

van der Waals interactions of polycyclic aromatic hydrocarbon dimers

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Density functional theory is in principle exact and includes also long-range interactions, such as the van der Waals interactions. These are, however, part of the exchange-correlation energy functional that needs to be approximated, and are absent in the local and semilocal standard implementations. Recently a density functional which includes van der Waals interactions for planar systems has been developed [Phys. Rev. Lett. **91**, 126402 (2003)], which we show can be extended to provide a treatment of planar molecules. We use this functional to calculate binding distances and energies for dimers of three of the smallest polycyclic aromatic hydrocarbons (PAHs)—naphthalene, anthracene, and pyrene. © 2005 American Institute of Physics. [DOI: 10.1063/1.1835956]

I. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are molecules that consist of fused carbon rings with the peripheral atoms terminated by covalent bonds to a hydrogen atom. In many respects they are interesting molecules. PAHs are very mutagenic and toxic,¹ and thus of interest from a biological point of view. They are exciting from a technological point of view, as they can self-assemble into stacks that possess important electronic properties, for example high conductivity.² Furthermore, it has recently been shown that some of the smallest of these molecules occur in the Red Rectangle nebula and they are thus the largest organic molecules found in space.³ No matter which of these aspects are at focus, experimental and theoretical studies are highly motivated. In particular, it is important to describe well the molecule–molecule interactions for the PAHs on the atomic level.

The internal structure of the PAH molecules is similar to that of the graphite plane. In particular, the large PAHs have bond lengths very similar to those of graphite. The dominating forces between PAH molecules are the dispersive, or van der Waals (vdW) forces, just as in the case for graphite planes. These similarities allow PAHs to be used as model systems for graphite studies, as done in a recent experimental study of the interlayer cohesive energy of graphite.⁴ There, the cohesive energy is determined by thermal desorption measurements of PAHs on a graphite surface, and reveals a binding energy of 52 ± 5 meV per carbon atom. In particular, the binding energy for a benzene molecule to the graphite surface is found to be about 500 meV, and the corresponding energy for naphthalene is 900 meV (including the hydrogen atoms).⁴

The interactions between PAHs have previously been treated by *ab initio* quantum chemistry methods with some success. For example, Ref. 5 considers interactions in the naphthalene dimer and the naphthalene–anthracene complex. However, such studies are computationally very demanding and therefore few in number. The interactions of pairs of the smallest aromatic molecule, i.e., benzene, have been much more explored.^{6–10} Even in that case, computations are labo-

rious and have not yet resulted in a complete understanding of the interactions and structure in terms of binding distances and energies.

Density functional theory (DFT) is more easily applied to systems with many atoms. However, so far DFT has mainly been successful for dense materials and molecules, including valence bonds, as the standard implementations lack the ability to include the important vdW forces. In the past few years an improved method to treat these within DFT has been developed for the case of plane–plane interactions.^{11,12} This method includes a vdW correction to the otherwise standard calculations. An estimate of the graphite interlayer distance that is comparable to this experimental value can be calculated, while the regular DFT implementations alone fail at the task.¹² As the vdW forces are expected to add a significant correction to the standard DFT results also when calculating interactions between PAH molecules, it is reasonable to try to extend this functional to also treat planar, but finite, molecules.

In this work we study the interactions within dimers of three of the smallest PAHs, naphthalene, anthracene and pyrene ($C_{10}H_8$, $C_{14}H_{10}$, and $C_{16}H_{10}$), by extending the non-local density functional method mentioned above. We mainly concentrate on dimers where the molecules are placed exactly on top of each other (AA structure), and perform calculations for a parallel-displaced (AB) structure, similar to that of graphite, for the naphthalene dimer only. We have also obtained results using the functional to treat the dimer of the benzene molecule (C_6H_6), which are presented elsewhere.¹³

II. METHOD TO INCLUDE LONG-RANGE INTERACTIONS

The interaction between two PAH molecules, when calculated by standard DFT in the generalized gradient approximation (GGA), shows the same problems as recently described for the calculation of the interaction between graphite sheets.¹² The energy profile as a function of separation distance does not have a minimum in the revPBE (Ref.

