Hydrogen is frequently touted as the “fuel of the future” because of its huge potential as clean energy source, although the large-scale adoption of this technology has yet to be realized. One of the remaining barriers to the utilization of hydrogen energy is an efficient and inexpensive means of hydrogen storage. In this work we investigate the nature of this process by first principle calculation.

In particular, we study the way in which the $\text{H}_2$ molecule can interact with graphene sheet through physisorption and chemisorption mechanism.

The first mechanism involves the condensation of the hydrogen molecule on the graphene as a result of weak van der Waals forces, while the chemisorption mechanism involves the preliminary dissociation of the $\text{H}_2$ molecule and the subsequent reaction of hydrogen atoms with the unsaturated C-C bonds to form C-H bonds.

To study carefully the possible physisorbed configurations on the graphene sheet, we take in to account van der Waals (vdW) interactions in DFT using the new method (DFT/vdW-WF) recently developed in our group and based on the concept of maximally localized Wannier functions.

There are three possible way in which the $\text{H}_2$ molecule can adapt to the structure of graphene: the hollow, the bridge and the top site called H, B and T configurations, respectively. We find the hollow site to be most stable physisorbed state with a binding energy of -50 meV. This value, in agreement with experimental results, is also compared with other vdW-correction methods as described in the following paper.

Diffusion of the physisorbed configurations on the graphene sheet and activated reaction pathways in which the molecule starts from a physisorbed configuration to end up in a chemisorbed configurations have also been studied.

Keywords: Density functional theory, first principles, physisorption and chemisorption

1. Introduction

Carbon-based nanomaterials like graphite (G), have attracted much attention because of their suitability as materials for gas storage. In particular, the reported high hydrogen uptake of these materials make them attractive for hydrogen storage devices in fuel-cell-powered
electric vehicles [1]. Among the available carbon nano-
materials, the graphene sheet is the simplest one and
may store hydrogen on both side of its structure.

Understanding the hydrogenation of graphene lay-
ers is important from several perspectives. For example,
Elias et al. [2] demonstrated the reversible transition of
graphene layers from semimetallic to semiconducting af-
ter hydrogenation. This is an important issue to help the
use of graphene layers in microelectronics.

To address the problem of hydrogen storage is
also very important to understand the interplay be-
tween molecular physisorption and atomic chemisorp-
tion. These are also the two possible ways in which the
hydrogen molecule may interact with carbon materials.
Many theoretical calculations have been published on the
physisorption states of hydrogen molecule on graphene
using Density Functional Theory (DFT) and indicating
binding energies of the order of 80-90 meV [3],[4].

Unfortunately, the majority of these article neglects
the importance of van der Waals (vdW) interactions for
these kind of systems.

In our work, we properly take into account vdW
interaction in DFT using the DFT/vdW-WF method [5],
[6], recently developed in our group and based on the
concept of maximally localized Wannier functions. This
new technique aims at combining the simplicity of the
semiempirical formalism with the accuracy of the first
principles approaches.

Our calculations so far show the catalytic effect due
to the graphene surface on the dissociation energy of the
isolated H₂ molecule.

Finally, we use different schemes to include vdW
interactions in the DFT calculations and compare our
results with recent literature [7],[8],[9],[10],[11] recently
published on these systems, where non covalent interac-
tion are taken in to account.

2. Methods

2.1. DFT calculations

Calculations were performed with the CPMD pack-
age [12]. This is a general ab initio Car-Parrinello mole-
cular dynamics code [13], based on density functional
theory.

For all the calculations, the generalized gradient ap-
proximation (GGA), in the PBE flavor [14], was adopted
for the exchange-correlation contribution.

Although sometimes PBE provides reasonable esti-
mates for the interaction energy in weakly bound systems
due to a favorable errors or cancellations, this agreement
should be considered accidental because it is not able to
reproduce genuine vdW effects, therefore including vdW
corrections is essential.

Only valence electrons were treated explicitly and
interactions with the ionic cores were described by
norm-conserving pseudopotentials generated according
to the prescription due to Troullier and
Martins [15].

The Graphene sheet was model using a
periodically-repeated slab with a single layer of 32 C
atoms.

The symmetry of the cell was hexagonal with the
following dimensions a ~18.6 bohr, b = a and c ~46.5
bohr and a vacuum region of 17 Å wide along z, sepa-
rates the repeated images of the slabs.

