A comparative investigation of an AB- and AA-stacked bilayer graphene sheet under an applied electric field: A density functional theory study*

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An AB- and AA-stacked bilayer graphene sheet (BLG) under an electric field is investigated by *ab initio* calculation. The interlayer distance between the two layers, band structures, and atomic charges of the system are investigated in the presence of different electric fields normal to the BLG. The AB-stacked BLG is able to tune the bandgap into 0.234 eV with the increase of the external electronic field to 1 V/nm, however, the AA-stacked BLG is not sensitive to the external electric field. In both the cases, the spacing between the BLG slightly change in terms of the electric field. The charges in the AB-stacked BLG are increased with the increase of the electric field, which is considered to be the reason that causes the bandgap opening in the AB-stacked BLG.

Keywords: graphene, bandgap, density functional theory study

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1. Introduction

Graphene, a single layer of carbon sheet, has become a research hotspot recently due to its potential replacement of Si material as the future of nanoscale electric devices.[1] It is now well known that intrinsic graphene is a semiconductor with zero band gap. However, the absence of a bandgap in the electronic spectrum of intrinsic graphene has to be conquered before the widespread application of graphene can take place. To open and tune the gap of graphene, a lot of methods have been applied, such as depositing graphene onto a substrate,[2] patterning graphene into nanoribbons,[3] doping other elements into graphene,[4] hydrogenating graphene,[5] and applying external stress on graphene,[6] etc.

By adding one more layer onto the single layer graphene, bilayer graphene has a completely different band structure. Generally, the AB-stacking system has attracted much attention, since it is a stable material and is used in common graphene-based devices. The AB-stacked bilayer graphene (BG) is a zero bandgap semiconductor in the pristine form. But a non-zero bandgap can be induced if the symmetry of the two layers is broken, such as through chemical doping.[7] In particular, the bandgap of the BG can be tunable through an electric field normal to the surface.[8] The alternative system, the AA-stacking BLG, has some special physical properties due to its unique structure. However, it has been seldom reported. Recent experiments indicated the possibility of the preparation of AA-stacked BLG, for instance, high-density plasma in hydrogen–methane mixtures can synthesize it on a diamond substrate, and mixtures of hydrogen and propane synthesized it on the C-terminated 4H–SiC (0001) surface in chemical vapor deposition reactors.[9,10]

In this work, density functional theory (DFT) is used to investigate the electric properties of the pristine AB- and AA-stacked BLG in the presence of an electric field ($F < 1$ V/nm). The density of states, the change of structure parameters, and the charge distribution on atoms are discussed. As far as we know, there is no report about AA-stacked BLG under F and the difference of AA and AB-stacked BGL under F was neglected before.

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2. Methods

All the DFT calculations are performed using the DMOL3 code.[11] The generalized gradient approximation (GGA) with the revised Perdew–Burke–Ernzerhof (RPBE) functional is employed as the exchange and the correlation function.[12] The energy cutoff is 600 eV for geometry optimization. In the simulation, a three-dimensional periodic boundary condition is taken. For the bilayer graphene, a 2×2 supercell of two layers of carbon atoms with a vacuum width of 2.5 nm is constructed. Two systems have 16 carbon atoms in a unit cell. The distance between the two layers of carbon atoms is set as 0.34 nm, which is the same as that of graphite. The Monkhorst–Pack grid k-point is set as $12\times12\times1$. In order to investigate the effect of an electric field on the atomic configuration, electronic structure and electron distribution of the bilayer system, an external electric field normal to the layer with various values is applied.

3. Results and discussion

Firstly, we calculate the structure parameters of graphite and diamond and the results are listed in Table 1. As shown in the table, they are consistent with the results of reported LDA and GGA calculations, although they are a little smaller than the experimental results. Thus, Table 1 confirms the validation of the simulation method.

Table 1. The structure parameters of graphite and diamond.

Structures	Values/Å	LDA/Å	Experiment/Å LDA/Å	GGA/Å	
Graphite	a	2.446	2.46[a]	2.455[d]	2.465[d]
	c	6.442	6.67[b]	6.712[d]	8.64[d]
P diamond	a	3.534	3.57[c]	3.529[d]	3.578[d]

[a]Ref. [21], [b]Ref. [22], [c]Ref. [23], [d]Ref. [24].

