

Accurate Description of van der Waals Complexes by Density Functional Theory Including Empirical Corrections

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Abstract: An empirical method to account for van der Waals interactions in practical calculations with the density functional theory (termed DFT-D) is tested for a wide variety of molecular complexes. As in previous schemes, the dispersive energy is described by damped interatomic potentials of the form C_6R^{-6} . The use of pure, gradient-corrected density functionals (BLYP and PBE), together with the resolution-of-the-identity (RI) approximation for the Coulomb operator, allows very efficient computations for large systems. Opposed to previous work, extended AO basis sets of polarized TZV or QZV quality are employed, which reduces the basis set superposition error to a negligible extend. By using a global scaling factor for the atomic C_6 coefficients, the functional dependence of the results could be strongly reduced. The “double counting” of correlation effects for strongly bound complexes is found to be insignificant if steep damping functions are employed. The method is applied to a total of 29 complexes of atoms and small molecules (Ne, CH₄, NH₃, H₂O, CH₃F, N₂, F₂, formic acid, ethene, and ethine) with each other and with benzene, to benzene, naphthalene, pyrene, and coronene dimers, the naphthalene trimer, coronene · H₂O and four H-bonded and stacked DNA base pairs (AT and GC). In almost all cases, very good agreement with reliable theoretical or experimental results for binding energies and intermolecular distances is obtained. For stacked aromatic systems and the important base pairs, the DFT-D-BLYP model seems to be even superior to standard MP2 treatments that systematically overbind. The good results obtained suggest the approach as a practical tool to describe the properties of many important van der Waals systems in chemistry. Furthermore, the DFT-D data may either be used to calibrate much simpler (e.g., force-field) potentials or the optimized structures can be used as input for more accurate *ab initio* calculations of the interaction energies.

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Introduction

The van der Waals (dispersive) interactions between atoms and molecules play an important role in many chemical systems. They are in detailed balance with electrostatic (ES) and exchange-repulsion (ER) interactions, and together, they control for example, the structures of DNA and proteins, the packing of crystals, the formation of aggregates, host–guest systems, or the orientation of molecules on surfaces or in molecular films.

Theoretically, the ER and ES effects can already be described relatively accurately at a mean-field (i.e., Hartree–Fock, HF) level of theory while the dispersive part is a pure electron correlation effect.¹ In the framework of standard *ab initio* wave function theory² it can be described by double excitations between occupied and virtual orbitals of the supermolecule (coupled monomer single

excitations). Accurate computations based on, for example, coupled-cluster methods like CCSD(T), however, suffer from unacceptable computation times even for medium-sized systems, and can thus routinely be applied only to benchmark studies of small complexes. Cheaper alternatives like second-order Møller–Plesset perturbation theory (MP2),³ on the other hand, are computationally simpler and thus more widely used. However, especially for dispersive π – π interactions standard MP2 systematically overestimates the binding energies and underestimates intermolecular

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equilibrium distances (see, e.g., refs. 4 and 5, and references therein).

Although today the most widely used theoretical approach to molecular structure, the density functional theory (DFT),^{6,7} includes electron correlation effects in an approximate manner, it is now clear that almost all gradient-corrected density functionals are unable to describe dispersive interactions (see, e.g., refs. 8–10, and references therein). Although this problem now has become a very active field of research (see refs. 11 and 12, and references therein), it seems to be very difficult to account for dispersion within the standard Kohn–Sham picture of DFT. These nonlocal, long-range electron correlations already appear for vanishing overlap of the electron densities of the fragments. Accordingly, they have only a tiny effect on the electron density of the fragments that is furthermore buried by the influences of the chemical environment. In the author's opinion, all nonempirical attempts to introduce van der Waals interactions in DFT will finally end up with methods that will be at least as complex as the simplest wave function (i.e., MP2) methods. Another empirical strategy to solve the problem is to modify¹³ or to combine¹⁴ existing density functionals to reproduce, for example, the interaction potentials of rare gas dimers. These approaches cannot be considered as successful in a sense that the modified functionals are not applicable (transferable) for different systems (e.g., Ne₂ vs. Kr₂ vs. (cytosine)₂).¹³ The recently proposed XLYP functional¹⁴ has solely been tested on He₂, Ne₂, and (H₂O)₂ and thus, its “real” performance cannot be judged.

In recent publications^{9,12,15} it was shown, however, that a pragmatic way to remedy this problem is to add an empirical potential of the form $C_6 R^{-6}$ to the usual DFT energy, where R are interatomic distances and C_6 are the dispersion coefficients. A similar correction has been proposed earlier within a tight-binding DFT model¹⁶ that has subsequently been applied to stacking interactions of DNA intercalators.¹⁷ The first work in similar directions based on the Hartree–Fock (HF) method goes back to Ahlrichs et al.¹⁸ (the Coulomb-correlated HF method of Clementi¹⁹ also includes a similar dispersive term). Although encouraging results have been obtained in the framework of DFT,^{9,12,16} we think that part of the criticism of such an approach in ref. 20 i.e., “... a more thorough testing procedure is needed ...,” is certainly true. In fact, the limited number of systems studied up to now do not allow any conclusive answer on the general applicability of the model.

In the same spirit, Gonzalez and Lim²¹ corrected the Hartree–Fock interaction potentials of large aromatic systems. This study, however, suffers from too small basis sets (i.e., 6-31G) resulting in large basis set superposition errors (BSSE) for binding energies and intermolecular distances. Furthermore, because the monomer geometries and their electric multipole moments are usually more accurate at the DFT level, there seems to be little reason to follow HF based approaches further. Another perspective of DFT is the use of efficient representations of the Coulomb operator (see below), which speed up calculations for large molecules by a factor of about 10 compared to analogous HF treatments.

In the present work, a practical method for the study of large van der Waals complexes based on efficient DFT computations is presented. It is tested on a wide variety of different systems namely complexes of atoms and small molecules (Ne, CH₄, NH₃, H₂O,

CH₃F, N₂, F₂, formic acid, ethene, and ethine) with each other and with benzene, to benzene, naphthalene, pyrene, and coronene dimers, the naphthalene trimer and a coronene · H₂O complex. Because of their importance in biochemistry H-bonded as well as stacked dimers of DNA bases (CC, AT, and GC) are also investigated. Opposed to statements in ref. 9 it will be shown here, that a $C_6 R^{-6}$ type correction to DFT (termed DFT-D) is indeed generally applicable, and that tailoring the mathematical form of the potential to specific systems is not necessary. After an outline of the form of the correction proposed here in the next section, and of the technical details in the Technical Details section, the results for the above-mentioned systems together with available literature data are discussed (Results and Discussion).

