances the performances of DH over a wide variety of benchmark sets (including for instance reaction energies and barriers or conformers stabilities) and not only the behavior of functionals on dispersion dominated test cases.

This finding also holds for DH since the relatively small MP2 contribution seems not to be able to fully recover dispersion interactions in the full distance range.^{7,13,16,17}

In this context, following the same 'parameter free' philosophy used by Adamo and Barone¹⁸ and Ernzerhof and Scuseria¹⁹ for the development of the well performing^{20–25} PBE0 global hybrid, recently Adamo and co-workers developed a new DH, the so-called PBE0-DH, which includes the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional in a double hybrid formulation without inclusion of any empirical parameters.^{26–28} The fraction of HF-like exchange and MP2 correlation were indeed fixed making use of theoretical constraints and physical considerations and not fitted to any experimental sets. In particular, making use of the adiabatic connection,²⁹ the PBE0-DH model was formulated as

$$E_{xc}^{\text{PBE0-DH}} = \frac{1}{2}(E_x^{\text{HF}} + E_x) + \frac{1}{2}\left(\frac{7}{4}E_c + \frac{1}{4}E_c^{\text{MP2}}\right) \quad (2)$$

The exact-like exchange contribution is here fixed to 0.5, which is indeed close to the value obtained in the B2PLYP model by fitting (0.53), while the MP2 correlation contribution included (0.125) is significantly lower than those of others double hybrids (ex. 0.27 for B2PLYP).