The structure parameters of a free-standing BLG without an electric field are listed in Table 2. AB-stacked BLG spacing is 3.405 Å, which is equal to the spacing in graphite. The spacing of AA-stacked BLG is 3.393 Å in our simulation, which is slightly less than ∼3.55 Å, which was measured by high-resolution transmission electron microscopy and electron diffraction.[9] Dahn *et al.* measured 3.706 Å, which is caused by lithium intercalating AA with the presence of the alkali metal atoms.[13] The AB-stacked BLG is more stable than the AA-stacked BLG, since the total energy of the former is 0.039 eV per atom smaller than that of the latter, a finding consistent with earlier works.[9] Their binding energy difference is 0.111 eV per atom in our works.

The conduction and the valence bands are calculated along K, M, K in the BZ (Fig. 1). It is well known that the AB-stacked BLG has a zero band gap just at the Dirac point and the BLG maintains the metallic properties, which is demonstrated by our simulation zero bandgap in Fig. 1(a). However, the bandgap of the AA-stacked BLG is 0.492 eV, a Dirac-type dispersion relation as shown in Fig. 1(c). The intersection of the bands is located symmetrically in the vicinity of the K point. Its electron distribution pattern is a sixfold symmetry pattern, close to the isolated monolayer graphene, which causes linear dispersion bands. In the case of the AB-stacked BLG, the distribution of the electron density is threefold patterns of the electron density, which leads to a hyperbolic highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) band dispersion. The difference of the distribution of electron density results in the distinctness of band structure between AA- and AB-stacked BLGs.

Table 2. The structures of BLG graphite.

Structures	Method	Spacings/Å	Reference
AA-stacked	calculated	3.393	this work
	calculated	3.5	Ref. [9]
	experimental	3.55	Ref. [9]
	experimental	3.706	Ref. [13]
AB-stacked	calculated	3.405	this work
	calculated	3.3	Ref. [9]
	experimental	3.35	Ref. [9]

