Interaction energies of monosubstituted benzene dimers
via nonlocal density functional theory

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We present density-functional calculations for the interaction energy of monosubstituted benzene dimers. Our approach utilizes a recently developed fully nonlocal correlation energy functional, which has been applied to the pure benzene dimer and several other systems with promising results. The interaction energy as a function of monomer distance was calculated for four different substituents in a sandwich and two T-shaped configurations. In addition, we considered two methods for dealing with exchange, namely using the revPBE generalized gradient functional as well as full Hartree–Fock. Our results are compared with other methods, such as Møller–Plesset and coupled-cluster calculations, thereby establishing the usefulness of our approach. Since our density-functional based method is considerably faster than other standard methods, it provides a computational inexpensive alternative, which is of particular interest for larger systems where standard calculations are too expensive or infeasible.

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I. INTRODUCTION

With the vast development of computational facilities in the last decade, it is now possible to analyze small aromatic systems numerically with high precision. Particular interest has emerged for the non-covalent van der Waals interaction, important in many areas and responsible for phenomena, such as DNA base pair bonding, protein structure and folding, and organic molecule crystallization. While the full DNA structure itself is still out of scope, calculations for the benzene dimer, which is the simplest prototype of aromatic $\pi-\pi$ interaction, have been reported.\textsuperscript{1-4} A step toward larger systems are calculations for substituent effects on the benzene dimer.\textsuperscript{5} State-of-the-art tools for such calculations are second-order Møller–Plesset (MP2) perturbation theory and coupled-cluster calculations with singles, doubles, and perturbative triples (CCSD(T)). These methods, especially the latter, are regarded as highly accurate and reliable. Unfortunately, their application to large systems is time consuming and computationally very demanding. Furthermore, the results might depend on the basis set used and elaborate techniques are necessary to estimate the basis set limit.

Density functional theory (DFT), especially in the form of various generalized gradient approximations (GGA) including those with no empirical input,\textsuperscript{6,7} have had a degree of success in describing dense bulk matter,\textsuperscript{8} and isolated molecules.\textsuperscript{9} For molecules, this performance has been further improved by the use of various empirical and hybrid methods. However, for van der Waals complexes and sparse matter including many layered structures, polymer crystals, organic molecular crystals and the like, such methods either give sporadic results or fail completely. In particular, the importance of DFT-based methods for calculations of molecular clusters has been minor. The reason for this is that the domi-
nant part of the stabilization energy in many cases comes from the dispersion energy, which is usually not included correctly in DFT. Moreover, functionals of the GGA type often do not even predict a binding of molecular dimers. Therefore, considerable effort has been devoted to develop DFT based methods that are capable of treating van der Waals systems. Among these are methods with empirical damping functions, self-consistent charge-density functional tight-binding methods, and self-consistent LCAO methods with standard pseudopotentials.

Recently, a new approach using a van der Waals density functional (vdW-DF) with a nonlocal correlation-energy has been developed. This formalism includes van der Waals forces in a seamless fashion and the applicability of this approach was first demonstrated for bulk layered systems such as graphite, boron nitride, and molybdenum sulfide. Similarly, it has been applied to two-layer dimers of these same materials and the benzene dimer in a number of geometries, where it also proved to give a realistic description. More recently, it has been applied to naphthalene, anthracene, and pyrene dimers where for naphthalene it gives a creditable comparison with recent CCSD(T) results. These larger dimers show the power of the method for more sizable systems where CCSD(T) results appear to be nonexistent. In addition, there have been promising applications to a molecule physisorbed on an infinite surface, as well as to a bulk crystal of polyethylene.

In this paper, we investigate the capability of vdW-DF to describe larger systems. We go beyond the pure benzene dimer and use the nonlocal functional to calculate the effect of the substituents OH, CH$_3$, F, and CN. These each replace an H atom on one of the molecules of the benzene dimer, and among other things act as electron donors (OH and CH$_3$) or acceptors (F and CN), as discussed by Sinnokrot and Sherrill, who performed MP2 and
CCSD(T) calculations. Our results show that vdW-DF, which is much faster than MP2 and CCSD(T), gives interaction energies and distances comparable with these standard methods. Furthermore, it generates the correct energy ordering of different substituent structures. Thus, it is a promising method for larger applications such as DNA base-pair stacking and beyond, as well as for various types of extended systems where wave function methods are typically impractical.

