Layer Antiferromagnetic State in Bilayer Graphene : A First-Principle Investigation

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The ground state of bilayer graphene is investigated by the density functional calculations with local spin density approximation. We find a ground state with layer antiferromagnetic ordering, which has been suggested by former studies based on simplified model. The calculations prove that the layer antiferromagnetic state (LAF) is stable even if the remote hopping and nonlocal Coulomb interaction are included. The gap of the LAF state is about 1.8 meV, comparable to the experimental value. The surface magnetism in BLG is of the order of $10^{-2}\mu_B/nm^2$.

Graphene, the star material nowadays, has shown many exotic physical properties and promised great potentials in developing new electronics devices[1–4]. However, one major roadblock for the practical applications of graphene in electronics is the small on/off ratio due to its gapless ground state. One alternative way to overcome the difficulty is exploiting the AB-stacked bilayer graphene (BLG) instead, where a gap can be formed and tuned by chemical doping or external electric field[5,6]. For example, the unipolar transport has been demonstrated in a field effect transistor based on BLG[7], and high frequency manipulation of the BLG quantum dot has been realized[8]. Recently, the results of several experiments on the ultraclean suspended BLG suggest that an intrinsic gap may exist at the charge neutrality point, which is attributed to the formation of certain ordered ground states due to spontaneously symmetry broken[9–14]. The nature of the correlated ground state is still unclear and highly debated, and different candidate states have been proposed theoretically, such as the layer antiferromagnetic (LAF) state, quantum anomalous Hall state, quantum spin Hall state, as well as a gapless nematic state[15–22].

The LAF state is one of the most possible candidates for the correlated ground state of BLG, which spontaneously breaks both the spin rotational and sublattice symmetry. By quantum Monte Carlo, renormalization group, and mean field methods based on a Hubbard model, the LAF is shown to be stable over a wide range of parameter range[23–25]. However, to determine the correlated ground state of BLG, two important factors have been ignored in a simple Hubbard model, which only focuses on the local Coulomb interaction. One is the influence of other components of the Coulomb interaction beyond the Hubbard U term, i.e. the long or short range nonlocal Coulomb interaction. Although these terms are much smaller than the on-site Coulomb interaction, some recent theoretical works indicate that these terms do affect the correlated ground state of BLG[26,27]. The other is effect of the remote hopping terms, which essentially modifies the parabolic feature of the energy bands near the Fermi level at high symmetry points. Furthermore, the choice of the model parameters also strongly influences the calculating results.

In this work, we study the ground state of BLG via density functional theory (DFT) calculations with local spin density approximation (LSDA). The results clearly indicate an insulating LAF ground state with an energy gap about 1.8 meV, which is of the same order of magnitude of the experimental value, i.e about $2 \sim 3$ meV[12–14]. This is different from the former DFT calculations on BLG in which a gapless ground state is predicted if the spin degree freedom is not considered[28]. We show that DFT calculation is helpful to investigate the correlated ground state of BLG, especially the LAF state. Most importantly, we prove that the LAF state is stable in BLG even in the presence of nonlocal Coulomb interaction and remote hopping, which are naturally included in DFT calculation. It provides an essential support to the LAF ground state. Furthermore, compared with other theoretical methods, the first principles calculations give a more quantitative description about the LAF ground state of BLG. The physical quantities which can be detected in experiments, e.g. spin distribution between sites and layers, are given in a more accurate way without empirical parameters.

The DFT calculations of the electron structures for BLG are performed with the ABINIT software package[29]. There are four carbon atoms in the primitive cell of the AB-stacking BLG, and the geometry structure of a 2×2 supercell is shown in Fig. 1 (a). In each layer, there are two sublattice, i.e. sublattice A and B. We use the experimental value of the layer separation 3.35 Å , since the van der Waals interactions can not be captured by DFT calculation[30]. A 23.4 Å vaccum layer is used to separate the BLGs in the calculations with periodic boundary condition. The cutoff energy for the plane wave basis set is

chosen as 40 Ha, and the Troullier-Martins (TM) norm-conserving pseudopotential for the carbon element was exploited. The k points for sampling the Brillouin zone (BZ) is generated by a 60×60 Monkhorst-Pack (MP) grid. In order to investigate the possible spin order, the LSDA is exploited to the exchange-correlation functional, and the converge criteria for the total energy difference is 10^{-10} Ha.