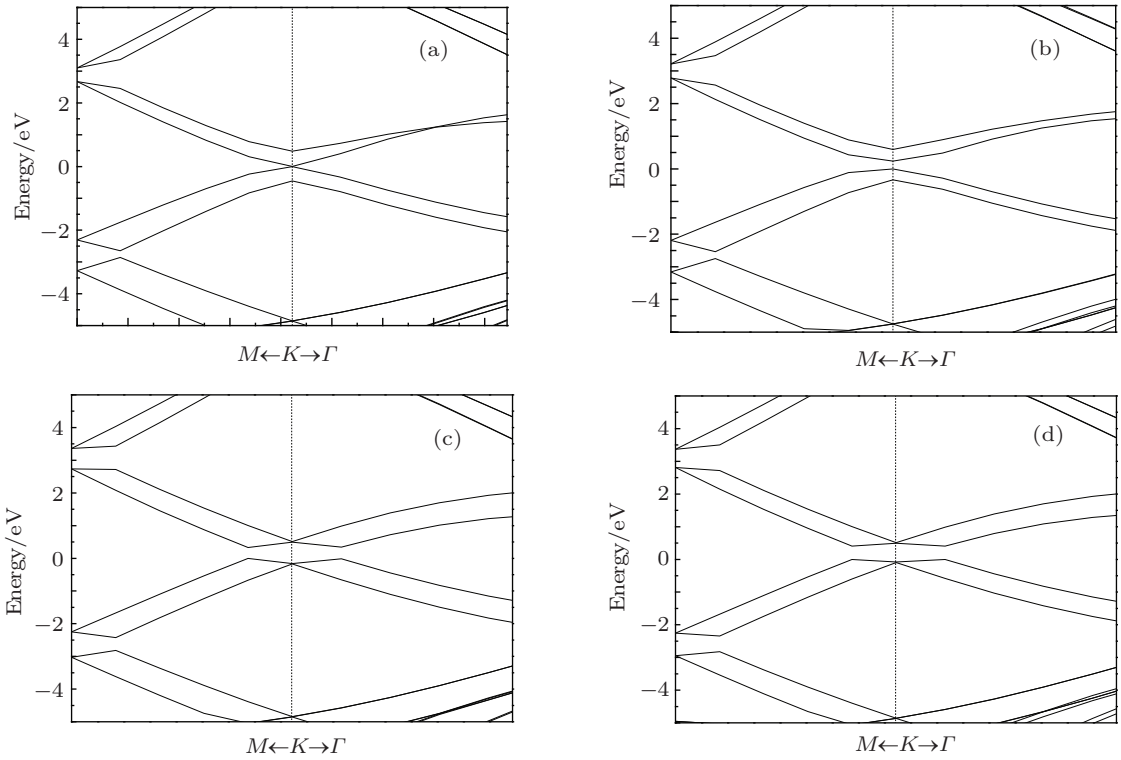


Fig. 1. The band structure of the BLG graphene: (a) the AB-stacked graphene without F, (b) the AB-stacked graphene under 1 V/nm, (c) the AA-stacked graphene without F, and (d) the AA-stacked graphene under 1 V/nm.

For the graphene-based devices where graphene is normally deposited on SiO_2 substrate, the breakdown benchmark of the electric field is 1 V/nm, above which the SiO_2 substrate would be cracked and would fail. Therefore, we explore the bandgap under 1 V/nm for use in common graphene-based devices. The band-gap change under an electrical fields is shown in Fig. 2(a). In the case of the AB-stacked BLG, the band gap increases with the increase of the electric field, which is consistent with the result of Ref. [8]. In addition, Castro *et al.* observed a tunable electronic gap in a biased graphene bilayer on an SiO_2 substrate through magneto-transport measurements and predicted a band gap larger than 0.2 eV in the presence of an electric field below 1 V/nm.[14] Novoselov *et al.* reported that the tunable electronic gap can be changed from 0 to 0.3 eV by using an electric field below 1 V/nm.[15] In our work, the band gap at 1 V/nm is 0.234 eV, which also agrees with the results mentioned above. The band structure of the AB-stacked BLG under 1 V/nm is shown in Fig. 2(b). We can see that a gap of 0.234 eV is present between the conductive and occupied bands at the K point near the Fermi level.

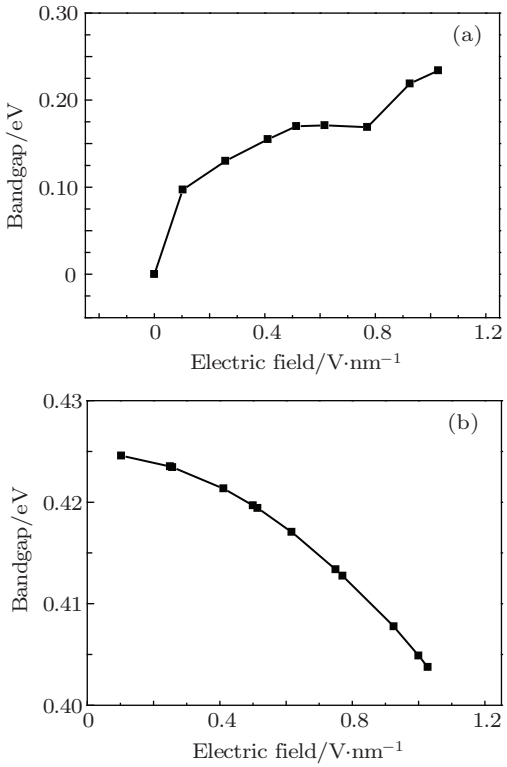


Fig. 2. Band gap opening of BLG (F <1 V/nm): (a) the AB-stacked BLG and (b) the AA-stacked BLG.

