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# Electron transfer study between hydrogen molecules and graphene surface

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**Abstract.** Electron transfer studies on the interaction of graphene surface and hydrogen ( $H_2$ ) molecules have been carried out. The calculations were based on the Density Functional Theory (DFT) with a basis set of Generalized-Gradient-Corrected PBE method approach (Perdew-Burke-Ernzerhof). The results showed that the optimum distance (lowest potential energy) between hydrogen molecules on the surface of the graphene was 3.2 Å, and the partial density of state (PDOS) calculation showed that the hydrogen-graphene system band gap was 2.51 eV. The electron transfer shown by the isosurface value indicates that the electron transfer from the  $p$  sub orbitals from the surface of the graphene to the hydrogen molecular orbitals was +0.3603  $e/\text{Å}$ .

## 1. Introduction

Experiments related to hydrogen compounds as energy resources in the modern era, have attracted great attention from researchers, especially on their use as energy and their storage in a material [1-6]. The nature of hydrogen gas that is reactive and flammable, causing difficulties in the storage process.

Research on the role and synthesis of graphite as a hydrogen storage medium was initiated by Chambers et al. [7]. Then, Kim and Park [8] observed that the micropore size of the porous carbons had an important role in the hydrogen adsorption at 77 K. In 2002, Browning et al. [9], carried out a synthesis of carbon nanofiber which have a high potential as a hydrogen storage medium because it was able to adsorb hydrogen by more than 4% by weight, but not yet close to the target of 6.5% by weight (the ratio of the weight of hydrogen stored in the media system, with a volume density of 62 kg  $H_2/m^3$ ).

Modeling  $H_2$  storage in a carbon-based material, specifically graphene and nanotubes, remains a challenge both in laboratory research and modeling. Computational studies on the investigations of hydrogen storage with a graphene system are not many, so the interaction of hydrogen molecules on graphene system is worth to be studied. Therefore, this research is focused on computational studies of  $H_2$  gas interaction with graphene material and the transfer electron during the interactions.

## 2. Methods

### 2.1. Computational Details

Determination of electron structure and interaction energy was calculated through the UNIX-based PWScf Quantum Espresso Schrodinger program [10]. Visualization of the program uses the UNIX-based XcryDen program [11]. In the study of interactions between hydrogen molecules on the surface of graphene, three positions of hydrogen molecules with the surface of graphene are chosen, namely:



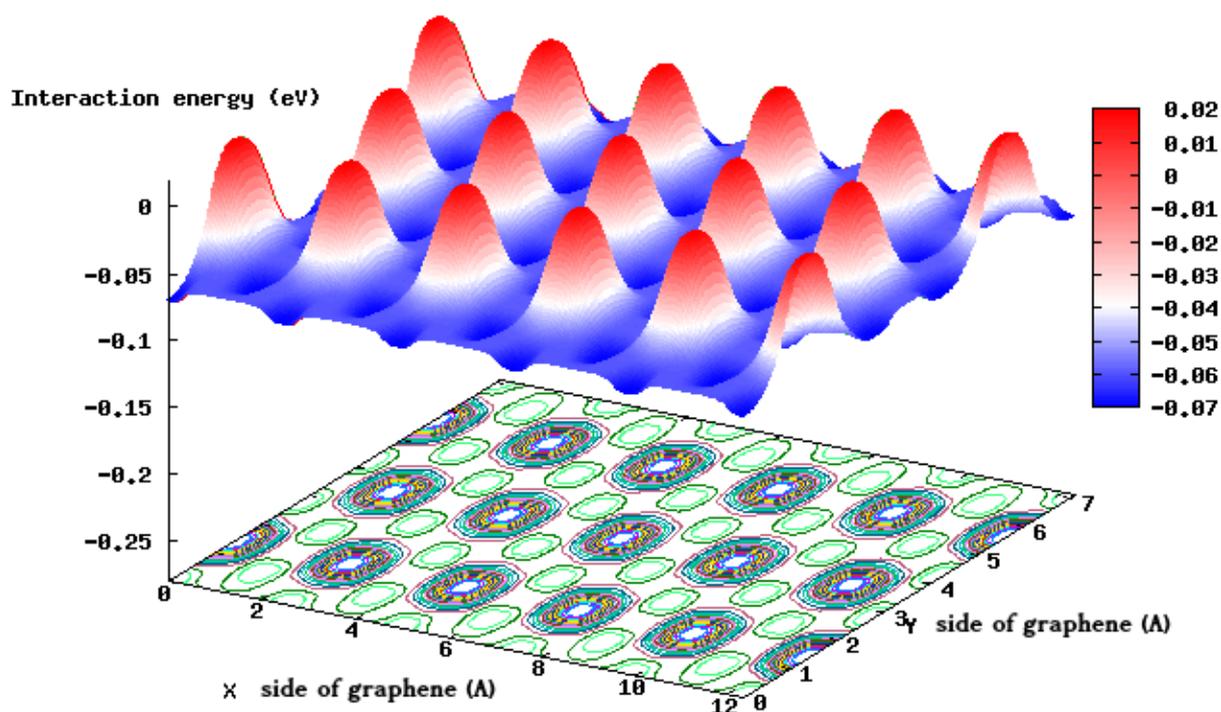
top (one hydrogen atom of the hydrogen molecule was above the carbon atom), bridge (one hydrogen atom was between two carbon atoms), and hollow (one hydrogen atom was at the top of the six carbon atom resonance ring). Calculations for different orientation of hydrogen molecules, eg parallel hydrogen position or helicopter position above the graphene surface, were not carried out.

