A van der Waals density functional study of adenine on graphene: single-molecular adsorption and overlayer binding

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Abstract
The adsorption of an adenine molecule on graphene is studied using a first-principles van der Waals functional, vdw-DF (Dion et al 2004 Phys. Rev. Lett. 92 246401). The cohesive energy of an ordered adenine overlayer is also estimated. For the adsorption of a single molecule, we determine the optimal binding configuration and adsorption energy by translating and rotating the molecule. The adsorption energy for a single molecule of adenine is found to be 711 meV, which is close to the calculated adsorption energy of the similarly sized naphthalene. On the basis of the single-molecular binding configuration, we estimate the cohesive energy of a two-dimensional ordered overlayer. We find a significantly stronger binding energy for the ordered overlayer than for single-molecule adsorption.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Physisorption of small biomolecules on inert surfaces acts as a laboratory of molecular interactions and is an excellent starting point for addressing molecular recognition and self-organization processes. By studying these systems we gain insight into the delicate balance between intermolecular forces that contribute to supramolecular binding, for example, the unique identification of antigens and their binding sites in our biochemistry.

It is natural to begin an investigation of molecular interactions and organization by focusing on key building blocks, like the nucleic acids or the amino acids. Three-dimensional biopolymer systems, like the DNA double helix or proteins, permit folding of an extreme complexity that limits direct access to most of the structure, and direct experimental probing of the atomic-scale organization is difficult. Theoretical modeling must therefore map out interactions and organization not only between primary but also secondary and higher order structure in the absence of any calibration with experiments. In contrast, trapping nucleobases on inert surfaces not only simplifies the possibilities for structural reorganizations but also makes the molecular interactions accessible to direct characterization through advanced atomic-scale experiments.

Adenine is one of the nucleobases of DNA. The molecule has been investigated in numerous sophisticated surface experiments that have characterized both the physisorption and self-organization or overlayer formation on inert substrates, ranging from the insulating MoS₂ [1] over the semi-metallic graphite [1–5] to surfaces of noble metals like Cu and Ag [6, 7]. The experimental characterization includes thermal desorption spectroscopy (TDS) [5] for a direct measurement of the physisorption energy, and scanning tunneling microscopy [1–4], atomic force microscopy [3], and low-energy electron diffraction [4] for explicit identification of the adenine assembly into regular overlayers.
Here we apply density functional theory calculations (DFT) with a fully nonlocal density functional method, vdW-DF [8, 9], that provides a first-principle account of dispersive or van der Waals (vdW) forces. The method permits a parameter-free description of a broad spectrum of sparse matter [10]: materials which have regions with voids in the electron distributions, such as molecular systems. Unlike the semi-empirical DFT-D methods, it does not involve an arbitrariness in the construction of a damping function. The vdW-DF method has previously been used to describe binding in a large range of material systems, for example dimers of benzene [9, 11], nucleobases [12, 13], polymers [14], nanotubes [15], simple oxides [16], and molecular crystals [17, 18] systems. It has furthermore been used to characterize the physisorption of organic molecules on coinage metals (Au, Ag, Cu) [19–23], on MoS2 [24], on Si [25], on alumina [26], and on graphene [26, 27]. In short, it is a versatile method.

By comparing directly with experimental measurements the vdW-DF method has been documented to provide good results for benzene and naphthalene on graphene [27, 28]. This suggests that vdW-DF should provide a good description of the adenine physisorption. The simple form of the nonlocal interactions leading to the formation of a two-dimensional overlayer crystal. These results can be directly compared with experiments. For an adenine molecule on graphene we find here an adsorption energy of 711 meV at an equilibrium separation of 3.5 Å, whereas the adenine molecules adsorb with the energy 1006 meV/molecule in the overlayer crystal in very good agreement with experiment [5].

In the following, section 2 describes how we use the vdW-DF method for the present adsorbate system. In section 3 we discuss the framework of the method in relation to some other methods used for this system, and in section 4 we present and discuss our results for the configuration and binding of the single adenine adsorbate and an estimate of the binding energy of adenine in the overlayer. Section 5 contains our conclusions.

