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## HYDROGEN STORAGE ON GRAPHENE SHEET: PHYSSORPTION, DIFFUSION AND CHEMISORBED PATHWAYS BY FIRST PRINCIPLES CALCULATIONS

## MAGAZYNOWANIE WODORU NA ARKUSZU GRAFENU: ANALIZA ŚCIEŻEK FIZYKOSORPCJI, DYFUZJI I CHEMISORPCJI METODĄ OBLICZEŃ AB INITIO

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 H<sub>2</sub> 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 H<sub>2</sub> 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 H<sub>2</sub> 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

Ze względu na możliwość magazynowania wodoru na arkuszu grafenu, badamy naturę tego procesu metodą obliczeń ab initio. Cząsteczka H<sub>2</sub> może oddziaływać z grafenem na dwa sposoby: fizykosorpcję i chemisorpcję.

Mechanizm fizykosorpcji polega na kondensacji cząsteczki wodoru na grafenie na skutek słabych oddziaływań van der Waalsa, podczas gdy mechanizm chemisorpcji polega na wstępnej dysocjacji cząsteczki H<sub>2</sub> i następnie reakcji atomów wodoru z niewysycenymi wiązaniami C-C co umożliwia tworzenie wiązań C-H.

W celu zobrazowania mechanizmu fizykosorpcji cząsteczek H<sub>2</sub> na arkuszu grafenu, analizujemy oddziaływania van der Waalsa (vdW) stosując teorię funkcjonału gęstości (DFT) za pomocą nowej metody (DFT/vdW-WF) niedawno opracowanej w naszej grupie na podstawie koncepcji maksymalnie zlokalizowanych funkcji Wanniera.

Analizujemy możliwość absorpcji w różnych miejscach siatki grafenu i orientację cząsteczki H<sub>2</sub> w stosunku do płaszczyzny siatki grafenu. Najbardziej stabilnym miejscem fizykosorpcji jest wewnątrz pierścienia grafenu z energią wiązania -50 meV. Wartość ta, zgodna z wynikami doświadczeń, jest także porównywana wartości uzyskanych innymi metodami korekcji vdW.

Typowe bariery energetyczne charakteryzujące ścieżkę dyfuzji, są rzędu ~10 meV.

Sytuacja jest inna, gdy cząsteczki wodoru pokonują barierę energetyczną i chemisorbuja jako jeden atom wodoru na powierzchni grafenu. Bariery energetyczne w tym przypadku wynoszą około 2-3 eV, w zależności od wybranej ścieżki reakcji.

### 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

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electric vehicles [1]. Among the available carbon nanomaterials, the graphene sheet is the simplest one and may store hydrogen on both side of its structure.

Understanding the hydrogenation of graphene layers is important from several perspectives. For example, Elias et al. [2] demonstrated the reversible transition of graphene layers from semimetallic to semiconducting after 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 between molecular physisorption and atomic chemisorption. 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 H<sub>2</sub> 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 interaction are taken in to account.

## 2. Methods

### 2.1. DFT calculations

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

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

Although sometimes PBE provides reasonable estimates 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  $a \sim 18.6$  bohr,  $b = a$  and  $c \sim 46.5$  bohr and a vacuum region of 17 Å wide along  $z$ , separates the repeated images of the slabs.

To sample the Brillouin zone only the  $\Gamma$  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 calculated 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 H<sub>2</sub> molecule with graphene sheet including vdW interactions [7], [10], our results, represent 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 concerns their failure to describe vdW interactions, and in particular the leading term  $-C_6/R^6$ , which result from electron correlation effects. An adequate treatment of these effects is nonetheless essential to study physisorption states, that are weakly-bonded configurations where vdW dispersion interactions play a key role. We overcame 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 conventional DFT approach. The MLWFs, a generalization of the localized Boys' orbitals [18] for systems characterized by periodic boundary conditions, allow the total electronic density to be partitioned into individual fragment contributions, in a chemically transparent fashion. Once the MLWFs are obtained, the leading  $-C_6/R^6$  vdW correction terms are evaluated 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.

