

Accuracy of Several Wave Function and Density Functional Theory Methods for Description of Noncovalent Interaction of Saturated and Unsaturated Hydrocarbon Dimers

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S Supporting Information

ABSTRACT: The proper description of noncovalent complexes is a notoriously difficult problem, especially for complexes dominated by the dispersion energy. Accurate and reliable results can be obtained using computationally demanding methods such as the coupled clusters with iterative treatment of single and double excitations and perturbative triples correction (CCSD(T)), close to the complete basis set (CBS) limit. The sizes of the noncovalent complexes of interest, however, often exceed the computational capability of available computer facilities and software. Computationally efficient yet accurate and reliable theoretical methods are highly desired. In this work, we assembled a small test set of noncovalent complexes of un/saturated α /cyclic hydrocarbon (HC) dimers in order to inspect the accuracy and reliability of several routinely used low-order scaling wave function (WFT) and density functional theory (DFT) methods. The test set comprises dispersion dominated complexes of two different monomer types, saturated and unsaturated. The unsaturated systems are relatively well populated in one of the most popular training data sets for noncovalent complexes, the S22 set of Jurečka et al. The opposite is true for saturated systems, for which rather poor performance of “approximate” methods has been observed. From the results shown in this work, it is clear that unsaturated, e.g., $\pi\cdots\pi$ stacked, covalent complexes are described more accurately on average. With the exception of a few “balanced methods”, such as MP2C, MP2.5, SCS-/SCS(MI)-CCSD, or DFT-D₃ with the TPSS and PBE functionals, a simultaneous description of saturated and unsaturated HCs introduces serious errors (i.e., more than 1 kcal/mol).

1. INTRODUCTION

Noncovalent interactions are notoriously known to be of crucial importance in many chemical systems and processes. Although the noncovalent interactions are, by at least an order of magnitude weaker compared to covalent interactions, the stability, structure and properties of e.g. biomolecular systems such as DNA, RNA or proteins is strongly influenced by these interactions.^{1–4} The most prevalent motifs of noncovalent interactions are the Hydrogen bonds (H-bonds), dispersion interactions (such as $\pi\cdots\pi$ stacking), X-H $\cdots\pi$ interactions (X = C, O, N, S), halogen bonds, etc.

Generally speaking, the accurate description of noncovalent interactions requires the use of the most sophisticated computational methods, taking electron correlation properly into account such as CCSD(T) at the complete basis set limit (CBS). However, different types of noncovalent interactions have different demands in terms of the level of sophistication of the applied computational method, when “limited” accuracy (e.g., ~ 0.1 kcal/mol) is desired. Whereas H-bonding interactions are dominated by the electrostatic interactions^{5–7} and can thus be reasonably well described by Hartree–Fock (HF), second-order Møller–Plesset perturbation theory (MP2),⁸ or density functional theory (DFT), the dispersion

interaction (and especially $\pi\cdots\pi$ stacking) or X-H $\cdots\pi$ interactions require highly correlated methods such as the coupled-clusters method with connected triple excitations.^{9–11}

The two driving forces behind the development of computational methods suitable for noncovalent interaction calculations can be immediately recognized, one leading toward the increase of accuracy and reliability and the second leading toward the size of the system that can be efficiently treated. Due to the nature of (*ab initio*) quantum chemical methods, these two forces have the opposite direction. An enormous effort has been invested in the past few years in the development of accurate yet computationally efficient methods,⁹ either based on wave function theory (WFT), (DFT), or even semiempirical (SE) treatment.

Within the WFT domain, the principal role of MP2⁸ is clearly recognized. MP2 is computationally very efficient and well parallelizable (depending on the algorithm applied, up to superlinear speedups can be achieved¹²) and at the same time covers a major portion of the electron correlation. MP2 thus fairly well describes the most important components of the

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interaction energy, such as the induction, charge-transfer, electrostatic, and exchange contributions and also the dispersion energy. The latter one, i.e., the dispersion energy, deserves special attention. As already shown by Cybulski and Lytle¹³ and by Heßelmann et al.,¹⁴ the dispersion energy within the MP2 supermolecular approach is covered only at the uncoupled Hartree–Fock level (UCHF), which tends to be overestimated 10–20%. This error is manifest mostly in the $\pi\cdots\pi$ stacked complexes, for which the MP2 method is known to largely overestimate the interaction energy. Several modifications of the MP2 scheme, motivated by various physical arguments, have been introduced in order to alleviate this failure, such as SCS-MP2¹⁵ and its variants,^{16–19} or dispersion corrected MP2 schemes^{20,21} with varying success.

Keeping in mind the $O(N^7)$ scaling of the CCSD(T) method with the calculated system size, the $O(N^5)$ scaling methods, such as MP2, are not the only option for saving computer time. A quite successful approach developed recently was the so-called MP2.5 method.²² MP2.5 is essentially a scaled MP3 method using an empirical scaling parameter of 0.5, where the scaling of the third-order correlation contribution proved to improve the accuracy over both MP2 and MP3 in most of the tested noncovalent complexes. MP3 has a similar computational advantage to MP2, that is, a potential for large-scale parallelization. Another option in the realm of the $O(N^6)$ scaling methods is to utilize the scaling of the different spin components in a manner similar to that used in SCS-MP2, for the CCSD method.^{23,24} Several resulting SCS-CCSD parametrizations proved to be a major improvement over CCSD itself, with accuracy often comparable to that of CCSD(T).

Massive development is also taking place in the field of DFT. Traditional DFT functionals are known not to be suitable for applications on noncovalent complexes, especially when the dispersion energy represents a substantial fraction of the interaction energy. Two major routes in the development of DFT methods for noncovalent interactions have been followed. One utilizes empirical corrections for the dispersion energy,^{25–28} and the second, a more “rigorous” technique, vaguely speaking “integrates” the dispersion energy directly into the (exchange-)correlation functional.^{29–31} The most appealing feature of DFT over WFT methods is their computational efficiency. However, if a particular DFT method is not noticeably faster than the HF method, the advantage is not so obvious. HF often represents a computational bottleneck of post-HF calculations, such as MP2, even if the formal scaling of a post-HF method is higher than $O(N^4)$. As already mentioned, e.g., MP2 is a noniterative method, and if the Resolution-of-the-Identity^{32,33} (RI) or Cholesky Decomposition (CD)⁵⁶ of Atomic Orbital (AO) integrals with its parallelization potential is utilized, an MP2 calculation is often completed in a fraction of the time required for the HF step.

The majority of the recently developed methods discussed above utilize one or more empirical parameters. Numerical values of these parameters usually result from a fit to some database of benchmark results, often comprising noncovalent interaction energies. One such database is the well-known S22 database of Jurečka et al.³⁴ This database was the first of its kind designed to cover most of the important interaction motifs and contains noncovalent complexes of sizes on the edge of the computational (i.e., CCSD(T)) capabilities at the time of its origin. S22 contains interaction energies for several challenging $\pi\cdots\pi$ stacked complexes, such as the benzene and uracil dimers and the adenine–thymine dimer, which are difficult to describe

at a theoretical level inferior to CCSD(T). However, as there are too many examples of H-bonding and stacking interactions, the set cannot be said to represent all noncovalent interaction types. This can lead to the failure of approximate methods parametrized against S22 applied on studies of noncovalent complexes dominated by different interaction types such as, for instance, the description of aliphatic hydrocarbon dimers using SCS-MP2.³⁵

For the purposes of this article, we have selected dispersion dominated noncovalent complexes of saturated and unsaturated hydrocarbons (HCs). The goal is to demonstrate the differing accuracy of commonly used computational methods for aliphatic (poorly represented in S22) and $\pi\cdots\pi$ dispersion dominated complexes (fairly well represented in S22). We investigate a series of unsaturated molecules, either conjugated polyenes or (aromatic) cyclopolyenes, and a series of saturated acyclic and cyclic polycarbons. At first glance, it may appear that this is an artificially assembled test set without any direct relevance for, e.g., biologically relevant systems, but we believe the opposite is true. While the importance of stacking interactions in DNA or proteins⁹ is notoriously known, the importance of the aliphatic dispersion interaction is often not appreciated enough. According to Berka et al.,³⁶ aliphatic–aliphatic (so-called “hydrophobic”) interactions between amino acid residues are the most abundant in proteins, especially in a protein’s hydrophobic core. Aliphatic–aliphatic interactions also play a key role in membranes. Furthermore, in situations where the stacked geometry of a complex of aromatic species is not the most populated (e.g., in proteins³⁶), the magnitude of the interaction is not so much different than that of aliphatic complexes. Thus a “disproportional” parametrization of an approximate method toward excellent performance on $\pi\cdots\pi$ stacked complexes is not the best route for development of a widely applicable method for noncovalent interactions.

