Double-hybrid density functionals with long-range dispersion corrections: higher accuracy and extended applicability†

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Received 29th March 2007, Accepted 4th May 2007
First published as an Advance Article on the web 29th May 2007
DOI: 10.1039/b704725h

The objective of this work is the further systematic improvement of the accuracy of Double-Hybrid Density Functionals (DHDF) that add non-local electron correlation effects to a standard hybrid functional by second-order perturbation theory (S. Grimme, *J. Chem. Phys.*, 2006, **124**, 034108). The only known shortcoming of these generally highly accurate functionals is an underestimation of the long-range dispersion (van der Waals) interactions. To correct this deficiency, we add a previously developed empirical dispersion term (DFT-D) to the energy expression but leave the electronic part of the functional untouched. Results are presented for the S22 set of non-covalent interaction energies, the G3/99 set of heat of formations and conformational energies of a phenylalanyl–glycyl–glycine peptide model. We furthermore propose seven hydrocarbon reactions with strong intramolecular dispersion contributions as a benchmark set for newly developed density functionals. In general, the proposed composite approach is for many chemically relevant properties of similar quality as high-level coupled-cluster treatments. A significant increase of the accuracy for non-covalent interactions is obtained and the corrected B2PLYP DHDF provides one of the lowest ever obtained Mean Absolute Deviations (MAD) for the S22 set (0.2–0.3 kcal mol^{-1}). Unprecedented high accuracy is also obtained for the relative energies of peptide conformations that turn out to be very difficult. The significant improvements found for the G3/99 set (reduction of the MAD from 2.4 to 1.7 kcal mol^{-1}) underline the importance of intramolecular dispersion effects in large molecules. In all tested cases the results from the standard B3LYP approach are also significantly improved, and we recommend the general use of dispersion corrections in DFT treatments.

1. Introduction

The development of new functionals in the framework of Kohn–Sham (KS) Density Functional Theory (DFT)[1] is a continuing process that has kept scientists busy since the formulation of this approach was published.[2–4] Whenever a new functional is developed, several constraints and different concepts guide its origin. There seems to be some agreement in the theoretical community that there are at least two fundamental requirements for a good density functional approach. First, it has to be accurate for basic physical/chemical properties such as energy and molecular structure, and second, it should be applicable in general chemistry, *i.e.*, from metals and inorganic clusters to (metal)organic chemistry and in biochemical applications. This is far from being trivial as general electronic structure, the relevant electron correlations and the dominant interaction types (covalent/ionic *vs.* dispersion (van der Waals)) change considerably in chemistry. This is the reason why most new functionals are validated against large benchmark test sets with chemically diverse entries.[5,6] During the last few years, however, the early euphoria about the accuracy of DFT has been replaced by a more realistic view on its strengths and weaknesses. Nowadays, the focus has moved to more problematic cases and outliers,[7–14] which also in our view will push the development of functionals further.

These preliminary considerations were also the driving force for our recent work.[15] Triggered by the idea that not only exchange but also the correlation part in KS-DFT has non-local orbital-dependent components, recently, a new semi-empirical hybrid functional with corrections from perturbation theory, termed B2PLYP, has been proposed.[15] The idea has its roots in the Görling–Levy Perturbation Theory (GL-PT).[16,17] In the method, first a standard hybrid-functional containing common semi-local Generalised Gradient Approximations (GGA) for exchange (X) and correlation (C) is defined. With this hybrid-GGA, a normal, self-consistent KS calculation is carried out. The resulting KS orbitals and eigenvalues are then subsequently used as input for a standard second-order Møller–Plesset type perturbation theory[18] correction that replaces part of the semi-local GGA correlation. Therefore, the name Double-Hybrid Density Functionals (DHDF) seems appropriate for this new class of density functionals (for related methods consisting of DFT and wave function parts in the broadest sense see *e.g.* ref. 19–24).

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† Electronic supplementary information (ESI) available: Detailed results for the G3/99, S22 and peptide benchmark sets and Cartesian coordinates for the molecules in the IDHC7 set. See DOI: 10.1039/b704725h

In further studies, the success of this approach has been well documented. The DHDF are very accurate for thermodynamic data yielding the smallest Mean Absolute Deviation (MAD) ever obtained by a density functional for the full G3/05 test set.[25] Very encouraging results have also been reported for barrier heights,[26] isomerisation energies[27] and for transition metal reactions.[28] Using an analytical gradient, it could also be shown for a diverse set of molecules that B2PLYP provides very good molecular structures (including transition metal complexes) comparable to those from CCSD(T).[29]

However, a very basic deficiency of the DHDF employing standard exchange and correlation components was obvious from the very beginning. Because the GGA kernel completely lacks attractive dispersive (van der Waals, vdW) interactions[30,31] and the perturbation correction replaces only part (about 25%) of the semi-local correlation, typical vdW complexes were found to be underbound[15] (although improved compared to *e.g.*, B3LYP[32,33]). Recent work on electronically quite simple chemical reactions[12,34] indicates that non-local electron correlations on medium and long-range length scales are of utmost importance not only for non-covalently bound complexes but also play a significant role for the thermodynamics of large molecules. This and the topic of intramolecular dispersion is a main aspect of our work.

