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Benchmarking dispersion and geometrical counterpoise corrections for cost-effective large-scale DFT calculations of water adsorption on graphene

Marco Lorenz,* Bartolomeo Civalleri,† Lorenzo Maschio,‡ Mauro Sgroi,§ Daniele Pullini¶

June 20, 2014

Abstract

The physisorption of water on graphene is investigated with the hybrid DFT-functional B3LYP combined with empirical corrections, using moderate-sized basis sets such as 6-31G(d). This setup allows to model the interaction of water with graphene going beyond the quality of classical or semiclassical simulations, while still keeping the computational costs under control. Good agreement w.r.t. CCSD(T) results is achieved for the adsorption of a single water molecule in a benchmark with two DFT-functionals (PBE, B3LYP) and Grimme’s empirical dispersion and counterpoise corrections. We apply the same setting to graphene supported by epitaxial h-BN, leading to an increased interaction energy. To further demonstrate the achievement of the empirical corrections, we model, entirely from first principles, the electronic properties of graphene and graphene supported by h-BN covered with different amounts of water (1, 10 water molecules per cell and full coverage). The effect of h-BN on these properties turns out to be negligibly small, making it a good candidate for a substrate to grow graphene on.

Keywords: DFT, B3LYP, dispersion, graphene, adsorption

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The adsorption of water on graphene is computationally investigated via density functional theory (DFT) combined with empirical corrections. This allows for going beyond the quality of classical or semiclassical simulations, while still keeping the computational costs under control. To model the water adsorption, we used 1 and 10 water molecules per cell, as well as a full coverage of the graphene surface. Additionally, we apply the same setup to hexagonal boron nitride supported graphene.
1 INTRODUCTION

The interaction of water with graphene\textsuperscript{1–5} layers is of high technological interest, mainly because water in gas phase is a constituent of air, and as a consequence is always present in open-air devices; nevertheless, quantifying the effect of water molecules on the physical properties of graphene is very important to gauge the quality of packaging of graphene based devices which contribute to increase the final cost of these product type. The topic has then attracted much attention, both from the experimental\textsuperscript{6,7} and theoretical point of view. The problem has been tackled both at meso-scale\textsuperscript{8} and at a micro/nano-scale\textsuperscript{9,10}, on single-layer, multi-layer or supported\textsuperscript{11,12} graphene. Several other water-graphene studies can be cited\textsuperscript{13–16}.

On the other hand, there is a substantial interest in the substrate underneath the graphene layer (that can be the same on which graphene has been grown, or not\textsuperscript{8,17}) and to understand its effects. One goal is to minimize the influence of the substrate in order to maintain the extraordinary properties of graphene. A good candidate is then epitaxial hexagonal boron nitride (h-BN): The cell parameters show only a mismatch of 2\%\textsuperscript{18}, preventing graphene from altering its structure so that changes in its properties can remain minimal.

The three-component system just described represents a real challenge from the computational point of view, mainly because of the predominant role of dispersive forces. The description of the weak water-layer interactions are generally treated through classical methods,\textsuperscript{8} that allow for large droplets (up to 4000 water molecules) to be simulated using Molecular Dynamics (MD) simulations\textsuperscript{19,20}. Evidently, these methods do not permit the calculation of the electronic structure.

DFT methods have been applied to much smaller models (up to 6 water molecules) to gain more quantum-chemical insight,\textsuperscript{10,21,22} which unveiled the delicacy of the problem. The correct description of weak interactions, in fact, constitutes a tough challenge for quantum mechanical methods\textsuperscript{23}. In particular, London dispersion forces are not captured by methods not going beyond the mean-field approximation, so that for its proper inclusion the system has in principle to be treated as a many-body problem\textsuperscript{24,25}. For solid state calculations,
post-Hartree Fock methods\textsuperscript{26–30} have become available mainly during the last decade. Such methods, however, remain very costly and applicable to model systems (up to 100 atoms for local MP2\textsuperscript{31}). High-quality level studies have been applied to graphene-derived materials,\textsuperscript{32} as well as to the water/graphene interaction\textsuperscript{16,33–35}.

An alternative – though less rigorous – way of including dispersion interactions are empirical corrections to the energy. In this way the costs stay moderate and extended systems can be treated routinely. Recently, Grimme and collaborators introduced their so called Grimme dispersion correction to DFT (denoted as DFT-D\textit{n}).\textsuperscript{36–38} The empirical correction can be obtained at different levels ($n$=2, 3, $3+E^{(3)}$) and was initially calibrated for molecular systems (using a benchmark set of molecules). The D2 correction for B3LYP has been recalibrated for solids by Civalleri et al.\textsuperscript{39} (hereafter denoted as B3LYP-D*), taking into account the higher overlap of Bloch functions in periodic systems compared to atomic orbitals in molecules. Other proposals in the same spirit have been presented in recent years\textsuperscript{40,41}, but none will be considered in this work.

The graphene/substrate interaction, however, is easier to be studied at the quantum chemical level than water/graphene, but not less delicate, and depending on the nature of the substrate. Quite a number of studies have been presented in the last few years\textsuperscript{18,42–50} though not many of them take into account dispersion interactions.

Apart from the level of theory, the use of atom-centered basis functions (i.e. Gaussian-type orbitals, as employed by the CRystal\textsuperscript{51} \textit{ab initio} code, to represent the Bloch functions) leads to an inter- and intramolecular basis set superposition error (BSSE). However, in contrast to a plane wave basis, where artificial replicas of the system in the nonperiodic $z$ direction are needed, it allows for a proper 2-D description. The standard Boys-Bernardi counterpoise correction (BB-CP)\textsuperscript{52} corrects for the intermolecular BSSE, but still the intramolecular BSSE remains. Most importantly, BB-CP techniques cannot be used in automatic geometry optimizations or MD simulations. The geometrical CP-correction (gCP) proposed by Grimme et al.\textsuperscript{53} maps the BB-CP onto a semi-empirical atom-pairwise potential. Recently, periodic boundary conditions and unit cell gradients have been included in the gCP code\textsuperscript{54}, making it applicable for crystals. The BSSE error is particularly relevant for small-to-medium basis sets and, therefore, it hampers the use of cheaper basis sets when
dealing with systems of increasing size and complexity.

