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Accuracy of intermolecular interaction energies, particularly those of hetero-atom containing molecules obtained by DFT calculations with Grimme's D2, D3 and D3BJ dispersion corrections

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Abstract

Intermolecular interaction potentials for the benzene, propane, perfluoromethane, furan, thiophene, selenophene, pyridine, phosphorine dimers and the benzene-methane, benzene-chlorobenzene, benzene-bromobenzene complexes were calculated using the BLYP, B97 (B98), BP86, BPBE, PBE, PW91, B3LYP, B3PW91, BMK, PBE1PBE, APF, ωB97 (ωB97X), CAM-B3LYP, LC-ωPBE, B2PLYP, mPW2PLYP, TPSS, M06L, M05, M052X, M06, M062X and M06HF functionals with Grimme's dispersion correction methods of the D2, D3 and D3BJ versions. The calculated potentials were compared with the CCSD(T) level potentials to evaluate the accuracy of the dispersion corrected DFT methods for calculating the intermolecular interaction energies of hydrocarbon molecules and molecules including hetero atoms (N, P, O, S, Se, F, Cl and Br). The performance of the calculations depends strongly on the choice of functional and dispersion correction method. Neither combination of the functionals and the dispersion correction methods can reproduce well the CCSD(T) level interaction potentials of all the complexes. The improvement of the functionals from GGA to hybrid GGA, meta GGA or meta hybrid GGA is not essential for improving the performance. The significant functional dependence suggests that the scaling factors, which were determined for each functional by fitting, are the cause of the dependence. The performance of the calculations of hydrocarbon molecules is much better than the molecules including hetero atoms. Smaller number of molecules including hetero atoms were used for the reference data of the fitting compared with hydrocarbon molecules, which will be one of the causes of the worse performance of the calculations of molecules including hetero atoms.

Introduction

Detailed information on intermolecular interactions (noncovalent interactions) is important in various research fields of chemistry and biochemistry. Intermolecular interactions control the structures of liquids[1,2] and crystals,[3,4] and also affect their physical properties. In addition, intermolecular interactions play important roles in controlling three-dimensional structures of polymers[5] and biomolecules and molecular recognition processes.[6-8] *Ab initio* molecular orbital calculations are becoming powerful methods for elucidating the details of intermolecular interactions (magnitude and origin of attraction and directionality).[6,9] Accurate intermolecular interaction energies can be obtained, if a sufficiently large basis set is used and electron correlation is properly corrected. The intermolecular interaction energies obtained by coupled-cluster calculations with single and double substitutions with non-iterative triple excitations [CCSD(T)] using large basis sets near the basis set limit are close to the experimental values in the gas phase.[10] However, the CCSD(T) calculations with large basis sets are computationally too demanding for studying intermolecular interactions of large molecules, as the computational time required for CCSD(T) calculation is proportional to seventh power of the number of basis functions.

The density functional theory (DFT) calculations are widely used for studying large molecules, as the DFT calculations are less computationally demanding. Unfortunately, however, the DFT calculations using popular functionals such as BLYP, B3LYP and PBE cannot accurately evaluate the dispersion interactions.[11,12] Accurate evaluation of the dispersion interactions is often crucial for studying intermolecular interactions of organic molecules, as the dispersion interactions are the primary source of the attraction between organic molecules, if the polarity of interacting organic molecules are not strong.[13,14] Therefore, accurate evaluation of the dispersion interactions is extremely important for studying the intermolecular interactions in molecular liquids, organic crystals, polymers and biomolecules. Recently several dispersion correction methods for DFT calculations were developed.[15-18] The dispersion corrected DFT calculations using the correction methods proposed by Grimme and coworkers, which are implemented in several quantum chemical calculation programs, are widely used.[19-21] The accuracy of the intermolecular interaction energies obtained by the dispersion corrected DFT calculations depends on the choice of functional and dispersion correction method significantly. Although several studies were reported on the accuracy of dispersion corrected DFT calculations,[22-27] there still remains ambiguity on the effects of the choice of functional and dispersion correction method on the accuracy of dispersion corrected DFT calculation. Especially the accuracy of the calculations of the interaction energies of molecules containing heteroatoms is not clear, although their dispersion correction methods were developed for 94 elements.[20,21] In addition, only few were reported on the accuracy of the intermolecular interaction potentials obtained by the dispersion corrected DFT calculations, although several studies were reported on the accuracy of the interaction energies calculated for the geometries registered in data base such as GMTKN55. In this paper, we calculated intermolecular interaction potentials of 11 complexes of organic molecules including molecules containing heteroatoms using several functionals and Grimme's dispersion correction methods. The calculated interaction potentials were compared with the CCSD(T) level interaction potentials to evaluate the accuracy of the dispersion corrected DFT calculations. The interaction potentials for the complexes of hydrocarbon molecules and molecules including hetero atoms (N, P, O, S, Se, F, Cl and Br) were studied.

Computational methods

The Gaussian 16 program[28] was used for the *ab initio* molecular orbital and DFT calculations. The geometries of isolated molecules were optimized at the MP2/cc-pVTZ level.[29,30] The optimized geometries were used for the calculations of intermolecular interaction potentials without further geometry optimizations. The basis set superposition error (BSSE)[31] was corrected for all interaction energy calculations using the counterpoise method.[32] The cc-pVTZ basis set was used for the dispersion-corrected DFT calculations. The BLYP,[33,34] B97 (B98),[36] BP86,[36] BPBE,[37] PBE,[37] PW91,[38] B3LYP,[39] B3PW91,[39] BMK,[40] PBE1PBE,[41] APF[42], ωB97 (ωB97X),[43] CAM-B3LYP,[44] LC-ωPBE,[45] B2PLYP,[46] mPW2PLYP,[47] TPSS,[48] M06L,[49] M05,[50] M052X,[51] M06,[52] M062X[52] and M06HF[53] functionals and Grimme's dispersion correction methods of the D2, D3 and D3BJ (D3 with Becke-Johnson damping) versions[19-21] were used for the calculations. All the possible combinations of the above functionals and the dispersion correction methods allowed in the Gaussian 16 program were tested. The default ultrafine integral grid was used for DFT calculations, except the calculations using the M06L, M06, M062X, M06HF functionals, where the superfine grid was used.[28] Because some of the potentials obtained using these functionals with the ultrafine grid have kinks and discontinuities. The intermolecular interaction potentials for the benzene, propane dimers and the benzene-methane complex were calculated to evaluate the accuracy of the dispersion corrected DFT calculations in calculating the dispersion interactions of the hydrocarbon molecules. Those for the pyridine, phosphorine, furan, thiophene, selenophene, perfluoromethane dimers, and the benzene-chlorobenzene, benzene-bromobenzene complexes were calculated to evaluate the calculations of the dispersion interactions of molecules including pnictogen, chalcogen and halogen atoms. The geometries of the complexes are shown in Figure 1. The configurations of the pyridine, phosphorine, furan, thiophene and selenophene dimers where a pnictogen or calcogen atom has contact with another aromatic ring were selected for the calculations, although these configurations do not correspond to the energy minimum structures. These geometries were selected, since they are suitable for the evaluation of the accuracy of the calculations of the dispersion interactions of the hetero atoms, owing to the short contact of the heteroatom and the aromatic ring. The second order Mϕller-Plesset (MP2) level interaction energy at the basis set limit [$E_{\mathrm{MP2(limit)}}$] for the complex was estimated by Helgaker et al.'s method[54] from the calculated MP2 level interaction energies (E_{MP2}) using the aug-cc-pVTZ and aug-cc-pVQZ basis sets. The CCSD(T) level interaction energy[55] at the basis set limit [$E_{\mathrm{CCSD(T)(limit)}}$] was calculated as the sum of the $E_{\mathrm{MP2(limit)}}$ and the estimated CCSD(T) correction term [the difference between the CCSD(T) and MP2 level interaction energies, ΔCCSD(T) = $E_{\mathrm{CCSD(T)}} - E_{\mathrm{MP2}}$] at the basis set limit [ΔCCSD(T)(limit)], which was estimated from the difference between the calculated CCSD(T) and MP2 level interaction energies using the aug-cc-pVDZ basis set.[56,57] The details of the estimation procedure of the $E_{\mathrm{CCSD(T)(limit)}}$ are shown in supplementary information.

