Structural and electronic properties of few-layer graphenes from first-principles

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The first-principles calculation method has been used to obtain structural and electronic properties of few-layer graphenes (FLG’s) with and without a cross-film external electric potential, \( V_{\text{ext}} \). It is found that the AB stacking is more favorable than the AA stacking and the calculated layer spacing for the two-layer AB stacked FLG is only 2.725 Å, which is substantially reduced from that of the bulk graphite of 3.257 Å. The two-layer AB stacked FLG is found to exhibit a semi-metal–semiconductor transition under \( V_{\text{ext}} \) qualitatively in agreement with previous studies. However, the energy gap, \( E_g \), is not limited at 0.3 eV as obtained in previous first-principles calculation due to the reduced interlayer spacing. The threshold of the semi-metal–semiconductor transition is 0.04 Volts. \( V_{\text{ext}} \) also induces \( E_g \)'s in 3- and 4-layer AB stacked FLG’s. However, in these FLG’s the induced \( E_g \)'s are small within 0.1 eV.

1 Introduction Nanoscale graphite derived materials have been investigated intensively due to its technological importance. Research interests on graphite-based materials include (1D) nanotubes [1], 0D carbon toroids [2, 3], 1D nanographite monoribbons [4–8], and 2D nanographite multiribbons [9–11] due to their possible applications and unique size and dimensionality dependent characteristics. Carbon nanotubes have been considered as energy and gas storage devices, sensors, field emission device, and nanodevices [12]. Recently, fabrication of ultra thin films of carbon atoms has been achieved [13–17]. The ultra thin carbon films are called few-layer-graphene (FLG), which are piles of a few layers of graphenes along the \( c \)-axis. FLG-based devices can be obtained by exfoliation of the small mesa of highly oriented pyrolytic graphite. [15–18]. A graphene layer consists of carbon atoms arranged in a planar honeycomb hexagonal network, in which carbon atoms form sp\(^2\) bonding and have a three-fold coordination. Graphene layers can be stacked in AA or AB sequences along the \( c \)-axis. Among them, the AB-stacking sequence is most common in natural graphite [19]. The electronic and magnetic properties of FLG have been studied intensively [20–51]. Unconventional quantum Hall effect has been found by Novoselov et al. [45] and McCann and Fal’ko [46] carried out the first theoretical study of electronic bands at low energy in bilayer graphene. In review articles, Geim and Novoselov [52] and Katsnelson [53] have discussed the new physics and potential applications revealed in this two-dimensional material.

The van der Waals force has been considered to contribute to the binding of graphite layers [54, 55] in bulk graphite. Since the van der Waals force is via dynamic interactions between instantaneous fluctuating dipoles, it does not involve direct coupling through overlapping of \( p_z \)-orbitals of adjacent graphene layers. Since the carbon atom has an atomic radius of 0.91 Å [56], the exponentially decaying tail of its \( p_z \)-orbital is not negligibly small at a distance of 1.7 Å from the nucleus, so that the \( p_z \)-orbitals of the carbon atoms in adjacent graphite layers with a separation of 3.337 Å [57] should have a significant overlapping. Thus, the contribution of the direct coupling between the \( p_z \)-orbitals of adjacent graphene layers to the interlayer interaction energy should not be negligible and should be considered. Indeed, Charlier, Gonze, and Michenaud have performed first-principles calculations to show weak coupling between \( p_z \)-orbitals of graphene layers in bulk graphite [11]. Yoshizawa et al. using the second-order perturbation theory concluded that the well-known ABAB
stacking of layers in graphite was a consequence of orbital interaction between layers. [47] Since the p$_z$-orbital has an exponentially decaying tail, the direct coupling between p$_z$-orbitals of adjacent graphene layers is expected to depend sensitively on the interlayer spacing. Thus, it is important to use first-principles calculation method to optimize the layer spacing through total energy calculations for FLG’s, which has been ignored in previous theoretical studies.

