

# First-Principle Density-Functional-Theory Calculation of Water Molecule on Graphene Defects

MARHAMNI. SYAPUTRA<sup>a,b</sup>, MINEO SAITO<sup>c</sup>

<sup>a</sup>Grad. School of Natural Sci. and Tech., Kanazawa University, Kakuma, Kanazawa, 920-1192 Japan, E-mail: marhamni@cphys.s.kanazawa-u.ac.jp

<sup>b</sup>Faculty of Mathematics and Natural Sciences, Institut Teknologi Bandung, Jl. Ganesha 10, Bandung 40132 Indonesia, E-mail: marhamni@students.itb.ac.id

<sup>c</sup>Institute of Science and Engineering, Kanazawa University, Kakuma, Kanazawa 920-1192 Japan, E-mail: m-saito@cphys.s.kanazawa-u.ac.jp

**Abstract.** *We investigate structural and electronic properties of water molecules adsorbed on graphene by using the density functional theory based on the generalized gradient approximation. We use pseudopotentials and plane wave basis set to study water molecules interacting with a perfect graphene, and graphene defects such as monovacancy, divacancy, and Stone Wales defect. It is found that adsorption energies in the case of defects are smaller than that of the perfect graphene. It is concluded that the perfect graphene and graphene defects are hydrophobic since the calculated adsorption energies are small.*

**Keywords:** graphene defect, density functional theory.

## 1 Introduction

Graphene, which is one of the allotropes of carbon, has an atomic one-mono layer and can be extracted from graphite [1]. Because of its unique properties, its nanoscale electronics device application is expected. The band structure of graphene has the zero-gap which is the main obstacle when we use graphene as a semiconductor. There are several methods that are used to break the linear dispersion of the graphene band structure: Impurities, defect, and substrates modify the electronic properties. Water adsorption on graphene shows that the tunable bandgap of graphene up to 0.21 eV which was clarified by controlling the absolute humidity level [10]. An advantage of this method is its reversibility and also chemically inertness of the graphene surface.

The purpose of this paper is to investigate the interaction of graphene with a single water molecule and water clusters. We calculate the adsorption energy up to four water molecules on the perfect graphene and graphene defects. We find that the perfect graphene surface provides the higher adsorption energy than defect graphene surfaces. It is found that the perfect graphene and graphene defects are hydrophobic since the calculated adsorption energies are small.

## 2 Computational Details

Density functional theory (DFT) is carried out by using the PHASE code [11]. We apply the generalized gradient approximation (GGA) for exchange-correlation potential instead of the local density approximation (LDA). It has been known that GGA gives good result for the calculation of H<sub>2</sub>O cluster and graphene: the GGA gives excellent results for the dimmer energy and bond lengths of water molecule [2]. We choose 25 Rydberg and 230 Rydberg for the cut off energies of the plane wave basis set and charge density, respectively. We use the 4x4 supercell with the 6x6x1 mesh grids in the Brillouin zone integration.

### 3 Result

#### A. Geometry Optimization

First, we determine the stable geometry of a single water molecule on the graphene. The optimized geometry of a single water molecule on the perfect graphene is shown in Table 1 and Figure 1.

In Table 1, our results are compared with those of some references. Bond length ( $d_{OH}$ ) and bond angle ( $\theta_{HOH}$ ) are 1.2% higher and 0.01% lower than the corresponding values of the isolated water ([4], [5]). Meanwhile the distance between the oxygen atom and graphene surface ( $d_{CO}$ ) is 0.2% lower than previous theoretical result based on the GGA [9]. The average bond length between two nearest atoms ( $d_{CC}$ ) in graphene is close to that of the experimental result [3] for the pure perfect graphene. In Table 2, we show the calculated values of graphene defects. The parameter  $d_{OH}$  for the graphene defect surfaces is slightly higher than the perfect graphene. Moreover, the values for  $d_{CO}$  and  $\theta_{HOH}$  are slightly lower than that of the perfect graphene.

Table 1. Optimized geometry of the water molecule on perfect graphene surface: bond length  $d_{OH}$ , bond angle  $\theta_{HOH}$  and the distance  $d_{CO}$  between of oxygen atom and graphene surface.

Parameter	Present calculation	Expt
$d_{OH}^o$ (Å)	0.9688	0.957 <sup>4,5</sup>
$\theta_{HOH}$ (degree)	104.49	104.5 <sup>4,5</sup>
$d_{CO}^o$ (Å)	3.60	3.61 <sup>9</sup>
$d_{CC}^o$ (Å)	1.419	1.42 <sup>3</sup>

Table 2. Optimized geometry of water molecule on graphene defects.

Parameter	Monovacancy graphene	Divacancy graphene	SW Defect graphene
$d_{OH}^o$ (Å)	0.9691	0.9690	0.9695
$\theta_{HOH}$ (degree)	104.43	104.38	104.30
$d_{CO}^o$ (Å)	3.604	3.590	3.589

