Adsorption of the water molecule on monolayer graphene surface has effect on its optical properties

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Abstract. The adsorption of water molecules on the surface of a monolayer graphene can be studied with the Materials Studio software and be applied density function theory from first principles. By studying the interaction of graphene with water molecule, it uses DFT (density function theory) with the PBE-GGA (the generalized gradient approximation of Perdew-Burke-Ernzerhof) and Periodic plane model, on the one hand working out the adsorption energy, and on the other hand getting related optical properties. It is shown that a single water molecule on graphene has very small adsorption energy, mainly owning to the van der Waals interactions. Graphene has high hydrophobic; adsorbed water molecule has little effect on the electronic structure of the graphene. The optical properties of the graphene have changed after the adsorption.

1. Introduction
Graphene is a single layer of graphite as the basic unit. Unique two-dimensional structure gives it attractive physical properties, such as excellent optical properties and special band structure [1]. In recent years, graphene becomes popular with the large number of researchers. For adsorption, graphene is an excellent material due to its several useful properties [2]. Because of its essentially two-dimensional structure, it almost completely exposed to the environment, leading to being significantly influenced by surrounding environment. There are numbers of literature in the study of alkali metal atoms [3], inert gas, and hydrocarbon [4], etc. adsorb on graphene. Whether in daily life or scientific researches, water plays a crucial role in the surface. The adsorption of water on the surfaces of metals has been studied in lubrication, corrosion, electrochemical and catalytic in the industrial production due to its important role. All kinds of researches are in progress and are going deep into smaller scale gradually; finally focus on the atomic scale [5].

In the experiment, a major problem exists in the calculation of a single water molecule adsorbs on the surface: Water molecules are so easy to form clusters that limit the study of adsorption.
Theoretically, distribution and hydrogen bonding of water molecules may cause difficulties in the calculation of water molecules interact with the material surface. To calculate the electronic structure and various properties, density functional theory is used in usual.

In recent years, the studies of water molecules adsorption on graphene surface are increasing, examples are as follows: Jie Ma studied the adsorption and diffusion of water on graphene from first principles [6], P. Cabrera San Felix, researches the structure of water on the surface of graphite [7], Gabor Nagy studied the water structure at the graphite surface by STM measurements [8] etc.. On the influence of the adsorption of water molecules on graphene, the article illustrates a hydrophobic related theory about graphene was written by Leenaerts O [9].

Based on the results of their study, Materials Studio software simulation calculation is applied in adsorption of water molecules on the monolayer graphene surface, using the first principles density functional theory with the generalized gradient approximation and periodic plane model. In this paper, the interaction between different water molecules and graphene is primarily a van der Waals interaction. The influence on monolayer graphene adsorbed by water molecules is explained and the corresponding optical properties are calculated.

2. Computational details
All computations have been done using the CASTEP (Cambridge Serial Total Package) programs in Materials Studio and using DFT (Density Functional Theory) to describe the exchange-correlation potential. Moreover, these use a plane-wave basis set with ultra soft pseudo potentials. PBE version of GGA (the General Gradient Approximation) was used rather than PW91[10], which mainly describing gas phase water adsorption on metal surfaces. Under the condition of the gas phase study, it is common to select the B3LYP version of GGA. Here, the paper doesn’t need to accurately describe approximate degenerate of many clusters of water molecules of isomers. So researches don't need pay attention to the differences of these methods in detail, but focus on the selected part.

Monolayer Graphene crystals model is a two-dimensional hexagonal grid with repetition structure. Considering the boundary conditions and computing time, typically graphene is replaced by a hexagonal 4 x 4 x 1 supercell sample model in simulation calculation, and it have used a vacuum gap of 15 Å (see figure 1). Numerical test results show that the structure can not only satisfy the accuracy of all calculation, but also won't make a too large amount of calculation.

![Figure 1. Monolayer graphene.](image)

Because water molecules relatively far from the plane, it makes no difference whether use a metallic or insulator treatment. Self-consistent iteration method (SCF) was used in the energy calculation with 1000 iteration steps, and ultra soft pseudo potential in Reciprocal space used BFGS algorithm.

In geometry optimization, system total energy convergence value is 1×10^-6 eV/atom, the force on the atom is 0.03 eV, maximum stress is 0.05 Gpa, the maximal displacement of 0.01 angstrom, and cut-off energy is 310.0 eV. Self-consistent calculation of irreducible Brillion k point 3×3×2 is produced by the program automatically, with BFGS algorithm geometry optimization and surface relaxation.
Water molecules adsorbed on the surface at random. In order to simulate the adsorption of water molecules on the graphene in reality, combining with numerical simulation conditions, and respectively adding one water molecule, two water molecule and three water molecules in random location and random direction to realize geometry optimization. Following calculations have been done on the basis of optimized structure.

