Electronic and magnetic properties of bilayer graphene with intercalated adsorption atoms C, N and O

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Abstract

We present an ab-initio density function theory to investigate the electronic and magnetic structures of the bilayer graphene with intercalated atoms C, N, and O. The intercalated atom although initially positioned at the middle site of the bilayer interval will finally be adsorbed to one graphene layer. Both N and O atoms favor the bridge site (i.e. above the carbon-carbon bonding of the lower graphene layer), while the C atom prefers the hollow site (i.e. just above a carbon atom of the lower graphene layer and simultaneously below the center of a carbon hexagon of the upper layer). Concerning the magnetic property, both C and N adatoms can induce itinerant Stoner magnetism by introducing extended or quasilocalized states around the Fermi level. Full spin polarization can be obtained in N-intercalated system and the magnetic moment mainly focuses on the N atom. In C-intercalated system, both the foreign C atom and some carbon atoms of the bilayer graphene are induced to be spin-polarized. N and O atoms can easily get electrons from carbon atoms of bilayer graphene, which leads to Fermi level shifting downward to valence band and thus producing the metallic behavior in bilayer graphene.

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**Introduction:** Since the discovery of monolayer graphene in the year 2004 [2], this two-dimensional material remains in the focus of active research motivated by its novel physical properties and a promising potential for applications [3–5]. Experimental groups have enabled preparation and study of systems with one or a small number of graphene layers [6]. Bilayer graphene, which is made of two stacked graphene layers, is considered to be particularly important for electronics applications because of its special band structure [7]. Coupling of the two monolayer graphene sheets in the usual A-B stacking of bilayer graphene yields pairs of hyperbolically dispersing valence and conduction bands that are split from one another by the interlayer interaction [8]. The band gap of the bilayer can be easily opened when a difference between the electrostatic potential of the two layers is introduced, either by chemical doping or by applying gate voltage [9–17], which makes graphene channels have a high resistance for the OFF state. Angle-resolved photoemission (ARPES) measurements indicate such a gap in potassium doped bilayer graphene epitaxially grown on SiC [14], and infrared spectroscopy measurements also detect the similar gap in the electrostatically gated bilayer graphene [10–12].

In this work, we carried out first-principle calculations and theoretical analysis to explore the electronic and magnetic properties of bilayer graphene with intercalated atoms C, N and O. The calculations were performed using the projector augmented wave (PAW) formalism of density functional theory (DFT) as implemented in the Vienna *ab initio* simulation package (VASP) [18]. Because generalized gradient approximation (GGA) [19] gives essentially no bonding between graphene planes and leads to excessively large values of bilayer distance [13], we performed the calculations within the localized density approximation (LDA). We find that LDA gives rise to a bilayer distance of 3.34 Å, in good agreement with the experiment value. Some previous investigations used LDA to optimize the structure to get a reasonable bilayer distance, and subsequently used GGA to calculate the electronic structure [9]. To keep consistent, we use LDA in all our calculations for the investigated system. An energy cutoff of 400 eV for plane-wave expansion of the PAWs is used. The model system here consists of a 4 × 4 supercell with a foreign atom intercalated between the two coupling graphene layers. The supercell parameters are set to be the same as $a = b = 9.84$ Å in the $xy$ plane ($a$ and $b$ indicate the crystal lattice constants). The Brillouin zone is sampled using a $11 \times 11 \times 1$ Γ centered k-point grid. For geometry optimization, all the internal coordinates are relaxed until the Hellmann-Feynman forces are less than 0.01 eV/Å.
vacuum thickness along the z axis is 16 Å to avoid the interaction between graphene layers of adjacent supercells.

We considered the \(\tilde{\text{A}}\)-B Bernal stacking structure for bilayer graphene. Top-view for the bilayer graphene is shown in Fig. 1(a), in which violet color is for the lower layer, and gray color is for the upper layer. Seen from the top-view, ‘\(\tilde{\text{A}}\)’ position in the lower layer coincides with ‘B’ position in the upper layer, ‘A’ position in the upper layer is exactly the center of the hexagon of the lower graphene layer from the top-view, and ‘\(\tilde{\text{B}}\)’ position in the lower layer is right the center of the hexagon of the upper graphene layer. The foreign atom is intercalated between the upper and lower graphene layers and is initially positioned in the middle position of the bilayer distance. Three kinds of initial positions are considered for each intercalated atom: bridge, top and hollow positions, which are noted in the following by using subscript “\(\text{Bri}\)”, “\(\text{Top}\)”, and “\(\text{Hol}\)” when needed, for example, we use \(N_{\text{Bri}}\) to indicates the bilayer system with \(N\) atom positioned at the bridge site. Bridge site is above the carbon-carbon bonding in the lower graphene layer, top site indicates the middle position between the coinciding positions ‘\(\tilde{\text{A}}\)’ and ‘B’, and hollow site is just above a carbon atom of the lower graphene layer and simultaneously below the center of a carbon hexagon of the upper layer. The structure relaxation calculations show that, if the intercalated atom is initially positioned at the bridge or hollow site, it will finally be adsorbed to one graphene layer and away from the other layer. While for the top site, the foreign atom will keep being located in the middle position of the bilayer interval.