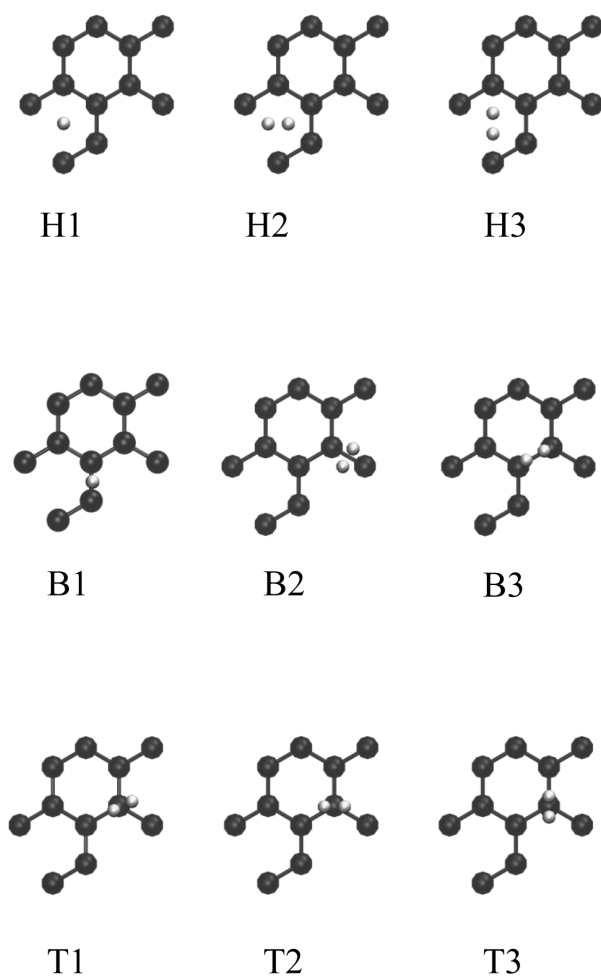


Fig. 1. Physisorbed configurations sites for the  $H_2$  on graphene. H, B and T letter stands for hollow, bridge and top site, respectively

### 2.4. Adsorption on graphene

The adsorption energy of a  $H_2$  molecule on a pristine graphene layer is calculated as  $E_{binding} = E_{H_2-graphene} - E_{H_2} - E_{graphene}$ , 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 state can also diffuse over the graphene surface overcoming small energy barriers with diffusion barrier ( $\Delta E_{barr}$ ) calculated just as a difference between the final and initial physisorbed state.

$\Delta E_{barr}$  is about of 10 meV for hollow configurations (H3 and H1) diffusing on the graphene surface through the bridge (B3 and B2) configurations. Similar  $\Delta E_{barr}$  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.

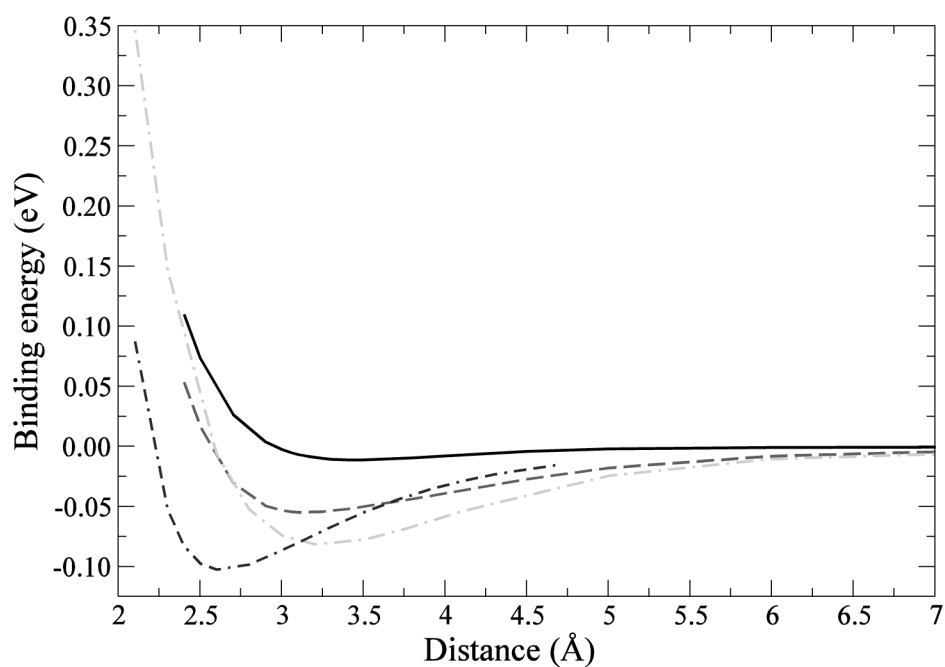


Fig. 2. Physisorption of  $H_2$  molecule on graphene for the H3 configuration. Pure DFT calculations are indicated by a solid line (black), DFT/vdW-WF results by a long-dashed line (red), vdW-DF by a dashed dotted line (green), and DFT-D by a dashed-dotted lines (blue)

