

A System-Dependent Density-Based Dispersion Correction

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Abstract: Density functional approximations fail to provide a consistent description of weak molecular interactions arising from small electron density overlaps. A simple remedy to correct for the missing interactions is to add *a posteriori* an attractive energy term summed over all atom pairs in the system. The density-dependent energy correction, presented herein, is applicable to all elements of the periodic table and is easily combined with any electronic structure method, which lacks the accurate treatment of weak interactions. Dispersion coefficients are computed according to Becke and Johnson's exchange-hole dipole moment (XDM) formalism, thereby depending on the chemical environment of an atom (density, oxidation state). The long-range $\sim R^{-6}$ potential is supplemented with higher-order correction terms ($\sim R^{-8}$ and $\sim R^{-10}$) through the universal damping function of Tang and Toennies. A genuine damping factor depending on (iterative) Hirshfeld (overlap) populations, atomic ionization energies, and two adjustable parameters specifically fitted to a given DFT functional is also introduced. The proposed correction, dDXDM, dramatically improves the performance of popular density functionals. The analysis of 30 (dispersion corrected) density functionals on 145 systems reveals that dDXDM largely reduces the errors of the parent functionals for both inter- and intramolecular interactions. With mean absolute deviations (MADs) of 0.74–0.84 kcal mol⁻¹, PBE-dDXDM, PBE0-dDXDM, and B3LYP-dDXDM outperform the computationally more demanding and most recent functionals such as M06-2X and B2PLYP-D (MAD of 1.93 and 1.06 kcal mol⁻¹, respectively).

Introduction

Kohn–Sham density functional theory (DFT)¹ offers a powerful and robust methodology for investigating electronic structures of many-body systems, providing a practical balance of accuracy and computational cost unmatched by other methods. Despite this success, the commonly used semilocal approximations have difficulties in properly describing attractive dispersion interactions that decay with R^{-6} at large intermolecular distances. Even in the short to medium range, most semilocal density functionals fail to give an accurate description of weak interactions.^{2–4}

Accurate treatment of weakly interacting systems is crucial, especially in the field of biomolecules (stacking of

DNA,⁵ protein folding⁶), host–guest chemistry, surface chemistry, and condensed phases of organic molecules. Yet, even seemingly innocuous looking reactions such as alkane isomerization energies and Pople's isodesmic bond separation equations (BSEs),^{7,8} where formal bond types are preserved, suffer from errors at standard DFT levels.^{9–12}

SAPT (DFT)^{13–15} gives highly accurate interaction energies for two or three interacting closed-shell subsystems, but the method is not applicable to intramolecular interactions. Around the energy minimum, dispersion-corrected atom-centered potentials (DCAPs)^{16–22} or specifically fitted density functionals^{23–28} have led to satisfactory results. Nevertheless, both approaches intrinsically lack the ability to recover the long-range $\sim R^{-6}$ attractive form. Conceptually, the simplest remedy is to correct for the missing

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interaction *a posteriori* by adding an attractive energy term summed over all atom pairs in the system. The strategy was originally proposed to improve Hartree–Fock energies (known as HF-D)^{29–32} and was later applied to DFT.^{2–4,33} With parameters for most elements in the periodic table, Grimme’s parametrization³⁴ is the best known DFT-D variant. Since then, there has been considerable interest in finding an optimal parametrization.^{34–52} DFT-D is generally accurate for the treatment of intermolecular interactions, but proper description of weak intramolecular interactions is trickier.^{12,53,54} Specific fitting to a suitable training set⁴⁰ decreases the “intramolecular” error, albeit we have recently shown that the two parametrizations can be unified using a physically motivated damping function called dD10.⁴⁶

Our dD10 correction⁴⁶ is, however, restricted to only a few elements (H, C, N, O) and, like most DFT-D schemes, employs system-independent dispersion coefficients. The present work overcomes these limitations by combining the efficiency of a new damping criterion with the attractiveness of deriving system-dependent dispersion coefficients. Akin to our former correction,⁴⁶ two damping functions are used jointly to treat both intra- and intermolecular weak interactions consistently. System-dependent dispersion coefficients are computed on the basis of the analytical approximation of the Becke and Johnson^{37,55–60} (BJ) exchange-hole-dipole moment (XDM) formalism.^{61,62} Iterative Hirshfeld weights⁶³ are used to partition the dispersion coefficients among the atoms.^{43,64} A genuine and universal damping criterion based on iterative Hirshfeld weights is introduced for the first time. Our approach has the additional advantage of easily incorporating higher order dispersion coefficients absent in, for instance, the related C₆-only scheme of Tkatchenko and Scheffler.⁴⁵ With only two fit parameters, this new dDXDM correction solves difficulties arising from elements positioned in different chemical environments (i.e., selecting a dispersion coefficient^{33–35}) and is easily applicable to every element of the periodic table.

The next sections give details on the implementation and computations. The performance of dDXDM, on test sets featuring both intra- and intermolecular weak interactions, is then compared with the interaction energies of (un)corrected popular functionals (BP86,^{65–67} BLYP,^{65,68} BHH-LYP,⁶⁹ B3LYP,^{70,71} PBE,⁷² and PBE0^{73,74}) and established DFT-methods designed to better describe weak interactions (B97-D,³⁴ B2PLYP-D,^{75,76} and M06–2X²⁴).

Theory

The basic form of our correction is the Tang and Toennies (TT) damping function⁷⁷

$$E_{\text{disp,dDXDM}} = - \sum_{i=2}^N \sum_{j=1}^{i-1} \sum_{n=3}^5 f_{2n}(bR_{ij}) \frac{C_{2n}^{ij}}{R_{ij}^{2n}} \quad (1)$$

where N is the number of atoms in the system and b is the TT-damping factor (*vide infra*). The correction is called dDXDM6 if only the first term is retained in the multipole expansion ($n = 3$, corresponding to C₆) and is called dDXDM otherwise ($n = 5$, up to C₁₀). $f_{2n}(bR_{ij})$ represents the “universal

damping functions”⁷⁷ that are specific to each dispersion coefficient and that serve to attenuate the correction at short internuclear distances to account for overlapping densities.

$$f_{2n}(x) = 1 - \exp(-x) \sum_{k=0}^{2n} \frac{x^k}{k!} \quad (2)$$

This coming section describes the procedure employed for the determination of the two nontrivial arguments of eq 1: (i) the dispersion coefficients and (ii) the damping factor b .