The binding energy is defined as: \(dE = E_{\text{graphene}} + E_{\text{atom}} - E_{\text{total}}\), where \(E_{\text{graphene}}\) is the energy of the clean bilayer graphene, \(E_{\text{atom}}\) stands for the energy of the single foreign atom, and \(E_{\text{total}}\) is the total energy of the bilayer graphene with the intercalated atom. The binding energy, the distance between the foreign atom and its nearest C atom, and the interlayer distance of the doped bilayer graphene are illustrated in Table I. Comparing the data in Table I, we find both N and O atoms favor the bridge site, while the C atom prefers the hollow site. No intercalated atom is stable at the top site. At the top position, the relaxation calculations show that nearest C-N bonding is about 1.83 Å, and C-O bonding is about 1.74 Å, which is much larger than the typical lengths of C-N (1.47 Å) and C-O (1.42 Å)\cite{20}, implying the physisorption rather than the chemisorption. For the hollow site, O atom is adsorbed to the layer which provides the nearest C atom, and away from the hexagonal
O atom and the nearest C atom form the C=O bonding with the length of 1.39 Å, smaller than the length of C-O bonding in the \( \text{O}_{\text{Bri}} \) structure (1.44 Å). The calculation shows \( \text{N}_{\text{Hol}} \) structure doesn’t exist because of the negative binding energy. Concerning the bilayer distance, with the foreign atom intercalated in the bilayer space, the distance is enlarged for all the investigated systems.

Figure 1 displays the ground states for C, N and O configurations, where Fig. 1(b), (c) and (d) are the \( \text{C}_{\text{Hol}} \), \( \text{N}_{\text{Bri}} \), and \( \text{O}_{\text{Bri}} \) structures, respectively. In the \( \text{C}_{\text{Hol}} \) system, the optimized interlayer distance is about 3.39 Å, which is a little larger than the value of 3.34 Å for the pure bilayer graphene. Calculations show that C-C bonding in the upper layer nearly keeps unchanged. The carbon atom which is right below the foreign C is pushed down, forming a “dumbbell” at the saddle point. The foreign C bonds with the adjacent three carbon atoms with bonding length being 1.54 Å, which is a standard length for \( sp^3 \) hybridization [20]. In \( \text{N}_{\text{Bri}} \) system, the bilayer distance is enlarged to the value of 3.87 Å, and the length of C-N is 1.43 Å, indicating the chemically adsorption not the physically adsorption. The two carbon atoms bonded with N atom are drawn out of the graphene layer, and the C-C bonding is 1.55 Å, which implies \( sp^3 \) hybridization of the two carbon atoms. In \( \text{O}_{\text{Bri}} \) system, bilayer distance is about 3.76 Å, length of C-O bonding is 1.44 Å, and the two carbon atoms bonded with O atom are also drawn out of the graphene layer with the C-C bonding is 1.51 Å. Obviously, N and O atoms have the similar ground state structure.

Side-view of the charge distributions for \( \text{C}_{\text{Bri}} \), \( \text{N}_{\text{Bri}} \), and \( \text{O}_{\text{Bri}} \) systems are displayed in Fig. 2. Although \( \text{C}_{\text{Bri}} \) structure is not the ground state for C-intercalated system, we show its charge contour together with those of \( \text{N}_{\text{Bri}} \) and \( \text{O}_{\text{Bri}} \) systems, to provide a clear comparison. We know O atom is lack of two electrons, when it is adsorbed in the bilayer graphene, it strongly interacts with its adjacent carbon atoms and get electrons from them (see the upper panel of Fig. 2). N atom lacks three electrons, it also gets electrons from its adjacent carbon atoms (see the middle panel of Fig.2). C atom lacks four electrons to get saturated, and it tends to share electrons with its adjacent carbon atoms in bilayer graphene (see the lower panel of Fig. 2). All these three atoms show strong interaction with lower graphene layer. Concerning their interactions with the upper graphene layer, judging from Fig. 2, C atom has the strongest interaction with the upper layer, N is the second, and O is the third. We compare the stable positions for C, N and O atoms in monolayer and bilayer graphene, as
illustrated in table II. It is clear that N atom has the same stable position in both monolayer and bilayer graphene, so does the O atom. C adatom is stable at the bridge site in monolayer graphene, and Hollow site in bilayer graphene. We believe the different stable positions for C atom results from its interaction with the upper graphene layer.