Theory

The dispersion corrected total energy is

$$E_{MF-D} = E_{MF} + E_{\text{disp}} \quad (1)$$

where E_{MF} is the usual mean-field energy (i.e., HF or DFT) and E_{disp} is an empirical dispersion correction given by

$$E_{\text{disp}} = -s_6 \sum_{i=1}^{N_{\text{at}}-1} \sum_{j=i+1}^{N_{\text{at}}} \frac{C_6^{ij}}{R_{ij}^6} f_{\text{dmp}}(R_{ij}). \quad (2)$$

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 (see below) and R_{ij} is the interatomic distance. Note, that E_{disp} is a model-dependent quantity with no real physical meaning. A more rigorous partitioning of intermolecular energies in, for example, ES, ER, and E_{disp} contributions can be obtained in the framework of symmetry-adapted perturbation theory (SAPT²²). To avoid near-singularities for small R , a damping function f_{dmp} must be used which is given by

$$f_{\text{dmp}}(R) = \frac{1}{1 + e^{-\alpha(R/R_0-1)}} \quad (3)$$

where R_0 is the sum of atomic van der Waals radii. This and other functions of similar type have been discussed in detail in refs. 9 and 12. Eq. (3) is chosen because it decays at small R fast enough to zero such that the dispersion corrections between atoms well below typical van der Waals distances are negligible and thus, “normal” bonds are not significantly affected by the correction. Note that the damping function of Gonzalez and Lim²¹ does not fulfill this requirement and can thus only be applied if weakly interacting fragments can be defined (i.e., it is not applicable to intramolecular dispersion in, for example, proteins). To get consistent van der Waals radii R_0 for arbitrary elements it is decided to derive them purely from theoretical data. The radius of the 0.01 au electron density contour from ROHF/TZV computations of the atoms in the ground state scaled by a factor of 1.22 is taken (this scale factor should work for first and second-row atoms). The resulting van der Waals radii R_0 , which are, however, similar to

Table 1. Atomic C_6 Parameters (s_6 Not Included) and van der Waals Radii Used.

	H	C	N	O	F	Ne
$C_6/\text{Jnm}^6\text{mol}^{-1}$	0.16	1.65	1.11	0.70	0.57	0.45
R_0/pm	111	161	155	149	143	138

those used in the literature, are given in Table 1. The value of $\alpha = 23$, which determines the steepness of the damping function, is used as in previous work.¹²

Different combination rules for the composed C_6^{ij} coefficients have been carefully tested for many complexes. It turned out, however, that the observed effects were always smaller than those introduced by the finite AO basis and the choice of the density functional (the same argumentation holds also for higher order dispersion terms like C_8 , which are considered in other approaches⁹). Thus, further search for the optimum dispersion function in that direction seems not warranted, and finally, a simple average of the form

$$C_6^{ij} = 2 \frac{C_6^i C_6^j}{C_6^i + C_6^j} \quad (4)$$

is used.²³ The atomic C_6 coefficients are taken from the work of Wu and Yang,¹² but have been averaged over the possible hybridization states of the atoms. A distinction of different hybridization states would clearly improve the flexibility of the correction, but seems to be problematic in cases where the hybridization states of the atoms are not well defined. The errors due to the use of atomic instead of hybridization-dependent C_6 coefficients may be on the order of 10–20% of the binding energy when, for example, saturated and unsaturated hydrocarbons are compared. This, however, is on the order of the effects of the chosen density functional, and thus, in the spirit of “Ockhams razor,” the simpler model will be considered. The values for fluorine and neon have been adjusted to reproduce intermolecular distances and binding energies of complexes of CH_3F with methane and ethine, and of Ne_2 and benzene · Ne, respectively. Note that changing the C_6 values by $\pm 10\%$ has only a small impact on the results when compared to other theoretical or experimental data, which show, in general, relatively large scatter. The values used are given in Table 1. Depending on the actual mean field (or density functional), the atomic C_6 coefficients are scaled by the factor s_6 to account for the different behavior of the intermolecular potential especially at intermediate distances. Optimum scale factors of 1.4, 1.3, and 0.7 have been obtained for the functionals BLYP,^{24,25} BP86,^{24,26,27} and PBE²⁸ by using the systems **1–3**, **5–19**, as a “fit-set” of molecules.

As an example, in Figure 1 the dispersion contribution to the interaction potential for two carbon atoms ($s_6 = 1.0$) is shown. It is seen, that pure R^{-6} behavior is retained up to typical van der Waals distances between carbon atoms (about 340 pm as, e.g., in graphite). Significant interactions are provided in regions down to about 270–280 pm where the overlap of the densities is still small, while there is negligible contribution for distances below 250 pm where DFT starts to account for chemical bonding. Note that more

slowly decaying damping functions as suggested in ref. 12 seem to be somewhat unphysical because the perturbatively obtained R^{-6} behavior of the interaction is not valid anymore at short distances.¹

Technical Details of the Calculations and Choice of the AO Basis Set

Equation (2) and its analytical derivative with respect to nuclear displacements have been implemented in the dscf, grad, ridft, rdgrad, and egrad modules of the TURBOMOLE^{29,30} program system.

Opposed to previous work, relatively large AO basis sets are employed in the present study that eliminate to a large extend the basis set superposition error (BSSE). The remaining (small) BSSE effects are “absorbed” into the empirical potential. This approach avoids the laborious computation of the usual counterpoise-correction (CP),^{31,32} and furthermore, leads to a consistency of energies and geometries (the cheapest way to obtain CP corrected optimized geometries requires a factor of about three to four more computation time compared to an uncorrected treatment, see ref. 33). It seems important to mention here that the CP correction is mandatory when correlated wave function methods are used. When dispersion is dominant for the interaction the BSSE is often several times larger than with mean-field methods like DFT or HF. The scale factor s_6 for the C_6 coefficients has been obtained by adjusting some calculated binding energies (ΔE) and intermolecular distances in the test set of systems to experimental or reliable theoretical values. For this purpose, valence triple zeta (TZV)³⁴ basis sets with two sets of polarization functions, i.e., TZV(2d,2p) in standard notation, are employed (the exponents of all polarization functions are taken from Dunning's cc-pVXZ ($X = \text{T, Q}$) basis sets³⁵). This choice yields BSSE less than 10–20% of the binding energy in most cases studied, and such basis sets can be used routinely also for very large systems. Furthermore, also the BSSE for intermolecular distances with the TZV(2d,2p) set is found to be < 2 –3 pm. This is illustrated in Table 2, where a detailed basis set

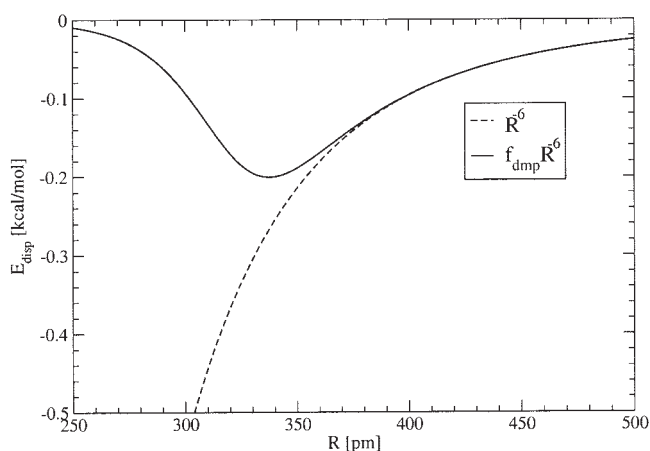
**Figure 1.** Dispersion contributions to the interaction potentials for two carbon atoms ($s_6 = 1.0$) separated by a distance R . The dashed line shows the undamped potential for comparison.