14) flavor of GGA. The PW91 (Ref. 15) flavor produces a binding, however at unphysically small binding energy and at a separation much too large. To correct this shortcoming, a density functional which includes van der Waals interactions was developed for planar systems and successfully applied to the graphite planes and few other cases of planar structures.^{11,12,16}

The functional is based on the assumption that the interacting, parallel and planar sheets are approximately translationally invariant. The charge density is laterally averaged and given by $n(z)$, where z is the direction perpendicular to the sheets. The dielectric function, here Fourier-transformed in the lateral direction, is modeled by a plasmon-pole approximation

$$\epsilon_k(z, iu) = 1 + \frac{\omega_p^2(z)}{u^2 + \nu_F^2(z)q_k^2/3 + q_k^4/4}, \quad (1)$$

where the plasmon frequency ω_p is defined by $\omega_p^2(z) = 4\pi n(z)$, the Fermi velocity is given by $\nu_F(z) = (3\pi^2 n(z))^{1/3}$, and $\omega = iu$ is the frequency. We here use atomic units. The three-dimensional wave vector for the system q_k is divided into a two-dimensional component within the plane, \mathbf{k} , and a one-dimensional component perpendicular to the plane, q_\perp , such that $q_k^2 = k^2 + q_\perp^2$. q_\perp is taken to be a constant, materials dependent parameter introduced to compensate for the locality of ϵ_k in the z -direction.

By applying a static, homogeneous electric field to one graphite plane in the direction perpendicular to the plane the effective (linear) susceptibility χ_{eff} can be computed within standard DFT. The χ_{eff} for the dielectric model (1) must correspond to this value at frequency $u=0$, and thereby a value for q_\perp is obtained. Applying the dielectric model (1) the nonlocal vdW interaction energy of two graphite sheets can be calculated from Ref. 11,

$$E_c^{\text{nl}}/A = - \lim_{L \rightarrow \infty} \int_0^\infty \frac{du}{2\pi} \int \frac{d^2k}{(2\pi)^2} \ln \frac{\phi'(0)}{\phi_0'(0)}. \quad (2)$$

Here the potential $\phi(z)$ fulfills the differential equation $(\epsilon_k \phi')' = k^2 \epsilon_k^2 \phi$ with boundary conditions $\phi(0)=0$ and $\phi(L)=0$. $\phi_0(z)$ is the vacuum solution. The system is considered enclosed in a long box of length L .

We would like to extend this functional to also include treatment of planar, but finite molecules. The PAH molecules do not quite have translational invariance, even if repeated periodically, although for very large PAHs this is a good approximation. When averaging the electron density in the plane of the molecule we must take care to only include those regions of space where the molecule is present, and exclude the vacuum regions between the periodic images of the molecules. Thus we need to find the lateral size of the molecule, A_{mol} , as experienced by the vdW forces. This was discussed in Ref. 13, and will be summarized below.

Apart from the compensation due to finite molecule sizes in the xy -directions, we keep the same general scheme as in the plane-plane case.^{12,16} This scheme is as follows. The standard implementations provide a local density approximation (LDA) or a semilocal (GGA) approximation to the exchange-correlation energy functional. When calculating

the energy in the new scheme^{12,16} we keep the exchange energy of the GGA-revPBE functional, as this functional is fitted to exact exchange.¹⁷ Then we take the local part of the correlation, which is calculated in LDA, and finally add the nonlocal correlation E_c^{nl} . The total energy by the vdW-DF method is thus given by

$$E_{\text{vdW-DF}} = E_{\text{GGA,revPBE}} - E_{\text{GGA},c} + E_{\text{LDA},c} + E_c^{\text{nl}}, \quad (3)$$

where the first term on the right-hand side is the self-consistently obtained energy using the revPBE functional. The correlation energy in GGA, $E_{\text{GGA},c}$, is substituted with the one of LDA, $E_{\text{LDA},c}$, and the new nonlocal correlation is given by the last term, E_c^{nl} . The energies obtained according to Eq. (3) will be referred to as obtained in the vdW-DF scheme. We are aware that revPBE-exchange has a tendency to be too repulsive, but it is the best approximation to exact exchange currently available to us.^{11,16}

