

Comment on “Theoretical study of the dynamics of atomic hydrogen adsorbed on graphene multilayers”

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It is shown that the theoretical prediction of a transient magnetization in bilayer and multilayer graphene (Moaied *et al.*, Phys. Rev. B 91, 155419, 2015) relies on an incorrect physical scenario for adsorption, namely one in which H atoms adsorb barrierless on graphitic substrates and form a random adsorption pattern of monomers. Rather, according to experimental evidence, H atom sticking is an activated process and adsorption is under kinetic control, largely ruled by a preferential sticking mechanism that leads to stable, non-magnetic dimers at all but the smallest coverages (<0.004). Theory and experiments are reconciled by re-considering the hydrogen atom adsorption energetics with the help of van der Waals-inclusive density functional calculations that properly account for the basis set superposition error. It is shown that today van der Waals-density functional theory predicts a shallow physisorption well that nicely agrees with available experimental data, and suggests that the hydrogen atom adsorption barrier in graphene is 180 meV high within ~ 5 meV accuracy.

In a recent study¹ Moaied *et al.* discussed the fascinating possibility that H atoms adsorbed on bilayer (BLG) and multilayer (MLG) graphene may temporarily occupy one sublattice only, thereby displaying a transient ferromagnetic behavior. The latter is characterized by a very high Curie temperature² and supposedly lasts hours if the substrate is kept at moderately low temperatures ($\sim 0^\circ$ C according to the results of the kinetic simulations of Ref. 1). The rationale behind this finding is that, differently from what happens in single layer graphene (SLG), a sublattice imbalance results in the MLG surface from interlayer interactions (assuming Bernal stacking), and this translates into a smaller chemisorption energy for H adsorbing at an α site (with a C underneath) than for H at a β site (without a C atom underneath). As a consequence, the desorption rate is larger for α hydrogens than for β hydrogens, and may determine a temporary excess population on β sites.

The above finding relies on the assumption that the adsorption and desorption kinetics lead to negligible formation of nonmagnetic dimers, otherwise H atoms would get trapped in more stable structures and be only able to leave the surface at high temperatures ($T > 400$ K) as H₂ molecules³. The authors of Ref. 1 did consider diffusion-mediated dimer formation and clustering, but overlooked the possible occurrence of a preferential sticking mechanism that favors adsorption of H atoms in pairs⁴. The latter is in fact the main pathway forming the experimentally observed hydrogen dimer structures³⁻⁵, since H atom diffusion hardly occurs in graphene⁴ and only sets in upon hole doping⁶. Had the authors of Ref. 1 used randomly arranged dimers, desorption would have hardly

resulted in a temporary sublattice imbalance (and related magnetization).

Preferential sticking is a simple manifestation of the huge impact that sticking of hydrogen atoms has on the graphene electronic structure⁸. In fact, the adsorbate-induced midgap state accompanying adsorption (semi)localizes around the adatom, in the opposite sublattice, and (exponentially) increases the reactivity of specific lattice positions by decreasing the energetic barriers that projectile gas-phase atoms need to overcome for sticking at those positions^{4,8}. Adsorption becomes barrierless or only weakly activated in the so-called *para* and *ortho* positions next to a previously adsorbed species^{4,8} – in sharp contrast to what happens for isolated lattice sites^{4,8,11-19} – and this makes clustering possible already at very small coverages, irrespective of the mobility of the adsorbed species. In fact, at a coverage of only *ca.* 0.004, more than 75% of atoms were found in dimer structures, a percentage well in excess to the predictions of a random adsorption model⁴.

The height of the adsorption barrier is yet unknown with precision, but its existence is undeniable. Without an energy barrier for adsorbing H atoms no preferential sticking would occur and a random arrangement of monomers would be the most likely outcome at any coverage, in contrast to observations^{4,5,9}. In addition, cold atomic beams would be effective in depositing H atoms on room temperature surfaces, something that has been ruled out with dedicated experiments using an inductively coupled plasma source delivering ~ 0.025 eV H atoms¹⁰. These results have a firm experimental^{4,5,9,10} and theoretical^{4,8,11-19} basis and are at the origin of puzzling issues in the chemistry and physics of the Universe⁷.