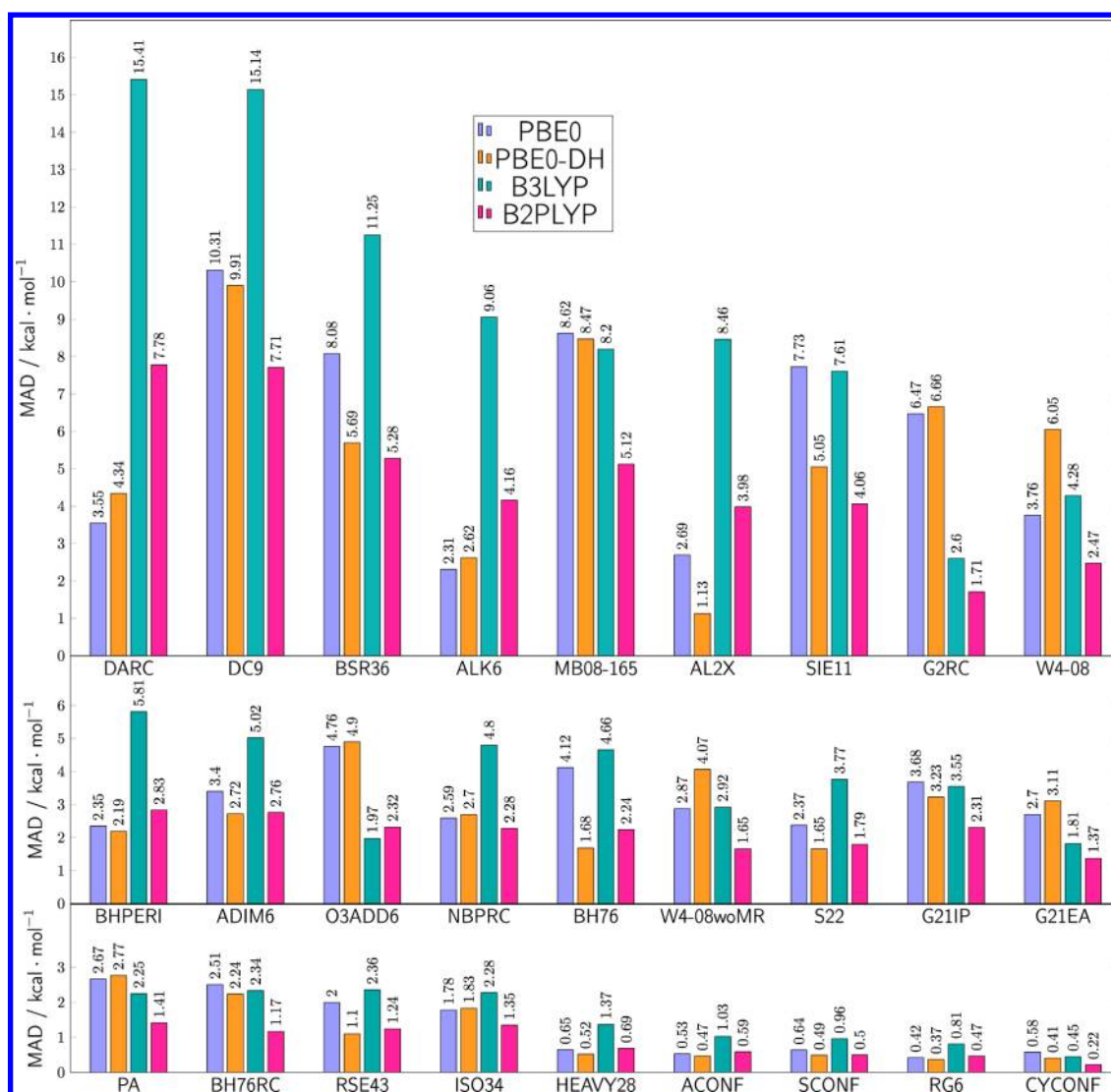


Figure 1. MAD (in kcal/mol) computed with the PBE0, PBE0-DH, B3LYP, and B2PLYP functionals over the subsets of the GMTKN30 database.

The aim of the present paper is to test the performances of the B2PLYP and PBE0-DH functionals with respect to the parent hybrids, (PBE0 and B3LYP) taken as representative of the parametrized and nonparametrized families over a relevant benchmark set, that is the GMTKN30 recently developed by Goerigk and Grimme.^{15,30}

In the present paper, two DH functionals possessing the same level of complexity will be considered, both of them not taking into account neither explicit dispersion corrections nor spin scaled MP2 contributions.

The GMTKN30, recently used to probe the performances of many functionals of different rung^{15,17,31,32} and including 1218 single point calculations and 841 data points, is providing reliable results for functional performances since it is extended version of the GMTKN24 database, which includes thermochemistry, kinetics and noncovalent interactions. This extended version presents six new and three modified subsets including oligomerizations and H₂ fragmentations of NH₃/BH₃ systems, isomerization energies of large organic molecules, fragmentation and dissociation reactions of alkaline and alkaline-cation-benzene, bond separation reactions of saturated hydrocarbons, interactions energies of *n*-alkane dimers, -binding energies of

noncovalently bond dimers, interaction energies of rare gas dimers, and heavy element hybrids.

The paper is structured as follows: after a brief description of the computational details, the performances of the four functionals will be assessed first by comparing the overall behavior and then by comparing in details the outcomes of the four functionals on different subsets. Finally some general conclusions will be drawn.

2. COMPUTATIONAL DETAILS

The PBE0-DH functional has been implemented in a local version of the Gaussian program,³³ so that all the standard features, including analytical derivatives for geometry optimization, harmonic frequencies and properties, are also available. In analogy with previous work (see for instance references 17, 31, 32), the performances of the PBE0, B3LYP, B2PLYP, and PBE0-DH functionals have been tested using the GMTKN30 database. The IDISP, ISOL22, WATER27, and PCONF subsets were not considered in the present study due to the too large size of the molecules contained in these subsets, not fitting our local computational resources.

In order to compare the obtained results with the values presented by Grimme, the same basis sets were used here. In

particular, the large Ahlrichs' type quadruple- ζ basis set def2-QZVP,³⁴ which is expected to provide converged results even for DHs, has been used. Indeed, it has been shown that, even if DH approaches could have a significant larger dependency on basis set then corresponding non-DH forms, due to the presence of the MP2 component, a quadruple- ζ is sufficient to reach the convergence limit.^{16,35} Regarding the calculations of electron affinities (subset G21EA), diffuse s and p functions were taken from the Dunning aug-cc-pVQZ,³⁶ which allows obtaining the aug-def2-QZVP basis.

3. RESULTS AND DISCUSSION

In order to analyze the results obtained first the overall performances of the PBE0-DH on the GMTKN30¹⁵ database will be discussed (section 3.1) and then the accuracy of the four functionals will be analyzed on the different subsets (sections 3.2–3.8). For the sake of clarity, several subsets have been grouped based on the property they are aimed to benchmark (see Table 1). In such a way, first subsets concerning thermochemistry (decomposition and atomization energies) will be discussed followed by those related to adiabatic processes (ionization potential, electron and proton affinities). Next, the performances of the functionals, on reactivity related properties (barriers, reaction energies, conformers' relative energies), will be discussed and finally subsets concerning difficult cases for DFT (including SIE and systems dominated by non covalent interactions) will be considered. This partition is clearly arbitrary, and as previously mentioned, and it does not intend that dispersion interactions play a role only in the case of the latter subsets since, as previously reported in literature, inclusion of dispersion terms globally ameliorate the DHs behavior also for other properties, including reaction energies and barriers or isomer relative stabilities.^{15,37}

3.1. PBE0-DH Overall Performances on the GMTKN30 Set. As previously discussed, the GMTKN30¹⁵ set is a very complete benchmark able to assess the behavior of functionals on very different and difficult properties. It is thus interesting to compare the performances of the PBE0-DH with respect to the PBE0 functional on this set in order to evaluate if the improvements observed going from the hybrid to the double hybrid in previous works on the G2 set are extensible to wider benchmark sets.

