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Physisorption of nucleobases on graphene: a comparative van der Waals study

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Abstract

The physisorption of the nucleobases adenine (A), cytosine (C), guanine (G), thymine (T), and uracil (U) on graphene is studied using several variants of the density functional theory (DFT): the generalized gradient approximation with the inclusion of van der Waals interaction (vdW) based on the TS approach (Tkatchenko and Scheffer 2009 *Phys. Rev. Lett.* **102** 073005) and our simplified version of this approach (here called sTS), the van der Waals density functional vdW-DF (Dion *et al* 2004 *Phys. Rev. Lett.* **92** 246401) and vdW-DF2 (Lee *et al* 2010 *Phys. Rev. B* **82** 081101), and DFT-D2 (Grimme 2006 *J. Comput. Chem.* **27** 1787) and DFT-D3 (Grimme *et al* 2010 *J. Chem. Phys.* **132** 154104) methods. The binding energies of nucleobases on graphene are found to be in the following order: $G > A > T > C > U$ within TS, sTS, vdW-DF, and DFT-D2, and in the following order: $G > A > T \sim C > U$ within DFT-D3 and vdW-DF2. The binding separations are found to be different within different methods and in the following order: $DFT-D2 < TS < DFT-D3 \sim vdW-DF2 < vdW-DF$. We also comment on the efficiency of combining the DFT-D approach and vdW-DF to study systems with van der Waals interactions.

(Some figures may appear in colour only in the online journal)

1. Introduction

In general, density functional theory (DFT), whether with the local density approximation (LDA) or with a generalized gradient approximation (GGA), is not expected to provide an accurate description of the van der Waals (vdW) interactions, owing to the built-in locality of their exchange–correlation functionals. One of the current challenges is to accurately account for the van der Waals forces (London dispersion forces) in DFT simulations [1].

Over the years, many schemes have been proposed for incorporating vdW interactions into DFT calculations. The vdW density functional (vdW-DF), proposed by Dion *et al*, takes the vdW interactions into account in a seamless manner [2]. More recently, a new version of vdW-DF, called

vdW-DF2 [3], has been developed with better predictions of binding energies and binding distances. In short, the exchange–correlation functional in vdW-DF (and vdW-DF2) consists of three terms: the exchange energy E_X^{GGA} calculated from a GGA functional (revPBE [4] for vdW-DF and PW86 [5] for vdW-DF2), the local correlation energy E_C^{LDA} calculated using the LDA approximation, and the nonlocal correlation energy E_C^{nl} .

The most popular approach for taking into account the dispersion interactions missing in standard DFT calculations is, however, to add a pairwise interatomic C_6R^{-6} term (or higher order terms C_8R^{-8} , $C_{10}R^{-10}$) to the DFT energy [6–16]. Such methods, often called DFT-D, in general result in reasonable dispersion corrections to the total energy. The major advantages of such methods are that they require

only a small additional computational effort and that they are easy to integrate into available DFT codes. Since there are many different forms of DFT-D, we limit ourselves here to briefly describing the ones adopted in this work. The most widely used method of the DFT-D category—proposed by Grimme [7], often called DFT-D2—calculates the C_6^i coefficient of an atom i from the ionization potential and static dipole polarizability that are calculated using DFT/PBE0 and then calculates the C_6 coefficient for a pair of atoms according to $C_6^{ij} = \sqrt{C_6^i C_6^j}$. This simple approach works very well and gives reasonable results. However, this method has the drawback that its C_6 coefficients are system independent. The most recent development in this genre is the DFT-D3 also proposed by Grimme and colleagues [8]. In this newer version of DFT-D, the dispersion coefficients are computed from first principles on the basis of a large database of such coefficients calculated accurately for any pair of atoms from H to Pu and on the coordination number of atoms in the system under study. Tkatchenko and Scheffer [16] have also proposed a sophisticated way of computing system-dependent C_6 coefficients for atoms in molecules by scaling free-atom values provided by Chu and Dalgarno [17] using the free-atom densities and Hirshfeld-partitioned effective atomic volumes. These values are then used to compute corrected energy values in a DFT-D manner. This approach (TS) gives good results for the S22 set [18].