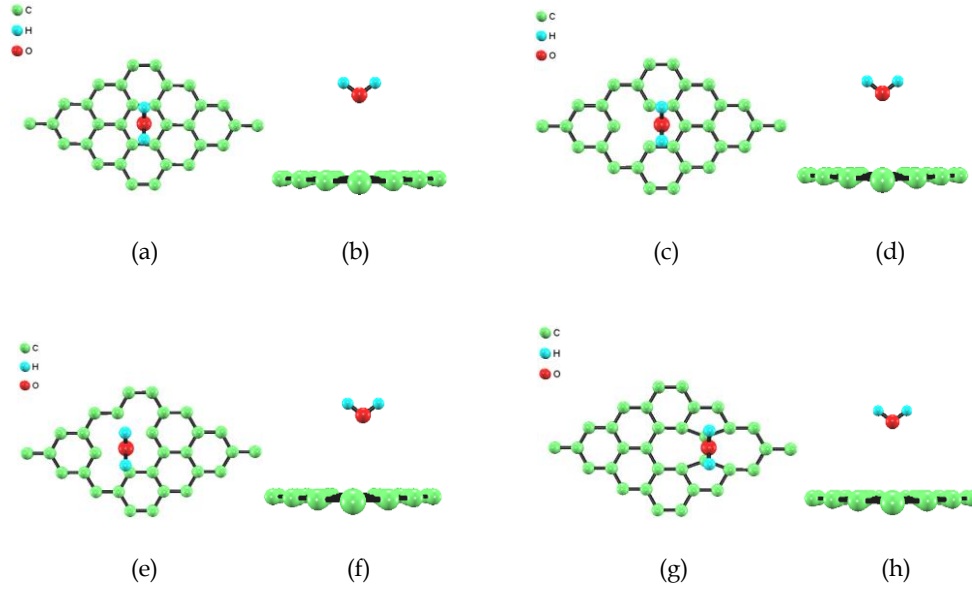


Figure 1. Atomic configurations of the most stable system of a single water molecule on graphene surfaces. Water molecule on perfect graphene (top view (a), side view (b)), graphene monovacancy (top view (c), side view (d)), graphene divacancy (top view (e), side view (f)) and graphene SW defect (top view (g), side view (h))

#### B. Adsorption energy

Calculated adsorption energies are presented in Table 3. The adsorption energies sensitively depend on orientation of water molecule as were shown in the past computational studies [7]. We find that the most stable geometry has the up orientation and the most stable site is the hexagon center as shown in Fig. 1. We estimate the adsorption energy by using the equation  $E_{ads} = (E_{graph} + E_{water}) - E_{tot}$ , where  $E_{graph}$  is the energy of the perfect graphene,  $E_{water}$  is the energy of the isolated water and  $E_{tot}$  is the energy of the water on graphene.

Table 3. The adsorption energies  $E_{ads}$  of a single water molecule and four water molecules on: monovacancy, divacancy, and SW defect.

Type of graphene sheet	$E_{ads}$ (meV) of 1 $H_2O$	$E_{ads}$ (meV) of 4 $H_2O$
Perfect graphene	64	23
Monovacancy	26	22
Divacancy	22	19
SW Defect	24	15

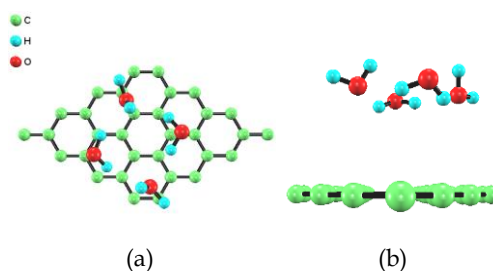


Figure 2. Cluster of four water molecules on perfect graphene: (a) top view, (b) side view

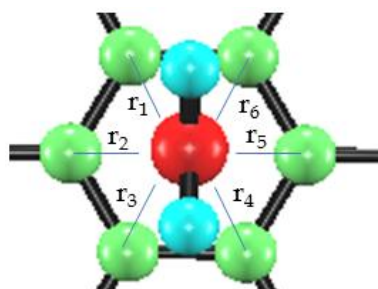


Figure 3. Single water molecule adsorbed on the perfect graphene surface: There are six nearest neighbor carbon atoms and  $r_1$  to  $r_6$  indicate the distance between the oxygen in the water molecule and the carbon atoms.

In Table 3, we find that the adsorption energy for the divacancy is the lowest whereas the energy of the perfect graphene is the highest. On the perfect graphene surface, a single water molecule interacts with the six nearest carbon atoms (see Fig. 3), while water molecules on the monovacancy and divacancy interact with five and four nearest carbon atoms, respectively. Water molecule on the SW defect, interacts with only two nearest carbon atoms. Therefore, it is expected that the interaction between the defects and water molecule is weak compared with that between the perfect graphene and water molecule. These weak interactions in the cases of defects induce low adsorption energies.

To confirm the above argument, we measure the average distances of nearest carbon atoms of the oxygen atom in water molecule. The average distances are  $3.87\text{\AA}$  for on perfect graphene,  $3.99\text{\AA}$  for the monovacancy,  $4.11\text{\AA}$  for the divacancy and  $3.92\text{\AA}$  for the SW defect. The average distance for the SW defect is between those of the monovacancy and divacancy. So, we conclude that as the distance becomes small, the adsorption energy increases.

We next study the cases that four water molecules are adsorbed on graphene. We construct a cluster of four water molecules. After obtaining the optimized geometry, we place this cluster on the graphene surface to attain the stable system (in Fig. 2). The adsorption energies for the four water molecules on graphene are shown in Table 3. If we increase the number of molecules, the adsorption energy tends to decrease. Water molecules favor interact each other since the average binding energy per molecule among them in cluster becomes large (see Table 4) as the number of molecule increases. The above results indicate that graphene is hydrophobic.

Table 4. The total binding energy ( $E_b$ ) of cluster and the average binding energy ( $E_b/\text{mol}$ ) per water molecule in cluster.

$n \text{ H}_2\text{O}$	$E_b(\text{eV})$	$E_b(\text{eV})/\text{mol}$
2	0.229	0.115
3	0.492	0.164
4	1.297	0.324

#### 4. Conclusions

We use the DFT to calculate the water on graphene. We find that there is a weak interaction between water molecules and graphene. This weak interaction can be seen from the small adsorption energy comparing with the binding energy of water cluster. The decreasing order of the adsorption energy is perfect graphene, monovacancy, SW defect and divacancy. Adsorption energy decreases as the number of water molecules increase, indicating that the graphene is hydrophobic [7].

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