In the Figure 1, the Mean Absolute Deviation (MAD) computed for the functionals studied on each subset is reported. For the sake of clarity, in this figure, the subsets were classified in decreasing order in mean absolute deviation.

Overall, among the 27 subsets, the PBE0-DH functional performs better than the PBE0 for 16 subsets, which is actually only slightly more than half of the subsets. Based on this result, one could thus consider the PBE0-DH functional as only a minor improvement with respect to PBE0 at, however, much larger computational cost. Indeed, it should be underlined that the improvements in term of absolute value in MAD computed on the 16 subsets for which PBE0-DH outperforms PBE0 is often large, whereas for the 11 sets where PBE0 performs better than PBE0-DH, actually, the performances of the two functionals are almost equivalent, and relatively small MADs are found for both. Therefore, globally, PBE0-DH represents, even on the larger GMTKN30 set, a real improvement with respect to the corresponding global hybrid. Considering the MAD obtained for each set with the four functional some few general trends can be found. Regarding the thermochemistry, (here represented by the MB08-165,³⁸ W4-08, and W4-

08woMR¹¹ subsets) if B2PLYP represents a systematic improvement with respect to B3LYP, PBE0-DH only slightly improves the PBE0 performances on the MB08-165 set and actually provides a larger MAD (of 2.29 kcal/mol) in the case of the W4-08 set.

Generally, double hybrids provide better reaction energies, even if the PBE0-DH performances are slightly worse than PBE0 for the DARC³⁹ set (of 0.79 kcal/mol in MAD), indeed PBE0 and PBE0-DH strongly outperform both B3LYP and B2PLYP. The same conclusion holds for barrier heights that are normally better reproduced using double hybrid functionals. For instance, in the case of the BH76^{40,41} subset, going from PBE0 to PBE0-DH determine a reduction of the MAD from 4.12 to 1.68 kcal/mol.

A remarkable improvement of global hybrid performances is also observed on sets related to self-interaction error (ex. SIE11³⁰). The computed decrease in MAD is clearly related to the increase of the HF-like exchange contribution in the double hybrid, thus reducing the SIE. The same overall behavior is also observed for the AL2X³⁹ subset, containing the dimerization energies of AlX₃ compounds, which can indeed be related to overdelocalization problems. Finally, double hybrids, due to the presence of a MP2 contribution, actually improve the performances on all sets testing the capability of functional on weak interaction such as the BSR36^{42–46} subset for which a decrease in MAD of 2.39 kcal/mol is computed going from PBE0 to PBE0-DH. Analogously, an improvement in the performances on subsets probing dispersion interactions was also found (ex. 0.72 kcal/mol for S22 and 0.68 kcal/mol for ADIM6^{46,47}). The performance on the latter data sets might be further improved by adding a specific correction for dispersion^{7,13,15,48} which is, however, beyond the scope of this work.

3.2. Decomposition and Atomization Energies. For the MB08-165³⁸ set, containing the decomposition energies of artificial molecules, significant MADs are computed for all considered functionals (from 5.12 kcal/mol for B2PLYP to 8.62 kcal/mol for PBE0). These large deviations are also related to the nature of the set, since the reference data are often very large so that the MADs obtained are, on a relative scale, not so large. Indeed, on such subset B2PLYP represents a net improvement with respect to B3LYP while PBE0-DH only very marginally ameliorates the PBE0 results. Furthermore, if B2PLYP systematically yield better results than B3LYP also on the W4-08 set, containing the atomization energies of 99 small artificial molecules, and on the W4-08 woMR set, obtained by removing 16 cases multireference cases from the W4-08,¹¹ this is not the case for PBE0-DH, which actually provides always larger errors than PBE0 on this two subsets. More generally, from these three subsets, it seems that while in the case of parametrized functional a global improvement of performances is obtained when going from hybrid to double hybrid, in the case of parameter free functional based on the PBE formulation an overall degradation of the performances is obtained at double hybrid level on the W4 sets.