The variety of the methods gives rise to questions of how the results obtained from each method compare and whether there are reliable and efficient ways of getting a preliminary idea of the importance of vdW interactions in a system of interest. Motivated by our interest in molecular adsorption on surfaces, our aim in this work is to compare the feasibilities of three of the promising approaches for including vdW interactions to the problem: vdW-DF, DFT-D, TS, and a few of their variants. In doing so, we have come up with a simplification of TS ourselves, which we will describe in some detail below. For our prototype systems we have chosen the adsorption of DNA fragments on graphene. The energetic ordering of these simple organic molecules on graphene is not only of intellectual interest but also useful for the elementary steps toward the understanding of the interactions of DNA with carbon nanotubes (CNTs) which have many potential applications in medical treatments [19], separation of CNTs [20, 21], chemical sensors [22], and others [23–26].

In early experiments, using scanning tunneling microscopy (STM) and atomic force microscopy (AFM), Tao and Shi [27] showed that adenine and guanine form a flat monolayer on graphite at a distance of about 3 Å. More recently, it has been shown that the strength of interaction between DNA nucleobases and graphene in alkaline solution varies in the order guanine (G) > adenine (A) > cytosine (C) > thymine (T) and in pure water varies in the order A > T > C [28]. The relative strength of these nucleobase–graphene interactions has also stimulated a great deal of theoretical investigation. Using DFT, Ortman *et al* [29] found the adenine–graphite separation to be 3.1, 4.0, or 3.4 Å, depending on the functional chosen—the LDA, the

GGA using the PW91 functional, or the GGA supplemented by the London dispersion formula, respectively. Within the LDA with additional calculations that uses the Hartree–Fock approach coupled with second-order Møller–Plesset perturbation theory (MP2), Gowtham *et al* [30] reported that the binding of DNA nucleobases on graphene follows the order of G > A \approx T \approx C > uracil (U). Invoking DFT-D [29], Antony and Grimme reported the sequence to be G > A > T > C > U [31]. Furthermore, employing the Hartree–Fock approximation with the addition of the vdW interaction and a solvation energy based on the AMBER generalized Born model (in [28]), Varghese *et al* [28] reported that the binding sequence is G > A \approx T > C.

In this work, we first propose a simplified version of the TS approach (referred to as sTS) to quantitatively optimize the geometric structures of DNA nucleobases on graphene. Then, starting with those structures, we carry out self-consistent vdW-DF calculations to further optimize the structures. Next, we compare the results for binding energies and binding distances of nucleobases on graphene from the TS, sTS, DFT-D2, DFT-D3, vdW-DF, and vdW-DF2 methods. Finally, we compare the computational costs associated with each of these approaches. It should be noted that all methods mentioned above are undergoing code optimization and that the results presented here may not necessarily represent the relative efficiency of these codes for all systems and at all times.

2. Computational details

Our total-energy calculations are carried out within DFT using the real space GPAW code which implements the grid-based projected augmented wave (PAW) method [32]. To avoid finite-size effects, we use a supercell of about $17.14 \times 17.33 \times 19.80 \text{ \AA}^3$ consisting of a graphene sheet of 112 C atoms and a DNA nucleobase whose plane is parallel to that of the graphene sheet. Given the large size of the supercell, the Brillouin zone is sampled only at the Γ point. The grid spacing is set at about 0.15 Å in order to minimize the ‘egg-box’ effect.

2.1. The method of incorporating van der Waals interactions into density functional theory simulations

We have described briefly DFT-D2, DFT-D3, TS, vdW-DF, and vdW-DF2 in the introduction (section 1). Here, we present only our simplification of the TS approach in order to propose the sTS.

There are two attributes of the TS approach that we found formidable in performing ionic structural relaxations. First, the implementation of the Hirshfeld partitioning is computationally intensive. Second, the vdW correction for the force calculation is not incorporated in an obvious manner. The reason for the latter is that the dependence of the Hirshfeld partitioning on the positions of ions in the system (which is needed to calculate the gradient of energy correction) is not clearly defined. To overcome this problem we do not calculate C_6 for every ionic iteration during the relaxation process; instead we fix the vdW radii and the

effective C_6 coefficients at their values in the clean graphene sheet and in isolated molecules. We call this method sTS (s stands for simplified), for brevity in the rest of the text.