In this paper, we propose to extend the DHDF by a long-range dispersion term to cure the remaining problems in a very simplistic manner. Our very well tested empirical correction based on damped, atom-pairwise $-C_6 \cdot R^{-6}$ potentials (DFT-D)[35,36] is used (for a recent review, see ref. 37, for related methods, see ref. 38–41). It seems important to mention at this point that we keep the entire approach as non-empirical as possible, *i.e.*, the electronic part of the DHDF is not modified and only *one* scaling factor in the dispersion correction is adjusted, as suggested originally.[35]

In the following, we first provide a short review of the underlying ideas of our approach and then present results for three standard test sets: the S22 set of non-covalent interactions,[42] the G3/99 set of heat of formations,[7] and a conformational energy benchmark of a phenylalanyl–glycyl–glycine petide model.[43] Additionally, we present results for some challenging hydrocarbon reactions as test cases (IDHC7 set) where medium- to long-range electron correlations have dramatic energetic consequences. All in all, our composite approach consisting of pure KS-DF (GGA), wave function (perturbative) and classical ($-C_6 \cdot R^{-6}$) parts provides extremely high accuracy in general chemistry applications, including now also non-covalent (vdW) interactions. Compared to recent attempts that are based on highly parameterised (kinetic energy density dependent) functionals (37 free parameters),[6] our method is based on physical insight of the correlation problem. It contains only few parameters that have been specially adjusted (two parameters in the DHDF have been determined previously and one additional scaling factor is considered here).

2. Theory

The new ingredient in double-hybrid functionals is the mixing of a second-order perturbation correlation term (PT2) to semi-local GGA type correlation (C) in complete analogy to the replacement of semi-local GGA exchange (X) by 'exact' Hartree–Fock (HF) exchange, as in conventional hybrid functionals.[15] Using the two mixing parameters a_x and a_c the total exchange–correlation energy reads

$$E_{XC} = (1 - a_x)E_X + a_x E_{HF} + (1 - a_c)E_C + a_c E_{PT2}. \quad (1)$$

The Møller–Plesset type perturbation correction term[18] (in spin–orbital notation) is given by

$$E_{PT2} = \frac{1}{4}\sum_{ia}\sum_{jb}\frac{|(ij||ab)|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}. \quad (2)$$

and is taken non-selfconsistently as an add-on to the hybrid-GGA part. It is based on the KS orbitals *ijab* with eigenvalues ε. The (small) contributions from single excitations due to the non-vanishing occupied-virtual KS-Fock-Matrix elements are neglected. In general, any density functional can be used for the GGA part in eqn (1) but up to now only standard functionals have been tested (although one could also think of specially adjusted/designed ones). In a recent study of the full G3/05 benchmark set,[25] we found the mPW exchange functional[44] in conjunction with LYP correlation,[45] called mPW2PLYP ($a_x = 0.55$, $a_c = 0.25$), to be the winner with the original B2PLYP ($a_x = 0.53$, $a_c = 0.27$) using B88 exchange[46] being second best.

As already noted in the introduction, the relatively small perturbation correction can not overcompensate the excessive repulsive behaviour of the GGA parts in the long-range regime and thus, typical vdW complexes are underbound at the B2PLYP level.[15] The replacement of B88 by mPW exchange improved the situation as expected, but mPW2PLYP is still not as accurate for typical vdW complexes (as will be shown below) as required in biochemical applications.

A basic assumption of the present work is that electron correlation effects operate on different length scales that are (at least to a large degree) decoupled, and hence the contributions can be treated separately. This is illustrated in Fig. 1.

Common semi-local exchange–correlation functionals account (by construction) only in relatively high-density regions for static and dynamic correlation effects, but these decay (due to the density decay) exponentially. There are, however, even

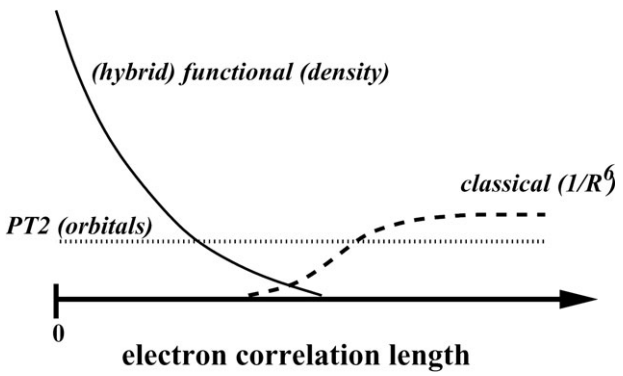

Fig. 1 Schematic description of the present composite approach with basically different methods for different electron correlation length scales. Note, that not potentials (or energies) but the methodical contribution in different regions of interelectronic distances is shown.

in the medium distance range non-local correlation effects that are related to the involved orbitals in a very system-dependent manner, as discussed in detail recently for the seemingly simple case of alkane isomerisation.[12] Such effects are treated in the DHDF mainly by the perturbative (PT2) part. In the long-range regime, the non-local correlations become less system dependent and are insignificantly influenced by quantum mechanical (overlap) effects. They can therefore be treated by classical potentials that employ the known asymptotic R^{-6} dependence of the dispersion energy.[47] This long-range dispersion correction must be damped in order to avoid double-counting effects. Our (obviously empirical) approach thus tries to incorporate all relevant correlation effects in a simple (separable) but well-defined and physically founded manner. The only known basic deficiency of the present approach (apart from the general requirement for conventional KS-DFT of having an electronically well-behaved single-reference system) is connected to the Self-Interaction Error (SIE) of the GGAs used. These effects are, however, alleviated by the use of relatively large amounts ($\approx$50%) of SIE-free HF exchange (for a recent SIE-free functional, see ref. 48).

For the dispersion correction we use (in a black-box manner) the now well established approach from ref. 36 that has been described before in ref. 35, and is based originally on a correction for Hartree–Fock.[49,50] The total energy for any density functional (including DHDF) is given by

$$E_{\text{DFT-D}} = E_{\text{KS-DFT}} + E_{\text{disp}}, \tag{3}$$

where $E_{\text{KS-DFT}}$ is the conventional KS-DFT self-consistent-field total energy and E_{disp} is an empirical dispersion correction given by

$$E_{\text{disp}} = -s_6 \sum_{i=1}^{N_{\text{at}}-1} \sum_{j=i+1}^{N_{\text{at}}} \frac{C_6^{ij}}{R_{ij}^6} f_{\text{dmp}}(R_{ij}). \tag{4}$$

Here, N_{at} is the number of atoms in the system, C_6^{ij} denotes the dispersion coefficient for atom pair ij, s_6 is a global scaling factor that only depends on the functional used and R_{ij} is an interatomic distance. A very appealing feature of DFT-D is that only one parameter has to be adjusted, *i.e.*, here we have to determine two new s_6 coefficients for mPW2PLYP and B2PLYP.

