Itinerant Flat-Band Magnetism in Hydrogenated Carbon Nanotubes

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We investigate the electronic and magnetic properties of hydrogenated carbon nanotubes using
ab initio spin-polarized calculations within both the local density approximation (LDA) and
the generalized gradient approximation (GGA). We find that the combination of charge transfer
and carbon network distortion makes the spin-polarized flat-band appear in the tube’s energy
gap. Various spin-dependent ground state properties are predicted with the changes of the radii,
the chiralities of the tubes and the concentration of hydrogen (H). It is found that strain or
external electric field can effectively modulate the flat-band spin-splitting, and even induce an
insulator-metal transition.

Keywords: hydrogenated carbon nanotube, density functional calculation, spin-polarized elec-
tronic structure, strain effect, electric field effect

I. INTRODUCTION

Much attention has long been devoted to finding macroscopic magnetic ordering phenomena in organic
materials. Experimentally, ferromagnetism has been discovered in pure carbon systems, such as carbon
foam, graphite, oxidized C_{60} and polymerized rhombohedral C_{60}^{1–5}, which has stimulated renewed interests
in their fundamental importance and potential applications in high-technology, e.g., the spintronics. Much
theoretical work has been done to study magnetism in nanographites
6–10, C_{60} polymers
11, and all-carbon
nanostructures
12,13. However, the microscopic origin of ferromagnetism remains controversial.

The recent proton irradiation experiments in graphite
2,3 have shown the importance of hydrogen in inducing the magnetization instead of magnetic
impurities. Disorder induced by He
+ ions irradiation does not produce such a large magnetic moment as
obtained with protons
14. Theoretically, the possible magnetism arising from the adsorption of hydrogen
atom on graphite has been studied
15–19. It can be easily speculated that hydrogen can trigger the sp^{2}\text{-}sp^{3}
transformation, promoting the magnetic ordering in other carbon structures, especially carbon nanotubes
with a surface of positive curvature.

Herein, we focus on the electronic and magnetic properties of single-walled carbon nanotubes (SWNTs) with
hydrogen atoms adsorbed on their surfaces. Our results show that hydrogenated carbon nanotubes are on the
verge of magnetism instability, and the combination of charge transfer and carbon network distortion drives flat-
band ferromagnetism. To our knowledge, this is the first comprehensive ab initio study on the physical origin of
flat-band ferromagnetism in the real carbon nanotube materials. Moreover, the applied strain and external
electric field are found to have a strong influence on the flat-band spin-splitting, resulting in the variation of spin-

II. RESULTS AND DISCUSSION

FIG. 1: Schematic geometrical structures of hydrogenated zigzag (top panels) and armchair (bottom panels) tubes in the
higher hydrogen concentration A with one hydrogen per tube period, or the lower hydrogen concentration B with one hy-
drogen per every two tube periods. Blue (grey) balls represent the hydrogen (carbon) atoms.

Interestingly, instead of the simple sp^{2} bonds in graphite, the bonds in carbon nanotubes are of sp^{2}\text{-}sp^{3} character due to the
tube’s curvature effect, making the hybridization of σ, σ^{*}, π and π^{*} orbitals quite larger, especially for small-
diameter tubes. Thus the magnetic property of hydrogenated SWNTs are more complicated than that of hy-
drogenated graphite, with a large dependence on the radii, the chiralities, and hydrogen concentration. Here,
two types of linear hydrogen concentration A and B are shown in Fig. 1. There is one hydrogen atom per tube
period in the higher concentration A, and one hydrogen atom per every two tube periods in the lower concen-
tration B. The higher H concentration leads to a larger structure deformation, as can be seen in Fig. 1. Stable

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C-H bond length is 1.1 Å, typical of covalent bonding (cf. 1.09 Å in methane). Recently, the cooperative alignment of the absorbed atoms has been observed in graphene experimentally\textsuperscript{15}. In the case of carbon nanotubes, the absorption of hydrogen on tube wall is easier than that on graphene due to the curvature effect\textsuperscript{16}. Moreover, the adatoms’ cooperative alignment can be enhanced by high curvature regions of nanotube\textsuperscript{16}, that can result from pressure\textsuperscript{17}, compression transverse to its axis\textsuperscript{18}, or tube-substrate interaction\textsuperscript{19}.