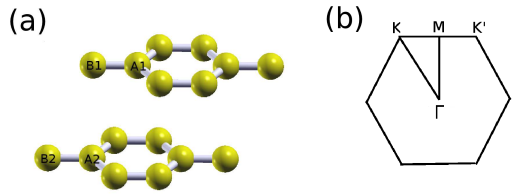

FIG. 1. (Color online) (a) The geometry structure of a 2×2 supercell of BLG. The four carbon atoms in the primitive cell are denoted as A1, B1, A2, and B2 respectively; (b) Brillouin zone (BZ) of BLG. Γ, M, K, and K' denote the high symmetry points in BZ.

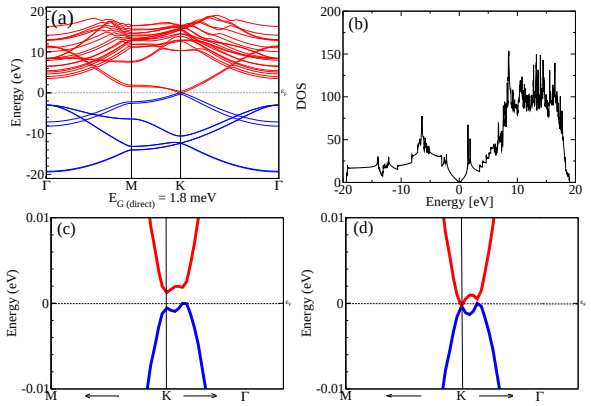

FIG. 2. (Color online) (a) Band structure of BLG from DFT+LSDA calculations; (b) DOS of BLG from DFT+LSDA calculations; (c) Fine band structure of BLG around Dirac point K from DFT+LSDA calculations; (d) Fine band structure of BLG around Dirac point K from DFT+LDA calculations.

The band structures and density of states (DOS) of BLG from the DFT+LSDA calculations are shown in Fig. 2 (a) and (b) respectively. A fine band structure around the Dirac point K is shown in Fig. 2 (c), where we present our most encouraging result, a minor band gap opened around the Dirac point K. The calculated band gap $E_{gap} \approx 1.8$ meV is comparable to the experimental values $2 \sim 3$ meV[12–14], considering that LSDA calculations usually underestimate the band gap. For comparison, we also perform the DFT+LDA calculation without including the spin degrees of freedom. In Fig. 2 (d), we show the fine band structure from this calculation, which reproduces previous studies[28]. No energy gap is found in this case. We see the trigonal warping in the energy band, which results from the remote hopping. Note that, for trigonal warping, there are three additional touching points at the Fermi level near K point in addition to the Dirac point. But in Fig. 2 (d) we only show one of the three touching points, since the other two are not on the high symmetry line. As shown in Fig. 2 (c), these degeneracies are all lifted if we include the spin degree of freedom in the calculation.

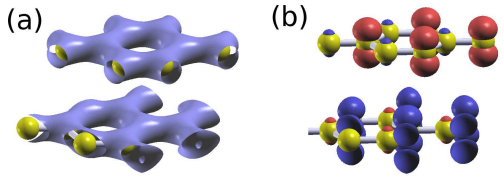

FIG. 3. (Color online) (a) Isosurface of the charge distribution with isovalue 0.15; (b) Isosurface of the spin polarization distribution with isovalue 2.5×10^{-5}(red) and -2.5×10^{-5}(blue).