i. Dispersion Coefficients and Atomic Partitioning Weights. Dispersion coefficients are computed according to Becke and Johnson’s XDM formalism,^{37,55–60} as efficiently implemented in Q-Chem by Kong and co-workers.^{61,62} The C_6^{ij} , C_8^{ij} , and C_{10}^{ij} coefficients between atoms i and j are, for instance, obtained according to

$$C_6^{ij} = \frac{\alpha_i \alpha_j \langle M_1^2 \rangle_i \langle M_1^2 \rangle_j}{\alpha_j \langle M_1^2 \rangle_i + \alpha_i \langle M_1^2 \rangle_j} \quad (3)$$

$$C_8^{ij} = \frac{3}{2} \frac{\alpha_i \alpha_j (\langle M_1^2 \rangle_i \langle M_2^2 \rangle_j + \langle M_2^2 \rangle_i \langle M_1^2 \rangle_j)}{\alpha_j \langle M_1^2 \rangle_i + \alpha_i \langle M_1^2 \rangle_j} \quad (4)$$

$$C_{10}^{ij} = 2 \frac{\alpha_i \alpha_j (\langle M_1^2 \rangle_i \langle M_3^2 \rangle_j + \langle M_3^2 \rangle_i \langle M_1^2 \rangle_j)}{\alpha_j \langle M_1^2 \rangle_i + \alpha_i \langle M_1^2 \rangle_j} + \frac{21}{5} \frac{\alpha_i \alpha_j \langle M_2^2 \rangle_i \langle M_2^2 \rangle_j}{\alpha_j \langle M_1^2 \rangle_i + \alpha_i \langle M_1^2 \rangle_j} \quad (5)$$

where α_i are atomic polarizabilities and $\langle M_l^2 \rangle$ atomic expectation values of squared multipoles ($l = 1, 2, 3$ for dipoles, quadrupoles, and octupoles, respectively) given by

$$\langle M_l^2 \rangle_i = \sum_{\sigma} \int w_i(r) \rho_{\sigma}(r) [r_i^l - (r_i - d_{X\sigma})^l]^2 d^3r \quad (6)$$

In eq 6, $\rho_{\sigma}(r)$ is the spin density, $d_{X\sigma}$ the dipole moment of the exchange-hole and its reference electron, approximated according to the Becke–Roussel model,⁷⁸ and $w_i(r)$ represents atomic partitioning weights.

Becke and Johnson⁵⁶ used classical Hirshfeld weightings:⁷⁹

$$w_{i,\text{HC}}(r) = \frac{\rho_i^{\text{at}}(r)}{\sum_n \rho_n^{\text{at}}(r)} \quad (7)$$

where ρ_i^{at} is the sphericalized free atomic density of atom i , weighted by the superposition of all ρ_i^{at} with all atoms n positioned as in the real molecule. The classical Hirshfeld scheme depends on the (arbitrary) choice of the atomic reference densities. Molecules with large ionic character, such as LiF, offer a clear illustration of this dependence. If one uses the typical superposition of neutral atomic densities (i.e., Li⁰ and F⁰), the atomic charges have an absolute value of 0.57. However, a value of 0.98 is obtained when Li⁺ and F[−] densities are considered.⁶³ This arbitrariness can be overcome by using the iterative version of the Hirshfeld partitioning procedure, called Hirshfeld-I.⁶³ In the k th iteration, the weight for atom i is given by

$$w_{i,\text{HI}}^k(r) = \frac{\rho_i^{k-1}(r)}{\sum_n \rho_n^{k-1}(r)} \quad (8)$$

Conveniently, the first iteration can use neutral atomic densities, leading to the classical Hirshfeld charges. Of course, the electronic populations, $N_i = \int w_i(r) \rho(r) dr$, are usually fractional numbers, and the corresponding densities are thus computed according to⁸⁰

$$\rho_i^k = \rho_i^{N_i} = \rho_i^{n+x} = x \cdot \rho_i^{n+1} + (1-x) \cdot \rho_i^n \quad (9)$$

where n is the integer part of N_i and $x = N_i - n$. The partitioning is converged if the electronic populations do not change significantly between two iterations (the convergence criterion was set to a root-mean-square deviation of 0.0005 au). Compared to the rest of the correction, the iterative scheme is computationally demanding, as integration over the entire grid is necessary for each iteration.⁸¹ For this reason, we also report values based on the classical Hirshfeld partitioning.

Finally, the determination of the dispersion coefficients from eqs 3–5 also depends on atomic polarizabilities. We herein follow Becke and Johnson's proposal to exploit the proportionality⁸² between polarizability and volume to estimate the effective atom in molecule (AIM) polarizabilities from tabulated free atomic polarizabilities:⁸³

$$\alpha_i = \frac{\langle r^3 \rangle_i}{\langle r^3 \rangle_{i,\text{free}}} \alpha_{i,\text{free}} = \frac{\int r^3 w_i(r) \rho(r) d^3r}{\int r^3 \rho_{i,\text{free}}(r) d^3r} \alpha_{i,\text{free}} = \frac{V_{i,\text{AIM}}}{V_{i,\text{free}}} \alpha_{i,\text{free}} \quad (10)$$

ii. The Damping. A key component of our dDXDM correction is the damping factor b . We showed previously⁴⁶ that the performance of the TT-damping function is improved by the introduction of a second damping function to prevent corrections at covalent distances. In the full TT model,⁷⁷ the attractive potential should give relatively strong contribution at short distances in order to soften the repulsive Born–Mayer potential. In contrast, a correction to DFT necessitates additional damping as density functionals better describe the region of strong density overlap (short-range). We herein introduce a variable, damped b , in which the second damping is intrinsically absorbed as an alternative to our previous model using a Fermi damping function.⁴⁶ In Tang and Toennies' seminal work,⁷⁷ the damping parameter b is also the range parameter of the repulsive Born–Mayer potential and thus depends on the two interacting atoms. Later, the same authors converted b from a constant into a function:⁸⁴ for an arbitrary repulsive potential $V(r)$,

$$b(r) = -\frac{d \ln V(r)}{dr} \quad (11a)$$

Here, we replace the distance dependence by the following form:

$$b(x) = F(x) \cdot b_{ij,\text{asym}} \quad (11)$$

x and $F(x)$ are respectively the damping argument and the function for $b_{ij,\text{asym}}$, the TT-damping factor associated with two separated atoms. $b_{ij,\text{asym}}$ is computed according to the combination rule:^{85,86}

$$b_{ij,\text{asym}} = 2 \frac{b_{ii,\text{asym}} \cdot b_{jj,\text{asym}}}{b_{ii,\text{asym}} + b_{jj,\text{asym}}} \quad (12)$$