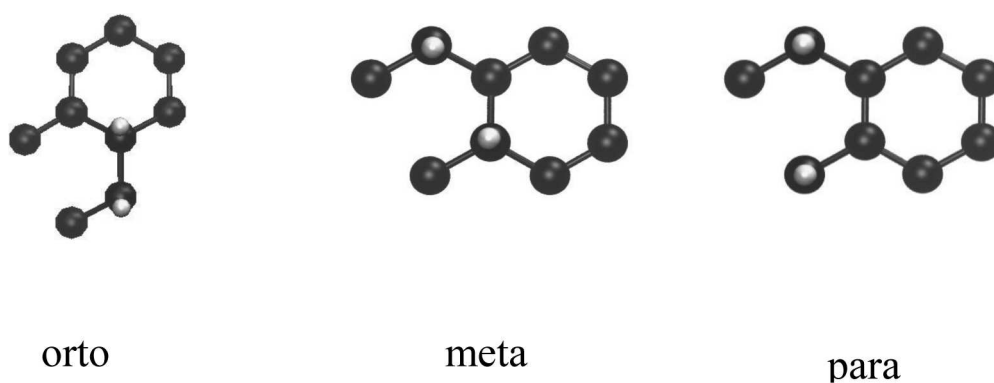


Fig. 3. Chemisorbed state of the dissociated hydrogen  $H_2$  molecule on graphene. Orto, meta and para are related to the position of the H atom on the C atoms: on two adjacent C atoms, on two alternate C atoms and on two opposite C atoms in the ring, respectively

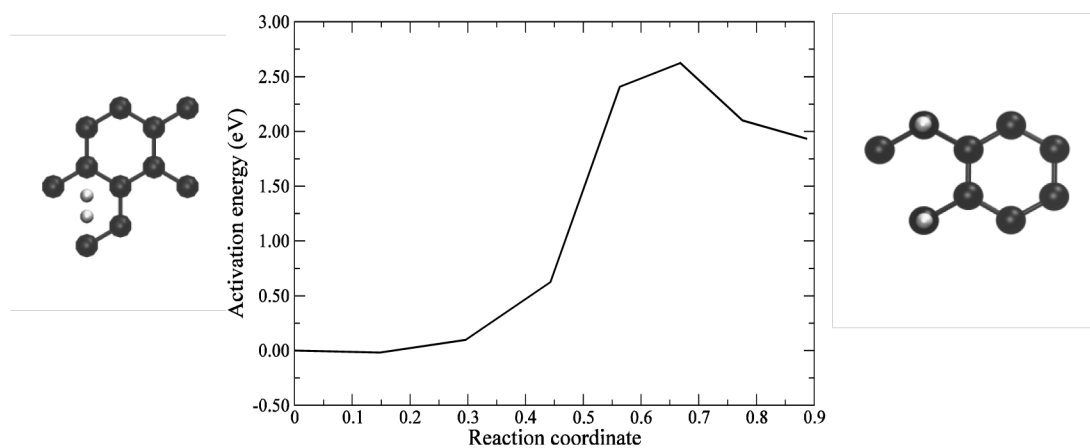


Fig. 4. Path from the H3 physisorbed state on graphene to the para chemisorbed state

Although the chemisorbed state is the only way to keep the hydrogen atom on the graphene sheet, the dissociation process of H<sub>2</sub> 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 H<sub>2</sub> 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 sp<sup>3</sup> bond length of 1.53 Å in diamond while it is much longer than 1.42 Å for the sp<sup>2</sup> 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 sp<sup>2</sup> bonding to sp<sup>3</sup> 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 process from endothermic to exothermic.

Other possible paths, however, involved as a final products orto and meta chemisorbed states. The activation energies associated to these paths are higher than 3 eV.

### 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].

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 H<sub>2</sub> on highly symmetric site of graphene (orto, 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 H<sub>2</sub> molecule. This results is perfectly in agreement with literature[12] and suggest the graphene as a good candidate for hydrogen storage.

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