Recently, Novoselov et al. found FLG’s to be a two-dimensional semi-metal with a tiny overlap between valence band and conduction band, and they exhibit a strong ambipolar electric field effect such that electrons and holes in concentrations up to $10^{13}$/cm$^2$ with room-temperature mobilities of ~10000 cm$^2$/Vs can be induced by applying gate voltage [13]. Novoselov et al. envisioned the usage of FLG as a metallic field effect transistor [28, 29]. Recently, Ohta et al. [42] by selectively adjusting the carrier concentration in each layer of a bilayer graphene found that changes in the Coulomb potential led to control of the gap, $E_g$, between valence and conduction bands, which suggested the potential application of bilayer graphene to switching functions in atomic scale electronic devices. Castro et al. also observed field induced energy gap in graphene bilayer by Shubnikov–de Haas analysis of magnetotransport [43]. The opening up of the energy gap under a perpendicular applied electric field for AB stacked FLG’s has been confirmed by theoretical calculations by Stauber et al. [24], McCann [33], Lu et al. [34] using the empirical tight-binding method and Aoki and Amawaski [41] using the first-principles pseudopotential method and Min et al. [44] using all-electron linearized augmented plane wave plus local-orbital method. McCann and Fal’ko [46] also predicted the opening of an energy gap. Recently, Oostinga et al. also found that an applied electric field can open up a band gap in bilayer graphene [48]. For the electronic switch application, a first-principles calculation to reveal the threshold of the semi-metal–semiconductor transition and the dependence of $E_g$ on the external potential or the electric field will be useful. Although, Min et al. have calculated the energy gap of the bilayer graphene as a function of the external potential, they chose a bulk-graphite-like interlayer spacing of 3.35 Å and didn’t optimize the interlayer spacing, which has been argued above to be important.

In this paper, the first-principles total energy calculation has been performed to show that the AB stacking is more favorable than the AA stacking for FLG’s as experiments indicated and to find that the equilibrium interlayer spacing of these FLG’s, especially that of the intensively studied AB stacked bilayer FLG, differ from that of the bulk graphite. As to be described and explained later, the interlayer spacing of the AB stacked bilayer FLG is substantially reduced from that of the bulk graphite, which suggests that the interlayer interaction energy for the AB stacked bilayer FLG be different from that derived from bulk graphite. The electronic structures obtained in this study qualitatively agree with previous first-principles calculations. However, there are quantitative differences with previous first-principles calculations which used fixed bulk-graphite-like interlayer spacing.

2 Calculation method The first-principles calculation method used in this study is the modified pseudofunction (PSF) method [58, 59]. In this method, the $z$-component of the Coulomb potential is calculated numerically by solving the Poisson equation, where the $z$-coordinate is perpendicular to graphene layers. The potential, which includes Coulomb and exchange-correlation potentials within the local density approximation (LDA) of Hedin and Lundqvist [60], was divided into spherical potentials within the muffin-tin spheres and a plane-wave expanded potential that extends through the film. PSF’s are smooth mathematical functions constructed by extending the muffin-tin-orbital tails into muffin-tin spheres. They are simply devised to calculate the interstitial and nonspherical parts of Hamiltonian matrix elements efficiently through plane waves using the fast Fourier transform technique. The muffin-tin radius chosen for the carbon is 0.688 Å.

In the PSF method, the pseudofunctions are expanded in three-dimensional plane waves even for a film [58]. To limit the number of plane waves used to expand the PSF’s, a criterion, $R_{G_{\text{max}}} > n$, where $n = 3, 5$ or 7, respectively, for s-, p-, and d-orbitals, is usually used, where $R$ is the muffin-tin radius of the C atom and $G_{\text{max}}$ is the magnitude of the largest wave vectors along the reciprocal basis vectors and the $z$-axis, which is normal to the film. Let $b_i$ and $b_i$ be the two hexagonal reciprocal basis vectors and $b_i = 2\pi/d_i$, where $d$ is greater than the thickness of the film [58], the total number of plane waves for PSF’s is $(2n_i + 1)$ with $n_i = G_{\text{max}}/b_i$ for $i = 1, 2$ and 3. Since the charge density is the absolute square of the wavefunction, the charge density as well as the potential is expanded by $(4n_i + 1)(4n_i + 1)$ plane waves. In this study $n_1 = n_2 = 5$ are chosen, which corresponds to $R_{G_{\text{max}}} = 9.7$. Due to the relatively large spacing between adjacent graphene layers, it is expected that the spatial region, in which the exponentially decaying p$_z$-orbitals of the C atoms in two adjacent graphene layers overlap significantly, is small, so that a large $n_z$, which yields sufficient number of short-wavelength z-component plane waves, is required to properly resolve the fine details of the overlapping and coupling of p$_z$-orbitals. An $n_z = 23$, which corresponds to $R_{G_{\text{max}}} = 22$ and a shortest wavelength of 0.2 Å, is used.

