

Calculation of Intermolecular Interactions in the Benzene Dimer using Coupled-Cluster and Local Electron Correlation Methods

J. Grant Hill and James A. Platts*

*School of Chemistry, Cardiff University, Park Place,
Cardiff CF10 3AT, UK*

Hans-Joachim Werner†

*Institut für Theoretische Chemie, Universität Stuttgart, Pfaffenwaldring 55,
70569 Stuttgart, Germany*

Abstract

Potential energy surfaces for the parallel-displaced, T-shaped and sandwich structures of the benzene dimer are computed with density fitted local second-order Møller-Plesset perturbation theory (DF-LMP2) as well as with the spin-component scaled (SCS) variant of DF-LMP2. While DF-LMP2 strongly overestimates the dispersion interaction, in common with canonical MP2, the DF-SCS-LMP2 interaction energies are in excellent agreement with the best available literature values along the entire potential energy curves. The DF-SCS-LMP2 dissociation energies for the three structures are also compared with new complete basis set estimates of the interaction energies obtained from accurate coupled cluster (CCSD(T)) and DF-SCS-MP2 calculations. Since LMP2 is essentially free of basis set superposition errors, counterpoise corrections are not required. As a result, DF-SCS-LMP2 is computationally inexpensive and represents an attractive method for the study of larger π -stacked systems such as truncated sections of DNA.

1 Introduction

The benzene dimer has three main conformations of interest on its potential energy surface (PES): the parallel-displaced (PD) structure, the T-shaped (T) structure and the sandwich (S) structure. Previous theoretical investigations^{1–12} have shown that the PD and T structures are minima, whilst the S structure is a transition state linking the two. The large interest in this dimer arises from the prevalence of $\pi - \pi$ stacking in biological systems, especially in stabilising the structure of DNA and proteins,^{13–17} this being the prototypical example of such interactions.

The permanent dipole moment possessed by the T-shaped benzene dimer has allowed for its detection and characterisation by microwave spectroscopy.¹⁸ The lack of such a dipole in the PD configuration means that this evidence does not rule out its existence. Indeed, hole-burning spectroscopy suggests the presence of more than a single isomer of the benzene dimer.¹⁹

The London dispersion interaction that is instrumental in the binding of all three dimer structures is not described by Hartree-Fock theory. Therefore, a correlated description of the electrons is required to produce even a qualitatively accurate picture. The computationally

*E-mail: platts@cf.ac.uk.

†E-mail: werner@theochem.uni-stuttgart.de

inexpensive density functional theory (DFT) is generally not considered to be a suitable method for computing interaction energies for π -stacked systems, since most of the popular exchange-correlation functionals fail to predict an attractive binding. It should be noted, however, that several newly developed functionals have been shown to provide acceptable results for this type of intermolecular interaction. Examples are functionals such as PWB6K,²⁰ M05-2X,²¹ BH&H,¹⁰ vdW-DF,¹² and BR and XX.²² Nevertheless, the results obtained with these methods are less reliable than those obtained with accurate wave-function based methods.

Much better results than with the supermolecular DFT methods can be obtained using density functional theory symmetry adapted intermolecular perturbation theory (DFT-SAPT)²³ in which only the intramolecular correlation is described by DFT. The efficiency of this method has recently been enhanced using density fitting (DF) approximations, and very good results were obtained for the benzene dimer.²⁴ However, this method is still rather expensive and can only be applied to dimers.

Singles and doubles coupled cluster theory with perturbative treatment of triple excitations (CCSD(T)) is currently believed to be the most accurate method for computing dispersion interactions. It provides binding energies of excellent quality (provided basis sets of at least aug-cc-pVTZ quality are used), and such results are invaluable as benchmarks for testing lower-level methods and in the parameterising of new force fields. However, the large associated computational cost, including the $n + 1$ (where n is the number of monomers) calculations in the full basis set of the system required for the counterpoise correction (CP), renders the approach prohibitively expensive for application to larger systems.

Unfortunately, the computationally much less expensive second-order Møller-Plesset perturbation theory (MP2) rather strongly overestimates the dispersion forces. Grimme has proposed a modification to MP2 that scales the energy contributions from parallel- and antiparallel-spin pairs of electrons by separate factors.²⁵ This technique is known as spin-component-scaled MP2 (SCS-MP2). Whilst the empirical scaling means that the methodology can no longer be considered truly *ab initio* in nature, previous calculations as well as the results in the current paper show that it provides a substantial correction to the MP2 overestimation of the dispersion energy at no extra cost. Grimme and co-workers have already applied SCS-MP2 successfully to several examples of intermolecular interactions involving π -stacking. They predicted optimised geometries for cyclophanes that are very close to those from X-ray crystal structure determination experiments,²⁶ and computed accurate interaction energies for stacked dimers and trimers of pyridine,²⁷ as well as for dimers of azulene.²⁸

For the computation of intermolecular interactions, local electron correlation methods²⁹⁻³¹ have proven to be particularly useful, as by construction they are virtually free of basis set superposition errors (BSSE).³⁰⁻³³ This makes it possible to perform geometry optimisations for larger clusters without counterpoise corrections. Linear scaling of the computational cost as a function of the system size has been demonstrated for local MP2 (LMP2)^{34,35} as well as for local coupled cluster methods such as LCCSD(T),³⁶⁻³⁸ making it possible to treat much larger systems than with conventional methods. A further reduction of the computation time by about one order of magnitude can be achieved by density fitting (DF) approximations of the electron repulsion integrals.^{39,40} Density fitting approximations can also be applied to the initial Hartree-Fock (HF) step of the DF-LMP2 calculations,^{41,42} and this is denoted in this paper as DF-HF⁴² (some authors use the acronym RI-HF⁴¹ for the same method).

The purpose of the current investigation is to establish the accuracy of DF-SCS-LMP2 by

comparison of potential energy curves for the benzene dimer with the best available CCSD(T) results. It will be shown that DF-SCS-LMP2 yields accurate interaction energies at low computational cost and therefore appears to be a suitable method for investigating larger π -stacked systems.

2 Computational Procedure

All calculations were carried out with the MOLPRO package of *ab initio* programs.⁴³ Interaction energies for the benzene dimer were calculated using conventional MP2 and CCSD(T) methods, as well as with density fitted local MP2 (DF-LMP2). Only the valence electrons were correlated. Calculations that compensated for BSSE did so with the counterpoise (CP) method of Boys and Bernardi.⁴⁴ The monomer geometry of benzene was optimised using DF-LMP2 and then kept frozen in the single point calculations of the interaction energy. For comparison, a number of calculations were also performed using monomer geometries from previous work.^{7,45} The initial Hartree-Fock orbital optimisation for all DF-LMP2 calculations used the DF-HF method, while the standard HF method was used in the conventional MP2 and CCSD(T) calculations. In calculations where the SCS approximation has been applied, the default scaling factors of 6/5 for antiparallel spins and 1/3 for parallel spins were used.