In order to identify the nature of the ground state of BLG further, we analyze its charge density and spin-polarization distributions. The isosurface of the charge density is illustrated in Fig. 3 (a), which is basically extended along the C-C bonds in each layer. We estimate the charge on each atom using the Hirshfeld method[32]. Calculations with LDA and LSDA give the same charge distributions. It implies that the energy gap in LSDA calculation has nothing to do with the charge redistribution. We then check the spin distribution. The calculation with LDA does not give any spin ordering, since the spin degree of freedom has been ignored in this case. But in the calculation with LSDA, we find a special spin ordering, i.e. layer antiferromagnetic order. The spin ordering is shown clearly in Fig. 3 (b). The spin polarization is mainly localized around the A1 and B2 atoms. By the Hirshfeld method, we get the spin polarization around A1 atom is about 5.5×10^{-4}, and that around B2 is -5.5×10^{-4}. Note that, for spin polarization, we mean $n_\uparrow - n_\downarrow$ where $n_\uparrow$ ($n_\downarrow$) is the charge number with up spin (down spin). For the A2 and B1 atoms, the spin polarization is very tiny, and at least one order of magnitude smaller. We see that the spin ordering between two nearest neighbor sites are all antiferromagnetic. The numerical results show that the net spin in each layer is nonzero but that of the whole system is zero. The spin structure in each layer is antiferrimagnetic and the spin polarization of two layers are of opposite sign. That is just the layer antiferromagnetic state predicted by former mean field studies. In Ref. 33, considering the experimental value of the gap 2 meV, self-consistent mean field calculation gives similar spin ordering, and the largest spin polarization on one atom is of the order of 10^{-4}, which is in qualitatively or semi-quantitatively agreement with our DFT results. Because that the remote hopping and nonlocal Coulomb interaction are naturally included in DFT calculation, the LAF state we found here indicate that the LAF state is stable even in the presence of remote hopping and nonlocal Coulomb

interaction. It offers an essential support to former mean field studies. We emphasize here that DFT calculation is the best way so far to investigate the influences of remote hopping and nonlocal Coulomb interaction. Meanwhile, our DFT calculation shows that the surface magnetism is about $10^{-2}\mu_B/nm^2$, which can be detected in experiment by spin-polarized scanning tunneling microscopy. We note that the surface magnetism has been reported in trilayer and 8-layer graphene systems[34–36].

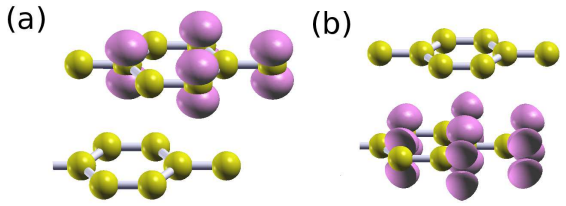

FIG. 4. (Color online) Isosurfaces of the norm of the wavefunction (spin up) for states at K point. (a) The state on valence band; (b) the state on conductance band. The isovalue is 30 here.

Another confirmation of the LAF state is its peculiar wave function near the Fermi level. In noninteracting case, the low energy states of BLG has a pseudospin symmetry, i.e. the layer symmetry, in addition to the normal spin and valley symmetry[16]. As mentioned before, electron-electron interaction can spontaneously break some symmetry and induce several possible correlated ground states. In LAF state, layer symmetry is broken for each spin direction, because the two layers have opposite spin polarization. In other words, for up spin, the states on conductance band near the Fermi level are localized on one layer, while that on the valence band are on the other. For down spin, the layer dependence is inverted. These features of the wave function of LAF state have been demonstrated clearly in former studies based on simplified model[26,33]. Our first principles results of the BLG wave function also have these features. Taking one spin direction for example (saying up spin), we plot the wave functions for both conductance and valence bands at K point in Fig. 4 (a) and (b). As we expected, the state on valence (conductance) band is on the top (bottom) layer. However, the wave function for the states a little away from the Fermi level does not have such spin and layer dependent distribution. Actually, the wave functions for these states spread uniformly among the two layers. The results here confirm that the electron-electron interaction in BLG system only influence the low energy states very close to the Fermi level. And only these states have the spin ordering.

In summary, the first principles calculations have been performed to investigate the ground state of BLG. The LAF ground state is found in the LDSA calculations and a reasonable energy gap compared with the experimental results is obtained. This calculation proves that the LAF state in BLG is stable in the presence of remote hopping and nonlocal Coulomb interaction. Our calculations also give the values of some key physical quantities of the LAF states. The largest spin polarization on one atom is about 5.5×10^{-4}. The surface magnetism is of the order of $10^{-2}\mu_B/nm^2$.

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