In view of the above, the assumption of Moaied *et al.* of a random adsorption model and the results of their ex-

tensive first principles investigation¹ appear rather surprising. The authors of Ref. 1 used a modern density functional including a nonlocal correlation energy term to describe van der Waals (vdW) interactions, *i.e.* a theory level substantially higher than many other used in previous reports on the subject^{4,8,11–13,15,16}, and found no energetic impedement for gas-phase H atoms to adsorb on the surface. The transition state barrier separating the physisorption from the chemisorption minima was located significantly below the asymptotic energy (by about 150 meV), thereby challenging the above mentioned consolidated observations pointing toward an activated adsorption of gas-phase H atom species.^{4,8,11–13,15,16} This finding suggests a serious failure of vdW-DFT, and calls for a deep reconsideration of the energetics of H atom adsorption on SLG and BLG and a reconciliation between theory and experiments.

In the rest of this Comment we shall address precisely these issues focusing on two key aspects affecting the DFT results, that is (i) the truncation errors associated with the use of atom-centered basis sets and (ii) the choice of the van der Waals functional. We shall show that currently available vdW-inclusive density functionals, when corrected or freed from basis-set truncation errors, predict a sizable adsorption barrier and, in addition, a shallow physisorption well that nicely agrees with available experimental data. We will further argue that the $\alpha - \beta$ sublattice chemisorption energy difference in BLG and MLG is considerably smaller than the estimate from Ref. 1, and probably irrelevant for any practical purpose. This is a consequence of the weaker interaction that we find between graphene layers and that is consistent with the known cohesive and exfoliation energies appropriate for graphite. Importantly, the present study highlights the need of curing the side-effects related to the use of atom-centered basis sets. Thanks to their computational efficiency, these compact sets are indeed becoming increasingly popular but, if not properly handled, they may compromise the accuracy attainable nowadays by the most recent density functionals.

We begin by critically re-analyzing H atom adsorption on SLG. As mentioned above, and differently from many previous reports^{4,8,11–13}, Moaied *et al.*¹ used vdW-inclusive DFT calculations to describe H sticking in SLG and BLG. They employed the SIESTA simulation method²⁶ whereby the Kohn-Sham (KS) orbitals are expanded on a set of atomic-like orbitals with compact support, a very efficient strategy that allows one to easily handle hundreds (and thousands) of atoms and to obtain, *e.g.*, adsorption energies which are well converged with respect to the simulation cell. It is known though that such an approach is plagued by the Basis Set Superposition Error (BSSE)²⁷, an error due to the geometry dependency of the basis-set and the related variation of the truncation error across the system configuration space. BSSE is the overestimate of the interaction energy between two systems due to the better description that results from the proximity of the two fragments.

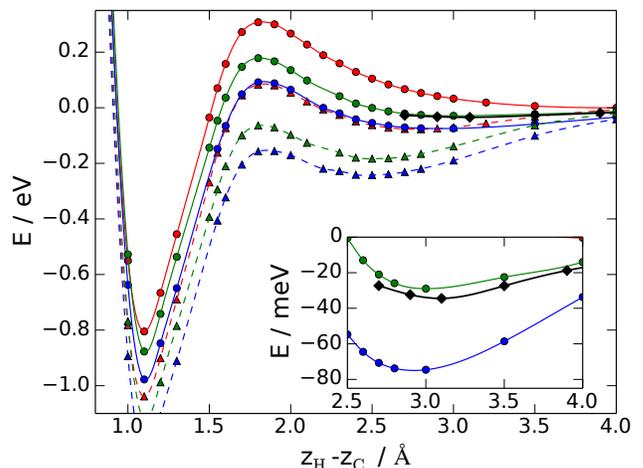


Figure 1. Adsorption energy curves for H adsorption on graphene. Results are shown for different functionals (PBE²¹ in red, vdW-DF^{22,23} in blue and vdW-VV²⁴ in green), both without (triangles) and with (circles) CP correction of the BSSE. Solid and dashed lines are spline interpolations to guide the eyes. The inset is a blow-up of the physisorption region where the benchmark results from Ref. 25 (black) are made more visible.

