Effects of different hydrogen distributions on the magnetic properties of hydrogenated single-walled carbon nanotubes

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The magnetic properties of the hydrogenated single-walled carbon nanotubes (SWNTs) have been studied by the first-principles calculations. It is found that different distributions of hydrogen atoms on the SWNT surfaces have a significant effect on the magnetic order of the hydrogenate SWNTs. More importantly, it has been shown that in general there exist two types of the hydrogen adsorption sites on the SWNT external surface, forming two different structures of the hydrogenated SWNTs, i.e., the so-called *AA* and *AB* structure, among which the latter has lower total energy than the former. The flat bands appear at the Fermi energy in the *AA* structures, favoring spontaneous magnetism, but not in the *AB* structures, making the composite system always stay in the nonmagnetic ground state.

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The carbon systems have long been considered as the most promising candidates of the magnets without the *d* electrons.[1] Recent reports on magnetic carbon, such as hydrogenated nanographite ribbon,[2,3] oxidized C_{60} (Ref. 4) and polymerized rhombohedral C_{60},[5] etc., have stimulated renewed interests[6] in the carbon systems as the new possible magnetic materials made exclusively of the light elements because of their fundamental importance and great potential applications in high-technology, e.g., the spintronics.

Some investigations have demonstrated that the hydrogenation of a carbon system is an important and efficient method to yield magnetism. For example, it is shown by the tight-binding model[2] that spontaneous magnetization could appear in the nanographite ribbon for the monohydrogenated zigzag edges. And it is also shown by first-principles calculations[3] that a finite spontaneous magnetization may appear in a hydrogenated graphene ribbon, in which one edge is composed of monohydrogenated carbon atoms and another edge is made of dihydrogenated ones. Recent experiments[7] and theory[8] indicate that proton irradiation triggers ferromagnetism in originally nonmagnetic samples of the carbon system, while He ion bombardment has a much smaller effect. All the above works show that hydrogen plays an important role in the magnetic ordering of the carbon system.

Due to a similarity between the carbon nanotubes and the graphite, there have been some works on the hydrogenation of carbon nanotubes, including the hydrogen-induced magnetism in carbon nanotubes.[9] It is obvious that the different hydrogen adsorptions on the single-walled carbon nanotubes (SWNT) surfaces will affect their physical properties. For example, it is shown in Ref. 10 that the different distributions of hydrogen atoms on the SWNT surfaces affect the electronic and atomic structure of the system significantly. However, because of the interaction of hydrogen with the nanotubes[11] or with the defects such as vacancies in the nanotubes,[12] and the possible mobility of the hydrogen,[13] it is very difficult to identify clearly the real possible hydrogen adsorption activities. In order to understand the adsorption mechanism to some extent, many static calculations by using the first-principle methods have been done.

Recently, Duplock *et al.*[14] have shown theoretically that the adsorption of atomic hydrogen on the graphene opens a substantial gap between its occupied and unoccupied bands, accompanying by a spin-polarized gap state, which can be quenched by the Stone-Wales defects. And they also suggested it is true for certain SWNTs. However, they did not discuss if the long-range magnetic order could exist in their hydrogenated graphene. Considering that the adsorption site of the hydrogen atom is bound to be related to the magnetic property of the system, demonstrated by some previous works[2,3] on the graphene, we will in this paper study how different adsorption sites of hydrogen on the SWNT surfaces affect their spin polarization and magnetic properties, and make a comparative study of their ground state energies, electronic structures, and magnet properties.