Results and discussion

Comparison with CCSD(T) calculations

The intermolecular interaction potentials calculated for the 11 complexes at the HF, MP2 are CCSD(T) levels are shown in Figure 1S. The MP2 and CCSD(T) interaction energies are estimated values at the basis set limit ($E_{\mathrm{MP2(limit)}}$ and $E_{\mathrm{CCSD(T)(limit)}}$). The HF interaction energy was calculated using the aug-cc-pVQZ basis set. The comparison of the HF and CCSD(T) level potentials shows that the attraction increases greatly by the electron correlation correction, which shows that the strong dispersion interactions exist in the 11 complexes. The strong dispersion interactions observed in the 11 complexes show that these complexes are appropriate for the evaluation of the accuracy of the calculations of the dispersion interactions. The intermolecular interaction energies calculated for the benzene dimer using several basis sets are shown in Figure 2S to show the basis set effects on the calculated interaction energies. Detailed discussion on the effects of electron correlation and basis set effects on the calculated interaction energies are shown in supplementary information.

The intermolecular interaction potentials obtained by the dispersion corrected DFT calculations were compared with the CCSD(T) [$E_{\mathrm{CCSD(T)(limit)}}$] level interaction potentials to evaluate the accuracy of the intermolecular interaction energies obtained by the dispersion corrected DFT calculations as shown in Figures 3S-13S in supplementary information. The deviations of calculated interaction energies from the $E_{\mathrm{CCSD(T)(limit)}}$ at the potential minimum of CCSD(T) level potential were calculated. The ratios of the deviations to the CCSD(T) level interaction energies (deviation ratios) are summarized in Table 1. The absolute deviations of the calculated equilibrium distances are less than 0.2 Å, when the absolute deviation ratios of calculated interaction energies are less than 20 %. The mean absolute deviation ratios (MADRs) for the 11 complexes are summarized in Table 2.

GGA (BLYP, BP86, BPBE, PBE, PW91, B97D) functionals

The performance of these GGA functionals with the dispersion corrections depend strongly on the choice of functional and dispersion correction method. The combinations of the BLYP and PBE functionals with the D3 correction and the PBE functional with the D3BJ correction show the best performance among the combinations of the six GGA functionals with the dispersion corrections. The MADRs for the calculations of the 11 complexes from the CCSD(T) calculations are 9-12 % as shown in Table 2. The MADRs for the combinations of the B97 and PBE functionals with the D3 correction (19 and 9 %) are nearly identical to the MADRs for the combinations of these functional with the D3BJ correction (22 and 9 %), while the MADRs for the combinations of the BLYP, BP86, BPBE functionals with the D3 correction (12, 22 and 23 %) are significantly smaller than the MADRs for the combinations of these functionals with the D3BJ correction (19, 39 and 40 %). The D3 correction often shows better performance compared with the D3BJ correction, when these GGA functionals are used for the calculations. The combinations of these GGA functionals with the D2 correction have larger MADRs (20-40 %) compared with the D3 and D3BJ corrections. The MADRs for the calculations of the three complexes of hydrocarbon molecules using the combination of the BLYP and PBE functionals with the D3 correction and the PBE functional with the D3BJ correction (9, 11 and 7%) are close to the MADRs for the calculations of other complexes including hetero atoms using the same combinations (13, 9, 10 %), while the calculations of the complexes including hetero atoms have larger MADRs compared with the calculations of the complexes of hydrocarbon molecules when other combinations are used. For example, the MADRs for the calculations of hydrocarbon molecules using the B3LYP functional with the D3BJ correction is 8%, while the MADRs for the calculations of molecules including hetero atoms is 23 %. The B97D functional, which includes the D2 correction, shows very good performance in the calculations of hydrocarbon molecules. The MADRs for the calculations of the three complexes of hydrocarbon molecules using the B97D functional is 10 %. Although some combinations have small MADRs for the calculations of the 11 complexes (about 10 %), no combinations of these GGA functionals and the dispersion corrections show good performance for the calculation of the perfluoromethane dimer (absolute deviation ratios are 21-135 %) except the combination of the PBE functional and the D3 correction (absolute deviation ratio is 4 %). Unfortunately, the performance of this combination for the calculations of the propane and phosphorine dimers is not good (absolute deviation ratios are 21 and 23 %) as shown in Table 1. The calculations using these GGA functionals without the dispersion correction have very large MADRs, since these functionals hardly evaluate the attraction in these complexes.

Hybrid GGA (B3LYP, B3PW91, BMK, PBE1PBE, APFD, ωB97XD) functionals

The performance of these hybrid GGA functionals with the dispersion corrections depend strongly on the choice of functional and dispersion correction method as in the case of the GGA functionals. The combinations of the B3LYP and PBE1PBE functionals with the D3 or D3BJ correction show the best performance among the combinations of these six hybrid GGA functionals with the dispersion corrections. The MADRs for the calculation of the 11 complexes using these combinations are 11-15 % as shown in Table 2. The APFD functional, which includes dispersion correction, and the combination of the B3PW91 functional with the D3 correction also show good performance. The MADRs of these methods are both 18 %. The combination of the B3PW91 functional with the D3BJ correction, those of the BMK functional with the D3 and D3BJ corrections have larger MADRs (30-58 %). The interaction potentials calculated using the BMK functional with the dispersion corrections show strange behavior even after the dispersion correction. The calculated potentials using the BMK functional often have highly repulsive region when molecules are well separated as shown in Figures 3S-13S. The potentials calculated using BMK functional with the dispersion correction do not agree with the CCSD(T) level potentials. The MADRs for the combinations of the B3LYP, BMK and PBE1PBE functionals with the D3 correction (13, 50 and 12 %) are nearly identical to the MADRs for the combinations of these functionals with the D3BJ correction (15, 58 and 11 %), the MADRs for the combination of the B3PW91 functional with the D3 correction (18 %) are smaller than the MADRs for the combination of this functional with the D3BJ correction (30 %). The combination of the B3LYP functional with the D2 correction has larger MADRs (30 %) compared with the combination with the D3 or D3BJ correction (13 and 15 %). The MADRs using the ωB97DX, which includes the D2 correction, is 23 %. The MADRs for the calculations of the three complexes of hydrocarbon molecules obtained using the combination of the PBE1PBE functional with the D3 correction (12 %) is close to that for the calculations of other complexes including hetero atoms using the same combination (12 %), while the calculations of the complexes including hetero atoms have larger MADRs compared with the calculations of the complexes of hydrocarbon molecules when other combinations are used. Although some combinations have small MADRs for the calculations of the 11 complexes, no combinations of these hybrid GGA functionals and the dispersion corrections show good performance for the calculation of the perfluoromethane dimer (absolute deviation ratios are 22-246 %) except the combination of the PBE1PBE functional with the D3 correction and the ωB97XD functional (absolute deviation ratios are 10 and 17 %). Unfortunately, the performance of these methods for the calculations of the pyridine dimer is not good as shown in Table 1. The calculations with the B3LYP, B3PW91, BMK, PBE1PBE and APF functionals without the dispersion correction have very large MADRs.