In order to avoid near-singularities for small R and electron correlation double-counting effects, a damping function f_{dmp} must be used, which is given by

$$f_{\text{dmp}}(R_{ij}) = \frac{1}{1 + e^{-d(R_{ij}/R_r - 1)}}, \tag{5}$$

where R_r is the sum of atomic vdW radii. We recently re-determined these radii and the atomic C_6 coefficients for the elements H–Xe and the damping factor d in eqn (5) (for details, see ref. 36). Note, that neither the functional form nor the atomic parameterization (except for s_6) of the DFT-D correction is specially adjusted for the DHDF. For the pairwise dispersion coefficients we employ a simple geometric mean of the form

$$C_6^{ij} = \sqrt{C_6^i C_6^j}. \tag{6}$$

The recently proposed functional (and basis set)-dependent scaling of the vdW radii[41] in a closely related DFT-D scheme seems to be incompatible with the present DHDF, as this would lead to electron correlation double-counting at very large distances.

3. Computational details

All computations are performed with a locally modified version of the TURBOMOLE 5.7[51] code in which our DHDF and the DFT-D method are implemented. The KS-DFT calculations are carried out with the dscf direct self-consistent field code.[52,53] If not mentioned otherwise, the following setup is used for single point energy calculations: a triple-ζ basis set with a large set of polarisation functions (TZV(2df,2pd) also named TZVPP),[54] a fine (multiple) grid (m4),[53] and all electrons included in the correlation treatment. The perturbation correction is obtained within the Resultion-of-Identity (RI) approximation[55,56] using auxiliary basis sets from the TURBOMOLE library.[56,57] The dispersion correction is used in its revised form as described in detail in ref. 36, where the re-optimised C_6 coefficients and atomic vdW radii are tabulated. The geometries employed in the single-point calculations are mostly taken from previous work[11,12,25,37,58] and have been (if not mentioned otherwise) optimised at the B3LYP/TZV(2d,2p) level. The geometries for the S22[42] and peptide[43] benchmark sets were kindly provided by Hobza and his group. The computations of the heat of formations for the G3 set are performed as described in detail in ref. 25 using a very large CQZV3P basis set[59] including core-polarisation functions.

4. Results and discussion

4.1 Determination of the s_6 coefficients

Although one might consider a re-fit of all three empirical parameters in our energy expression (eqn (1) and (3)), we decided to keep everything as simple and non-empirical as possible and thus solely adjust the s_6 scaling factor of the dispersion correction for the two DHDFs. A complete re-fit is computationally very demanding and depends strongly on the reference sets used, because a_x and a_c are already optimised (on relatively small systems) and the dispersion correction only adds significantly for larger systems due to the damping function. Thus, the results for atomisation energies of smaller molecules are almost unaffected by the dispersion correction (see Section 4.2). We thus decided to adjust s_6 for non-covalent interactions as recommended in ref. 36 (and as done similarly for other functionals). As a training set, the now well established S22 benchmark of non-covalent binding energies[42] has been chosen because it covers various interaction types like H-bonding, dispersion dominated, and mixed cases. The reference data have been obtained by Jurecka *et al.*[42] with a standard extrapolation procedure to the complete basis set limit at the MP2 level and a CCSD(T) correction term. The estimated accuracy of the reference data is about 2–3% of ΔE. The thus obtained s_6 coefficients are then subsequently used in further validation studies on thermodynamic and conformational benchmarks.

The MAD from the reference values has been chosen as quality criterion. In Fig. 2, the MAD for the S22 set with B2PLYP is plotted as a function of the s_6 parameter in steps of

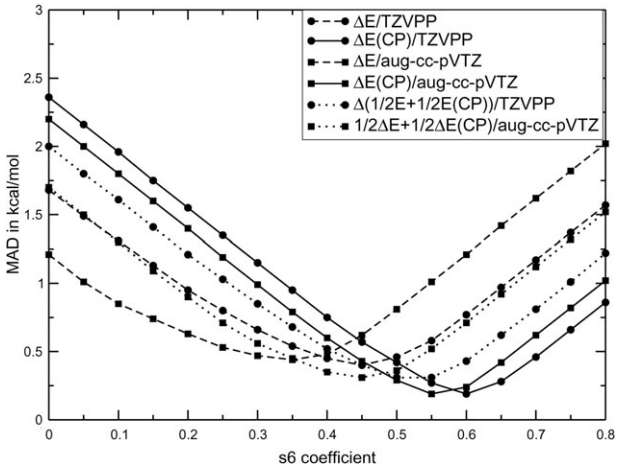

Fig. 2 Mean absolute deviations of B2PLYP for the S22 benchmark set for different s_6-values and with two basis sets (TZVPP and aug-cc-pVTZ). ΔE and ΔE(CP) refer to uncorrected and counterpoise corrected binding energies, respectively, and $\frac{1}{2}\Delta E + \frac{1}{2}\Delta E(CP)$is their average.

0.05. Analogous computations have been performed with the mPW2PLYP functional (not shown).

Because we adhere to a general quantum chemical model that should be applicable not only for inter-molecular complexes, it does not seem straightforward how to deal with finite basis set effects. Thus, three types of binding energies are considered: uncorrected (ΔE), counterpoise corrected[60,61] (ΔE(CP)) and the mean of both $\left(\Delta E(\mathrm{HCP}) = \frac{1}{2}\Delta E + \frac{1}{2}\Delta E(\mathrm{CP})\right)$, because the CP method typically overestimates the Basis Set Superposition Error (BSSE). We show results with a standard TZVPP[54] basis that is often used in routine chemical applications and the aug-cc-pVTZ[62] basis set, which represents some kind of standard for the study of vdW complexes.

