DSD-BLYP: A General Purpose Double Hybrid Density Functional Including Spin Component Scaling and Dispersion Correction[†]

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Received: July 29, 2010; Revised Manuscript Received: September 30, 2010

We present a general purpose double-hybrid DFT parametrization based on the BLYP functional, spin-component scaled (SCS) MP2-like correlation and a dispersion correction, called DSD-BLYP. Six training sets were used, including main group and transition state thermochemistry, kinetics, and dispersion forces. This new parametrization is usually 10−15% more accurate than the already exceptional B2GP-PLYP double hybrid, at the same computational cost. Its principal benefit is greater robustness for systems with significant nondynamical correlation. If a scaling factor is included in the harmonic frequency calculations, B2GP-PLYP was found to give very accurate results for kinetics, thermochemistry, and frequencies.

I. Introduction

The quest for a universal DFT method is an ongoing hot issue.[1−3] The formulation and parametrization of functionals has grown in complexity as more properties for more diverse molecular systems are intended to be addressed. Some of the most important properties to take into account are thermodynamics and kinetics of main group and transition metal species, atomization energies, and weak interactions (H bonds or van der Waals). In addition, the treatment of species with pronounced multireference character poses challenges of its own. In this study we try to deal with all of these issues with a reparametrization of: (1) a BLYP[4,5] based double hybrid (DH) functional;[6,7] (2) spin-component scaling (SCS) on the MP2-like perturbation based on the Kohn−Sham orbitals;[8,9] and (3) dispersion correction (D) for long-range interactions.[10]

In a seminal paper,[11] Perdew proposed the "Jacob's Ladder" hierarchy of functionals, ascending from the Earth of Hartree theory (null exchange, null correlation) to the Heaven of chemical accuracy and beyond. Each rung on the ladder represents an additional type of information being introduced into the exchange-correlation functional. At the first rung, only the local density is available, leading to the LDA (local density approximation) or LSDA (local spin density approximation). At the second rung, the reduced density gradient is introduced, leading to the various GGA (generalized gradient approximation) functionals such as BLYP, PBE, etc. At the third rung, the Laplacian of the density or the kinetic energy density (which has similar information content) is introduced, leading to meta-GGA functionals such as TPSS and M06L. At the fourth rung, dependence on the occupied orbitals is introduced: two special cases are hybrid GGAs (such as B3LYP and PBE0) and hybrid meta-GGAs (such as BMK and M06). At the fifth rung, dependence on the virtual orbitals is introduced: one special case thereof are double hybrids. These mix a certain amount of MP2-like correlation with the DFT correlation, in addition to combining Hartree−Fock exchange with the DFT exchange (like the traditional hybrid functional).

The idea of carrying out perturbation theory in a basis of Kohn−Sham orbitals was, to the authors' knowledge, first suggested by Görling and Levy.[12] Building on this work, Grimme proposed the first practical double-hybrid functional, namely, B2-PLYP,[1,6] according to

$$E_{xc} = (1 - c_x)E_{x,B88} + c_x E_{x,HF} + (1 - c_c)E_{c,LYP} + c_c E_{c,MP2} \quad (1)$$

where $E_{x,B88}$ and $E_{c,LYP}$ are the DFT exchange and correlation terms (Becke88[4] and Lee−Yang−Parr[5] in this study) $E_{c,MP2}$ is the MP2-like perturbational term based on the KS orbitals, and $E_{x,HF}$ is the exact exchange contribution. In the B2-PLYP parametrization the coefficients were set to $c_x = 0.53$ and $c_c = 0.27$.

Several reparametrizations were subsequently proposed, such as the B2-P3LYP functional of Benighaus et al.[13] (with a distance-dependent scaling factor for the MP2 term) and our own B2GP-PLYP ($c_x = 0.65$, $c_c = 0.36$).[7] The latter has the desirable property that it simultaneously yield accurate thermochemistry and barrier heights. Both Grimme[6] and the present group[7] considered different GGA and meta-GGA exchange and correlation functional. As it turns out, pretty much any good exchange functional is adequate. However, the LYP correlation functional outperforms all the others in this setting.[7]

Spin-component scaling MP2 (SCS-MP2)[1,8,9] is a method first derived by Grimme, where the same spin and opposite spin perturbational terms are multiplied by different scaling coefficients (c_s and c_o, respectively). The same-spin correlation energy (also called triplet or parallel spin) is associated with long-range, nondynamical effects; opposite spin (also singlet or antiparallel spin) is associated with short-range, dynamical correlation.[8] In the original work of Grimme, the values for c_o and c_s were set to 6/5 and 1/3, respectively.[8] Further studies recognized the validity of these parameters,[14−25] with the notable exception of dispersion forces and H-bonds,[26−34] where long-range effects are dominant and c_s may grow, eclipsing c_o. Recently, the SCS concept was also extended to higher level post HF methods such as SCS-MP3[14,35,36] and SCS-CCSD.[37,38]

London-type empirical correction (D)[10] is a simple and very fast molecular mechanics term for long-range interactions of the van der Waals type, and hydrogen bond types. Especially the former interactions are traditionally underestimated by DFT methods (with some notable exceptions as the M06 funtional[39,40]). The addition of the D correction has proven invaluable to improve DFT functionals[7,10,41−44] but can also be used as an add-on for ab initio methods.