Now, let us study electronic structures of hydrogenated SWNTs, taking the zigzag (8,0), (9,0), and armchair (5,5) and (10,10) tubes as examples. Fig. 2 presents their ground state band structures obtained by using spin-polarized LDA (\textit{left panels}) and GGA (PBE exchange correlation functional) (\textit{right panels}). In spin-unpolarized LDA and GGA paramagnetic (PM) band structures (not shown here completely), a common feature is that hydrogen atom induces a half-filled flat-band in the tube’s energy gap around $\epsilon_F$ due to the odd electrons in compounds, as seen in the LDA-PM ground state band structure of (5,5)-B in Fig. 2. Apparently, flat-band creates an extremely high density of states around $\epsilon_F$, and if the Coulomb interaction between itinerant electrons in the band is introduced, magnetic instability would occur. It has been shown that flat-band leads to ferromagnetism for certain models\textsuperscript{20}. In hydrogenated SWNTs, the spin-spin interaction plays a similar role as the Coulomb one, and lifts the spin degeneracy of the flat band. As a result, the flat-band’s spin-splitting magnitude and the energy position relative to $\epsilon_F$ determine the ground state properties of system. As we can see in the right panels of Fig. 2, the spin-splitting magnitude has increased after introducing the generalized gradient correction in the exchange correlation functional, compared to the LDA without correction (\textit{left panels}), which makes ferromagnetic (FM) state become more favorable in energy. The adsorption of hydrogen atom is found to hardly affect the gaps of zigzag (8,0) and (9,0) tubes\textsuperscript{21}, while a large tube’s energy gap is opened in the metallic armchair (5,5) and (10,10) tubes. In the LDA results, (8,0)-A,B, (5,5)-A and (10,10)-A exhibit FM semiconducting characteristic, whereas (9,0)-A,B and (10,10)-B are FM metals. (5,5)-B has a PM metallic ground state under LDA. However, the enhanced spin-splitting in GGA makes (9,0)-A,B and (10,10)-B present a FM semiconducting behaviour, not metallic one under LDA. Furthermore, a FM metallic state is produced for (5,5)-B, not the PM metallic one obtained by LDA.

In order to investigate the physical origin of flat-band ferromagnetism, we plot the spin-up density of the full-occupied GGA flat-band of (9,0)-B (black band, see Fig. 2) in Fig. 3. A $sp^3$-like hybridization is induced on the carbon atom attached to the hydrogen atom, leading to whole carbon network distortion, accompanied by charge transfer from hydrogen to the bonded carbon atom (0.352 and 0.334 electron for LDA and GGA (PBE), respectively). Magnetism is strong itinerant in both circumferential and tube axial directions, arising from the hybridization of H-$s$ orbital with tube-$\pi$ orbitals. Magnetic moment per unit cell is 0.63 and 0.96 $\mu_B$ in LDA and GGA, respectively.

Obviously, this $s-\pi$ hybridization is relevant to structure distortion and affects the flat-band spin-splitting magnitude. To get such an insight, we carried out both LDA and GGA calculations on the undistorted (9,0)-B structure with only the location of hydrogen atom relaxed. Charge transfer still exists, and the band structures plotted in Fig. 3(c) clearly show a disappearance of the flat-band spin-splitting and also magnetism. Weak magnetic moment 0.2 $\mu_B$ per unit cell appears even if on-site Coulomb repulsion $U = 3.0$ eV\textsuperscript{22} is considered.

\*FIG. 2: Spin-polarized LDA (\textit{left panels}) and GGA (\textit{right panels}) ground state band structures of hydrogenated zigzag (8,0) and (9,0), and armchair (5,5) and (10,10) tubes in the two different systems A (top panels) and B (bottom panels). Insets show the band structures around $\epsilon_F$ in an enlarged energy scale. The Fermi level is set at zero. Spin-up and spin-down channels are represented by black and cyan, respectively.\*
in the LDA+U calculation. These results indicate that only charge transfer is not sufficient to induce a large magnetic moment, therefore structure distortion is indispensable. As a result, we can anticipate that the applied strain could tune the physical properties of hydrogenated SWNTs by affecting the spin-splitting of flat-band. We applied a 4% stretch or compression strain along the tube axis, then the atomic positions were optimized again. Corresponding ground state electronic structures are given in Figs. 3(d)-3(e). As expected, strain do has an important effect on the magnetic ground state properties. The 4% axial stretch strain causes the length of C-C bonds, beneath the H atom, further stretched and deviate from the regular value of 1.42 Å, which enlarges the energy gap, as shown in Fig. 3(d). Even a metal-insulator transition is found in LDA band structure, accompanied by an increase in the magnetic moment to 0.96 $\mu_B$ (normally 0.63 $\mu_B$). Under 4% axial compression strain, the compound presents the metallic or semiconducting characteristic similar to those without strain in both LDA and GGA, but the magnetic moment in LDA is reduced to 0.53 $\mu_B$. Under both axial strains, the transferred charge remains to be $0.35 \sim 0.36$ electron in LDA and $0.33 \sim 0.34$ electron in GGA, proving that carbon network distortion plays a very important role in the flat-band spin-splitting. Of course, flat-band and magnetism would also disappear if we remove the hydrogen atom from the distorted SWNTs, indicating the necessity of hydrogen in inducing the ferromagnetic ordering, which is similar to the role of so called “carbon radicals” in magnetic all-carbon structures.\(^7\)