Several different optimized models’ vertical view can be seen as follows (in figure 2).

![Figure 2. (a) 1 H$_2$O; (b) 2 H$_2$O; (c) 3 H$_2$O.](image)

1. One water molecule model is shown in figure 2(a): Water molecule present bridge site; the oxygen atom is just above the middle of the carbon-carbon bond; two hydrogen molecules are symmetrically distribute on both sides of the carbon-carbon bond, and the height of the water molecules from graphene is 3.26358 Å.

2. Two water molecule model is shown in figure 2(b): Both of two water molecules present bridge site; two oxygen atoms are located in two carbon-carbon bonds in different carbon rings; length between water molecules is 3.430 Å; and the heights of the water molecules from graphene are 3.04383 Å and 2.94343 Å.

3. Three water molecule model is shown in figure 2(c): Three water molecules are located above three different carbon rings. One of a water molecule hydrogen atoms pointing down; lengths between water molecules are 2.961 Å and 2.955 Å. It became a small cluster of water molecule, conforming to liquid water, and the heights of the water molecules from graphene are 3.24965 Å, 3.42859 Å and 3.8967 Å.

3. Results and discussion

Optimization of the lattice constant of graphene is 2.4638 Å, being in good agreement with the theoretical value of 2.46 Å. The water molecule’s O-H bond length in the first model, after optimized is about 0.9903 Å and O-H bond angle is 104.534°; The water molecules’ O-H bond lengths in the second model after optimized are about 0.9700 and 0.96941 Å ,and O-H bond angles are 104.067°, 104.745°; The water molecules’ O-H bond lengths in the third model after optimized are about 0.9864, 0.9691, 0.9696 Å, and O-H bond angles are 104.305°, 104.938°, 105.301°; conforming to the actual weather conditions of water molecule bond length of 0.97 and bond angle of 104.00°.

Thus, it can be seen that Supercell geometry optimization and water molecules geometry optimization’s results are accord with the theory. The method to select the model is properly and the calculation method is feasible.

3.1. Adsorption energy

Adsorption energy can reflect the strength of the interaction between the graphene and the water molecules, defining as equation (1):

$$E_{ad} = E_{total} - (E_{H_2O} + E_{gra})$$ (1)

In the equation, $E_{ad}$ is the adsorption energy; $E_{total}$ is system total energy of a single water molecule adsorbed on the monolayer graphene; $E_{H_2O}$ is water molecule energy; $E_{gra}$ is the monolayer graphene energy.
The energy of one water molecular adsorption on graphene Ead is -0.0213952 eV; the energy of adsorption of two water molecular on graphene Ead is -0.0203484 eV in average; the energy of adsorption of three water molecular on graphene Ead is -0.0244898 eV in average.

The results of optimized structure and adsorption energy can be analyzed as follows: In the first two models, water molecule only interacts with graphene surface and the interaction between water molecules is so small that can be ignored when calculating. In the third model, located on the edge of the periodic structure will result in the interaction between two water molecules, leading to water molecules form changed after the optimization. Water molecules form clusters and adsorption energy in equation (1) will be an error.

Calculation of adsorption energy use PBE in GGA includes van der Waals interactions. It can be seen that the interaction of water molecules and graphene is so small that Van der Waals interaction plays a main role. Because the C-C bond between carbon atoms is highly saturated in graphene, making the interaction of water molecules and graphene is very weak, that id the structure of graphene is high hydrophobicity structure.

Observing the data, the water molecules average adsorption energy of different models are very similar to each other, which showing that the number of adsorbed water molecules have no effect on the average adsorption energy. The conclusion is in accordance with and the water adsorption on the graphite surface [11].

3.2. Density of states

In the figure 3, monolayer has a summit value is 57.68912 electrons/eV in the point of -265.65 eV, and a fragment of summits exist between -19.4235 eV to 4.232958 eV. In this section, a summit value 34.22898 electrons/eV exists at the point of -0.04977 eV. For the model of adsorption, summits height and scope of the original image is few changes [12]. Compared with the monolayer graphene, a water molecule adsorbed on graphene cause a small height (3.932914 electrons/eV) adding at the point of 504.888 eV. Two or three water molecules adsorption on graphene follows the same rule.

![Figure 3. Density of state](image)
Figure 3(a) monolayer graphene; (b) A water molecule adsorption on graphene; (c) Two water molecule adsorption on graphene; (d) Three water molecules adsorption on graphene [13]. Only the valence electrons were considered without the inner electrons.