Electric properties of the AB-stacked BLG under an electric field are investigated. While the electric field is less than 1 V/nm, the band gap opening is able to gradually tune to 0.236 eV. The electrical field slightly affects the geometric deformation, so spacing change contributes to the band gap opening a little. The spacing in terms of the change of the electric field is shown in Fig. 3. While $F < 1$ V/nm, spacing variation is extremely small. The distance variation is within 0.2%. The correlation between the spacing and band gap is not obvious, as illustrated in Fig. 3. In the same figure, it is shown that the Mulliken charge population of the atoms. Under the electric field, electrons are unbound. It is noted that electrons accumulate along the bilayer structure and the number of charges increases with the increase of the electric field. The positive electrons are scattered on bottom layer and the negative ones are on the top layer, while the electric field is pointing from bottom to top. The accumulated electrons are localized on the BLG and are accordant to the applied electric field. The build-in F trends to confront outside F, very familiar with the build-in F in p–n junction. The charges play an important role for band gap opening. The absolute charges are not large, however, the external electric field re-arranges them along two layers and the nano scale spacing renders that a few charges build a great build-in static perpendicular field. The two layers may counteract with each other and decline the polar moments of the entire graphene structure under an electric field. With higher electron density, it should be that the overlap between the π orbitals of the adjacent BLG increases. Ohta *et al.* also pointed out that sufficient asymmetry was enhanced with higher doping by potassium adsorption, which unambiguously opened the band gap.[16] Sano and Otsuji thought that in order to open the BLG, a 0.3-eV 10^{13}-cm^{-2} doping concentration is required.[17] Higher doping generates more charges and augments the higher build static field. Moreover, this charge transfer indicates that the formation of a chemical bond between layers replaces the previous week van der Waals interaction. It is noted that generally greater Mulliken charges correlate with a larger band gap in the AB-stacked BLG. The charges, which are induced and re-arranged by the applied electric field, promote structure asymmetry of the AB-stacked BLG and result in the magnitude of band gap opening.

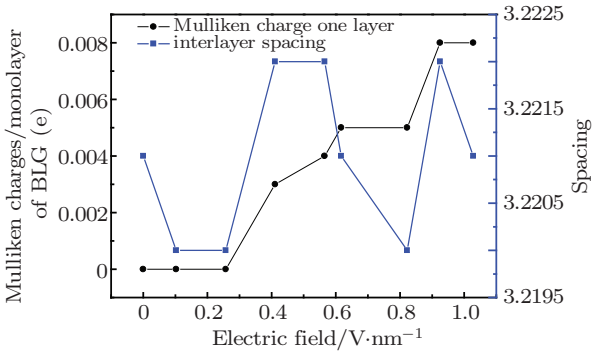


Fig. 3. (colour online) Mulliken charges of one-layer carbon atoms and spacing in the AB-stacked BLG in terms of applied electric fields.

However, the AA-stacked BLG is not sensitive to F, as shown in Fig. 2(b). Its band gap only drops to 0.021 eV with the increase of the electric field to 1 V/nm, whose span is less than one tenth of the variation in the AB-stacked BLG. The fixed spacing indicates that the overlap of the p_z orbitals does not alter. The dispersion relation is linear, so the shift arising from the overlap of the adjacent carbon layer does not happen. It is noted that the spacing changes and the Mulliken charge variation with the increase of F are zero in the AA-stacked BLG. This is considered to be the main reason that a very slight band gap is found in the AA-stacked BLG. The electron distribution pattern of the AA-stacked BLG is a sixfold symmetry pattern and that of the AB-stacked BLG is threefold patterns of electron density. The difference of the distribution of electron density and the structure results in the dissimilarity of the charge distribution under F. The charges, which are induced and re-arranged by the applied electric field, promote structure asymmetry of the AB-stacked BLG and result in the magnitude of band gap opening.

4. Conclusions

In short, the bandgap of AA-stacked BLG is less sensitive to F and less stable than the AB-stacked BLG. Its spacing and Mulliken charge are unchanged under F. A sixfold symmetry pattern of the electron distribution causes linear dispersion bands, 0.492 eV without F. For the AB-stacked BLG, its spacing variation may influence its band gap, since the distance change means altering the third nearest neighbor coupling, the coupling between layers modifies the overlap of p_z orbitals. Charge distribution changes under F cause asymmetry and tune the band gap from 0 to 0.234 eV while F increases to 1 V/nm. Our

study illustrates AB- and AA-stacked BLG properties for their potential usage in future graphene-based devices.[18−20]

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