2. Computational method

We use the first-principles vdW-DF method within DFT [8], calculating the vdW-DF energies in a post-GGA procedure similar to previous studies [11, 16, 21, 26, 27, 29]. We calculate the vdW-DF total energy, \( E^{\text{vdW–DF}} \), for a number of positions of the adenine molecule above graphene, as described in section 4. For each position, a self-consistent GGA (sc-GGA) calculation is carried out, from which the GGA-based total energy \( E^{\text{GGA}} \) and the sc-GGA electron density \( n \) are obtained. In a post-processing phase, we use \( n \) to evaluate long-range correlation contributions that arise from the vdW interactions, \( E^{\text{nl}} \) and then in a systematic way combine the sc-GGA results and the nonlocal results to obtain \( E^{\text{vdW–DF}} \). This procedure is described below and is further detailed in several other publications [11, 27, 29].

For the sc-GGA calculations we utilize the plane-wave code DACAPO [30] with the PBE exchange–correlation [31]. We use ultrasoft pseudopotentials, a 2x2x1 sampling of the Brillouin zone in the Monkhorst–Pack scheme, a wavefunction energy cutoff at 500 eV, and a fast Fourier transform (FFT) grid with a maximum of 0.15 Å between nearest-neighbor gridpoints.

The correlation part of the energy in \( E^{\text{vdW–DF}} \) can be split into a nearly local part \( E_0 \) and a part that includes the most nonlocal interactions \( E^{\text{nl}}_c \),

\[
E_c = E_0 + E^{\text{nl}}_c. \tag{1}
\]

The nearly local part is approximated by the correlation of the local density approximation (LDA) \( E^{\text{LDA}}_c \), and the nonlocal correlation functional is given by the integral

\[
E^{\text{nl}}_c[n] = \frac{1}{2} \int n(r)\phi(r)r' \phi(r')n(r'). \tag{2}
\]

Reference [8] contains the explicit form of the kernel \( \phi \). The vdW-DF total energy can thus be written as the sum 

\[
E^{\text{vdW–DF}} = E_0 + E^{\text{nl}}_c \quad \text{where the } E_0 \text{ term includes kinetic and electrostatic terms in addition to GGA exchange and LDA correlation:}
\]

\[
E_0 = E^{\text{GGA}}_\text{tot} - (E^{\text{GGA}}_c - E^{\text{LDA}}_c). \tag{3}
\]

This splits off the nonlocal part of the calculation, that needs a slightly different treatment than the nearly local term \( E_0 \).

As in recent applications [11, 14, 17, 29] of vdW-DF we use the revPBE [32] GGA exchange in the post-processing phase. From the total energy of the sc-GGA calculations we therefore subtract the PBE exchange energy and instead add the revPBE exchange energy. The revPBE exchange energy is calculated from the charge density \( n \) that is provided by the sc-GGA calculations. The revPBE exchange functional is known to be overly repulsive in the binding region [8]. For a range of systems, vdW-DF with revPBE exchange provides good values for the binding energy and quite good, but consistently overestimated binding separations. The development of an exchange functional companion to the nonlocal correlation of vdW-DF is an active research field showing promising results [16, 33–35, 37].

The adsorption energy is given by the difference between \( E^{\text{vdW–DF}} \) for the optimal configuration and for a reference system corresponding to isolated fragments (molecules). Since intra-molecular and intra-sheet contributions dominate \( E^{\text{vdW–DF}} \) we must use the same numerical approximations in the two calculations. To conveniently cancel parameter-sensitive contributions, the reference calculation for the sc-GGA part is done in a manner different from the nonlocal correlation part. The difference in total energy \( E^{\text{vdW–DF}} \) of the adsorbate system compared to that of separated fragments, the cohesive energy \( E_c \), is thus the sum of two terms

\[
E = \Delta^0 E_0 + \Delta^{\text{nl}} E^{\text{nl}}_c \tag{4}
\]

where the \( \Delta^0 \) and \( \Delta^{\text{nl}} \) denote the use of two different sets of reference calculations. At the optimal position of the adenine on graphene (figures 1 and 2) the binding energy \( E_b \) is found

5 Local in correlation.
Figure 1. The molecular configuration of adenine on graphene as determined in our vdW-DF study. Dark (blue) circles are N atoms, medium gray (brown) circles are C atoms, and the small white circles are H atoms. The light-colored background illustrates the underlying graphene.

2.1. Reference calculations for the sc-GGA part

For the calculations of the single adenine molecule adsorbed on graphene the reference sc-GGA calculation uses the same unit cell as the adsorbate system, but in a configuration where the adenine molecule is lifted 9 Å away from the graphene sheet:

$$\Delta^0 E^0 = E^0 - E^0_{\text{ref}}$$

(5)

where $E^0_{\text{ref}}$ is the reference calculation. This distance of 9 Å is fully sufficient for the GGA calculations which only include interactions acting at a much smaller distance. By using the same unit cell for the reference calculation as for the full calculation, we cancel a small spurious contribution from the regions of very low electron density in the sc-GGA calculation [11, 16, 36, 37].