The $b_{ii,\text{asym}}$ values are estimated^{87,88} by the square root of the atomic ionization energy $\sqrt{I_i}$ taken from the literature.⁸⁹ Inspired by the approach of Tkatchenko and co-workers,^{45,90} the atom in molecule character is taken into account through a cubic root scaling of the ratio between the free atom and the AIM volume. After introduction of the parameter b_0 , which determines the strength of the correction in the medium range, we arrive at

$$b_{ii,\text{asym}} = b_0 \cdot \sqrt{2I_i} \cdot \sqrt[3]{\frac{V_{i,\text{free}}}{V_{i,\text{AIM}}}} \quad (13)$$

Equation 14 proved to be the most robust form for the damping function⁹¹

$$F(x) = 1 - \frac{2 \arctan(a_0 \cdot x)}{\pi} \quad (14)$$

where the fitted parameter a_0 adjusts the short-range behavior of the correction.

The last element of the correction is the damping argument x

$$x = \text{abs} \left(q_{ij} + q_{ji} - \frac{(Z_i - N_i) \cdot (Z_j - N_j)}{r_{ij}} \right) \frac{N_i + N_j}{N_i * N_j} \quad (15)$$

where Z_i and N_i are the nuclear charge and Hirshfeld population of atom i (*vide supra*), respectively. The overlap population⁹² $q_{ij} = \int w_i(r) w_j(r) \rho(r) dr$ is a covalent bond index, and the fraction term in the parentheses is an ionic bond index.⁹³ The multiplicative factor, $(N_i + N_j)/(N_i \cdot N_j)$, serves to attenuate the damping of $b_{ij,\text{asym}}$ for heavier atoms (containing more electrons). Note that the damping function has an adequate form (i.e., $F(0) = 1$ and $F(\infty) = 0$), given that x is large for atoms near each other and vanishes with increasing r_{ij} distance.

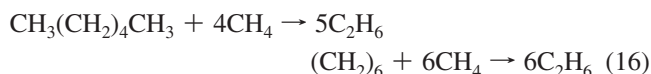
This is the first example for which the damping of an atom pair-wise dispersion correction depends on Hirshfeld (overlap) populations rather than on “critical” or “van der Waals” radii. Our approach is, however, similar in spirit to Slipchenko and Gordon's⁹⁴ overlap-matrix-based formula employed within the framework of the effective fragment potential method.

To summarize, the presented dDXDM correction uses electronic structure information to determine dispersion coefficients and two fitted damping parameters that are the strength of the TT-damping (b_0) and the steepness factor (a_0).

Determination of the Adjustable Parameters

In line with our former work,^{40,46} the chosen fitting procedure ensures a successful treatment of both weak intra- (short-range) and inter- (long-range) molecular interactions. From

a theoretical perspective, typical weakly bound systems, such as rare gas dimers, seem the appropriate choice as a training set. However, the description of rare gas dimers by standard density functionals is not consistent; for instance, PBE overbinds the helium dimer and underbinds the argon dimer (see the Supporting Information). Such behavior is not easily improved by a dispersion correction and highlights that inclusion of rare gas dimers into the training set does not necessarily guarantee a generally improved treatment of weak intra- and intermolecular interactions.^{95,96} In contrast, we and others demonstrated that the large DFT errors in the description of alkane intramolecular interactions (e.g., isomerization energies) are systematic^{9,12} and conveniently reduced by a dispersion correction.^{40,76,97–99} Our recent work, introducing a flexible TT-based correction,⁴⁶ demonstrated that using alkane reaction energies as a training set results in a highly transferable correction, which outperforms others, even for systems well outside the range of the training set (e.g., intermolecular complexes).⁴⁶ Akin to our former fitting procedure, the two parameters (a_0 and b_0) are fitted for each functional as to minimize the mean absolute deviation (MAD) over five reaction energies that are the Pople's isodesmic bond energy separation reaction of *n*-hexane and cyclohexane,



the folding energy of $\text{C}_{22}\text{H}_{46}$, and the isomerization energy of *n*-octane and *n*-undecane to 2,2,3,3-tetramethylbutane and 2,2,3,3,4,4-hexamethylpentane, respectively.

The best fit parameters are given in the Supporting Information for dDXDM (i.e., iterative Hirshfeld weights and terms up to C_{10}), dDXDMc (using classical Hirshfeld weights), dDXDM6 (iterative Hirshfeld weights, only up to C_6), and dDXDM6c (classical Hirshfeld weights and only up to C_6). Short form parenthetical notations that are used in the text refer to the two levels of correction with or without the parentheses (e.g., dDXDM6(c) refers to dDXDM6 and dDXDM6c).

Table S1 and Figure S1 (Supporting Information) illustrate that, for the models including terms up to C_{10} , best fit a_0 and b_0 correlate well with each other. There is also a good correlation between each of the fitted parameters and the repulsive character of the functional, as represented by the error in the methane dimer interaction energy shown in Figure S2 (Supporting Information).^{100,101} In contrast, the C_6 -based corrections show poor (dDXDM6) or even no (dDXDM6c) correlation between a_0 and b_0 . The missing higher order dispersion terms in dDXDM6c are compensated by relatively higher b_0 values.¹⁰² The a_0 parameters adjust accordingly following the repulsive character of the functional to prevent a too strong correction in the short range. These results emphasize the physical relevance of including higher dispersion terms to achieve a more consistent correction.

Test Sets

The robustness of the dDXDM correction is tested on seven illustrative sets featuring both intra- and intermolecular weak interactions, as described hereafter.