This paper is organized as follows: Section II describes the energy functional and the details of its evaluation. In Sec. III, we give computational details. Our results are analyzed in Sec. IV, where we also compare with other numerical methods. We conclude in Sec. V and give an outlook for future work.

II. VAN DER WAALS DENSITY FUNCTIONAL (VDW-DF)

At the heart of every DFT calculation lies the energy functional $E[\rho]$, which depends on the electron density $\rho$. For our calculations we used the following particular functional with nonlocal correlation energy,

$$E[\rho] = T_s[\rho] + V_{pp}[\rho] + J[\rho] + E_x[\rho] + E_L^c[\rho] + E_{NL}^c[\rho],$$

which was especially designed to include the van der Waals interaction. Here, $E$ is the total energy functional of the dimer, $T_s$ is the single-particle kinetic energy, $V_{pp}$ is the ionic pseudopotential functional, and $J$ describes the Coulomb interaction. For the exchange functional $E_x$ we used the revPBE parameterization of GGA. Furthermore, $E_L^c$ denotes the local part of the correlation, which was evaluated using LDA. The nonlocal part can be
written as

\[ E_{\text{NL}}^{\rho}[\rho] = \frac{1}{2} \int \int d^3r \, d^3r' \rho(\vec{r}) \phi(\vec{r}, \vec{r}') \rho(\vec{r}') , \]  

(2)

where \( \phi(\vec{r}, \vec{r}') \) is a function depending on \(|\vec{r} - \vec{r}'|\) and \( \rho \) in the vicinity of \( \vec{r} \) and \( \vec{r}' \). Details about its construction can be found in Ref. [10]. No empirical input was applied.

For the charge density \( \rho \), we used the result of a self-consistent DFT calculation utilizing the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. With this charge density we then evaluated the functional from Eq. (1). Differences in interaction energies for charge densities resulting from other exchange-correlation functionals turned out to be negligible.

**III. COMPUTATIONAL METHODS**

Our self-consistent DFT calculations for obtaining the charge density \( \rho \) were performed with the planewave code ABINIT. We used Troullier-Martins pseudopotentials with a kinetic energy cutoff of 50 Rydberg. The dimers and monomers were placed in boxes of such size that one system and its mirror image is separated by 15 to 20 Å of vacuum. This distance proved to be sufficient for the charge density to approach zero well before the supercell edge, which eliminates any interaction between periodic replica, aside from the possibility of electrostatic as discussed below. Even with this conservative box size, the calculations of this GGA part go quickly, requiring only around two hours on a single processor (e.g. Athlon MP2000+) for each position of the monomers considered.

Most parts of the energy functional from Eq. (1) were also directly evaluated in ABINIT. Only the nonlocal correlation part was calculated in a post-process procedure. Thereby, we
computed $E_c^{NL}$ on a real space grid with a spacing equal to the Fourier transform spacing in the plane wave calculations, and then we performed a numerical integration as described in Ref. [10]. This procedure, as currently coded, requires a computer time comparable to the DFT calculation. Although optimization of the code could substantially cut this time, that effort is probably unnecessary, as the time for the straightforward GGA calculation of the above paragraph will dominate as the system size increases.

At this point we should mention another promising complementary method (SAPT-DFT), a density functional based version of symmetry adapted perturbation theory (SAPT), which uses time-dependent DFT to calculate the dispersion contribution. This complementary procedure appears to have advantages and disadvantages with respect to our much simpler one. First, it gives an energy curve closer to CCSD(T) than vdW-DF for the benzene dimer in the sandwich geometry and also for rare gas dimers. Furthermore, with recent optimization, the computer time required for benzene is (like vdW-DF) comparable to that of an ordinary density functional calculation. It appears likely that for systems this size or a little larger, this better accuracy may continue. However, the computer time of SAPT-DFT scales as the fifth power of the basis size, so that its application will rapidly become impractical as the system size increases, as opposed to vdW-DF, which will continue to scale as an ordinary DFT calculation. In addition, SAPT-DFT is not a density functional; its application necessitates the identification of individual fragments, so it cannot be seamless as fragments merge together to become single entities. It is also not obvious how it might be applied to a single fragment for which dispersion interaction between different ends or parts is important; nor to an extended system that cannot be divided into individual summable finite parts. Being a simple density functional, vdW-DF can do all of the above. In summary,
it can be applied to calculations of all types and sizes for which an ordinary LDA or GGA calculation can. These complementary aspects of SAPT-DFT and vdW-DF render both methods important to pursue.