Long-range-corrected hybrid GGA (CAM-B3LYP, LC-ωPBE) functionals

The combinations of these long-range-corrected hybrid GGA functionals with the D3 or D3BJ correction show good performance. The MADRs for the calculation of the 11 complexes are 8-17 % as shown in Table 2. The MADRs are close to those for the calculations using the PBE (GGA) and B3LYP (hybrid GGA) functionals with the D3 or D3BJ correction (MADRs are 9-15 %). The combination of the CAM-B3LYP functional with the D3BJ correction shows better performance than the combination of this functional with the D3 correction, while the D3 and D3BJ corrections show nearly the same performance for the calculations using the LC-ωPBE functional. The four combinations show better performance in the calculations of hydrocarbon molecules

(MADRs are 0-13 %) compared with the calculations of complexes including hetero atoms (MADRs are 10-20 %) as in the cases of many combinations of the GGA and hybrid GGA functionals with the D3 and D3BJ corrections. Although the combination of the CAM-B3LYP functional with the D3BJ shows good performance in most of the calculations, the calculations of the perfluoromethane and pyridine dimers using this combination have large absolute deviation ratios (20 %). The combinations of the LC-ωPBE functional with the D3 and D3BJ correction have large absolute deviation ratios (23-47 %) in the calculations of the perfluoromethane, furan, and pyridine dimers. The calculations with these two functionals without dispersion correction have very large MADRs (138 and 143 %).

Double hybrid (B2PLYPD, mPW2PLYPD) functionals

The performance of these double hybrid functionals is not good. The calculations using these functionals underestimate the attraction significantly even after the dispersion corrections. The MADRs for the calculations of the 11 complexes using the B2PLYPD and mPW2PLYPD, which include the D2 correction, are 101 and 87 % as shown in Table 2. The combination of the B2PLYP functional with the D3 and D3BJ corrections still have large MADRs (95 and 92 %). Although the merit of the perturbation theory correction used for these double hybrid functionals were often claimed,[46,47] the comparison of the calculated interaction energies using the double hybrid functionals with those by the CCSD(T) calculations shows that these double hybrid functionals are not appropriate for evaluating the dispersion interactions.

Meta GGA (TPSS, M06L) functionals

The performance of these meta GGA functionals depends on the choice of functional and dispersion correction method as shown in Table 2. The combinations of the TPSS functional with the D3 or D3BJ correction show good performance. The MADRs for the calculations of the 11 complexes are 11 and 13 %. The combination of the M06L functional with the D3 correction has larger MADRs (26 %). The combinations of the two functionals with the dispersion corrections show better performance in the calculations of hydrocarbon molecules compared with the calculations of complexes including hetero atoms as in the cases of the GGA and hybrid GGA functionals. Although the combination of the TPSS functional with the D3 correction shows good performance in most of the calculations, the calculations of the phosphorine dimer using this combination have a large absolute deviation ratio (24 %). The combination of the

M06L functional with the D3 correction shows good performance only in the calculations of limited complexes (the benzene, propane, furan and pyridine dimers). The calculations using the M06L functional without the dispersion correction has larger MADRs (42 %) compared with the calculations with the D3 correction. The calculations using the TPSS functional without the dispersion correction has very large MADRs (165 %).

Meta hybrid GGA (M05, M052x, M06, M062x, M06HF) functionals

The performance of the calculations using these meta hybrid GGA functionals are similar to that using the M06L functional as shown in Table 2. The performance of these functionals without the dispersion correction is much better than the BLYP and B3LYP functionals as shown in Table 1. The MADRs for the calculations of 11 complexes using these functionals are 32-87 %, while those using the BLYP and B3LYP functionals without the dispersion correction are 218 and 184 %. The interaction potentials calculated using these meta hybrid GGA functionals without the dispersion correction have potential minima as shown in Figures 3S-13S, in contrast to the potentials calculated using the BLYP and B3LYP functionals, which do not have potential minima. However, the interaction potentials calculated using these functionals without the dispersion correction underestimate the attraction substantially compared with the CCSD(T) level potentials in general, although it was often claimed that these functionals show much better performance compared with the popular functionals in calculations of weak intermolecular interactions such as the π/π and CH/π interactions, where the dispersion interactions are mainly responsible for the attraction.[12] The D3 correction improves the performance of the calculations using these functionals as in the case of the M06L functional. The MADRs are 13-26 % after the D3 correction. The interaction potentials obtained using these functionals with the D3 correction do not always agree with the CCSD(T) level potentials.

Comparison of functionals

The comparison of the calculated interaction potentials for the 11 complexes with the CCSD(T) level potential shows that the choice of functional and dispersion correction method is the accuracy-determining factor. The calculated interaction potentials depend strongly on the choice of functional and dispersion correction method.

The improvement of the functionals from GGA to hybrid GGA, meta GGA or meta hybrid GGA is not essential for improving the performance of the calculations. The functional dependence of the performance within the functionals in the same category is often significantly large. For example, the combination of the BLYP functional with the D3 correction shows much better performance (MADRs is 12 %) compared with the BPBE functional with the D3 correction (22 %), although both functionals are GGA functionals. The different performance is also observed in the comparison of the B3LYP and BMK (hybrid GGA) functionals with the D3 correction (13 and 50 %) and the in the comparison of the TPSS and M06L (meta GGA) functionals with the D3 correction (11 and 26 %). On the other hand, the combination of the BLYP (GGA) functional with the D3 correction, that of the B3LYP (hybrid GGA) functional with the D3 correction and that of the TPSS (meta GGA) functional with the D3 correction show nearly the same performance (MADRs are 12, 13 and 11 %).

The performance of the dispersion correction depends on the dispersion coefficients and scaling factors used in the D3 and D3BJ corrections. The dispersion coefficients (C_6 and C_8) for each atom pair were determined by time-dependent DFT calculations,[20] while the scaling factors were determined for each functional by least square fitting.[20] The poor performance was observed in some combinations of the functionals and the dispersion correction methods, which suggests that the scaling factors used for the dispersion corrections will be the cause of the problem.