In the present paper, all the numerical calculations have been performed in the local spin density approximation (LSDA)+*U* by using the VASP[15,16] code. That is because in a few cases treated by only LSDA calculation, although there is no magnetic moment appearing in the system, the flat bands appear in it. Based upon the well-known theory on the flat band magnetism, including the electron correlations in the flat band would make it spin polarized. So, in this case, the LSDA+*U* calculation is more appropriate to treat the magnetism of the system. Also, in order to compare the results obtained in different cases more properly, we have simply treated all the systems by the same LSDA+*U* calculation. Here, the on-site Coulomb repulsion of *U*=3.0 eV, and the exchange *J*=0.9 eV have been used in the LSDA+*U* calculations, the similar value of *U* and *J* have also been adopted in other similar calculations.[17,18] The ion-electron interaction is modeled by the projector augmented wave (PAW)[19,20] potentials. A kinetic energy cutoff of 400 eV is found to converge the total energy to within 1 meV. Generally, a *k*-point mesh of $(1 \times 1 \times 5)$ (Gamma point included) is found to be sufficient to make convergence of the total energy within the order of meV. The supercell geometry for the SWNT has been used, in which the tubes are aligned in a hexagonal array with the adjacent intertube distance of at
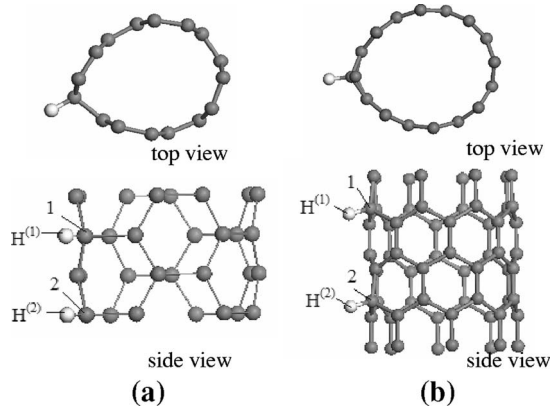
FIG. 1. Schematic of the geometrical structures of the hydrogenated (a) (4, 4) SWNT and (b) (8, 0) SWNT. Here, the dark and white balls represent the carbon and hydrogen atoms, respectively.

least 10 Å, sufficient to prevent the tube-tube interactions. All atoms are fully relaxed by a conjugate-gradient algorithm until the change in energy upon ionic displacement is below 0.1 meV.

In this paper we consider two different SWNTs: the armchair (4, 4), and the zigzag (8, 0) SWNT, among which the former is metallic, but the latter is semiconducting. The unit cell for the hydrogenated SWNT is taken in our calculations as a two-period length of the tube with two hydrogen atoms adsorbed on its external surface because the hydrogen atom is found by our numerical calculations to be absorbed more easily on the external surface of the SWNT. The geometrical structures of the hydrogenated (4, 4) and (8, 0) SWNTs are shown in Fig. 1, in which the dark and the white balls represent the carbon and the hydrogen atoms, respectively. The two hydrogen atoms are marked as $H^{(1)}$ and $H^{(2)}$, which bond to the carbon atom C1 and C2, respectively. Then, we fix the adsorption site of $H^{(1)}$, and change the adsorption site of $H^{(2)}$. In order to see clearly different adsorption sites of the $H^{(2)}$, a plane picture of Fig. 1 is given in Fig. 2, which is obtained by cutting the SWNTs in Fig. 1 along their tube axis. In
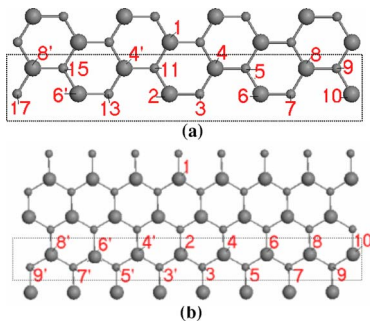

FIG. 2. (Color online) A plane picture of Fig. 1, obtained by cutting the SWNT along its tube axis. (a) (4, 4) SWNT; (b) (8, 0) SWNT. The bigger and smaller balls represent the A and B sites of carbon atoms, which are marked by some integers. C1 is the atom bonded by $H^{(1)}$, and then $H^{(2)}$ is made to bond to different carbon atoms in the dashed frame, respectively, obtaining other different structures. In the frame, relative to C1, the carbon atoms marked by 4′, 6′, 8′ are equivalent to C4, C6, C8, respectively.

TABLE I. Different magnetic properties of a hydrogenated (4, 4) SWNT with different adsorption positions of the second H atom, whose period is two times that of the pure (4, 4) SWNT. Here, the first H atom has been bonded to C1.