This investigation employed the aug-cc-pVnZ (where $n = 2-5$) augmented correlation consistent basis sets of Dunning *et al.*⁴⁶ as the AO basis set. Calculations with the full aug-cc-pV5Z basis were not possible due to linear dependency problems (the smallest eigenvalue of the metric was smaller than 10^{-8}). This problem could be avoided by using the standard cc-pVnZ sets for hydrogen. In the following, the full aug-cc-pVnZ basis sets will be denoted AVnZ, and the sets in which the aug-cc-pVnZ sets were used for C and cc-pVnZ for H will be denoted AVnZ*. The largest basis set employed in this work, namely AV5Z*, included 2184 contracted basis functions for the benzene dimer. This basis is about twice as large as the biggest basis used for the benzene dimer reported so far.

The corresponding aug-cc-pVnZ MP2-fitting auxiliary basis sets (where n retains the same value as in the AO basis) of Weigend *et al.*⁴⁷ were employed in the DF-LMP2 calculations, and the cc-pVnZ JK-fitting auxiliary basis sets of Weigend⁴⁸ were utilised in the DF-HF calculations. In the calculations with AVnZ* basis sets the non-augmented cc-pVnZ MP2-fitting bases were used for hydrogen. Local fitting domains as proposed in Refs. 40, 42 were not used in this work, since this can lead to large errors in counterpoise calculations due to the fact that in CP calculations the fitting domains would be restricted to the monomer for which the energy is computed, and fitting functions on the other (dummy) monomer would be missing. However, it would be possible to make local fitting approximations if no CP corrections were applied. This would lead to linear scaling of the computational cost with molecular size and might be useful for the treatment of larger clusters.

The orbital localisation required for DF-LMP2 was performed using the Pipek-Mezey method.⁴⁹ The localisation of the π -orbitals in benzene is not unique, i.e., there is a redundant linear combination of orbital rotations that does not change the localisation criterion. Therefore, to ensure convergence of the localisation procedure, a Newton-Raphson algorithm was employed. The matrix of second derivatives of the localisation criterion with respect to the orbital rotations was constructed and diagonalised, and the eigenvector corresponding to the zero eigenvalue that results from the redundancy was eliminated.

Another problem was that the standard Pipek-Mezey (PM) method lead to very poor localisation when the larger diffuse basis sets were used, due to the localisation tails arising from the diffuse basis functions. More effective localisation can be obtained by eliminating the contributions of the diffuse basis functions to the localisation criterion. This can simply be achieved by setting the corresponding rows and columns of the overlap matrix used in the PM localisation to zero. In all calculations presented in this work, the contributions of the two most diffuse functions of each angular momentum type at each atom were eliminated in this way, so that well localised orbitals were obtained.

In local correlation calculations excitations are restricted to subspaces (domains) of projected atomic orbitals (PAOs) that are spatially close to the dominant parts of the localised molecular orbitals from which the excitations are made.²⁹⁻³¹ The orbital domain selection was carried out as described by Boughton and Pulay,⁵⁰ using a completeness criterion of 0.985. As an additional constraint it was required that only atoms were included in a domain whose Löwdin charges were larger than 0.01 for C and 0.2 for H. The domains of the three benzene π -orbitals were merged, leading to three identical domains that include the p_π AOs of all 6 carbon atoms. The energy is then invariant with respect to unitary transformations among the π orbitals and thus to the redundant orbital rotations mentioned above. The domains of all C-H and C-C σ -bonds just included the PAOs at the corresponding two atoms.

The domains were determined at a large intermolecular distance and kept fixed in the calculations of the PES. This does not only lead to smooth potentials, but also minimises basis set superposition errors as at large intermolecular distances the domains of each molecule only include PAOs located on the same molecule. The number of non-redundant PAOs on each molecule at large distances is $N - m$, where N is the number of basis functions and m the number of occupied orbitals at one molecule. As the molecules approach each other, the PAOs at the two molecules start to overlap, and it can happen that for one molecule more than $N - m$ PAOs become non-redundant. If the domains are then determined at shorter distances the domains would grow, leading to steps on the potential. The energy lowering due to the additional PAOs can be regarded as BSSE. We note that this problem did not occur in the current calculations, i.e., the same number of non-redundant functions was found at all intermolecular distances. Nevertheless, it is recommended always to determine the domains at large distances in calculations of intermolecular interactions.

It should also be noted that all intermolecular pairs must be fully included in the local calculations (in LCCSD(T) calculations intermolecular pairs should be treated as *strong pairs*); the neglect of very distant pairs or the use of multipole approximations of distant pair energies⁵¹ would lead to steps on the PES at the distances where these approximations are invoked. In order to avoid such problems, a procedure has been implemented in MOLPRO which detects individual molecules and automatically includes all necessary intermolecular pairs in the LMP2 or LCCSD calculations.

3 Results and Discussion

To date the best theoretical approaches give practically isoenergetic binding energies for the PD and T structures of the benzene dimer. Sinnokrot and Sherrill⁸ produced estimated CCSD(T)/aug-cc-pVQZ* energies of -2.63 and -2.61 kcal mol⁻¹ for those two systems, respectively. These estimates are based on CCSD(T) calculations with a small basis set (aug-cc-pVDZ for C and

cc-pVDZ for H), with basis set corrections from MP2 added. In their MP2/aug-cc-pVQZ* g -functions on C and f -functions on H were neglected (note that this aug-cc-pVQZ* basis is not the same as our AVQZ* basis). The same methodology gave a binding energy for the sandwich configuration of $-1.70 \text{ kcal mol}^{-1}$.⁸ These CCSD(T) values are consistent with the experimental dissociation energy of $2.4 \pm 0.4 \text{ kcal mol}^{-1}$.⁵² The MP2/aug-cc-pVQZ interaction energies of $-4.79 \text{ kcal mol}^{-1}$ for the PD structure, $-3.54 \text{ kcal mol}^{-1}$ for the T structure and $-3.37 \text{ kcal mol}^{-1}$ for the S structure⁸ highlight the MP2 overestimation of the binding energy.