Table 2. Calculated^a (DFT-D-BLYP, $s_6 = 1.4$) Intermolecular Distances (R , in pm) and Binding Energies (ΔE , in kcal/mol) for Three Complexes with Different AO Basis Sets.

AO basis	(Benzene) ₂ (D _{6h})		Benzene · H ₂ O (C _s)		(Cytosine) ₂ (C _i)	
	R^b	$-\Delta E$	R^c	$-\Delta E$	R^d	$-\Delta E$
DZV(d)	378	1.82	316	5.68	315	13.86
TZV(d,p)	390	1.15	331	4.20	321	10.93
TZV(2d,2p) ^e	390	1.21	333	3.66	323	11.14
TZV(2df,2pd)	390	1.18	333	3.57	322	10.77
QZV(2df,2pd)	390	1.04	335	3.13	322	10.19
QZV(3d2f,3p2d)	390	1.02	335	3.05	322	10.17

^aFully optimized geometries.

^bDistance between the rings.

^cDistance between the ring plane and the oxygen atom.

^dAveraged distance between the planes of the two cytosine molecules.

^eThe CP corrected binding energies for the three systems are -0.97 , -2.60 , and -10.15 kcal/mol, respectively.

study for the optimized distances and binding energies of three representative complexes with increasing interaction strengths is presented.

Obviously, basis sets smaller than TZV (i.e., split-valence sets like DZV(d) or 6-31G*) yield unreliable results, while the distances seem already relatively accurate at the TZV(d,p) level. As expected, the interaction energies are more sensitive but seem to be within 10–20% of the limiting values with the TZV(2d,2p) set. With this basis the BSSE as obtained from CP calculations is about 20 and 30% of ΔE for the benzene dimer and the complex with water, respectively, but only 9% for the cytosine dimer. The TZV(2d,2p) set is employed for geometry optimization and also recommended for large-scale applications in practice. However, the ΔE values as obtained in single-point calculations using the larger QZV(2df,2pd) basis³⁶ are also discussed in the following. Note further that diffuse basis functions that are necessary in correlated (e.g., MP2) calculations to accurately describe the fragment polarizabilities do not necessarily improve the description of weak complexes when DFT approaches are applied. If used together with small valence basis sets they sometimes artificially increase the BSSE. Furthermore, all standard density functionals exhibit large errors for the exchange-correlation potential far away from the nuclei (too fast asymptotic decay) where the diffuse functions have their largest probability. Also, from the computational effort point of view it seems thus most effective to employ valence basis sets in DFT-D treatments that are flexible enough to provide accurate electrostatic interactions. When the present approach is employed together with near complete basis set expansions or those which do not suffer from significant BSSE (i.e., plane wave basis sets) it is recommended to adjust the scale factor s_6 accordingly. In general, it is noticed that the BSSE is largest for atoms and small (less than 4–5 atomic) molecules. In larger systems, where each atom is surrounded by “shells” of other atoms, the BSSE diminishes because the atomic basis is completed by remaining functions of other atoms.

To keep the calculations tractable, the resolution-of-the-identity (RI) approximation for the Coulomb operator³⁷ (also called “density fitting”^{38–40}) is employed in all treatments. This reduces the computation times by a factor of 5–10 for the larger systems at no significant loss of accuracy. In test calculations RI errors for the binding energies of less than <0.01 kcal/mol have been obtained. The RI auxiliary basis sets⁴¹ are taken from the TURBOMOLE library.⁴²

One of the disadvantages of the dispersion corrected DFT approach compared to the analogous HF treatment is the necessity of numerical quadrature. The numerical noise of the calculated energies and gradients due to grid errors are of particular importance for the convergence of the geometry optimization process of weak complexes with shallow potential surfaces. To get smooth convergence, the use of relatively large grids especially in the radial dimension is recommended (grid = m4, grid = m5, or grid = 3, radsiz = 10 in the TURBOMOLE notation, the latter grid and Becke’s weighting scheme was used throughout this work). When using other programs, careful checks on the simultaneous energy and gradient convergence should be performed and in case of divergence, increasing the grid size is mandatory.

All geometries were fully optimized in the mentioned point group without any further constraints. If the structure of the complex was not clear from the beginning the optimization was performed in the C_1 point group and the resulting (if higher) symmetry is given. Tight convergence criteria for the geometry optimization (i.e., change in energy between two cycles $<10^{-7}$ E_h) are used which is mandatory to obtain reliable intermolecular distances. Note, that full geometry optimization is rarely performed in the study of larger van der Waals complexes, and thus, literature data sometimes have to be taken with care. For example even for the weakly interacting case of the benzene dimer, changes of the monomer geometries upon complexation are on the order of 0.1 pm and 0.2 degree for bond lengths and angles, respectively. In the case of stronger interactions (e.g., the DNA bases) the effects are more than one order of magnitude larger and should be considered in accurate work. Note further, that some of the investigated complexes may not be true minima on the potential energy surface (PES). In the present context this, however, does not significantly influence the general conclusions because the PES are usually very flat and small changes of the orientations of the fragments leads only to minor changes of the interaction energies. All reported theoretical binding energies ΔE refer to pure electronic energies, i.e., zero-point vibrational as well as thermal corrections are neglected.

Results and Discussion

Initially, the pure (nonhybrid) gradient-corrected functionals BLYP,^{24,25} BP86,^{24,26,27} and PBE²⁸ have been tested. Although the exchange part of BP86 and BLYP is the same, it turned out, however, that BLYP provides clearly superior results. Especially a uniformly consistent description of the interactions between saturated fragments and those between π systems could not be obtained with BP86. Therefore, in the following, only results with PBE and BLYP are presented. PBE is chosen because it represents one of the rare functionals (along with PW91¹⁰) that at least

qualitatively account for some dispersive interactions (see below). Note that other functionals can be used as well when only one parameter (s_6) is adjusted. For that purpose it has been found to be sufficient to perform calculations of the interaction energies for a few typical systems with fixed geometries. Before turning to the results for individual complexes, a closer look to the behavior of the two functionals used with respect to closed-shell interactions seems appropriate. The potential energy curve for the stacking of two cytosine molecules (frozen monomer geometry, antiparallel orientation with the center-of-masses exactly above each other) serves as an example (see Figure 5). The stacking of DNA base pairs has been studied in great detail theoretically⁴³ and these systems were also used to calibrate modified density functionals¹³ and the other DFT models including dispersive corrections.^{12,16}