To sample the Brillouin zone only the Γ point was
considered. The Kohn-Sham orbitals were expanded in
plane waves up to an energy cutoff of 70 Ry, which
is sufficient to yield converged structural properties for
these kind of systems.

As better explained in the following section, we cal-
culated vdW corrections with various methods.

Complementary DFT calculations have therefore
been performed with Quantum-Espresso package [16],
adopting ultrasoft pseudopotentials, where vdW-DF
method [17] has been implemented.

Although some works have already been reported
on the interaction of H₂ molecule with graphene sheet
including vdW interactions [7], [10], our results, rep-
resent a step forward to include vdW interaction in a
simple and accurate way, in a reasonable agreement with
those obtained by very sophisticated quantum-chemistry
methods like CCSD and MP2 [10].

2.2. Treatment of the van der Waals interactions

A known drawback of standard DFT methods con-
cerns their failure to describe vdW interactions, and in
particular the leading term -C₆/R₆, which result from
electron correlation effects. An adequate treatment of
these effects is nonetheless essential to study physisorp-
tion states, that are weakly-bonded configurations where
dth W dispersion interactions play a key role. We over-
came the DFT limitations by applying the DFT/vdW-WF
method reported in full detail in Ref. [5],[6]. The method
is based on the generation of the maximally localized
Wannier functions (MLWFs) and uses as only input the
ground state Kohn-Sham orbitals computed in the con-
ventional DFT approach. The MLWFs, a generalization
of the localized Boys’ orbitals [18] for systems charac-
terized by periodic boundary conditions, allow the total
electronic density to be partitioned into individual frag-
ment contributions, in a chemically transparent fashion.
Once the MLWFs are obtained, the leading -C₆/R₆ vdW
correction terms are e valuated by suitable expressions
for long range interactions between separated fragments of matter [19],[5]. The method has been already successfully applied to small molecules, bulk, and surface systems [20],[6].

To confirm our results and to test our method, we have also calculated vdW corrections with other methods like the well-known "seamless" vdW-DF method [17] based on the calculation of the non local correlation energy and a semiempirical approach: the DFT-D method [21] which consists of adding a $-C_6/R^6$ dispersion correction to the conventional Kohn-Sham DFT energy, where the vdW interactions are described via a simple pair-wise force field.

### 2.3. Hydrogen physisorption on graphene

Several calculations have been performed on the static configurations of the graphene-hydrogen system. Fig. 1 shows the nine configurations of the $H_2$ molecule in the hollow, bridge and top configurations where the hydrogen molecule has the axis aligned parallel or perpendicular to the graphene surface. Hollow, bridge and top sites are defined by the H, B and T letter, respectively.

![Fig. 1. Physisorbed configurations sites for the $H_2$ on graphene. H, B and T letter stands for hollow, bridge and top site, respectively](image)

#### 2.4. Adsorption on graphene

The adsorption energy of a $H_2$ molecule on a pristine graphene layer is calculated as $E_{\text{binding}} = E_{H_2-graphene} - E_{H_2} - E_{graphene}$, where $E_{H_2-graphene}$ is the energy of the system (graphene and $H_2$), while $E_{H_2}$ and $E_{graphene}$ are the energies of the isolated fragments, respectively.

Our calculations show that the most stable configuration, once including the vdW corrections, is the H3 one.

Fig. 2 shows the potential energy surface for the adsorption site H3 where the binding energy were reported as a function of the distance between the graphene sheet and the hydrogen molecule’s center of mass, ranging this from 2 to 7 Å.

The higher energy curve of Fig. 2 corresponds to the results of pure DFT calculations, while including vdW interactions, the binding energy increases by 30 or 40 meV with respect to the pure DFT results.

Our calculations with the DFT/vdW-WF[5] method gives a binding energy of -50 meV with a minimum at 3.2 Å. This value is in very good agreement with the experimental value of -47.6 meV by Mattera et al. [22] for graphite, and corrected for graphene.

The semiempirical approach DFT-D [21] and the "seamless" method vdW-DF [17], overestimate the interaction between the graphene and the $H_2$ molecule, and are in worse agreement with the experimental value [22] giving the binding energy of -98 meV at 2.8 Å and -81 meV at 3.2 Å, respectively.

The physisorbed stated can also diffuse over the graphene surface overcoming small energy barriers with diffusion barrier ($\Delta E_{\text{barr}}$) calculated just as a difference between the final and initial physisorbed state.