Three of the sets assess Pople's isodesmic bond separation equation reactions^{7,8} of saturated hydrocarbons (H, R, and C for chains, rings, and cages, respectively). As in ref 46, B3LYP/6-311+G** geometries and thermal corrections are included, and reference values are derived from experimental heats of formation.¹⁰³

The "intramolecular dispersion interactions in hydrocarbons" (IDHC)⁷⁶ set contains two isomerization reactions (*n*-octane and *n*-undecane to the fully branched isomer), two folding reactions of large hydrocarbon chains ($\text{C}_{14}\text{H}_{30}$ and $\text{C}_{22}\text{H}_{46}$), the dimerization of anthracene, and the hydrogenation reaction of [2.2]paracyclophane to *p*-xylene. Geometries and reference values are taken from ref 76.

The S22⁹⁶ set validates the performance of the correction on noncovalent complexes, while the P76 set test probes peptide conformational energies.¹⁰⁴ P76 contains 76 conformations of five small peptides having aromatic side chains (FGG, GFA, GGF, WG, and WGG). For these two sets, geometries and reference values (estimated CCSD(T)/CBS) are taken from the literature.^{105,106}

The last test set (EX3) exclusively features weak interactions involving heavy atoms in the dimers of pnictogen trihalides (NF_3 , NCl_3 , PCl_3 , PBr_3 , and AsBr_3).¹⁰⁷ Geometries (counterpoise corrected df-MP2/aug-cc-pVTZ) were taken from ref 107. Reference values (estimated CCSD(T)/CBS) were computed at the counterpoise corrected level¹⁰⁸ according to

$$\begin{aligned} E(\text{CCSD(T)/CBS}) &= \text{HF/AVQZ} + \\ &\quad \text{CCSD-F12b/CBS(AVTZ/AVQZ)} + \\ &\quad \text{(T)/CBS(AVDZ/AVTZ)} \quad (17) \end{aligned}$$

where aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ are abbreviated by AVDZ, AVTZ, and AVQZ, respectively. These computations were performed with Molpro2009.1¹⁰⁹ at the F12 level,¹¹⁰ with the HF energy containing the CABS single correction and the triples being based on F12 amplitudes. The *g* functions are omitted in all aug-cc-pVQZ computations, except for the heaviest dimer (i.e., $(\text{AsBr}_3)_2$). The extrapolation functional proposed by Helgaker and co-workers^{111,112} ($E_n^{\text{corr}} = E_{\text{CBS}}^{\text{corr}} + AX^{-3}$ with $X = 2, 3$, and 4 for AVDZ, AVTZ, and AVQZ, respectively) is applied *a posteriori* to the CCSD-F12b and (T) correlation energies.¹¹³ The T1 diagnostic was below 0.02 and the D1 diagnostic¹¹⁴ around 0.04, except for NCl_3 , where $\text{D1} \approx 0.065$ (monomer and dimer) is indicative of a multireference character. The NBr_3 dimer was discarded from the test set due to its $\text{D1} \approx 0.085$ and an unreliable basis-set convergence.

The performance of the dDXDM correction was further examined on four potential energy profiles: (a) the stacked benzene dimer (geometry and reference values taken from refs 115 and 116, respectively), (b) a propane dimer conformation (geometry based on the experimental geometry¹¹⁷ and arranged like in ref 118), (c) a benzene– H_2S complex (geometry and reference from ref 116), and (d) a benzene– H_2O complex (orientation analogous to the benzene– H_2S conformation, with the same benzene geometry¹¹⁹ and the experimental water geometry).¹¹⁷ For b and c, reference values were computed at the counterpoise corrected level.¹⁰⁸

$$E(\text{CCSD(T)/CBS}) = \text{df-MP2/CBS(AVDZ,AVTZ)} + \Delta\text{CCSD(T*)-F12b/AVDZ}$$

where $\Delta\text{CCSD(T*)-F12b/AVDZ}$ is the difference between df-MP2-F12 and CCSD(T*)-F12b evaluated with the aug-cc-pVDZ basis set, and (T*) stands for the perturbative triple corrections improved by scaling by the ratio of df-MP2-F12/df-MP2.¹²⁰

Finally, to ensure that the corrections do not affect covalent bonds, the performance on six representative atomization energies (AE6) and barrier heights (BH6)¹²¹ was investigated. Geometries and reference values were obtained from the Minnesota database collection.¹²² Errors for these two test sets are given in the Supporting Information.

Computational Methods

B97-D and B2PLYP-D computations with the cc-pVTZ basis set^{123–125} were performed with Turbomole 5.10^{126,127} using the resolution of identity (RI-MP2)¹²⁸ with matching auxiliary basis functions¹²⁹ to speed up B2PLYP. M06-2X energies were computed with NWChem 5.1^{130,131} using the “xfine” grid. All of the other computations were performed with a developmental version of Q-Chem 3.2.¹³² The cc-pVTZ basis set^{123–125} was used except for the potential energy curves, for which the larger aug-cc-pVTZ basis set was employed. The energy differences between cc-pVTZ and the larger aug-cc-pVTZ basis set were found to be negligible compared to the error of the method against the reference value¹³³ (e.g., the averaged total MAD for PBE/cc-pVTZ, 4.27 kcal mol^{−1}, differs by only 2%, 0.08 kcal mol^{−1}, from PBE/aug-cc-pVTZ, 4.20 kcal mol^{−1}; see Table S2 Supporting Information).

To ensure a consistent treatment between intra- and intermolecular interaction, no basis set superposition correction was applied (e.g., P76 contains peptide conformations with intramolecular interactions resembling closely those of intermolecular complexes in the S22 test set).

XDM-based corrections were done post-SCF. The iterative Hirshfeld partitioning was implemented using sphericalized restricted–open atomic densities computed on the fly (i.e., functional specific) with a 99/590 Euler–Maclaurin–Lebedev^{134,135} grid. The energy profiles were computed with a 99/302 Euler–Maclaurin–Lebedev grid. Otherwise, the SG1 grid¹³⁶ was used.

Results and Discussion

Figure 1 summarizes the mean absolute deviation for established methods tested on the seven sets described above. The difference between “standard” and “recent” functionals (M06-2X, B97-D, and B2PLYP-D) is significant for all of the test sets (averaged total MAD 5.0 vs 1.5 kcal mol^{−1}). As noted previously,⁴⁶ the performance of the recent functionals on hydrocarbon reaction energies (H, R, C, and IDHC) is significantly better than that of the standard ones (MAD of 3.8 and 12.9 kcal mol^{−1}, respectively), although chemical accuracy has yet to be obtained.