The C_Hol structure is favored as the ground state for C atom intercalated in the bilayer graphene. The spin-resolved band structures and density of states (DOS) for C_Hol system are shown in Fig. 3. Fig. 3(a) and (b) are the band structures for the majority spin and minority spin, respectively. It is clearly seen that impurity bands for the majority and minority spin components lie, respectively, lower and higher than the Fermi level. In the spin-resolved total DOS (see Fig. 3(c)), two narrow peaks at the opposite side of the Fermi level are observed, indicating the itinerant magnetism triggered by the intercalated C atom. In the following, we will find the itinerant magnetism comes from not only the foreign C atom, but also the carbon atoms of the bilayer graphene. In the orbital-resolved PDOS of the foreign C atom, s state and p state have peaks in the same energy range, which is indicative of the sp^3 hybridization. The C-C bonding between the foreign C and the nearest carbon atoms with the value of 1.54 Å, is also a proof of the sp^3 hybridization, which has been pointed in the previous analysis. When the spin degree of freedom is neglected, our calculation from first principle predicts a twofold degenerate peak at the Fermi level (Fig. 3(e)), but the spin unpolarized state is not the ground state. Including the spin degree of freedom, the balance between the majority and minority spin components will be destroyed. The spin density distribution of the lower graphene layer of the C_Hol system are shown in Fig. 3(f). Both the foreign C atom and the pushed down carbon atom are magnetic, yet we cannot see their magnetic moment distribution in Fig. 3(f), because they are not in the lower graphene plane. Seen from the top-view, these two carbon atoms occupy coinciding positions, which are noted in Fig. 3(f) by the letter ‘C’. The three nearest carbon atoms bonded with the foreign C atom are nearly nonmagnetic and the next-near-neighbors are magnetic. On the whole, the total magnetic moment of the C_Hol system is about 1.32 µB, and the magnetic moment distributions show threefold symmetry, which is similar with the hydrogen adsorption on the graphene plane [23].

Spin-resolved band structure and density of states for N_Bri system are shown in Fig. 4, where Fig. 4(a) and (b) show the band structure for majority and minority spin, respec-
tively, and Fig. 4(c) and (d) display the total DOS of N_{Br} system and PDOS of N atom, respectively. In the total DOS, very narrow and sharp peak at the Fermi level is observed. We draw the PDOS of N atom and find the peak arises from from the N adsorption and the N atom is nearly 100% spin polarized. In the band structure, we find the very localized states at the Fermi level in the minority spin band structure. Such quasilocalized states give rise to the strong Stoner magnetism with magnetic moment of 0.65 \( \mu_B \) located at the N atom. In the PDOS of N atom, between the energy \(-0.5\) eV and \(-1\) eV, another narrow peak is obtained. Both in the majority and minority spin band structures, the corresponding flat impurity bands in the energy range from \(-0.5\) eV to \(-1\) eV are observed. In addition, both in the majority and minority band structures, the characteristic conical point at K point still can be clearly identified, implying the bilayer graphene is not strongly perturbed by the N atom. The critical difference is that, in freestanding graphene the Fermi level coincides with the conical point, while the Fermi level obtained in N-intercalated system is shifted downward and becomes below the conic point. A shift downwards (upwards) means the holes (electrons) are donated by the adsorption atom. The manganese doping (electron donor) results in the upward shift of the Fermi level, reported by previous investigations \[9\].