Because the GGA part of our calculation is performed on a system consisting of replicas of the relevant molecular complex separated by 40 Bohr on a simple cubic lattice, one must consider the possibility of spurious electrostatic interactions between these replicas showing up in our results. Of course, the pure benzene monomer does not have a permanent dipole moment. On the other hand, the dipole moments of the substituted benzene range from \( \sim 0.4 \) debye for toluene to \( \sim 4 \) debye for benzonitrile. The Coulomb energy associated with this interaction is easily calculated using a method attributed to Lorentz\(^{34}\) (see Jackson\(^{35}\) for a more easily accessible description). We find that this Coulomb energy ranges from \( \sim 0.05 \) kcal/mol for benzonitrile and becomes two orders of magnitude smaller for toluene. The former number is comparable to the numerical accuracy of our calculations. We cite it because it is a hard number that must reasonably be expected to be larger than any induced electrostatic interactions, which we will estimate below. This direct interaction obviously cancels out of our calculation exactly when the subtraction is made to find the energy of interaction between the two parts of each molecular complex. However, the dipole moment of the complex in one supercell can induce a changed charge distribution in each of the two molecules in an adjacent supercell, thereby changing the electrostatic interaction between the latter. This interaction does not cancel out, but can be estimated from the dipole moments and polarizabilities involved. We find that it gives a contribution ranging from \( \sim 10^{-4} \) kcal/mol for the \( \text{CH}_3 \) substituted dimer to \( \sim 10^{-2} \) kcal/mol for the \( \text{CN} \) substituted one. On the level of the other inaccuracies in our calculation, these errors are completely
negligible.

Of the exchange functionals tried earlier,\textsuperscript{10,14,19} Zhang and Yang’s “revPBE” was the closest to Hartree–Fock (HF) for the dimers compared.\textsuperscript{10,19} However, it was clear that the magnitude of its slope was a little too big in the binding region. This lead to the speculation that the equilibrium distances with revPBE exchange, which were also a little too big, would be improved if full HF exchange were used instead. This conjecture was verified in Ref. [20], where the use of HF exchange instead of revPBE exchange in the functional of Eq. (1) was fully implemented and applied to the benzene dimer in several different configurations. There, the exchange $E_x$ was evaluated both with the revPBE exchange functional and HF, and the various tradeoffs evaluated and discussed. Here, we do the same for the substituted dimers. For HF exchange we used the general ab-initio package GAMESS,\textsuperscript{36} using a triple zeta valence (TZV) basis set.

\section*{IV. RESULTS AND DISCUSSION}

We calculated interaction energies for three typical configurations of the dimer,\textsuperscript{1–4} as depicted in Fig. 1. In the sandwich structure, the two monomers are arranged parallel in such a way that the centers of the rings are on top of each other. In the T-shaped structure, the two monomers form an angle of 90°, where one monomer is placed right above the center of the other ring. We have chosen a configuration in which the substituent points away from the other ring [T-shaped(1)] and a similar configuration in which both monomers are rotated by 90° [T-shaped(2)]. For our calculations we have considered four different substituted molecules, namely phenol, toluene, fluorobenzene, and benzonitrile (whose substituents are
OH, CH$_3$, F, and CN, respectively). In addition, we also calculated the pure benzene dimer, whose “substituent” we refer to as “H”. In all cases, we define “distance” as the distance from the center of the benzene ring to the center of the aromatic ring containing the substituent. All atomic positions for the monomers were optimized during the self-consistent DFT calculations, however, for the calculations of interaction energies, the two constituent monomers were considered “rigid” and only the intermonomer distance was changed.

A. Sandwich configuration

Results for the interaction energy as a function of the distance for the sandwich configuration are plotted in Fig. 2. Each line depicted consists of 20 points for distances from 3 to 8 Å. The data was then fitted with splines to be continuous. As expected, for short distances all curves show strong repulsion, whereas for large distances the interaction vanishes. Furthermore, all curves show a pronounced minimum around 4 Å. Values for the interaction energy at these minima can be found in Table I, where we also compare with other numerical methods. Unfortunately, corresponding experimental values are not available, however, we want to mention that some experimental studies of substituent effects in related systems are reported,$^{37,38}$ but it is difficult to reliably extract correct binding energies.