It could be difficult to relate this behavior to the intrinsic characteristic of the functionals, since all their different components (HF exchange, MP2 contribution, and so on) are entangled with each other. However, from one side, it should be considered that both B3LYP and B2PLYP are parametrized on thermochemistry. On the other side, it is not surprising that, at least for atomization energies, the increasing of HF-like exchange leads to a significant improvement of the

performances.^{49,50} Such amelioration is larger for B3LYP/B2PLYP than for PBE0/PBE0-DH. A similar behavior could be expected also for self-interaction effects, where the error decreases as the HF-like exchange increases.⁵¹

On the other hand, when considering bond separation reactions (i.e., the BSR36 set^{42–46}), a systematic and sizable improvement of the performances is obtained when going from global hybrids to double hybrids, the MAD of the B2PLYP and PBE0-DH functional being of the same order of magnitude (5.28 and 5.69 kcal/mol, respectively)

3.3. Adiabatic Processes. In order to estimate the performances of the functionals in the prediction of adiabatic processes, three different subsets, namely the G21IP, G21EA,⁵² and the PA^{53–55} ones, will be considered probing, respectively, adiabatic ionization potential and electron and proton affinities.

In particular, considering the G21IP and G21EA sets, the first includes 36 adiabatic ionization potentials of atoms and small molecules while the second collects 25 adiabatic electron affinities. Both sets are taken from the G2-1 set, and in both cases, the B2PLYP functional provides the best results with a MAD of 2.31 and 1.37 kcal/mol, respectively. For the G2IP set, only two reactions (including the ionization potential of Be and B) present an absolute deviation larger than 5.0 kcal/mol, and they actually represent the worst case for all functionals with MAD of 7.19 kcal/mol (B2PLYP), 6.70 kcal/mol (B3LYP), 7.95 kcal/mol (PBE0DH), and 8.03 kcal/mol (PBE0) for the ionization of beryllium and 5.89 kcal/mol (B2PLYP) 9.21 kcal/mol (B3LYP), 7.72 kcal/mol (PBE0-DH), and 8.98 kcal/mol (PBE0) for the IP of bore. When looking at the ionization of the oxygen atom, which was considered as the most difficult reaction of this set for GGA functionals (GMTKN24), we can observe a significant improvement of the performances when going from hybrids to double hybrids. The computed reduction of the error going from PBE0 (5.34 kcal/mol) to PBE0-DH (1.98 kcal/mol) is indeed large (3.36 kcal/mol) and is actually even larger in the case of the B3LYP/B2PLYP with errors from 9.50 kcal/mol (B3LYP) to 2.32 kcal/mol (B2PLYP).

Overall, the same conclusion drawn for the G21IP subset also holds for the G21EA set, with the B2PLYP results providing the lowest MAD (1.37 kcal/mol for B2PLYP). Indeed, the good performances obtained with B2PLYP (and B3LYP) on these subsets were somehow expected since this family of functionals was optimized on the G2 databases, of which the G21IP and G21AE are part. Surprisingly, the PBE0-DH functional does not significantly improve the performances of PBE0 on the G21EA sets, actually increasing the MAD of 0.41 kcal/mol.

Analogously for the PA set, including 12 adiabatic proton affinities of four conjugated polyenes (reference values based on CCSD(T)/CBS⁵⁵ and eight small molecules (based on vibrationally back corrected reference values^{53,54}), B2PLYP and B3LYP results are sizably better than PBE0-DH and PBE0 ones. Excluding the four polyenes from the set (the most affected by overdelocalization problems) allows reducing the MAD of all functionals to 0.46 kcal/mol (B2PLYP), 0.81 kcal/mol (B3LYP), 1.38 kcal/mol (PBE0), and 1.60 kcal/mol for PBE0-DH, respectively. The largest errors on the set are indeed related, for all functionals, to the prediction of proton affinity of C₈H₁₀. In such a case, errors of 5.53 kcal/mol (B2PLYP), 8.00 kcal/mol (B3LYP), 6.62 (PBE0-DH), and 7.17 kcal/mol for PBE0 are computed.

More generally, although the MAD are relatively low for all four functionals (i.e., below 3.7 kcal/mol) as in the case of

atomization and dissociation energies, B3LYP and B2PLYP seem to better perform with respect to PBE0 and PBE0-DH for the description of adiabatic ionization potential and electron and proton affinities. Moreover, a systematic improvement of the global hybrid performances is only obtained using parametrized functionals.

3.4. Barriers Heights and Reaction Energies. Let us first focus on the performances obtained for barrier heights using two subsets, the BHPERI⁵⁶ and the BH76^{40,41} ones. The first set contains 26 barrier heights of reactions involving pericyclic cyclopentadiene while the BH76 set includes the HTBH38⁴⁰ set, composed of forward and reverse barrier of 19 hydrogen atom transfer reactions, and the NHTBH38⁴¹ set, containing forward and reverse barrier of heavy atom transfer and nucleophilic substitution.