In the present work, we first benchmark the combination of DFT-D\textit{n} (\textit{n}=2/*, 3, 3+E^{(3)}) and gCP with two different DFT functionals (PBE and B3LYP) by studying the adsorption of a single water molecule on graphene against CCSD(T) results recently reported by Voloshina et al.\textsuperscript{35}. Tiny interaction energies in the range of physisorption (50-200 meV) open up perfect test conditions for the empirical corrections. The investigation is then extended to h-BN supported graphene. Once defined the optimal computational setup and method among, we tackle the simulation of more complex models, i.e. 10 water molecules per cell and the full coverage of the surface. The aim is to move towards more realistic systems, still maintaining the substantial quantum-chemical character of the simulation to study the electronic structure of the examined systems. For this purpose we use the B3LYP functional because is known that hybrid HF/DFT functionals allow for a better prediction of the band gap of solids\textsuperscript{55,56}.

The paper is structured as follows: In Section 2 we present the computational setup used. In Section 3 we carry out the benchmark and get an insight into the optimal approach to be used for our target application. In Section 4 we apply this approach to the study of different amounts of water on graphene and graphene/h-BN. In Section 5 conclusions are drawn and some future work is noted.

2 COMPUTATIONAL DETAILS

2.1 Parameters of the DFT calculations

Calculations were performed with a development version of the CRYSTAL09 periodic ab initio code\textsuperscript{57} by using an all-electron Gaussian-type basis set and the PBE functional as well as the B3LYP hybrid functional\textsuperscript{58–60}. In particular, the latter hybrid functional has recently been applied to the study of structural, vibrational and optical properties of semiconducting C and BN nanostructures\textsuperscript{61–65}. Hybrid functionals have been reported to be more accurate
than both Hartree-Fock and pure DFT approaches in the prediction of the band gap\textsuperscript{55,56}, static polarizability and first hyper-polarizabilities\textsuperscript{66–68} and vibrational features of solids\textsuperscript{69}.

The level of accuracy in evaluating the bielectronic Coulomb and Hartree-Fock exchange series is controlled by five parameters $T_i$ ($i = 1, ..., 5$)\textsuperscript{57}. $T_1$ and $T_2$ refer to the Coulomb integrals, $T_3$, $T_4$, and $T_5$ to the exchange ones: integrals are either approximated or disregarded when the overlap between the corresponding basis functions is below $10^{-T_i}$. More details on these truncation criteria can be found in Ref. 57. To get directly comparable results to Voloshina et al.\textsuperscript{35}, we choose $7771580$.

In Sec. 3, the threshold on the SCF energy was set to $10^{-6}$ ha. For the systems investigated in Sec. 4, a full relaxation of both atomic positions and lattice parameters was carried out. The threshold on the SCF energy in this case was set to $10^{-9}$ ha. Optimized geometries for the different structures can be found in the supplementary material\textsuperscript{70}.

The reciprocal space was sampled along the two lattice vectors according to a sublattice with a shrinking factor set to 12, corresponding to 74 independent $k$ vectors in the irreducible part of the Brillouin zone for the B-UP/DOWN structures (\textit{vide infra} Fig. 1), and to 43 in all the other structures.

The DFT exchange-correlation contribution is evaluated by numerical integration over the unit cell volume. In CRYSTAL, radial and angular points of the grid are generated through Gauss-Legendre radial quadrature and Lebedev two-dimensional angular point distributions. A (75, 974)p grid was used, corresponding to a pruned grid with 75 radial and 974 angular points (XLGRID keyword in the CRYSTAL09 manual\textsuperscript{57}).

We use empirical corrections to the energy/gradient proposed by Grimme and co-workers\textsuperscript{36,37,37}. They correct the KS-DFT energy with a dispersion $E_{\text{disp}}$ and a counterpoise term $E_{\text{gCP}}$,

$$E_{\text{tot}} = E_{\text{KS-DFT}} + E_{\text{disp}} + E_{\text{gCP}}. \quad (1)$$

A conceptional overview over different levels of empirical dispersion corrections (D2/*, D3, D3+E\textsuperscript{(3)}) and the geometrical counterpoise correction (gCP) is presented in the supplementary material\textsuperscript{70}. An important difference between D2/* and D3/D3+E\textsuperscript{(3)} is the degree of empiricism. The former uses system-independent empirical dispersion coefficients, while the
latter incorporates non-empirical (apart from the short-range-damping), pairwise-specific, chemical environment-dependent dispersion coefficients obtained from first-principle calculations for molecular systems with time-dependent DFT. The corresponding parameters are taken from Ref.s 36,37,39,53 and can also be found in the supplementary material\textsuperscript{70}.

2.2 Basis sets

We targeted small to intermediate sized basis sets capable to reproduce the essential features (geometry, interaction energy, electronic structure) of the system of interest. Our interest here is, in fact, to set up a methodology that is capable to treat systems with a reasonably large number of molecules adsorbed on the graphene surface.