The minima of the MAD with respect to the varied s_6 coefficient are relatively pronounced in all cases, indicating the physical significance of the added dispersion energy. Without CP correction (and for the aug-cc-pVTZ basis in particular) the minima occur for smaller s_6 values, indicating significant BSSE. The best results with very small MADs of about 0.25 kcal mol^{-1} are obtained at the ΔE(CP) level with both basis sets for s_6 values between 0.55 and 0.6. At the ΔE(HCP) level the optimum s_6 values are smaller (between 0.45 and 0.55) and a slightly larger MAD of about 0.3 kcal mol^{-1} is obtained. We finally decided to take $s_6 = 0.55$ as some kind of compromise for our method (best ΔE(CP)/aug-cc-pVTZ result and simultaneously good performance of ΔE/TZVPP), which is dubbed B2PLYP-D when this correction is applied. Similar considerations lead to $s_6 = 0.40$ for mPW2PLYP-D.

In comparison to other density functionals, these values are quite small (for most GGAs $1.0 < s_6 < 1.25$ holds except for PBE, where $s_6 = 0.75$[36]). This comes as no surprise because parts of the dispersion effects are already covered by the perturbation term. Although B2PLYP has the larger perturbation correction and a smaller fraction of GGA correlation ($a_c = 0.27$ *vs.* $a_c = 0.25$), mPW2PLYP has the smaller s_6 coefficient. This is attributed to the different long-range behaviour of the mPW compared to the B88 exchange functional, as intended originally.[44]

Table 1 lists a statistical assessment for the S22 set with mPW2PLYP-D and B2PLYP-D, as well as for the DHDF without dispersion correction. Only ΔE(HCP) values are discussed.

The gain in accuracy due to the dispersion correction is remarkable. The MAD decreases by about 1–1.5 kcal mol^{-1} for each level of theory and also the error spread ($\Delta_{\mathrm{max-min}}$) decreases substantially. Slightly better results are obtained with the TZVPP basis set. The lowest MAD of 0.3 kcal mol^{-1} is obtained at the B2PLYP-D/TZVPP level, which is one of the best results ever obtained for a quantum chemical method for this benchmark set (the hitherto best other results are also listed in Table 1). This average deviation is also close to the estimated error of the CCSD(T) reference data. As shown in Table 2, which contains the results for individual complexes, almost no bias with respect to H-bonded or dispersion dominated (stacked) complexes is observed for the corrected DHDF. Note also the very small error spread (last column in Table 1) indicating the absence of outliers.

4.2 Heat of formations for the G3/99 test set

In order to test the general applicability of our model in thermochemical applications, we chose the common G3/99 set of heat of formations (HOF) with 223 entries. The accurate computation of atomisation energies requires very different qualities of a density functional than the determination of non-covalent complex binding energies. There is, however, also a deep relation of the two subjects. The G3/99 set comprises relatively large molecules which should contain

Table 1 Performance for the S22 set of non-covalent interaction energies at different levels of theory. The statistics for the first eight entries refers to the mean of the ΔE and ΔE(CP) values. The statistical descriptors are the Mean Deviation (MD), Mean Absolute Deviation (MAD) and the difference of maximum and minimum deviations ($\Delta_{\mathrm{max-min}}$). All values are in kcal mol^{-1}

Method	MD	MAD	$\Delta_{\mathrm{max-min}}$
This work			
B2PLYP/TZVPP	−2.0	2.0	7.0
B2PLYP/aug-cc-pVTZ	−1.7	1.7	6.0
B2PLYP-D/TZVPP	0.2	0.3	1.4
B2PLYP-D/aug-cc-pVTZ	0.5	0.5	1.2
mPW2PLYP/TZVPP	−1.3	1.4	6.2
mPW2PLYP/aug-cc-pVTZ	−1.1	1.1	5.6
mPW2PLYP-D/TZVPP	0.3	0.5	2.5
mPW2PLYP-D/aug-cc-pVTZ	0.6	0.6	2.1
Other methods			
MP2/CBS[a]	−0.8	0.8	2.9
BLYP-D/TZVPP[b]	−0.3	0.5	2.0
SCS-MP2/TZVPP[c]	0.3	0.5	2.5
SCSN-MP2/CBS[d]	−0.3	0.3	1.7
DFT-D-TPSS/6-311++G(3df,3pd)[e]	—	0.3	1.5

[a] Complete basis set (CBS) extrapolated (aug-cc-pVXZ, $X = 3, 4$) MP2, not CP-corrected from ref. 70. [b] BLYP with dispersion correction, not CP-corrected from ref. 71. [c] Spin-component scaled (SCS)-MP2, not CP-corrected from ref. 70. [d] Reparametrised SCS-MP2 for nucleobases,[72] CBS-extrapolated (aug-cc-pVXZ, $X = 3, 4$), not CP-corrected from ref. 70. [e] TPSS with dispersion correction from ref. 41.

Table 2 Performance for the S22 set of non-covalent interaction energies for mPW2PLYP-D and B2PLYP-D. Listed are the reference binding energies ΔE_{ref}, the unscaled ($s_6 = 1$) dispersion correction ΔE_{disp}, and the deviations based on $^1/_2\Delta E + {}^1/_2\Delta E$(CP) values with the TZVPP basis set. All values are in kcal mol^{-1}