Fig. 4 summaries structure information and ground state properties of hydrogenated zigzag ($n,0$) ($n=6-12$) and armchair ($n,n$) ($n=5-11$) tubes in both A and B cases (see Fig. 1). Generally speaking, magnetic moment per unit cell has increased gradually with the change of tube index $n$ (top panels), and approaches a saturation value in both LDA and GGA results. In ($n,0$)-A case, magnetic moment curve presents oscillation behavior (especially in LDA) that might be relevant to periodic change of the band gap in zigzag-type tubes. The higher concentration A-type compounds have a larger magnetic moment than that of the lower concentration B-type compounds, especially in smaller diameter tubes. In the bottom panels of Fig. 4, the curves of energy difference ($E_{PM} - E_{FM}$) between FM and PM states per unit cell vs tube index $n$ present a similar trend as found in the curves of magnetic moment vs $n$. Introducing of the generalized gradient correction enhances the spin-splitting, as discussed for Fig. 2, which leads that the FM state becomes more favorable in GGA than in LDA, evidenced by the energy difference $E_{PM} - E_{FM}$. These reveal that magnetic properties of hydrogenated carbon nanotubes are affected by the structure characteristic of the SWNTs host, and the concentration of hydrogen.

Finally, we also investigate the effect of transverse electric fields in the Y direction of cross section (see Fig. 3(a)). Absorption of H atom makes SWNT become a polar organic compound. Here, the polar C-H bond is just along the Y direction. It can be anticipated that charge redistribution driven by an external electric field could occur, which would induce a subtle change of electronic structure. Both LDA and GGA simulations on (10,10)-A reveal the spin-dependent effect of applied external electric fields with a magnitude of $0.1 \sim 0.4$ V/Å.

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**FIG. 3:** The 0.003 Å$^{-3}$ magnetization density isosurfaces for the full-occupied spin-up GGA flat-band in (9,0)-B: (a) top view, and (b) front view. Spin-polarized LDA and GGA ground state band structures for (9,0)-B: (c) with only the location of hydrogen atom relaxed, (d) under the 4% axial stretch strain, (e) under the 4% axial compression strain.

**FIG. 4:** From the top down, the evolution of magnetic moment per unit cell and energy difference ($E_{PM} - E_{FM}$) per unit cell vs the tube index $n$. Left panels are from spin-polarized LDA, and right panels are from spin-polarized GGA (PBE).
illustrated in Fig. 5. Compared with Fig. 2, the applied field gradually decreases the gap between spin-up and down flat band at 0.1 and 0.2 V/Å, finally closes it and directly drives an insulator-metal transition at 0.3 V/Å in LDA and 0.4 V/Å in GGA. This effect is different from the case of graphene nanoribbons, where the band gap closure takes place only for one spin channel. The fantastic “beating” behaviour of spin-polarized flat-band under the external electric field can be used for designing quantum switches.

We have demonstrated how the combined effect of charge transfer and carbon network distortion makes spin-polarized flat-band appear in the tube’s carbon: Explicit evidence of ferromagnetism induced by proton irradiation. Carbon 2004, 42, 1213-1218.

IV. THEORETICAL METHODS AND MODELS

We carried out the numerical calculations using the Vienna ab initio Simulation Package (VASP) within the frameworks of spin-polarized local density approximation (LDA) and generalized gradient approximation (GGA) (PBE exchange correlation functional). The ion-electron interaction was modeled by the projector augmented wave (PAW) method with a uniform energy cutoff of 400 eV. We used periodic boundary conditions and a supercell large enough to prohibit the electronic and the dipole-dipole interactions between neighboring tubes. The spacing between k points was 0.03 Å⁻¹: 1×1×8 k-point sampling in (n,0)-Å, 1×1×4 in (n,0)-B, 1×1×14 in (n,n)-A, and 1×1×7 in (n,n)-B. The geometrical structures of hydrogenated SWNTs were optimized by employing the conjugate gradient technique, and in the final geometry no force on the atoms exceeded 0.01 eV/Å.
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