$\Delta E_{\text{barr}}$ is about of 10 meV for hollow configurations (H3 and H1) diffusing on the graphene surface through the bridge (B3 and B2) configurations. Similar $\Delta E_{\text{barr}}$ have been calculated for displacement across “the top” site directly above a carbon atom.

The barriers for physisorbed states are low and hence the adsorbed species can easily desorb at room temperature on a time scale of nanoseconds.

Therefore, the only way to keep such a system stable on a reasonable time scale for practical applications is to reach a chemisorbed state.

#### 2.5. Chemisorbed state on graphene

Fig. 3 shows the three possible way in which the $H_2$ molecule can dissociate on the hexagon ring: orto, meta and para positions.
Fig. 2. Physisorption of H$_2$ molecule on graphene for the H3 configuration. Pure DFT calculations are indicated by a solid line (black), DFT/vdW-WF results by a long-dashed line (red), vdW-DF by a dashed dotted line (green), and DFT-D by a dashed-dashed-dotted lines (blue).

Fig. 3. Chemisorbed state of the dissociated hydrogen H$_2$ molecule on graphene. Orto, meta and para are related to the position of the H atom on the C atoms: on two adjacent C atoms, on two alternate C atoms and on two opposite C atoms in the ring, respectively.

Fig. 4. Path from the H3 physisorbed state on graphene to the para chemisorbed state.
Although the chemisorbed state is the only way to keep the hydrogen atom on the graphene sheet, the dissociation process of H₂ molecule is not spontaneous at room temperature and need to be activated.

We study this process using the Nudge Elastic Band (NBE) [23] method, as implemented in Quantum Espresso package, to find the structure of the transition state (TS) and the minimum energy pathway between the physisorbed and chemisorbed state of H₂ molecule on graphene.

The favorable configuration is obtained when two H atoms are adsorbed on the opposite site (para position) of same hexagon ring of graphene (see Fig. 3) and in agreement with Miura [8] and Ao. [24].

The para configuration is characterized by a the C-H bond length of 1.12 Å, the C atoms move up by about 0.32 Å and with a distortion of a dihedral angle of 30°, while the C-C bond length elongates to 1.51 Å.

This is similar to the sp³ bond length of 1.53 Å in diamond while it is much longer than 1.42 Å for the sp² carbon length. The reconstruction of the graphene layer was also reported by Miura [8], who predicted that the C atoms bonded with the H atoms move out of the graphene plane by 0.35 Å [8]. In this case the carbon hexagon becomes more chemically active as it turns from sp² bonding to sp³ like bonding.

The path where the H3 configuration goes to the para configuration has the lowest energy barrier of 2.62 eV.

The transition state TS is characterized by a broken H-H bond and by the formation of a new bond C-H (1.14 Å length). Also the surface deforms quite a lot to form this new C-H bond. In fact, the dihedral angle varies from 180° from the pristine graphene to 163° in the hydrogenated graphene. Our result agrees also with the recent work from McKay et al. [9] where they show that applying an external stress to the graphene substrate can lower the barrier by a factor of 6 and change the state is the hollow site with a binding energy of -50 meV. This value is in good agreement with experimental results and is also compared to that obtained by other vdW correction methods [21].

The analysis of diffusion paths among physisorbed states show that molecular hydrogen can diffuse at room temperature from one configuration to another with energy barriers of about 10 meV.

The situation is different when the hydrogen molecules approach the carbon surface and dissociate allowing the chemisorption on the graphene surface, provided that they are able to overcome the activation energy barriers.

In particular, we calculate the potential energy surfaces for the dissociative adsorption of H₂ on highly symmetric site of graphene (ortho, meta and para position).

The lowest activation barrier of 2.67 eV is that one that describes the process going from the hollow physisorbed state to the para chemisorbed state. Other energy paths are characterized by higher activation barriers (3.0 eV).

Moreover, our calculations show the effect of the catalytic effect of the surface on the dissociation process of H₂ molecule. This results is perfectly in agreement with literature[12] and suggest the graphene as a good candidate for hydrogen storage.

3. Conclusions

We explored several adsorption sites and orientation of hydrogen molecule relative to the graphene plane: hollow, bridge and top site. The most stable physisorbed state is the hollow site with a binding energy of -50 meV. This value is in good agreement with experimental results and is also compared to that obtained by other vdW correction methods [21].

REFERENCES


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