Entry		ΔE_{ref}[a]	ΔE_{disp}	Deviation (ref−theor.) mPW2PLYP-D	B2PLYP-D
Hydrogen bonded complexes					
1	$(NH_3)_2$	−3.17	−1.39	0.70	0.48
2	$(H_2O)_2$	−5.02	−0.78	0.80	0.45
3	Formic acid dimer (C_{2h})	−18.61	−2.52	1.44	0.82
4	Formamide dimer (C_{2h})	−15.96	−2.66	0.91	0.41
5	Uracil dimer (C_{2h})	−20.65	−3.33	0.69	0.23
6	2-pyridoxine · 2-aminopyridine	−16.71	−3.97	1.12	0.89
7	Adenine · thymine WC	−16.37	−4.24	0.76	0.48
Complexes with predominant dispersion contribution					
8	$(CH_4)_2$ (D_{3d})	−0.53	−0.83	0.07	−0.13
9	$(C_2H_4)_2$ (D_{2d})	−1.51	−2.14	0.19	−0.01
10	Benzene · CH_4 (C_3)	−1.50	−2.18	0.03	−0.08
11	Benzene dimer (C_{2h})	−2.73	−5.71	−0.44	−0.21
12	Pyrazine dimer (C_s)	−4.42	−6.21	−0.41	−0.16
13	Uracil dimmer (C_s)	−10.12	−9.01	−0.25	0.02
14	Indole · benzene	−5.22	−8.54	−1.06	−0.53
15	Adenine · thymine stack	−12.23	−13.22	−0.45	0.29
Mixed complexes					
16	Ethene · ethane (C_{2v})	−1.53	−0.99	0.24	0.07
17	Benzene · H_2O (C_s)	−3.28	−2.34	0.52	0.38
18	Benzene · NH_3(C_s)	−2.35	−2.28	0.23	0.12
19	Benzene · HCN (C_s)	−4.46	−3.10	0.60	0.50
20	Benzene dimer (C_{2v})	−2.74	−3.64	0.08	0.08
21	Indole · benzene T-shape	−5.73	−5.31	0.18	0.31
22	Phenol dimer	−7.05	−4.09	0.38	0.23

[a] Estimated CCSD(T) complete basis set limit from ref. 42.

significant contributions from intramolecular dispersion (which is more-or-less neglected in common functionals). This is indeed the case and *e.g.*, for *n*-octane we obtain a dispersion correction to the HOF of 9.2 kcal mol^{-1} at the B2PLYP-D level (see also below).

A statistical summary of our results is given in Table 3 and histograms with error distributions are depicted in Fig. 3. For comparison, also B3LYP values with ($s_6 = 1.05$[36]) and without the dispersion correction are included.

The improvements that are achieved by applying the DFT-D model are remarkable and even B3LYP benefits from the dispersion correction. This interesting finding is related to the increasing errors for larger systems that were observed already some years ago[7] for B3LYP, and that have been attributed to an accumulation of errors of local correlation effects. Our results presented here show that this is not the major reason and that failures in describing dispersion effects play a major role. Because dispersion is a long-range phenomenon (using our damping function, typical correlation distances are >300–400 pm), these effects only show up for larger molecules (>10–20 atoms). This is clearly seen in the error distributions (Fig. 3), which become more symmetric (and smaller) upon application of the dispersion correction. This is further underlined with a few molecules of different size taken from the set whose HOF are given in Table 4.

Perusing Table 4, one finds that the dispersion correction mostly works in the right direction (stabilising the molecule with respect to the atoms) but that it is <2 kcal mol^{-1} for the systems with four or less non-hydrogen atoms (first group). For larger molecules (groups 2 and 3), the correction becomes very significant and it is noted that not only sheer size but the shape and the elemental composition of the molecule determines the size of the correction.

A very encouraging result of this part of our study is that the re-scaled DFT-D correction that has been derived from vdW

Table 3 Performance of B3LYP, B2PLYP, and mPW2PLYP with and without the dispersion correction for the G3/99 set of heat of formations. The statistical descriptors are the Mean Deviation (MD), Mean Absolute Deviation (MAD) and the difference of maximum and minimum deviations ($\Delta_{max-min}$). All values are in kcal mol^{-1}

Functional	MD	MAD	$\Delta_{max-min}$
This work			
B3LYP	−4.6	5.6	25.5
B3LYP-D	−1.3	3.1	23.3
B2PLYP	−1.7	2.4	20.2
B2PLYP-D	0.0	1.7	15.5
mPW2PLYP	−1.4	2.1	16.2
mPW2PLYP-D	−0.2	1.7	15.7
Other functionals[a]			
TPSS		5.6	
MPW1B95		4.9	
M05-2X[b]		4.2	
B97-2		4.1	
O3LYP		4.0	
X3LYP		4.0	
B1B95		3.7	
B98		3.4	
MCY1[c]		3.1	

[a] Taken from ref. 5. [b] Taken from ref. 73. [c] Taken from ref. 48.

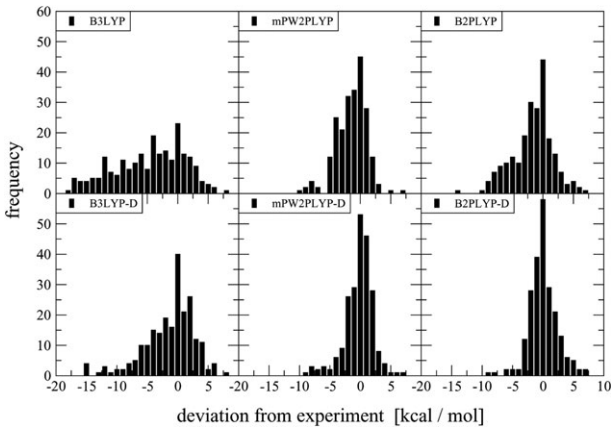

Fig. 3 Comparison of error distributions (binning in a 1 kcal mol^{-1} range) for heat of formations of the G3/99 set for density functionals without (top) and with (bottom) dispersion correction.

complexes is fully applicable also for conventional thermodynamics without any further re-fit of the electronic part. One of the reasons for this and the absence of double-counting effects is that the two (electronic) parameters of DHDF have been adjusted on relatively small systems (G2 subset[63]) and that the damping function effectively removes over-correlation in these cases.