Although the curve from the standard DFT-BLYP treatment exhibits only a very flat bonding region between 400 and 450 pm with about -2 kcal/mol depth due to ES interactions, the PBE functional implicitly accounts for some van der Waals attraction as indicated by a much smaller intermolecular distance (about 360 pm) and stronger binding (-3.6 kcal/mol). This different behavior of PBE opposed to B88 based functionals has been observed recently also in a study of weak $C-H \cdots F-R$ interactions⁴⁴ (see also ref. 45). As can be seen by comparison with the relatively accurate SCS-MP2⁴⁶ curve, both DFT-D approaches yield very good results. Compared to pure MP2, the SCS-MP2 method reduces the interaction energy by about 2 kcal/mol, which agrees well with the difference between CCSD(T) and MP2 reported for similar structures in ref. 47. A similar value for ΔE of -8.3 kcal/mol obtained at the MP2/6-311G(2d,2p) level ($R = 330$ pm⁴³) results from a fortunate error cancellation between the incomplete AO basis and the tendency of MP2 to overestimate stacking interactions. The DFT-D-PBE curve is almost parallel to that from SCS-MP2 while the depth of the DFT-D-BLYP potential agrees better with the SCS-MP2 reference. Note that both DFT-D curves are much closer to each other compared to uncorrected DFT. This could be achieved by the scaling factor s_6 . There are,

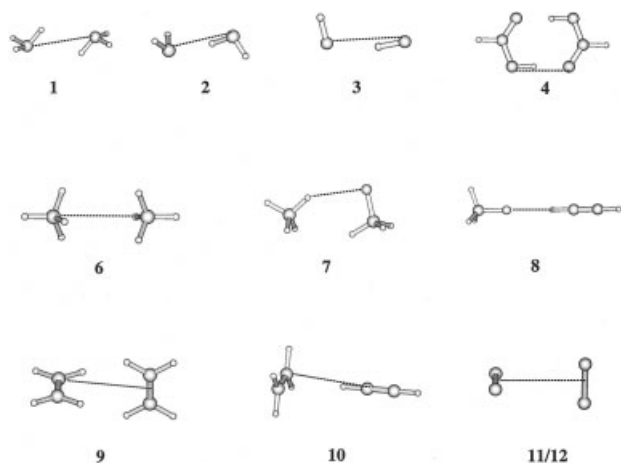


Figure 2. Optimized structures (DFT-D-BLYP/TZV(2d,2p)) of the investigated nonaromatic complexes. Dashed lines define the intermolecular distances.

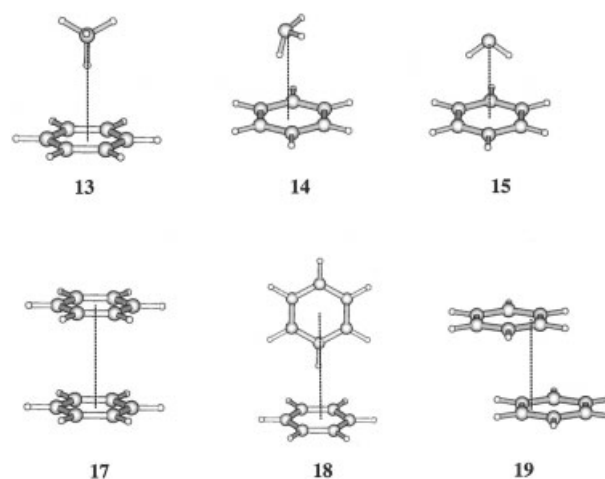


Figure 3. Optimized structures (DFT-D-BLYP/TZV(2d,2p)) of the benzene complexes. Dashed lines define the intermolecular distances.

however, remaining differences between BLYP and PBE in the description of saturated vs. π systems that are discussed below.

The structures of all investigated complexes are shown in Figures 2–4. The optimized intermolecular distances and the corresponding interaction energies ΔE are gathered together with reference data in Table 3 (BLYP) and 4 (PBE). In the following discussion the systems are grouped according to chemical structure and type of interaction.

Hydrogen-Bonded Complexes

Strong hydrogen bonds are already described very accurately with most standard density functionals.¹⁰ The dispersion contributions to ΔE of about 10–30% in these systems are implicitly accounted for by DFT because opposed to most van der Waals complexes, the fragment electron densities significantly overlap. Any of the empirical C_6R^{-6} approaches will thus introduce some “double-counting” of correlation effects that have been ignored so far. The H-bonded complexes in the series NH_3 , H_2O , HF , and formic acid will serve as extreme examples how large these effects are. Note that steep damping functions as used here are mandatory to retain the original DFT description as close as possible in these systems.

For $(NH_3)_2$, which is a borderline case for hydrogen bonding, the DFT-D-BLYP results for the binding energy and R are better than with pure DFT. This is consistent with the large dispersion contribution to ΔE of about 60% for this system.¹⁰ The DFT-PBE method without any correction already overbinds for $(NH_3)_2$. For the other complexes the DFT-D binding energies with both functionals are too low compared to uncorrected DFT. This overbinding, however, does not exceed 10% with BLYP and the intermolecular distances are almost unaffected and still very accurate. It is interesting to note that although the DFT-D ΔE values are worse compared to those from DFT, the difference between the binding energy of water and HF dimers (about -0.4 kcal/mol) is improved by the dispersion correction. Comparing the functionals PBE and BLYP it is seen that the PBE interaction energies are about 0.4–0.5 kcal/mol (1.9 kcal/mol for $(HCOOH)_2$) lower compared

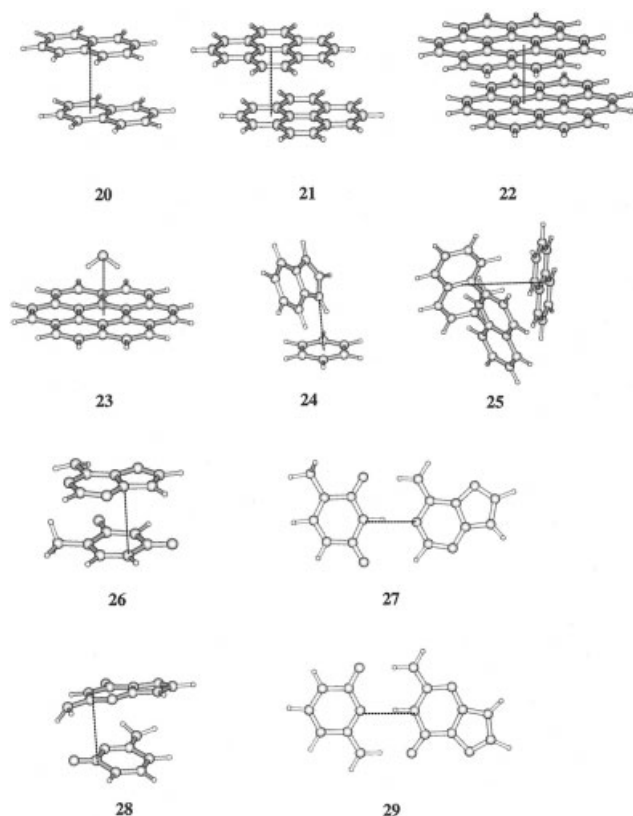


Figure 4. Optimized structures (DFT-D-BLYP/TZV(2d,2p)) of the larger aromatic complexes and base pairs. Dashed lines define the intermolecular distances.

to BLYP mainly because the pure DFT data already show this difference.