For a given external electric potential, $V_{\text{ext}}$, across FLG, there is a constant external electric field, $E = V_{\text{ext}}/t$, perpendicular to the plane of FLG, i.e. along the $z$-axis, where $t$ is the thickness of the FLG. In the current PSF formulation, the electric potential function of $z$ due to $E$ is expanded in plane waves. It has been tested that the linear external potential can be accurately expanded by plane waves [61]. Note that this linear potential is an external potential like the potential due to the positive and negative charges in the
two electrodes of a capacitor with FLG lying between the two electrodes. The total potential seen by an electron in FLG is the sum of this external potential and the Kohn–Sham effective potential, which includes Coulomb or Hartree potential due to ion cores and valence electrons and the exchange-correlation potential within LDA. The Kohn–Sham potential depends on the linear external potential through self consistent response or rearrangement of electrons to this external potential. In the calculation of the self-consistent potentials, the six special-$k$-point scheme of Cunningham for hexagonal two-dimensional lattice [62] is used to approximate the integration over the first Brillouin zone.

3 Calculation results and discussion

3.1 Interlayer spacing The equilibrium lattice constant obtained as the minimum of the calculated total energy per primitive cell, $E_{\text{tot}}$, as a function of the hexagonal lattice periodicity for a single graphene layer is 2.408 Å, which is about 2% smaller than the experimental lattice constant of graphite of 2.4612 Å [63] at room temperature and 2.4589 Å [57] at low temperature. Since the bonding between adjacent graphene layers is weak in comparison with the intralayer sp$^2$ bonding, it is reasonable to fix this calculated equilibrium lattice constant for thicker FLG’s. The total energies per primitive cell of the bilayer FLG as functions of the interlayer distance for AA and AB stacking are shown in Fig. 1. The calculated equilibrium layer spacing for AA and AB stacking are 2.821 Å and 2.725 Å, respectively, which are substantially reduced from the calculated equilibrium layer spacing of 3.257 Å for bulk graphite. The calculated layer spacing for bulk graphite is 2.4% less than the experimental value of 3.337 Å [57].

Within a few percent underestimate of the lattice constant as well as the interlayer spacing is typical of the LDA calculation. Note that Trickey et al. also obtained a contracted layer spacing of 2.707 Å for bilayer graphite. [49], though they obtained a relaxed spacing of 3.437 Å later [50]. Van der Waals forces are thought to be the binding mechanism between different graphene sheets in graphite. The Van der Waals interaction stems from truly non-local correlation and is not contained in LDA. Thus, the present study does not include the contribution from the Van der Waals interaction. Since the Van der Waals interaction described by the Lennard–Jones potential is weak and acting at a long distance, the reasonable layer spacing obtained in this study may suggest that for FLG’s the direct coupling between p-orbitals may be equally important. This study also finds that if the exponentially decaying p-orbitals are not described by sufficient number of short-wavelength plane waves, the coupling between p-orbitals is not adequately treated and the AB stacking becomes less favorable than the AA stacking in disagreement experiment.