We have thus tested two basis sets, 6-31G(d)\textsuperscript{71,72} and def2-SVP\textsuperscript{73}. The number of basis functions in both basis set is the same (H [2s], B/C/N/O [3s,2p,1d]) except an additional p-function for hydrogen in the def2-SVP basis set. Since exponents of carbon basis functions in graphene lower than about 0.17 Bohr\textsuperscript{−2} cause severe convergence problems in the SCF-procedure due to near (or even) linear dependencies in the basis set, we increased diffuse exponents by hand to a value at which the calculation is stable. For the 6-31G(d) basis set the most diffuse exponent of the sp-function on carbon was increased from 0.1687144 Bohr\textsuperscript{−2} to 0.19 Bohr\textsuperscript{−2}, and denoted in the following as 6-31g(d)-spC0.19. For the def2-SVP basis set we increased the lowest exponent of the p-function on carbon from 0.15268613795 Bohr\textsuperscript{−2} to 0.17 Bohr\textsuperscript{−2}, denoted as SVP-pC0.17. The increasing of the exponents leads to a mismatch of the basis set specific gCP correction. We then performed test calculations to estimate the introduced error for the PBE functional. Very small differences with respect to the original basis sets are obtained. Results are reported and discussed in the supplementary material\textsuperscript{70}.


3 RESULTS I: BENCHMARK OF DFT-D\textit{N}+GCP METHODS

3.1 Water molecule on graphene

In this section, we very briefly review the literature discussing theoretical results for the interaction of a single water molecule with graphene. Then, we assess the examined DFT methods as augmented with the DFT-D\textit{n} and gCP corrections on this model system against reference data. All of the dispersion corrections are well-defined. We do not yet have D3 or D3+E[3] for the gradients, so it is good to know how D2/D\textit{g} behaves, because we use it afterwards for the calculations including structural optimizations.

3.1.1 Results from other investigations

Several quantum chemical investigations of single-molecule of water on graphene, at different levels of theory, can be found in literature\textsuperscript{12,15,16,22,35,74,75}. A table with distances and energies is given in the supplementary material\textsuperscript{70}. The most studied arrangement of water on graphene is with C-DOWN geometry (see Fig. 1). Results for high-level theoretical methods, as DFT-SAPT, RPA, MP2 or CCSD(T), give an adsorption energy that ranges between -100 and -140 meV and an equilibrium distance of about 2.60 - 2.80 Å, with a reasonable agreement among them.

A few studies have been published on different geometries\textsuperscript{35,74}. Results from Ref. 35 and 74 are similar, with the main difference being the reversed stability of the C-DOWN and T-DOWN conformation, but the relative stability differs just by 15 meV (i.e. a few tenth of kcal/mol).

As already discussed in the Sec. 1, ordinary DFT provides no reasonable equilibrium distances, clearly seen for the non-dispersion-corrected PBE results of Voloshina \textit{et al}. Instead, all dispersion corrected or dispersion including methods reproduce the equilibrium distances well. The empirical dispersion corrections capture the essence of the interaction, although its error is usually about ± 30% w. r. t. CCSD(T).

The differences in the water–graphene distance is much less sensitive to the method, and
different flavors of DFT-D provide results that are in substantial agreement with LMP2 and CCSD(T) results.

Overall, the most sophisticated investigation has been done by Voloshina et al.\textsuperscript{35} and gains the local MP2 as well as the local CCSD(T) results via the periodic\textsuperscript{26,27,76,77} and incremental method.\textsuperscript{78–81} The CCSD(T) results are generally assumed to be beyond chemical accuracy (i.e. 1 kcal/mol = 43.4 meV)\textsuperscript{1} and hereafter they will be considered as the reference data to compare with and benchmark the DFT-D+gCP methods under investigation.

3.1.2 Our structural models

Following Ref. 35, a (3 × 3) graphene supercell (18 carbon atoms) was used to model the adsorption of a single H\textsubscript{2}O molecule on graphene. The water molecules then are 7.38 Å apart and assumed to be non-interacting. The C-C distance in graphene is set to the experimental value of 1.421 Å, the oxygen-hydrogen distance to 0.9584 Å and the hydrogen-oxygen-hydrogen angle to 104.45 degrees. Different positions and orientations of water are considered, varying only the distance between water and graphene. The six different structures are depicted in Fig. 1 and read: B-UP/-DOWN (middle of the carbon-carbon bond), C-UP/-DOWN (center of the six-fold carbon-ring), T-UP/-DOWN (top of the carbon atom). The distance of water and the graphene sheet is defined as the distance of oxygen-graphene in the UP-structures and as the distance of hydrogen-graphene in the DOWN-structures (note that in other studies also for the DOWN-structures the oxygen-graphene distance might be

\textsuperscript{1}It can be generally questioned if the results in Ref. 35 are actually beyond chemical accuracy or not, since they are hindered by two additional types of errors: (a) are obtained from cluster calculations; the calculation in this case is not periodic, but done on a very large, not infinite system, because graphene is a conductor so periodic MP2/(T) diverge, while with “finite graphene” a small, artificial band gap is introduced; (b) a finite basis set (cc-pVDZ for graphene and aug-cc-pVTZ for water), i.e. not at the basis set limit, is used. Nevertheless it is reasonable to assume these errors are cancelled out in a large part when computing energy differences, and these can be considered accurate enough to (1) describe the right order of stability of the UP and DOWN configurations at a given position (B, C, T), differing maximally 33 meV, (2) describe the right order of stability of the different positions, differing maximally 17 meV and (3) provide a systematic error of the adsorption energies of all structures small enough (i.e. close to the limit of the method, see above) to describe those tiny adsorption energies. Nonavailability of experimental data prevents from being able to falsify this assumption.
Figure 1: Details of the six considered (periodic) structural models B-UP/-DOWN, C-UP/-DOWN, T-UP/-DOWN, with a single graphene sheet and a graphene sheet supported by h-BN. A 3x3 supercell contains one single water molecule being then 7.38 Å apart (visually emphasized by showing three water molecules).