To quantify this error in the present problem we re-computed the adsorption profile using exactly the same set up of Ref. 1, with the SIESTA simulation code²⁶, and accounting for the BSSE. Fig. 1 reports the adsorption energy curves corresponding to different functionals, as obtained by fixing the value of $z_H - z_C$ and relaxing the remaining coordinates, z_H (z_C) being the height of the incoming H (the binding C) atom above the surface. (The reasons behind this choice of the “reaction coordinate” will be outlined below, at the end of this comment). Both bare and corrected results are reported, BSSE being here corrected with the popular *a posteriori* counterpoise (CP) correction²⁸. The latter, though not entirely free of problems²⁹, represents a pragmatic and sound way to reduce the overbinding due to the use of atomic orbital (AO) sets, since it only requires additional single point calculations with “ghost atoms” that re-define, for each geometry, the appropriate asymptotic situation to compare with. As can be seen in Fig. 1, BSSE strikingly affects the shape of the adsorption energy curve and results in a severe overestimation of the physisorption binding energy and underestimation of the barrier height. When BSSE is properly accounted for, no physisorption is present when using semilocal functionals (which is a well known shortcoming of standard DFT), while the vdW functionals present a dispersive well in the order of tens of meV. Because of this, the accuracy of the DFT calculations by Moaied *et al.* is clearly questionable much above the meV range claimed by the authors.

Fig. 1 also shows the physisorption curve that results from a correlated-wavefunction calculation of the energy of a H atom approaching coronene, a cluster model of

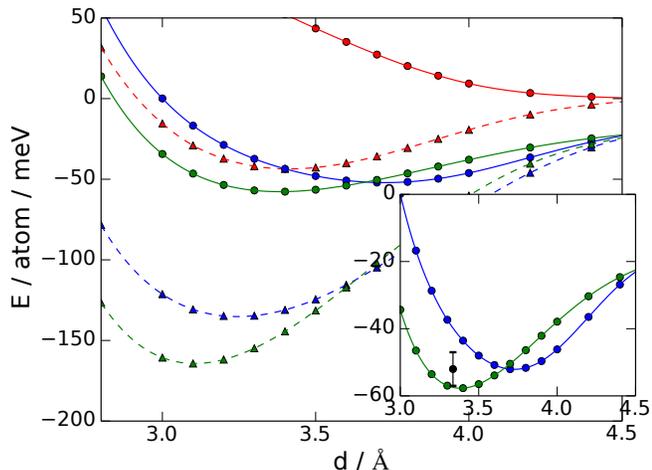


Figure 2. Interlayer interaction energy in BLG. Results are shown, as function of the interlayer distance d , for different functionals (PBE in red, vdW-DF in blue and vdW-VV in green), affected by the BSSE (triangles) and corrected with the CP method (circles). Solid and dashed lines are spline interpolations to guide the eyes. The inset is a zoom-in of the physisorption region, where the black dot marks the cohesive energy of graphite of Ref. 35.