In the calculations for the overlayer of adenine on graphene the contributions to $\Delta^0 E^0$ are obtained in three steps, as indicated in figure 3. In each step, the reference calculation uses the same unit cell as the full calculation. First, the adenine overlayer crystal (o), shown in figure 2 and sketched in figure 3(a), is lifted off as an intact sheet (s) from the sheet of graphene to a distance 9 Å above graphene (figure 3(b)). We denote the energy cost per molecule of this process by $\Delta^0 E^0_{o-s}$. Then the sheet of the adenine crystal is split into ribbons (r) of width one adenine molecule (figure 3(c)), with energy cost $\Delta^0 E^0_{s-r}$ per molecule, and finally the ribbons are disassembled into individual molecules (m), $\Delta^0 E^0_{r-m}$ (figure 3(d)). In total, the contribution to the overlayer cohesion energy per adenine molecule is

$$\Delta^0 E^0 = \Delta^0 E^0_{o-s} + \Delta^0 E^0_{s-r} + \Delta^0 E^0_{r-m}.$$  

(6)

The quantity $\Delta^0 E^0$ could also have been obtained by simply taking all five fragments (graphene and four adenine molecules) far apart within the unit cell, but this would require an unreasonably large unit cell, both for the GGA reference calculations and all other GGA calculations of the molecule overlayer on graphene.

2.2. Reference calculations for the nonlocal part

Our implementation of (2) is sensitive to the choice of grid on which the charge density is described. To avoid adverse effects of this sensitivity we use a charge density grid with a volume per grid point smaller than $(0.15 \, \text{Å})^3$ in all our DACAPO calculations. Further, for every adsorbed adenine configuration we carry out a separate reference calculation of the isolated molecule where the molecule is locally placed in the same position relative to the charge density grid. A similar reference calculation for graphene is carried out once, since this sheet is kept fixed. The contribution of the nonlocal correlation to the adsorption energy is thus

$$\Delta^{\text{nl}} E^{\text{c}} = E^{\text{c, system}} - E^{\text{c, adenine}} - E^{\text{c, graphene}},$$

(7)

with obvious definitions of terms.

Figure 2. A two-dimensional adenine crystal on graphene: the configuration used in our estimate of the binding energy. There are four molecules in the rectangular unit cell. Same color coding of atoms as used in figure 1.
molecules in order to calculate adsorbed adenine molecules (black) in a two-dimensional crystal on graphene (medium gray/brown). (b) Lifting off the sheet of adenine supercell of $7 \times 7$ graphene unit cells (containing a total of 98 graphene carbon atoms) in the plane of the sheet makes the inter-adsorbate interactions negligible (less than 0.5 meV) even for the evaluation of the nonlocal correlation. With this unit cell, the minimum distance between any two atoms on two different adenine molecules is larger than 10 Å.

In the evaluation of $E^\text{nl}$ from (2) the electron density from several neighboring supercells within the plane may be included, in order to capture the full extent of the adenine–graphene interaction. Based on the decay of vdW forces at large separations, we can efficiently evaluate $E^\text{nl}$ by introducing two radius cutoffs $|\mathbf{r} - \mathbf{r}'| < R_1$. Around a given point in space, a full grid sampling is used for the $E^\text{nl}$ evaluation in the volume within the smallest radius, while the volume outside the smallest, but within the largest radius, is evaluated using a sampling of half the grid points in all directions. Use of $R_1 = 6.0$ Å and $R_2 = 23.0$ Å converges the contribution to the binding energy to sub-meV. Details of the implementation are given in [18].

3. Other computational methods

To describe the adsorption of adenine on graphene, an organic molecule interacting with a chemically inert surface, it is imperative that the vdW forces are well described. The vdW-DF is a first-principles DFT method, relieving some of the short-comings of previous (semi-)local approximations of the exchange–correlation term $E^\text{xc}$ in DFT, such as the GGA approximation. It combines the excellent description of short-range interactions already present in GGA with good descriptions of the longer-ranged vdW interactions (including systems where the binding equilibrium configuration has a range of distances over which the vdW interaction acts).