2. ELECTRONIC STRUCTURE METHODS

In order to compare the tested computational methods, we calculated the most accurate interaction energies obtainable at a particular theoretical level in terms of convergence toward the CBS limit. As rather different basis sets and CBS extrapolation schemes had to be set up for different computational methods, let us analyze them one by one. Let us finally note that in all the correlated WFT calculations, the frozen core approximation was utilized along with the counterpoise (CP) correction³⁷ for the Basis Set Superposition Error (BSSE).

Benchmark interaction energies were obtained at the approximate CCSD(T)/CBS level. We took advantage of the well-known rate of convergence of the second- and post-second-order correlation contributions by calculating them using the largest basis sets possible, which varied according to the size of the system

$$\Delta E_{\text{CBS}}^{\text{CCSD(T)}} = \Delta E_{\text{CBS}}^{\text{MP2}} + (\Delta E^{\text{CCSD(T)}} - \Delta E^{\text{MP2}})_{\text{small basis set}} \quad (1)$$

where $\Delta E_{\text{CBS}}^{\text{MP2}}$ is the sum of the HF term, $\Delta E_{\text{CBS}}^{\text{HF}}$, and the second-order correlation term $\Delta E_{\text{CBS}}^{\text{MP2corr}}$. The first of these terms was approximated by the HF value calculated with the aug-cc-pVQZ basis set, which is known to be essentially converged toward the CBS limit.³⁸ The second term, the MP2 correlation energy, was extrapolated according to Halkier et al.³⁹

$$E_X^{\text{corr}} = E_{\text{CBS}}^{\text{corr}} + BX^{-3} \quad (2)$$

from aug-cc-pVTZ and aug-cc-pVQZ basis sets. The CCSD(T) calculations were done consistently using the aug-cc-pVDZ basis set. According to several benchmark investigations,^{10,21,40} use of the aug-cc-pVDZ basis set is known to deliver accuracy in the $\Delta E^{\text{CCSD(T)}}$ term of about 0.1 kcal/mol for complexes similar to those calculated in this work. For the smallest complexes, with monomers containing less than five carbon atoms, CCSD(T)/aug-cc-pVTZ calculations were computationally feasible and thus were employed here, as they serve as even more accurate benchmarks.

The methodology for obtaining interaction energies using $O(N^6)$ scaling methods, i.e., iterative SCS-CCSD²³ and SCS(MI)-CCSD²⁴ and noniterative MP2.5,²² is analogous to the one used for CCSD(T)/CBS, i.e.

$$\Delta E_{\text{CBS}}^{\text{post-MP2}} = \Delta E_{\text{CBS}}^{\text{MP2}} + (\Delta E^{\text{post-MP2}} - \Delta E^{\text{MP2}})_{\text{small basis set}} \quad (3)$$

where the “post-MP2”, as clear from the designation, stands for the post-MP2 method, such as CCSD or MP3. Despite the fact that, due to the computational efficiency of these methods we could have afforded to use larger basis sets, we decided to use exactly the same ones as for the CCSD(T) calculations. Since both CCSD and MP3 have similar basis set convergence patterns as CCSD(T), it is more appropriate to use the same basis sets in order to make comparisons.

Rather diverse methodologies were applied for the $O(N^5)$ scaling methods under consideration, i.e., SCS-MP2,¹⁵ SCS(MI)-MP2,¹⁷ DW-MP2,¹⁹ MP2C,²¹ and the $O(N^4)$ scaling SOS-MP2¹⁸ and SOS(MI)-MP2¹⁷ methods (abbreviation “MI” stands for “Molecular Interactions”). SCS-MP2 interaction energies were calculated in series of both augmented and nonaugmented cc-pVXZ, $X = D, T, Q$ basis sets, while other spin-component scaled variants of MP2 were calculated only in series of nonaugmented cc-pVXZ basis sets. The primary reason for using nonaugmented basis sets results from the fact that “(MI)” spin-component scaling coefficients were parametrized only for these types of basis sets. Therefore, calculating all the spin-component scaled MP2 methods using the same types of basis sets does not penalize any particular parametrization. SCS-MP2 interaction energies obtained using the series of augmented basis sets will serve the comparison with nonaugmented results in order to validate their use. Basis set extrapolations were carried out analogously to $\Delta E_{\text{CBS}}^{\text{MP2}}$ from eq 1.

In the so-called “dispersion-weighted” MP2, DW-MP2,¹⁹ interaction energies are calculated as

$$\Delta E_{\text{DW-MP2}} = w\Delta E_{\text{MP2}} + (1 - w)\Delta E_{\text{SCS-MP2}} \quad (4)$$

where “ w ” is a system-dependent weight factor defined in ref 19. Explicitly correlated MP2 energies required for calculation of “ w ” were carried out using the series of aug-cc-pVXZ basis sets ($X = D, T, Q$), utilizing the “3C” ansatz, in analogy with works of Marchetti and Werner.^{19,41} Due to the fact that the weight factor contains two empirical parameters fitted against the explicitly correlated CCSD(T*)-F12a interaction energies for the S22 database, DW-MP2 results are not extrapolated.

The MP2C calculations were performed using the series of aug-cc-pVXZ basis sets ($X = D, T, Q$), and the resulting total MP2C interaction energies were extrapolated according to a $1/X^3$ formula.

All the HF, MP2, and post-MP2 calculations were performed using the MOLPRO package⁴² of ab initio programs utilizing the density fitting approximation, when applicable. For HF

calculations, cc-pV(X+1)Z/JKFIT and, for MP2 (and its spin-component scaled variants), aug-cc-pV(X+1)Z/MP2FIT auxiliary basis sets were used for (aug-)cc-pVXZ orbital basis sets of cardinality “ X ” ($X = D, T, Q$).

Two different DFT approaches capable of describing dispersion interactions were used in this work. One set of tested DFT methods comprised (several variants of) the empirical dispersion energy based on the C_6R^{-6} formula. Another DFT approach applied was the M06-2X functional developed by Truhlar and Zhao,^{29–31} inherently capable of describing the dispersion energy.