graphene²⁵. This latter quantum chemistry study predicts a stable physisorption minimum at the “hollow” position (*i.e.*, above the center of a carbon hexagon) that is only 5.0 meV deeper than that at the “top” position shown in Fig. 1. The corresponding physisorption binding energy of 39.7 meV is in excellent agreement with the value of 39.2 ± 0.5 meV inferred for SLG from the position of the selective adsorption resonances observed in H atom scattering off graphite³⁰, thus making the results of Ref. 25 a reliable benchmark for the physisorption regime. It can be appreciated from Fig. 1 that the vdW-DF functional adopted by Moaied *et al.*¹ - the one developed by Dion *et al.*²², in the efficient implementation given by Román-Pérez and Soler²³ - largely overestimates the binding energy in this regime, even when corrected for the BSSE. Several non-local functionals^{31–34} behave rather similarly, being simple variants of the original version proposed by Dion *et al.*²². The notable exception is the recent functional developed by Vydrov and Van Voorhis²⁴ (vdW-VV), whose CP-corrected physisorption curve reported in Fig. 1 is seen to agree rather well with the benchmark. Such functional predicts a binding energy to the top site of 29 meV, only ~ 5 meV smaller than the benchmark, and thus appears to be the most accurate for the problem at hand (and likely for many other, since Vydrov and Van Voorhis reported analogous accuracy on several examples of this kind²⁴). Accordingly, the vdW-VV energy of 179 meV at the top of the barrier in Fig. 1 represents the most appropriate value of the height of the adsorption barrier for H on graphene, with an estimated accuracy of ~ 5 meV.

BSSE affects similarly the binding between graphene layers, which is at the origin of the sublattice imbalance

method	E_{BLG}	E_{coh}	E_{ex}	E_{cle}
vdW-DF/PW	46	51	51	58
vdW-DF/DZP/CP	51	54	53	56
vdW-VV/PW	47	54	54	62
vdW-VV/DZP/CP	49	54	55	63

Table I. Some significant energies (in meV per atom) in BLG and graphite, as obtained with vdW-DF and vdW-VV using either plane-waves or the DZP atomic orbital set (in conjunction with the counterpoise correction) and the experimental lattice parameters of graphite. E_{BLG} is the binding energy in bilayer graphene, whereas E_{coh} , E_{ex} and E_{cle} are, respectively, the interlayer cohesive energy, the exfoliation energy and the cleavage energy of graphite.

in BLG invoked by Moaied *et al.*¹. Such attractive interaction represents indeed a restoring force opposing to the surface puckering that accompanies hydrogen adsorption, and it acts differently depending on whether the H atom adsorbs on the “softer” β site or on the “stiffer” α site, thereby determining the limiting value Δ_∞ that the $\beta - \alpha$ chemisorption energy difference, $E_b(\beta) - E_b(\alpha)$, takes in the diluted limit. Fig. 2 shows the interlayer interaction energy of BLG (per C atom in one layer), as obtained with the SIESTA DZP set for different functionals, at several values of the distance d between the two layers (arranged in Bernal stacking). The binding energy in BLG is not experimentally known, but its value is bound from above by the interlayer cohesive energy of graphite³⁶, namely 52 ± 5 meV/atom according to Zacharia *et al.*³⁵ [from plane wave (PW) calculations we estimate that the graphite cohesive energy is *ca.* 10% larger than the binding energy in BLG, see Table I below]. In Fig. 2 the experimental result by Zacharia *et al.* is placed at an interlayer distance of 3.336 Å, corresponding to the interlayer spacing in graphite³⁷, and clearly shows that the BSSE associated with the adopted DZP set makes any functional considered largely overbinding; even the semilocal functional PBE turns out to be binding and, surprisingly, predicts a minimum at the correct d value (~ 3.41 Å) and with a reasonable depth (~ 43.6 meV). Upon correcting the data according to the CP scheme only the non-local functionals, as expected, predict interlayer binding. vdW-VV appears again more accurate than vdW-DF in the equilibrium position but they both overestimate the energy, especially in light of the fact that the reference cohesive energy needs to be reduced to give the binding energy in BLG. However, BSSE is not the only truncation error, and the CP correction is not exact. In fact, additional plane wave calculations performed with Quantum Espresso³⁸ predict BLG to be slightly less bound when compared to AO-based calculations with the same functionals at the same geometry; see Table I for a summary of the BLG and the MLG energetics, as obtained with the above vdW functionals using either plane-waves or atomic-orbital sets³⁹.