The dispersion correction (D) has a Lennard-Jones attraction potential, damped at short distances (f_{dmp} function):

$$E_{\text{disp}} = -s_6 \sum_{i=1}^{N_{\text{at}}-1} \sum_{j=i+1}^{N_{\text{at}}} \frac{c_6^{ij}}{R_{ij}^6} f_{\text{dmp}}(R_{ij}) \qquad (2)$$

$$f_{\text{dmp}}(R_{ij}) = \left\{ 1 + \exp\left[-\alpha\left(\frac{R_{ij}}{s_R R_r} - 1 \right) \right] \right\}^{-1} \qquad (3)$$

The D term includes three adjustable parameters (which could in principle be optimized for each method). The linear s_6 parameter modulates uniformly the dispersion forces; for B3LYP it was set at 1.05, PBE0 at 0.70, BMK at 0.65, and M06 at 0.25; MP2 is known to overestimate dispersion forces, and the calculated s_6 resulted negative, with a value of −0.16; SCS-MP2 method inverts the s_6 value to 0.17.[7] The second parameter, s_R, defines the position of the damping cutoff (usually set to unity), and the third, α, modulates the slope of the sigmoid damping (usually set to 20). The amount of dispersion is normally adjusted a posteriori; i.e., the parameter values were set over the established methods, without altering them to accommodate this dispersion supplement.

The objective of the present research was to study the impact of the three combined techniques (DH, SCS-MP2, and D correction) using a general purpose training set and subsequently create a reparametrized SCS double-hybrid from this information, which we shall denote DSD-BLYP. The general energy formula to minimize corresponded to

$$E_{xc} = (1 - c_x)E_{x,B88} + c_x E_{x,HF} + c_c E_{c,LYP} + c_o E_{c,MP2}^o +$$
$$c_s E_{c,MP2}^s + E_D \qquad (4)$$

Herein $E_{c,MP2}^o$ and $E_{c,MP2}^s$ are the opposite spin and same spin MP2-like correlation energies, respectively, and E_D is the dispersion correction, dependent on its three parameters (s_6, s_R, and α). The dispersion is now simultaneously optimized alongside the quantum mechanical parameters. A similar approach was recently studied by Head-Gordon and co-workers in his B97X-2 functional.[45]

II. Theoretical Methods

For the sake of clarity, and owing to the high number of acronyms that appear in this work, we cite here all the *abbreviations* used:

Methods. DH: double hybrid. SCS: spin component scaling. Frozen: frozen core MP2 correlation. Full: all electrons MP2 correlation. D: dispersion correction. c_o: opposite spin coefficient. c_s: same spin coefficient. s_6: linear scaling of the dispersion correction. s_R: radius of the dispersion cutoff. α: slope of the dispersion cutoff.

Training Sets. W4-08: total atomization energies. DBH24: main group reaction barriers. S22: dispersion forces. Pd:

oxidative addition reactions on a Pd atom. Grubbs: metathesis reactions on Ru complexes. MB: mindless benchmark (main group random thermochemistry).

A. Training Sets. To obtain the parameters for a general purpose double hybrid, six training sets were used:

(1) The W4-08 set of Karton et al.[7] for atomization energies. Atomization thermochemistry is a thorny problem, since the correlation energy greatly differs between molecules and their separated atomic components. This set has 101 molecules, from where 14 are of a high multireference nature.

(2) The DBH24 set of Zheng et al.[46] for reaction kinetics. Energies of activation have been a difficult challenge for DFT methods that are usually optimized for thermochemistry. Transition states, with their stretched bonds, may have more electronic self-repulsion and multireference issues than minimum energy states. This set includes heavy atom transfers, hydrogen tranfers, nucleophilic substitutions, and unimolecular and association reactions.

(3) The S22 set of Jurečka and co-workers[47] for van der Waals and hydrogen bonds. A posteriori dispersion corrections were intended for this kind of systems.[48]

(4) Reactions at a Pd center, according to Quintal et al.[49] This set extends the kinetic contribution of the DBH24 group by including prototype oxidative addition reaction barriers on a bare transition metal.

(5) Grubbs set of Ru olefin metathesis catalyst, by Zhao and others.[34] This includes several intermediates and transition states on the reaction profile. The incorporation of this ensemble of states in the training set provides weight for more accurate transition metal energies. Dispersion corrections are necessary in this group due to the size of the molecules and the long distance between moieties.

(6) The mindless benchmark set (MB) of Korth and Grimme.[50] The energies of 167 eight-atom "random" molecules are considered here. The reference energy consists in the hydrides (elements from groups 1−4) and diatomic molecules (groups 5−7) that can be generated from each "random" molecule, with the addition of H_2 to fill the stoichiometry. The almost arbitrary characteristics of this big number of reactions makes the MB set an important factor for main group thermochemistry considerations. The response of the set to the parameters is similar to the response of the average of all the six groups, so it can be deemed as a broad and worthwhile training set (although it was computationally the most expensive of all the six groups).

On each set the root-mean square deviation (RMSD) was used. We decided to minimize the arithmetic mean of the six RMSD, assigning the same weight to all the sets.