The standard DFT calculations are performed by the plane-wave pseudo-potential based program Dacapo.¹⁸ We use a hexagonal unit cell of size (17.112 Å, 17.112 Å, 26 Å) except for pyrene where the size is (21.39 Å, 21.39 Å, 20 Å). In order to simulate infinite separation between the molecules, corresponding to very small or no intermolecular interaction, we use a large size especially in the z -direction. This is also facilitated by the short-range nature of the common DFT-implementation. The plane-wave cutoff energy value is 450 eV, for which the energies are well-converged.

III. RESULTS FOR THE PAH MOLECULES

A. In-plane structure and energies

We determined the (relaxed) structures of the isolated molecules within the GGA-revPBE approximation. As the size of the PAH molecules increases, the PAH carbon-to-carbon bond lengths converge to the one found in graphite sheets. The deviations in length in the side bonds are consistent with the trends found for large PAHs in Ref. 19, and the calculated bond lengths are in agreement with experimental data²⁰ where data exist.

We further calculated the cohesive energy, E_{coh} , for the molecules, defined as the difference in total energy of an isolated molecule E_{mol} (in revPBE) and the constituent parts of carbon and hydrogen in graphite and the hydrogen molecule:

$$E_{\text{coh}} = E_{\text{mol}} - N_C E_C^{\text{graph}} - 2N_H E_{\text{H}_2}, \quad (4)$$

where N_C (N_H) is the number of carbon (hydrogen) atoms, and E_C^{graph} and E_{H_2} are the energies for a carbon atom in an isolated graphite plane, and a H_2 -molecule, respectively. The cohesive energies are given in Table I.

B. Compensating for the finite molecule size

Although the PAH molecules are relatively extended in the xy -plane, in our DFT calculations they do not cover the plane, to avoid artificial interactions sideways. To find the laterally averaged charge density $n(z)$ we must determine the area of the molecule that is effective in the dispersive interactions, A_{mol} .¹³ Thus, we take into account that the elec-

TABLE I. The cohesive energies E_{coh} , calculated as shown in Eq. (4), and the molecule areas A_{mol} obtained by requiring that q_{\perp} equals that for a graphite sheet.

	E_{coh} [meV]	A_{mol} [\AA^2]
Naphthalene (C_{10}H_8)	205	73
Anthracene ($\text{C}_{14}\text{H}_{10}$)	91	93
Pyrene ($\text{C}_{16}\text{H}_{10}$)	77	101

tron density calculated self-consistently within DFT originates only from the region in the plane occupied by the molecule and not from the vacuum surrounding it. With a correct A_{mol} attributed to the computed electron density $n(z)$ we can obtain a correct q_{\perp} . Alternatively, by estimating q_{\perp} by some other method, we can calculate an adequate molecule area and proceed from there.

The major contributors to the molecule profile and to the electric response in the PAH molecules are the carbon atoms. We therefore use the calculations performed for graphite planes as a base, and we assume that the value of q_{\perp} found for a graphite sheet also describes the PAH molecules. As discussed in Ref. 13 the quality of this estimate increases for increasing PAH size. For the graphite planes q_{\perp} is calculated to be 0.756 a.u., which we use to calculate a corresponding molecule area A_{mol} . These areas are presented in Table I. Our calculations also show that there is little sensitivity of the results on the exact choice of A_{mol} while q_{\perp} is more important.

C. Dimer binding energies and separations

We have mainly considered PAH dimers in the AA structure, where the molecules are exactly on top of each other. These are judged to be energetically less favorable than the parallel-displaced structures and also, at least in the case of benzene and naphthalene dimers, the T-shape structures.^{5,21} Our method is not applicable for calculations of T-shaped dimers, but applies to cases where the aromatic rings in the dimer molecules are parallel. However, as the T-shaped structure goes from being nearly isoenergetic with the parallel-displaced one for the benzene dimer⁵ to being less favorable for the naphthalene dimer,²¹ we conclude that the parallel-displaced structures are more relevant than the T-shaped ones also for the anthracene and pyrene dimers. In fact, for large PAHs it is expected that the most stable structure is one of the parallel-displaced ones, namely the AB structure, which is known to be favored by graphite. In this work we concentrate mainly on the AA structure (inset in Fig. 1), because our method of lateral density averaging is more accurate if the centers of the molecules are directly on top of each other, but in principle it is a reasonable approximation also for small deviations of the positions. Further, determining the exact position of an AB-dimer is not trivial in our scheme, as will be discussed later.