The evaluation of the performance of the D3 and D3BJ corrections show that the performance of the calculations of the complexes of hydrocarbon molecules are much better than that of the calculations of molecules including hetero atoms in most cases. For example, the MADRs for the calculations of hydrocarbon complexes using the B97 and B3LYP functionals with the D3 correction are both 9 %, while the MADRs for the calculations of molecules including hetero atoms using the same method are 23 and 15 %. The same trend was observed for other combinations in general excluding very few exceptions. Although several reference data were used for the fitting of scaling factors,[20] large number of reference data are hydrocarbon molecules and molecules including many carbon atoms. The large numbers of molecules including many carbon atoms used for the fitting will be responsible for the good performance of the calculations for the interactions of hydrocarbon molecules. Previously reported benchmarks of D3 and D3BJ corrections show that the overall performance of these corrections is good.[20,21] But these benchmarks did not focus on the performance of the dispersion corrections for the calculations of hetero atoms separately, although the corrections were developed for 94 elements.

In contrast to the calculations of hydrocarbon molecules, the calculations of interactions of molecules including hetero atoms often show poor performance (MADRs are lager then 20 %) as shown in Table 2. Smaller numbers of molecules including hetero atoms were used for the reference data for the fitting compared with molecules including carbon atoms, which will be one of the causes of the worse performance of the calculations of the interactions of molecules including hetero atoms compared with hydrocarbon molecules. In addition, the performance of the calculations depends on the choice of hetero atom. The calculations for the perfluoromethane and furan dimers with the dispersion corrections show worse performance compared with the calculations for the molecules including other hetero atoms. This hetero atom dependence also suggests that the choice of molecules used for reference data in the fitting affects the accuracy of the dispersion correction. The interactions of DNA base pairs, amino acid pairs, alkane dimers, and rare gas dimers and conformers of tripeptide, sugar, alkane and cysteine were used for the reference data for the fitting.[20] The calculations of the perfluoromethane dimer with the D3 or D3BJ corrections often show bad performance as shown in Tables 1 and 2. The addition of many fluorine compounds to the reference data will help to improve the performance of the dispersion correction for fluorine compounds. Although oxygen and nitrogen atoms are included in the molecules used for the reference data, most of the systems including oxygen and nitrogen atoms in the reference data are hydrogen bonded complexes of base pairs and amino acid pairs, in which the contribution of the dispersion interactions of oxygen and nitrogen atoms are not significant compared with the stacked geometries and the geometries of the furan and pyridine dimers used for this work. The addition of complexes with large contribution of the dispersion interactions by hetero atoms to the reference data for the fitting will be helpful for improving the performance of the dispersion correction for hetero atoms.

The same scaling factors, which were determined for each functional, were used in the calculations of the dispersion interactions for all atom pairs in the corrections, which can be one of the causes of the poor performance of the calculations of molecules including hetero atoms. The scaling factors for the C_6 coefficients used in the D3 and

D3BJ corrections is unity, while the scaling factors for the C_8 coefficients are different depending on the functional, which reflects the different repulsive behavior of the functionals.[21] This means that the functional dependent behavior of repulsive interactions is corrected by the adjustable scaling factor for the C_8 coefficients of the dispersion interactions. It is well known that the repulsive interactions of some atoms (hydrogen, halogen etc.) have strong anisotropy. The magnitude of anisotropy depends on the type of atom. On the other hand, the repulsive behavior was corrected by the scaling of the isotropic dispersion interactions, which were calculated from the distance between atoms in the D3 and D3BJ corrections. The same scaling factors, which were determined for each functional, are used for the calculations of the dispersion interactions for all atom pairs to correct the repulsion behavior. It is questionable that the atom pair dependent repulsion behavior can be accurately corrected using the same scaling factors for the isotropic dispersion interactions. This will be another possible cause of the poor performance of the dispersion corrections in the calculations of molecules including some hetero atoms.

Comparison of D2, D3 and D3BJ corrections

The interaction potentials calculated for the 11 complexes using five functionals (BLYP, PBE, TPSS, B3LYP and B97) with the three dispersion correction methods (D2, D3 and D3BJ) are compared with the CCSD(T) level interaction potential as shown in Figures 2-5, 14S-20S. We chose these functionals because the combinations of these functionals with the three dispersion corrections methods are allowed in Gaussian 16 program and therefore these functionals are convenient for comparing the performance of the three dispersion correction methods. In addition, the potentials calculated using these functionals with the dispersion correction show relatively good agreement with the CCSD(T) level potential. In addition to these potentials, the potentials calculated using the ωB97XD functional and those calculated using the CAM-B3LYP, LC-ωPBE functionals with the D3 and D3BJ corrections are also shown.

The comparison of the D2, D3 and D3BJ corrections shows that the performance of the D3 and D3BJ corrections are much better than the D2 correction in general as reported previously.[20] Although the D3BJ correction is an improved version of the D3 correction, The performance of the D3BJ correction is not always better than the D3 correction. In the calculations of the interaction potentials for the benzene, thiophene, selenophene dimers, the D3 correction shows better performance compared with the D3BJ correction.

The depth of interaction potentials depends on the version of dispersion correction method. The potentials calculated with the D3BJ correction often have deeper potential minima compared with those calculated with the D3 correction. Most of the potentials calculated for the benzene, thiophene, slelnophene, pyridine, phosphorine dimers and the benzene-chlorobenzene, benzene-bromobenzene complexes with the D2 correction underestimate the attraction, while those for the propane, perfluoromethane, furan dimers and the benzene-methane complex with the D2 correction overestimate the attraction. Similar results were obtained in the calculations using other functionals.

The difference between two damping methods used in the D3 and D3BJ corrections was discussed by Grimme et al. They reported that the differences between the two methods are much smaller than the overall dispersion effect.[21] They reported that the dispersion correction using the zero-damping used for the D3 correction underestimates the dispersion correction compared with the BJ-damping used for the D3BJ correction at short distances. The different behavior of the dispersion correction at short distances can be one of causes of the frequently observed larger attraction by the D3BJ correction compared with the D3 correction.

Interaction energies for each complex

The intermolecular interaction potentials for the 11 complexes obtained by DFT calculations using various functionals and the three dispersion correction methods are compared with the CCSD(T) [$E_{\mathrm{CCSD(T)(limit)}}$] level potentials as shown in Figures 3S-13S. The agreement with the CCSD(T) level potential depends strongly on the choice of functional and dispersion correction method. Each complex shows different dependence. Table 1 shows that neither combination of functionals and dispersion correction methods can reproduce well the CCSD(T) level interaction potentials of all the complexes. We will discuss the dependence using the calculations of representative four complexes (benzene, perfluoromethane, furane and thiophene dimers). The detailed discussion on the calculated potentials for each complex is shown in supplementary information.

The interaction potentials calculated for slipped-parallel benzene dimer using the selected functionals with dispersion correction methods are compared with the CCSD(T) level interaction potential as shown in Figure 2. Table 1 shows that 20 combinations of the functionals with the dispersion correction methods show very good performance. The absolute deviation ratios from the CCSD(T) calculations are 0-10 %. The very good performance of several combinations of the functionals with the dispersion correction is also observed in the calculations of the interaction potentials of other hydrocarbon molecules. The comparison of the interaction potentials calculated for the propane dimer and the benzene-methane complex by the dispersion corrected DFT calculations with the CCSD(T) level potentials are shown in Figures 14S and 15S.