The vdW force originates primarily from the most loosely bound electrons, which for molecular monomers are in states modified by chemical bonding. It is not directed through nuclear centers, as assumed by some semi-empirical methods. In the vdW-DF method the vdW interaction is correctly described as an effect originating in the tails of the electron distribution, and it is well suited to include effects of image planes [17].

In recent years the system of adenine on graphene or graphite has also been studied by other methods. One of them, which has become very popular for van der Waals systems, is a hybrid method that uses a force field between the nuclei to calculate the dispersion energy and forces, coupled with standard DFT for the other forces, including Pauli repulsion and electrostatic interactions. It has been used by the authors of [38, 39] to study adenine on graphene. Methods similar to that have been widely used [40–48]. The force fields used have typically been heavily parametrized empirically, although less so in the most recent forms. For example, a very recent semi-empirical version appears to provide numerically good results [48].

Reference [49] is another recent study addressing the adsorption of nucleobases on graphene. They use
Hartree–Fock (HF) calculations coupled with Møller–Plesset perturbation theory (MP2), in addition to LDA-based\(^6\) DFT. The approach of HF with MP2 is obviously accurate if the (in principle infinite) sheet of graphene is represented by a sufficiently large flake of graphene, but the approach is then also very expensive. Thus, to keep the computational expense down often rather small graphene flakes are used. The graphene flakes, terminated by hydrogen atoms, are polycyclic aromatic hydrocarbon (PAH) molecules. In section 4 we discuss the effect of mimicking the graphite substrate by PAH molecules of insufficient extension.

Results of the above studies are mentioned in and compared to our vdW-DF results in section 4.

\(^6\) LDA-based DFT cannot be used as a substitute for the inclusion of vdW interactions. As pointed out by Harris already in 1985 [50] ‘LDA predicts attraction between all systems at large separation mainly because it assigns an unphysically long range to exchange interactions and not because, in any sense, it simulates van der Waals interactions’. This issue is summarized and discussed also in [33]. In some flat systems the numerical results predicted by LDA happen to end up in the range of the physical results for these unphysical reasons, whereas in other geometries the LDA gives results that are not in accordance with experiment nor with more accurate methods [14, 51, 52].

### Table 1. Single-adenine-molecule adsorption, the values of the energy terms and distance \(d\) at the optimal vdW-DF binding position, the binding energy \(E_b\), and the minima of the revPBE and PBE GGA calculations.

| Term                     | \(d (\text{Å})\) | \(E (\text{meV})\) |
|--------------------------|------------------|-------------------|
| \(\Delta^0 E^0\)       | 420              |
| \(\Delta^9 E^9\)       | 1131             |
| \(E = \Delta^0 E^0 + \Delta^9 E^9\) | 3.5 | -711  |
| \(E_b\) (single molecule) | 711 meV        |
| \(\Delta^0 E_{\text{GGA}}^{\text{tot}}\) with revPBE GGA | 5.0 | -11   |
| \(\Delta^0 E_{\text{GGA}}^{\text{tot}}\) with PBE GGA | 4.0 | -45   |

### 4. Results and discussions

The optimal molecular configuration of adenine adsorbate is determined by first placing the molecule relative to the sheet of graphene in a configuration that resembles AB stacking of graphite. Next, we calculate the optimal distance to the graphene sheet. Then we rotate and translate the molecule in the plane until optimal in-plane positions are found, within the accuracy of the method. We here only consider positions with the adenine molecule parallel to the plane of graphene.

#### 4.1. Single-molecule adsorption

Using the updated in-plane configuration, shown in figure 1, we determine the cohesive energy curve \(E(d)\) as a function of the distance to the surface in the direction perpendicular to the surface, \(d\) (figure 4). We find that the molecule binds at \(d = 3.5\) Å above graphene, with a binding energy \(E_b = 711\) meV. The exchange part of revPBE is overly repulsive [8] at this distance and thus we expect our value for the binding energy to be somewhat too small. For naphthalene, an aromatic molecule with approximately the same number of electrons as adenine, [27] reports a binding energy of 763 meV, using the same vdW-DF method and choice of exchange functional as used here. In contrast, as shown in table 1 for adenine and in [27] for naphthalene, pure GGA functionals such as revPBE or PBE bind at unphysically large binding distances (4–5 Å) at unphysically low binding energies (<50 meV).

For the single adenine molecule, rotation around the hexagon shows little variation in energy (inset of figure 4). Roughly 90% of this small variation originates from the \(E_0\) part of the total energy. This confirms that the directional dependence of the vdW interaction is small.