Structure kind	The carbon atom bonded to $H^{(2)}$	The total energy per unit cell (eV)	Magnetic moments per unit cell (μ_B)
	C2	−321.06	1.79
	C4	−320.38	1.50
AA	C6	−320.69	1.0
	C8	−320.75	0.99
	C10	−320.89	1.0
	C3	−321.85	0.32
	C5	−321.22	0.07
	C7	−321.22	0
AB	C9	−321.09	0.03
	C11	−321.96	0
	C13	−321.15	0.39
	C15	−321.17	0
	C17	−321.09	0

Fig. 2(a), all the carbon atoms shown in the dashed frame locate on the same armchair edge as the C2, in which relative to C1, there are 13 inequivalent carbon atom sites. And the C4′ means that this carbon atom site is equivalent to the C4 site due to the symmetry of (4, 4) SWNT, and so on for those C6′, C8′. Therefore, in Fig. 1(a), if we fix the position of $H^{(1)}$, and then change the position of $H^{(2)}$, making $H^{(2)}$ bonded to C3, C4–C17, respectively, there would be another 12 hydrogenated structures, which are different from that shown in Fig. 1(a). We treat the (8, 0) SWNT in the same way, whose hydrogenated structure is shown in Fig. 1(b), and mark those inequivalent carbon atom sites located on the same zigzag edge, shown in Fig. 2(b). Another eight different hydrogenated structures could be obtained from that shown in Fig. 1(b).

We have calculated the total energy and magnetic moments of these different structures for both (4, 4) and (8, 0) SWNTs, and given the obtained results in Table I and Table II, respectively, from which some general characteristics of the hydrogenated SWNTs are found as follows: (1) Those configurations with $H^{(2)}$ bonded to even number carbon atoms, e.g., C2, C4, etc., have larger magnetic moments, but those of $H^{(2)}$ bonded to the odd number carbon atoms, e.g., C3, C5, etc., have very small or zero magnetic moments. (2) The total energies of the former configurations are always higher than those of the latter, meaning the hydrogenated SWNTs prefer the nonmagnetic ground states.

It is well known that in the unit cell of an infinite SWNT there are two inequivalent carbon atoms, which can be called as A-type and B-type site in this paper. Therefore, we can divide all carbon atoms in the dashed frames of Fig. 2 into the same A-type and B-type site, i.e., all the even number carbon atoms in the frames are equivalent to the atom C1, called as A-type site, but those odd number carbon atoms are inequivalent to C1, called as B-type site. In order to distin-

TABLE II. Different magnetic properties of a hydrogenated (8, 0) SWNT with different adsorption positions of the second H atom, whose period is two times that of the pure (8, 0) SWNT. Here, the first H atom has been bonded to C1.

Structure kind	The carbon atom bonded to $H^{(2)}$	The total energy per unit cell (eV)	Magnetic moments per unit cell (μ_B)
	C2	−639.24	1.98
	C4	−639.48	0.46
AA	C6	−639.29	1.99
	C8	−639.39	1.73
	C10	−639.56	0.45
	C3	−640.07	0
AB	C5	−639.95	0
	C7	−639.91	0
	C9	−639.66	0

guish them, we have used the bigger and smaller balls to represent the *A*- and *B*-type sites, respectively, in the figures. It is obvious that for the structures of $H^{(2)}$ bonded to the even number carbon atoms, the two H atoms are adsorbed on the same *A*-type sites, called as *AA* structures, while for that of $H^{(2)}$ bonded to odd number carbon atoms, both H atoms lie on the different *A*- and *B*-type sites, respectively, which can be called as *AB* ones in the following.