The already very accurate DHDF (MAD of 2.4 and 2.1 kcal mol^{-1} for B2PLYP and mPW2PLYP, respectively) are further improved and the MAD is reduced to very small values of 1.7 kcal mol^{-1}, which is much less than with the best other density functional (3.1 kcal mol^{-1} with MCY1,[48] for results with more conventional ones, see Table 3). Also the maximum errors (outliers) are smaller and the functionals are now competitive to the G3 model, which has a MAD of 1.1 kcal mol^{-1} for this test set.[7] Note in this context that also the G3 approach contains four empirical parameters and that the DHDF results are obtained in only a small fraction of computation time. Together with the density fitting (RI) approximation, DHDF computations are routinely possible for systems with 100–200 atoms, which is out of reach for the G3 procedure.

Table 4 Examples from the G3/99 set of Heat Of Formations (HOF). The difference between theoretical and experimental HOF for B2PLYP and B2PLYP-D is given. The entries have been grouped by the number of heavy atoms, and within these subgroups the five entries with the largest effect on the dispersion correction have been selected. All values are in kcal mol^{-1}

		Deviation (exp.-theor.)	
Entry number		B2PLYP	B2PLYP-D
Less than 4 heavy atoms			
83	C_3H_8	−2.8	−0.4
109	CH_3NHCH_3	−1.6	0.5
110	$C_2H_5NH_2$	−0.9	1.1
146	$(CH_3)_2CH$	−0.6	1.2
119	C_2H_5SH	−2.3	−0.6
116	CH_3OCH_3	−2.0	−0.3
4 to 6 heavy atoms			
158	C_6H_{14}	−9.1	−1.4
204	$(CH_3)_3COCH_3$	−8.5	−1.5
156	C_6H_{12}	−9.1	−2.3
153	C_5H_{12}	−8.0	−1.4
157	C_6H_{14}	−7.4	−0.9
More than 6 heavy atoms			
162	C_8H_{18}	−10.5	−1.3
160	C_7H_{16}	−9.0	−1.1
208	$((CH_3)_2CH)_2O$	−9.3	−1.8
164	$C_{10}H_8$	−1.2	4.5
190	$C_2H_5CH(CH_3)NO_2$	−3.5	2.0

4.3 Conformational energies for a polypeptide model

As a third test, we study conformational (relative) energies of the phenylalanyl–glycyl–glycine peptide as suggested by Reha *et al.*[43] The eleven most stable conformers (based on their MP2 results with complete basis set extrapolation and CCSD(T) corrections) are investigated. We computed single point energies (TZVPP basis) based on their MP2 geometries and take the global minimum found in the previous study as a reference point. The relative energies compared to this conformer are plotted at different levels of theory in Fig. 4. Test calculations for some conformers with even larger QZV3P basis sets resulted in insignificant changes of these values (<0.1 kcal mol^{-1}).

Although the conformers considered have very different structures (*e.g.* π-stacked, partially and completely unfolded) the energies are found to be in a relatively small range of 2.5 kcal mol^{-1}, indicating the flatness of the potential energy surfaces for folding processes. We applied various quantum chemical methods to this problem and found it to be very difficult. Standard functionals as *e.g.*, B3LYP fail completely and not only incorrectly predict the spatially more extended conformers 2 and 5 to be lower in energy, but furthermore scatter strongly for the other structures. B3LYP and other uncorrected functionals provide unphysically rough (spiky) potential energy surfaces for such intrinsically smooth processes (for another recent example, see ref. 64). This is partially

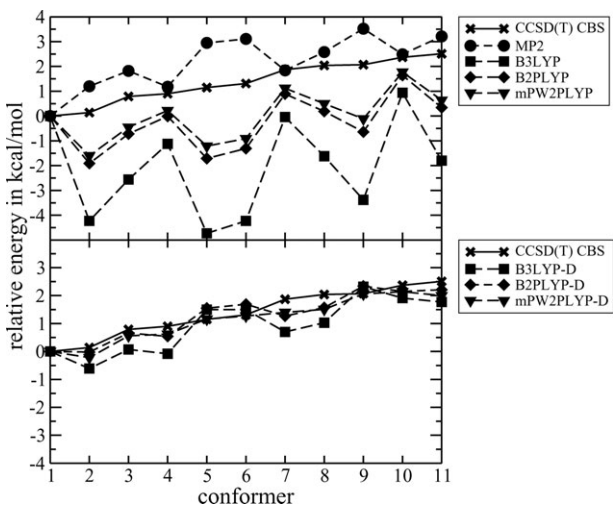

Fig. 4 Relative energies (TZVPP AO basis) for different conformers of phenylalanyl–glycyl–glycine at various levels of theory. The energy of the first conformer is set to zero. Top: MP2 and uncorrected functionals, bottom: functionals with dispersion correction. The CCSD(T) reference data are from ref. 43.

improved by the dispersion correction, as seen clearly by the much better B3LYP-D data. However, the desired accuracy is not obtained at this level (and in particular the right prediction of the energetically lowest structure) and we speculate that this is due to system(orbital)-dependent, medium-range correlation effects. This view is supported by the results of the DHDF, which are better than B3LYP but also miss part of the relevant interactions. These are again very accurately provided by the dispersion correction, and thus the B2PLYP-D and mPW2PLYP-D results are found to be in almost perfect agreement with the reference data. Although they both predict a different global minimum (conformer two), this is less than 0.25 kcal mol^{-1} more stable than conformer one, which is well within the estimated error of the reference data. Note, that MP2, which is often considered as some kind of 'gold standard' by theoretical biochemists for such applications, performs worse than the corrected DHDF due to a general overestimation of correlation effects when π-systems are involved (see *e.g.*, ref. 65–67).

4.4 Strong intramolecular dispersion effects in hydrocarbons

Encouraged by the previous results, we decided to apply the corrected DHDF to other challenging cases and pay particular attention to size effects. We consider non-polar hydrocarbon reactions here that involve strong intramolecular dispersion contributions but no complicated electrostatic or charge-transfer effects. In some cases, also a balanced description between short and medium-ranged electron correlation due to bond rearrangements is required. We propose this set of seven reactions and conformational changes as a general benchmark for DFT that is termed IDHC7 (intra-molecular dispersion, seven hydrocarbons). The results are listed in Table 5 and the more complicated molecular structures are shown in Fig. 5.