One can envisage various orientations for the PD structure, which differ by rotations of the monomers about their C_6 axes. We have compared two such structures, one in which the horizontal displacement between the two monomers is perpendicular to a C–C bond (see A in Figure 1) and the second where the displacement is in the direction of a C–H bond (see B in Figure 1). Sherrill *et al.*⁸ used orientation A, but Heßelmann *et al.*²⁴ orientation B. We have carried out optimisations of the distances R_1 and R_2 for the PD structures A and B as well as for the S and T structures using the DF-LMP2 and DF-SCS-LMP2 methods and basis set AVTZ*. The monomer structures ($R_{CC} = 1.3915 \text{ \AA}$ and $R_{CH} = 1.0800 \text{ \AA}$) were taken from previous work^{7,45} and kept fixed. No CP corrections were applied in the optimisations, since the BSSE in LMP2 calculations is very small (see below). The optimised distances and corresponding interaction energies are summarised in Table 1. Orientation B is found to be slightly more strongly bound at both the DF-LMP2 and DF-SCS-LMP2 levels. The DF-SCS-LMP2 interaction energies of the PD and S structures are very close to the CCSD(T) values of Sinnokrot and Sherrill, while the binding energy of the T-structure is somewhat too small. Also the optimised DF-SCS-LMP2 distances R_1 and R_2 are close to the CCSD(T) values of Sinnokrot and Sherrill. In contrast, the strong overbinding of DF-LMP2 (without SCS correction) leads to significantly too short intermolecular distances. The overbinding of MP2 is particularly strong for the PD and S structures where the binding is purely due to the dispersion energy, while the effect is smaller for the T-structure which is also stabilised by quadrupole-quadrupole interactions.

Table 2 shows a comparison of conventional CCSD(T), MP2, and SCS-MP2 interaction energies for the AVDZ* and AVTZ* basis sets. The AVTZ* basis set is significantly larger (720 contracted functions) than any basis set previously reported for CCSD(T) calculations on the benzene dimer. The calculations were performed at the optimised DF-SCS-LMP2 structures discussed above. It can be seen that MP2 does not only overestimate the binding energy, but also the basis set effect. This means that adding a MP2 basis correction to the CCSD(T) value, as done by Sinnokrot and Sherrill, will somewhat overestimate the basis set limit. For the PD structure, the $\Delta\text{CCSD(T)} = E_{\text{CCSD(T)}} - E_{\text{MP2}}$ corrections amount to $1.76 \text{ kcal mol}^{-1}$ and $1.81 \text{ kcal mol}^{-1}$ for the AVDZ* and AVTZ* basis sets, respectively. As shown by Sinnokrot and Sherrill⁸ these values are strongly dependent on the intermolecular distance. Using the AVDZ* basis, these authors obtained values of $1.67 \text{ kcal mol}^{-1}$ and $2.18 \text{ kcal mol}^{-1}$ at 3.6 \AA and 3.4 \AA , respectively (our values were obtained at 3.54 \AA , see Table 1). The SCS-MP2 values are in much better agreement with CCSD(T), and the basis set effect is also close to that from CCSD(T) (except for the T-structure, for which SCS-LMP2 slightly underestimates the binding energy and the basis set effect). The $\Delta\text{CCSD(T)}$ corrections for SCS-MP2 only amount to $0.171 \text{ kcal mol}^{-1}$ and $0.159 \text{ kcal mol}^{-1}$ for the two basis sets, respectively. It is also of interest to compare the triples corrections $\Delta(\text{T}) = E_{\text{CCSD(T)}} - E_{\text{CCSD}}$ for the two basis sets, because it has sometimes been argued that one could compute this with a smaller basis set than the CCSD

energy. For the PD structure the corrections amount to 0.968 kcal mol⁻¹ and 1.091 kcal mol⁻¹ for the AVDZ* and AVTZ* basis sets, respectively. Thus, the triples effect increases by about 10% from AVDZ* to AVTZ*, and adding the AVDZ* value to the CCSD/AVTZ* energy would underestimate CCSD(T) interaction energy by about 0.12 kcal mol⁻¹. Finally we note that the effect of the density fitting approximation on the interaction energies is less than 0.01 kcal mol⁻¹ and thus negligible.

Table 3 shows a more extensive study of the basis set convergence for HF, DF-SCS-MP2, and DF-SCS-LMP2 for the series of AVnZ* basis sets. Comparison of AVnZ and AVnZ* indicates that the lack of diffuse functions on H has a negligible effect on MP2 binding energies (0.04 kcal mol⁻¹ for AVTZ and AVTZ*: see Supporting Information for the AVnZ data). Estimates for the basis set limits have been obtained by extrapolating the individual AVQZ* and AV5Z* correlation energies added to the AV5Z* HF energies. For the extrapolation, the dependence of the correlation energy on the cardinal number n is described by $E_n = E_{CBS} + An^{-3}$.^{53,54} Such extrapolations are well established for MP2, but this is not yet the case for LMP2. When extrapolating LMP2 energies, one must of course ensure that the domains are exactly the same for all basis sets. Even if this is the case, the basis set dependence is different than for MP2 because increasing the basis set improves the domain approximation. Whether the n^{-3} dependence is still appropriate in this case has not yet been investigated systematically. The extrapolated DF-LMP2 and DF-SCS-LMP2 values in Table 3 should therefore be regarded with some caution. However, it is noteworthy that the counterpoise corrections computed from the extrapolated energies are very small in all cases, which gives confidence to the extrapolation approximation.

The results in Table 3 and in the Supporting Information firstly demonstrate that the CP-corrected HF values, which are repulsive, are basically converged with the AVTZ basis set. Additionally, the HF CP correction is reasonably small (0.21 kcal mol⁻¹ for the PD (B) structure) for this basis. The DF-SCS-MP2 interaction energies converge much more slowly with basis set size, and the CP correction is significantly larger than for HF (1.4 kcal mol⁻¹ for AVTZ). Using the AVnZ* basis sets, in which diffuse functions on the hydrogen atoms are omitted, leads only to very small changes in the CP-corrected interaction energies, but reduces the BSSE. For DF-SCS-LMP2, the CP correction is almost the same as for HF, i.e., there is virtually no BSSE on the correlation contribution. In the basis set limit, the DF-SCS-LMP2 interaction energy is about 0.05 kcal mol⁻¹ less negative than the (CP-corrected) DF-SCS-MP2 value. This is most likely due to the missing contributions of one class of ionic excitations, where from one monomer one electron is excited within the same monomer and the other to the virtual orbitals of the other monomer. These excitations are excluded in the local calculations by construction.³² Also absent in the local calculations are double excitations from one monomer to the virtual basis of the other monomer. These are the excitations which are responsible for BSSE. For medium size basis sets (e.g. AVTZ*) the neglect of the CP correction leads to some error compensation, and the uncorrected values are therefore in closer agreement with the CP-corrected conventional interaction energies. Thus, it is recommended not to apply counterpoise corrections to the LMP2 or SCS-LMP2 values.