It can be seen in Table I that the values for the binding distances are approximately 10% larger than the corresponding MP2 values and about 5% larger than CCSD(T) values. Numbers for the interaction energies are in between MP2 and CCSD(T) values, and about 25% larger compared to CCSD(T). This can be partly explained by the fact that DFT calculations underestimate the quadrupole moment by as much as 20%. $^{39}$ This makes our
interaction energies too large, since not enough repulsion is considered.

In a simple picture, as pointed out by Sinnokrot and Sherill,\textsuperscript{5} one could think of the substituents as electron donors (OH, CH\textsubscript{3}) or electron withdrawing (F, CN). In terms of a Hunter–Sanders model,\textsuperscript{40} where electrostatics is assumed to determine changes in binding, one would expect to find that dimers with F and CN substituents bind more strongly than the pure dimer, whereas OH and CH\textsubscript{3} bind more weakly. On the contrary, they found increased binding for all the substituted species. A subsequent breakdown\textsuperscript{5} using SAPT with a modest basis set showed these differences to be distributed among a number of different energy components, whose individual values were rather sensitive to the precise values of intermonomer distance. We might expect the binding from dispersion to increase due to the addition of substituents, as they would be expected to reduce the energy gap for electronic particle-hole excitations, and hence increase the polarizability of the substituted monomer. However, SAPT calculations showed this effect to be too small to alone explain the differences. Nevertheless, it was clear that dispersion was by far the largest individual attractive component of the energy, and the necessity to be able to calculate this with little variation in fractional error for each substituted species is crucial to obtain a correct overall picture.

In the light of the above, it is an important challenge to the vdW-DF density functional to see if it can reproduce the changes that occur upon substitution, and hence it is interesting to look at our predicted interaction energies relative to those of the pure benzene dimer. Numbers for these values at the corresponding minimum are collected in Table II. If we also normalize the distance such that it is measured relative to the benzene binding distance, the plot in the right panel of Fig. 2 is obtained. Here, we also added the CCSD(T) minimum
points so that a direct comparison is possible. It can be seen clearly that the DFT method is in very good agreement with the CCSD(T) calculations. Similarly, we predict a bond length contraction of \(\sim 0.1\ \text{Å}\) for all the substituents, in agreement with the CCSD(T) calculations. In general, while all interaction energies depend somewhat upon the specific details of the calculation, the relative energies for the different substituents are almost independent thereof.

**B. T-shaped(1) and T-shaped(2) configuration**

Results for interaction energies of T-shaped(1) and T-shaped(2) dimers are plotted in Figs. 3 and 4. All curves show pronounced minima around 5.25 Å. Values for \(E_{\text{int}}\) at the minimum points and relative to the benzene dimer can again be found in Tables I and II, respectively. It can be seen immediately that the effect of substitution in the T-shaped configurations is much weaker. The difference in \(E_{\text{int}}\) for the strongest and weakest binding substituents is only approximately half of what it is in sandwich configuration.

As mentioned before, the quadrupole-quadrupole interaction within DFT is underestimated. For sandwich structures, this leads to a binding that is too strong, since not enough repulsion is considered. For T-shaped configurations, however, the quadrupole-quadrupole interaction constitutes an attraction, since the monomers form an angle of 90°. Here, the underestimation will lead to a binding which is too weak. The effect will be smaller though, because the T-shaped binding distances are larger than the sandwich ones. As a result, the vDW-DF interaction energies now show a weaker binding compared to MP2 and CCSD(T). The binding order, on the other hand, is in perfect agreement. In particular, the isoenergetic levels of H and OH in T-shaped(1) and T-shaped(2) configuration are well reproduced.
As for the sandwich structure, we calculated the interaction energies in reference to the benzene dimer and its binding distance. The results are depicted in the right graphs of Figs. 3 and 4. Again, it can be seen that the DFT method is generally in quite good agreement with the CCSD(T) calculations.

C. Hartree–Fock exchange

As pointed out in Ref. [20], using HF exchange instead of revPBE while evaluating the functional of Eq. (1) influences binding distances and interaction energies. While the exchange energy might alter the shape of the potential curve to a smaller or greater extent, it is the nonlocal correlation energy functional that allows to treat van der Waals systems within a DFT approach. As we will see below, the binding order of different substituents is actually independent of the exchange functional used and thus, it is governed by the nonlocal correlation energy and other components of the total energy. From this point of view, it seems conceivable to utilize even other exchange functionals than revPBE or HF. However, there is one important point to keep in mind: Within a given covalently bonded monomer the full HF interaction can be long ranged, because the Coulomb interaction can extend from one end of a molecular orbital to another, whereas the proper inclusion of correlation will shield this interaction, yielding an effectively short-ranged Coulomb interaction (aside from van der Waals effects). In ordinary DFT (either LDA or GGA) this is handled by making both exchange and correlation short-ranged, thus mixing their definitions in this respect.