B. Basis Set. In this study we used basis sets of considerable size to focus only on the parameters of the functional. Owing to the perturbative term in the double hybrids, they require a more complete basis set than regular DFT methods. Therefore, for the W4-08 and DBH24 sets we used the aug′-pc3 basis set of Jensen,[51−55] with diffuse functions on non-hydrogen atoms and adding a high exponent d function for the W4-08 to properly account for high oxidation states. For the rest we used the Weigend and Ahlrichs Def2 bases:[56,57] Def2-TZVP for S22 and Grubbs, as the size of the molecules made it arduous to climb to a quadruple-ζ type of functions (following past practice,[7,41] we added half the counterpoise correction in the S22 set to correct for the basis set superposition error[48]); Def2-QZVP was applied to MB, and Def2-QZVPP to the Pd set.

C. Full vs Frozen Core MP2 Correlation. The B2GP-PLYP functional was optimized including full MP2 correlation (taking

TABLE 1: Same (c_s) and Opposite (c_o) Spin Coefficients of the MP2 Perturbation and s_6 Term of the Dispersion Correction, RMSD of Each Training Set and Total Error Mean Deviation for Different MP2+D Combinations

	MP2	MP2-D[a]	SCS-MP2	SCS-MP2-D[a]	SCS-MP2-D*[b]
c_s	1	1	0.33	0.33	0.54
c_o	1	1	1.20	1.20	1.09
s_6	0	−0.29	0	0.24	0.12
W4-08[c]	9.34	9.34	5.66	5.68	5.68
non MR	9.40	9.40	5.59	5.62	5.59
MR	8.97	8.95	6.03	6.01	6.18
DBH24	7.26	7.37	8.69	8.60	8.17
S22[d]	1.14	1.24	1.53	1.18	1.05
Pd	4.20	4.02	1.71	1.76	1.97
Grubbs	5.46	3.92	3.15	2.80	2.88
"mindless"	6.11	6.30	8.44	7.94	6.68
mean	5.58	5.36	4.86	4.66	4.40

[a] s_6 optimized for this training set. s_R and α set to default values, 1 and 20, respectively. [b] s_6, c_o, and c_s coefficients optimized for this training set. [c] Full W4-08 set, and discrimination between high- and low-multireference systems. [d] Including one-half the counterpoise correction.

into account core electrons). Using frozen core correlation (all valence electrons plus outer s and p core orbitals of third row and later alkali and alkaline earth atoms) changes the optimum parameters of the double hybrid functionals; the MP2 weight will be slightly augmented to compensate for the neglected core correlation. In this work both full and frozen core correlation were considered.

D. Software. The calculations were carried out using Gaussian09.[58] Dispersion corrections were added by means of a simple Fortran program developed in-house. It is possible to run the jobs specifying all the necessary parameters through "iop" keywords. One can save a huge amount of computer time by extracting the same and opposite spin perturbational energies from the Gaussian output (E2 values under the line "spin components of T(2) and E(2)"), and altering the c_o and c_s coefficients in a spreadsheet program. The linear s_6 value of the D correction can be treated the same way.

III. Results and Discussion: Training Sets

A. SCS-MP2-D. To understand the influence of the long-range dispersion correction on the MP2 spin components, a pure MP2+D study was considered. With the conventional MP2 (c_o and c_s equal to one), the optimal s_6 value for the training set was −0.29, confirming the overestimation of weak forces by second-order perturbational theory. The negative s_6 value corrects the excess of dispersion forces produced at the MP2 level (an excess that would be mitigated by the MP3 method). Nevertheless, the improvement of adding the D term is negligible, except for the Grubbs set (see Table 1). The SCS-MP2 approach slightly improves the mean deviations, notably for the Pd, Grubbs, and W4-08 sets, but worsening the MB, DBH24, and S22 ones. Again the D correction does not improve significantly the mean deviation of the SCS-MP2. The resulting s_6 value is now positive, indicating an underestimation of long-range interactions by the small c_s coefficient.