As for the dispersion corrected DFT methods, i.e., “DFT-D”, we used the empirical dispersion correction according to Jurečka et al.,^{25,26} “ D_J ”, as well as the D_2 ²⁷ and D_3 ²⁸ corrections developed by Grimme and co-workers. According to suggestions of the authors, we used the TPSS⁴³ and PBE^{44,45} functionals along with the 6-311++G(3df,3pd)^{46–48} basis set in combination with D_J . For the D_2 and D_3 dispersion correction terms, the TPSS, PBE, and BLYP functionals were used along with the def2-QZVP⁴⁹ basis set. All DFT-D calculations were done using the TURBOMOLE package.⁵⁰

Calculations using the M06-2X functional utilized the aug-cc-pVTZ basis set and were performed using the Gaussian '09 program package.⁵¹

3. COMPLEXES INVESTIGATED

Geometries of the complexes considered in this work, except for the benzene dimer, which was taken from the S22 data set,³⁴ were obtained in a three-step optimization procedure. The first step involves geometry optimization of the isolated monomers, which was carried out at the MP2/cc-pVTZ level. The optimized acyclic saturated, small cyclic saturated (cyclopropane and cyclobutane), as well as the cyclic unsaturated HCs were planar in the carbon backbone. The (most stable) *trans*-1,3-butadiene and *trans*-1,3,5-hexatriene were planar as well, but the cyclopentane and cyclohexane possessed the envelope and chair conformations, respectively.

In the second step of the optimization, a few starting geometries for each dimer were “manually” prepared and optimized at the DFT-D/TPSS/6-311++G(3df,3pd) level. For each saturated acyclic and cyclic HC dimer, we selected and further analyzed typically three different conformations. The number of analyzed structures was eight and five for the acyclic unsaturated HC dimers and the cyclobutadiene dimer, respectively. In all of these dimer geometries, the monomers were mutually parallel except for the cyclopentane and cyclohexane dimers, due to their monomer geometry. By consideration of several different starting dimer conformations, we increased the probability of converging to the global minimum on the potential energy surface (PES). A more rigorous approach would rely on quenching, metadynamics, or some other similar scheme, but for the sake of this study, it is not critical to work with the exact minimum energy structures. A reliable theoretical method should deliver acceptable accuracy for a reasonably wide range of nonequilibrium geometries, but the most representative certainly is the performance on an equilibrium structure. In the last step, the “global minimum” structure is selected from the optimized structures as the one with the lowest CP corrected MP2/aug-cc-pVTZ interaction energy.

As was already mentioned, the optimized dimers, except for the cyclopentane and cyclohexane dimers, have parallel configuration. The monomers in the 1,3-cyclobutadiene,

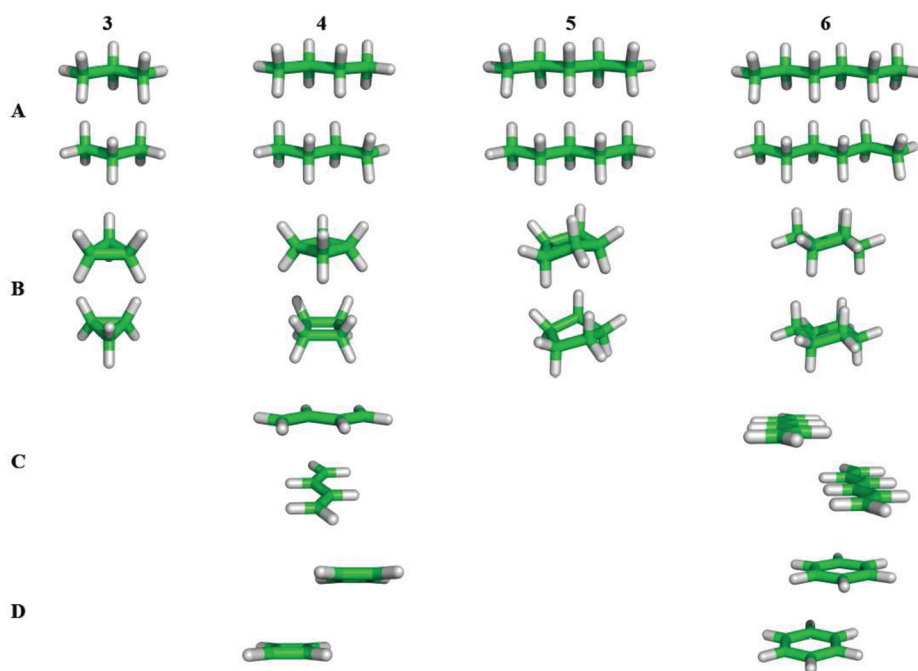


Figure 1. The optimized structures of studied saturated acyclic (A), saturated cyclic (B), unsaturated acyclic (C), and unsaturated cyclic (D) HCs dimers.

benzene, and 1,3,5-hexatriene dimers are mutually displaced, while in the 1,3-butadiene dimer, the monomers are mutually twisted by approximately 90° around the axis perpendicular to the monomer planes. The cyclopropane and cyclobutane are bound in tight parallel-like configuration with the monomers rotated around the centroid of the molecules by about 180° and 90° , respectively. The saturated acyclic HC monomers are mutually rotated around the two peripheral carbon atoms by 180° . The optimized HCs' dimer structures are shown in Figure 1, and the atomic coordinates are provided in the Supporting Information.

4. RESULTS

The interaction energies of the studied systems were calculated at the DFT level with an empirical correction for the dispersion energy (BLYP, PBE, and TPSS DFT functionals with Jurečka's D_j and Grimme's D_2 and D_3 corrections) as well as without, using Truhlar's M06-2X method. The WFT studies were carried out at the HF, MP2, modified MP2 (MP2C, DW-MP2, SCS-MP2, and SCS(MI)-MP2), and post-MP2 (MP2.5, CCSD, SCS-CCSD, SCS(MI)-CCSD and CCSD(T)) levels.

The calculated interaction energies are shown separately for acyclic saturated HC dimers, Table 1, cyclic saturated HC dimers, Table 2, and finally the unsaturated acyclic and cyclic HC dimers, Table 3. Graphical representations of the accuracy of the tested methods are found in Figures 2, 3, and 4, where each figure shows the deviation of a particular computational method from the estimated CCSD(T)/CBS reference. Positive deviations indicate overestimation of the stabilization energy with respect to the reference, whereas negative deviations indicate the opposite.

A detailed discussion on the obtained results is found in sections 4.1, 4.2, and 4.3.

4.1. DFT Method with Dispersion Correction. The (empirically corrected as well as plain) DFT methods involved in this study represent, to the best of our knowledge, the most

routinely used approaches for calculation of noncovalent interactions at this theoretical level. Except for Truhlar's M06-2X method, all tested methods are "standard" DFT functionals (i.e., TPSS, PBE, and BLYP) with different versions of the empirical correction for the dispersion energy, i.e., D_j , D_2 , and D_3 , as referenced above. As will be discussed further, quite a diverse performance, in terms of the accuracy for comparable computational cost, is obtained.

Despite the fact that the DFT methods are almost exclusively applied without CP corrections for the BSSE, we have carried out the calculations including the CP correction as well to make sure that the sources of errors have different origins.

Let us start with the discussion concerning results obtained for *saturated acyclic HCs*, as shown in Table 1 and Figures 2 and 3. The benchmark order of stability for the propane to hexane dimers is correctly reproduced by all the DFT methods. Generally, the absolute stabilization energies are overestimated by as much as 0.84 to 1.96 kcal/mol (for the DFT- D_j propane and hexane dimers) or slightly underestimated by 0.09 to 0.03 kcal/mol (for M06-2X propane to pentane dimers). The DFT results differ mutually by about the same magnitude, because the M06-2X method reproduces the CCSD(T)/CBS benchmarks the most faithfully for these complexes.