We repeated all calculations from above using HF exchange instead of revPBE. The results for all configurations are plotted in Fig. 5. In general, the effect of using HF exchange
instead of revPBE is a stronger binding at shorter distances. Values for the interaction energy at the minimum points can be found in Tables III and IV where we refer to the DFT calculations with HF exchange as vdW-DF(HF). Remarkably, the relative order of interaction energies for different substituents is the same with HF and revPBE exchange. It can also be seen that the effect of using HF exchange instead of revPBE is stronger in the T-shaped configuration than in the sandwich structure. However, it is clear that the energy differences between the benzene dimer and the four substituted ones are not in such good agreement with CCSD(T) as the results using revPBE were. As the substituted monomers are significantly longer and presumably more easily polarized than benzene alone, one can speculate that this poorer agreement is due to the lack of long range shielding of the Coulomb potential in the HF approximation, as discussed in the above paragraph. Alternatively, it could be due to the lack of self-consistency of simply substituting the self-consistent HF exchange energy for the self-consistent GGA one, which is a related problem. In any case, the larger issue of the consistency of various exchange approximations with the correlation method used is an important one, and a subject of further study.

However, with respect to the grosser effects of HF exchange, we find results similar to Ref. [20], in particular an improvement in the binding distances. The vdW-DF(HF) values are now within \( \sim 1\% \) of the CCSD(T) values. On the other hand, the interaction energies now show a stronger binding than the vdW-DF results. The use of HF exchange also corrects the relation of interaction energies between T-shaped and sandwich structures: While vdW-DF always predicts the sandwich structure to be lower in energy, vdW-DF(HF) reverses this order and gives stronger binding for all T-shaped structures, in agreement with CCSD(T) calculations.\(^5\)
V. CONCLUSIONS

We have presented DFT-based calculations for systems that exhibit van der Waals type bonding. In particular, we investigated substituent effects on benzene dimers for several different substituents. Our method gives useful approximations for interaction energies and binding distances, when compared with state-of-the-art wave function methods, which are computationally much more demanding. In addition, the changes produced by the substituents as given by our vdW-DF method were quite close indeed to those predicted by CCSD(T). Our DFT based method offers a computationally inexpensive alternative that can speed up calculations drastically, and in addition make applications to extended systems possible. To be specific, our calculations require only slightly more computer time for large systems than the GGA type of DFT calculations that they replace. With this in mind, it is a promising candidate for larger applications, such as DNA base-pair stacking, which is already work in progress. The method is also applicable to extended systems where wave function methods are infeasible.

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TABLE I: Comparison of interaction energies $E_{\text{int}}$ and binding distances $R$ for all substituents, calculated with different methods. MP2 and CCSD(T) values are taken from Ref. [5], where calculations were performed with an aug-cc-pVTZ basis set.