In contrast to the calculations of the interaction potentials of hydrocarbon molecules, most of the combinations of functionals and dispersion correction methods show the poor performance in the calculations of the interaction potentials for the perfluoromethane and furan dimers as shown in Table 1. Most of the potentials calculated using various functionals and dispersion correction methods do not well reproduce the CCSD(T) level potentials. The 0-10 % absolute deviation ratios were observed in the calculations of the perfluoromethane dimer using only four combinations and those of the furan dimer using only three combinations. The interaction potentials calculated for the perfluoromethane and furan dimers using the selected functionals with the dispersion correction methods are compared with the CCSD(T) level potential as shown in Figures 3 and 4. Most of the potentials calculated for the two dimers with the D3 or D3BJ correction underestimate the attraction compared with the CCSD(T) calculations. The potentials calculated for the perfluromethane and furan dimers using the PBE functional with the D3 correction are very close to the CCSD(T) level potentials (absolute deviation ratio is 4%), while this combination shows poor performance in the calculation of the interaction potential for the propane dimer as shown in Figure 14S (absolute deviation ratio is 21%). The potential calculated for the propane dimer using the PBE functional with D3 correction overestimates the attraction compared with the CCSD(T) level potential.

Unlike the calculations of the interaction potentials for the perfluoromethan and furan dimers, several combinations of functionals and dispersion correction methods show very good performance in the calculations of the interaction potentials for the thiopehene dimer as shown in Table 1. 13 combinations of the functionals with the dispersion correction show 0-10 % absolute deviation ratios. The dependence of the performance on the functional and dispersion correction method observed in the calculations of the thiophene dimer is similar to that observed in the calculations of the benzene dimer. The calculated interaction potentials for the thiophene dimer using the selected functionals with the dispersion correction methods are compared with the CCSD(T) level potential as shown in Figure 5. The potentials obtained using several functionals with D3 or D3BJ correction are very close to the CCSD(T) level potential. Similar dependence is observed in the calculations of the benzene-chlorobezene, benzene-bromobenzene complexes, and selenophene, phosphorine dimers as shown in Table 1. Several combinations of functionals and D3 or D3BJ correction show very good performance in the calculations of these four complexes. On the other hand, different dependence on functional and dispersion correction method is observed in the calculations of the pyridine dimer as shown in Table 1. Different combinations of functionals and dispersion correction methods show very good performance in the calculations of the pyridine dimer. The calculated interaction potentials for the five complexes using the selected functionals with the dispersion correction methods are compared with the CCSD(T) level potential as shown in Figures 16S-20S.

Conclusion

The intermolecular interaction potentials for 11 complexes of hydrocarbon molecules and molecules including hetero atoms obtained by DFT calculations using various functionals with three versions of Grimme's dispersion corrections were compared with CCSD(T) level interaction potentials. The comparison shows that the accuracy of calculated interaction potentials depends strongly on the choice of functional and dispersion correction method. The functional and dispersion correction method must be selected with great care depending on the complex to calculate sufficiently accurate interaction potential. The performance of the D3 and D3BJ corrections is much better than the D2 correction in general. Although the D3BJ correction is an improved version of the D3 correction, the performance of the D3BJ correction is not always better than the D3 correction. The improvement of the functionals from GGA to hybrid GGA, meta GGA or meta hybrid GGA is not essential for improving the performance of the dispersion corrected DFT calculations. The performance depends strongly on the choice of the functional even within the functionals in the same category. The performance of the calculations for the interactions of hydrocarbon molecules is much better than that for the molecules including hetero atoms, although the D3 and D3BJ corrections were developed for 94 elements. Many combinations of the functionals and the dispersion correction methods show very good performance in the calculations of interactions of hydrocarbon molecules. On the other hand, only limited numbers of combinations show good performance in the calculations of molecules including some hetero atoms. The performance of the dispersion correction depends on the dispersion coefficients and scaling factors used in the dispersion correction. The dispersion coefficients (C_6 and C_8) were determined by time-dependent DFT calculations, while the scaling factors were determined for each functional by least square fitting. The strong functional dependence of the performance suggests that the scaling factors used for the dispersion corrections will be the cause of the problem. Although many hydrocarbon molecules and molecules including large numbers of carbon atoms were used for reference data of the fitting of the scaling factors, only small numbers of molecules including hetero atoms were used for the reference data, which will be the cause of the better performance of the D3 and D3BJ corrections for the calculations of hydrocarbon molecules compared with the calculations of molecules including hetero atoms. The same scaling factors, which were determined for each functional, were used for the calculations of the dispersion interactions for all atom pairs in the D3 and D3BJ dispersion correction to correct the functional dependent repulsion behavior. It is questionable that the different repulsion behavior depending on the atom pairs can be accurately corrected using the same scaling factors for the isotropic dispersion interactions. This will be another possible cause of the poor performance of the dispersion corrections in the calculations of molecules including hetero atoms.

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Conflicts of interest

There are no conflicts to declare.

Electronic supplementary information (ESI)

Estimation procedure of CCSD(T) level interaction energy at the basis set limit, Effects of basis set and electron correlation correction, Interaction energies for each complex, Geometries of complexes, Comparison of HF, MP2 and CCSD(T) level intermolecular interaction potentials, Basis set effects on B3LYP-D3 (B3LYP functional with Grimme’s D3 dispersion correction), HF, MP2 and CCSD(T) level intermolecular interaction potentials calculated for slipped-parallel benzene dimer, Comparison of intermolecular interaction potentials obtained by DFT calculations using several functionals and Grimme's dispersion correction methods with CCSD(T) level intermolecular interaction potential. Files for calculated interaction energies of each complex.

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Table 1 Deviation ratio of calculated interaction energy by DFT method from CCSD(T) level interaction energy. The combinations displayed in green have absolute deviation ratios of 0-10%. Those displayed in yellow have absolute deviation ratios of 10-20%. Other combinations displayed in pink have larger deviation ratios[a]