The MADs for the best performing variant of the correction (–dDXDM i.e., iterative Hirshfeld weights and terms up

to C₁₀) are shown in Figure 2a. Note that (un)corrected B2LYP (0.47 B88 + 0.53 HF + 0.73 LYP, same functional contributions as in B2PLYP⁷⁵) is not intended for “real world” applications but provides insight into the good performance of B2PLYP-D. Overall, dDXDM largely improves the parent functionals, yielding low errors. Over the seven corrected functionals tested, the averaged total MAD (TMAD) is 0.9 kcal mol^{−1} (min 0.74 (PBE0-dDXDM); max 1.11 (BLYP-dDXDM)), significantly lower than for the recent M06-2X, B97-D, and B2PLYP-D (1.5 kcal mol^{−1}, min 1.06 (B2PLYP-D)). The correction improves the IDHC energies for both PBE and HF (MAD of 12.3 and 22.2 kcal mol^{−1}, respectively) to a respectable mean absolute deviation of 1.6 kcal mol^{−1}. B2LYP- and BHHLYP-dDXDM give remarkably low MADs of 0.6 and 0.9 kcal mol^{−1} (B2PLYP-D gives 1.6 kcal mol^{−1}), while BLYP-dDXDM performs less convincingly (MAD of 3.6 kcal mol^{−1}) for this set. The robustness and range of applicability of dDXDM combined with various functionals is further illustrated by the consistent improvement of alkane BSE reaction energies and weak intermolecular interactions: averaged MADs for the HRC, P76 (relative conformational energies of small peptides), and S22 (intermolecular weak interactions) sets are 1.4, 0.7, and 0.9 kcal mol^{−1}, respectively, corresponding to roughly 10, 50, and 30% of the deviations of the uncorrected values (12.9, 1.3, and 3.2 kcal mol^{−1}). The 0.5 kcal mol^{−1} averaged MAD for the pure inorganic test set (EX3; vs an uncorrected 3.9 kcal mol^{−1}) is also rewarding. It is worthwhile noting that the proposed corrections do not affect significantly properties such as atomization energies and barrier heights (see the Supporting Information).

PBE0-dDXDM is the most accurate combination presented herein (TMAD of 0.74 kcal mol^{−1}) but dDXDM with the popular B3LYP functional is, as well, very satisfactory (TMAD of 0.82 kcal mol^{−1}). The best corrected GGA, PBE-dDXDM, performs nearly as well as PBE0-dDXDM with a TMAD of 0.84 kcal mol^{−1}. Such a performance is of interest for applications to large systems (or even bulk materials), where hybrid functionals are computationally considerably more demanding. Nevertheless, hybrid functionals, which generally outperform the GGA in many thermochemistry applications, provide the best dDXDM corrected results.

Classical Hirshfeld Partitioning and C₆-Only Dispersion Corrections. The reliability of simpler variants of the correction, i.e., including only terms up to C₆ or using Hirshfeld classical instead of iterative weights, has also been evaluated. The use of the classical Hirshfeld weights is of practical interest, as it is significantly less computationally demanding than the iterative version. In the BJ formalism, C₈/R^{−8} and C₁₀/R^{−10} terms are relatively inexpensive but have non-negligible contributions to the interaction energy at short internuclear separations.^{49,58,102} A comparison with the C₆ truncation is thus of theoretical relevance.

Figure 2a (dDXDM) and b (dDXDM6) reveal that the BSE of alkane cages, the IDHC, and the EX3 test sets are most affected by the truncation. Whereas the first two sets are characterized by a high number of short-range interactions, the effect in the EX3 interaction energies is more difficult

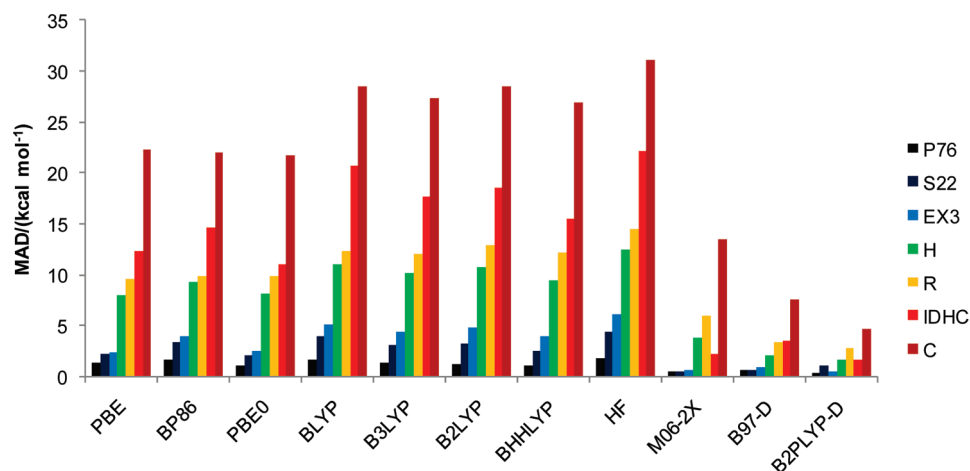


Figure 1. Performance for commonly used functionals: Mean absolute deviations for binding energies for noncovalent complexes (S22 and EX3); relative conformational energies of five small peptides (P76); and bond separation energies over hydrocarbon chains (H), rings (R), and cages (C) and for reaction energies of the test set “intramolecular dispersion interactions” (IDHC) using the cc-pVTZ basis set.