As shown in figure 4, water molecules state of density. It can be seen clearly that the extra wave was due to the superposition of a part of the water molecules density of state.

3.3. Band structure

Band structure of graphene is shown in figure 5. Because graphene is a two-dimension crystal with hexagonal symmetric structure consisting of a bipartite lattice of two triangular sub-lattices, four valence electrons are tied to the C nucleus tightly and each atom is tied to its three nearest numbers via σ bonds which are a result of sp2 hybridization of 2s, 2px and 2py orbitals for the three valence electrons. Near the Fermi surface level, 2pz orbitals make the main contribution, which is π bond.

Graphene energy gap is zero. The conduction band and valence band intersect at the Dirac point, there are two atoms per unit cell and hence there are two electrons per unit cell. When the lower π band is completely filled full, leaving the upper π* band empty completely, Fermi surface is just located in the intersection point. Fermi surface E=0. Under the Fermi surface, electronic state is the corresponding with zorbitals bonding state; above the Fermi surface energy level, electronic state is the corresponding π* orbitals anti-bonding.

After the adsorption of water molecules, the band structure of graphene does not change, that is water molecules has little influence on the band structure of graphene.
3.4. Optical properties

In this paper, the calculation of optical properties is under polarized light, and parameters are as follows: Graphene has zero band gap; the scissors operator is 0 eV; the polarization direction of the polarized light is (1 0 0).

Limitations: the calculation of optical properties in CASTEP based on the electronic structure, but it doesn’t contain the excited states, so it has some influence on the accuracy of optical computing. For example, the transition of the electric field inside the material is considered no attenuation while the transition is calculating, but in fact not the case.

![Figure 6. Absorption.](image)

Figure 6 is the absorption rate. The absorption coefficient is usually referred to the material energy attenuation when the electromagnetic waves pass through the unit thickness of material [14].

Absorption spectrums are calculated by CASTEP is only considered about intrinsic absorption. Seeing the curves in the figure, on the same wave band, the absorption rate is arranged as follows: one water molecular adsorption on graphene > two water molecular adsorption on graphene > three water molecular adsorption on graphene.

Absorption coefficient equation is as follows:

$$\alpha(\omega) = \frac{\omega \varepsilon_2(\omega)}{nc}$$

(2)

According to the relationship of quantum mechanics energy equation:

$$E = hv = \hbar \omega = \hbar c k = \frac{pc}{\hbar}$$

As is known to all, the wavelength of visible light is 390 nm to 780 nm; the frequency of the corresponding is 3.84×10^14 to 7.70×10^14 Hz, that is 1.6 eV to 3.2 eV. In the figure, light absorption in the range of 0 ~ 17 eV; a summit located in 2 eV and the absorption coefficient is 0 when the frequency is greater than 17 eV.

When light through the model, in visible band graphene shows favourable nonlinear optical absorption properties, the adsorption of one water molecular model is a little smaller than pure graphene. Owing to the zero gap of graphene and its wide wave band adsorption, graphene is easy to saturate to light. Therefore, graphene has low light saturation flux, so it has prospects for practical application such as manufacturing optical photonic crystals, fiber laser and laser switch in the area of the optical field.

Figure 7 is light conductivity, calculating by $\sigma = \sigma_1 + i\sigma_2$, the phenomenon of the conductance change of the semiconductor material is caused by illumination change is called photoconductive effect.
This parameter is used to describe the optical properties of the metal, but the CASTEP expand the scope of it to insulators and semiconductors. As for the metal, the main difference in calculating process is the real component is closely related to an internal band when considering Conversion relationship in optical spectroscopy while the other does not consider these factors.

Figure 7. Conductivity. (a) conductivity Re; (b) conductivity Im.

In figure 7(a), the light conductivity of the graphene in the real number part is very strong in the low-frequency part, but will be weak in the high-frequency part. The summit value 76 of graphene located in 1 eV. When one, two and three water molecular adsorption on graphene, the summit value drops to 73, 21 and 19 respectively. In the low-frequency part of the imaginary, the light conductivity value of the graphene is bigger than others, then dropping to 0 in the high-frequency part. The summit value of pure graphene is 51 at 2 eV, and dropping to 50, 15, 15 when one, two and three water molecular adsorption on it, then they are all quickly dropping to near zero. It shows that the optical conductivity of graphene is very big in infrared wave band, but it decreased after adsorbing water molecular.

Figure 8. (a) Dielectric function Re; (b) dielectric function Im.

Figure 8 is the dielectric function.

Imaginary part of a dielectric function expresses the transition information between band gaps, and reflects the solid band structure and various kinds of spectral information. It depends on the size of the electron transition energy of conduction band and valence band. In fact, it is the electronic absorption spectrum of the transition between the bands.