	C_6H_6 dimer	C_3H_8 dimer	C_6H_6-CH_4	CF_4 dimer	C_6H_5Cl-C_6H_6	C_6H_5Br-C_6H_6	C_4H_4O dimer	C_4H_4S dimer	C_4H_4Se dimer	C_5H_5N dimer	C_5H_5P dimer
GGA											
BLYP	-215	-186	-173	-230	-218	-170	-254	-181	-176	-331	-262
BLYP+D2	-26	19	-12	24	-48	-23	-41	-53	-29	-47	-75
BLYP+D3	2	20	6	-41	0	11	-16	-3	5	-4	-24
BLYP+D3BJ	14	-4	-7	-62	-1	11	-24	21	34	-4	29
BP86	-192	-180	-159	-291	-199	-152	-261	-160	-147	-311	-216
BP86+D2	-27	0	-18	-69	-49	-23	-74	-49	-18	-63	-52
BP86+D3	14	13	9	-108	6	18	-32	7	24	-1	8
BP86+D3BJ	32	-15	-7	-135	7	24	-38	36	58	2	72
B98	-134	-101	-88	-122	-131	-98	-157	-107	-103	-216	-158
B97D (D2)	-6	24	0	35	-39	-7	-37	-41	-11	-38	-47
B97+D3	-9	15	3	-69	0	-1	-50	-7	7	-39	-13
B97D3 (D3BJ)	25	13	10	-53	-17	14	-24	20	28	-1	34
BPBE	-229	-225	-197	-324	-243	-185	-311	-198	-183	-379	-265
BPBE+D3	9	4	3	-117	4	21	-49	2	25	-18	4
BPBE+D3BJ	39	-20	-10	-131	6	25	-43	35	58	-1	75
PBE	-132	-97	-87	-118	-125	-96	-147	-102	-96	-203	-149
PBE+D2	-14	32	14	41	-18	-4	-14	-22	-4	-26	-32
PBE+D3	-1	21	12	4	-13	-5	1	-8	-5	-11	-23
PBE+D3BJ	1	11	9	-21	-13	-3	-11	4	7	-13	5
PW91	-120	-81	-72	-68	-112	-86	-122	-90	-85	-179	-133
Hybrid GGA											
B3LYP	-185	-151	-139	-184	-184	-143	-218	-154	-150	-287	-226
B3LYP+D2	-20	28	3	39	-35	-14	-31	-42	-21	-39	-62
B3LYP+D3	-8	14	4	-26	-8	4	-20	-5	5	-23	-27
B3LYP+D3BJ	9	3	2	-42	-2	9	-21	16	27	-9	20
B3PW91	-198	-185	-160	-260	-206	-156	-266	-169	-157	-328	-229
B3PW91+D3	5	5	4	-79	-5	11	-41	-3	14	-24	-7
B3PW91+D3BJ	22	-15	-5	-102	-2	14	-45	22	40	-17	48
BMK	-133	-143	-117	-354	-143	-111	-237	-118	-108	-242	-157
BMK+D3	0	-9	1	-246	28	37	-92	21	49	-35	32
BMK+D3BJ	40	-22	-4	-240	22	35	-66	44	75	-2	83
PBE1PBE	-133	-100	-85	-124	-127	-97	-158	-105	-98	-214	-151
PBE1PBE+D3	-7	15	13	-10	-12	-3	-16	-7	-1	-28	-20
PBE1PBE+D3BJ	4	4	10	-28	-9	0	-20	5	10	-22	10
APF	-160	-135	-116	-180	-159	-121	-202	-131	-122	-261	-183
APFD	23	17	11	22	6	17	32	23	22	2	21
wB97	-25	-6	5	-88	-24	-13	-55	-18	-7	-46	-15
wB97X	-37	-10	-1	-74	-33	-19	-58	-24	-18	-64	-35
wB97XD (D2)	12	28	17	-17	-39	-13	-38	-30	-16	-21	-25
Hybrid GGA + LC correction											
CAM-B3LYP	-147	-105	-96	-117	-140	-110	-162	-120	-118	-223	-182
CAM-B3LYP+D3	-22	12	6	-13	-14	-6	-22	-12	-7	-37	-38
CAM-B3LYP+D3BJ	0	0	1	-20	-13	-3	-16	3	6	-20	-1
LC-wPBE	-138	-118	-97	-152	-143	-107	-185	-122	-113	-239	-164

LC-wPBE+D3	-6	6	10	-40	-10	3	-36	-9	4	-42	-12
LC-wPBE+D3BJ	16	-4	7	-47	-7	6	-30	7	18	-23	25
Double hybrid											
B2PLYP	-190	-150	-136	-167	-190	-145	-222	-160	-160	-301	-241
B2PLYPD (D2)	-104	-56	-62	-50	-112	-78	-124	-102	-92	-171	-156
B2PLYP + D3	-102	-66	-62	-95	-94	-65	-118	-79	-74	-155	-132
B2PLYPD3 (D3BJ)	-87	-72	-65	-94	-94	-65	-123	-70	-64	-168	-110
mPW2PLYP	-162	-114	-103	-99	-156	-120	-173	-132	-135	-250	-207
mPW2PLYPD (D2)	-99	-45	-49	-15	-99	-70	-102	-90	-85	-155	-145
Meta GGA											
TPSS	-167	-140	-124	-162	-169	-130	-200	-139	-131	-263	-192
TPSS+D2	-9	31	10	50	-27	-7	-23	-33	-8	-26	-36
TPSS+D3	-1	12	7	-11	-16	-3	-15	-13	-5	-15	-24
TPSS+D3BJ	8	-5	-1	-36	-14	-2	-24	5	13	-15	18
M06L	-25	-7	-47	58	-57	-40	-42	-56	-43	-34	-53
M06L+D3	-1	15	-27	75	-35	-26	-10	-37	-27	4	-27
Meta hybrid GGA											
M05	-99	-52	-55	-62	-93	-69	-90	-80	-82	-146	-131
M05+D3	-11	29	15	14	-12	-4	12	-10	-14	-15	-37
M052X	-49	-24	-22	-17	-49	-42	-66	-44	-48	-99	-70
M052X+D3	-3	16	12	21	-16	-19	-10	-14	-24	-32	-31
M06	-40	-4	-44	-53	-69	-50	-84	-53	-40	-68	-47
M06+D3	24	49	-1	6	-28	-20	-9	-15	-10	22	3
M062X	-26	-15	-14	-21	-35	-32	-55	-30	-28	-55	-36
M062X+D3	-6	5	3	-8	-14	-19	-27	-13	-14	-22	-13
M06HF	-55	-34	-40	-47	-67	-62	-81	-53	-58	-111	-65
M06HF+D3	-13	2	-9	-15	-36	-41	-30	-25	-36	-51	-29

[a] The deviation of calculated interaction energy from the CCSD(T) level interaction energy at the basis set limit at the potential minimum of CCSD(T) level potential is calculated. The ratio of the deviation to the CCSD(T) level interaction energy (deviation ratio) is shown in %. The deviation ratio is positive, if DFT calculation overestimates the attraction, while the deviation ratio is negative, if DFT calculation underestimates the attraction. The deviation ratio is less than -100 %, if the calculated interaction energy by DFT calculation is positive.