The vertical vibrational states of the adenine molecule adsorbed on graphene may be estimated by solving the one-dimensional Schrödinger equation for the cohesive energy potential shown in figure 4. We find that the ground state energy when including zero-point vibrations is \(-707.6\) meV (up from the result \(-711\) meV without zero-point vibrations) and the first and second excited states are found at \(-700.7\) and \(-693.9\) meV. This spectrum of lowest lying states closely resembles that of a harmonic oscillator at frequency around 6.8–6.9 meV.

The wavefunctions of the three lowest vibrational states are illustrated in the bottom panel of figure 4, offset with their vibrational energies. The spatial extension of these lowest...
vibrational state wavefunctions is about 0.3 Å. In combination with the small energy changes for lateral motion (illustrated also by the effect of rotational displacement of adenine, shown in the inset of figure 4) we conclude that the precise position of the adenine molecule on graphene has very little bearing on the binding energy.

In this work and most of the work cited here only the interaction from one graphite layer, graphene, is included. If the molecules adsorb at a (multilayer) graphite surface the layers below the top graphite layer also contribute to the interaction, but the contribution has previously been shown to be at a very low level (3%, as discussed in [27]). We therefore ignore multilayer effects here.

Other groups have studied the adsorption of single molecules on graphene using other theory methods. Using DFT-D methods, Ortmann et al [38] found a binding energy of 1.01 eV, and a separation of 3.4 Å while more recently Antony et al [39] found binding at 0.91 eV and 3.0 Å. Both results are for single molecules adsorbed on graphene. Unlike the above-mentioned and the present study, the MP2 calculations of Gowtham et al [49] use an adenine molecule with a methyl group attached. They find a binding energy 0.94 eV and separation 3.5 Å.

4.2. Graphene size convergence test study

We use calculations of the long-range correlation contribution, $\Delta E_{nl}^{\alpha}$, to estimate the effect of using small PAH molecules as substitutes for graphene in the MP2 calculations of [49] and other similar studies. We perform a number of crude but generous test calculations. The tests are available directly from the vdw-DF method simply by restricting the cutoff radii $R_1$ and $R_2$ in the $\Delta E_{nl}^{\alpha}$ calculations by the value $R_{cut}$.

Figure 5 illustrates the convergence of $\Delta E_{nl}^{\alpha}$ with $R_{cut}$. The value of $R_{cut}$ sets the amount of interactions with graphene included. Figure 5 shows that for $R_{cut}$ $\approx$ 9 Å about 1% of the interaction is discarded. In the production runs we find that at more than 6 Å distance between interacting points only every second grid point in each direction needs to be included, which is reflected in our choice of $R_1 = 6$ Å and $R_2 = 23$ Å.

For our convergence tests we further do not include any pairs of points in space $r$ and $r'$ that have $|r - r'| > R_{cut}$. The value $R_{cut} = 9$ Å corresponds approximately to the use of a 96 C atom PAH molecule as a representant for the sheet of graphene, for which we therefore predict that ~1% of the interaction (compared to graphene) is lost.

For smaller $R_{cut}$ the convergence is much worse, as illustrated in the inset of figure 5. If we include only a radius of 4 Å, corresponding approximately to the inclusion of 24–30 C atoms of graphene in the $\Delta E_{nl}^{\alpha}$ calculation (2) we loose 21% of the interaction contribution. We therefore estimate that the use of a 28 C atom PAH molecule in [49] misses an important part of the long-range interaction compared to the use of graphite or a larger size of PAH molecule.

Our convergence tests are not fully equivalent to using PAH molecules to model graphene, such as done in the MP2 calculations. This is because for this $E_{nl}^{\alpha}$ calculation any point on the adenine molecule is paired with all grid points at a distance less than $R_{cut}$, even those outside the volume covered by a PAH model substitute. At a specified cutoff radius $R_{cut}$ this test is therefore more generous than a similar calculation using a PAH molecule having roughly the radius $R_{cut}$.

Another test of the effect of using small PAH molecules instead of graphene as a substrate is reported in [39], using actual PAH molecules but an empirical dispersion term (via DFT-D). There, similar results were found: reducing the size of the PAH molecule from 150 C atoms to 24 C atoms caused a loss of 24% of the dispersion interaction (from $-32.9$ to $-24.9$ kcal mol$^{-1}$ for adenine). The use of a 150 C atom PAH molecule roughly corresponds to the value 11 Å of our cutoff radius $R_{cut}$, where we find very little (~0.4%) loss of interaction compared to a converged size (figure 5).

