Enhanced spin-orbit coupling in hydrogenated and fluorinated graphenes studied from first principles

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(Dated: July 22, 2009)

Abstract

The spin-orbit couplings (SOCs) of hydrogenated and fluorinated graphenes are calculated from the first principles method. It is found that the SOC-induced band splittings near their Fermi energies can be significantly enhanced to the order of $10^{-2}$ eV from the original about $10^{-6}$ eV of the pure graphene, which is comparable to those found in the diamond and even the archetypal semiconductors. And two different mechanisms are proposed to explain the SOC enhancements in these two systems. The huge SOC enhancements are found to come not only from the sp$^3$ hybridization of carbon atoms, but also from the larger intrinsic SOC of the fluorine atom than the carbon one. We hope many interesting phenomena caused by the SOCs (e.g. the spin Hall effect) can be observed experimentally in these systems.

PACS numbers: 73.22.-f, 61.48.De, 71.70.Ej, 71.15.Mb

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I. INTRODUCTION

The graphene, a single layer graphite, has attracted much attentions of researchers since its discovery in 2004 [1] due to its unique two-dimensional (2D) geometrical structure and Dirac-Fermion’s electronic properties [2]. Many works focus on its transport properties since the charge carrier mobilities of the graphene can reach to more than $10^4 \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ [1, 3, 4]. In addition, the graphene might also be a promising material for spin transport [5] and other spintronics applications, such as the spin-qubits [6], due to the weak spin-orbit coupling (SOC) of carbon atom. This is true since many theoretical works show that the SOC-induced band gap at the $K$ point (i.e. Dirac point) of the graphene is very small, which is at the order of $10^{-6} \sim 10^{-5} \text{eV}$ [7, 8, 9, 10].

However, although the weak SOC is good for transporting spin information, but it is probably not favored by others. As we known, the SOC is related to many interesting phenomena, such as optical dichroism, anomalous Hall effect, and spin Hall effect, among which the spin Hall effect especially offers a possibility of pure electrically driven spintronics in semiconductors and simple metals [11, 12]. Unfortunately, the tiny SOC in a pure graphene makes impossible to observe experimentally the proposed spin Hall effect even the temperature goes down to 0.01 K [7, 8, 9].

Therefore, it is quite meaningful and important to study how to enhance the SOC of the graphene for other applications. In fact, the curvature effect can mix the $\pi$ and $\sigma$ electrons in the graphene and enhance the SOC significantly [8], which has been experimentally found in the single-walled carbon nanotube (SWNT) [13]. Our recent first principles calculation shows that the SOC-induced band splitting can reach to several meV in small diameter SWNTs [14]. Another possible method to enhance the graphene’s SOC is to form sp$^3$ bonds by the impurities adsorbed on the sp$^2$ graphene, which has been proposed by Neto and Guinea very recently [15]. They show that the impurities can induce the sp$^3$ distortion of the flat graphene, leading to a large SOC enhancement in it, which possibly reaches to about 10 meV, the same order as the intrinsic SOC in the carbon atom.

On the other hand, a new kind of 2D crystal, called graphane, has been firstly predicted theoretically [16] and then synthesized recently in the experiment [17]. The graphane is nothing but a fully hydrogenated graphene (H-graphene), in which the hydrogen atoms change the hybridizations of carbon atoms from sp$^2$ to sp$^3$, removing the conducting $\pi$
bands near the Fermi energy of the pure graphene. As a result, the H-graphene is a wide gap semiconductor, which can also be considered as a 2D-like diamond. In fact, even far before the H-graphene is found, the fluorinated graphite (F-graphite) has been synthesized and calculated [18, 19, 20]. It is then straightforward that the fluorinated graphene (F-graphene) can also exist and be easily synthesized just like the F-graphite. The F-graphene has the similar sp³ hybridizations as the H-graphene and is also a wide gap semiconductor. However, since fluorine has a much larger electronegativity than hydrogen, we expect that in the F-graphene, the charge transfer between the graphene and dopants is quite different from that in the H-graphene. And the SOC in a fluorine atom itself is also different from those in the hydrogen and carbon atoms.

Based on the above arguments, we have used the first-principles method to calculate the practical sizes of SOC in the H-graphene and F-graphene. The paper is organized as follows. In Sec. II, the computational method and details are described. The main numerical results and discussions are given in Sec. III. Finally, in Sec. IV, a conclusion is presented.