(a) UP (b) DOWN

(i) middle of the C-C-bond - B (ii) center of the 6-fold C-ring - C (iii) top of the C-atom - T

3.1.3 Adsorption energy profiles

We have calculated adsorption energies and equilibrium distances for the six different geometries (vide infra Figure 1) using the same strategy as in Ref. 35. For brevity, we discuss here only two of the adsorption energy curves, namely for the C-UP structure with PBE- and B3LYP-functionals (Fig. 2) corrected for BSSE with the gCP and the BB-CP method. Other curves can be found in the supplementary material.

The adsorption energy profile for the C-UP structure shows most clearly the differences between gCP and BB-CP corrections, as well as the differences between different levels of dispersion corrections for both PBE and B3LYP functionals with respect to CCSD(T).

The equilibrium distance is also affected by the type of the dispersion correction. In the
Figure 2: Adsorption energy curves of different orientations of water on graphene.
Table 1: DFT-D<sub>n</sub> counterpoise corrected adsorption energies in meV and equilibrium distances in Å, as well as the maximum (MaxD) and mean absolute deviation (MAD). PBE and B3LYP values are calculated with the 6-31G(d)-spC0.19 basis set, while CCSD(T) and MP2 values are taken from Voloshina et al. with a cc-pVDZ basis set for graphene and aug-cc-pVTZ basis set for water<sup>35</sup>. The minima are obtained through a least-square polynomial fit.

<table>
<thead>
<tr>
<th>Method</th>
<th>BB-CP-PBE-&lt;sup&gt;D2&lt;/sup&gt;</th>
<th>BB-CP-PBE-&lt;sup&gt;D3&lt;/sup&gt;</th>
<th>BB-CP-PBE-&lt;sup&gt;D3+E&lt;sup&gt;3&lt;/sup&gt;&lt;/sup&gt;</th>
<th>BB-CP-B3LYP-&lt;sup&gt;D*&lt;/sup&gt;</th>
<th>BB-CP-B3LYP-&lt;sup&gt;D3&lt;/sup&gt;</th>
<th>BB-CP-B3LYP-&lt;sup&gt;D3+E&lt;sup&gt;3&lt;/sup&gt;&lt;/sup&gt;</th>
<th>gCP-PBE-&lt;sup&gt;D2&lt;/sup&gt;</th>
<th>gCP-PBE-&lt;sup&gt;D3&lt;/sup&gt;</th>
<th>gCP-PBE-&lt;sup&gt;D3+E&lt;sup&gt;3&lt;/sup&gt;&lt;/sup&gt;</th>
<th>gCP-B3LYP-&lt;sup&gt;D*&lt;/sup&gt;</th>
<th>gCP-B3LYP-&lt;sup&gt;D3&lt;/sup&gt;</th>
<th>gCP-B3LYP-&lt;sup&gt;D3+E&lt;sup&gt;3&lt;/sup&gt;&lt;/sup&gt;</th>
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<td>E&lt;sub&gt;ads&lt;/sub&gt;</td>
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<td>d&lt;sub&gt;0&lt;/sub&gt;</td>
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</tr>
<tr>
<td>B-UP</td>
<td>3.05 (-102)</td>
<td>3.09 (-99)</td>
<td>3.27 (-53)</td>
<td>3.25 (-60)</td>
<td>3.15 (-53)</td>
<td>3.19 (-58)</td>
<td>3.16 (-72)</td>
<td>3.17 (-65)</td>
<td>3.30 (-54)</td>
<td>3.29 (-65)</td>
<td>3.30 (-58)</td>
<td>3.14 (-88)</td>
</tr>
<tr>
<td>C-UP</td>
<td>3.06 (-102)</td>
<td>3.09 (-98)</td>
<td>3.18 (-57)</td>
<td>3.28 (-63)</td>
<td>3.29 (-57)</td>
<td>2.96 (-82)</td>
<td>3.06 (-83)</td>
<td>3.07 (-76)</td>
<td>3.19 (-58)</td>
<td>3.21 (-69)</td>
<td>3.22 (-62)</td>
<td>3.02 (-82)</td>
</tr>
<tr>
<td>T-UP</td>
<td>3.06 (-102)</td>
<td>3.08 (-101)</td>
<td>3.29 (-52)</td>
<td>3.35 (-58)</td>
<td>3.36 (-52)</td>
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<td>3.29 (-64)</td>
<td>3.30 (-57)</td>
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<tr>
<td>B-DOWN</td>
<td>2.84 (-113)</td>
<td>2.80 (-115)</td>
<td>2.72 (-109)</td>
<td>2.83 (-105)</td>
<td>2.90 (-105)</td>
<td>2.67 (-122)</td>
<td>2.92 (-115)</td>
<td>2.92 (-109)</td>
<td>2.95 (-104)</td>
<td>2.81 (-124)</td>
<td>2.81 (-116)</td>
<td>2.81 (-118)</td>
</tr>
<tr>
<td>C-DOWN</td>
<td>2.61 (-123)</td>
<td>2.66 (-126)</td>
<td>2.63 (-117)</td>
<td>2.83 (-110)</td>
<td>2.83 (-102)</td>
<td>2.58 (-138)</td>
<td>2.74 (-124)</td>
<td>2.74 (-116)</td>
<td>2.78 (-112)</td>
<td>2.75 (-120)</td>
<td>2.75 (-123)</td>
<td>2.75 (-129)</td>
</tr>
<tr>
<td>T-DOWN</td>
<td>2.69 (-135)</td>
<td>2.70 (-136)</td>
<td>2.87 (-133)</td>
<td>2.88 (-103)</td>
<td>2.89 (-96)</td>
<td>2.66 (-124)</td>
<td>2.81 (-116)</td>
<td>2.81 (-109)</td>
<td>2.84 (-138)</td>
<td>2.81 (-122)</td>
<td>2.81 (-114)</td>
<td>2.79 (-119)</td>
</tr>
</tbody>
</table>

*MaxD*<sub>0</sub> = 0.25 | 0.24 | 0.25 | 0.25 | 0.17 | 0.17 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12

*MaxD*<sub>MAD</sub> = 0.03 | 0.12 | 0.24 | 0.24 | 0.24 | 0.24 | 0.24 | 0.24 | 0.24 | 0.24 | 0.24 | 0.24 | 0.24 | 0.24 | 0.24

**case of PBE** the D2 correction provides a different minimum than the D3 and D3+E<sup>(3)</sup> corrections, while in the case of B3LYP the D* correction is usually in line with the D3 and D3+E<sup>(3)</sup> corrections (which is likely an effect of the recalibration for solids<sup>39</sup>).