In summary, it can be concluded that the empirical correction slightly deteriorates the DFT results for strongly bound systems. The effect is more pronounced for PBE than for BLYP. However, for structures the differences are negligible and for the interaction energies they are on the order of basis set incompleteness effects and seem thus not too relevant in practical applications involving such bonding situations (more realistic examples are discussed later).

Complexes of Nonaromatic Molecules

This group of test systems mainly consists of monomers with σ -bonds only. Two unsaturated complexes studied previously^{10,48} (π complex of ethene and the C—H/ π complex of ethine and ethene) and the N₂ dimer are also included. Because fluorine containing compounds have not been investigated so far with approaches like DFT-D, complexes of CH₃F and (F₂)₂ are studied. For the former compounds accurate MP2 data already exist.⁴⁴

In general, the DFT-D predictions with both functionals are in good agreement with the reference data. Because of the significant BSSE obtained with the TZV(2d,2p) basis for these small systems, only the binding energies using the larger basis set will be dis-

cussed. Except for the CH₃F • ethine complex with the BLYP functional, the DFT-D errors for intermolecular distances R are below 10 pm. The errors of the binding energies are usually below 0.1–0.2 kcal/mol. Furthermore, the predictions for the very weakly bound complexes **5**, **6**, and **11–12** are of the same accuracy as for the other systems, which involve some attractive ES contributions. Comparing the results of the two functionals it is noticed that PBE provides slightly shorter R and lower ΔE values. Note that at the uncorrected DFT-BLYP level only complexes **8** and **10** are bound indicating dominant ES interactions in these systems. As noted before, the PBE functional simulates to some extent dispersive interactions, and thus all complexes are weakly bound at this level. However, the ΔE values from DFT-PBE are much too small and the dispersive correction considerably improves also here.

Complexes with Benzene

Small Molecules

Complexes of benzene with atoms and small molecules have been studied before at various levels of theory (see, e.g., refs. 9, 19, 49, and 50) although very accurate CCSD(T) data are still missing. The adducts studied range from nonpolar (Ne, CH₄) to polar molecules (NH₃ and H₂O) where ES interactions become more important. For the complex with methane we investigate the more stable structure where one C—H bond points towards the center of the benzene ring. The potential energy surfaces (PES) of the complexes with NH₃ and H₂O are extremely flat, that is, within an energy range of about 0.1–0.2 kcal/mol strong changes in the position above the benzene plane are observed. The DFT-D optimized structure for the NH₃ complex has low symmetry where one of the N—H bonds points onto a carbon atom or a carbon–carbon bond. For the complex with water a structure with C_{2v} symmetry is found that contradicts predictions from MP2 calculations.⁵⁰ Compared to the MP2 reference data, the DFT-D distances of the heavy atom (C, N, or O) with respect to the benzene ring are

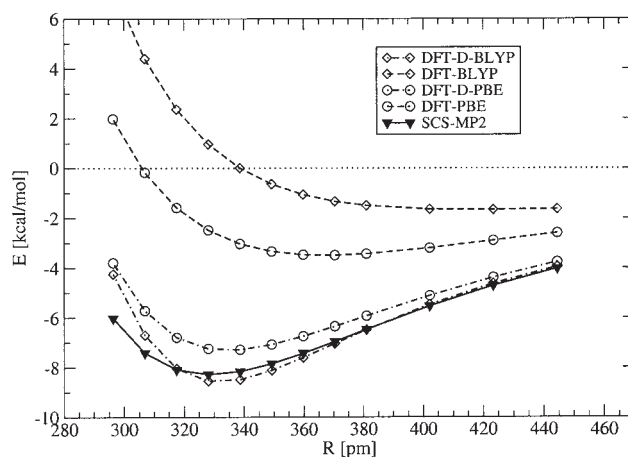


Figure 5. Dependence of the interaction energy on the vertical separation for the cytosine base pair (antiparallel oriented, planar fragments, C_i symmetry, QZV(2df,2dp) AO basis). The counterpoise-corrected SCS-MP2(FC) values are included as reference.

Table 3. Calculated Intermolecular Distances (R , in pm), Pure DFT Interaction Energies (ΔE_{DFT} , in kcal/mol, Using the DFT-D Optimized Geometry) and Binding Energies Including the Dispersion Correction (ΔE , in kcal/mol) at the DFT-D-BLYP/QZV(2df,2pd)//DFT-D-BLYP/TZV(2d,2p) Level of Theory. For comparison, ΔE values using the TZV(2d,2p) AO basis (in parentheses) as well as available reference values are also included.