2.2. Relaxation procedures

In the first step of geometric relaxation, our calculations are carried out within DFT, employing the GGA, using the plane-wave pseudopotential method implemented in the VASP 5.2 code [33–35] with the PAW [36, 37] pseudopotentials. The supercells and Brillouin zone sampling are the same as described above. We set the kinetic energy cutoff for plane-wave expansion at 500 eV. We use the PBE functional [38] to describe the exchange and correlation of electrons. Our local implementation is available for performing structure relaxation also with DFT-D2, DFT-D3, or other similar approaches. However, in this work, we do not use DFT-D2 or DFT-D3 for preliminary structure optimization. After a quick test of finding the binding distance between graphene and adenine, we find that DFT-D2 predicts much smaller binding distances than are obtained from vdW-DF2. The TS approach also predicts shorter binding distance than vdW-DF2 but in general these distances are larger than that obtained by DFT-D2. As our proposed sTS method provides binding distances that are similar to that obtained by the TS method, we decided to take advantage of sTS's simplicity for preliminarily structural relaxation. In fact, there is almost no extra cost in performing single-point calculations using sTS in comparison with that of regular DFT. Thus, we are able to perform 360° rotations of the nucleobases around their 'center of mass' in 5° steps when optimizing the starting orientation of the nucleobases on the graphene sheet. The initial separations between the nucleobases and graphene are set to 3.2 Å. Within the sTS approach, the vdW force between a pair of atoms i and j is calculated by using

$$F_{\text{vdW}}^{ij} = -\nabla E_{\text{vdW}}^{ij}.$$

The forces acting on the ions are then calculated by adding these vdW forces to the DFT-based forces calculated by the Hellmann–Feynman theorem [39]. This force correction accounts for the vdW interaction when performing structural relaxations. All structures are relaxed until all force components acting on each individual atom are less than 0.02 eV \AA^{-1} . Once the structures are optimized, the 360° rotations are performed once again to ensure that the nucleobases are not trapped in a local minimum orientation. The geometries obtained for the nucleobases on graphene are then optimized once again using the vdW-DF as implemented in the GPAW code. The advantage of the above procedure is that the equilibrium structures that have been optimized using the sTS approach provide excellent starting points for more sophisticated calculations using vdW-DF. Relaxations stop when all components of forces acting on each ion are smaller than 0.05 eV \AA^{-1} , when using GPAW.

2.3. Binding energies

From the optimized structures, by calculating the total energy of various systems with different distances between nucleobases and graphene sheet, we derive a full binding energy profile for each system. The binding energy of a nucleobase on the graphene sheet is calculated by using

$$E_b = -(E_{\text{sys}}^{\text{tot}} - E_g^{\text{tot}} - E_m^{\text{tot}}),$$

where $E_{\text{sys}}^{\text{tot}}$, E_g^{tot} , and E_m^{tot} are the total energies of the nucleobase–graphene system, of the clean graphene, and of the nucleobases in the same supercell, respectively. By fitting a few calculated points near the minimum of the binding energy profile to a third-order polynomial, we obtain the binding energy and binding distance between each nucleobase and graphene. This process is repeated for different approaches: sTS, TS, DFT-D2, DFT-D3, vdW-DF, non-self-consistent (nsc) vdW-DF, vdW-DF2, and nsc vdW-DF2. By 'non-self-consistent' we mean that the vdW energy is evaluated on the basis of the charge density generated by a prior GGA–PBE calculation.

3. Results and discussion

3.1. Adsorption structures

The optimized orientations of nucleobases physisorbed on a graphene sheet are presented in figure 1. These orientations of C, G, and U on graphene are in good agreement with those reported by Antony and Grimme [31], while those of A and T are not. In comparison with the results reported by Gowtham *et al* [30] for nucleobases on graphene, we get similar orientations for A and U but not for G, T, and C.

3.2. Comparison of binding energies

In table 1 we present the binding energies and binding distances of all five nucleobases on graphene. The data are also visualized in figure 2. Since there is no clear experimental evidence about the binding energies or binding distances of all five nucleobases on graphene, we cannot comment on the accuracy of any of the above methods. For comparison, we take the vdW-DF2 results as the 'benchmark'. As shown in figure 2 and in table 1, TS and also sTS approaches predict higher binding energies in comparison to other mentioned approaches (about 200 meV higher). The stronger binding of molecules on graphene predicted using the TS approach has been mentioned elsewhere [40]. The point here is that sTS gives results that are very similar to those obtained by TS. The interesting results in table 1 also point to: (1) all methods provide the same order for the binding of the DNA fragments on graphene; (2) within each method the spread in the binding energy for the five fragments lies between 200 and 300 meV.