The last conclusion we can draw from Table 3 is that the DF-SCS-MP2 basis set error of the AVTZ* basis amounts to ≈ 0.2 kcal mol⁻¹ for the PD structure. Adding this correction to the CCSD(T) value of Table 2 yields an estimate for the CCSD(T) basis set limit of -2.72 kcal mol⁻¹ for the interaction energy of the PD(B) structure. This is slightly more negative

than the CCSD(T)/aug-cc-pVQZ* estimate of $-2.63 \text{ kcal mol}^{-1}$ of Sinnokrot and Sherrill, which was based on CCSD(T) calculations with a smaller basis set and an MP2 basis set correction. Sinnokrot and Sherrill obtained a CCSD(T)/AVDZ* value of $-2.22 \text{ kcal mol}^{-1}$, very close to our value of $2.225 \text{ kcal mol}^{-1}$ (the intermolecular distance is slightly different). To this an MP2 basis set correction of $-0.41 \text{ kcal mol}^{-1}$ was added. The corresponding basis set correction $E(\text{MP2/CBS}[45]) - E(\text{MP2/AVDZ}^*)$ amounts to $0.56 \text{ kcal mol}^{-1}$, whilst the SCS-MP2 correction is $0.48 \text{ kcal mol}^{-1}$. Adding similar corrections to the CCSD(T)/AVTZ* interaction energies for the S and T structures yields estimates of the CBS limits of 1.71 and $2.68 \text{ kcal mol}^{-1}$, respectively, in good agreement with the (probably less accurate) estimates of Sinnokrot and Sherrill.⁸

The potential energy curves for the vertical separation (R_1 in Figure 1) in the parallel-displaced (PD (A)), T-shaped and sandwich configurations of the benzene dimer are presented in Figures 2, 3 and 4, respectively. A horizontal scan for the parallel-displaced dimer with the vertical separation fixed at 3.4 \AA is shown in Figure 5. In these calculations the DF-LMP2/aug-cc-pVTZ optimised benzene monomer geometry ($R_{CC} = 1.3956 \text{ \AA}$ and $R_{CH} = 1.0830 \text{ \AA}$) was used, which is in excellent agreement with the MP2/aug-cc-pVTZ values of 1.3942 and 1.0823 \AA ,⁷ and the reference geometry from Gauss and Stanton of 1.3915 and 1.0800 \AA .⁴⁵ The canonical MP2 and CCSD(T) results include the CP correction, while the LMP2 and SCS-LMP2 ones are without CP correction. The CCSD(T) points are the values of Sherrill *et al.*,⁸ computed as $E_{\text{CCSD/AVDZ}^*} + E_{\text{MP2/aug-cc-pVQZ}^*} - E_{\text{MP2/AVDZ}^*}$, where in the aug-cc-pVQZ* basis all g -functions on carbons and all f -functions on hydrogens were omitted.

Figures 2-5 show that CP uncorrected DF-LMP2 binding energies very closely reproduce the CP corrected MP2 ones along the entire potential energy scans. In fact, the energies are so close that in many places it is difficult to visually distinguish between the curves on the scale of the figures. The DF-SCS-LMP2 values almost quantitatively reproduce the approximate CCSD(T)/aug-cc-pVQZ* results of Sherrill *et al.* for the entirety of the potential energy curves, with the difference in energy typically not more than $0.1 \text{ kcal mol}^{-1}$. As also seen from Table 2, the worst performance of DF-SCS-LMP2 is in the case of the T-shaped dimer configuration, but with a difference in interaction energy of $\approx 0.25 \text{ kcal mol}^{-1}$ this is still remarkably accurate.

4 Conclusions

It has been shown in the past that SCS-MP2 much improves the overestimation of dispersion energies by MP2.^{25-28,55} The current work supports these findings and demonstrates that the combination of spin-component scaling with density fitting and local approximations is particularly compelling. In the current application, density fitting reduces the CPU-times by one order of magnitude as compared to standard integral-direct calculations when the AVTZ basis set is used. This consistent with timings given in previous work.^{40,42} Due to the fact that the computational cost of DF methods grows only cubically with basis set size, the savings are even more pronounced for larger basis sets. This has made it possible in the current work to use basis sets up to quintuple zeta quality and to obtain extrapolated results that should be very close to the basis set limit.

It has been demonstrated that the BSSE is rendered practically negligible by the local correlation treatment, provided the BSSE is small at the HF level. The CP uncorrected DF-SCS-LMP2 interaction energies are in excellent agreement with those of CP corrected DF-SCS-

MP2. This makes it possible to avoid CP corrections, which is especially useful for larger clusters, since for a cluster of n molecules the number of calculations in the full basis set is reduced from $n + 1$ to 1. It is also possible to compute analytical DF-SCS-LMP2 energy gradients and to perform geometry optimisations of molecular clusters without the need for counterpoise corrections. In the current work this has been used to optimise the 3 considered structures of the benzene dimer at the DF-SCS-LMP2/AVTZ* level.

The DF-SCS-LMP2/AVTZ interaction energies reproduce the approximate CCSD(T)/aug-cc-pVQZ* results of Sherrill *et al.* along the entire potential energy curves within 0.1–0.2 kcal mol⁻¹. This also means that DF-SCS-LMP2 predicts almost the same optimal separation between the benzene monomers as the higher level CCSD(T) method. For the T-shaped configuration the experimental separation is well reproduced.

The excellent performance of DF-SCS-LMP2 is particularly striking when comparing the computational cost. Using the MOLPRO quantum chemistry package,⁴³ a CCSD(T)/AVTZ* calculation (720 basis functions) took 95.1 hours CPU-time on a single 2.4 GHZ opteron processor with 8 GB of memory (PD structure, C_{2h} symmetry, including integration and Hartree-Fock). Of this time, the CCSD (integral transformation and 11 iterations) took 13.3 hours and the perturbative triples correction 80 hours. This does not include the counterpoise correction, which requires substantial additional computational effort. A corresponding DF-HF/DF-SCS-LMP2 calculation (using C₁ symmetry) takes about 30 minutes on the same machine, thus being almost 200 times faster. This ratio is even more in favour of DF-SCS-LMP2 when the CP correction is applied to CCSD(T) to compensate for the BSSE.

Whilst the purpose of this investigation was to assess the suitability of using DF-LMP2 and DF-SCS-LMP2 in the prototypical π -stacking system of the benzene dimer, the results are extremely encouraging. The rather low cost of DF-SCS-LMP2 with reasonably large basis sets and the potentially linear scaling nature of DF-LMP2 suggest that this methodology is readily applicable to larger systems, such as the stacking of DNA base pairs. Further applications of this methodology to larger systems are currently underway.