| method     | sandwich $R$ [Å], $E$ [kcal/mol] | T-shaped(1) $R$ [Å], $E$ [kcal/mol] | T-shaped(2) $R$ [Å], $E$ [kcal/mol] |
|------------|----------------------------------|-------------------------------------|-------------------------------------|
| H          | MP2 3.70, −3.26                  | 4.89, −3.46                         | 4.89, −3.46                         |
|            | estd. CCSD(T) 3.90, −1.80        | 4.99, −2.62                         | 4.99, −2.62                         |
|            | vDW-DF 4.10, −2.37               | 5.28, −2.28                         | 5.28, −2.28                         |
|            | vDW-DF(HF) 3.83, −2.93           | 4.90, −4.40                         | 4.90, −4.40                         |
| OH         | MP2 3.60, −3.75                  | 4.90, −3.42                         | 4.90, −3.52                         |
|            | estd. CCSD(T) 3.80, −2.17        | 5.00, −2.58                         | 5.00, −2.67                         |
|            | vDW-DF 4.03, −2.79               | 5.27, −2.28                         | 5.26, −2.41                         |
|            | vDW-DF(HF) 3.74, −3.85           | 4.88, −4.45                         | 4.90, −4.39                         |
| CH$_3$     | MP2 3.65, −3.96                  | 4.90, −3.39                         | 4.80, −3.89                         |
|            | estd. CCSD(T) 3.80, −2.27        | 5.00, −2.55                         | 5.00, −2.95                         |
|            | vDW-DF 4.04, −2.95               | 5.25, −2.27                         | 5.24, −2.62                         |
|            | vDW-DF(HF) 3.75, −3.81           | 4.87, −4.26                         | 4.88, −4.82                         |
| F          | MP2 3.70, −3.81                  | 4.90, −3.61                         | 4.90, −3.17                         |
|            | estd. CCSD(T) 3.80, −2.29        | 5.00, −2.77                         | 5.00, −2.38                         |
|            | vDW-DF 4.03, −2.85               | 5.28, −2.46                         | 5.29, −2.23                         |
|            | vDW-DF(HF) 3.75, −3.98           | 4.89, −4.81                         | 4.91, −4.05                         |
| CN         | MP2 3.60, −4.86                  | 4.80, −4.11                         | 4.90, −3.08                         |
|            | estd. CCSD(T) 3.80, −3.05        | 4.90, −3.25                         | 5.00, −2.20                         |
|            | vDW-DF 3.97, −3.68               | 5.22, −2.86                         | 5.31, −2.01                         |
|            | vDW-DF(HF) 3.70, −5.16           | 4.86, −5.37                         | 4.92, −3.85                         |
TABLE II: Interaction energies relative to the benzene dimer in [kcal/mol]. MP2/aug-cc-pVTZ and CCSD(T)/aug-cc-pVTZ values are taken from Ref. [5].

| Structure         | OH     | CH₃    | F      | CN     |
|-------------------|--------|--------|--------|--------|
| **sandwich structure** |        |        |        |        |
| MP2               | −0.49  | −0.70  | −0.55  | −1.60  |
| estd. CCSD(T)     | −0.37  | −0.47  | −0.49  | −1.25  |
| vDW-DF            | −0.42  | −0.58  | −0.48  | −1.31  |
| vDW-DF(HF)        | −0.92  | −0.88  | −1.05  | −2.23  |
| **T-shaped(1) structure** |        |        |        |        |
| MP2               | 0.04   | 0.07   | −0.15  | −0.65  |
| estd. CCSD(T)     | 0.04   | 0.07   | −0.15  | −0.63  |
| vDW-DF            | 0.00   | 0.01   | −0.18  | −0.58  |
| vDW-DF(HF)        | −0.05  | 0.14   | −0.41  | −0.97  |
| **T-shaped(2) structure** |        |        |        |        |
| MP2               | −0.06  | −0.44  | 0.29   | 0.39   |
| estd. CCSD(T)     | −0.05  | −0.33  | 0.24   | 0.42   |
| vDW-DF            | −0.13  | −0.34  | 0.05   | 0.27   |
| vDW-DF(HF)        | 0.01   | −0.42  | 0.35   | 0.55   |
FIG. 1. Models of the dimer, where we have used a CH$_3$ substituent as example in a) sandwich configuration, b) T-shaped(1) configuration, and c) T-shaped(2) configuration. The distance is measured between the centers of the rings.

FIG. 2. Results for the interaction energy $E_{\text{int}}$ as a function of the monomer separation in sandwich configuration. In the left panel, the absolute energy values are plotted over the absolute distance. In the right panel, the energy and distance are plotted with respect to the minimum energy and distance of the benzene dimer. In addition, the CCSD(T) minimum points are depicted as corresponding larger symbols.

FIG. 3. Results for the interaction energy $E_{\text{int}}$ as a function of the monomer separation in T-shaped(1) configuration. (left) The absolute energy and distance are plotted. (right) Energy and distance are given in reference to the minimum energy and distance of the benzene dimer. In addition, the CCSD(T) results are depicted.
FIG. 4. Results for the interaction energy $E_{\text{int}}$ as a function of monomer separation in T-shaped(2) configuration. (left) The absolute energy and distance are plotted. (right) Energy and distance are given in reference to the minimum energy and distance of the benzene dimer. The CCSD(T) minimum points are also depicted as corresponding symbols.

FIG. 5. Interaction energy $E_{\text{int}}$ as a function of the distance for sandwich, T-shaped(1), and T-shaped(2) configuration, where Hartree-Fock exchange was used.
T. Thonhauser et al., Fig. 2
T. Thonhauser et al., Fig. 3
T. Thonhauser et al., Fig. 4
T. Thonhauser et al., Fig. 5