In Figure 1 the impact of the dispersion term on the c_o and c_s terms can be observed. An optimization of the two perturbational terms when the s_6 value is altered shows the long-range scope of the same spin MP2 correlation. The higher s_6, the less we need $E_{c,MP2}^s$. At the same time the short-ranged c_o term rises moderately, to compensate for the loss of overall correlation.
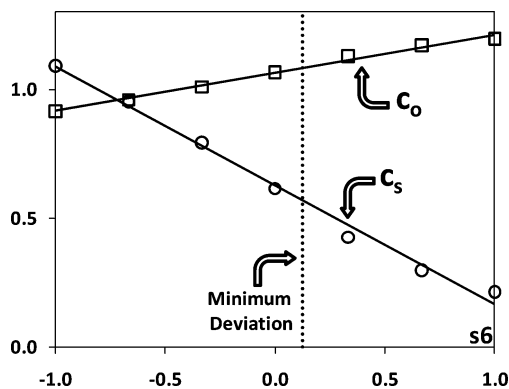
Figure 1. Same spin (c_s) and opposite spin (c_o) MP2 coefficients vs s_6 dispersion value. The values correspond to a minimum in the mean deviation of the six training sets. The global minimum lies at $s_6 = 0.12$.
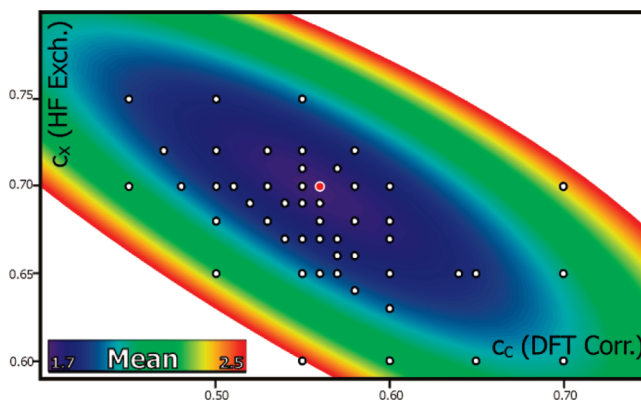
Figure 2. Mean deviation as a function of DFT correlation (c_c) and Hartree−Fock exchange (c_x) coefficients (c_o, c_s, and s_6 optimized for each coordinate). White dots indicate actual data points. The red dot denotes the full minima at $c_c = 0.56$, $c_x = 0.70$, $c_s = 0.40$, $c_o = 0.46$, and $s_6 = 0.37$. The α value was 60. These data correspond to a frozen core MP2-like step.

Note that on every case where dispersion correction is added to MP2 based calculations, the sum of c_s ("long range" MP2) and s_6 is less than 1, since second-order perturbation overestimates dispersion forces.

From the errors appearing on Table 1 the notion of different correlation for different properties can be confirmed. A gloomy conclusion that can be drawn from Table 1 is the inability of these types of parametrized MP2 methods to effectively cope with all chemical properties. SCS-MP2-D can be very accurate only when the chemical problem is narrowly defined.[14−25]

B. DH+SCS+D. Double hybrids have been found to be very effective,[1,7,13,41,59,60] so we expected a more efficient behavior than the previously studied MP2. To test for the improvement of the SCS+D approach, we compared the DSD-BLYP errors with the errors from the general purpose double hybrid B2-GP-PLYP-D (using all electron correlation).[7]

Figure 2 shows the mean deviation surface for the training set as a function of the DFT correlation and HF exchange (c_o, c_s, and s_6 optimized), with a frozen core correlation. The surface has a typical elliptical paraboloid shape[7] with a minima at $c_c = 0.56$, $c_x = 0.70$, $c_s = 0.40$, $c_o = 0.46$, and $s_6 = 0.37$. The α dispersion parameter was set to 60, as a tighter cutoff was found to be slightly advantageous. s_R was left at the default value of 1, which we verified to be approximately optimum for this method. The average MP2 and HF percentages (43,70) are slightly higher than in B2-GP-PLYP-D (36, 65). When the more expensive full MP2 correlation was considered, the optimum

TABLE 2: HF Exchange (c_x), DFT Correlation (c_c), Same (c_s), and Opposite (c_o) Spin Coefficients of the MP2 Perturbation, s_6 Term of the Dispersion Correction, RMSD of Each Training Set and Total Error Mean Deviation for DSD-BLYP and B2GP-PLYP-D,[7] and for Comparison B3LYP-D, M06-D, and BMK-D (in kcal/mol)

	DSD-BLYP (frozen)[a]	DSD-BLYP (full)[b]	B2GP-PLYP-D[c]	B3LYP-D[d]	M06-D[e]	BMK-D[f]
c_x	0.70	0.69	0.65			
c_c	0.56	0.54	0.64			
c_s	0.40	0.37	0.36			
c_o	0.46	0.46	0.36			
s_6	0.37	0.41	0.40	1.05	0.25	0.65
W4-08[g]	2.66	2.66	3.17	5.40	4.60	5.52
non MR	2.21	2.24	2.12	4.61	3.86	3.27
MR	4.53	4.42	6.68	8.83	7.75	12.38
DBH24	0.97	0.98	0.98	5.24	3.01	1.68
S22[h]	0.35	0.39	0.32	0.81	0.35	0.61
Pd	0.91	0.80	0.51	1.76	5.83	7.87
Grubbs	1.02	1.06	1.39	4.26	1.21	6.47
"mindless"	4.46	4.23	5.38	8.61	7.54	7.60
mean[i]	1.73	1.69	1.96	4.35	3.76	4.96

[a] Frozen core MP2 correlation. [b] Full (all electrons) MP2 correlation. [c] The mean deviation for B2GP-PLYP (without D) is 3.03. [d] The mean deviation for B3LYP (without D) is 6.63. [e] The mean deviation for M06 (without D) is 4.15. [f] The mean deviation for BMK (without D) is 5.10. [g] Full W4-08 set, and discrimination between high and low multireference systems. [h] Including half of the counterpoise correction. [i] Arithmetic mean of all six RMSD values.

parameters were $c_c = 0.54$, $c_x = 0.69$, $c_s = 0.37$, $c_o = 0.46$, and $s_6 = 0.41$.