With a MAD of 5.81 kcal/mol, the BHPERI⁵⁶ set seems to represent a difficult benchmark for B3LYP. Among all reactions, the worst performances were indeed obtained for the 1,3-cyclopentadiene in C₂ symmetry. Nonetheless, the performances are significantly improved going to B2PLYP (MAD of 2.83 kcal/mol) or using functionals belonging to the PBE0 family. In this set, PBE0-DH was actually particularly accurate, since only four absolute deviations are above 3.0 kcal/mol and, among those four reactions, only two are above 4.0 kcal/mol (1,3 cyclopentadiene and cis-triscyclopropacyclohexane). B2PLYP presents eight reactions with an associate absolute error above 4.0 kcal/mol whereas B3LYP gives 18 reactions above 4.0 kcal/mol, and among them, five are above 10 kcal/mol.

Considering the BH76 subset, the advantages related to the use of double hybrids instead of global hybrids are clear. Indeed, for B2PLYP and PBE0-DH, MADs of 2.24 and 1.68 kcal/mol are respectively computed with respect to 4.66 and 4.12 kcal/mol obtained at B3LYP and PBE0 level. Using PBE0-DH, only one reaction (the reverse reaction of H + NO₂ → OH + N₂) presents a MAD above 5.0 kcal/mol. The same holds for B2PLYP with two MADs above 5.0 kcal/mol. On the other hand, 21 barriers heights are computed above the reference values of more than 5.0 kcal/mol for PBE0 and 32 for B3LYP. For all functionals, the worst results are obtained for the barriers height associated to the reaction previously cited, with MADs computed to be 6.17 kcal/mol for PBE0-DH, 6.47 kcal/mol for B2PLYP, and even larger for B3LYP and PBE0 (10.16 and 14.17 kcal/mol, respectively).

For the corresponding reaction energies (included in the BH76RC^{40,41}) the computed MADs are overall smaller, the largest MAD being 2.51 kcal/mol at PBE0 level. As in the case of the barrier, the largest errors are also associated to the H + NO₂ → OH + N₂ reaction. Indeed, with an error of 5.62 kcal/mol for the PBE0-DH, 5.16 kcal/mol for B2PLYP, and 10.17 kcal/mol for PBE0, the performances are far from the MADs associated to this set, which are quite low (ex. 1.17 kcal/mol for B2PLYP and 2.24 for PBE0-DH). Overall, in this set, double hybrids represent an improvement with respect to global hybrids. This is actually not the case when considering the reaction of addition of ozone on ethane or ethyne, contained in the O3ADD6⁵⁷ subset. For both reactions the formation energy of the primary ozonide, the barrier height and the association energy of van der Waals complex were actually computed but the associated errors change as a function of the property considered. All functionals give pretty accurate results for the association energy of the van der Waals (vdW) complex: when computing the MAD regarding only the vdW association

energy, we observe variations from 0.13 kcal/mol for B2PLYP to 0.81 kcal/mol for B3LYP. PBE0 and PBE0-DH yield a similar behavior with MADs of 0.33 and 0.38 kcal/mol for PBE0 and PBE0-DH, respectively. The barrier height is correctly described by all functionals except PBE0 for which errors ranging from 4.93 to 6.04 kcal/mol are computed. When analyzing the formation energy of the primary ozonide, the PBE0 family is not able to give accurate results (errors ranging from 7.09 to 11.4 kcal/mol), giving a global MAD for this subset largely higher than for B3LYP family. The same conclusion holds for the reaction energies included in the G2RC set, which is part of the G2/97 set regarding the heats of formation.⁵⁸ Also, in this case, B2PLYP and B3LYP give results (MAD of 1.71 and 2.60 kcal/mol, respectively) in better agreement with the reference data than PBE0 or PBE0-DH (MAD of 6.47 and 6.66 kcal/mol, respectively). Indeed, for PBE0 and PBE0-DH, the error associated to fourteen and twelve reactions, respectively, among the twenty-five present in this set, is above 5.0 kcal/mol.

Very large MADs are also computed when considering the MAD associated to 14 Diels–Alder reactions, studied in the DARC³⁹ set. For this set all functionals show large MADs, the PBE0 one providing the smallest MAD on this set (3.55 kcal/mol). The MAD slightly increases for the corresponding double hybrid (4.34 kcal/mol for PBE0-DH), and it is substantially larger in the case of both B3LYP and B2PLYP (15.41 and 7.78 kcal/mol, respectively). Overall, these results indicate that the (over)delocalization issue, responsible for the large errors on the DARC set, is far to be a problem solved even when using double hybrid functionals.

