

Study of Carbon Nanomaterials Based on Density Functional Theory

メタデータ	言語: eng 出版者: 公開日: 2017-10-05 キーワード (Ja): キーワード (En): 作成者: メールアドレス: 所属:
URL	http://hdl.handle.net/2297/37354

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Dissertation

Study of Carbon Nanomaterials based on Density Functional Theory

Graduate School of Natural Science & Technology
Kanazawa University

Major subject: Division of Mathematical and Physical Sciences

Course: Computational Science

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Abstract

Carbon nanomaterials have attracted much attention because they are candidates for post-silicon materials. Since carbon nanotubes (CNTs) were detected and graphene was isolated from graphite, comprehensive studies have been carried out with the aim of exploiting the properties of these materials. In this study, by using first principles calculations, we study the interlayer distance of the two-layer graphene and atomic hydrogen adsorption in graphenes and CNTs. We first study layer distance of the two-layer graphene. We use a recently developed van der Waals density functional theory (VDWDFT) as well as the local density approximation (LDA). Both methods give successful results for graphite; i.e. the calculated interlayer distances are comparable with the experimental value. We find that the interlayer distance of the two-layer graphene is close to that of graphite. We also find that the AA stacking structure of the two-layer graphene has higher energy than that of the AB stacking one and the layer distance of the AA stacking is larger than that of the AB stacking. It is thus suggested that the interlayer distance becomes somewhat large when the stacking deviates from the AB stacking.

Next, we study hydrogen monomers and dimers in graphene, the armchair edge (5, 5) carbon nanotube (CNT), and the zigzag edge (10, 0) CNT because the presence of hydrogen atoms could change the electronic properties of graphenes and CNTs, where those hydrogen atoms are chemically attached. We find that the monomers in the above three carbon nanomaterials have the magnetic moment of $1 \mu_B$. In the case of the CNTs, the hydrogen atoms are located on the outer side of the CNTs. In the most stable structures of the dimers in the above three carbon materials, the two hydrogen atoms are bonded to host carbon atoms, which are nearest-neighbors. In the case of graphene, the two atoms are located on opposite sides, whereas in the case of the armchair edge (5, 5) CNT and zigzag edge (10, 0) CNT, both hydrogen atoms are located on the outer side. The electronic structures of the most stable geometries are found to be nonmagnetic. However, when the two hydrogen atoms are bonded to second-nearest-neighbor carbon atoms, the magnetic moment is found to be $2 \mu_B$.

Extended Description

Carbon nanomaterials have attracted much attention because they are candidates for post-silicon materials. Since carbon nanotubes (CNTs) were detected [1] and graphene was isolated from graphite [2], comprehensive studies have been carried out with the aim of exploiting the properties of these materials. In this study, by using first principles calculations, we study the interlayer distance of the two-layer graphene and atomic hydrogen adsorption in graphenes and CNTs.

We first study the interlayer distance of the two-layer graphene. Graphene has been attracting wide scientific interests because of novel electronic properties. To study the electronic properties of few-layer graphenes, it is essential to clarify the interlayer distance but the distance is still unclear. We employ the recently developed van der Waals density functional theory (VDWDFT) [3] as well as local density approximation (LDA). We first carry out LDA calculations of the graphite having the AB stacking structure. Our calculated layer distance is 3.35 Å; therefore, our calculations well reproduce the experimental value (3.35 Å) [4]. The determined interlayer distance (3.60 Å) of the AA stacking structure is larger than that of the AB stacking structure (3.35 Å). By using VDWDFT calculations; we find that the interlayer distance of the AB stacking structure is 3.50 Å, which is close to previously calculated result based on the VDWDFT (3.59 Å) [5]. As well as the LDA calculations; the VDWDFT calculations lead to the conclusion that the interlayer distance of the AA stacking structure (3.65 Å) is larger than that of the AB stacking structure (3.50 Å). Also by using VDWDFT calculations; we find that the interlayer distance of the two-layer graphene having AB stacking structure (3.49 Å) and AA stacking structure (3.65 Å) are close the corresponding values of the graphite. So we conclude that the interlayer distance of the two-layer graphene is close to that of the graphite. We also

find that interlayer distance of the metastable AA stacking structure of the two-layer graphene is larger than that of the AB stacking. It is thus suggested that the interlayer distance becomes somewhat large when the stacking deviates from the AB stacking.

Next we study atomic hydrogen adsorption in graphene, the armchair edge (5, 5) CNT, and the zigzag edge (10, 0) CNT. Whereas the hydrogen molecules are physisorbed on carbon materials, hydrogen atoms are chemisorbed. This hydrogen chemisorbed significantly affects the electronic properties of carbon nanomaterials. To understand the effect of the hydrogen adsorption, the study of the monomers and dimers is necessary since they are fundamental hydrogen impurities in carbon materials.