Table 2 includes the RMSD for each group in the training set plus the total mean deviation for DSD-BLYP (full and frozen correlation), B2GP-PLYP-D, and for comparison B3LYP-D, M06-D, and BMK-D. As can be seen, the mean error deviation for the DSD-BLYP is 14% more accurate than the already outstanding B2GP-PLYP-D (at least for the present training set), with a good performance along all the sets. Noteworthy is the atomization energy improvement (W4-08), especially for the difficult multireference systems. This suggests that the main benefit of an SCS double hybrid approach is robustness rather than accuracy. This raises the question about whether the SCS approach can deal with nondynamical correlation. In the MP2 cases of Table 1 we have already witnessed some progress on this aspect.

A comparison between the frozen core and the all-electron correlated DSD-BLYP shows a slight improvement upon considering the core electrons. However, with a parametrization suited for a frozen core (with a compensating higher correlation), the difference is minimal, while the frozen-core variant offers a significant gain in computer time.

In non-SCS double hybrid parametrizations, the sum of the MP2 and DFT correlation is usually set to one, preventing double counting (or undercounting) of this energy component. In the SCS method, the fact that we consider two components for the MP2 energy makes this constraint harder to fulfill. Therefore, in this work the c_s and c_o coefficients were not attached to the DFT correlation weight. In spite of that, the sum of the *opposite* spin component and the LYP correlation (both short-range) naturally came close to one (exactly one for the all electron MP2). Ideally, the sum of long-range components (c_s and s_6 dispersion factor) should also be close to one, but second-order perturbational theory has a tendency to overbind, as explained previously in section III.A. To compensate for this overbinding, the sum of these two terms is smaller than one. In a higher level perturbation theory with an improved dispersion correction, we would expect this sum to be exactly one, thus making possible the elimination of one of the parameters.

The simple hybrid DFT functionals tested (B3LYP, M06, and BMK) have strengths and weaknesses on different sets, but the overall performance is similar to that of the MP2 and SCS-
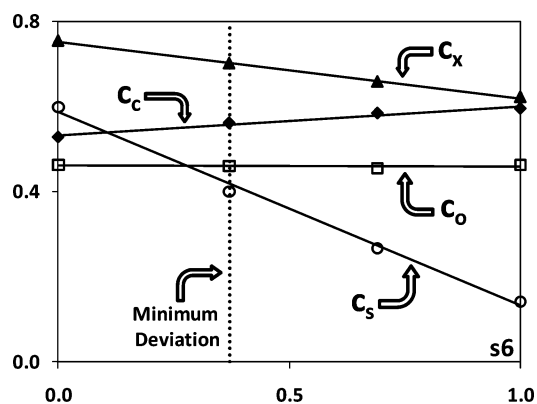
Figure 3. Same spin MP2 (c_s), opposite spin MP2 (c_o), DFT correlation (c_c), and HF exchange (c_x) coefficients, vs s_6 dispersion value. The values correspond to a minimum in the mean deviation of the six training sets. The global minimum lies at $s_6 = 0.37$.

MP2 methods (compare with Table 1). Again, for each property we see that a different correlation treatment is needed.

In Figure 3 we study again the impact of the s_6 dispersion coefficient on the rest of the parameters. The same effect on c_s and c_o as previously seen for SCS-MP2 can be observed (see Figure 1): the long-range same spin component is much more sensitive to the dispersion correction than the other parameters. HF exchange is slightly lowered also, denoting the positive influence of higher exact-exchange on weak forces where pure DFT traditionally fails.

IV. Results and Discussion: Validation Sets

Several difficult systems outside the training set were considered to test the DSD-BLYP (full and frozen core correlation) functional vis-à-vis the B2GP-PLYP (full correlation) double hybrid, plus B3LYP, M06, and BMK simple hybrids. Unless specified, all the results are the RMSD of the whole set in kcal/mol, including dispersion corrections and in the aug′-pc3+d basis set. Detailed tables of each set are relegated to the Supporting Information.

A. NHTBH38 (Non Hydrogen Transfer Barrier Heights).[61] This set consists of small molecule, main group, non-H atom transfer reactions. The BMK functional, optimized for kinetics,

has an excellent performance with an RMSD of 1.79. M06 is still adequate (2.92), while B3LYP grossly underestimates most of the barriers (RMSD = 5.95, signed average error = −4.76). B2GP-PLYP provides an outstanding RMSD of 1.65 (not surprising, considering that one of the two training sets for this functional was DBH24). DSD-BLYP slightly worsens (1.93 and 1.89, frozen core and full correlation, respectively).

The reaction H + F2 → HF + F is the most conspicuous outlier on this set. Excluding it, the RMSD of B2GP-PLYP goes to 1.35, while for the DSD-BLYP falls to 1.06 and 1.07 (frozen and full correlation). M06 and BMK does not significantly change, but B3LYP improves to 5.60, suggesting that the BLYP DFT part is a main factor on the difficulties dealing with F transfers.

Notably, B2GP-PLYP yields better NHTBH38 performance without the D correction (RMSD of 1.59), while DSD-BLYP worsens (1.98 and 1.94). As explained in the Introduction, in the former method the dispersion correction is an add-on on an already optimized functional, whereas in the latter the parametrization of D is an integral part of the functional. Also, the tighter cutoff ($\alpha = 60$ instead of the default 20) makes D interfere less with the short-range correlation.