References

- [1] P. Hobza, H. L. Selzle, and E. W. Schlag, *J. Am. Chem. Soc.* 116 (1994) 3500.
- [2] P. Hobza, H. L. Selzle, and E. W. Schlag, *J. Phys. Chem.* 100 (1996) 18790.
- [3] R. L. Jaffe and G. D. Smith, *J. Chem. Phys.* 105 (1996) 2780.
- [4] P. Hobza, V. Špirko, H. L. Selzle, and E. W. Schlag, *J. Phys. Chem. A* 102 (1998) 2501.
- [5] S. Tsuzuki, T. Uchimaru, K. Matsumura, M. Mikami, and K. Tanabe, *Chem. Phys. Lett.* 319 (2000) 547.
- [6] S. Tsuzuki, K. Honda, T. Uchimaru, M. Mikami, and K. Tanabe, *J. Am. Chem. Soc.* 124 (2002) 104.
- [7] M. O. Sinnokrot, E. F. Valeev, and C. D. Sherrill, *J. Am. Chem. Soc.* 124 (2002) 10887.
- [8] M. S. Sinnokrot and C. D. Sherrill, *J. Phys. Chem. A* 108 (2004) 10200.

- [9] O. A. Zhikol, O. V. Shishkin, K. A. Lyssenko, and J. Leszczynski, *J. Chem. Phys.* 122 (2005) 144104.
- [10] M. P. Waller, A. Robertazzi, J. A. Platts, D. E. Hibbs, and P. A. Williams, *J. Comput. Chem.* 27 (2006) 491.
- [11] Y. C. Park and J. S. Lee, *J. Phys. Chem. A* 110 (2006) 5091.
- [12] A. Puzder, M. Dion, and D. C. Langreth, *J. Chem. Phys.* 124 (2006) 164105.
- [13] J. D. Watson and H. C. D. Crick, *Nature* 171 (1953) 737.
- [14] L. S. Lerman, *J. Mol. Biol.* 3 (1961) 18.
- [15] S. K. Burley and G. A. Petsko, *Science* 229 (1985) 23.
- [16] C. A. Hunter, J. Singh, and J. M. Thornton, *J. Mol. Biol.* 218 (1991) 837.
- [17] G. B. McGaughey, M. Gagne, and A. K. Rappe, *J. Biol. Chem.* 273 (1998) 15458.
- [18] E. Arunan and H. S. Gutowsky, *J. Chem. Phys.* 98 (1993) 4294.
- [19] W. Scherzer, O. Kratzschmar, H. L. Selzle, and E. W. Schlag, *Z. Naturforsch., A* 47 (1992) 1248.
- [20] Y. Zhao and D. G. Truhlar, *Phys. Chem. Chem. Phys.* 7 (2005) 2701.
- [21] Y. Zhao, N. E. Schultz, and D. G. Truhlar, *J. Chem. Theory Comput.* 2 (2006) 364.
- [22] A. D. Becke and E. R. Johnson, *J. Chem. Phys.* 123 (2005) 154101.
- [23] G. Jansen and A. Heßelmann, *J. Phys. Chem. A* 105 (2001) 11156.
- [24] A. Heßelmann, G. Jansen, and M. Schütz, *J. Chem. Phys.* 122 (2005) 014103.
- [25] S. Grimme, *J. Chem. Phys.* 118 (2003) 9095.
- [26] S. Grimme, *Chem. Eur. J.* 10 (2004) 3423.
- [27] M. Piacenza and S. Grimme, *Chem. Phys. Chem.* 6 (2005) 1554.
- [28] M. Piacenza and S. Grimme, *J. Am. Chem. Soc.* 127 (2005) 14841.
- [29] P. Pulay, *Chem. Phys. Lett.* 100 (1983) 151–154.
- [30] S. Saebø and P. Pulay, *Annu. Rev. Phys. Chem.* 44 (1993) 213–236.
- [31] C. Hampel and H.-J. Werner, *J. Chem. Phys.* 104 (1996) 6286–6297.
- [32] M. Schütz, G. Rauhut, and H.-J. Werner, *J. Phys. Chem. A* 102 (1998) 5997.
- [33] N. Runeberg, M. Schütz, and H.-J. Werner, *J. Chem. Phys.* 110 (1999) 7210.
- [34] M. Schütz, G. Hetzer, and H.-J. Werner, *J. Chem. Phys.* 111 (1999) 5691–5705.
- [35] G. Hetzer, M. Schütz, H. Stoll, and H.-J. Werner, *J. Chem. Phys.* 113 (2000) 9443–9455.
- [36] M. Schütz and H.-J. Werner, *Chem. Phys. Lett.* 318 (2000) 370–378.

- [37] M. Schütz, *J. Chem. Phys.* 113 (2000) 9986–10001.
- [38] M. Schütz and H.-J. Werner, *J. Chem. Phys.* 114 (2001) 661–681.
- [39] O. Vahtras, J. Almlöf, and M. W. Feyereisen, *Chem. Phys. Lett.* 213 (1993) 514.
- [40] H.-J. Werner, F. R. Manby, and P. J. Knowles, *J. Chem. Phys.* 118 (2003) 8149.
- [41] F. Weigend, *Phys. Chem. Chem. Phys.* 4 (2002) 4285.
- [42] R. Polly, H.-J. Werner, F. R. Manby, and P. J. Knowles, *Mol. Phys.* 102 (2004) 2311.
- [43] H.-J. Werner, P. J. Knowles, R. Lindh, M. Schütz, P. Celani, T. Korona, F. R. Manby, G. Rauhut, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, A. W. Lloyd, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, R. Pitzer, U. Schumann, H. Stoll, A. J. Stone, R. Tarroni, and T. Thorsteinsson, MOLPRO, version 2006.1, a package of ab initio programs, see <http://www.molpro.net>.
- [44] F. Bernardi and S. F. Boys, *Mol. Phys.* 19 (1970) 553.
- [45] J. Gauss and J. F. Stanton, *J. Phys. Chem. A* 104 (2000) 2865.
- [46] R. A. Kendall, T. H. Dunning, and R. J. Harrison, *J. Chem. Phys.* 96 (1992) 6796.
- [47] F. Weigend, A. Köhn, and C. Hättig, *J. Chem. Phys.* 116 (2002) 3175.
- [48] F. Weigend, *Phys. Chem. Chem. Phys.* 4 (2002) 4285.
- [49] J. Pipek and P. G. Mezey, *J. Chem. Phys.* 90 (1989) 4916.
- [50] J. W. Boughton and P. J. Pulay, *J. Comput. Chem.* 14 (1993) 736.
- [51] G. Hetzer, P. Pulay, and H.-J. Werner, *Chem. Phys. Lett.* 290 (1998) 143.
- [52] J. R. Grover, E. A. Walters, and E. T. Hui, *J. Phys. Chem.* 91 (1987) 3233.
- [53] T. Helgaker, W. Klopper, H. Koch, and J. Noga, *J. Chem. Phys.* 106 (1997) 9638.
- [54] A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, and A. K. Wilson, *Chem. Phys. Lett.* 286 (1998) 243.
- [55] M. Gerenkamp and S. Grimme, *Chem. Phys. Lett.* 392 (2004) 229.