As can be seen from Figure 2, the quality of the DFT results is the most diverse, particularly for this category of complexes. The performance of the empirically corrected DFT method utilizing the TPSS and PBE functionals greatly depends on the level of the dispersion correction used. While DFT- D_j /TPSS reaches the maximum error for the hexane dimers, almost 2 kcal/mol, the same functional when combined with the latest generation of Grimme's dispersion correction, i.e., DFT- D_3 /TPSS, delivers the second most accurate description for these complexes with an absolute error below 0.3 kcal/mol. On the other hand, the performance of the DFT methods utilizing the BLYP functional is only slightly improved using $-D_3$ instead of the $-D_2$ empirical dispersion correction. Moreover, the second

Table 1. The DFT, MP2, Modified-MP2, and Post-MP2 Interaction Energies [kcal/mol] for Dimers of Acyclic Saturated HCs—Propane, Butane, Pentane, and Hexane

method	propane	butane	pentane	hexane	method	propane	butane	pentane	hexane
DFT-DJ/TPSS ^a	−2.899 (−2.694)	−4.123 (−3.833)	−5.355 (−4.983)	−6.610 (−6.150)	SCS-MP2/cc-pV (DT)Z	−1.096	−1.600	−2.132	−2.662
DFT-DJ/PBE ^a	−2.666 (−2.480)	−3.694 (−3.425)	−4.740 (−4.392)	−5.813 (−5.379)	SOS-MI-MP2/ cc-pV(DT)Z	−1.672	−2.441	−3.223	−4.015
DFT-D2/TPSS ^a	−2.820 (−2.791)	−4.032 (−3.981)	−5.255 (−5.182)	−6.490 (−6.390)	SSS-MI-MP2/cc- pV(DT)Z	−1.409	−2.050	−2.718	−3.385
DFT-D2/PBE ^a	−2.860 (−2.836)	−4.001 (−3.956)	−5.136 (−5.071)	−6.296 (−6.207)	SCS-MI-MP2/ cc-pV(DT)Z	−1.490	−2.169	−2.872	−3.577
DFT-D2/BLYP ^a	−2.646 (−2.627)	−3.925 (−3.887)	−5.203 (−5.145)	−6.510 (−6.429)	SOS-MP2/cc-pV (TQ)Z	−1.158	−1.668	−2.201	−2.737
DFT-D3/TPSS ^a	−2.238 (−2.209)	−3.120 (−3.069)	−4.034 (−3.961)	−4.951 (−4.852)	SCS-MP2/cc-pV (TQ)Z	−1.185	−1.706	−2.252	−2.799
DFT-D3/PBE ^a	−2.406 (−2.382)	−3.300 (−3.256)	−4.222 (−4.158)	−5.154 (−5.065)	SOS-MI-MP2/ cc-pV(TQ)Z	−1.597	−2.305	−3.026	−3.758
DFT-D3/BLYP ^a	−2.576 (−2.557)	−3.726 (−3.688)	−4.854 (−4.797)	−6.033 (−5.952)	SSS-MI-MP2/cc- pV(TQ)Z	−1.313	−1.888	−2.493	−3.097
M06-2X ^a	−1.966 (−1.877)	−2.886 (−2.749)	−3.745 (−3.569)	−4.649 (−4.424)	SCS-MP2/ cc-pV(TQ)Z	−1.422	−2.048	−2.699	−3.352
DF-HF/CBS	2.135	3.106	3.983	4.917	SCS-MP2/aug- cc-pVDZ	−0.799	−1.181	−1.602	−2.016
DF-MP2/CBS	−2.116	−3.048	−3.988	−4.946	SCS-MP2/aug- cc-pVTZ	−1.060	−1.531	−2.032	−2.532
MP2C/aug-cc- pVDZ	−1.699	−2.449	−3.204	−3.972	SCS-MP2/aug- cc-pVQZ	−1.130	−1.626	−2.148	−2.672
MP2C/aug-cc- pVTZ	−2.055	−2.924	−3.785	−4.665	SCS-MP2/CBS	−1.181	−1.695	−2.233	−2.774
MP2C/aug-cc- pVQZ	−2.144	−3.042	−3.938	−4.852	MP2.5/CBS ^b	−1.934 (−1.929)	−2.734 (−2.727)	−3.540	−4.360
MP2C/CBS	−2.210	−3.128	−4.050	−4.989	CCSD/CBS ^b	−1.545 (−1.463)	−2.160 (−2.043)	−2.784	−3.418
DW-MP2/aug- cc-pVDZ	−1.178	−1.695	−2.244	−2.793	SCS-CCSD/ CBS ^b	−2.165 (−2.130)	−3.055 (−3.001)	−3.942	−4.849
DW-MP2/aug- cc-pVTZ	−1.199	−1.723	−2.275	−2.828	SCS-MI-CCSD/ CBS ^b	−2.215 (−2.173)	−3.127 (−3.061)	−4.035	−4.964
DW-MP2/aug- cc-pVQZ	−1.202	−1.727	−2.280	−2.834	CCSD(T)/CBS ^b	−2.055 (−2.064)	−2.912 (−2.921)	−3.772	−4.649
SOS-MP2/cc-pV (DT)Z	−1.161	−1.696	−2.255	−2.815					

^aThe results in parentheses are the CP corrected interaction energies. ^bThe $\Delta E^{\text{post-MP2}}$ term calculated using the aug-cc-pVTZ basis sets

generation of Grimme's dispersion correction has a unique property of delivering results of about the same quality for these complexes, irrespective of the DFT functional used.

The effect of the CP correction is noticeable only in the case of the DFT-D_j/TPSS method, where it leads to a decrease of the error by about 0.2 to 0.5 kcal/mol for propane to hexane dimers.

Table 2, as well as Figures 2 and 3, present the results obtained for the DFT calculations of *cyclic saturated HCs*. In contrast to the results for the acyclic saturated HCs, the span of errors is notably narrower, about 1.2 kcal/mol (maximum reached for the DFT-D_j/TPSS cyclopentane dimer), but the reference order of stability, i.e., cyclopentane > cyclobutane > cyclohexane > cyclopropane dimers, of the dimers is incorrectly reproduced by the DFT-D_j/PBE, DFT-D₃/TPSS, and DFT-D₃/PBE methods. According to the CCSD-(T)/CBS benchmark, cyclobutane is only 0.2 kcal/mol more stable than cyclohexane, while the opposite is predicted by the three aforementioned DFT methods. DFT-D_j/PBE predicts cyclohexane to be more stable than cyclobutane by about 0.25 kcal/mol, the DFT-D₃ methods based on the TPSS and PBE functionals predict these differences to be about 0.19 and 0.25 kcal/mol, respectively. It is worth noting that all of the tested WFT methods predicted the order of stability correctly, as discussed below. Surprisingly, the DFT-D₃/TPSS method is the most accurate one for these types of complexes, measured by the maximum deviation from the reference. The maximum error is reached for the cyclohexane dimer, where the DFT-D₃/TPSS underestimates the

stability of the complex by 0.35 kcal/mol, while all other complexes are described accurately within an error of 0.1 kcal/mol.

Inclusion of the CP correction does not improve the performance of the DFT methods utilizing the “-D₃” dispersion correction, neither does it eliminate the wrong ordering of the stability of the complexes in all of the problematic cases. What is, however, significantly improved is the performance of the “most outlying” DFT-D_j/TPSS method, leaving the DFT-D₂ methods as the worst performer.

The DFT results for both cyclic and acyclic unsaturated HC dimers with alternating double bonds are summarized in Table 3 and graphically shown in Figures 2 and 3. This is the most diverse set of complexes, because it comprises both the cyclic and acyclic monomers with delocalized unsaturated as well as aromatic character. Nevertheless, more accurate results are (both expected and) obtained compared to the saturated HC dimers. This can be attributed to the fact that one of the complexes of this subset, the benzene dimer, is a notorious member of most of the noncovalent complex benchmark data sets used for parametrization of (empirical dispersion corrected) DFT methods.