B. HTBH38 (Hydrogen Transfer Barrier Heights).[61] This set is similar to the previous one but is focused on H-transfers exclusively. B3LYP, M06, and BMK have RMSDs of 5.78, 2.56, and 2.14, respectively. B2GP-PLYP improves to 1.40, while DSD-BLYP on the frozen core and full versions has an exceptionally good RMSDs of 1.02 and 0.97 kcal/mol, respectively.

For this set, neglecting the dispersion correction improves the RMSD for all the methods (B2GP-PLYP = 1.15, DSD-BLYP = 0.91 and 0.85, B3LYP = 5.09, M06 = 2.41, and BMK = 1.69). The probable reason is that D energies are parametrized for neutral atoms, without taking into account their chemical states and environment. Improvements on this aspect are already on their way.[62]

C. Hydrogen Bonds. Here we consider Boese's[63] set for the dissociation of 16 H-bonded dimers. As in the S22 training set, we included here half the counterpoise correction.[48] The resulting RMSDs for B3LYP, M06, and BMK were 0.95, 0.40, and 0.39. B2GP-PLYP has an error of 0.51, and DSD-BLYP (frozen and full forms) 0.40 and 0.38.

Without the dispersion there is a striking improvement for the double hybrids (B2GP-PLYP = 0.26, DSD-BLYP(frozen) = 0.22, DSD-BLYP(full) = 0.23). The mean signed error is very close to zero, so any D correction will probably overbind the fragments. It is advisable to completely neglect D corrections for double hybrids on H-bonds systems, as the bare double hybrids have already a superb performance in this set.

D. van der Waals Complexes. Let us turn to Zhao and Truhlar's[64] set for the dissociation of 28 weak interaction dimers. Again, half of the CP correction was added.[48] The errors for B3LYP, M06, and BMK were 0.82, 0.49, and 0.52; for B2GP-PLYP 0.47; for DSD-BLYP(frozen) 0.40, and for DSD-BLYP(full) 0.42.

Strangely, as in the previous H-bonds set the inclusion of dispersion correction marginally worsens the results for the DHs. This may be caused by the small size of the molecules involved in this set, while the D add-on is most useful on bigger size systems (like the S22 and Grubbs sets). The errors without D were B2GP-PLYP = 0.37, DSD-BLYP(frozen) = 0.34, and DSD-BLYP(full) = 0.37.

E. Monoligated Zn(II). The set due to Rayón et al.[65] for 19 binding energies of neutral and anionic ligands on a Zn(II) atom.

DFT functionals systematically (and severely) overestimate the binding energy, while MP2 was found to yield results very close to CCSD(T).[65] Double hybrids still inherit the "sins" of DFT but are mitigated by the perturbational correction. It seems that cationic systems still provide a challenge for DHs. The RMSDs obtained here with Def2-TZVPP basis set augmented with a diffuse function were B3LYP = 13.72, M06 = 8.62, BMK = 14.51, B2GP-PLYP = 6.56, DSD-BLYP(frozen) = 4.35, and DSD-BLYP(full) = 5.88. The signed average error was almost the same as the RMSD (with negative sign), indicating the systematical overestimation of the binding energy. Again, the dispersion correction is counterproductive in this set containing small molecules. Without D, the errors were B2GP-PLYP = 5.95, DSD-PLYP(frozen) = 3.90, and DSD-BLYP(full) = 5.38.

F. Pericyclic Reactions. Houk and co-workers[66,67] proposed a test set of 11 pericyclic reactions. For eight of them W1 reference energies are also available.[7,68] For this set the aug′-pc2+2d basis set was used. The results show a strong degradation of accuracy in the double hybrids when dispersion is included, to the point that they perform worse than simple hybrids. Excluding dispersion, DHs are promising methods, with B2GP-PLYP turning in the best performance. The results taking as a reference the W1 values are, with dispersion: B3LYP = 2.56, M06 = 2.18, BMK = 2.32, B2GP-PLYP = 2.65, DSD-BLYP(frozen) = 2.76, DSD-BLYP(full) = 2.86. Without dispersion: B3LYP = 3.21, M06 = 2.08, BMK = 2.73, B2GP-PLYP = 1.69, DSD-BLYP(frozen) = 1.95, DSD-BLYP(full) = 1.86.

G. Alkanes Thermochemistry and Isomerization Energies.[69] A set of 19 alkanes, from one to eight carbon atoms, calculated with the pc3 basis set. In this group total atomization energies (TAE) and all the possible isomerizations were studied. It has been shown[68] that on this set dispersion corrections are critical for the TAE estimation. This was confirmed here, even for the M06 functional where the s_6 coefficient is just 0.25. Isomerizations are less needy of D corrections, probably because of error compensation. The TAE RMSD values are B2GP-PLYP = 1.00, DSD-BLYP(frozen) = 0.44, DSD-BLYP(full) = 2.79, B3LYP = 0.61, M06 = 0.70, and BMK = 5.14. For isomerizations: B2GP-PLYP = 0.19, DSD-BLYP(frozen) = 0.48, DSD-BLYP(full) = 0.53, B3LYP = 0.43, M06 = 1.08, and BMK = 1.01. Considering both tests, DSD-BLYP(frozen), B3LYP, and B2GP-PLYP are the most robust methods. Including full correlation in DSD-BLYP strangely underbinds the molecules, providing less accurate TAE.