II. COMPUTATIONAL METHODS

The spin-orbit couplings in the three different systems, i.e., the pure graphene, H-graphene and F-graphene have been calculated by the density functional theory in the local density approximation implemented in the VASP [21, 22] code, in which the projected augmented wave (PAW) method [23, 24] and the Ceperley-Alder-type exchange-correlation are used. The plane-wave cutoff energy is 520 eV throughout the calculations. A supercell is used to simulate the two dimensional structures, in which the closest distance between two nearest layers is taken to be at least 10 Å. A uniform grid of 20 × 20 × 1 k points is used for pure graphene and 10 × 10 × 1 k points for H-graphene and F-graphene. Both of the atomic positions and the in-plane lattice constant are firstly optimized without SOC and the residual forces at all atoms are less than 0.005 eV/Å. Once the optimized structure is obtained, the band structures with and without the SOC are calculated. By comparing the two band structures, the SOC-induced band splitting can be obtained.

We use the same 'chair' structure in the H-graphene as that in the reference [16], whose binding energy is about 0.06 eV/atom lower than the 'boat' structure. The F-graphene is constructed by replacing the hydrogen atoms in the H-graphene with fluorine ones. As a
TABLE I: The calculated bonding length, bond angles, energy gap, and SOC-induced band splitting near the Fermi energy in the pure graphene, H-graphene and F-graphene. The value of diamond is the experimental one.

|                | graphene | H-graphene | F-graphene | diamond |
|----------------|----------|------------|------------|---------|
| C-C (Å)        | 1.413    | 1.516      | 1.553      | 1.544   |
| C-H(F) (Å)     | -        | 1.117      | 1.365      | -       |
| ∠ C-C-C (°)    | 120.0    | 111.6      | 110.6      | 109.5   |
| ∠ C-C-H(F) (°) | -        | 107.3      | 108.3      | -       |
| Energy gap (eV)| 0        | 3.38       | 2.96       | 5.48    |
| SOC size (meV) | $10^{-3}$| 8.7        | 27.4       | 6.0     |

FIG. 1: (Color online) The band structure of pure graphene with SOC.

reference, the band structure and SOC of the pure graphene is also calculated.

III. RESULTS AND DISCUSSIONS

A. Pure graphene

The pure graphene is well known to be a zero gap semiconductor, whose band structure is given in Fig.1. The linear band structures of $\pi$ electrons touch exactly on the Fermi energy at the $K$ point. When the SOC is turned on, a small gap can be opened at this point, which is at the order of $10^{-6}$ eV. This is because in the pure graphene only the $\pi$ electrons hopping
between the two next nearest neighbor carbon atoms can contribute to the SOC, which is the second order process and quite tiny \([7, 8, 9]\). However, at the Γ point, the two-folding degenerate valence band splits by about 9.4 meV, which is caused by the \(\sigma\)-electrons and much larger than that at the \(K\) point.

Since only the electrons near the Fermi energy participate the transport process, some spin-related phenomena cannot be observed until the temperature is as low as 0.01 K. In order to get a large SOC at the Fermi energy, we have to use the \(\sigma\) electrons. The recently discovered H-graphene gives us such a system, where the \(\pi\) bands are removed by the hydrogen atoms and the \(\sigma\) bands become the highest occupied molecular state (HOMO) at the Γ point. We expect a large SOC can be found in the H-graphene.

**B. H-graphene**

First of all, we can see from Table I that the bond lengths of C-H and C-C are 1.117 and 1.516 Å, respectively, which are well consistent with Sofo et al.’s results \([16]\). The angle between the C-C and C-H bonds is about 107.3° and that between the two C-C bonds is about 111.6°. All these bond lengths and angles are much like the ones in the diamond rather than in the pure graphene, indicating that the H-graphene is a pure sp\(^3\) carbon system and is somewhat like to a flat 2D diamond. The band structure of chair-type H-graphene is given in Fig. 2, from which it can be clearly seen that the H-graphene is a wide direct
FIG. 3: (Color online) The band structure of F-graphene with SOC. The inset shows the detailed band structure near the Γ point.

gap semiconductor with its band gap of about 3.38 eV, which is underestimated due to the well-known DFT band gap problem. A recent GW calculation shows that the band gap of H-graphene is 5.4 eV, which is very close to that of the diamond [25].