The first case is the dimerisation of anthracene. It has been found that intramolecular dispersion (as well as short-range correlation) plays a crucial role for the computation of the dimerisation energy ΔE.[11] Transformations of π to σ-bonds, change of aromatisation energy and stacked π-systems are involved. As discussed in ref. 11, all known density functionals fail even to get a correct sign for ΔE. Although the DHDFs fail as well, they are closest to the reference ΔE value of about −9 kcal mol^{-1}. Applying the dispersion correction yields values of −3.9 and −6.1 kcal mol^{-1} for mPW2PLYP-D and B2PLYP-D, respectively, in reasonable agreement with the reference.

In the second example, the hydrogenation reaction of [2.2]paracyclophane to *p*-xylene is considered. Due to the ethano-bridges, the two (distorted) aromatic units of the phane are clamped together, resulting in inter-atomic distances (280–310 pm[67]) that are below typical vdW radii for carbon. This in turn results in strong energy contributions when the system is split into two *p*-xylene molecules that, however, remain aromatic. Because of the short distances between the rings, the corresponding attractive part of the interaction has been termed 'overlap-dispersive'.[67] Its account requires orbital-dependent terms and this reaction thus represents an important test of the present approach. As can be seen from Table 5, B3LYP yields a huge error of about 18 kcal mol^{-1} (the cyclophane is too unstable) for ΔE due the missing correlation effects. This error is reduced with the pure DHDF to about 10 kcal mol^{-1} and, together with the dispersion correction, they yield deviations of 0.7 and 3.6 kcal mol^{-1} for B2PLYP-D and mPW2PLYP-D, respectively. For B2PLYP-D this is within the errors of the experimental reference value.[68]

The next entry considers the known DFT problem to predict the right energy for branching isomerisations in long alkane chains.[12] In this case, medium- as well as long-range electron correlation contributions are important and are the reason for the failure of common functionals (except for the new M05-2X approach that computes this value for at least eight carbon atoms correctly, see ref. 69). As in the case of the anthracene dimer, the uncorrected DHDF are qualitatively wrong but closer to the true answer than conventional functionals like B3LYP due to the PT2 term. Again, outstanding accuracy is obtained with the dispersion correction resulting in errors <0.5 kcal mol^{-1} for both functionals in the case of *n*-octane. Also the isomerisation of the even more extreme example of *n*-undecane to the sterically overcrowded hexamethylpentane isomer is treated accurately. In that case, the DHDF are probably even better than the SCS-MP2 reference that slightly underestimates dispersion in saturated molecules

Table 5 Performance of the DHDF (TZVPP AO basis) in comparison to B3LYP for hydrocarbon reactions and conformational changes with strong intramolecular dispersion effects (IDHC7 set). MAD is the Mean Absolute Deviation. All energies are in kcal mol^{-1}

	ΔE					
Reaction	Ref.	mPW2-PLYP	mPW2-PLYP-D	B2-PLYP	B2-PLYP-D	B3-LYP
$2C_{14}H_{10} \rightarrow C_{28}H_{20}$[a]	−9.0[b]	4.8	−3.9	6.6	−6.1	25.4
[2.2]paracyclophane + $2H_2 \rightarrow 2p$-xylene[c]	−58.5[d]	−68.0	−62.1	−67.3	−59.2	−76.7
n-octane → tetramethylbutane[e]	1.9[f]	2.8	−1.4	3.2	−2.4	8.5
n-undecane → hexamethylpentane[e]	9.4[g]	16.7	8.5	17.4	6.1	26.9
$C_{14}H_{30}$ (linear) → $C_{14}H_{30}$ (folded)[h]	2.2[i]	5.3	3.1	5.6	2.6	7.5
$C_{22}H_{46}$ (linear) → $C_{22}H_{46}$ (folded)[h]	−3.6[i]	8.2	−1.1	9.9	−3.4	18.0
$C_{30}H_{62}$ (linear) → $C_{30}H_{62}$ (folded)[h]	−8.8[i]	8.6	−4.9	11.0	−8.2	22.9
MAD		9.7	2.5	10.6	1.2	19.9

[a] Geometries optimised at the MP2/TZV(d,p) level. [b] DMC and QCISD(T) data, see ref. 11. [c] Geometries optimised at the PBE-D/TZV(2d,2p) level. [d] Derived from experimental HOF[68] and PBE-D/TZV(2d,2p) vibrational/thermal corrections. [e] Geometries optimised at the MP2/TZV(d,p) level. [f] Derived from experimental HOF, see ref. 12. [g] SCS-MP2/CQZV3P, taken from ref. 12. [h] Geometries optimised at the B97-D/TZV(d,p) level, taken from ref. 37. [i] MP2/aug-cc-pVTZ//BLYP-D/TZV(p,d), taken from ref. 37.

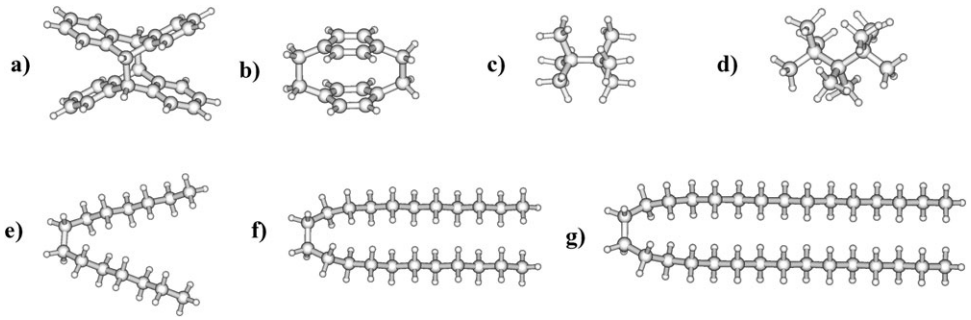

Fig. 5 Structures of the hydrocarbons in the IDHC7 test set with stronger dispersion effects: (a) dimer of anthracene, (b) [2.2]paracyclophane, (c) tetramethylbutane, (d) hexamethylpentane, (e)–(g) folded alkane chains.

like alkanes.[70] Note, the huge and unacceptable B3LYP error of about 17.5 kcal mol^{-1}.