Dielectric function spectrum peaks are formed by electron transition from the valence band to the conduction band; transitions satisfy to selection rule which corresponding to the width value of band gap. The position of the absorption peak was not corresponding with band difference well, because of
the relaxation effect when the transition energy absorption by electronic in the process of transition, leading to the deviation. In band structure, there are many levels have contributed to the same peak by directly or indirectly transition, so we can't simply use two energy levels difference to calculate, and can't simply think crystal absorption spectrum is caused by a single transition.

Imaginary part of dielectric function equation (3) as follows:

$$\varepsilon(q) \rightarrow O_u, h\omega = \frac{2e^4\pi}{Q\varepsilon_0} \sum_k \delta(E_k^u - E_k^v - E)$$

In equation (3), q is a vector in the First Brillouin zone, and the physical meaning is the change of electronic before and after the transition. Because the photon momentum is far smaller than the electron momentum, the electron momentum remains the same approximately. So q tends to be 0, and Ou is a zero vector, and the $\Omega$ refers to the original cell volume.

Graphene has a zero band gap, and its spectrum produced by the electron transition between energy levels. In the real part, the curve of one water molecule adsorption on graphene is coincident with pure graphene, and going down with energy’s growth in the low energy part. The minimum value is -500 at 0.8 eV, growing with energy, arriving at value 0 at 2.5 eV, saturated. Adsorption of two or three water molecules change smoothly. In the imaginary part, curve monotonous gently fall; Dielectric function of graphene and one water molecule adsorption model changes more than the adsorption of two or three water molecules. That is the more water molecular adsorption on graphene, the more energy is loss.

Figure 9 is the refractive index n and k.

Figure 9 is the refractive index n and k. The equation of refractive index n and k is as follows:

$$n(\omega) = \frac{1}{\sqrt{2}} \left\{ \left( e_1^2 + e_2^2 \right)^{1/2} + e_1 \right\}^{1/2}$$

$$k(\omega) = \frac{1}{\sqrt{2}} \left\{ \left( e_1^2 + e_2^2 \right)^{1/2} - e_1 \right\}^{1/2}$$

The refractive index is the light attenuation in the crystal. In figure 9, all curves have no peak, and attenuation rate drop to zero in low energy part soon. At about 2eV, graphene refractive index k is 27, and the refractive index value is almost zero in the high energy region (more than 15 eV). It shows that graphene absorption is very weak for high-frequency electromagnetic wave. Analysis of the figure shows that only one water molecule adsorption on graphene has little effect on transparency.

Figure 10 is a loss function.
The energy loss function in theory is $\text{Im}(-1/\varepsilon)$, it is deduced by experiments Optical energy loss function $\text{Im}[−1/\varepsilon(\omega)]$. If $q \neq 0$, energy loss function is $\text{Im}[−1/\varepsilon(q,\omega)]$.

In figure 10, the energy loss maximum value is at about 5 eV; in addition, there are secondary energy loss values at about 1 eV and 8 eV. For graphene, every C atom is tied to each other via $\sigma$ bonds that lie in the graphene plane with angles of 120°, 2s, 2p$^x$ and 2p$^y$ orbitals form to $sp^2$ hybridization. The electron is in the 2p$^z$ orbital that is orthogonal to the monolayer graphene. Plasma excitation peaks at 5 eV and 8 eV are caused by $\pi$ and $\sigma$electrons transit to excited states, but plasma excitation peak at 1 eV is caused by secondary plasma excitation of $\sigma$electrons.

The main peak of energy loss of water molecular adsorption on graphene is at 4.3 eV, and second peaks of energy loss are at 1 eV and 7.5 eV. In figure 10, the more adsorption of water molecules, the bigger the energy loss.

All above is optical properties simulation model of graphene and different water molecular adsorption on graphene calculated by CASTEP. CASTEP provides the calculation of polarization system, but only in the same spins conversion. But in reality, due to the complexity of the incident light, geometrical structure on the material surface is not idea; and because the polarization effect exist in the crystal structure, causing the dielectric coefficient may not isotropic. These factors will hinder us to predict the optical properties of the material, leading to a random error.

4. Conclusions
Based on the first principles calculation of plane wave ultra-soft pseudo-potential technology, it was performed by the Density Function Theory (DFT). The plane wave function was studied on different number of water molecules adsorption on the monolayer graphene, electronic structure total energy shows that the nature of the adsorption is physical adsorption, and the adsorption is very weak. The density of states are analyzed, and optical properties including absorption rate, dielectric function, refractive index n and k, loss function are calculated.

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