On the other hand, relatively low MADs are computed for radical stabilization energies (RSE34^{59,60} set) and H₂ activation (NBPRC^{30,61} set). For the RSE43 set the performances obtained with double hybrids are systematically better than those of corresponding global hybrids: PBE0-DH and B2PLYP provide MADs of 1.10 and 1.24 kcal/mol, respectively, to be compared to 2.00 and 2.36 kcal/mol for PBE0 and B3LYP, respectively. Overall, for this set the PBE0 family performs slightly better than the B3LYP one. In the case of the NBPRC set, the rather poor performances of B3LYP, already been pointed out in the literature⁶² (MAD of 4.8 kcal/mol), are overcome by PBE0, PBE0-DH, and B2PLYP, all providing similar results with MADs around in the range 2.7 (PBE0-DH) to 2.28 kcal/mol (B2PLYP).

The ALK6⁴⁸ set, containing three decomposition reactions energies of alkaline metal complexes and three dissociation reaction energies of alkaline-cation–benzene complexes actually allows to probe the performances of the functionals on reactions dominated by London dispersion. Globally, the PBE0 family shows smaller MAD already at global hybrid level (2.31 kcal/mol for PBE0 and 2.62 kcal/mol for PBE0-DH) while for the B3LYP family larger errors are computed both at global (9.06 kcal/mol) and double (4.16 kcal/mol) hybrid level, the largest contribution to the MADs coming from the three dissociation reactions of alkaline-cation–benzene complexes.

Finally, the AL2X subset, which contains the binding energies of seven dimers of AlX₃ (X = H, CH₃, F, Cl, and Br), has been considered as a probe over delocalization problems in DFT.³⁹ The performances of both PBE0 and PBE0-DH functionals are rather good with MADs of 2.69 and 1.13 kcal/mol, respectively. In particular, for the PBE0-DH functional, the error ranges from 0.06 kcal/mol (for the

Al₂(CH₃)₄ → 2Al(CH₃)₂ reaction) to 3.49 kcal/mol (for the Al₂H₆ → 2AlH₃ reaction). On the other hand, the errors associated to both the B3LYP and B2PLYP functionals are in average higher. At B2PLYP level, for six over seven reactions, errors between 3 and 5 kcal/mol are found, whereas for B3LYP, for the same six reactions, discrepancies between 6.5 and 12.5 kcal/mol are computed.

Nonetheless, for both families of functionals, double hybrids represent, for this subset, a sizable improvement with respect to global hybrids.

3.5. Conformers and Isomers. The ACONF,⁶³ SCONF,⁶⁴ and CYCONF⁶⁵ sets all include conformers relative energies. The associated MADs are very low and actually all functionals are very accurate, although a systematic improvement when going from hybrid to double hybrids can be found.

For the ACONF subset, the computed MADs range from 0.47 kcal/mol (PBE0-DH) to 1.03 kcal/mol (B3LYP). The SCONF follows the same qualitative and quantitative behavior while for the CYCONF set even smaller MADs are computed ranging from 0.22 kcal/mol (B2PLYP) to 0.58 kcal/mol (PBE0).

The ISO34⁶⁶ subset (containing isomerization of organic molecules) shows similar results although slightly higher MADs are computed with respect to the ACONF, SCONF, or CYCONF sets with MADs ranging from 1.35 kcal/mol (B2PLYP) to 2.28 kcal/mol (B3LYP). Therefore, the problems associated with the use of GGAs on this set seem to be solved by the use of global hybrids and double hybrids.

Analyzing the results of this set in more details, for each functional, only two reactions (tetramethylbutane → *n*-octane and toluene → norbornadiene for the B3LYP family and tetramethylbutane → *n*-octane and hexanoic acid → *t*-butanoate for the PBE0 family) present a difference from the reference values larger than 5.0 kcal/mol.

As previously mentioned, inclusion of dispersion correction is indeed expected to ameliorate the results over this set as demonstrated by previous works.^{7,13,16,17}

3.6. Dispersion and Noncovalent Interactions. The four sets probing dispersion and noncovalent interactions, namely ADIM6,^{40,41} S22,^{48,67,68} HEAVY28⁴⁸ and RG6,^{69–72} are, as expected, all characterized by a systematic and sizable improvement of global hybrids' behavior by inclusion of MP2 contributions.

On the S22 subset, probing functionals' behavior on noncovalent interactions, the performances of the two double hybrids are significantly better than those of the corresponding global hybrids: using PBE0-DH allows to decrease the MAD of 0.72 kcal/mol. The same holds for B2PLYP, decreasing the MAD of about 1.98 kcal/mol with respect to the MAD computed at B3LYP level.