Table 2 Mean absolute deviation ratio of calculated interaction energies by dispersion corrected DFT method to CCSD(T) level interaction energy. The minimum and maximum deviation ratios are shown in parenthesis. The calculations with D2, D3 and D3BJ corrections are displayed pink, yellow and bule, respectively.[a]

	Hydrocarbon[b]	Other[c]	Total[d]
GGA			
BLYP	191 (-215~-173)	228 (-331~-170)	218 (-331~-170)
BLYP+D2	19 (-26~19)	43 (-75~24)	36 (-75~24)
BLYP+D3	9 (2~20)	13 (-41~11)	12 (-41~11)
BLYP+D3BJ	8 (-7~14)	23 (-62~34)	19 (-62~34)
BP86	177 (-192~-159)	217 (-311~-147)	206 (-311~-147)
BP86+D2	15 (-27~0)	50 (-74~-18)	40 (-74~0)
BP86+D3	12 (9~14)	26 (-108~24)	22 (-108~24)
BP86+D3BJ	18 (-15~32)	47 (-135~72)	39 (-135~72)
B98	108 (-134~-88)	137 (-216~-98)	129 (-216~-88)
B97D (D2)	10 (-6~24)	32 (-47~35)	26 (-47~35)
B97+D3	9 (-9~15)	23 (-69~7)	19 (-69~15)
B97D3 (D3BJ)	16 (10~25)	24 (-53~34)	22 (-53~34)
BPBE	217 (-229~-197)	261 (-379~-183)	249 (-379~-183)
BPBE+D3	5 (3~9)	30 (-117~25)	23 (-177~25)
BPBE+D3BJ	23 (-20~39)	47 (-131~75)	40 (-131~75)
PBE	105 (-132~-87)	130 (-203~-96)	123 (-203~-87)
PBE+D2	20 (-14~32)	20 (-32~41)	20 (-32~41)
PBE+D3	11 (-1~21)	9 (-23~4)	9 (-23~21)
PBE+D3BJ	7 (1~11)	10 (-21~7)	9 (-21~11)
PW91	91 (-120~-72)	109 (-179~-68)	104 (-179~-68)
Hybrid GGA			
B3LYP	158 (-185~-139)	193 (-287~-143)	184 (-287~-139)
B3LYP+D2	17 (-20~28)	35 (-62~39)	30 (-62~39)
B3LYP+D3	9 (-8~14)	15 (-27~5)	13 (-27~14)
B3LYP+D3BJ	5 (2~9)	18 (-42~27)	15 (-42~27)
B3PW91	181 (-198~-160)	221 (-328~-156)	210 (-328~-156)
B3PW91+D3	5 (4~5)	23 (-79~14)	18 (-79~14)
B3PW91+D3BJ	14 (-15~22)	36 (-102~48)	30 (-102~48)

BMK	131 (-143~-117)	184 (-354~-108)	169 (-354~-108)
BMK+D3	3 (-9~1)	68 (-246~49)	50 (-246~49)
BMK+D3BJ	22 (-22~40)	71 (-240~83)	58 (-240~83)
PBE1PBE	106 (-133~-85)	134 (-214~-97)	127 (-214~-85)
PBE1PBE+D3	12 (-7~15)	12 (-28~-1)	12 (-28~15)
PBE1PBE+D3BJ	6 (4~10)	13 (-28~10)	11 (-28~10)
APF	137 (-160~-116)	170 (-261~-121)	161 (-261~-116)
APFD	17 (11~23)	18 (2~32)	18 (2~32)
ωB97	12 (-25~5)	33 (-88~-7)	27 (-88~5)
ωB97X	16 (-37~-1)	41 (-74~-18)	34 (-74~-1)
ωB97XD (D2)	19 (12~28)	25 (-39~-13)	23 (-39~28)
Long-range-corrected hybrid GGA			
CAM-B3LYP	116 (-147~-96)	147 (-223~-110)	138 (-223~-96)
CAM-B3LYP+D3	13 (-22~12)	19 (-38~-6)	17 (-38~12)
CAM-B3LYP+D3BJ	0 (0~1)	10 (-20~6)	8 (-20~6)
LC-ωPBE	118 (-138~-97)	153 (-239~-107)	143 (-239~-97)
LC-ωPBE+D3	7 (-6~10)	20 (-42~4)	16 (-42~10)
LC-ωPBE+D3BJ	9 (-4~16)	20 (-47~25)	17 (-47~25)
Double hybrid			
B2PLYP	159 (-190~-136)	198 (-301~-145)	187 (-301~-136)
B2PLYPD (D2)	74 (-104~-56)	111 (-171~-50)	101 (-171~-50)
B2PLYP + D3	77 (-102~-62)	102 (-155~-65)	95 (-155~-62)
B2PLYPD3 (D3BJ)	75 (-87~-65)	99 (-168~-64)	92 (-168~-64)
mPW2PLYP	126 (-162~-103)	159 (-250~-99)	150 (-250~--99)
mPW2PLYPD (D2)	64 (-99~-45)	95 (-155~-15)	87 (-155~-15)
Meta GGA			
TPSS	144 (-167~-124)	173 (-263~-130)	165 (-263~-124)
TPSS+D2	17 (-9~31)	26 (-36~50)	24 (-36~50)
TPSS+D3	7 (-1~12)	13 (-24~-3)	11 (-24~12)
TPSS+D3BJ	5 (-5~8)	16 (-36~18)	13 (-36~18)
M06L	26 (-47~-7)	48 (-57~58)	42 (-57~58)
M06L+D3	14 (-27~15)	30 (-37~75)	26 (-37~75)
Meta hybrid GGA			
M05	69 (-99~-52)	94 (-146~-62)	87 (-146~-52)
M05+D3	18 (-11~29)	15 (-37~14)	16 (-37~29)

M052X	32 (-49~-22)	54 (-99~-17)	48 (-99~-17)
M052X+D3	10 (-3~16)	21 (-32~21)	18 (-32~21)
M06	29 (-44~-4)	58 (-84~-40)	50 (-84~-4)
M06+D3	25 (-1~49)	14 (-28~22)	17 (-28~49)
M062X	18 (-26~-14)	37 (-55~-21)	32 (-55~-14)
M062X+D3	5 (-6~5)	16 (-27~-8)	13 (-27~5)
M06HF	43 (-55~-34)	68 (-111~-47)	61 (-111~-34)
M06HF+D3	8 (-13~2)	33 (-51~-15)	26 (-51~2)

[a] Absolute deviation ratios of calculated interaction energies are shown in Table 1. Mean absolute deviation ratios (MADRs), minimum and maximum deviation ratios are shown in %.

[b] MADRs of calculated interaction energies for three complexes of hydrocarbon molecules.

[c] MADRs of calculated interaction energies for other eight complexes including heteroatoms.

[d] MADRs of calculated interaction energies for 11 complexes.