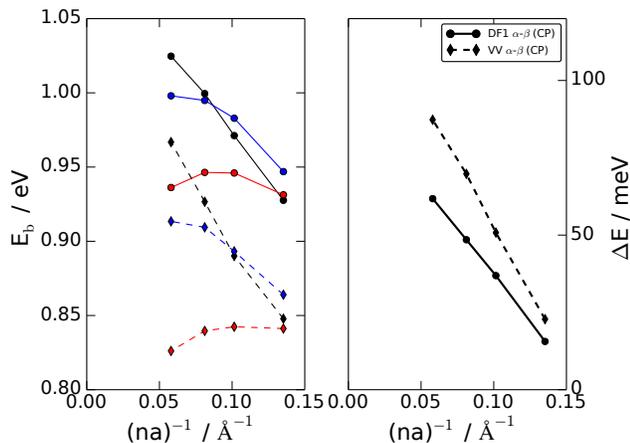


Figure 3. Hydrogen binding to SLG and BLG. Left: CP-corrected binding energy E_b as a function of inverse cell size, for vdW-DF (solid lines) and vdW-VV (dashed lines). Black symbols are for SLG, while red and blue symbols are for α and β sites in BLG, respectively. Right: the computed difference $E_b(\beta) - E_b(\alpha)$ in BLG, for vdW-DF (solid lines) and vdW-VV (dashed lines).

As stated above the interlayer interaction just described has important consequences for the chemisorption sublattice imbalance in BLG and MLG. Moaied *et al.*² found $\Delta_\infty = 85$ meV, a value which is likely overestimated by the incorrect description of binding in BLG. This is not due to the direct effect that the BSSE has on the BLG-H energetics, and it is not easily corrected with the CP scheme. Fig. 3 indeed shows that the BSSE has little effect on the limiting energy difference, which we too find to be ~ 85 meV when using vdW-DF and including the CP correction, and even larger with the more binding vdW-VV. However, Fig. 3 also shows that the effect of the interlayer interaction is overemphasized. From the left panel of Fig. 3, it can be seen that, in the diluted limit, the chemisorption energy on SLG is larger than the values it takes on BLG, in agreement with experimental observations²⁰. The reduction of binding energy when passing from SLG to BLG can be as large as 100 meV, a value which compares favorably with the interlayer interaction energy computed at the same theory level (Fig. 2, dashed lines), as it should do since this is the energy lost by the binding carbon atom when it is pulled out of the surface in the adsorption process. As shown above, though, such interaction energy is largely overestimated (by several tens of meV) in BLG because of the BSSE, and the same likely occurs for the SLG-BLG differences in the adsorption energetics and for the chemisorption sublattice imbalance Δ_∞ . Unfortunately, since the CP correction is *a posteriori* (*i.e.* it uses geometries which are optimized with the BSSE included) there is no simple way to fix the overbinding in BLG while computing the H adsorption energetics. The only remedy is to resort to (expensive) plane wave calculations extrapolated to the diluted limit, something that is well beyond the

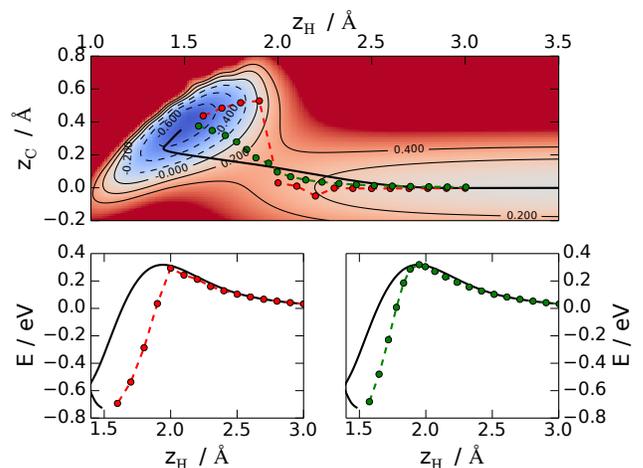


Figure 4. Top panel: the CP-corrected PBE potential energy surface describing H adsorption on SLG is shown as a function of z_H and z_C (see text for details). The black line follows the minimum energy path, while the red (green) line represents the path which results from constrained minimizations at selected values of z_H ($z_H - z_C$). The adsorption profile *vs.* z_H along the above paths, color coded as in the top panel.