Table 1: Optimised equilibrium structures of the benzene dimer using DF-LMP2 and DF-SCS-LMP2 and the AVTZ* basis (see text).

Structure	DF-LMP2			DF-SCS-LMP2		
	R ₁	R ₂	ΔE	R ₁	R ₂	ΔE
PD (A)	3.37	1.57	-4.427	3.55	1.63	-2.604
PD (B)	3.37	1.58	-4.437	3.54	1.68	-2.617
S	3.72	0.00	-3.187	3.89	0.00	-1.781
T	4.89	0.00	-3.257	5.04	0.00	-2.234

a) Fixed monomer structure: $R_{CC} = 1.3915 \text{ \AA}$, $R_{CH} = 1.0800 \text{ \AA}$

Table 2: Comparison of MP2 and CCSD(T) counterpoise corrected interaction energies of the benzene dimer using double and triple zeta basis sets^a. The difference between the interaction energies obtained with the two basis sets is given in parenthesis. The calculations were performed at the SCS-LMP2/AVTZ* optimised structures (see Table 1)

Method	PD(B)-structure		S-structure		T-structure	
	AVDZ*	AVTZ*	AVDZ*	AVTZ*	AVDZ*	AVTZ*
HF	3.533	3.515 (-0.038)	3.630	3.484 (-0.146)	0.714	0.796 (-0.082)
MP2	-3.982	-4.324 (-0.342)	-2.745	-3.038 (-0.293)	-2.975	-3.239 (-0.264)
CCSD	-1.257	-1.422 (-0.165)	-0.476	-0.631 (-0.155)	-1.745	-1.924 (-0.179)
CCSD(T)	-2.225	-2.513 (-0.288)	-1.310	-1.564 (-0.254)	-2.239	-2.492 (-0.253)
Δ (T)	-0.968	-1.091 (-0.123)	-0.834	-0.933 (-0.099)	-0.494	-0.568 (-0.074)
SCS-MP2	-2.396	-2.672 (-0.276)	-1.488	-1.737 (-0.249)	-2.057	-2.280 (-0.223)
DF-SCS-MP2	-2.388	-2.665 (-0.277)	-1.479	-1.732 (-0.253)	-2.053	-2.275 (-0.222)

a) AVDZ*: aug-cc-pVDZ for C, cc-pVDZ for H (336 basis functions)

AVTZ*: aug-cc-pVTZ for C, cc-pVTZ for H (720 basis functions)

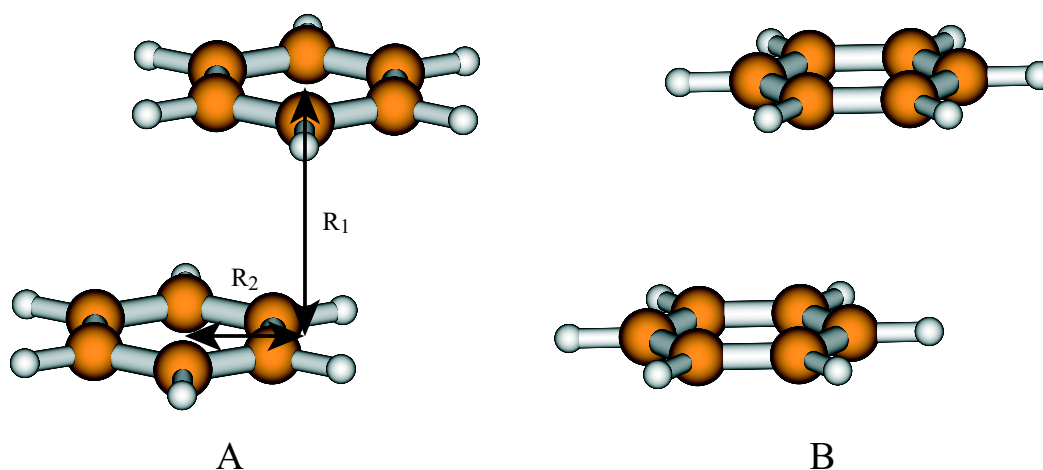


Figure 1: Possible orientations of the benzene dimer in the parallel displaced configuration. Orientation A shows a horizontal displacement along R_2 perpendicular to a C–C bond. Orientation B possesses a horizontal displacement in the direction of a C–H bond.

Table 3: Basis set dependence of interaction energies for the benzene dimer (in kcal mol⁻¹) using the AV n Z* basis sets^a.

Method	n	PD(B)			S			T		
		ΔE	ΔE_{CP}	BSSE	ΔE	ΔE_{CP}	BSSE	ΔE	ΔE_{CP}	BSSE
HF	2	2.732	3.544	-0.811	3.145	3.641	-0.495	0.098	0.719	-0.622
	3	3.318	3.522	-0.204	3.310	3.489	-0.179	0.667	0.801	-0.134
	4	3.469	3.517	-0.048	3.436	3.478	-0.042	0.758	0.793	-0.035
	5	3.504	3.515	-0.011	3.468	3.478	-0.009	0.785	0.793	-0.007
MP2	2	-6.486	-3.978	-2.508	-4.453	-2.739	-1.714	-4.867	-2.974	-1.893
	3	-5.471	-4.318	-1.154	-3.941	-3.033	-0.907	-4.033	-3.234	-0.798
	4	-4.867	-4.446	-0.421	-3.443	-3.123	-0.320	-3.646	-3.349	-0.297
	5	-4.689	-4.494	-0.195	-3.318	-3.158	-0.160	-3.520	-3.388	-0.131
	∞	-4.539	-4.542	0.003	-3.222	-3.195	-0.027	-3.416	-3.429	0.013
LMP2	2	-4.049	-3.475	-0.574	-2.801	-2.518	-0.282	-3.076	-2.583	-0.493
	3	-4.209	-4.023	-0.185	-3.037	-2.876	-0.160	-3.152	-3.028	-0.124
	4	-4.287	-4.241	-0.046	-3.037	-2.995	-0.041	-3.244	-3.208	-0.036
	5	-4.369	-4.360	-0.009	-3.074	-3.067	-0.007	-3.307	-3.301	-0.006
	∞	-4.491	-4.482	-0.009	-3.147	-3.143	-0.005	-3.403	-3.399	-0.004
SCS-MP2	2	-4.933	-2.388	-2.545	-3.236	-1.479	-1.756	-3.969	-2.053	-1.916
	3	-3.890	-2.665	-1.226	-2.696	-1.732	-0.965	-3.124	-2.275	-0.848
	4	-3.238	-2.778	-0.460	-2.160	-1.810	-0.350	-2.708	-2.383	-0.325
	5	-3.043	-2.823	-0.219	-2.022	-1.841	-0.180	-2.568	-2.421	-0.147
	∞	-2.874	-2.868	-0.006	-1.910	-1.874	-0.036	-2.452	-2.461	0.010
SCS-LMP2	2	-2.577	-2.001	-0.576	-1.624	-1.330	-0.294	-2.241	-1.748	-0.494
	3	-2.617	-2.428	-0.189	-1.781	-1.617	-0.163	-2.234	-2.107	-0.127
	4	-2.655	-2.606	-0.049	-1.751	-1.707	-0.044	-2.301	-2.263	-0.038
	5	-2.720	-2.711	-0.010	-1.774	-1.767	-0.007	-2.354	-2.347	-0.006
	∞	-2.826	-2.818	-0.008	-1.833	-1.830	-0.003	-2.438	-2.436	-0.003

a) ∞ denotes the complete basis set estimates obtained by extrapolating the $n = 4$ and 5 correlation energies(see text). Density fitting was used in all cases.