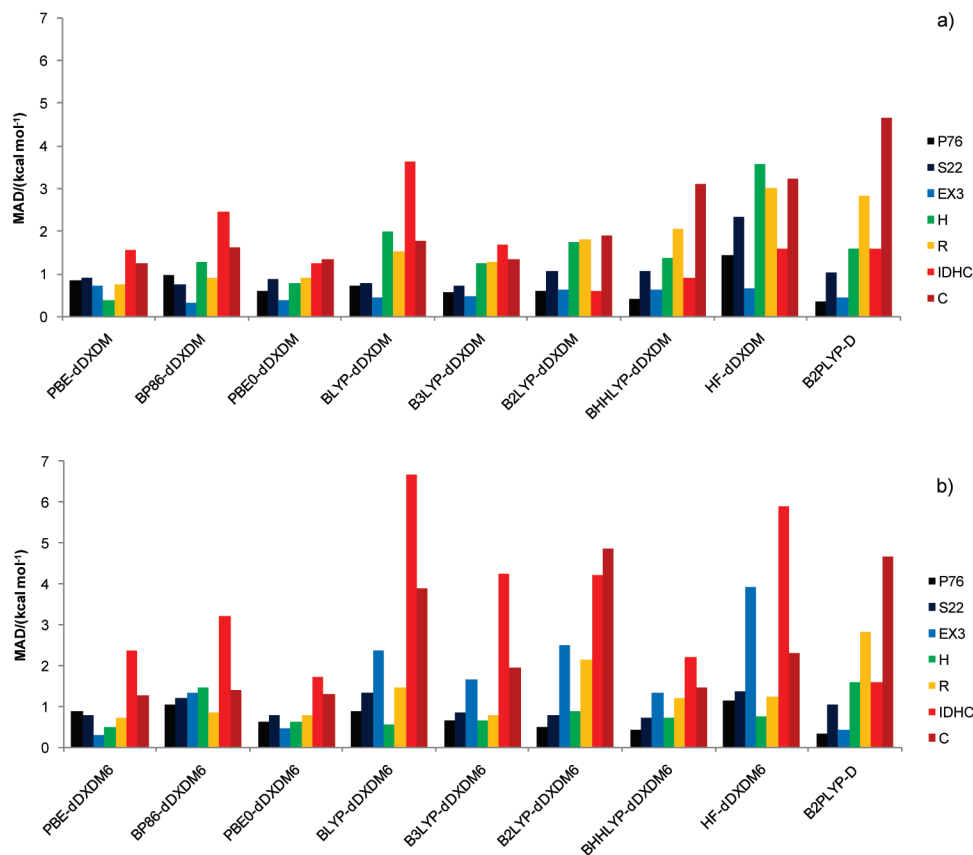


Figure 2. Performance for the iterative Hirshfeld-distributed dispersion coefficients up to C_{10} (a) and up to C_6 (b): Mean absolute deviations for binding energies for noncovalent complexes (S22 and EX3); relative conformational energies of five small peptides (P76); and bond separation energies over hydrocarbon chains (H), rings (R), and cages (C) and for reaction energies of the test set “intramolecular dispersion interactions” (IDHC) using the cc-pVTZ basis set. B2PLYP-D serves as an “internal standard”.

to interpret. Overall, only the combinations of dDXDM6 with PBE, PBE0, and BHHLYP match the dDXDM results closely.

For the higher-order multipole expansion, classical Hirshfeld weights result in larger errors than the iterative procedure (Figure 3). With an increase in averaged MAD from 0.9 (dDXDM) to 1.5 kcal mol⁻¹ (dDXDMc), the S22 test set is the most representative of the classical partitioning

limitation (underestimation of ionic characters).¹³⁷ As an example, the C_6 –(PBE) $O\cdots O/H\cdots H$ dispersion coefficients for the water dimer are 12.6/2.5 with classical Hirshfeld weights, compared to 21.2/0.9 with the iterative procedure. The key difference arises from the ionic bond index appearing in eq 13. The index for the $O\cdots O$ atom pair is 0.014 while using atomic densities (classical partitioning) and 0.15 after the iterative scheme. This difference translates

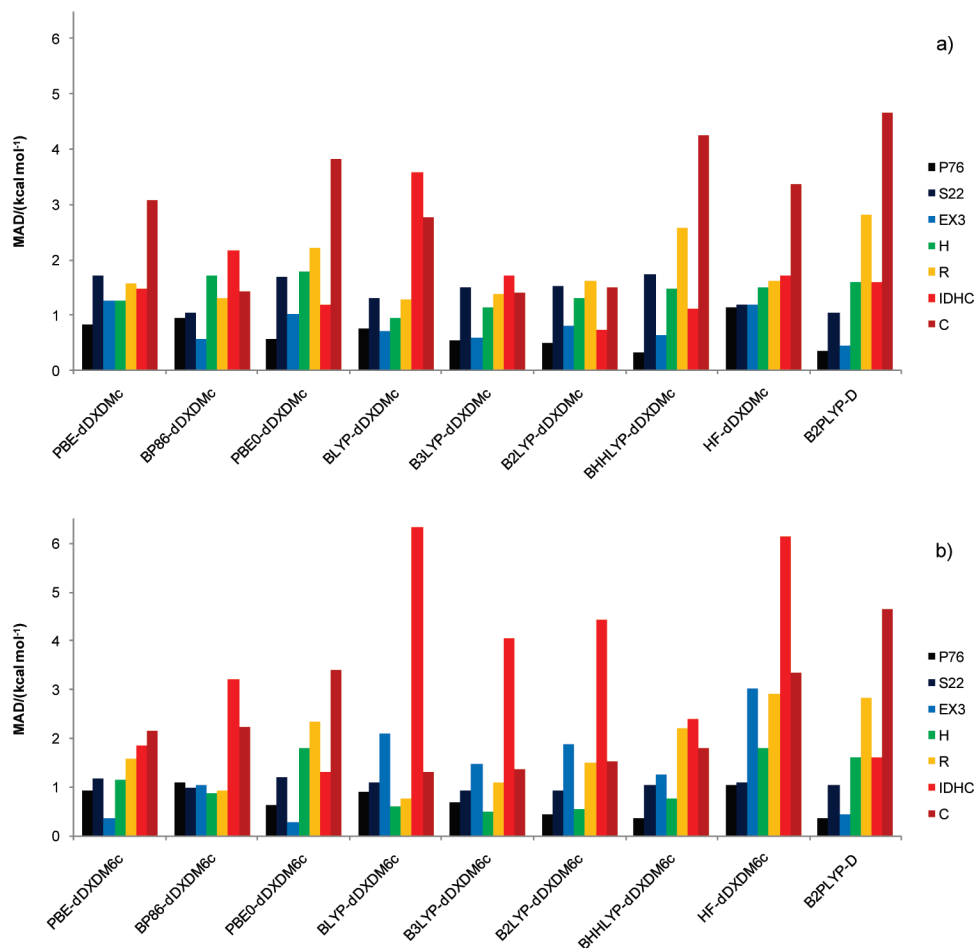


Figure 3. Performance for the classical Hirshfeld distributed dispersion coefficients up to C_{10} (a) and up to C_6 (b): Mean absolute deviations for binding energies for noncovalent complexes (S22 and EX3); relative conformational energies of five small peptides (P76); and bond separation energies over hydrocarbon chains (H), rings (R), and cages (C) and for reaction energies of the test set “intramolecular dispersion interactions” (IDHC) using the cc-pVTZ basis. B2PLYP-D serves as an “internal standard”.