All the approaches considered, except for TS and sTS, give very similar binding energies, which lie within a 70 meV range. vdW-DF2 gives the smallest binding energies while

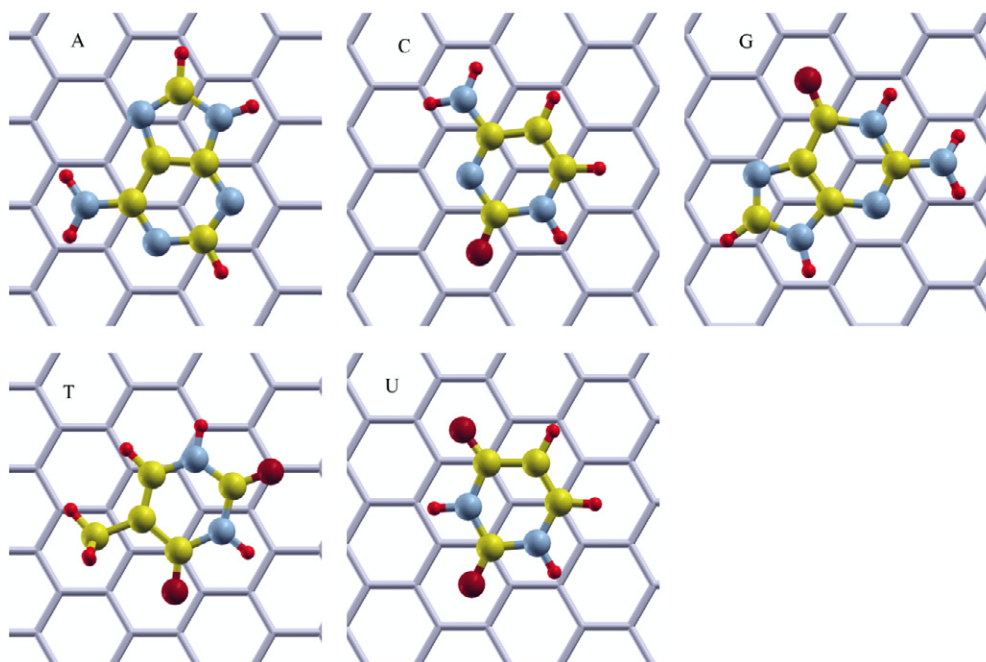


Figure 1. Optimized orientation of adenine (A), cytosine (C), guanine (G), thymine (T), and uracil (U) on graphene.

Table 1. Binding energies (meV) of nucleobases on graphene and optimized nucleobase–graphene separations (binding distances in Å, in parentheses).

Nucleobase	DFT-D				vdW-DF		vdW-DF2	
	sTS	TS	DFT-D2	DFT-D3	nsc	sc	nsc	sc
A	829 (3.29)	849 (3.28)	636 (3.18)	618 (3.38)	637 (3.50)	634 (3.50)	594 (3.37)	588 (3.39)
C	724 (3.32)	745 (3.31)	573 (3.20)	567 (3.38)	582 (3.50)	579 (3.51)	546 (3.38)	540 (3.41)
G	959 (3.26)	986 (3.25)	770 (3.13)	733 (3.33)	750 (3.45)	742 (3.45)	717 (3.33)	699 (3.35)
T	742 (3.35)	763 (3.34)	583 (3.22)	570 (3.42)	607 (3.53)	603 (3.53)	558 (3.41)	545 (3.43)
U	664 (3.31)	682 (3.30)	515 (3.20)	512 (3.38)	543 (3.49)	539 (3.49)	501 (3.37)	496 (3.39)

vdW-DF gives the highest binding energies except for the case of guanine. It is indeed interesting that the simplest and the earliest developed approach—DFT-D2—also yields accurate values of binding energies without demanding excessive computational resources. The newer approach in the DFT-D family, DFT-D3, also gives results that are comparable to those from vdW-DF and vdW-DF2. The binding energies obtained from DFT-D3 lie between those obtained by using vdW-DF2 and vdW-DF.

Although there are disagreements in predicting binding energies, the methods agree with each other very well that the strength of the interactions of the nucleobases on graphene follows the order $G > A > T > C > U$. However, the binding energies of T and C on graphene are predicted to be very

similar by DFT-D3 and vdW-DF2. The results are also in good agreement with earlier work [31].

It is worth mentioning that the binding energies obtained from the methods considered lie between the LDA and MP2 results reported in [30]. The results from the TS and the sTS methods are closer to the MP2 ones while results from the other methods are near the values obtained using LDA. It is interesting that the LDA results are actually closer to what we have taken here as our benchmark results, showing the effect of vdW interactions.