The same qualitative behavior is also observed for the RG6 and HEAVY28 sets, although for both sets very low MADs are already computed at global hybrid level. The worst results are indeed obtained at B3LYP level, but they are still very accurate with MADs of 0.81 and 1.37 kcal/mol associated to the RG6 and HEAVY28 sets, respectively.

For the ADIM6 set^{46,47} on the other hand, if the overall behavior is the same (that is sizable reduction of the MAD when going from hybrid to double hybrids and comparable absolute MAD for B2PLYP and PBE0-DH), the absolute value of the MADs are larger of 2.72 and 2.76 kcal/mol for PBE0-DH and B2PLYP, respectively.

3.7. Self-interactions Errors. Considering the more classical SI dominated cases contained in the SIE11³⁰ subset, although double hybrids clearly improve the performances of global hybrids, overall, the MADs of all four functionals are rather large. Indeed, for ten over eleven reactions present in this set, all functionals overestimate the reactions energies. A significant decrease of the MAD is indeed shown going from global to double hybrids of 2.68 kcal/mol for the PBE0 family and 3.55 kcal/mol for the B3LYP one. This behavior is clearly directly related to the higher percentage of Hartree–Fock exchange present in the double hybrid functional which partially corrects for the SIE.⁷³ Indeed, both double hybrids include roughly speaking 50% of HF-like exchange when only 25% and 20% are casted in PBE0 and B3LYP, respectively.

3.8. Nine Difficult Cases for DFT. The DC9 set groups nine cases considered as particularly difficult for DFT approaches. Since all reactions of this set do not share any common features, they will be discussed separately. Considering the reaction energy associated with the 2-pyridone → 2-hydropyridine,⁷⁴ of only −1.0 kcal/mol, it is clearly difficult to predict correctly not only its magnitude but also simply its sign. Among the four functionals, only PBE0-DH gives a qualitatively and quantitatively correct result predicting a reaction energy of −0.70 kcal/mol. The second reaction considered in this set deals with the isomerization of C₂₀ cage to its bowl isomer.⁷⁵ The relative stability (of −13.3 kcal/mol) of the isomers is affected by large errors, independently of the functional: indeed, the results are ranging from −4.05 kcal/mol (PBE0) to −42.78 kcal/mol (B3LYP). On the other hand, the energy difference between hepta-1,2,3,5,6 hexaene and hepta-1,3,5 tryne isomers, reported in the literature⁷⁶ as a very difficult case for DFT, seems to be better described going from hybrids to the corresponding double hybrids functionals: the PBE0 error (of 7.19 kcal/mol) is indeed reduced using the PBE0-DH to 2.23 kcal/mol and the same trend holds for the B3LYP family, with errors going from 8.14 (B3LYP) to 1.91 kcal/mol (B2PLYP). On the other hand, only PBE0-DH yields a relatively low error (of 3.82 kcal/mol) for the dimerization of tetramethyl–ethene to octamethyl–cyclobutane. For the isomerization⁷⁷ of (CH)₁₂, all DFT approaches fail with an deviation of 9.69 kcal/mol computed at B2PLYP, for an overall isomerization reaction energy of only −19.5 kcal/mol. B3LYP is even unable to yield the correct isomers relative stability, whereas the PBE0 family underestimates the reaction energy. On the other hand, for the isomerization reaction of carbo-[3]-oxacarbon⁷⁸ both B3LYP and B2PLYP provide relatively small errors (4.77 and 2.42 kcal/mol, respectively) while functionals of the PBE0 family yield unexpectedly large errors (23.40 and 21.91 kcal/mol for PBE0 and PBE0-DH, respectively). PBE0 (1.87 kcal/mol) is the only functional that gives coherent results for the cycloaddition between ethene and diazomethane.⁷⁹ None of the four functionals gives satisfactory energies for the decomposition of the Be₄ cluster into beryllium atoms.⁸⁰ Analogously, the decomposition⁸¹ of S₈ to diatomic S₂, is rather well described by functionals of the PBE0 family. Indeed, PBE0 gives an error of 3.93 kcal/mol, and this error decreases at PBE0-DH level to 0.39 kcal/mol. These rather good performances are opposed to the behavior of the B3LYP family, for which errors are ranging from 14.10 (B2PLYP) and 27.06 kcal/mol (B3LYP).