H. BMK Data Set. This set of Boese and Martin[68] comprises several subsets (neutral, anionic, cationic, dimers, TS, etc.) using experimental reference energies. These references are somehow dubious for the accuracy needed in the high level double hybrids for several reasons: not only are the reference data of the sets ultimately based on outdated JANAF values (sometimes with sizable uncertainties), but also their use intrinsically amounts to "comparing apples with oranges" as the experimental data include various effects (relativistic, anharmonicity, etc.) not included in the QM calculation. As long as RMSDs for DFT methods were an order of magnitude larger than these contributions this was effectively a nonissue, but we are presently in an accuracy range where this can no longer be ignored. Still, this set is useful as guidance. In this set DH functionals are clearly more accurate than simple hybrids, and the DSD-BLYP acts slightly better than B2GP-PLYP. Cationic molecules have the worst performance; this issue needs to be addressed in future double hybrid methods. All the specific information is summarized in the Supporting Information.

TABLE 3: RMSD Errors for the Extended S22 Set, in kcal/mol, for the Five Fraction Distances and the Total RMSD for the Whole Set

	DSD-BLYP (frozen)[a]	DSD-BLYP (full)[b]	B2GP-PLYP-D[b]	B3LYP-D	M06-D	BMK-D
0.9	0.53	0.59	0.36	0.95	0.45	0.84
1	0.35	0.39	0.32	0.81	0.35	0.62
1.2	0.21	0.21	0.28	0.57	0.48	1.23
1.5	0.16	0.16	0.18	0.33	0.29	0.80
2	0.05	0.05	0.05	0.08	0.11	0.24
total	0.31	0.34	0.27	0.64	0.36	0.82

[a] Frozen core MP2 correlation. [b] Full (all electrons) MP2 correlation.
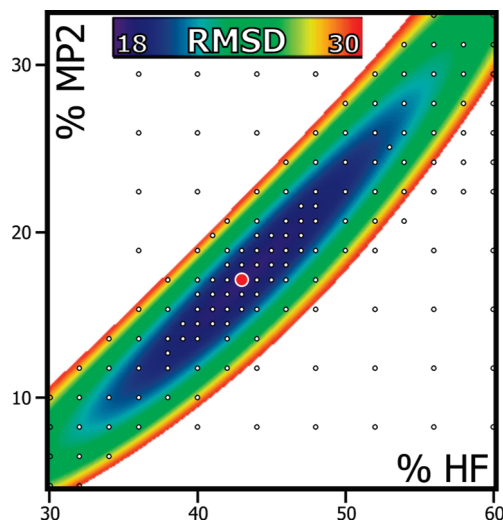
Figure 4. RMSD "canal" (in cm^{-1}) of the harmonic frequencies for the HFREQ27 set, as a function of the MP2-like correlation and HF-like exchange (see eq 1). The minimum (red dot) lies at 18% HF and 43% MP2, with an RMSD of 18.6 cm^{-1} (aug′-pc2+2d basis set level).

I. Extended S22 Set. The extended S22[70] set expands the original S22 set for dispersion forces by changing the distance between the monomers in such a way that the dissociation curve is better described. The arrangements are made by multiplying the equilibrium distance by the following factors: 0.9, 1 (the original S22), 1.2, 1.5, and 2. Herein we considered the same methodology that we used previously for the S22 set, i.e., Def2-TZVP basis set and including half the counterpoise correction.[48] The double-hybrid functionals and the M06 methods have good performance all along the dissociation curve, B2GP-PLYP-D resulting in the best method for this test, especially for the "squeezed" group with factor 0.9. The results are summarized in Table 3 (see the Supporting Information for detailed results).

V. A Note on Harmonic Frequencies

To test the performance of the double hybrids on harmonic frequencies computations, a set of 27 diatomic and small polyatomic molecules was studied, which we will denote HFREQ27. Full details on the molecules and the reference data employed (harmonic frequencies from experiment or high-level ab initio calculations) are given in the Supporting Information. Our estimations show that, similar to the W4-08 thermochemistry set and the DBH24 set for reaction kinetics,[7] the RMSDs of the frequencies form an error "canal" when graphed as a function of the exact exchange and MP2-like correlation, with a minimum at 18% HF and 43% MP2 (RMSD = 18.6 cm^{-1}, calculated at the aug′-pc2+2d basis set level, see Figure 4). This canal is displaced from the error canals of the W4-08 and DBH24 sets (see ref 7), implying that each one of these three properties requires different exchange−correlation coefficients.