### 2.2. Electronic Structure Calculations

In assessing the nature of solid system interactions, a change-correlation potential energy function was performed, which was based on the Density Functional Theory (DFT) with a basis set of Generalized-Gradient-Corrected PBE method approach (Perdew-Burke-Ernzerhof) [12]. This approach was chosen because it is more accurate for the atomic/molecular interaction system on a graph solid surface.

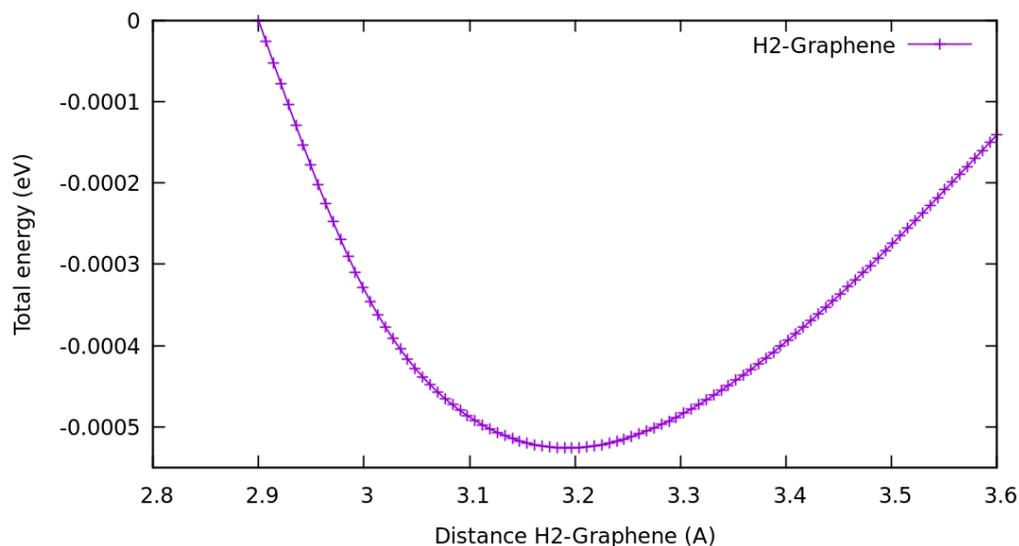
### 3. Result and Discussions

Calculation of the potential energy surface from the interaction of hydrogen molecules and the surface of the graphene was conducted by choosing the same distance between all points on the graphene surface and the hydrogen molecule. The potential energy surface curve (Figure 1) showed that hydrogen molecules in the top position produced low interaction energy (marked in blue), whereas hydrogen molecules in the bridge and hollow positions produced medium and high interaction energies (marked in white and red, respectively). This shows that the hydrogen molecule has the highest stability in the top position compared to the bridge and hollow positions. The difference in the interaction energy of each position can be expressed as follows  $E_{hollow} > E_{bridge} > E_{top}$ .



**Figure 1.** The contour and the potential energy surface of interaction between  $H_2$  molecules and graphene as a function of distance between  $H_2$ -graphene.

Calculation of the optimum distance between the hydrogen molecule and the graphene surface was done after calculating the value of the potential energy surface above, and the calculation was performed on the hydrogen molecule at the top position. Interactions between hydrogen molecules on the surface of graphene produced the optimum distance (lowest energy) (3.2 Å), with measurements ranging from 2.8 Å to 3.6 Å (Figure 2).

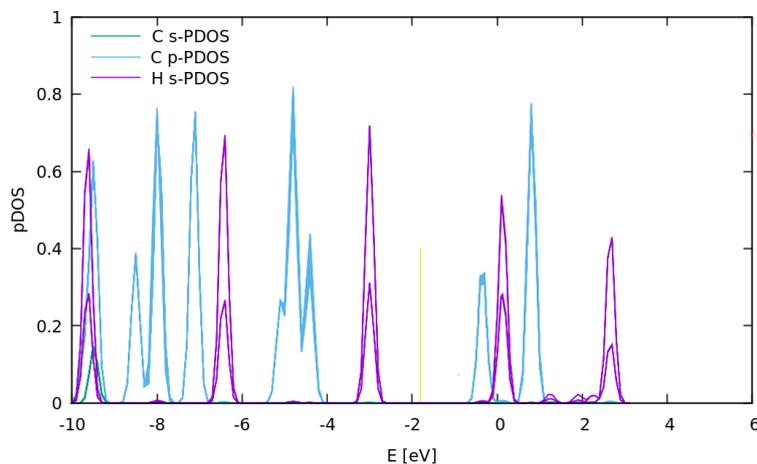


**Figure 2.** The potential energy of interaction of H<sub>2</sub> molecules and graphene as a function of distance between H<sub>2</sub>-graphene.