Band structure and density of states of O_{Br} system are displayed in Fig. 5, where Fig. 5(a), (b) and (c) are the band structure, total density of states, and partial density of states of O atom, respectively. The calculation shows the O_{Br} system is nonmagnetic. From the above analysis about N_{Br} and C_{Ho} systems, we see the impurity states localized around the Fermi level play an important role in the magnetic properties, and the intercalated atom itself is spin-polarized. In O_{Br} system, we do not get such localized states around the Fermi level, and the O atom is nonmagnetic. In the PDOS of O atom, we find the peak nearest to the Fermi level is around the energy of 0.75 eV. From the band structure, we can also see that the impurity state nearest to the Fermi level is at the energy of 0.75 eV. Like N_{Br} system, the O_{Br} system also undergoes a change from semimetal to metal, because O atom get electrons form graphene, thus the Fermi level shifts downward.

In summary, we calculated the structure, electronic and magnetic properties of the bilayer graphene with intercalated atoms C, N, and O by the \textit{ab-initio} density function theory. Impurities even at very low density may bring fruitful physical properties for bilayer graphene system. Structure relaxation shows that the intercalated atom although initially positioned
at the middle position of the bilayer distance, will finally be adsorbed to one graphene layer and away from the other layer. The bilayer distance is enlarged for all the investigated adsorption systems. Both N and O atoms are stable at the bridge site, while C atom is stable at the hollow site. Concerning the magnetic property, O-intercalated system is nonmagnetic, while N and C atoms can induce stoner magnetism by introducing extended or quasilocalized states around the Fermi level. Nearly 100% spin polarization is obtained in N-intercalated system and the magnetic moment focuses on the N atom. For C-intercalated system, the magnetic moment distributes on the foreign C atom and certain carbon atoms of the bilayer graphene. Both in N-intercalated and O-intercalated systems, the Fermi level is obviously shift downward, inducing the metallic behavior of the bilayer graphene.

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I. FIGURE CAPTIONS

Fig. 1 (a) ˜A-B Bernal stacking structure for bilayer graphene. (b) CHol system, where the atom in violet is the foreign C atom. (c) NBri system, where the atom in blue is the foreign N atom. (d) OBri system, where the atom in red is the foreign O atom.

Fig. 2 Side-view of charge contours for CBri, NBri and OBri systems, respectively.

Fig. 3 Electronic and magnetic structures of the CHol system. (a) Band structure of majority spin, (b) band structure of minority spin, (c) total density of states, (d) the orbital-resolved DOS for the foreign C atom, (e) density of states for spin unpolarized CHol system, (f) distribution of the spin density on the lower graphene layer.

Fig. 4 Spin-resolved band structure and density of states of NBri system. (a) Band structure of the majority spin; (b) band structure of the minority spin, (c) total density of states, (d) partial density of states of N atom.

Fig. 5 Band structure and density of states of OBri system. (a) Band structure, (b) total density of states, (c) partial density of states of O atom.

Table I The binding energy (dE), the length of bonding between the adsorption atom and its nearest C atom (aC-atom), and the bilayer distance of the adsorption system (dis.). The stable position for each intercalated atom is noted by box.

Table II The stable positions for adsorption atoms C, N, and O in monolayer and bilayer graphene.
This figure "fig1.jpg" is available in "jpg" format from:

http://arxiv.org/ps/1001.0803v1
| Position | C | N | O |
|----------|---|---|---|
| Top      | 1.31 | 0.37 | 1.45 | 1.68 | 2.10 | 2.80 |
| Hol      | 1.93 | --- | 1.45 | --- | 1.68 | 2.10 |
| Bri      | 1.86 | --- | 1.45 | --- | 2.10 | 2.80 |
| Bri      | --- | --- | 1.49 | 1.74 | 1.39 | 1.44 |
| bri      | --- | --- | 1.83 | --- | 1.43 | 1.44 |
| C-atom (Å) | 1.46 | 1.54 | 1.49 | 1.83 | 1.43 | 1.44 |
| dis. (Å) | 3.53 | 3.39 | 3.87 | 3.62 | 3.87 | 3.85 |
| dis. (Å) | 3.62 | 3.61 | 3.85 | 3.76 | 3.76 | 3.76 |
This figure "fig2.jpg" is available in "jpg" format from:

http://arxiv.org/ps/1001.0803v1
|       | C          | N          | O          |
|-------|------------|------------|------------|
| Monolayer | Bridge $^a$ | Bridge $^b$ | Bridge $^b$ |
| Bilayer  | Hollow     | Bridge     | Bridge     |

$^a$reference 20.
$^b$reference 21.
This figure "fig3.jpg" is available in "jpg" format from:

http://arxiv.org/ps/1001.0803v1
This figure "fig4.jpg" is available in "jpg" format from:

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