Complex		$-\Delta E_{\text{DFT}}$	DFT-D-BLYP		Reference		
			R	$-\Delta E$	R	$-\Delta E$	Method ^a
Hydrogen bonded complexes							
1	(NH ₃) ₂ (C_{2h})	2.17	327	3.18 (3.59)	317	3.0	MP2/MP4 ^b
2	(H ₂ O) ₂ (C_s)	4.53	293	5.42 (5.98)	292	4.8	MP2 ^c /CCSD(T) ^d
3	(HF) ₂ (C_s)	4.48	276	4.96 (5.48)	275	4.4	MP2 ^c /CCSD(T) ^d
4	(HCOOH) ₂ (C_{2h})	14.06	268	16.09 (16.60)	266	13.9	MP2 ^c /CCSD(T) ^d
Non-aromatic complexes							
5	(Ne) ₂ ($D_{\infty h}$)	−0.11	311	0.05 (0.20)	309	0.08	exp. ^e
6	(CH ₄) ₂ (D_{3d})	−0.80	363	0.31 (0.32)	360	0.5	MP2 ^d
7	CH ₃ F · CH ₄ (C_s)	−0.43	263	0.98 (1.17)	261	0.7	MP2 ^f
8	CH ₃ F · ethine (C_{3v})	1.21	230	1.62 (1.76)	219	1.7	MP2 ^f
9	(ethene) ₂ (D_{2d})	−1.22	373	1.36 (1.41)	380	1.3	MP2/CCSD(T) ^d
10	ethene · ethine (C_{2v})	0.38	389	1.35 (1.45)	382	1.52	MP2 ^c
11	(N ₂) ₂ (D_{2d})	−0.24	368	0.29 (0.19)	341	0.33	MP2 ^c
12	(F ₂) ₂ (D_{2d})	−0.40	304	0.27 (0.34)	306	0.27	MP2 ^c
Benzene complexes							
13	benzene · CH ₄ (C_{3v})	−1.00	381	0.90 (0.96)	362	1.6	MP2 ^c
14	benzene · NH ₃ (C_s)	0.25	362	1.78 (2.16)	345	2.4	MP2 ^c
15	benzene · H ₂ O (C_{2v})	0.70	333	3.13 (3.73)	321	3.9	MP2 ^g
16	benzene · Ne (C_{6v})	−0.41	341	0.24 (0.56)	330	0.43	exp. ^h
Benzene dimers							
17	(benzene) ₂ (D_{6h})	−3.11	390	1.04 (1.21)	370	1.8	MP2/CCSD(T) ⁱ
18	(benzene) ₂ (T, C_{2v})	−1.08	506	2.03 (2.20)	490	2.7	MP2/CCSD(T) ⁱ
19	(benzene) ₂ (PD, C_{2h})	−3.39	352	2.00 (2.18)	340	2.8	MP2/CCSD(T) ⁱ
Complexes of larger aromatic molecules							
20	(naphthalene) ₂ (C_i)	−6.31	345	5.34 (5.58)	350	6.2	MP2/CCSD(T) ^j
21	(pyrene) ₂ (C_{2h})	−11.36	343	11.82 (12.35)	353	13.1	exp. ^k /MP2 ^l
22	(coronene) ₂ (C_i)	−17.52	340	21.56 (22.21)	—	—	
	coronene · H ₂ O						
23	(C_{2v})	0.10	330	3.20 (4.09)	339 ^m	4.5	MP2 ⁿ
24	benzene · indole (C_1)	−0.20	334	4.78 (5.15)	316	5.9	MP2/exp. ^o
25	(naphthalene) ₃ (C_{3h})	−8.09	486	13.22 (13.82)	493	8.7	exp. ^p
DNA base pairs							
26	A · T (S, C_1)	−2.36	344	10.47 (11.27)	—	11.6	MP2/CCSD(T) ^q
27	A · T (WC, C_s)	10.91	284	15.01 (15.54)	—	15.4	MP2/CCSD(T) ^q
28	G · C (S, C_1)	5.16	317	15.30 (16.53)	—	16.9	MP2/CCSD(T) ^q
29	G · C (WC, C_s)	23.56	293	28.10 (28.82)	—	28.8	MP2/CCSD(T) ^q

^aThe first entry refers to the geometry, the second (if present) to the binding energy.

^bRef. 63.

^cThis work. Fully optimized RI-MP2(FC)/aug-cc-pVTZ⁶⁴ structures and counterpoise-corrected^{31,32} binding energies.

^dRef. 10.

^eRefs. 65 and 66.

^fRef. 44.

^gRef. 50.

^hRef. 67.

ⁱRef. 51.

^jRef. 55.

^kInterplanar distance in the crystal.⁵⁹

^lRef. 21.

^mValue of the triphenylene · H₂O complex from ref. 58.

ⁿRef. 58.

^oRef. 60.

^pRef. 57.

^qRef. 47.

consistently overestimated by about 10 pm. In part, this can be explained by a general exaggeration of the interactions with π systems by MP2. For example in the H_2O complex, the experimental R values range between 333 and 335 pm, which is in almost perfect agreement with the DFT-D data (330–333 pm). This view is also supported by the good agreement between theory and experiment for the neon complex where especially DFT-D-PBE is remarkably accurate.

The DFT-D binding energies again agree well with the reference data and the increase of stability in the order **16**, **13–15** is reproduced almost quantitatively. The largest deviation of about 0.7 kcal/mol is found with BLYP for the complex with methane. Compared to BLYP, the lower ΔE values obtained with PBE seem to be slightly superior for this group of complexes.

Dimers

A very sensitive test for the quality of the dispersion correction are the benzene dimers. Of the two lowest energy structures, the T-shaped is clearly preferred by HF and standard DFT methods because it has larger (attractive) electrostatic interactions than the parallel-displaced (PD) form, which is more stabilized by dispersion. Note, however, that only the T-shaped form is bound at the pure DFT-PBE level. According to CCSD(T)⁵¹ and recent SCS-MP2⁴⁶ results, the T and PD isomers are very close in energy, which is nicely reproduced by the DFT-D-BLYP method. The PBE functional slightly favors the C—H/ π interaction in the T-form compared to π stacking, which is also observed for larger aromatic complexes (see later). This is also indicated by the large R value computed with PBE for the stacked form **17**. The energy difference of the PD and T isomers with respect to **17** (which is not a true minimum, however) of about 1 kcal/mol is obtained correctly. The absolute binding energies from DFT-D are slightly lower than those from CCSD(T) but compare very well with recent SCS-MP2 data (about –2 kcal/mol)⁴⁶ and with experiment [–(1.6 – 2.4) kcal/mol for the T-shaped form, see ref. 51 and references therein].

The comparison of DFT-D and MP2 intermolecular distances is problematic for all aromatic compounds because MP2 in general overestimates dispersive π – π interactions. The counterpoise(CP)-corrected MP2 reference data⁵¹ have been obtained by rigid-monomer calculations of parts of the PES. Because of the small number of points used, the data are expected to be accurate to only about ± 3 pm. Furthermore, the CP correction usually overestimates the effect of BSSE and thus the reported values certainly represent an upper bound for MP2. A full geometry optimization⁵² of the T-shaped form using the aug-cc-pVTZ basis yields a center-of-mass distance of 479.5 pm, which is 16.5 pm smaller than the experimental value of 496 pm.⁵³ It is thus concluded that differences between the DFT-D and MP2 data (10–20 pm) at least in part result from a deficiency of MP2 and that the DFT-D results for benzene dimers can be considered as quite accurate (probably 5–10 pm too long).

Complexes of Larger Aromatic Molecules

Although the larger complexes of aromatic molecules are most interesting from the chemical point of view, it is worth mentioning that both experimental and theoretical data from the literature are

not always accurate enough to allow a definite assessment of the present approach. This should be kept in mind when the reference data in Tables 3 and 4 are discussed.

For the naphthalene and pyrene dimers, several different orientations of the monomers in stacked arrangements that are within an energy range of 1–2 kcal/mol are possible.^{54,55} The displaced structures **20** and **21**, that resemble the crystal structure of graphite, have been found to be the most stable isomers.^{21,55,56} In any case, the investigated structures seem representative for π – π interactions in large aromatic compounds. For the coronene dimer, which has not been investigated before, we also assume a graphite-like structure with C_i symmetry. The structure of the naphthalene trimer (threefold C—H/ π interactions) is very clear from experimental microwave data.⁵⁷ For the coronene · H_2O complex no other structural data are available and therefore the MP2 distance of the corresponding complex with triphenylene⁵⁸ is taken as reference.