The folding of molecular structures from spatially extended, linear to more dense, space-filling arrangements is an important elementary process in proteins, as already mentioned in the previous section. Here, we further study the effects of dispersion in a non-polar model system and also want to monitor the performance when going to really large systems with about 10^2 atoms. The example is taken from ref. 37 and is concerned with the energy difference between linear and *gauche* (singly-folded) alkane chains (C_nH_{2n+2}) of increasing length (n = 14, 22 and 30). In the folded state there are two almost perfectly aligned alkane chains that become more stable than the linear form due to intramolecular dispersion effects between n = 14 and 22. According to the MP2 reference data,[37] for n = 30 the folded form is already much more stable than the linear conformer. This behaviour is not even qualitatively obtained with standard functionals, and only with the dispersion correction are accurate results obtained. This also holds for the DHDF and, in particular, B2PLYP-D is very close to the reference data for all three chains lengths.

5. Summary and conclusions

In this paper, we have presented a composite approach to describe inter- and intra-molecular dispersion effects on different lengths scales accurately. First of all it corrects the systematic underestimation of long-range dispersion effects by the recently proposed Double-Hybrid Density Functionals (DHDF). In all test cases, excellent agreement with accurate reference data is obtained. The previously developed DFT-D model is used without any modifications and also the electronic part of the functionals was kept. The new approaches are dubbed B2PLYP-D with a s_6 dispersion scaling factor of 0.55 and mPW2PLYP-D, for which s_6 = 0.4.

As could be anticipated from the well documented reliability of the DFT-D method, this combination leads to a significant increase of the accuracy for non-covalent interactions. The B2PLYP-D functional now yields one of the lowest MADs ever reported for the S22 benchmark set (0.25 kcal mol^{-1}). Similarly, high accuracy could also be obtained for systems with strong intramolecular dispersion effects, *e.g.*, as shown for the folding of alkane chains and a tripeptide model. That the independently developed methods almost perfectly fit together is an intriguing (but far from trivial) result because of the double-counting problem of correlation effects. However, already the conformational benchmark for the tripeptide indicates that it is only the combination of orbital-dependent correlation terms (in the PT2 part of the functionals) and the long-range R^{-6} dependence (in the DFT-D model) together that provides outstanding accuracy competitive to coupled-cluster reference methods.

This view is further supported by the large improvements found for the G3/99 benchmark set of heat of formations that mainly stem from the large molecules in the test set. The DFT-D correction lowers the already small MADs provided by the DHDF (2.4 and 2.1 kcal mol^{-1} for B2PLYP and mPW2PLYP, respectively) further down to unprecedented DFT values of about 1.7 kcal mol^{-1}. Furthermore, even the standard B3LYP functional strongly benefits from the dispersion correction, which underlines the importance of intra molecular dispersion effects. The excellent results (reduction of the MAD from about 10 to 1–2 kcal mol^{-1}) for some very challenging reactions in organic thermochemistry (cyclophane fragmentation, branching of alkanes and the dimerisation of anthracene) further support the validity of our approach.

A very appealing feature of the proposed method is that it not only provides highly accurate thermochemistry (and kinetics) but also can lead to some qualitative understanding. In the total energy expression, the hybrid GGA, perturbative correlation and long-range dispersion parts are additive, which allows a simple partitioning of reaction or binding energies into physically meaningful components.

In summary, we recommend general use of dispersion corrected density functionals. Also, B3LYP has been improved significantly in almost all cases investigated. However, the double-hybrids offer higher accuracy for a wider range of applications with little more computational effort. They are free of over-fitting problems and contain only physically plausible components. From the purists point of view, the approach proposed here is certainly not satisfactory because our dispersion correction is not of electronic origin. We think, however, that it is, at the current stage of functional development, better to get the right answer for the right physical reason with a classical correction than to rely on error compensation or to resort to very empirical approaches. Also, on the negative side we note that the problem of self-

interaction error is still not really solved. This is important for future extensions of the DHDF to *e.g.*, excited states that are currently conducted in our laboratory. Of course, further testing of the entire approach is mandatory and the very interesting fields of large molecular geometries (analytical B2PLYP-D gradients are available[29]), vibrational frequencies of non-covalently bound systems or special electronic (spin-dependent) properties have not been explored yet. Furthermore, it seems clear that the more consistent account of intramolecular correlation effects in the corrected DHDF should be accompanied by similar improvements of solvation models, such that molecules in the gas and condensed phases are treated in a balanced manner.

In most applications, mPW2PLYP-D and B2PLYP-D perform similarly but the latter approach, which contains a more repulsive GGA part and a larger dispersion correction, seems to be slightly better overall. This confirms recent results for DFT-D in combination with GGAs, where BLYP is found to be superior to *e.g.* PBE.[71] The number of cases where the dispersion correction significantly improves the results by far exceeds the few examples where the corrected results are (mostly) slightly worse. Our results show that the future for thermodynamic predictions in chemistry including biochemistry and non-covalent interactions is bright. Using reasonable integral approximations and reliable AO basis sets, molecular DHDF computations are routinely possible for systems with 100–200 atoms, which is out of reach for any other quantum chemical method of similar accuracy and broad range of applicability.

6. Acknowledgement

The authors want to acknowledge financial support by the Deutsche Forschungsgemeinschaft within the SFB 424 "Molecular Orientation and its Functions in Chemical Systems" and want to thank C. Mück-Lichtenfeld and J. Antony for their help at some stages of this work.

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