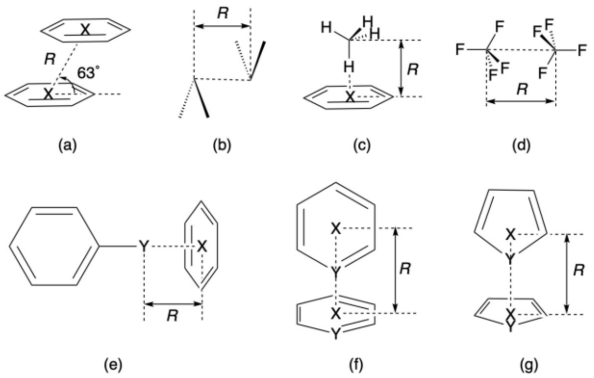
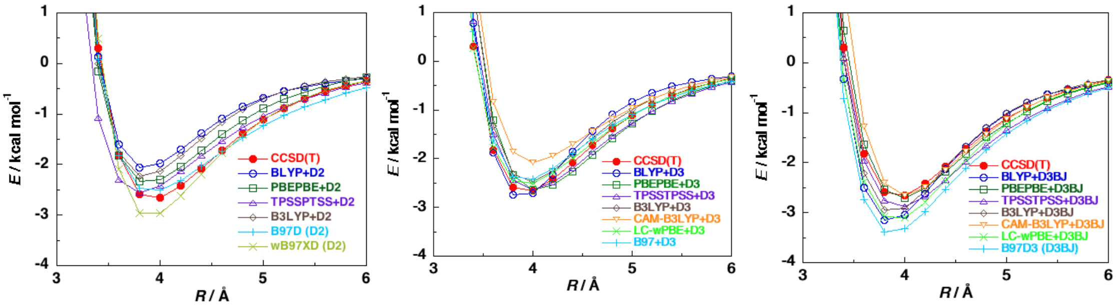
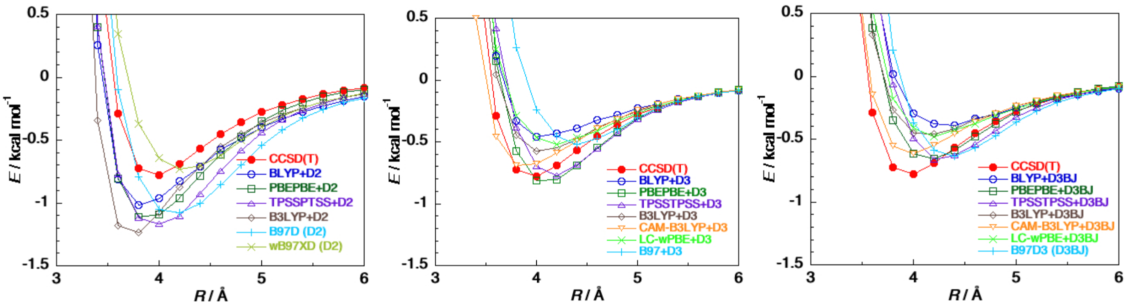


Figure 1. Geometries of complexes: (a) C_{2h} Benzene dimer; (b) C_{2h} Propane dimer; (c) C_{3v} Benzene-methane complex; (d) D_{3d} Perfluoromethane dimer; (e) C_{2v} Benzene-chlorobenzene and benzene-bromobenzene complexes, Y = Cl or Br; (f) C_s Furan, thiophene and selenophene dimers, Y = O, S or Se; (g) C_s Pyridine and phosphorine complexes, Y = N or P. The symmetry planes of two propane molecules are parallel. The line between the central carbon atoms is perpendicular to the symmetry planes of propane molecules.



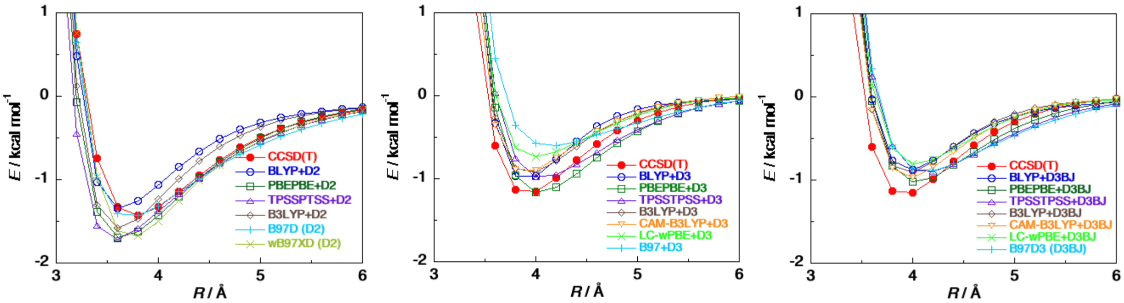
(a) D2 correction (b) D3 correction (c) D3BJ correction

Figure 2. Intermolecular interaction potentials calculated for C_{2h} slipped-parallel benzene dimer by DFT calculations with cc-pVTZ basis set using several functionals and Grimme's dispersion correction methods (a) D2 correction; (b) D3 correction; (c) D3 correction with Becke-Johnson damping. The CCSD(T) level interaction potential at the basis set limit is shown for comparison. The geometry of complex is shown in Figure 1. *R* is the distance between the symmetry centers of two benzenes.



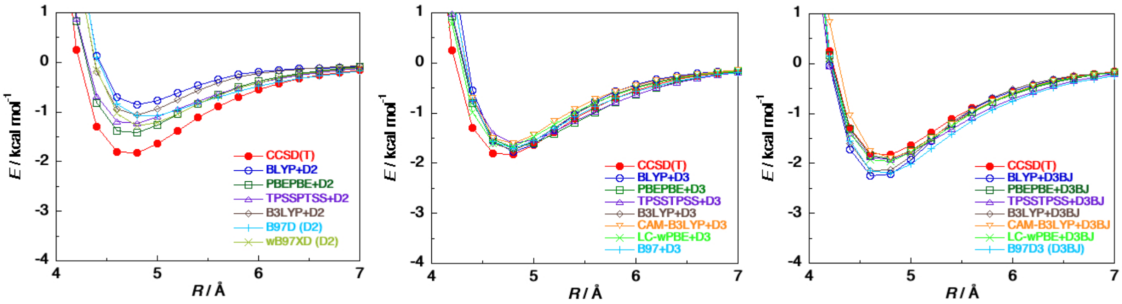
(a) D2 correction (b) D3 correction (c) D3BJ correction

Figure 3. Intermolecular interaction potentials calculated for D_{3h} perfluoromethane dimer by DFT calculations with cc-pVTZ basis set using several functionals and Grimme's dispersion correction methods (a) D2 correction; (b) D3 correction; (c) D3 correction with Becke-Johnson damping. The CCSD(T) level interaction potential at the basis set limit is shown for comparison. The geometry of complex is shown in Figure 1. The complex has C_{2h} symmetry. The symmetry axes of two propane molecules are parallel and the line connecting two central carbon atoms of propane molecules are perpendicular to the symmetry planes of propane molecules. R is the distance between the carbon atoms of perfluoromethanes.



(a) D2 correction (b) D3 correction (c) D3BJ correction

Figure 4. Intermolecular interaction potentials calculated for C_s furan dimer by DFT calculations with cc-pVTZ basis set using several functionals and Grimme's dispersion correction methods (a) D2 correction; (b) D3 correction; (c) D3 correction with Becke-Johnson damping. The CCSD(T) level interaction potential at the basis set limit is shown for comparison. The geometry of complex is shown in Figure 1. X is the midpoint between two carbon atoms connected to oxygen atom (C_2 and C_5). R is the distance between X of two furan rings.



(a) D2 correction (b) D3 correction (c) D3BJ correction

Figure 5. Intermolecular interaction potentials calculated for C_s thiophene dimer by DFT calculations with cc-pVTZ basis set using several functionals and Grimme's dispersion correction methods (a) D2 correction; (b) D3 correction; (c) D3 correction with Becke-Johnson damping. The CCSD(T) level interaction potential at the basis set limit is shown for comparison. The geometry of complex is shown in Figure 1. X is the midpoint between two carbon atoms connected to sulfur atom (C_2 and C_5). *R* is the distance between X of two thiophene rings.