The most notable difference with respect to the theoretical reference data is found for the interplanar distance in the pyrene dimer (343 and 351 pm with BLYP and PBE, respectively, opposed to 379 pm with MP2/6-31G). However, both DFT-D values agree quite well with the interplanar distance found in the crystal (353 pm⁵⁹). Also, the available geometry⁵⁵ of the naphthalene dimer [R = 350 pm, MP2+CCSD(T) correction] is in very good agreement with the DFT-D structures (345 and 350 pm with BLYP and PBE, respectively). Especially the DFT-D-BLYP results seem to be very consistent because a convergence with increasing number of aromatic rings in the series of dimers **20–22** (345, 343 and 340 pm) to the experimental R value observed for graphite (340 pm) is predicted. The R values from PBE are about 10 pm larger. At present, it is not clear how fast the convergence of this property with the size of the graphite fragment is but it seems very likely that the “true” R values are between those of BLYP and PBE. For the naphthalene trimer, both DFT-D values are in excellent agreement with experimental microwave data [486 (BLYP) and 489 (PBE) pm vs. 493 pm (exp.)⁵⁷].

The binding energies for the naphthalene trimer (–13.2 kcal/mol with BLYP) are lower than the experimental value (–8.7 kcal/mol⁵⁷) but this difference partly can be attributed to neglected vibrational contributions which may be around 1–2 kcal/mol. In light of the good accuracy of DFT-D for other systems of similar structure, however, it seems likely that the experimental value is too high. In any case, the DFT-D data represent a significant improvement compared to previous HF-D and MP2 calculations which overestimated the ΔE value by a factor of 2–3.²¹ All larger aromatic systems represent important tests for the correction because the pure DFT potentials are very repulsive (also for PBE in most cases) and the differential correction between the complex and the monomers is large (about 40 kcal/mol for **22**). Comparing the two functionals is found that PBE underbinds **20–22** relative to the naphthalene trimer with dominant C—H/ π interactions, which has already been observed for the benzene dimers. In passing, it is noted that the BSSE for the large aromatic systems is less than 5% with the TZV(2d,2p) AO basis, and furthermore, fairly constant for differently bound systems (**20–22** vs. **25**).

The coronene · H_2O complex has been studied before at the MP2 level⁵⁸ to extrapolate to the binding energy of a water molecule on graphite. In light of the problems of MP2 with

Table 4. Calculated Intermolecular Distances (R , in pm), Pure DFT Interaction Energies (ΔE_{DFT} , in kcal/mol, Using the DFT-D Optimized Geometry) and Binding Energies Including the Dispersion Correction (ΔE , in kcal/mol) at the DFT-D-PBE/QZV(2df,2pd)//DFT-D-PBE/TZV(2d,2p) Level of Theory. For comparison, ΔE values using the TZV(2d,2p) AO basis (in parentheses) as well as available reference values are also included.

Complex		$-\Delta E_{\text{DFT}}$	DFT-D-PBE		Reference		
			R	$-\Delta E$	R	$-\Delta E$	Method ^a
Hydrogen bonded complexes							
1	(NH ₃) ₂ (C_{2h})	3.14	318	3.61 (4.00)	317	3.0	MP2/MP4 ^b
2	(H ₂ O) ₂ (C_s)	5.45	289	5.90 (6.43)	292	4.8	MP2 ^c /CCSD(T) ^d
3	(HF) ₂ (C_s)	5.12	272	5.35 (5.85)	275	4.4	MP2 ^c /CCSD(T) ^d
4	(HCOOH) ₂ (C_{2h})	16.93	262	17.98 (18.52)	266	13.9	MP2 ^c /CCSD(T) ^d
Non-aromatic complexes							
5	(Ne) ₂ ($D_{\infty h}$)	0.12	296	0.21 (0.34)	309	0.08	exp. ^e
6	(CH ₄) ₂ (D_{3d})	0.04	367	0.56 (0.59)	360	0.5	MP2 ^d
7	CH ₃ F · CH ₄ (C_s)	0.48	263	1.16 (1.35)	261	0.7	MP2 ^f
8	CH ₃ F · ethine (C_{3v})	1.62	226	1.84 (1.96)	219	1.7	MP2 ^f
9	(ethene) ₂ (D_{2d})	0.32	375	1.56 (1.62)	380	1.3	MP2/CCSD(T) ^d
10	ethene · ethine (C_{2v})	1.20	384	1.71 (1.83)	382	1.52	MP2 ^c
11	(N ₂) ₂ (D_{2d})	0.20	361	0.49 (0.41)	341	0.33	MP2 ^c
12	(F ₂) ₂ (D_{2d})	0.20	304	0.53 (0.59)	306	0.27	MP2 ^c
Benzene complexes							
13	benzene · CH ₄ (C_{3v})	0.26	382	1.21 (1.25)	362	1.6	MP2 ^c
14	benzene · NH ₃ (C_s)	1.14	358	2.19 (2.56)	345	2.4	MP2 ^c
15	benzene · H ₂ O (C_{2v})	2.33	330	3.58 (4.17)	321	3.9	MP2 ^g
16	benzene · Ne (C_{6v})	−0.16	324	0.57 (0.59)	330	0.43	exp. ^h
Benzene dimers							
17	(benzene) ₂ (D_{6h})	−0.70	404	1.02 (1.21)	370	1.8	MP2/CCSD(T) ⁱ
18	(benzene) ₂ (T, C_{2v})	0.63	506	2.18 (2.33)	490	2.7	MP2/CCSD(T) ⁱ
19	(benzene) ₂ (PD, C_{2h})	−0.58	357	1.82 (1.95)	340	2.8	MP2/CCSD(T) ⁱ
Complexes of aromatic molecules							
20	(naphthalene) ₂ (C_i)	−1.62	350	3.87 (4.07)	350	6.2	MP2/CCSD(T) ^j
21	(pyrene) ₂ (C_{2h})	−2.68	351	7.93 (8.27)	353	13.1	MP2 ^l
22	(coronene) ₂ (C_i)	−4.89	349	12.95 (13.48)	—	—	
23	coronene · H ₂ O (C_{2v})	2.00	329	3.68 (4.31)	339 ^m	4.5	MP2 ⁿ
24	benzene · indole (C_1)	2.47	334	4.80 (5.48)	316	5.9	MP2/exp. ^o
25	(naphthalene) ₃ (C_{3h})	1.16	489	11.50 (12.14)	493	8.7	exp. ^p
DNA base pairs							
26	A · T (S, C_1)	−2.46	349	8.68 (9.42)	—	11.6	MP2/CCSD(T) ^q
27	A · T (WC, C_s)	13.97	280	16.11 (16.64)	—	15.4	MP2/CCSD(T) ^q
29	G · C (WC, C_s)	27.38	289	29.72 (30.46)	—	28.8	MP2/CCSD(T) ^q

^aThe first entry refers to the geometry, the second (if present) to the binding energy.