### 3.1.4 Energetics and geometries

Table 1 summarizes the empirically and fully counterpoise corrected equilibrium distances and adsorption energies for the 6 different structures for all the examined methods using the 6-31G(d)-spC0.19 basis set. Mean absolute deviation (MAD) and maximum deviation (MaxD) are also listed. In Figure 3 the (relative) errors are explicitly reported for the same data set and additionally for the SVP-pC0.17 basis set.

For both functionals, PBE and B3LYP, respectively, the MaxD of the equilibrium distance is reduced using the gCP correction instead of the BB-CP correction. It does not reach the accuracy of MP2, but since the potential is very shallow, a deviation of 0.06 Å means a negligible change in the adsorption energy of 1 meV. To point out the main difference in the equilibrium distances computed via the BB-CP and gCP correction: the UP configurations are much better described with the gCPC, while the DOWN configurations are also well-described with the BB-CPC.

The error of the adsorption energies is also reduced for gCP corrected functionals. The
Figure 3: (a) Relative errors of the equilibrium distances and (b) errors of the DFT-Dn counterpoise corrected adsorption energies with respect to the CCSD(T) counterpoise corrected adsorption energy with a cc-pVDZ basis set for graphene and aug-cc-pVTZ basis set for water from Ref. 35. Also the Vol-BB-CP-MP2 results as well as the Vol-BB-CP-PBE-D2 results are taken from Ref. 35. The three-body contribution $E^{(3)}$ is denoted as $E[3]$. The ordinates are chosen such that the results are directly comparable.

(a) Relative errors of the equilibrium distances with 6-31G(d)-spC0.19 (left side) and SVP-pC0.17 (right side) basis sets.

(b) Errors of the CPC adsorption energies with 6-31G(d)-spC0.19 (left side) and SVP-pC0.17 (right side) basis sets.
additional error of the empirical gCP correction seems to lead to a more fortune error cancellation.

In Table 1 the structures are ordered by increasing stability w.r.t. CCSD(T) adsorption energies. While MP2 fails in reproducing the order of B-UP and C-UP, all the DFT methods show a similar problem with the T-UP and T-DOWN structures, since they underestimate the adsorption energies such that it is the least or second least stable instead of the most stable within the rows of UP and DOWN structures, respectively. The difference between BB-CP and gCP corrected energies is that gCP moves the T-configurations from the least to the second least stable. BB-CP-B3LYP-D* coincidentally reproduces the correct order of stability in the DOWN-configurations (but not in the UP-configurations). Nevertheless, all DFT methods are able to distinguish between UP and DOWN configurations.

The quality of the results shows a moderate dependency on the basis set. Calculations with a def2-SVP basis set, shown in Fig. 3, reveal that in this case the equilibrium distances are much better described using gCP in combination with D3 or D3+E(3) dispersion correction than with BB-CPC-D3 or BB-CPC-D3+E(3), respectively. The adsorption energies are severely overestimated, especially for the DOWN-configurations.

Overall, the contributions of the different ingredients, the density functional, empirical dispersion correction, and geometrical counterpoise correction are the following: the density functional alone (PBE, B3LYP) does provide only a very shallow potential with small binding of the water molecule to graphene at completely unreasonable equilibrium distances (< 10 meV, not shown here, see e.g. Ref. 35). Adding the empirical dispersion correction at D2(/*)/D3/D3+E(3) levels, reasonable binding is introduced. For the B3LYP functional, the MAD with respect to CCSD(T) for the equilibrium distances is then 0.18-0.19 Å, and for the adsorption energies 25-31 meV (PBE: 0.14-0.27 Å, 20-40 meV). gCP then should mimic those results, but fortune error cancellations reduce the MAD of the equilibrium distance to 0.05-0.10 Å, and of the adsorption energies to 20-21 meV (PBE: 0.05-0.11 Å, 20-26 meV).

We infer from that that the B3LYP+gCP approach with all empirical dispersion corrections, in combination with the 6-31G(d)-spC0.19 basis set provides good equilibrium distances and adsorption energies at small costs and is therefore practical to use. Since for the gradients the D3 and D3+E(3) corrections are not yet available in CRYSTAL09, we stick to the D*
Table 2: DFT-Dn counterpoise corrected adsorption energies in meV and equilibrium distances in Å for a water molecule on graphene/h-BN. The minima are obtained through a least-square polynomial fit.