The order of stability according to our CCSD(T)/CBS benchmark is the following: hexatriene > benzene > butadiene > cyclobutadiene dimer. The difference between the stability of the hexatriene and benzene dimers is substantive, i.e., about 1.8 kcal/mol, while the difference between the butadiene and cyclobutadiene dimers is only about 0.3 kcal/mol. Similarly to

Table 2. The DFT, MP2, Modified-MP2, and Post-MP2 Interaction Energies [kcal/mol] for Dimers of Cyclic Saturated HCs—Cyclopropane Dimer, Cyclobutane Dimer, Cyclopentane Dimer, and Cyclohexane

method	cyclopropane	cyclobutane	cyclopentane	cyclohexane	method	cyclopropane	cyclobutane	cyclopentane	cyclohexane
DFT-DJ/TPSS ^a	−3.059 (−2.849)	−4.110 (−3.833)	−4.605 (−4.246)	−3.895 (−3.659)	SCS-MP2/cc-pV (DT)Z	−1.280	−1.674	−2.101	−1.574
DFT-DJ/PBE ^a	−2.491 (−2.295)	−3.494 (−3.245)	−4.117 (−3.796)	−3.747 (−3.535)	SOS-MI-MP2/ cc-pV(DT)Z	−1.794	−2.420	−2.986	−2.389
DFT-D2/TPSS ^a	−3.087 (−3.036)	−4.011 (−4.009)	−4.654 (−4.655)	−3.777 (−3.814)	SSS-MI-MP2/cc- pV(DT)Z	−1.659	−2.165	−2.661	−1.987
DFT-D2/PBE ^a	−3.093 (−3.048)	−3.945 (−3.958)	−4.471 (−4.489)	−3.611 (−3.666)	SCS-MI-MP2/ cc-pV(DT)Z	−1.718	−2.258	−2.775	−2.106
DFT-D2/BLYP ^a	−2.959 (−2.914)	−3.977 (−3.994)	−4.551 (−4.580)	−3.633 (−3.701)	SOS-MP2/cc-pV (TQ)Z	−1.361	−1.763	−2.169	−1.619
DFT-D3/TPSS ^a	−2.173 (−2.122)	−2.899 (−2.897)	−3.484 (−3.485)	−3.089 (−3.126)	SCS-MP2/cc-pV (TQ)Z	−1.405	−1.816	−2.228	−1.652
DFT-D3/PBE ^a	−2.308 (−2.263)	−3.074 (−3.087)	−3.608 (−3.626)	−3.326 (−3.381)	SOS-MI-MP2/ cc-pV(TQ)Z	−1.772	−2.347	−2.853	−2.229
DFT-D3/BLYP ^a	−2.602 (−2.556)	−3.513 (−3.530)	−4.116 (−4.144)	−3.270 (−3.338)	SSS-MI-MP2/cc- pV(TQ)Z	−1.602	−2.056	−2.496	−1.813
M06-2X ^a	−2.086 (−1.981)	−2.520 (−2.405)	−3.537 (−3.344)	−2.214 (−2.029)	SCS-MI-MP2/ cc-pV(TQ)Z	−1.683	−2.182	−2.648	−1.970
DF-HF/CBS	1.719	2.615	2.959	2.954	SCS-MP2/aug- cc-pVDZ	−0.967	−1.311	−1.651	−1.175
DF-MP2/CBS	−2.314	−3.087	−3.712	−2.934	SCS-MP2/aug- cc-pVTZ	−1.258	−1.643	−2.045	−1.500
MP2C/aug-cc- pVDZ	−1.826	−2.483	−2.889	−2.321	SCS-MP2/aug- cc-pVQZ	−1.341	−1.739	−2.147	−1.583
MP2C/aug-cc- pVTZ	−2.208	−2.925	−3.407	−2.741	SCS-MP2/CBS	−1.402	−1.809	−2.221	−1.643
MP2C/aug-cc- pVQZ	−2.307	−3.045	−3.537	−2.859	MP2.5/CBS ^b	−2.120 (−2.119)	−2.778 (−2.774)	−3.262	−2.548
MP2C/CBS	−2.379	−3.132	−3.632	−2.945	CCSD/CBS ^b	−1.725 (−1.654)	−2.232 (−2.128)	−2.605	−1.978
DW-MP2/aug- cc-pVDZ	−1.446	−1.827	−2.274	−1.646	SCS-CCSD/ CBS ^b	−2.279 (−2.268)	−3.044 (−3.001)	−3.546	−2.827
DW-MP2/aug- cc-pVTZ	−1.465	−1.858	−2.303	−1.676	SCS-MI-CCSD/ CBS ^b	−2.347 (−2.322)	−3.127 (−3.071)	−3.635	−2.899
DW-MP2/aug- cc-pVQZ	−1.462	−1.863	−2.308	−1.679	CCSD(T)/CBS ^b	−2.219 (−2.237)	−2.943 (−2.954)	−3.433	−2.743
SOS-MP2/cc-pV (DT)Z	−1.319	−1.742	−2.185	−1.670					

^aThe results in parentheses are the CP corrected interaction energies. ^bThe $\Delta E^{\text{post-MP2}}$ term calculated using the aug-cc-pVTZ basis sets

the cyclic saturated HCs, the order of stability is incorrectly predicted by some of the tested methods. The DFT methods augmented with the “-D₂” dispersion favor cyclobutadiene for the butadiene dimer, but only by about 0.05, 0.1, and 0.3 kcal/mol in the cases of DFT-D₂/TPSS, DFT-D₂/PBE, and DFT-D₂/BLYP, respectively.

Disregarding the DFT-D₂/BLYP results, the performance of the DFT methods is better for this category of complexes, as can be seen in Figures 2 and 3. The maximum absolute error with and without taking into account the DFT-D₂/BLYP results is 0.77 kcal/mol (butadiene dimer) and 0.55 kcal/mol (DFT-D₃/TPSS benzene dimer), respectively. If the CP correction is included, the maximum errors change slightly to 0.82 kcal/mol (butadiene dimer) and 0.46 kcal/mol (DFT-D₃/PBE benzene dimer).

The acyclic unsaturated HCs are generally described more accurately than the cyclic ones, except for the DFT-D₂/BLYP, DFT-D₃/BLYP, and M06-2X methods. The first of these methods delivers results consistently shifted with respect to the benchmark by about 0.7 kcal/mol. The DFT-D₃/BLYP stabilization energy for the butadiene dimer is somewhat accurate, but the result for the hexatriene dimer is overestimated by almost 0.5 kcal/mol. The opposite is true for the M06-2X method, which describes the hexatriene dimer to within 0.05 kcal/mol but slightly overestimates the stability of butadiene dimer by 0.3 kcal/mol.

The errors for the cyclobutadiene and benzene dimers are all roughly within the 0.5 kcal/mol error bars. Exceptional

accuracy, i.e., errors below 0.2 kcal/mol, is delivered by DFT/TPSS with “-D₂” and “-D₃” corrections as well as the M06-2X method.

4.2. Wave Function Methods—MP2 and the MP2-Based Methods. The related MP2-based approximate schemes are appealing computational methods because of their generally favorable ratios between accuracy and computational requirements. The notoriously known failure of the MP2 method to accurately describe the aromatic $\pi \cdots \pi$ stacked complexes was a main driving force in the development of modified MP2 schemes capable of overcoming this obstacle. Except for the MP2C method, all other MP2-based schemes tested in this work rely on the concept of separate scaling of the same-spin and opposite-spin components of the MP2 correlation energy. This strategy was in principle found to be successful; however, as the performance on the $\pi \cdots \pi$ stacked complexes is clearly enhanced, the description of other complex types, such as the saturated HCs, is not improved or even becomes worse.