into a strong/weak damping when iterative/classical Hirshfeld charges are used. As DFT methods correctly account for interaction energy between strongly polarized fragments (e.g., H bonds), higher iterative Hirshfeld charges (i.e., strong damping, small corrections) are better suited. In contrast, HF that systematically underestimates electrostatic interactions benefits from the larger dispersion corrections associated with the use of classical Hirshfeld weights. It is thus not surprising that Hartree–Fock gives its best results when combined with dDXDMc (TMAD of $1.3 \text{ kcal mol}^{-1}$, $\text{MAD}(\text{S22}) = 1.18 \text{ kcal mol}^{-1}$) and that HF-dDXDM is the least accurate variant (TMAD of $2.01 \text{ kcal mol}^{-1}$, $\text{MAD}(\text{S22}) = 2.32 \text{ kcal mol}^{-1}$). HF-dDXDMc could thus be a general alternative to the recent refined HF-D approach, which has been proven to be successful for intermolecular interactions.⁴⁸

For the reasons given above, the classical Hirshfeld partitioning performs better on the S22 set when terms only up to C_6 are included (see Figure 3b): excluding higher dispersion corrections attenuates the overcorrections of polar interactions. With TMADs below $1.0 \text{ kcal mol}^{-1}$, B3LYP-dDXDM6c and BHHLYP-dDXDM6c represent attractive alternatives to avoid the iterative scheme. As for the GGAs, PBE-dDXDM6c and BP86-dDXDMc are the most consistent over the seven sets tested (TMAD of 1.12 and $1.14 \text{ kcal mol}^{-1}$, respectively). Comparisons of B2LYP-dDXDM6(c)

to B2PLYP-D and B2LYP-dDXDM demonstrate that the C_6/R^6 -dispersion terms are not sufficient to correct B2LYP errors in the EX3 and IDHC sets. Including either higher dispersion terms semiempirically as in B2LYP-dDXDM(c) or adding a fraction of PT2 energy to give B2PLYP-D is crucial for these two test sets. Apart from those, B2LYP-dDXDM6(c) performs similarly to B2PLYP-D, even improving alkane BSE energies. Corrected B2LYP and B3LYP also tend to perform the same. The similarity relies on the fitting procedure used to determine the empirical parameters of both, B3LYP and B2PLYP.

Interaction Energy Profiles. Figure 4 shows potential energy curves of complexes typically underbound at the (hybrid)-GGA levels (stacked benzene dimer (a), propane dimer (b), and the benzene complex with water (c) and hydrogen sulfide (d)). The hybrid-meta-GGA M06-2X offers substantial improvement for the benzene– H_2S complex but under- and overbinds the stacked benzene dimer conformation and the water–benzene complex, respectively. PBE-dDXDM, B3LYP-dDXDM, and, to a lesser extent, B2PLYP-D overbind all four complexes, while the dDXDM6c corrections provide significantly better results for these weakly bound complexes (*vide infra*). Since B2PLYP-D suffers greatly from basis set superposition and incompleteness