The AB stacking is found to be 0.17 eV per primitive cell more favorable than the AA stacking. This result agrees with the experimental finding of the ABABAB... sequence in bulk graphite [57]. The substantially reduced interlayer spacing for the bilayer FLG suggests that graphene layers may form pairs. Thus, $E_{\text{tot}}$ calculations for four-layer graphenes with AA–AA and AB–AB stacking sequence are performed to see if this is the case. For the AA–AA case, the AA layer spacing and the spacing between the two AA pairs are 3.346 Å and 3.365 Å, respectively. As for the AB–AB case, the AB layer spacing and the spacing between the two AB pairs are 3.365 Å and 3.297 Å, respectively. The AB–AB case is found to be 0.13 eV/per primitive cell more favorable than the AA–AA case. These results suggest that graphene layers do not form into pairs. Thus, the average equilibrium layer spacing for 3-, 5-, 6-, 7-, and 8-layer AB stacked FLG’s are also calculated. The calculated average layer spacing for 2-, 3-, 4-, 5-, 6-, 7-, and 8-layer AB stacked FLG’s are 2.725, 3.389, 3.331, 3.317, 3.192, 3.220, and 3.220 Å, respectively, and are plotted in Fig. 2. This trend shows that the average layer spacing approaches the bulk value when the number of layers is increased. The reason why the layer spacing for the two-layer FLG is substantially reduced relative to those of thicker FLG’s is that in the two-layer graphene the p-orbitals of the carbon atoms in the top layer couple fully with the p-orbitals of the carbon atoms in the bottom layer which lie directly below those in the top layer, so that the coupling is stronger. In contrast, the p-orbitals of the carbon atoms in the interior layers are not coupled.

![Figure 1](https://example.com/fig1.png)

**Figure 1** Total energies per primitive cell vs. the interlayer distance for bilayer FLG with AA and AB stacking.

![Figure 2](https://example.com/fig2.png)

**Figure 2** Calculated average interlayer spacing for 2- to 8-layer AB stacked FLG’s. The dashed line shows the calculated interlayer spacing of the bulk graphite.
shared among the $p_z$-orbitals of the carbon atoms in two adjacent layers for thicker FLG's. The present results are in opposite to those obtained by Yumura and Yoshizawa that the layer spacing are relaxed and contracted for bilayer and trilayer graphenes, respectively, using the second-order perturbation theory to treat the Van der Waals interaction [51].

### 3.2 Electronic structures

The electronic structures and total energies per primitive cell of both AA and AB stacked two-layer FLG’s for $V_{\text{ext}} = 0.0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0$ and $4.5$ Volts have been calculated. In these calculations, the layer spacing is optimized for each $V_{\text{ext}}$ and each type of stacking through $E_{\text{tot}}$ minimization. The AB stacking is more favorable than the AA stacking by $\sim 0.2$ eV/primitive cell for all $V_{\text{ext}}$'s considered. The AB stacking is more favorable than the AA stacking by $\sim 0.2$ eV/primitive cell for all $V_{\text{ext}}$'s considered. The band structure of the AB stacked two-layer FLG for $V_{\text{ext}} = 0$ is shown in Fig. 3. In Fig. 3 the high symmetry $k$-points $\Gamma$, K and M are the Brillouin zone center, $(2/3, 0)$ and $(1/2, 1/2\sqrt{3})$, respectively, in the unit of $2\pi/\alpha$, where $\alpha$ is the lattice constant. The shape of the energy bands is similar to that obtained by first-principles calculations of Charlier, Gonze, and Michenaud [11] for bulk graphite and Latil and Henrard et al. [30] for two-layer FLG. At the $\Gamma$-point, the occupied energy levels shown in Fig. 3 are $-3.0$ eV, $-8.0$ eV, $-9.5$ eV, and $-21.5$ eV. Ohta et al. performed angle-resolved photoemission spectroscopy measurements obtained energy levels at the $\Gamma$-point relative to $E_F$ as $\sim -3.2$ eV, $\sim -8.0$ eV to $\sim -9.5$ eV, and $\sim -22.0$ eV [32]. The calculated values agree very well with data. In comparison, Latil and Henrard [30] obtained $-3.0$ eV, $-7.20$ eV, $-8.20$ eV and $-19.2$ eV, Min et al. [44] obtained $-3.0$ eV, $-7.0$ eV, and $-8.0$ eV (for the first three levels) and Trickey et al. [50] obtained $-4.0$ eV, $-7.5$ eV, $-8.7$ eV, and $-20.0$ eV, respectively, for the corresponding energy levels. The band structures in the vicinity of $E_F$ and in the vicinity of the K-point for $V_{\text{ext}} = 0$ and $4.5$ Volts are shown in Fig. 4 for the two-layer FLG with both AA and AB stacking. Figure 4 indicates that the AA-stacked film remains semi-metallic for the whole range of $V_{\text{ext}}$ considered. However, there is an energy gap, $E_g$, of 0.598 eV for $V_{\text{ext}} = 4.5$ eV for the AB stacked film. For $V_{\text{ext}} = 0$, there is a band overlapping of 9 meV, which is not resolved in Figs. 3 and 4. The tiny band overlapping has been observed by Novoselov et al. [13]. The $E_g$ vs. $V_{\text{ext}}$ curve is shown in Fig. 5. Aoki and Amawaski obtained $E_g = 0.12$ eV for $U = 0.26$ V, where $U$ is the interlayer energy difference [41], while Min et al. obtained $E_g \sim 0.19$ eV for the same $U$ [44]. If using the same rela-
tionship between $U$ and $U_{ext} = eV_{ext}$ ($e$ is the electronic charge) obtained by Min et al., the present study yields $E_g = 0.16$ eV for the same $U$, which is comparable with those obtained by Aoki and Amawaki and Min et al. The $E_g$ curve shows a threshold at $V_{ext} = \sim 0.04$ Volts, which implies a semi-metal–semiconductor transition. This low $V_{ext}$ threshold suggests that the two-layer AB stacked FLG can be fabricated into useful nanoscale electronic switch. The near-$E_g$ and near-K band structures for 3- and 4-layer AB stacked FLG’s are also calculated. For the 3-layer FLG, the semiconductor phase occurs for most of $V_{ext}$ within 4 Volts. However, the $E_g$’s are very small and vary within 76 meV, which is only a few times the room-temperature thermal excitation energy of 26 meV. As for the 4-layer FLG, there is a window of the semiconductor phase between 0.48 Volts and 1.52 Volts; the $E_g$ curve as a function of $V_{ext}$ is roughly a triangle with a maximum $E_g = \sim 0.1$ eV at $V_{ext} = \sim 1.0$ Volt. The result for 3- and 4-layer FLG’s suggests that only the 2-layer FLG is useful as a nanoscale electronic switch.