<table>
<thead>
<tr>
<th>Str.</th>
<th>D2</th>
<th>D3</th>
<th>D3-E10</th>
<th>D2</th>
<th>D3</th>
<th>D3-E10</th>
<th>D2</th>
<th>D3</th>
<th>D3-E10</th>
<th>D2</th>
<th>D3</th>
<th>D3-E10</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-UP</td>
<td>3.15</td>
<td>-65</td>
<td>3.28</td>
<td>-61</td>
<td>3.04</td>
<td>-92</td>
<td>3.05</td>
<td>-82</td>
<td>3.17</td>
<td>-66</td>
<td>3.20</td>
<td>-76</td>
</tr>
<tr>
<td>B-DOWN</td>
<td>2.72</td>
<td>-117</td>
<td>2.87</td>
<td>-104</td>
<td>2.65</td>
<td>-137</td>
<td>2.78</td>
<td>-129</td>
<td>2.79</td>
<td>-119</td>
<td>2.83</td>
<td>-115</td>
</tr>
<tr>
<td>C-DOWN</td>
<td>2.63</td>
<td>-127</td>
<td>2.80</td>
<td>-109</td>
<td>2.56</td>
<td>-154</td>
<td>2.70</td>
<td>-139</td>
<td>2.70</td>
<td>-129</td>
<td>2.76</td>
<td>-123</td>
</tr>
<tr>
<td>T-DOWN</td>
<td>2.78</td>
<td>-116</td>
<td>2.86</td>
<td>-112</td>
<td>2.87</td>
<td>-102</td>
<td>2.63</td>
<td>-139</td>
<td>2.77</td>
<td>-130</td>
<td>2.81</td>
<td>-114</td>
</tr>
</tbody>
</table>

correction for further investigations including geometry optimizations.

### 3.2 Water molecule on graphene/h-BN

We used the same setup for the case of graphene supported on a h-BN sheet (in the following denoted as graphene/h-BN). The structures are depicted in Fig. 1. For aligning the h-BN sheet, we chose the most stable structure according to Ref. 18, where one carbon is over boron, and the other carbon centered above a h-BN hexagon. The cell parameter mismatch of 2% (the one of graphene is smaller) is neglected and the cell parameters are fixed to be both the same (the buckling of BN after optimizing this structure is negligible). The distance of graphene to the h-BN sheet is set to the experimental one, i.e. 3.33 Å\textsuperscript{18}.

In Table 2 the equilibrium distances and adsorption energies of different water structures on a graphene/h-BN sheet calculated with PBE and B3LYP functionals and different empirical dispersion and CP corrections are listed. In this case, we were not able to find in literature reference data for comparison.

The equilibrium distances and adsorption energies generally show the same trends as in the water-graphene system. The gCP compared to the BB-CP correction shows shortened equilibrium distances and increased adsorption energies. The difference of the adsorption energy between the BB-CP and the gCP correction slightly becomes larger, indicating that the gCP correction is slightly more overestimating in this case compared to the single graphene sheet.

As for water/graphene, all DFT-Dn counterpoise corrected methods predict the C-DOWN
structure to be the most stable one. The oxygen is at the center of the ring but on top of the nitrogen atom of the h-BN sheet. Also, the C-UP structure is the most stable among the UP-structures.

Overall, the effect of the h-BN sheet is to slightly decrease water-graphene distances of about 0.02 Å and increase interaction energies of about 9-16 meV. For the UP structures, the differences in adsorption energy differences B3LYP-D* and B3LYP-D3+E(3) methods are quite small (about 2 meV), while for the DOWN structures the differences are bigger but still not more than 10 meV (< 9%). Compared to the water-graphene system this is a slight decrease (of about 2 meV) indicating that the difference between different dispersion corrections gets smaller when interaction energies get larger. The same trend is observed for the equilibrium distances.

4 Results II: Towards more realistic systems

From the results of Sec. 3 we single out B3LYP-D*+gCP as a suitable approach also for the study of systems with more water molecules (10 per cell and full coverage), adsorbed on free-standing graphene and h-BN supported graphene. Our target is to better understand the role of water molecules in tuning the electronic structure of the systems under investigation. We are especially interested to see whether the combination of the interaction with water and the support can open a gap in graphene. Moreover, we can also get some insights on the problem of the wettability of graphene and its transparency.

4.1 Structural models

For the different coverages of water molecules, as an initial structure a slab is cutted out from the dipole-free modification of ice Ih with a hexagonal arrangement of the oxygen sublattice. At variance with other works, this allows us to create a non polar water monolayer along the non periodic direction (i.e. z-axis). The structures were then fully optimized using the B3LYP-D*+gCP method with the above designated 6-31G(d)-spC0.19 basis set. We adopted for the study of 1 water molecule again a 3x3 supercell (18 carbon atoms/9 BN molecules per supercell, equivalent to 22% H2O-coverage), for 10 water molecules a 7x7 supercell.
Figure 4: Details of the optimized (periodic) water on graphene and graphene/h-BN structures (non polar in the $z$-direction): (a) 1 water molecule, (b) 10 water molecules, and (c) a water layer.

percell (98 carbon atoms/49 BN molecules per supercell, equivalent to 41% $\text{H}_2\text{O}$-coverage), and for the water layer/ full coverage a rectangular supercell generated by the expansion matrix \((\frac{2}{3}, -\frac{2}{3})\) (16 carbon atoms/8 BN molecules/4 water molecules per supercelle) (we have to note that since in a rectangular supercell the Dirac cone is not located on a special symmetry point, but on the path between $\Gamma$ and $X$, and thus creating an artificial band gap for graphene, we used for calculating the band structure and gap a 4x4 supercell with 32 carbon atoms/16 BN molecules/8 water molecules). The optimized structures are depicted in Fig. 4. These will be discussed in more detail in the following, but it is clear at a first glance that the effect of the BN substrate is nearly insignificant in the case of low and full coverage. In the 10-molecule droplet some minor difference due to the substrate can be seen.
Table 3: Adsorption energies and fundamental direct band gaps in meV of different amounts of water on graphene and graphene supported by a h-BN-layer. The ratio of water molecules in the system and water molecules at full coverage of the graphene surface is denoted as H$_2$O-coverage.