3.3. Comparison of binding distances

Unlike the distribution of binding energies, which shows some agreements between different approaches except for the TS

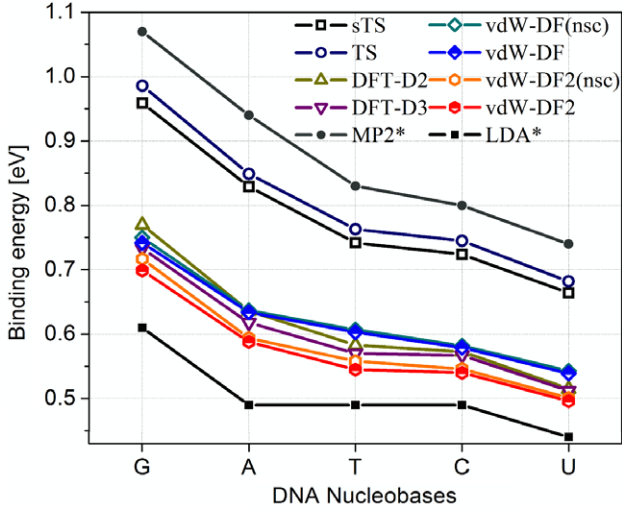


Figure 2. Binding energies of nucleobases on graphene calculated from different methods. The MP2* and LDA* results are from [30].

and sTS methods, the binding distances between nucleobases and graphene from each approach are clearly distinguished, as seen in figure 3. vdW-DF is well known for its overestimation of binding distances [3]. We also find that vdW-DF yields the longest binding distances in comparison to the other approaches considered. On the other hand, vdW-DF2, our benchmark for our purposes here, is expected to provide more realistic binding distances. Interestingly, DFT-D3 gives similar binding distances to vdW-DF2. Its results lie in the small range of variation of vdW-DF2 and nsc vdW-DF2. The binding distances given by the TS and sTS approaches are about 0.1 Å shorter than those given by vdW-DF2. DFT-D2 gives the shortest binding distances among the approaches considered with about or more than 0.2 Å deviation from the vdW-DF2 results.

3.4. Comparison of computational costs

In order to further investigate the computational costs of the methods considered, we perform single-point calculations for the same structure (guanine on graphene) with different approaches. For PBE, vdW-DF, and vdW-DF2 calculations, we have to use multi-processors, while we use a single processor for the TS, sTS, DFT-D2, and DFT-D3 correction calculations. We assume that linear scaling occurs and hence normalize the computational costs to that using a single processor. Using the GPAW code, we perform many sets of runs using PBE, vdW-DF, vdW-DF2, nsc vdW-DF, and nsc vdW-DF2 with different numbers of processors. For comparison, we select the ones with the best computer times. We find that use of eight processors is the best choice for PBE, nsc vdW-DF, and nsc vdW-DF2, while use of 64 processors is the best choice for vdW-DF and vdW-DF2. Because the required numbers of electronic iterations in PBE, vdW-DF, and vdW-DF2 are usually different and are around 30, we calculate the average time required by one electronic iteration and multiply it by 30 to get the normalized time for one self-consistent calculation.

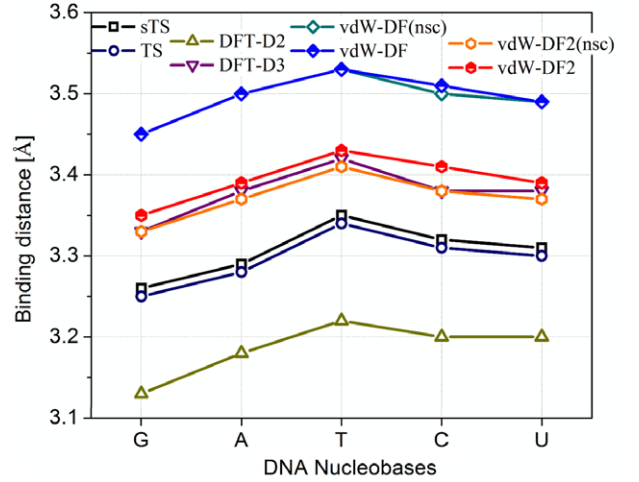


Figure 3. Binding distances of nucleobases on graphene calculated by different methods.

The sTS approach obviously requires the same computational effort as DFT-D2 does. The DFT-D3 requires a bit more computational effort than DFT-D2 because of the need to calculate the coordination numbers for all atoms. Nevertheless, this extra effort is not noticeable. All sTS, DFT-D2, and DFT-D3 corrections are performed using the VASP package with our locally added implementations. The additional costs of these corrections are usually small in comparison to the cost of a PBE calculation; thus it is safe to use those numbers to compare with computational time using the GPAW code.