As already mentioned, in practice, the MP2 correlation energy calculation for systems with several tens of atoms rarely presents the time-determining step. The MP2 method is thus applicable to most of the molecular systems investigated at the “O(N⁴) level” without an unbearable increase of computation time. However, there are two factors somewhat disfavoring MP2 compared to DFT. The first of these is the slow convergence of the correlation energy with the basis set size, and the second is the BSSE. These two factors are not completely independent, because

Table 3. The DFT, MP2, Modified-MP2, and Post-MP2 Interaction Energies [kcal/mol] for Dimers of Cyclic and Acyclic Unsaturated HCs—Butadiene, Hexatriene, Cyclobutadiene, and Benzene

method	butadiene	hexatriene	cyclobutadiene	benzene	method	butadiene	hexatriene	cyclobutadiene	benzene
DFT-DJ/TPSS ^a	-2.361 (-1.912)	-4.564 (-4.162)	-2.219 (-1.930)	-3.285 (-2.405)	SCS-MP2/cc-pV (DT)Z	-1.668	-3.428	-1.622	-2.492
DFT-DJ/PBE ^a	-2.531 (-2.185)	-4.440 (-4.127)	-2.323 (-2.088)	-2.980 (-2.274)	SOS-MI-MP2/cc- pV(DT)Z	-2.619	-4.337	-2.107	-4.035
DFT-D2/TPSS ^a	-2.135 (-2.079)	-4.429 (-4.373)	-2.180 (-2.129)	-2.784 (-2.697)	SSS-MI-MP2/cc- pV(DT)Z	-1.866	-4.140	-1.938	-2.775
DFT-D2/PBE ^a	-2.179 (-2.131)	-4.503 (-4.459)	-2.275 (-2.232)	-2.505 (-2.440)	SCS-MI-MP2/cc- pV(DT)Z	-2.043	-4.238	-1.999	-3.068
DFT-D2/BLYP ^a	-1.499 (-1.453)	-3.777 (-3.738)	-1.769 (-1.721)	-2.170 (-2.111)	SOS-MP2/cc-pV (TQ)Z	-1.993	-3.665	-1.801	-2.833
DFT-D3/TPSS ^a	-2.237 (-2.180)	-4.549 (-4.492)	-2.034 (-1.983)	-2.596 (-2.509)	SCS-MP2/cc-pV (TQ)Z	-1.972	-3.749	-1.833	-2.796
DFT-D3/PBE ^a	-2.327 (-2.279)	-4.559 (-4.514)	-2.196 (-2.153)	-2.425 (-2.360)	SOS-MI-MP2/cc- pV(TQ)Z	-2.687	-4.420	-2.197	-3.929
DFT-D3/BLYP ^a	-2.161 (-2.115)	-4.947 (-4.908)	-1.941 (-1.893)	-2.821 (-2.763)	SSS-MI-MP2/cc- pV(TQ)Z	-1.918	-4.122	-1.979	-2.696
M06-2X ^a	-2.569 (-2.351)	-4.447 (-4.208)	-1.936 (-1.748)	-2.652 (-2.325)	SCS-MI-MP2/cc- pV(TQ)Z	-2.163	-4.268	-2.069	-3.086
DF-HF/CBS	3.197	2.009	1.169	5.356	SCS-MP2/aug- cc-pVDZ	-1.561	-3.064	-1.527	-2.223
DF-MP2/CBS	-3.341	-5.401	-2.731	-4.956	SCS-MP2/aug- cc-pVTZ	-1.831	-3.469	-1.731	-2.597
MP2C/aug-cc- pVDZ	-1.945	-4.132	-1.719	-1.932	SCS-MP2/aug- cc-pVQZ	-1.925	-3.618	-1.811	-2.732
MP2C/aug-cc- pVTZ	-2.334	-4.651	-1.997	-2.476	SCS-MP2/CBS	-1.993	-3.727	-1.869	-2.831
MP2C/aug-cc- pVQZ	-2.473	-4.766	-2.125	-2.650	MP2.5/CBS ^b	-2.623 (-2.599)	-4.733	-2.229 (-2.220)	-3.188
MP2C/CBS	-2.575	-4.850	-2.219	-2.777	CCSD/CBS ^b	-1.512 (-1.358)	-3.534	-1.538 (-1.447)	-1.493
DW-MP2/aug- cc-pVDZ	-2.016	-4.073	-2.003	-2.856	SCS-CCSD/ CBS ^b	-2.328 (-2.207)	-4.394	-1.950 (-1.904)	-2.709
DW-MP2/aug- cc-pVTZ	-2.030	-4.128	-2.047	-2.867	SCS-MI-CCSD/ CBS ^b	-2.362 (-2.243)	-4.562	-2.030 (-1.974)	-2.704
DW-MP2/aug- cc-pVQZ	-2.043	-4.143	-2.057	-2.884	CCSD(T)/CBS ^b	-2.273 (-2.225)	-4.497	-1.995 (-1.966)	-2.732
SOS-MP2/cc-pV (DT)Z	-1.834	-3.489	-1.667	-2.768					

^aThe results in parentheses are the CP corrected interaction energies. ^bThe $\Delta E^{\text{Post-MP2}}$ term calculated using the aug-cc-pVTZ basis sets

the BSSE converges to zero when approaching the CBS limit. Still, the choice of the basis set in correlated WFT calculations is of higher importance than in DFT.

This section has a slightly different structure compared to the previous section dealing with DFT results. The results obtained for all the tested complexes are discussed at once for each of the MP2(-based) methods individually, in order to emphasize the imbalance of the description for different complex types.

Let us start with the performance of the MP2 itself. MP2 delivers surprisingly high accuracy in the description of saturated complexes, both acyclic and cyclic HCs, see Tables 1 and 2. Not only is the order of stability of these complexes correctly described but the maximum error with respect to the benchmark is only ~0.06 (3%) to ~0.30 (6%) kcal/mol for propane to hexane and ~0.09 (4%) to 0.28 (8%) for cyclopropane and cyclopentane, respectively. Despite the fact that all of the complexes investigated in this work are dispersion dominated, completely different accuracy is achieved for the unsaturated HCs.

The interaction energy of the benzene dimer is overestimated by about 2.2 kcal/mol (81%), which represents the largest error among all the WFT/DFT methods tested in this work. This discrepancy could change the ordering of stability of the tested complexes, but due to the fact that the stability of the hexatriene dimer is also overestimated by about 0.9 kcal/mol (20%), the benzene dimer is correctly predicted to be the second most stable complex. Surprisingly, the butadiene dimer is overstabilized more than the hexatriene dimer, by about

1 kcal/mol (49%) with respect to the benchmark, while the cyclobutadiene is overstabilized by only ~0.7 kcal/mol (38%).

The computationally cheapest techniques among the tested modified MP2 methods are the $O(N^4)$ spin-opposite scaled SOS-MP2¹⁸ and SOS(MI)-MP2 methods,¹⁷ the latter being parametrized for noncovalent interactions. According to the results shown in Figure 4, SOS-MP2 strongly underestimates the stability of acyclic saturated HCs, at most by 1.8 kcal/mol (39%) for the hexane dimer. In contrast, the stability of the cyclic unsaturated HCs is described quite accurately, the error for the benzene dimer being only about 0.1 kcal/mol (4%). The description of the saturated and unsaturated acyclic HCs delivered by SOS(MI)-MP2 is more accurate compared to SOS-MP2, but the stability of the benzene dimer, a member of the SOS(MI)-MP2 parametrization data set, is overestimated by 1.2 kcal/mol (44%).