It is clearly shown by a comparison of Fig.1 with Fig.2 that the π band in the pure graphene disappears in the H-graphene and the σ band at the Γ point becomes the top of its valence band. When considering SOC, the two fold degenerate σ-bands split near the Fermi energy at the Γ point with a gap of 8.7 meV, as shown in the inset of Fig.2. This value is at the same order as the intrinsic SOC of atomic carbon and greatly enhanced, compared with the negligible SOC near the Fermi level of the pure graphene, which is induced by the π-bands in it. This SOC-induced band splitting appears at the highest point of the valence band and is very similar to the SOC in the archetypical semiconductors [11].

C. F-Graphene

The fluorinated graphene is also calculated and its band structure is given in Fig.3. Obviously, the F-graphene has the similar band structure with the H-graphene, except that more valence bands are found in the F-graphene. The F-graphene is also a wide direct gap semiconductor with a band gap of 2.96 eV, a little smaller than that of the H-graphene. However, we also expect that the real band gap is about 5 eV if we take into account the same DFT underestimation of the band gap as in the H-graphene. This also gives us a
method to tune the band gap of pure graphene by using different adsorbed atoms.

In Table I, the C-C and C-F bond lengths in the F-graphene are shown to be 1.553 and 1.365 Å, respectively. The angle between the C-C and C-F bonds is about 108.3°, and that between the two C-C bonds is about 110.6°, which are all well consistent with the previous calculation [18]. Although the bond lengths are much longer than that in the H-graphene, the F-graphene is also a sp³ carbon system and therefore both of them have the similar band structures.

It is the most interesting to find that the SOC-induced band splitting in the F-graphene can reach to 27.4 meV near the Fermi energy, which is far bigger than that of carbon atom. We believe that this large SOC cannot be explained only by the sp³ hybridization of carbon atoms. What is the difference between the H-graphene and F-graphene? We think the main difference between them is that the fluorine atom has a much larger electronegativity than hydrogen atom. The charge transfers from the carbon atom to fluorine one in the F-graphene and the SOC splitting is contributed from both the carbon and fluorine atoms. In order to confirm this hypothesis, we have calculated the site and orbital projected wavefunction of HOMO at the Γ point, whose coefficient can give the band characteristics. The obtained results show that the HOMO state of the F-graphene consists of about 60% carbon’s p-electron and about 40% fluorine’s p-electron. It is known that the intrinsic SOC of the fluorine atom is quite larger, which is about 50 or 100 meV by different experiments [26]. So, the large SOC splitting in the HOMO state of the F-graphene comes mostly from that of the fluorine atom, whose mechanism is totally different from that in the H-graphene, where its HOMO state consists of almost 100% carbon’s p-electron. As a result, the SOC splitting near the Fermi energy in the H-graphene has the similar value as that of diamond or carbon atom, while the one in the F-graphene has a much bigger value.

IV. CONCLUSION

In summary, we have used the first-principles method to calculate the practical SOC-induced band splittings of the H-graphene and F-graphene. And two different mechanisms have been proposed to explain the great enhancements of the SOC splitting in both of them, in which the carbon atoms’ hybridizations become the sp³ from their original sp² due to the doped hydrogen or fluorine atoms, making the σ-bands move to the top of their valence bands.
bands and a large energy gap to be opened at there. The SOC induced band splitting near the Fermi energy of the H-graphene is found to reach to 8.7 meV, which is significantly enhanced by four orders from its original value near the Fermi energy of the pure graphene. More importantly, it is even enhanced to 27.4 meV in the F-graphene, which mainly comes from the larger SOC of fluorine atom than the carbon atom. These large SOC values are comparable, respectively, to those found in the diamond and archetypal semiconductors. So, we hope that the spin Hall effect and other SOC-related phenomena can be easily found in the H-graphene and F-graphene than that in the pure graphene.

Acknowledgments

This work was supported by the Natural Science Foundation of China under Grant No. 10874067, and also from a Grant for State Key Program of China through Grant Nos. 2004CB619004 and 2006CB921803. J.Z. is also supported by the China Postdoctoral Science Foundation funded project and the Jiangsu Planned Projects for Postdoctoral Research Funds.

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