In this study, we carry out first-principles calculations of hydrogen monomers and dimers in the graphene, armchair edge (5,5) CNT and zigzag edge (10,0) CNT. We perform spin-polarized generalized gradient approximation (GGA). Based on the result of the calculations, we determine the binding energy per hydrogen atom E_b of the C-H bond, which is defined as:

$$E_b = \frac{E(system) + n_H E_{at}(H) - E_t(hydrogenated\ system)}{n_H}, \quad (1)$$

where $E(system)$ is the total energy of the pristine system and $E_t(hydrogenated\ system)$ is that of the hydrogenated system. $E_{at}(H)$ is the energy of a single hydrogen atom and n_H is the number of hydrogen atoms in the hydrogenated system. We find in the monomer case the binding energies Eq. (1) in the CNTs (1.13 eV and 1.10 eV) are found to be much larger than that of the graphene (0.53 eV). Therefore, the CNTs are easily hydrogenated compared with the graphene. We find that the monomers in the above three carbon nanomaterials have the magnetic moment of $1 \mu_B$. In the case of CNTs, the hydrogen atoms are located on the outside of the CNTs. As shown in Fig. 1(a), the large spin density is located at the hydrogen site and the graphene sublattice. This graphene sublattice is different from the sublattice to which the hydrogen is bonded. This result indicates that the hydrogen s-orbital is hybridized with the wave function at the Dirac cone point of the graphene. The wavefunction having a nonzero amplitude at only one sublattice originates from those of the Dirac points. Similar hybridization occurs for the monomer in CNTs [Figs.1(b) and(c)].

Next, we study hydrogen dimer in graphene. In the most stable geometry of the dimer, both

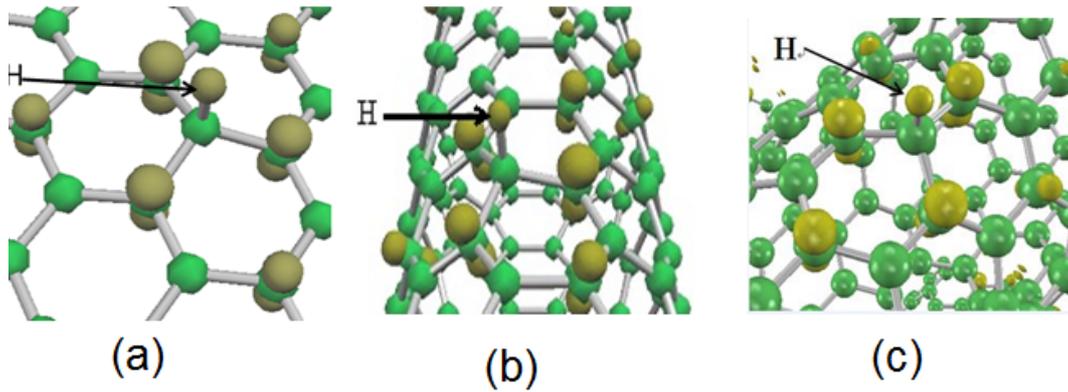


Figure 1: Spin densities of the hydrogen monomer in the graphene (a), CNT (5,5) (b) and CNT(10,0) (c). The isosurface value is $0.01 (a.u.)^{-3}$.

hydrogen atoms are bonded to carbon atoms which are nearest-neighbors. The two hydrogen atoms are located on opposite sides [Fig. 2(a)]. We find that the C1-C2 bond length [Fig. 2(a)] is 1.51 \AA , and the bond angle of H1-C1-C2 [Fig. 2(a)] is 107.8° . The bond length is close to the sp^3 bond length (1.54 \AA) in diamond and the bond angle is close to the sp^3 bond angle (109.5°).

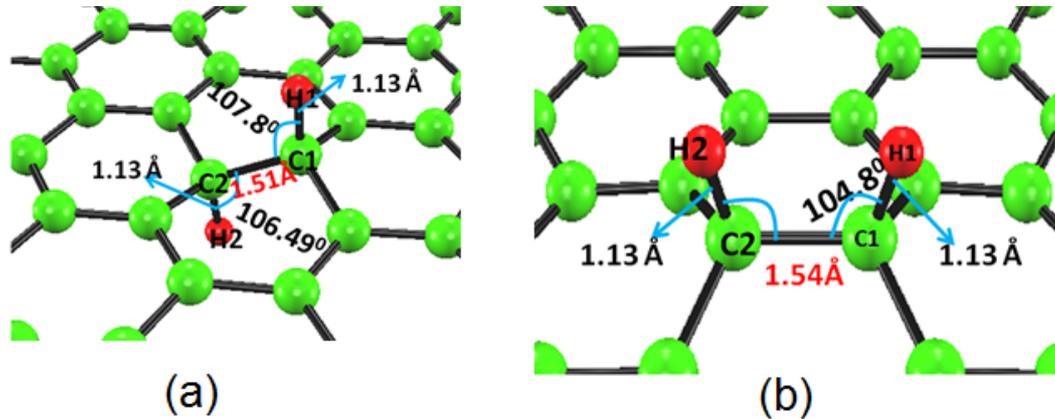


Figure 2: Nearest-neighbor geometrical configurations of the hydrogen dimers in graphene.