Scaling of both the same- and opposite-spin components of the MP2 correlation energy (reasoned in works of Szabados⁵² and Fink⁵³), as done in SCS-MP2¹⁵ or SCS(MI)-MP2,¹⁷ leads to improvement of the description of the problematic benzene dimer. The stability of the complex is overestimated by only 0.1 kcal/mol (4%) for SCS-MP2 and 0.4 kcal/mol (13%) for SCS(MI)-MP2, which are dramatic improvements over MP2 and its SOS variants. However, the performance of the SCS-MP2 method on saturated HCs is almost the same as that of SOS-MP2, and the same holds true for SCS(MI)-MP2 and SOS(MI)-MP2. The stability of the saturated HCs is strongly underestimated, in the case of SCS(MI)-MP2 even more

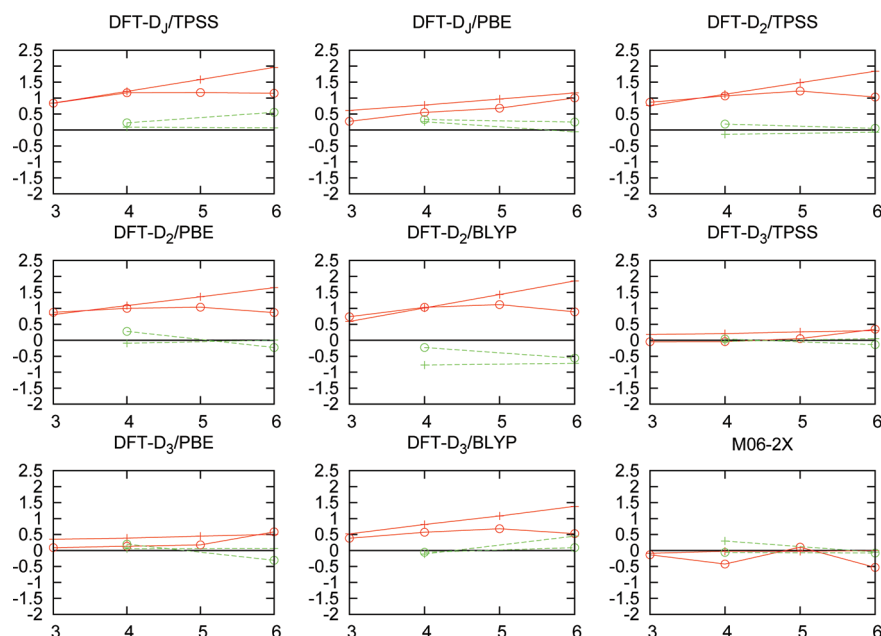


Figure 2. Errors [kcal/mol] of the DFT interaction energies *without the CP correction* wrt the CCSD(T)/CBS benchmark. Values on the x axis indicate the number of carbon atoms in monomers. Full lines correspond to saturated and the dashed lines, unsaturated HCs. Circles indicate cyclic and crosses, the acyclic structures.

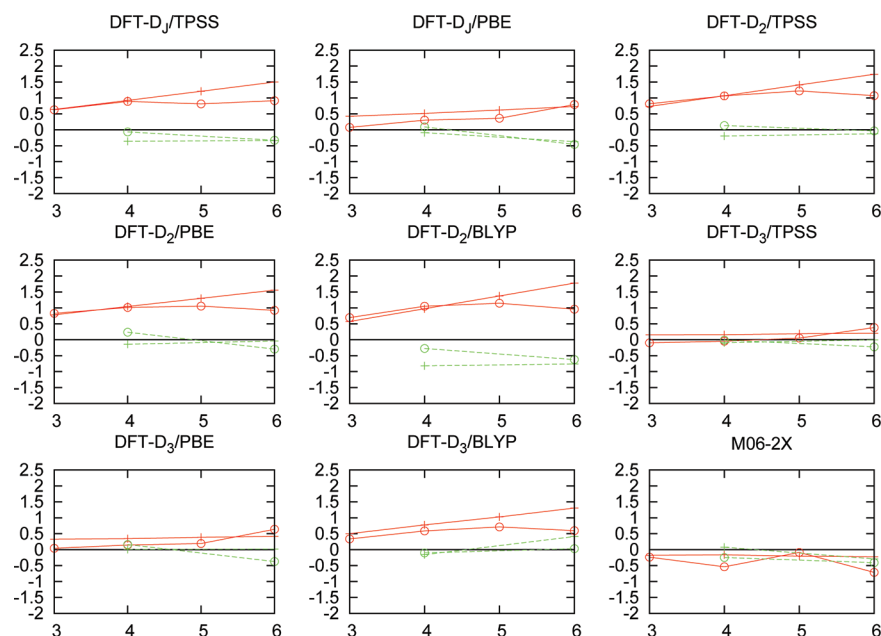


Figure 3. Errors [kcal/mol] of the DFT interaction energies *including the CP correction* wrt the CCSD(T)/CBS benchmark. Values on the x axis indicate the number of carbon atoms in monomers. Full lines correspond to saturated and the dashed lines, unsaturated HCs. Circles indicate cyclic and crosses, the acyclic structures.

compared to SOS(MI)-MP2. The maximum error is obtained for the hexane dimer, 1.3 kcal/mol (28%).

The last among the tested MP2-based methods with scaled spin components is the DW-MP2 method.¹⁹ The DW-MP2 method utilizes two fixed spin-component scaling parameters taken from SCS-MP2 and two optimized parameters contributing to the weight factor mixing the MP2 and SCS-MP2 energies. Statistical analysis of the performance of the DW-MP2 and SCS(MI)-MP2 methods on the S22 test set shown in refs 17 and 19 reveals almost identical accuracy for these two methods. The results obtained in this work also confirm this conclusion. The

absolute errors for the unsaturated complexes are below 8% (maximum of ~ 0.4 kcal/mol for the hexatriene dimer), but the ordering of stability is predicted incorrectly.

The DW-MP2 method predicts the cyclobutadiene dimer to be slightly more stable than the butadiene dimer, by 0.01 kcal/mol (the reference value is 0.25 kcal/mol in favor of the butadiene dimer). This is, however, only a “marginal” issue in comparison with the performance for the unsaturated HCs. Analogously to the performance of other aforementioned MP2-based methods, the stability of the unsaturated HCs is strongly underestimated. The maximum error is obtained for the hexane dimer, 1.8 kcal/mol

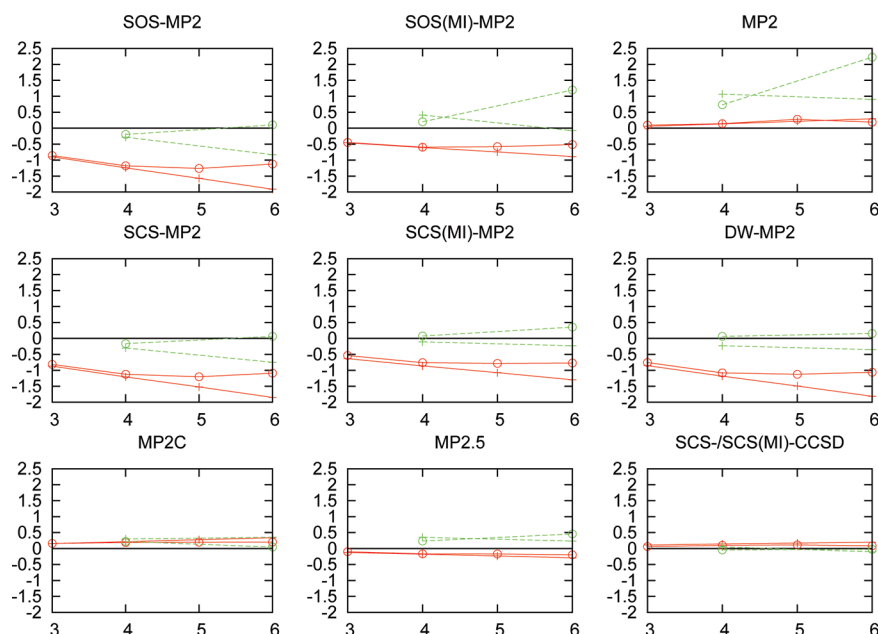


Figure 4. Errors [kcal/mol] of the WFT interaction energies wrt the CCSD(T)/CBS benchmark. Values on the x axis indicate the number of carbon atoms in monomers. Full lines correspond to saturated and the dashed lines, unsaturated HCs. Circles indicate cyclic and crosses, the acyclic structures.