The dimer interactions are calculated by locking the atoms of the dimer molecules into their position in an isolated molecule and varying the distance between the molecules, keeping the cell size. The total corrected energy for each system is computed according to Eq. (3) for each separation

TABLE II. Calculated binding distances and energies for the studied dimers. The dimer structure (AA or AB) is given in parenthesis. d_{ref} is the separation distance used as a reference for “far apart” molecules. Next, we report the binding energies and distances calculated with the PW91 functional (no binding at all observed with revPBE). Right two columns: Binding energies and distances calculated in our vdW-DF scheme.

	d_{ref} [\AA]	PW91		vdW-DF	
		E_b [meV]	d_b [\AA]	E_b [meV]	d_b [\AA]
Naphthalene (AA)	12	30	4.5	172	4.1
Anthracene (AA)	12	30	4.7	245	4.1
Pyrene (AA)	9.5	34	4.7	282	4.1
Naphthalene (AB)	13	30	4.2	247	3.7

distance. By subtracting a reference energy due to the molecules themselves, we obtain a corrected total-energy curve, which gives the binding distance and energy for the PAH dimers. For the reference energy we use a dimer calculation where the molecules are separated by a large distance, d_{ref} . The actual values of d_{ref} used are given in Table II.

We expect a positive binding energy, since PAHs easily self-assemble. As a background we outline results for the graphite system. The interlayer distance for the AB stacking in bulk graphite has been experimentally measured to be 3.35 \AA .²² The binding distance between two graphite sheets in the AB structure, calculated in the same vdW-DF scheme by Ref. 16 is 3.76 \AA , corresponding to the binding energy 24 meV/atom (which is compared to the experimental 34 ± 10 meV/atom from studies of collapsed carbon nanotubes). In similar calculations we have found a binding separation of 4.0 \AA and a binding energy of around 10 meV/atom for two graphite sheets in the AA structure.¹³ We expect the binding distance between the PAHs in the AB structure to be larger than that found for graphite sheets, due to the fewer interacting carbon atoms. We expect it to be larger still in the cases of AA-stacking compared to AB-stacking.

Figure 1 shows the total-energy curves for the studied PAH dimers in the AA structure, calculated for the molecule areas in Table I. For comparison, we also present results for the benzene dimer obtained in the same manner.¹³ Table II presents the binding distances and energies calculated in this fashion and also the ones obtained by the pure PW91-functional (the pure revPBE-functional does not result in any binding). As reported in Ref. 16, the PW91-functional provides unphysical binding distances and energies for the interactions between graphite planes. As seen here, also for our systems the PW91 potential gives much smaller binding energies and larger binding separations.

As expected, the binding distances found in our scheme are slightly larger than the distance between two graphite sheets in the AA stacking calculated in the same scheme, 4.0 \AA .¹³ Further, the binding distances for the PAHs are expected to converge to this value for larger PAHs. In our case all three studied dimers in the AA structure have the binding distance 4.1 \AA , with a weak tendency of decreasing this distance for increased PAH size. The results for the binding energies are in agreement with other calculations, as will be discussed below. Comparing the number of carbon atoms in the molecules, it is reasonable to expect that the binding