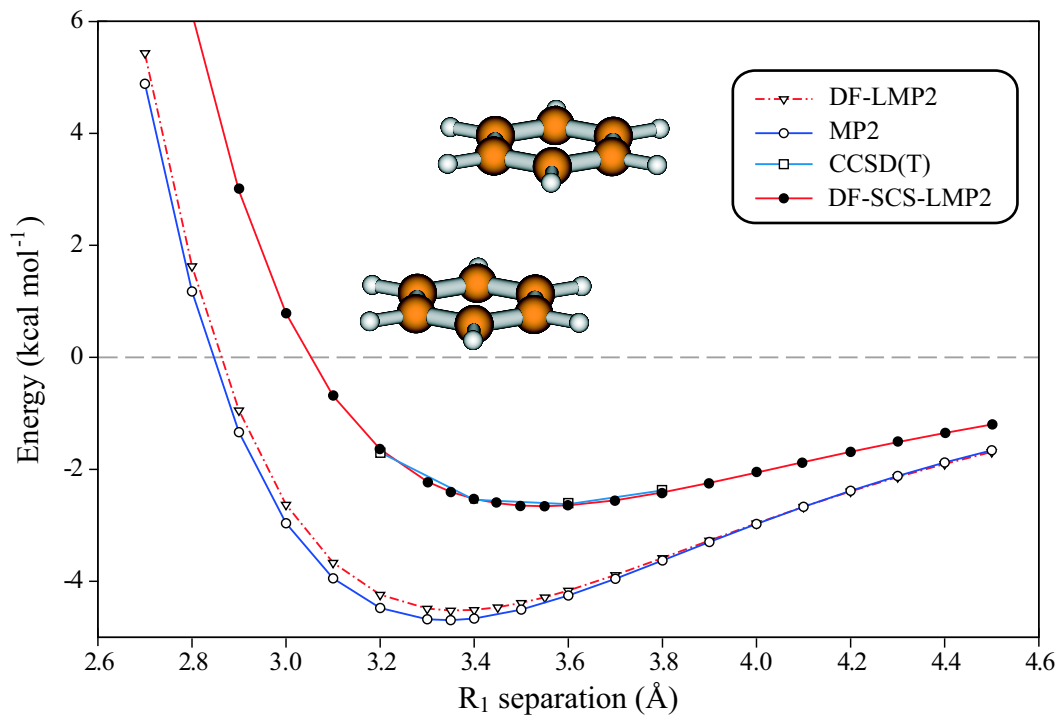


Figure 2: Potential energy curves for the parallel displaced configuration of the benzene dimer, horizontal separation fixed at 1.6 Å. In all MP2 and LMP2 calculations the aug-cc-pVTZ basis set was used. The CCSD(T) results are from Ref. 8 (see text). Only the MP2 and CCSD(T) values are counterpoise corrected.

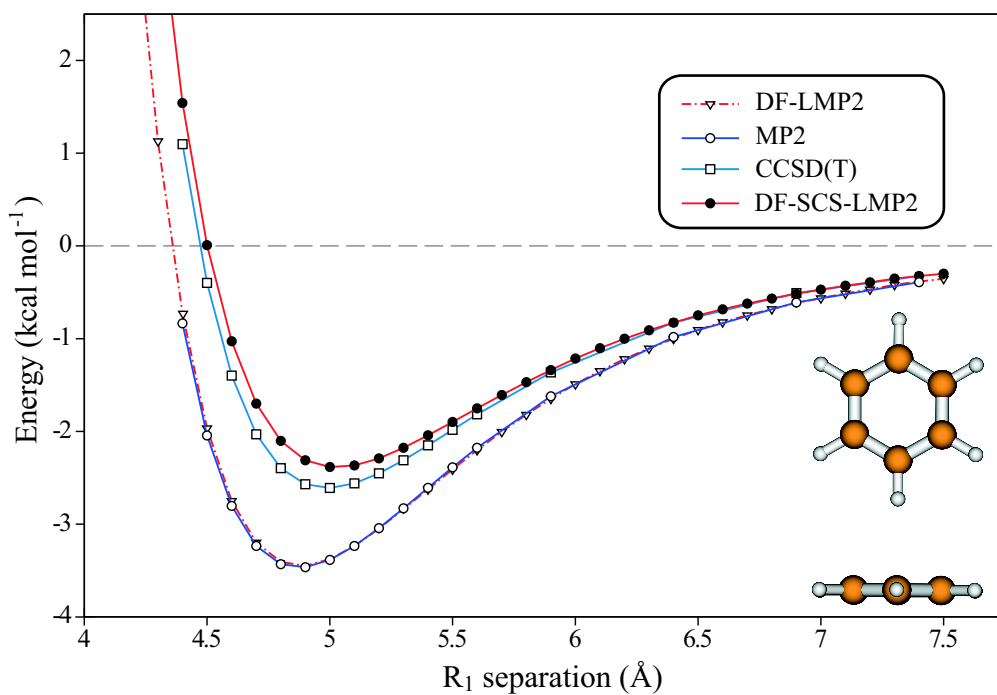


Figure 3: Potential energy curves for the T-shaped configuration of the benzene dimer. In all MP2 and LMP2 calculations the aug-cc-pVTZ basis set was used. The CCSD(T) results are from Ref. 8 (see text). Only the MP2 and CCSD(T) values are counterpoise corrected.