<table>
<thead>
<tr>
<th>System</th>
<th>$E_{ads}$</th>
<th>$E_{ads}/N_{H_{2}O}$</th>
<th>H$_2$O-coverage</th>
<th>Direct band gap</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 water-mol on graphene</td>
<td>-178</td>
<td>-178</td>
<td>22%</td>
<td>60</td>
</tr>
<tr>
<td>10 water-mol on graphene (non polar)</td>
<td>-748</td>
<td>-75</td>
<td>41%</td>
<td>6</td>
</tr>
<tr>
<td>water-layer on graphene (non polar)</td>
<td>-601</td>
<td>-75</td>
<td>100%</td>
<td>30</td>
</tr>
<tr>
<td>1 water-mol on graphene/BN</td>
<td>-194</td>
<td>-194</td>
<td>22%</td>
<td>88</td>
</tr>
<tr>
<td>10 water-mol on graphene/BN (non polar)</td>
<td>-816</td>
<td>-82</td>
<td>41%</td>
<td>87</td>
</tr>
<tr>
<td>water-layer on graphene/BN (non polar)</td>
<td>-670</td>
<td>-84</td>
<td>100%</td>
<td>85</td>
</tr>
</tbody>
</table>

### 4.2 Effects of water coverage

The fully optimized structure of the single water molecule is shown in Fig. 4(a), while adsorption energies and fundamental direct band gaps can be found in Table 3. The position of the oxygen is still in the middle of the six-fold carbon ring as for the C-type structures investigated in Sec. 3.1 but the orientation of the hydrogen atoms makes it comparable to a tilted DOWN-structure, where the two hydrogen atoms point to two carbon atoms, which are only one carbon atom apart. This minimum is 49 meV below the local minimum of a fully optimized C-DOWN structure, and shows an increased adsorption energy of -178 meV, compared to -129 meV of the optimized C-DOWN structure, and -127 meV of the C-DOWN structure investigated in Sec. 3.1.

The ten water molecules arrange in the center of the six-fold carbon rings, with a length of the hydrogen bonds of about 1.71 to 1.96 Å, compared to about 1.79 Å in ice. A rearrangement of the cluster in the z-direction is observed, i.e. one water-molecule is moving away from the graphene layer, while the other water molecules stay approximately in the plane.
In the case of the full coverage, there is an equivalent amount of water molecules centered on the middle of the carbon ring and on top of the carbon atoms. The lengths of the hydrogen bonds group into about 1.75 Å and about 1.95 Å, the latter to compensate the different lattice parameters of the ice-like layer and graphene. The adsorption energy per water molecule, as shown in Table 3, is rapidly decreasing when increasing the number of water molecules adsorbed. From one single water molecule to 10 water molecules the interaction energy drops to 60%, and then stays about constant for the full coverage. This can be easily explained by the competition between the weak water/graphene interaction and the stronger H-bonding within the water molecules in the cluster and in the monolayer.

Since in the case of 10 water molecules one water molecule is leaving the plane of the other nine water molecules and therefore most probably not directly interacting with the graphene layer, the quantity interaction per water molecule provides an underestimation, which can be taken into account by norming the interaction energy to nine water molecules, which would be then -83 meV. The full coverage then provides only 8 meV less attraction, indicating that with only few water molecules more, the interaction energy per water molecule does not decrease any more.

Since graphene is under observation as a candidate to substitute silicon–based electronics, we also focused our attention on the effect of water molecules on the electronic structure and band gap of graphene. Band structures of graphene and water/graphene, at different loading of water, are shown in Figure 5 (a) and (b), respectively. Comparing panels (1a) and (1b) of Figure 5 we can see that the electronic bands of graphene are unaltered by the adsorption of one water molecule, even though a tiny opening of the band gap is observed (see Table 3). For the water cluster and monolayer adsorbed on graphene, the band gap still remains very small, so that, the band structure of graphene is only marginally influenced by the presence of water. Test calculations with a higher quality basis set, i.e. VTZ-quality for graphene and aug-cc-pVTZ for water, as used in Ref. 35, show an only 5% wider band gap for the system 1 water molecule on graphene.
Interestingly, previous calculations for water monolayer on graphene adopted a structural arrangement of the molecules in which the dipole moment of water is aligned perpendicularly to the graphene sheet. This creates a net dipole along the \( z \)-direction that leads to a larger band gap opening.\(^{12,13}\) B3LYP-D\(^*\)+gCP calculations on such a polar water monolayer give an interaction energy of \(-304\) meV (i.e. \(-51\) meV per water molecule) and a band gap of \(105\) meV. However, this structural model is unphysical because it is unlikely that a polar surface can grow without any reconstruction. Furthermore, a droplet (or a film) of liquid water adsorbed on graphene shows a random orientation of the \( \text{H}_2\text{O} \) molecules, so that the net dipole moment would be zero.

In this respect the water-monolayer/graphene structure investigated in the present work is a more reliable model.

Nevertheless, a partial orientation of the water molecules, resulting in a net dipole moment\(^{83}\), can be the reason for the experimentally measured band gap of \(200\) meV at full saturation with water in an environmental chamber, as observed by Yavari et al.\(^6\). This discrepancy to our results might be attributed to the use of a \( \text{SiO}_2 \) substrate and its defects, as well as defects in the graphene sheet (caused by defects of the substrate and by the usually applied exfoliation technique), altering the response to the water molecules.

### 4.3 Effects of the h-BN substrate

Fig. 4 shows that the orientation and structure of the water molecules on h-BN supported graphene. Geometries are nearly the same as with graphene alone. For a single water molecule, e.g., the water molecule is slightly closer to the graphene sheet when supported by h-BN, with the hydrogen atoms being at about \(2.81/3.06\) Å with respect to \(2.79/2.95\) Å, and the oxygen atom is at \(3.07\) Å vs. \(3.04\) Å.