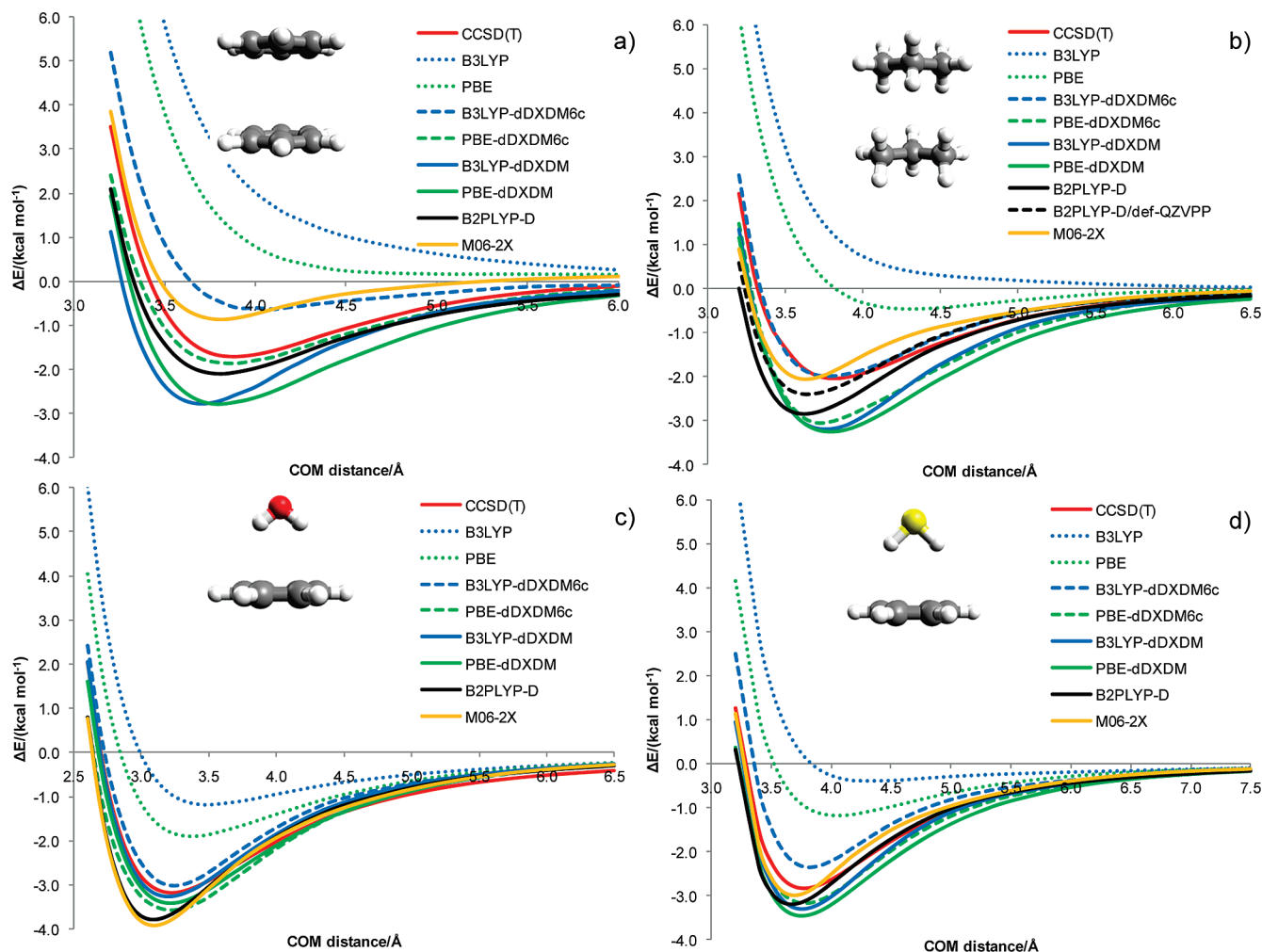


Figure 4. Interaction energy (ΔE) profiles for the (a) stacked benzene dimer, (b) propane dimer, (c) benzene–H₂O complex, and (d) benzene–H₂S complex. CCSD(T) references for a and d are taken from ref 116, while b and d are computed (see Test Sets). If not stated otherwise, density functional computations were performed with the aug-cc-pVTZ basis set.

Table 1. MAD (in kcal mol^{−1}) and Mean Absolute Relative Deviation (in percent) over All 67 Points of Figure 4

	MAD	mean absolute relative deviation
B3LYP	2.67	357.2
PBE	1.69	222.0
B3LYP-dDXDM6c	0.45	56.8
PBE-dDXDM6c	0.39	58.6
B3LYP-dDXDM	0.49	54.9
PBE-dDXDM	0.59	69.9
B2PLYP-D	0.47	81.8
M06-2X	0.41	75.2

errors,^{75,76} both B2PLYP-D/aug-cc-pVTZ and B2PLYP-D/def-QZVPP energy curves are reported for the propane dimer. As expected, the accuracy of the energy curve is drastically improved with the large def-QZVPP basis set.

The MAD and mean absolute relative deviation over all 67 points associated with the four potential energy curves are given in Table 1. Figure 5, on the other hand, displays the error in the propane dimer interaction energy. With the exception of PBE-dDXDM, all dispersion-corrected methods have MADs between 0.4 and 0.5 kcal mol^{−1}. PBE-dDXDM6c is the most accurate combination (MAD 0.39 kcal mol^{−1}). The distinctive performance of the current corrections is further emphasized by the remarkably low error in

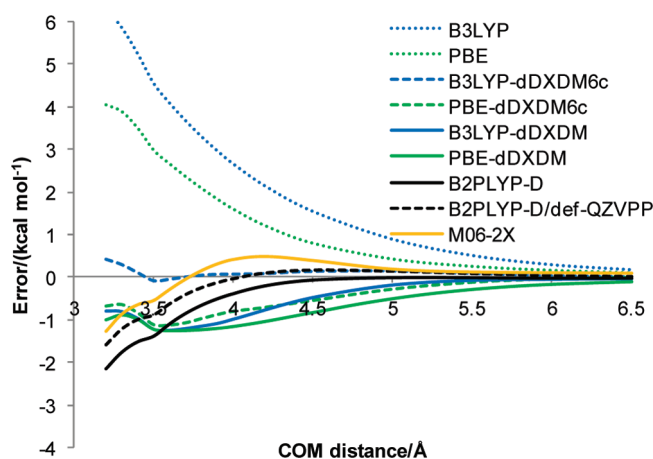


Figure 5. Errors (with respect to estimated CCSD(T)/CBS) in DFT interaction energies for the propane dimer.

both the short (i.e., repulsive wall) and long range of Figure 5. Overall, the error range spans between 55% (B3LYP-dDXDM) and 70% (PBE-dDXDM), thereby outperforming M06-2X (75%) and B2PLYP-D (80%) (Table 1).

As discussed earlier, DFT binding energies of the rare-gas dimers cannot be easily corrected by a dispersion correction. Nevertheless, those archetypical systems represent

a challenging set for testing the robustness of our correction, and their interaction energy profiles (i.e., helium, neon, and argon homodimers) are, for this reason, given in the Supporting Information (Figure S3). It can be seen that, whereas PBE overbinds after correction and is thus less satisfactory for rare-gas dimers, our corrected B3LYP and HF interaction energies compare well with M06-2X or B2PLYP-D, two other generally well performing approximations.

Conclusions

We have presented an improved scheme for computing system-dependent dispersion coefficients and damping parameters for a correction to density functional theory. The dispersion coefficients are evaluated exploiting the XDM formalism of Becke and Johnson^{37,55–59} and are distributed among the atoms according to $a(n)$ (iterative)⁶³ Hirshfeld⁷⁹ partitioning. The universal damping function of Tang and Toennies⁷⁷ is used with a damping factor depending on Hirshfeld (overlap) populations and charges as well as on two adjustable parameters. In addition to the fitted parameters and the density-based information, only free atomic polarizabilities and ionization energies are needed. Hence, the dDXDM correction is applicable to all elements of the periodic table and is easily combined with every density functional. This flexibility permits choosing a functional on the basis of its performance for properties not dominated by weak interactions (e.g., spin states and barrier heights), while still correcting any failures for weak interactions. The analysis of 30 (dispersion corrected) density functionals on 145 systems reveals that dDXDM(6c) largely reduces the error of the parent functionals for both inter- and intramolecular interactions. PBE0-dDXDM and PBE-dDXDM are the best performing hybrid-GGA and GGA, respectively, outperforming M06-2X and B2PLYP-D. The use of B3LYP-dDXDM is recommended as well, and it gives the second best overall performance.

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Supporting Information Available: Optimal a_0 and b_0 values for all corrections are given. (Corrected) PBE/aug-cc-pVTZ results are listed. Absolute and reaction energies for all systems and the detailed values used for estimating the CCSD(T)/CBS limit of the propane dimer and the benzene–H₂O complex are provided. Cartesian coordinates for the H, R, C test set, the propane dimer, and the benzene–H₂O complex as well as details on the rare gas dimers, barrier heights, and atomization energy test sets are also available.

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