The RMSDs obtained by our test methods are (in cm^{-1}, using the aug′-pc3+d basis set): B2GP-PLYP = 29.8, DSD-BLYP-(frozen) = 30.9, DSD-BLYP(full) = 31.1, B3LYP = 33.9, M06 = 47.5, and BMK = 58.0. As can be seen, these DHs do not improve over B3LYP but are far better than the other simple hybrids considered. We tested Grimme's B2-PLYP,[6] since its parameters (HF = 53%, MP2 = 27%) and performance are closer to the optimal for this test, and for comparison also MP2, both with all electrons correlated. The resulting RMSDs were B2-PLYP = 18.6 and MP2 = 44.0 cm^{-1}. Clearly B2-PLYP is by far the best of the methods considered for harmonic frequencies without applying scaling factors. The good performance of this functional was recently verified by Biczysko and others for harmonic and anharmonic vibration frequencies.[71]

However, as there is a typical systematic error on the frequencies calculations, it is customary to apply a scaling factor dependent on the theoretical method.[72,73] By optimizing the rms deviation, we obtained RMSD values of (in cm^{-1}; dimensionless scaling factor given in curly brackets) B2GP-PLYP = 17.7 {0.989}, DSD-BLYP(frozen) = 22.4 {0.990}, DSD-BLYP(full) = 23.6 {0.991}, B3LYP = 32.6 {1.004}, M06 = 46.6 {0.996}, BMK = 51.4 {0.988}, B2-PLYP = 17.4 {0.997}, and MP2 = 35.6 {0.988}. Including the scaling factor we see the improvement of all the DHs over the simple hybrids, especially B2GP-PLYP.

While it is possible to optimize double hybrids for each of the {frequencies, thermochemistry} and {thermochemistry, kinetics} pairs, a double hybrid that simultaneously gives near-optimal performance for all three cannot be found. We do note that B2-PLYP gives accurate frequencies and having a scaling factor of basically unity it can be said to be free of systematic bias. However, we found that simple frequency scaling makes B2GP-PLYP meet all three criteria.

It must be emphasized here the effect of the size of the basis set on the accuracy of the frequencies. It is well-known that DFT methods swiftly converge to the basis set limit, while post HF techniques require bigger basis sets. Herein, as well as the large aug′-pc3+d basis set used for validation, we considered the smaller aug′-pc2+2d to test for convergence and to estimate the canal of Figure 4. There is virtually no degradation of the performance on the simple hybrids when both basis sets are compared, but MP2 RMSD results are 30% less accurate with aug′-pc2+2d. Double hybrids inherit part of the convergence difficulties as they include a fraction of the perturbation term. Consequently, with the smaller basis set the DHs were found to be 10 to 15% less accurate than with aug′-pc3+d.

VI. Summary and Conclusions

In this study we present a new parametrization of a general purpose double hybrid DFT. It is based on the BLYP functional,[4,5] spin-component scaling on the MP2 correlation,[1,8,9] and a molecular mechanics type of dispersion correction.[10] We denote it DSD-BLYP.

Contrary to the common use of the D term as a parameter optimized over the untouched method, we minimized the error on the training set with the dispersion as an integral factor. Thus, five linear coefficients were optimized simultaneously: HF exchange (c_x), DFT correlation (c_c), same (c_s), and opposite (c_o) spin MP2 perturbation and the dispersion correction (s_6). The dispersion radius cutoff (s_R) was found to be optimal at the default value of one, while the "sharpness" of the cutoff (α) was set to 3 times the default value of 20, to interfere less with the short-range DFT and MP2 correlations.

To obtain a method as generally applicable as possible, six training sets were used: W4-08 for atomization energies,[7] DBH24 for kinetics,[46] S22 for weak interactions,[47] Pd for transition metals kinetics,[49] Grubbs for transition metals reactions,[34] and mindless benchmark for main group.[50]

For an appropriate level of accuracy big basis sets are needed, at least of polarized, augmented triple-ζ quality. A complete basis set extrapolation may be advisable, since the parametrization was done with high level basis sets. Convergence to a complete basis set was found to be (as expected) somewhere in the middle between the fast DFT and the slow MP2 convergence. There is no significant difference in quality between an all-electron or a frozen-core MP2 calculation, as long as the appropriate parametrization is used.

The dispersion correction is an essential and intrinsic part of the DSD-BLYP functional. Nevertheless, for small molecules and H-bonded systems it was seen to degrade the accuracy and may be discarded. Future dispersion corrections with better damping functions and parametrizations that take into account the chemical environment[62] may correct these deficiencies.

When different dispersion correction weights were considered, it was observed that the component most affected was the same spin MP2 correlation. This confirmed the fact that c_s corresponds to a long-range effect. The optimum sum of the dispersion correction plus same spin MP2 was lower than one, since MP2 tends to overbind. The DFT correlation plus the short-range opposite spin MP2 correlation indeed add up to unity (at least in the all-electron MP2 method).

Harmonic frequencies see an improvement in the double-hybrids compared to single-hybrid functionals. It is not possible to optimize DHs for frequencies, kinetics, and thermochemistry together, but with a scaling factor to correct the frequencies systematic bias, we found that B2GP-PLYP meets all three criteria.

The average improvement in the energy RMSDs of the DSD-BLYP over the already outstanding B2GP-PLYP[7] is around 10−15% (dependent on the property studied). This improvement comes at no cost, as the computational times for both methods are identical. In addition, DSD-BLYP offers significantly enhanced robustness for systems with significant nondynamical correlation.

Supporting Information Available: Reference energies, errors of each theoretical method, and statistics for the training and validation sets. This material is available free of charge via the Internet at http://pubs.acs.org.

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