From Tables I and II, we know the *AA* structures favor the appearance of magnetic moments, but the *AB* ones disfavor it. In all the *AA* structures, if the net spin of every hydrogen atom is positive, then the net spin of carbon atom on every *A* site is negative, making the absolute magnet moment on every *A* site very lower, nearly to be zero, but the net spin of carbon atom on every *B* site is positive, and the total magnetic moment of a single atom is larger, making the total magnetic moment of one unit cell positive. So, in general, the *AA* structures show a ferrimagnetic order, meaning the net spins on every two carbon atoms bonded together are always opposite in the *AA* structures. To understand it more clearly, we have shown in Fig. 3(a) the isosurfaces of the magnetization density on the specific *AA* structure of $H^{(1)}$-C1 and $H^{(2)}$-C2 at a density value of $0.012\mu_B$ Å^{-3}, from which it is seen that the magnetization density localizes on the three carbon atoms nearby the hydrogen atoms. For all

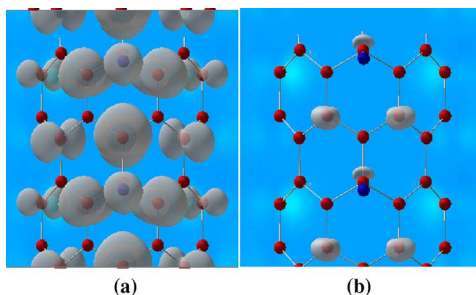**(a)**   **(b)**

FIG. 3. (Color online) The isosurfaces of the magnetization density at (a) $0.012\mu_B$ Å^{-3} and (b) $-0.012\mu_B$ Å^{-3}, on the $H^{(2)}$-C2 structure of the (8, 0) SWNT.

the *AB* structures, we found that the magnetic moment on every carbon atom is very small or nearly zero, showing no regular magnetic order.

It is very interesting to know why the *AA* and *AB* structures are so greatly different in inducing the magnetic order, and what is its microscopic origin. When the hydrogen atoms are adsorbed on the SWNTs, they will cause two primary changes, among which one is the charge transfer, and another is the structure distortion of the SWNT, especially around the hydrogen atoms. In order to identify their separate effects, we have made a similar calculation on a two-periods length of (8, 0) SWNT with one hydrogen adsorbed on it. After the geometry optimization, we found its magnetic moment is $0.8884\mu_\beta$. Then we removed the hydrogen atom from the above relaxed structure, and did not relax it any more, based on which its magnetic moment was again calculated, and found to vanish completely. On the other hand, for the same structure, we did not relax the nanotube, but only relaxed the C-H bond, and then calculated its magnetic moment directly. We have also found that the magnetism vanishes completely. The above calculations demonstrated that the charge transfer and the tube distortion caused by the hydrogen adatoms are all indispensable to the appearance of magnetism. On the other hand, in both of the *AA* and *AB* structures, we have found by our numerical calculations that the charge transfer and the local distortion around the hydrogen atoms have no distinct difference between the *AA* and *AB* structures. The interaction effect between two hydrogen atoms is not important either because the fundamental difference between both *AA* and *AB* structures is independent of the distance between two hydrogen atoms. Finally, it is found that the total magnetic moments are not the simple algebra sum of those induced by two isolated hydrogen atoms, but there exists an interference effect between them. So, the only possible reason to cause the large difference between the *AA* and *AB* structures is the different correlation effects in both structures induced by different topological hydrogen atom configurations of *AA* and *AB* sites.