Previously, the geometry where the two hydrogen atoms are located on the same side [Fig. 2)] was studied, [6] but we find that this geometry is metastable, i.e., its energy is 0.60 eV higher than that of the most stable geometry. The calculated bond angle of H1-C1-C2 [Fig. 2(b)] in the metastable geometry is 104.8° , which somewhat deviates from the sp^3 bond angle. As a result, the C1-C2 bond length (1.54 \AA) is longer than that (1.51 \AA) of the most stable geometry. Therefore, it is expected that the higher energy of the metastable geometry is due to

the deviation from the sp^3 hybridization.

We also study dimer on armchair edge (5,5) CNT [Fig. 3 (a)] and zigzag edge (10,0) CNT [Fig. 3 (b)]. In the most stable structure of the those structures, both two hydrogen atoms are located on the outer side. This is contrast to the case of graphene, where the two hydrogen atoms are located on the different sides [Fig. 2]. The difference between graphene and the CNTs is expected to originate from the fact that the CNTs have curvature. The binding energies of the most stable geometries are 1.65 and 1.60 eV for armchair (5, 5) and zigzag (10, 0) edges CNTs, respectively. These binding energies are much larger than that of graphene (1.16 eV).

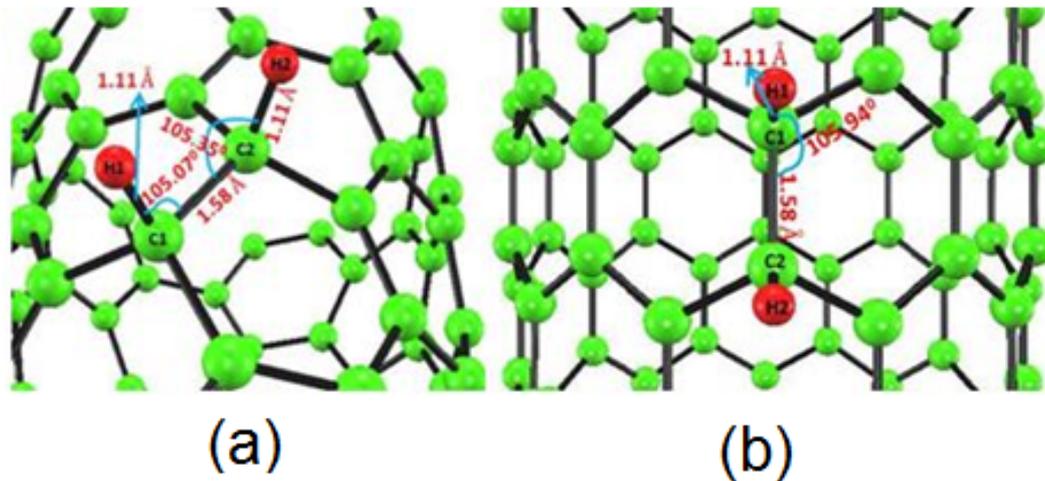


Figure 3: Most stable structures of the dimers in (a) armchair edge (5,5) CNT, and (b) zigzag edge (10,0) CNT.

The electronic structures of the most stable dimer geometries are found to be nonmagnetic. However, when the two hydrogen atoms are bonded to the second-nearest carbon atoms, the magnetic moment is found to be $2 \mu_B$. We found that when the two hydrogen atoms are bonded to third-nearest-neighbor carbon atoms, the electronic structure is nonmagnetic. In the nearest-neighbor and third-nearest-neighbor configurations, the two hydrogen atoms are bonded to different sublattices, i.e., the A and B sublattices. In this case, no spin polarization arises and magnetization is not achieved. On the other hand, when the two hydrogen atoms are bonded to the second-nearest-neighbor carbon atoms, both hydrogen atoms are bonded to the same (A) sublattice and the majority spin density appears at the B sublattices.

It is experimentally difficult to investigate the magnetic state in carbon nanomaterials by atomic hydrogen adsorption. Therefore, simulation is necessary to reduce the risk of error in producing material and also minimize enormous costs involved in any material handling project. Moreover, we can predict the property of the materials not existing in nature and design new materials. Thus, the above mentioned results are very important in the field of carbon nanomaterial and hydrogenation of carbon materials is a promising candidate of post-silicon materials.

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