4.3. Adenine overlayer

Some molecular adsorbates, such as adenine molecules [3, 4], can spontaneously form an ordered lattice on a graphite surface. Here we present an estimate of the formation energy of the two-dimensional adenine crystal. This calculation illustrates the potential of the vdw-DF method to discern the different phases of adsorbate crystals and can therefore lend credibility to interpretations of scanning tunneling microscopy images.

Figure 2 shows the molecular position on graphene for the two-dimensional adsorbate crystal. The crystal symmetry is chosen to be the same as that determined with the force-field calculations in [4], but with the molecules each in a configuration relative to graphene that is identical to our single-adsorbate result.

In the process of calculating the cohesive energy $E$ (the difference between the adenine overlayer on graphene and the adenine molecules all lifted off individually) a number of partial energy terms are calculated, corresponding to the terms illustrated in figure 3. These partial energy terms are provided in table 2.
We determine the binding energy of the adenine overlayer to be 1006 meV/molecule, which is larger than that of a single, adsorbed adenine molecule. The energetic gain of the system when single, adsorbed molecules are moved together to form an overlayer crystal (the overlayer formation energy), is found to be 295 meV/molecule in our not fully optimized overlayer crystal structure. This result shows that a two-dimensional ordered crystal structure is energetically much more preferred than isolated molecules on the surface, in agreement with experimental findings showing spontaneous formation of the adenine crystal overlayers [3, 4]. Using TDS the binding energy of adenine clusters on graphene has been measured to be 23.2 kcal mol$^{-1}$ (1006 meV/molecule) [5], in very good agreement with our results for the crystal overlayer.

The value of the overlayer formation energy may be compared to the energy gained by creating a free-floating two-dimensional adenine crystal (with the same structure as the overlayer) from isolated molecules, $E_b$(free-floating crystal) = 239 meV/molecule. The gain of assembling the crystal on graphene (295 meV/molecule) instead of away from graphene (239 meV/molecule) is a mere 56 meV/molecule, not insignificant but clearly smaller than the effect of the mutual binding of the adenine molecules. Of course, if the free-floating adenine molecules were allowed to assemble in the most optimal structure, the molecules would stack and the gain in binding energy would increase to about 300 meV/molecule, depending on the details [12].

### 5. Conclusions

We use the first-principles vdW-DF method to study the adsorption of adenine on graphene. We find that the adenine molecule is physisorbed at a distance 3.5 Å above graphene. We also find that the physisorption well is shallow and therefore small changes in position (all directions and rotations) lead to only small changes in adsorption energy; the molecule is mobile.

Our calculations show an adsorption energy of 711 meV/molecule for adenine molecules far apart on the surface, whereas molecules forming a two-dimensional overlayer cluster gain significantly more: 1006 meV/molecule, both situations compared to molecules floating off as a dilute gas.

The small barriers for changing the position, mentioned above, along with this 295 meV/molecule gain per molecule for moving molecules closer together, is consistent with the tendency of adenine on graphite to assemble into clusters of two-dimensional overlayers. We find that although it is more favorable for the adenine molecules to form the overlayer crystal at graphene, the largest part of the energy gain, about 239 meV/molecule, is also obtained in the (unphysical) situation of the adenine molecules being moved together into the same positions but without having graphite nearby. The role of a graphite surface in forming clusters therefore seems to be mainly to attract the molecules and orient them (flat on the surface) before assembly into cluster, rather than contributing any major part to the cluster formation energy.

In a crude estimate of the effect of using small PAH molecules to model the graphite surface we found that an important part of the long-ranged correlation effects are lost in such models. If a PAH molecule is used to model graphite, it must be significantly larger than the adsorbed molecule: in the case of adenine we estimate that a 96 C atom PAH molecule is the smallest acceptable, and for full convergence an even larger PAH molecule should be used. For comparison, a 96 C atom PAH molecule has the approximate radius 9 Å and the adenine radius is approximately 2.5 Å.

In summary, we find adsorption energies of adenine on graphene using vdW-DF. The energies are calculated both for single adenine molecules on graphene and a two-dimensional crystal overlayer of adenine on graphene. The adsorption energy is highest per molecule for the overlayer compared to single-molecular adsorption, in agreement with the tendency to cluster formation seen in experiment.

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