Since the TS approach uses the Hirshfeld partitioning to calculate the effective volume ratio of atoms in the system, the total cost for this approach would depend on how the routine of Hirshfeld partitioning performs. In general, the amount of computational effort for obtaining the effective volume ratio is appreciable, especially for big systems containing many atoms and large supercell. We rely on the GPAW code to calculate the effective volume ratios.

For the vdW-DF and vdW-DF2 functional calculations, the computational effort is dedicated to the six-dimensional integral of the nonlocal correlation energy E_C^{nl} . The integral is not only time-intensive but also memory-intensive (even with the aid of the Román-Peréz and Soler algorithm [41]) owing to the requirement of highly accurate charge density representation in a very fine 3D mesh (the grid spacing is about 0.07–0.08 Å in our calculations).

We understand that the amount of memory required by different approaches is a major factor in determining computational costs. However in this work, we do not evaluate the relative memory cost, and provide enough memory for all calculations and record only computational times.

In figure 4 we present the additional computational times that are required by different methods. They are calculated as the relative increase in time,

$$\frac{T - T_{PBE}}{T_{PBE}},$$

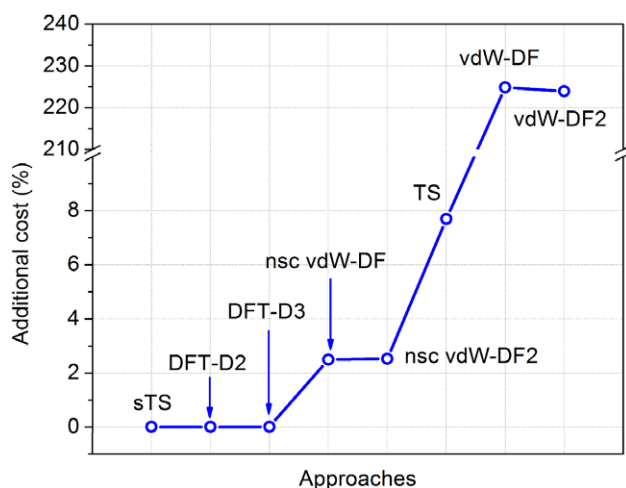


Figure 4. Comparison of computational costs. The additional times used by different approaches in comparison with time consumed by PBE calculation are normalized to that used by a single processor.

where T and T_{PBE} are the total computational times for using the approach considered and using the PBE functional, respectively. Among these, sTS, DFT-D2, and DFT-D3 are truly approaches with almost no additional cost for incorporating the vdW interactions into DFT simulations. The usage of vdW-DF and vdW-DF2 requires computational times that may not be feasible for some (large) systems. The applications of nsc vdW-DF or nsc vdW-DF2 do not cost much—only about 2.5% more time, while the application of the TS approach requires about 8% more computational time.

Our results also show that the difference between self-consistent and non-self-consistent calculations using the vdW-DF and vdW-DF2 functionals is small, which is in good agreement with what is reported in [42]. Here, the non-self-consistent vdW-DF functional calculations use the charge density generated from a PBE functional calculation.

4. Conclusions

Taking into account the accuracy of the approaches under consideration and the computational time required by each approach, we conclude that DFT-D3 is an excellent choice for this class of problems, in which we need to evaluate interactions between molecules and between molecules and less dense material, such as graphene. The accuracy of DFT-D3 for this class of problems has been also shown in [8]. We also find sTS to be very cost effective, and producing results on a par with TS.

It is important to mention that although the structures and orientations of the nucleobases on graphene, and the binding distances of the nucleobases and graphene are fully optimized using vdW-DF in a self-consistent manner, such structural optimization is computationally demanding. Nor is it a good idea to use DFT-D2 to perform calculations of the type considered here, as it predicts much shorter binding distances compared to the other approaches considered. As for the TS approach, its description of the correction for forces is still not clear, though a recent formulation of the method

may have addressed this issue [43]. Nevertheless, we have proposed a simplified method (sTS) as an efficient alternative for acquiring preliminary information about the extent of importance of vdW in a given system. At the very least it provides a good starting point in which one fixes the effective volume ratios of atoms as their values in a clean, isolated system. The relaxed structures obtained with sTS may then be used for further investigations of vdW interactions using more sophisticated techniques. While we have referred to the results obtained by vdW-DF2 as our benchmarks, validation of this assumption can only come from agreement with experimental data which we await.

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