In the case of 10 molecules, the hydrogen-bond lengths are between \(1.70\) and \(1.93\) Å, which is about the same as without h-BN. The atom closest to graphene/h-BN is an hydrogen atom and about \(2.32\) Å apart. An obvious difference is that two water molecules went out of the plane, indicating that the attractive force for the water cluster is not raising when adding the h-BN layer, and it rather rearranges itself but to interact with graphene/h-BN. The distance of graphene and h-BN is about \(3.22\) Å. When comparing the interaction energy
per water molecule (see again Table 3) with respect to the one for free-standing graphene, it can be seen that it slightly higher, but it rapidly decreases from -194 to -82 meV when passing from one to ten water molecules, and then does not change for the full coverage.

When graphene is supported on h-BN, band structures, as shown in Figure 5 (1c), (2c), and (3c) are not influenced by the interaction with the substrate. As expected, a band gap opening is observed but it is still very small and close to the graphene/h-BN system alone, that is 99 meV. The presence of adsorbed water molecules only slightly perturb the band structure. Overall, the h-BN substrate has a minor impact on the structure and the studied electronic properties (although it can be objected that this is an artefact of the simplified model used to describe the dispersion forces).

5 SUMMARY AND CONCLUSIONS

In the present work, we did a step forward in describing the water/graphene system with respect to classical and semiclassical simulations. We used the B3LYP-D*+gCP method, allowing for cost-effective quantum mechanical calculations and in turn to investigate the electronic properties of the water/graphene system at an unprecedented accuracy. We have shown that the effect of water on band structure of free-standing and h-BN supported graphene is negligible thus preserving the electronic properties of the system.

For that, we have assessed DFT methods (PBE and B3LYP) augmented with two empirical terms: one to include dispersion interactions (i.e. D2/*, D3 and D3+E(3))\textsuperscript{36–39} and the other one to correct for the BSSE, through the recently proposed geometrical counterpoise correction\textsuperscript{53,54}, in the study of the adsorption of water molecules (from one over ten per cell to full coverage) on graphene and h-BN supported graphene. In particular, we focused

\textsuperscript{2}Overall, the gCP correction allows to use intermediate sized basis sets like the 6-31G(d) one. This makes the calculation rather cheap even with a hybrid functional. For instance, the largest system we have investigated (i.e. 10 water molecules on graphene/h-BN) consists of 226 atoms with 2924 atomic orbitals in the unit cell, without symmetry operators. For an energy and gradient calculation at B3LYP level, which is representative of a typical run when doing a geometry optimization, takes 13.6 min for a single SCF cycle (14 iterations) and 49.6 min for a single gradient step on 64 cores (Intel Xeon E5-2680 @2.7 GHz) by using the massive parallel version of CRYSTAL.
Figure 5: The electronic band structure (10 bands) of graphene supercells and different amount of water molecules on graphene and graphene/h-BN. (1a/b/c) utilizes a 3x3 hexagonal supercell, (2a/b/c) a 7x7 hexagonal supercell, and (3a/b/c) a 4x4 hexagonal supercell. The supercells including only graphene are not fully exploiting translational symmetry in direct space and cause the bands in the Brillouin zone to fold, leading to differing band structures for 1a, 2a and 3a. The band gaps are explicitly listed in Table 3. There are no emerging water bands in the area of interest around the band gap.
on the gCP correction which is an inexpensive and effective way to remove both intra- and inter-molecular BSSE when using small-to-medium basis sets and permits to correct both energy and gradients.

In order to benchmark the empirical corrections, a model system composed of a single water molecule and a graphene layer has been considered. We have compared the adsorption energies and equilibrium distances computed with DFT-Dn+gCP methods to BSSE-free DFT-Dn results, corrected with the Boys-Bernardi approach, and to reference CCSD(T) results\(^3\). Computed data show that the B3LYP hybrid functional, in combination with gCP and all considered types of dispersion corrections, gives good results with respect to highly sophisticated methods like MP2 and CCSD(T) at a remarkably lower cost. In particular, DOWN structures are in very good agreement with CCSD(T), while UP structures show a larger error, but still well capture the essence of the interaction. We have then extended the calculations to h-BN supported graphene and more water molecules. Because of the interest of the studied systems for their electronic properties, we have taken advantage of the fact that the B3LYP hybrid functional provides better results than the semilocal PBE functional for both hydrogen-bonded systems and, in particular, for the prediction of the electronic band structure and the corresponding band gap.

We have shown that for one water molecule adsorbed on graphene, the presence of h-BN as a supporting material leads to a very small increase of the interaction energy. Furthermore, calculations on an increasing number of water molecules confirm that the interaction of water (molecule, cluster, layer) with graphene, when referred to a single water molecule, is somewhat small and, not unexpectedly, H-bonding between water molecules dominates with respect to weaker van der Waals interactions.

Overall, present results agree with recent experimental works and classical simulations on the wettability of graphene\(^7,8,19\). In fact, we have shown that for both free-standing and h-BN supported graphene: (i) van der Waals forces control the wetting; (ii) the electronic properties are not perturbed by the presence of water, when a physically motivated non-polar water monolayer model is adopted; and (iii) van der Waals forces dominate the h-BN interaction thus making it a good candidate for a substrate to grow graphene on it.

In this respect, the B3LYP method augmented with both dispersion correction and geomet-
rical counterpoise correction is a clear advantage to get more insights on electronic properties of graphene based materials and help to interpret results from experiments. This study has indeed demonstrated that B3LYP-D*+gCP can be fruitfully employed to investigate the graphene/water interaction with a good accuracy at a low computational cost.

In perspective, this will permit to extend the present work to study both the interaction of larger molecules on graphene and more complex graphene-based systems with a greater technological interest.

6 ACKNOWLEDGMENTS

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70. See Supplementary Material Document No.___________.