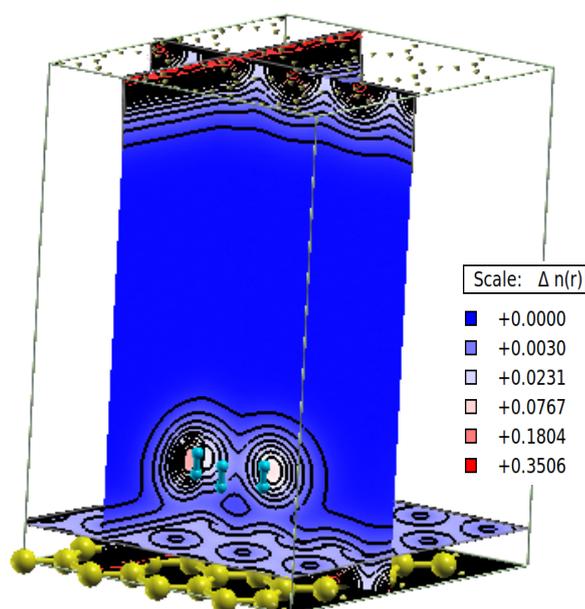
Calculation of electron density between several hydrogen molecules on the surface of graphene was performed by calculating pDOS (partial Density of State), which was a band gap calculation of the interaction between hydrogen molecules and graphene surface. This calculation showed a fairly strong interaction between s orbitals from hydrogen molecules and p orbitals from the surface of graphene. There was a uniform distribution of s orbitals of the hydrogen molecule, both in the valence band and in the conduction band, which showed the attraction of electrons from the hydrogen molecule by the graphene surface. In the valence band there was a weak interaction between the s orbitals of the hydrogen molecule and the s orbitals of each carbon atom in the energy region of -9.5 eV. This was indicated by the green color of the s orbital of the non-dominant carbon atom (Figure 3). Meanwhile, there was a strong contribution from the interaction of p atoms of carbon atoms with s molecules of hydrogen molecules. This was observed both in the valence band (from -10 eV to -1.8 eV) and the conduction band (from -1.8 eV to 3 eV). Whereas the Fermi energy, which was the band gap energy, was measured at -1.8 eV. So that, the interaction between the hydrogen molecule and the graphene surface produced a band gap of 2.51 eV.

To support the PDOS calculation data above, an isosurface calculation was performed between the hydrogen molecule and the graphene surface. By scanning the surface of graphene perpendicularly, the electron transfer occurred can be observed (Figure 4). The interaction between hydrogen molecules on the surface of graphene produced an electron transfer energy of 0.3506 e / Å from the hydrogen molecule's s orbitals. Electron transfer from hydrogen molecular s orbitals occurred because of the attractive force of atoms on the carbon's p orbitals from the surface of graphene. However, the overlap between the hydrogen molecular s orbitals and the carbon atom p orbitals did not form  $sp^3$  hybridization. This only resulted in a change in the character of carbon atoms from  $sp^2$  to  $sp^3$  of each graphene surface carbon atom that interacted with a hydrogen molecule. The red color in Figure 4 shows strong electron transfers with values of 0.3506 e / Å to 0.1804 e / Å. The electron transfer value was not strong enough to form covalent bonds with  $sp^3$  hybridization at the top position of the hydrogen molecule above the graphene surface. The blue color in Figure 4 shows that the covalent bonds in hydrogen molecules had non-polar characters (electronic transfer value of 0.0030 e / Å) while the light blue color indicates that covalent bonds in hydrogen molecules changed from non-polar to polar character (electron transfer value of 0.0231 e / Å). This character change indicates a strong interaction between the hydrogen

molecule at the top position with the surface of graphene so that graphene has the potential to be a hydrogen adsorbent material.



**Figure 3.** Partial density of state (PDOS) of the interactions between hydrogen molecules and graphene surface.



**Figure 4.** Electron transfer energy of the interactions between  $H_2$  molecules and graphene.

#### 4. Conclusions

Interactions between hydrogen molecules on the surface of graphene produced electron transfer energy of  $0.3506 \text{ e}/\text{\AA}$  from graphene p orbitals to hydrogen molecular orbitals. This interaction was considered as chemical adsorption because the interaction distance was  $3.2 \text{ \AA}$  and there was a change in character from  $sp^2$  to  $sp^3$  carbon atoms from graphene.

#### Acknowledgments

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