aims of this Comment. We can though provide a reasonable estimate of this error by comparing PW and AO results at a fixed supercell size. Using PWs³⁸ we find that the energy difference $E_b(\beta) - E_b(\alpha)$ in the 4×4 supercell ($na^{-1} = 0.101 \text{ \AA}^{-1}$) is more than halved with respect to the AO result, *i.e.* it goes from 37 (51) meV to 14 (24) meV for vdW-DF (vdW-VV). Hence the estimated value of Δ_∞ of Ref. 1 is likely too large by $\sim 50\%$ ($\sim 25\%$) in comparison to the BSSE-free vdW-DF (vdW-VV) result.

Finally, before concluding, we briefly comment on our choice of the adsorption coordinate ($z_H - z_C$), which may appear strange at first sight, being at odds with the common practice (z_H). This choice is arbitrary to a large extent, but is bound to be representative of the adsorption process under consideration; in particular, it must guarantee a faithful representation of the transition state region that is crucial for the adsorption dynamics⁴⁰. Fig. 4 shows the pitfalls of using z_H as representative coordinate. It displays the mass-weighted minimum energy (reaction) path⁴¹ for H adsorbing on SLG, superimposed on a two-dimensional cut of the potential energy surface (PES). The latter was obtained for collinear configurations of the hydrogen and the binding carbon atoms, at fixed values of their heights, by optimizing the remaining coordinates of a 6×6 supercell, using the PBE functional and including the counterpoise correction. As is evident from Fig. 4, because of the shape of the PES in the transition state region, a sudden jump occurs between the two sides of the barrier when following the PES minima at constrained z_H values. In this way, it is rather difficult (if not impossible) to locate the saddle point with precision, and the barrier height is most likely underestimated (bottom left panel). Moreover, this jump

determines a singularity in the adsorption profile, which Moaied *et al.* erroneously attributed to the spin symmetry breaking of their DFT calculation. The barrier does result from a crossing between different *adiabatic* curves⁸ but is smoothed already at the KS-DFT level of theory, as Fig. 4 unambiguously shows. On the contrary, the adsorption profile appears smooth and the barrier height more precisely determined when using $z_H - z_C$ as adsorption coordinate (bottom right panel).

To summarize, a recent DFT investigation of hydrogen adsorption on SLG and BLG using vdW-inclusive functionals challenged a number of well-established results. By critically re-analyzing the adsorption process we have reconciled theory and experiments and proved that the correct physical scenario for such a process involves formation of dimers (and larger clusters) at all but very small coverages, thereby undermining the founding assumptions behind the prediction by Moaied *et al.*¹

of a transient ferromagnetism in hydrogenated BLG and MLG.

Importantly, our results highlight the need of carefully controlling truncation errors such as the BSSE, especially when vdW interactions are of concern. Given the recent progress of DFT in describing vdW forces and the potentiality of AO-based DFT methods in handling systems that are much larger than PW methods allow to, an *a priori* scheme which can alleviate or correct the BSSE in a consistent way appears more timely than ever.

On the bright side, our study highlights the role of the adsorption barrier in determining the arrangement of the ad-species on the surface. Breaking the graphene sublattice degeneracy through interactions with other graphene layers or other 2D materials in close registry - a plausible route to magnetic graphene^{2,42} - is not likely to succeed unless, at the same time, such a barrier is made vanishingly small and preferential sticking silent.

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