In summary, even if it is difficult to find common trends over all the reactions of this subset, double hybrids globally increase the corresponding global hybrid performances over the DC9,

although their MADs still keep relatively high (9.91 and 7.71 kcal/mol for PBE0-DH and B2PLYP compared with 10.31 and 15.14 kcal/mol for PBE0 and B3LYP, respectively).

4. CONCLUSIONS

Overall, the improvement of the performances over the GMNTK30 set when going from global to double hybrids can be summarized by inspection of the MAD and RMSD on all the sets reported in Figures 2 and 3. For both the B3LYP and PBE0 family, going from global to double hybrid allows to obtain better agreement with the reference values (smaller RMSD and MAD).

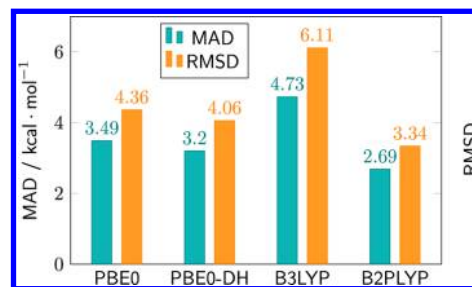


Figure 2. MAD and RMSD (in kcal/mol) computed with the PBE0, PBE0-DH, B3LYP, and B2PLYP functionals over the GMTKN30 set.

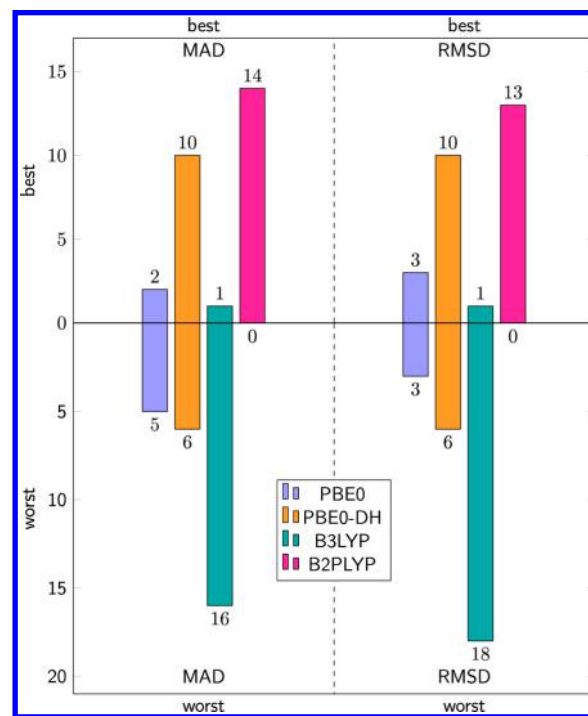


Figure 3. Count of best (up) and worst (low) MAD (left) and RMSD (right) obtained at PBE0, PBE0-DH, B3LYP, and B2PLYP functionals for all subsets of the GMTKN30 considered in this paper.

As clearly depicted in Figure 2, for the PBE0 family, the MADs decreases from 3.49 kcal/mol (PBE0) to 3.20 kcal/mol (PBE0-DH) which means an average decrease in error of 0.29 kcal/mol while a more important improvement is indeed found going from B3LYP (MAD of 4.73 kcal/mol) to B2PLYP (2.69 kcal/mol).

As evident from Figure 3, double hybrids are actually the best performing functionals for 24 over 27 subsets: 10 times, in the

case of PBE0-DH, and 14 times, in the case of B2PYLP. Of note global hybrids, such as PBE0 and B3LYP, are the best performing only when dealing with peculiar reaction and dissociation energies such as the ones of the DARC or ALK6 sets (for PBE0) or the O3ADD6 set (for B3LYP).

More interestingly, carefully analyzing the subsets for which either the PBE0-DH or the B2PLYP functional performs the best, the B2PLYP outperforms PBE0-DH for sets probing thermochemistry (such as MB08-165, G2RC, W4-08, W4-08woMR) adiabatic processes (G21EA, G21IP, PA), self-interaction error (SIE11) or difficult cases in DFT (DC9, ISO34) while PBE0-DH better performs for sets testing the functional performances on the prediction of reaction barriers (BHPERI, BH76), radical stabilization energies (RSE43), dispersion interactions (ADIM6, S22, HEAVY28), or conformers stability (SCONF, ACONF). In general, their behavior also parallel the performances of the corresponding global hybrids thus showing that there is still room for the development of new nonparameterized approaches to design new double hybrids. Indeed, it should not be forgotten that the functionals here considered do not include any specific London dispersion term. Work is in progress in order to properly include dispersion terms and increase functional efficiencies in order to fulfill the gap with the most performing parametrized DH.

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Notes

The authors declare no competing financial interest.

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