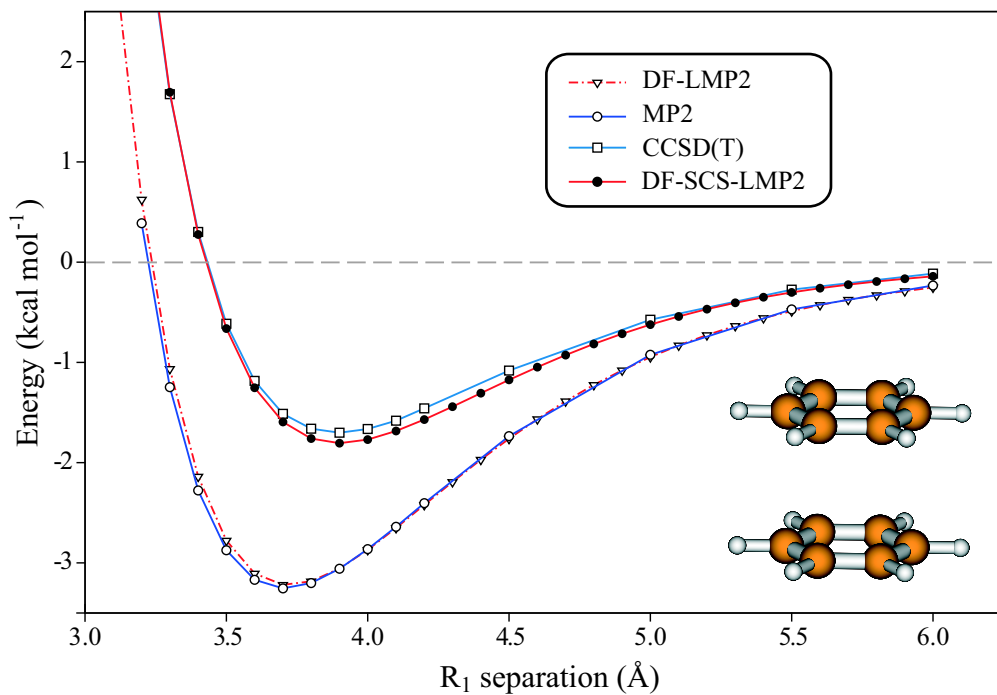


Figure 4: Potential energy curves for the sandwich configuration of the benzene dimer. In all MP2 and LMP2 calculations the aug-cc-pVTZ basis set was used. The CCSD(T) results are from Ref. 8 (see text). Only the MP2 and CCSD(T) values are counterpoise corrected.

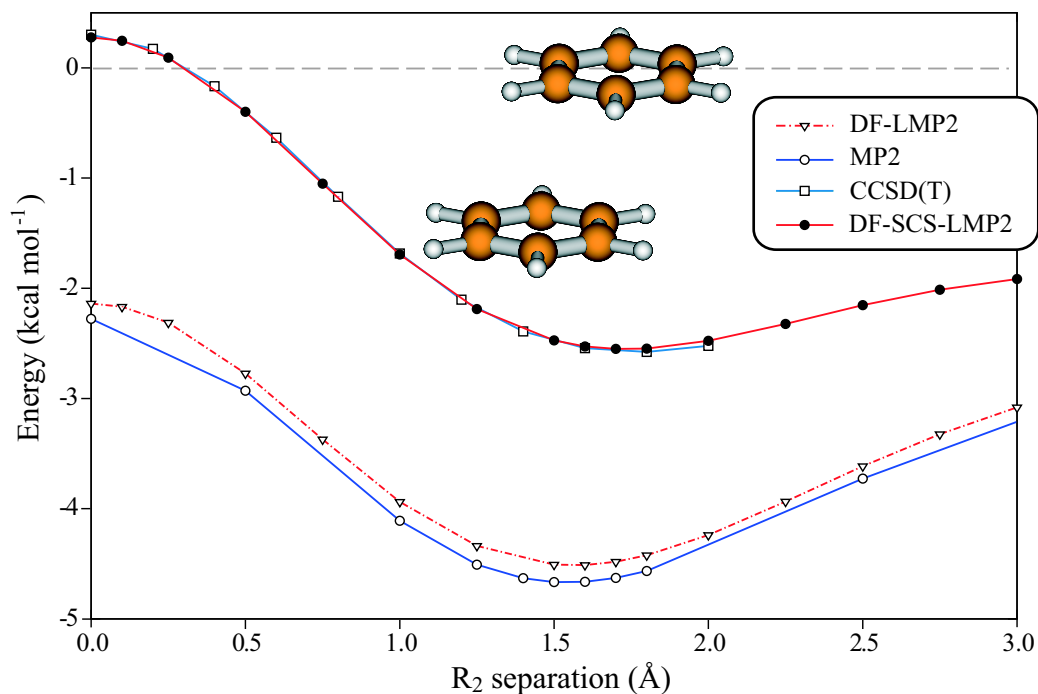


Figure 5: Potential energy curves for the parallel-displaced configuration of the benzene dimer with a vertical separation of 3.4 Å. In the MP2 and LMP2 calculations the aug-cc-pVTZ basis set was used. The CCSD(T) results are from Ref. 8 (see text). Only the MP2 and CCSD(T) values are counterpoise corrected.

Supporting Information

Table 4: Basis set dependence of interaction energies for the benzene dimer (in kcal mol⁻¹) using the AVnZ basis sets^a. Density fitting was used in all cases. The DF-SCS-LMP2 structures of Table 1 were used.

Method	n	PD(B)			S			T		
		ΔE	ΔE_{CP}	BSSE	ΔE	ΔE_{CP}	BSSE	ΔE	ΔE_{CP}	BSSE
HF	2	2.275	3.557	-1.283	2.697	3.637	-0.939	-0.321	0.780	-1.102
	3	3.310	3.524	-0.214	3.310	3.490	-0.179	0.610	0.794	-0.184
	4	3.461	3.517	-0.056	3.430	3.479	-0.048	0.751	0.793	-0.042
MP2	2	-7.308	-4.049	-3.259	-5.138	-2.800	-2.338	-6.037	-3.032	-3.005
	3	-5.699	-4.365	-1.334	-4.085	-3.065	-1.021	-4.503	-3.297	-1.207
	4	-4.967	-4.468	-0.499	-3.533	-3.142	-0.391	-3.802	-3.373	-0.429
LMP2	2	-4.551	-3.519	-1.031	-3.335	-2.570	-0.765	-3.604	-2.619	-0.985
	3	-4.265	-4.059	-0.206	-3.068	-2.892	-0.176	-3.300	-3.108	-0.192
	4	-4.302	-4.266	-0.037	-3.041	-3.009	-0.032	-3.283	-3.254	-0.029
SCS-MP2	2	-5.758	-2.444	-3.314	-3.910	-1.529	-2.382	-5.143	-2.095	-3.048
	3	-4.130	-2.705	-1.425	-2.850	-1.758	-1.092	-3.617	-2.329	-1.288
	4	-3.348	-2.798	-0.550	-2.256	-1.826	-0.430	-2.877	-2.404	-0.473
SCS-LMP2	2	-3.070	-2.038	-1.033	-2.146	-1.379	-0.767	-2.746	-1.761	-0.986
	3	-2.667	-2.457	-0.210	-1.809	-1.630	-0.179	-2.371	-2.175	-0.196
	4	-2.667	-2.629	-0.038	-1.753	-1.721	-0.033	-2.334	-2.304	-0.030