Stauber et al. [24] using the tight-binding model found that the energy bands near $E_g$ and the K-point of the two-layer FLG with an AB stacking become Mexican-hat-like similar to that obtained in the present study as shown in Fig. 4. A similar shape of the energy bands was also obtained by Min et al. [44]. Stauber et al. obtained a concave downward nonlinear dependence of the energy gap minimum, $\Delta g$, on the bias, $V$. $\Delta g$ saturates at $\Gamma_{interplane} \sim 0.3$ eV, where tinterplane is the inter-plane hopping parameter [24]. Min et al. obtained a similar dependence of $E_g$ on $V$ with a saturated $E_g$ of 0.3 eV [44], which is the same as that of Stauber et al. However, Fig. 5 indicates that the energy gap rises well beyond 0.6 eV. The present first-principles calculation suggests that $\Gamma_{interplane} > 0.6$ eV. The discrepancy with the results of Stauber et al. and Min et al. is clearly due to the substantially reduced interlayer spacing in the present case, which substantially enhances the interlayer coupling.

4 Conclusion Based on the first-principles electronic structure and total energy calculations, the AB stacking is found to be more favorable than the AA stacking in agreement with the experimental fact. The layer spacing of the two-layer FLG is found substantially reduced from those of thicker FLG’s, which suggests an enhancement of the interlayer interaction energy relative to that of the bulk graphite. The calculated average interlayer spacing for 2- to 8-layer FLG’s indicate that the interlayer spacing will approach the bulk-graphite value as expected. For the AB stacked 2-, 3-, and 4-layer FLG’s, an external electric potential, $V_{ext}$ opens up energy gaps. However, the $E_g$’s induced by $V_{ext}$ are small and within 0.1 eV for 3- and 4-layer AB stacked FLG’s. In contrast, induced $E_g$ increases monotonically beyond 0.6 eV with a threshold at $V_{ext} = 0.04$ Volts for the 2-layer AB stacked FLG, which suggests a semi-metal–semiconductor transition that can be utilized as a nanoscale electronic switch.

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References


[59] In the modified PSF method, the projections of the tailing functions of the muffin-tin orbitals of surrounding atoms onto a given atom are calculated using two-dimensional structure factors [K. Kambe, Z. Naturf. 22a, 322 (1967); 22a, 422 (1967); 23a, 1280 (1968)] rather than the partial waves of plane-wave expanded pseudofunctions in the original method [58].