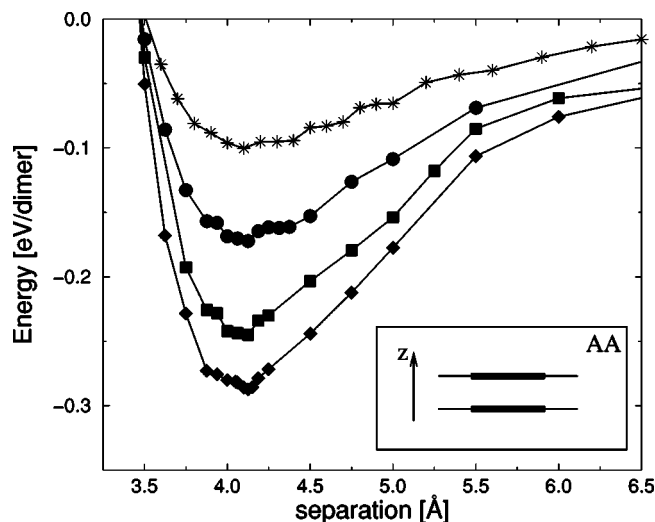


FIG. 1. Binding energy curves for the PAH dimers in the AA stacking: naphthalene (circles), anthracene (squares), and pyrene (diamonds), compared to a similar curve for the benzene dimer (stars) (Ref. 13). The zero point of the binding energy is taken to be the dimer interaction at separation d_{ref} , as found in Table II. The inset illustrates the geometry of the dimer, seen from the side.

energy of naphthalene is less than twice that of benzene, that of anthracene less than three times that of benzene, etc., which is what we find.

When studying the PAH dimer interactions in this work, we mainly concentrate on the AA structure. In principle other parallel types of stacking, as for instance the AB stacking similar to that of graphite can also be considered. However, it is not trivial to calculate the exact position of the small PAH molecules in an AB dimer, since the intramolecular bond lengths are not as symmetrical as in the graphite sheet, but are slightly distorted. In our case, we place the top molecule in such a way that a carbon atom is placed over the top of the geometrical center of the aromatic ring of the bottom molecule, as is the case in graphite AB stacking. In order to find the energetically most favorable position, one would ultimately need to be able to relax the positions of the atoms in the molecules with respect to both types of interactions, those already incorporated in the standard DFT implementations, and the weaker dispersive interactions from our correction. This is presently not implemented, but we can choose an approximate position based on symmetry and intuition. Relaxation of atomic positions without taking non-local correlations into account might not give physically sound results.

We perform such AB stacking calculations for the naphthalene dimer. The position of the dimer is approximated as shown in the schematic picture in the inset of Fig. 2 (the results are not very sensitive to this exact position). The same figure also shows the resulting energy curves, while the actual binding distances and energies are reported in Table II along with the results for the AA stacking. As evident from Fig. 2 and Table II the AB stacking gives a larger binding energy at a smaller binding distance than the AA stacking, supporting the idea of it being the more favorable structure, as is also the case for graphite sheets.

We can compare our results to recent CCSD(T) calcula-

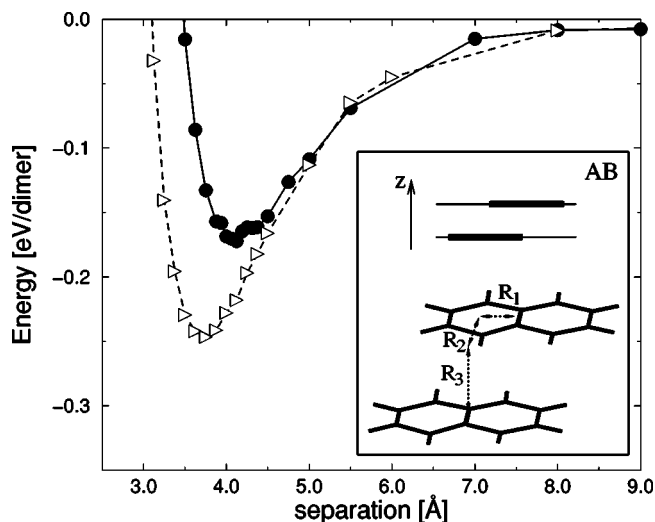


FIG. 2. Binding energy curves of a naphthalene dimer in the AA structure (circles), and in the AB structure (triangles). The inset shows a schematic picture of the AB structure. The position of the top molecule in the x - and y -directions is chosen to be such that the position of the carbon atoms resembles closely their positions in an AB-structure graphite, i.e., two of the carbon atoms of the top molecule are placed above the geometrical centers of the two aromatic rings of the bottom molecule. This leads to the in-plane displacements $R_1=1.2$ Å and $R_2=0.7$ Å. As shown by the total-energy curve, the optimum vertical separation for naphthalene in this structure is found at $R_3=3.7$ Å.