In order to study the magnetic properties, we should first study the electronic band structure of every different configuration, which is calculated by the LSDA+*U* method. It is found that the flat bands always appear at the Fermi energy in the band structure of the *AA* structures, but not in the *AB* structures. Here we have only shown some typical band structures in Fig. 4, which correspond to three different configurations of the (4, 4) tube with $H^{(2)}$ bonded to C2, C7, and C13, respectively. The spin-polarized flat bands of $H^{(2)}$-C2 structure (*AA* structure) appear at the Fermi energy, in which all branches for up and down electrons are split, making the system display a stronger magnetism. In the band structures of the $H^{(2)}$-C7 and $H^{(2)}$-C13 structures (*AB* structures), we have not found the flat bands at Fermi energy. And only for the $H^{(2)}$-C13 structure, there is a band crossing the Fermi level, causing a weak spin polarization. So, we conclude that the flat bands always appear at the Fermi energy for the *AA* structures, causing the appearance of a stronger magnetic order. On the other hand, the *AB* structures cannot induce the flat bands in their band structures, making its magnetic order very weak or completely lost. For the (8, 0) tube, we have done the same work as for the (4, 4) tube, and found the
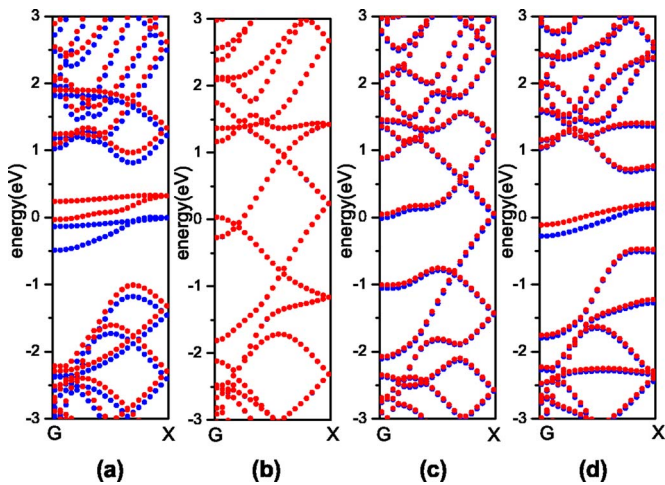
FIG. 4. (Color online) The LSDA+U electronic band structures of some different configurations for the (4, 4) SWNT, in which the spin-up and spin-down channels are represented by dark and light (blue and red online) lines, respectively. (a) $H^{(2)}$-C2, (b) $H^{(2)}$-C7, (c) $H^{(2)}$-C13. (d) The structure of a two-periods length of (4, 4) tube with only one hydrogen atom adsorbed on it.

same features as for the (4,4) tube. So, we will not make any more detailed analysis on them.

It is interesting to know what causes the large difference between the band structures of the AA and AB configurations. First, we show in Fig. 4(d) the LSDA+U electronic band structure of a two-periods length of (4,4) tube with only one hydrogen atom adsorbed on it, and see there is a flat band at the Fermi energy induced mainly by the hydrogen. Therefore, in the AA structures because $H^{(1)}$ and $H^{(2)}$ occupy the same topological type of adsorption sites, their effect on the band structures of the system can be added in phase, making the flat bands appear, which favors the magnetism. However, for the AB structures, since $H^{(1)}$ and $H^{(2)}$ occupy

the different topological types of adsorption sites there would be a phase difference between their quantum states, making their superposition more complicated than in the AA structures and causing the vanished flat bands at the Fermi energy, which is disadvantageous to the appearance of magnetism. In addition, the total energy of the AA structures is always higher than the AB structures, making the ground state of the hydrogenated SWNT nonmagnetic.

Needless to say, realization of the systems proposed here will be an experimental challenge. However, we think that it is not impossible. According to our results, in the systems we studied, it is found when the $H^{(2)}$ is far more from the $H^{(1)}$, the difference of the total energies between the neighboring AA and AB structures is lower. For example, for the $H^{(2)}$-C9 and $H^{(2)}$-C10 structures of the (8, 0) SWNT, the difference between their average energies/every atom is only 15 meV. So in this case, the migration barrier would be lower, and at a finite temperature the AA structure could be stable, making the magnetism available.

In summary, we have studied by the first-principle calculations the magnetic properties of the hydrogenated SWNTs, paying special attention to the effects on the magnetic order of the system due to different distributions of hydrogen atoms on the tube surface. Our obtained results have shown that the different distributions of hydrogen atoms affect significantly the magnet properties of the system. It is shown that the AA and AB hydrogenated structures display fundamentally different magnetic behaviors, among which the AA structure favors the appearance of spontaneous magnetism, but the ground state of AB structure is nonmagnetic. A possible reason for the difference between these two structures is the different topological configurations for the adsorption sites of hydrogen atoms in the AA and AB structures, making flat bands appear at Fermi level in the electronic band of the AA structure, but not in the AB one.

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