(39%), which is about 0.5 kcal/mol higher than that of SCS(MI)-MP2.

The MP2C method^{21,54} is based on the idea of substitution of the uncoupled Hartree–Fock dispersion energy from the supermolecular MP2 calculation with the coupled one from the time-dependent density functional response theory. In this respect, MP2C is not a genuine supermolecular approach because it incorporates (intermolecular) dispersion energy calculated from the separate monomers. The results shown in Figure 4 as well as Tables 1–3 clearly demonstrate both the accurate and stable performance on all the types of tested complexes. The errors are below ~ 0.4 kcal/mol (8% for hexatriene dimer), with a slight tendency of overestabilization.

4.3. Wave Function Methods—Post-MP2 Methods.

The $O(N^6)$ scaling post-MP2 methods, such as MP2.5²² and SCS-/SCS(MI)-CCSD,^{23,24} are computationally at least 1 order of magnitude more demanding than MP2 but still significantly cheaper than the “gold standard”, CCSD(T). Their applicability on larger molecular systems is naturally biased compared to MP2 or the DFT methods; however, there are certain factors that alleviate these limitations. The first factor is the faster convergence of the respective post-MP2 correlation energy contributions toward the CBS limit compared to the MP2 energy itself.⁵⁵ The post-MP2 correlation energy can thus be calculated using a smaller basis set and added as a correction to the “converged” MP2 energy. Second, the noniterative post-MP2 methods, such as the MP2.5 (i.e., MP3), can be almost ideally parallelized (i.e., linear scaling with increasing number of parallel processes) and, in combination with approximate two-electron integrals treatment⁵⁶ (e.g., CD, RI, etc.), are applicable to molecular systems of hundreds of atoms. The inevitable computational effort is naturally expected to be priced by the accuracy and reliability of results obtainable using the $O(N^5)$ and lower scaling methods.

Let us start with an analysis of the performance of the MP2.5²² method. MP2.5 delivers moderately accurate but well balanced results for both saturated and unsaturated HCs

dimers. According to Figure 4, the stability of the saturated HCs dimers is slightly underestimated, on average by ~ 0.3 kcal/mol (12%), whereas the opposite is true for the unsaturated HCs dimers, on average by ~ 0.2 kcal/mol (6%). The maximum error is obtained for the benzene dimer, about 0.5 kcal/mol (17%), which is worse than, e.g., all of the DW- and SCS-based MP2 methods. However, the relative error with respect to the cyclobutadiene or hexatriene dimer is only ~ 0.2 kcal/mol (12%), unlike in SCS-MP2/SCS(MI)-MP2/DW-MP2 where the relative error with respect to the hexatriene dimer is about 0.9/0.6/0.5 kcal/mol (49%/33%/29%).

The most computationally demanding among the tested approximate methods are SCS-CCSD²³ and SCS(MI)-CCSD.²⁴ These iterative $O(N^6)$ scaling methods are (in practice) more than an order of magnitude more expensive than MP2.5; thus accuracy close to the “benchmark” is expected to pay for the computational efforts. The obtained results for all the tested complexes confirm the capacity of these methods to substitute for the benchmark CCSD(T) approach where it is not feasible. The average unsigned error for the unsaturated HCs dimers is about 0.06 kcal/mol (2%), with the maximum of ~ 0.1 kcal/mol (2.3%) reached for the hexatriene dimer. The saturated HCs dimers are all slightly overestabilized by about 0.12 kcal/mol (3.8%) on average. The maximum error is reached for the hexane dimer, 0.2 kcal/mol (4%). The results obtained using SCS-CCSD and SCS(MI)-CCSD differ in the hundredths of a kcal/mol, so the accuracy of these two methods for the complexes under investigation is practically indistinguishable. Very similar conclusions concerning the excellent performance of MP2.5 and SCS(MI)-CCSD was obtained for the extended S66 data set containing more than 1100 equilibrium and nonequilibrium structures for 66 representative noncovalent complexes.⁵⁷

5. CONCLUSIONS

The small test set of saturated and unsaturated acyclic and cyclic HCs dimers with four to six carbon atoms in each monomer was assembled for the purpose of testing several popular WFT and DFT methods used for calculations of noncovalent complexes.

The choice of the complexes is based on the observation of a rather diverse performance of some of the routinely applied computational methods on these chemically close, yet quite different, molecular systems with respect to the character of the noncovalent interaction. The noncovalent interactions in these complexes are dominated by the dispersion force, having a different “flavor” in saturated and unsaturated HCs. Due to the existence of the notorious problem of the accurate description of the challenging $\pi\cdots\pi$ stacking complexes, several novel WFT/DFT computation schemes were developed with a special focus on this interaction motif. While addressing this issue, less attention was paid to the proper description of other important interaction types.

The complex geometries were fully optimized in a three-step procedure, which is assumed to deliver geometries close to the global minimum. For each of the complexes the benchmark interaction energies were calculated on the CP-corrected estimated CCSD(T)/CBS level obtained at the CP-corrected MP2 value extrapolated from aug-cc-pVTZ and aug-cc-pVQZ basis sets augmented with the CP-corrected Δ CCSD(T) term obtained with either aug-cc-pVDZ or aug-cc-pVTZ, depending on the complex size.

The DFT methods performed poorly for both acyclic and cyclic saturated HCs. Almost all of the tested DFT methods tend to overstabilize the complexes. This is particularly true for the DFT methods with “-D_j” and “-D₂” empirical corrections for the dispersion energy, in combination with BLYP, PBE, and TPSS DFT functionals, as well as for DFT-D₃/BLYP. With the exception of the DFT-D₂/BLYP, all of the aforementioned methods deliver satisfactory performance for the unsaturated HCs dimers. The performance of the DFT-D₃/PBE and M06-2X methods is clearly superior to the other ones, but still the errors exceed the value of ~ 0.5 kcal/mol (17% on average). The only reliable and accurate DFT method among the tested ones is the DFT-D₃/TPSS. The role of the CP correction for the BSSE was found to be insignificant.

The performance of the tested WFT methods is much more diverse compared to the DFT ones. Except for the few accurate and reliable methods, MP2C, MP2.5, and SCS-/SCS(MI)-CCSD, the stabilities of the saturated HCs were clearly underestimated. This is particularly unwelcome for the methods optimized for the best performance on noncovalent complexes, such as SCS(MI)-MP2 and DW-MP2. Taking into consideration the “price/performance” ratio, clearly the method of choice in this category is MP2C. MP2.5 delivers balance yet not the most accurate results. The SCS-/SCS(MI)-CCSD methods are clearly the most accurate ones; thus they could serve as an alternative benchmark in situations where the use of CCSD(T) is prohibitively costly. The computational cost penalty compared to, e.g., MP2C or even MP2.5, however, cannot be ignored.

■ ASSOCIATED CONTENT

■ Supporting Information

A list of optimized atomic coordinates [Å] of the HC dimers used in this work. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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