tions of the interaction energies of the benzene dimers and naphthalene dimers (AA and AB structures). The binding energy of 100 meV for the benzene dimer found at the separation of 4.1 Å in our scheme is discussed in detail in Ref. 13 and is in agreement with reported energies of 64–92 meV/dimer.^{7–9} However, these correspond to a binding distance which is somewhat smaller, 3.8 Å. The results for the naphthalene dimers (AA and AB structures) may be compared to the results of Ref. 21. Our AA structure is the same as their “sandwich”-structure, and we find a binding energy 172 meV/dimer compared to their 164 meV/dimer. Again, the distance found is larger in our case, 4.1 Å compared to their 3.8 Å.

Our AB structure corresponds approximately to the “slipped-parallel”-structure in Ref. 21. Our calculations are performed for a slightly different displacement of the top dimer in the x - and y -directions. As described in the inset in Fig. 2, we have $R_1=1.2$ Å and $R_2=0.7$ Å, while Ref. 21 found the optimum binding for $R_1=1.4$ Å and $R_2=1.0$ Å. Our values are as close as possible to the “ideal” AB case where the carbons of the two dimers arrange themselves in the same fashion as the carbon atoms in the AB graphite. As mentioned earlier and also found in Ref. 21, the exact values of R_1 and R_2 are not important, as the interaction potential is very shallow with regards to these in-plane displacements, while it depends substantially on the displacement in the vertical direction. For the optimum vertical separation, R_3 , we find the value of 3.7 Å which is slightly larger than the 3.5 Å reported by Ref. 21. The binding energy is in excellent agreement (247 meV/dimer compared to 248 meV/dimer in Ref. 21). Other calculations referred to in Ref. 21 were in the range 162–463 meV/dimer.

Further comparison can be made with the experimental study of the interlayer cohesive energy of graphite in Ref. 4, where PAH molecules on graphite are used. The binding energy for a benzene molecule on a graphite surface is found to be about 500 meV, and the corresponding energy for naphthalene is 900 meV. It can be assumed that the benzene and naphthalene molecules place themselves in a structure similar to the AB parallel-displaced one. Further, the binding energy of PAH to a graphite plane is expected to be larger than the binding energy of a corresponding PAH dimer. Our 247 meV/dimer for naphthalene in the AB structure differs from the measured 900 meV by a factor of 3.6, which we judge is somewhat too large an effect to be assigned to the difference described above. However, the value measured in Ref. 4 for benzene is also rather large, nearly five times larger than some of the reported binding energies for parallel-displaced benzene dimers, for instance 107 meV/dimer in Ref. 7. Thus we believe that other effects than those treated in our study influence the results of Ref. 4.

In summary, our results for the binding energies of AA and AB dimers of naphthalene, and AA dimers of anthracene and pyrene seem reasonable. In the case of the naphthalene dimers a comparison to other theoretical studies is possible and produces a very good agreement. The binding distances we find are slightly larger than those reported in other theoretical studies. There are so far very few theoretical works that treat complexes of large PAHs. Direct comparison with experiments is difficult, especially as we have concentrated on the AA structure which is not the most energetically favorable structure. However we have been able to relate our work to results of thermal desorption measurements of PAHs on graphite.

IV. CONCLUSION AND OUTLOOK

We have shown that it is possible to apply a recently developed density functional, which includes van der Waals interactions for planar systems, to also give an approximate treatment of dimers of planar PAH molecules. We have used this functional to calculate binding distances and energies for dimers of several of the smallest polycyclic aromatic hydrocarbons (PAHs)—naphthalene, anthracene, and pyrene, and obtained results consistent with other studies. The results indicate great promise for the vdW-DF method to sparse systems.

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