^bRef. 63.

^cThis work. Fully optimized RI-MP2(FC)/aug-cc-pVTZ⁶⁴ structures and counterpoise-corrected^{31,32} binding energies.

^dRef. 10.

^eRefs. 65, 66.

^fRef. 44.

^gRef. 50.

^hRef. 67.

ⁱRef. 51.

^jRef. 55.

^kInterplanar distance in the crystal.⁵⁹

^lRef. 21.

^mValue of the triphenylene · H₂O complex from Ref. 58.

ⁿRef. 58.

^oRef. 60.

^pRef. 57.

^qRef. 47.

extended π systems, the DFT-D data seem reasonable, although it should be mentioned that the increase of the binding energy when going from benzene to coronene (about 0.1 kcal/mol) is smaller than in the MP2 study (0.6 kcal/mol).

For the benzene \cdot indole N—H/ π complex (**24**) accurate experimental as well as theoretical data are available.⁶⁰ The experimentally derived interaction energy of -5.9 kcal/mol [$\Delta H_{\text{exp}}^0 - \Delta \text{ZPVE}(\text{MP2})$] is well reproduced by both DFT-D approaches (-4.78 and -4.80 kcal/mol with BLYP and PBE, respectively) that seem to be more accurate compared complete basis set MP2 estimates (-7.2 kcal/mol⁶⁰). All theoretical approaches predict a structure of the complex where the indole N—H bond points to the center of the benzene ring. As observed before, the R values from DFT-D (334 and 333 pm with BLYP and PBE, respectively) are larger than that from MP2 (316 pm). Also, the elongation of the N—H bond upon complex formation [0.3 pm with MP2/TZV(2df,2pd)⁶⁰] is predicted almost quantitatively by DFT-D (0.1 and 0.3 pm with BLYP and PBE, respectively).

DNA Base Pairs

From the extensively studied pairs of DNA bases⁴³ we chose the stacked (S) and H-bonded (Watson–Crick, WC) structures of adenine \cdot thymine (AT) and guanine \cdot cytosine (GC), respectively. As reference interaction energies, the recent values of Jurecka and Hobza⁴⁷ obtained at the complete basis set estimate MP2 level and corrected by small basis set CCSD(T) energies are taken. At the DFT-D-BLYP/TZV(2d,2p) level, the interaction energies are in excellent agreement with the reference data. The largest difference is 0.4 kcal/mol for GC(S) and all other values are within 0.1–0.2 kcal/mol of the reference data. The corresponding DFT-D-BLYP/QZV(2df,2pd) values are consistently 0.7–1.2 kcal higher. Note that the dispersion correction also improves the binding energies of the WC pairs by about 4–5 kcal/mol. This indicates that the hydrogen-bonding between these large π systems also includes a significant dispersion contribution and that “double-counting” effects (see earlier) seem to be negligible. These results suggest the DFT-D model as the method of choice for accurate studies of larger DNA fragments.

Compared to the DFTB approach including dispersion corrections,¹⁶ the present DFT-D ΔE values for the WC pairs are more accurate by about 4 kcal/mol.⁶¹ With the PBE functional, the stacked forms are slightly underbound relative to the H-bonded structures. For the GC(S) pair, no minimum was found with DFT-D-PBE but the geometry optimization converged instead to a H-bonded structure. This indicates the already mentioned tendency of PBE to disfavor stacked interactions. However, the GC(S) pair in general seems to be very close to a transition to a H-bonded structure. This is seen in the DFT-D-BLYP and MP2 structures where a large tilting of the molecular planes of G and C relative to each other is observed. The reason for this are probably the two very close $\text{NH}_2/\text{C}=\text{O}$ contacts that are present also in the stacked arrangement.

Summary and Conclusions

Two common density functionals augmented with an empirical correction for long-range dispersion effects have been used to

predict the structures and binding energies of a wide variety of weakly bonded molecular complexes. As in previous schemes, the dispersive correction term is described by a sum of damped interatomic potentials of the form $C_6 R^{-6}$ and added to the usual DFT energy. A steep damping function, averaged dispersion coefficients from the literature and theoretically derived van der Waals radii are employed. The finding that the two functionals PBE and BLYP, which show a very different behavior with respect to repulsive closed-shell interactions, give both accurate results seems to be very encouraging. Opposed to previous schemes of similar type, this different behavior is explicitly taken into account. The only necessary modification for different functionals concerns a global scaling factor for the atomic C_6 coefficients. At present, the relative performance of the DFT-D-BLYP and DFT-D-PBE models tested is difficult to judge because reliable experimental or theoretical data are missing, especially for the larger systems. DFT-D-PBE slightly favors interactions between saturated fragments compared to π – π interactions while the opposite is found for DFT-D-BLYP. On the basis of the present results, the DFT-D-BLYP approach can be recommended because it seems to yield more consistent results for the wide variety of systems studied (including hydrogen bonded complexes). Further refinement of the form of the dispersive interaction potential (damping function, combination rule for C_6 coefficients) is not warranted until more precise reference data become available. Parameter adjustments based on large basis set SCS-MP2 calculations⁴⁶ may provide a systematic route to a even more accurate description, although one should keep the inherent limitations of the method in mind (e.g. nonatomic additivity of dispersion in general or anisotropy of the fragment polarizabilities). The choice of hybrid functionals like B3LYP may also improve the results because the monomer geometries are more accurate, and especially extended π systems are better described by including a fraction of “exact” HF exchange. The prize to pay is, however, that one loses a major part of the efficiency of the RI technique, which then limits the size of the systems that can routinely be studied. A promising alternative may be meta-generalized gradient functionals like the recently proposed TPSS that yields good results for hydrogen-bonded systems.⁶²

In general, the accuracy of the DFT-D model for intermolecular distances is estimated to be about 5–10 pm for systems dominated by van der Waals interactions. The interaction energies are accurate to about 10–30% in most cases and the accuracy in general increases with the size of the systems. As long as larger monomers (>4–6 atoms) are considered and AO basis sets of at least polarized triple-zeta quality are used, BSSE effects are negligible at the DFT level and the laborious (and approximate) calculation of the counterpoise-correction can be avoided. This leads to a fully consistent description of geometries and other properties of the complexes. Another technical aspect of DFT calculations for weakly bonded systems that should be considered in the future is the error of numerical quadrature, which significantly worsens the convergence of the geometry optimizations.

From a practical point of view, there seem to be two major modes of operation for the DFT-D approach. First, large scale applications in, for example, supramolecular chemistry or biochemistry where both electrostatic and dispersive interactions are important now become possible. Second, the DFT-D data may

serve as input for other theoretical models, i.e., to calibrate simpler (e.g., force-field) potentials or the optimized structures can be used as input for more accurate and systematically improvable *ab initio* calculations of the interaction energies.

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