Influence of electric fields on absorption spectra of AAB-stacked trilayer graphene

Chih-Wei Chiu* and Rong-Bin Chen²

¹Department of Physics, National Kaohsiung Normal University, Kaohsiung 824, Taiwan
²Center of General Studies, National Kaohsiung Marine University, Kaohsiung 811, Taiwan

*E-mail: giorgio@fonran.com.tw; rbchen@mail.nkmu.edu.tw

Received April 22, 2016; accepted May 10, 2016; published online May 31, 2016

Since mono- and few-layer graphene sheets were first fabricated in 2004,¹ low-dimensional graphene-related systems have been of great interest in experimental and theoretical studies. The stacking order of the graphene sheets includes the basic stacking sequences of AA,² ³ AB,⁴ ᵆ ABC,⁴ ᵇ and AAB.⁹ ᵋ In the past, research studies focused primarily on the first three kinds of the stacking.¹⁻³,¹² AAB stacking is the last probable configuration in trilayer systems. Recently, AAB stacking has been verified using different methods, such as electrostatic-manipulation scanning tunneling microscopy (STM),¹³ mechanical cleavage,¹⁴ liquid-phase exfoliation of natural graphite,¹⁵ and growth on metal surfaces.¹⁶ AAB stacking can be synthesized using horizontal shifting of the top graphite layer along the armchair direction.¹³ That is to say, the stacking configuration is continuously changed by the STM tip. Furthermore, AAB stacking has been found in the STM image of a sample obtained after fresh cleaving with either a scalpel or scotch tape.¹⁴

Theoretical studies on the electro-optical properties of trilayer graphene in the AAA,¹⁷ ABA,¹⁸ and ABC¹⁷,¹⁹ stacking configurations have been performed in previous studies. In this work, we mainly discuss the effects of an electric field on the rich band structures and optical absorption spectra of AAB-stacked trilayer graphene. The lowest symmetry of the geometric structure enriches the electronic structure, and thus, complicates the absorption spectra and electro-optical properties. Comparisons with trilayer graphene in the AAA, ABA, and ABC stacking configurations are also made.

The π-electronic structure of AAB-stacked trilayer graphene (AAB-TLG), arising primarily from the 2p orbitals, is calculated using the generalized tight-binding model. The two sublattices in the l-th (l = 1, 2, 3) layer are denoted as A¹ and B¹. The bottom two layers, shown in Fig. 1, are arranged in the AA-stacking configuration, in which all carbon atoms have the same (x, y) projections. The third layer can be obtained by shifting the first (or the second) layer by a distance b along the armchair direction. In this system, the A atoms (white) have the same (x, y) coordinates, whereas the B atoms (black) on the third layer are projected at the hexagonal centers of the other two layers. The interlayer distance and the C–C bond length are, respectively, d = 3.37 Å and b = 1.42 Å. There are six carbon atoms in a primitive unit cell. The zero-field Hamiltonian, which is built using the six tight-binding functions of the 2p orbitals, is dominated by the intralayer and interlayer atomic interactions γ. There exist 10 kinds of atom–atom interaction, which correspond to the 10 atomic hopping integrals in the Hamiltonian matrix. γ₀ = −2.569 eV represents the nearest-neighbor intralayer atomic interaction; γ₁ = −0.263 eV and γ₂ = 0.032 eV represent the interlayer atomic interactions between the first and second layer; γ₃ = −0.413 eV, γ₄ = −0.177 eV, and γ₅ = −0.119 eV are associated with the interlayer atomic interactions between the second and third layer; γ₆ = −0.013 eV, γ₇ = −0.0177 eV, and γ₈ = −0.0119 eV refer to the interlayer atomic interactions between the first and third layers; and γ₉ = −0.012 eV corresponds to the difference in the chemical environment of A and B atoms. The hopping integrals γ₁, γ₂, and γ₃ belong to the vertical interlayer atomic interactions, whereas all others are non-vertical.

The zero-field band structure of AAB-TLG consists of three pairs of conduction and valence subbands dispersed in the energy-wave-vector space along Γ → K → M → Γ. The pairs are labeled E¹⁻¹γ, E²⁻²γ, and E³⁻³γ according to the magnitude of the K-state energy in an increasing order, as indicated by the black curves in Fig. 2. In the vicinity of the
Fermi energy $E_F = 0$ (lower inset), the first pair of subbands, $E^{0\ast}_1$ and $E^{0\ast}_2$, have strong oscillatory energy dispersions. The conduction and valence states start from the extreme points of roughly $\pm 4\,\text{meV}$ at the K point. Along the KM or the KΓ direction, they reach the second points (the $b_1$ states) of $\pm 46\,\text{meV}$, and exhibit oscillatory variations at the third points (the $b_2$ states) at $\pm 4\,\text{meV}$, and then, change monotonically. The narrow gap $E_F \approx 8.2\,\text{meV}$ is located at the K point. Furthermore, both the $b_1$ and $b_2$ states form a circular constant-energy contour with the K point as its center in the energy-wave-vector space. Specifically, the two-dimensional (2D) constant-energy loops can be regarded as 1D energy bands; that is, they can display square-root asymmetric peaks in their spectra. Concerning the sombrero-shaped $E^{0\ast}_1$ and $E^{0\ast}_2$ bands, the energy difference between the two extreme points is relatively narrow, at roughly 20\,\text{meV}. Far from $E_F$, the monotonic parabolic bands, $E^{\ast}_1$ and $E^{\ast}_2$, possess band-edge states at roughly 0.46 and $\sim 0.51\,\text{eV}$. The special electronic structures distinguish AAB stacking from the other stacking configurations. For the middle energy, the states at the M point are saddle points, i.e., the state energy is a maximum (minimum) along $K \rightarrow M$ ($M \rightarrow \Gamma$). Therefore, there exists a larger density of states at the energy of the M points ($E^{\ast}_M$).

The energy dispersions of the AAB stacking are drastically changed in the presence of a perpendicular electric field $F_z$ (expressed in units of V/Å). As $F$ increases from zero, the effects are as follows. For low energy, the $b_1$ and $b_2$ states move farther away from the K point, and $|E^{0\ast}_{b_1}|, |E^{0\ast}_{b_2}|$ values increase. Both $|E^{0\ast}_{b_1}|$ and $|E^{0\ast}_{b_2}|$ rise and then fall, with the former exhibiting a significant change. The energy gap might depart from the K point to the $b_2$ state; it increases to the maximum value of 0.125\,\text{eV} at $F \sim 0.1$, and then, is reduced at higher field strengths ($F > 0.1$) (upper inset). Furthermore, $|E^{0\ast}_K|$ decreases and then increases, whereas $|E^{0\ast}_K|$ and $|E^{0\ast}_M|$ increase monotonically. The middle energy first-pair (third-pair) subbands are close to (distant from) the low energy, which means that $|E^{0\ast}_M|$ (|$E^{0\ast}_M$|) decreases (increases). $E^{0\ast}_M$ decreases and then increases slightly, whereas $E^{0\ast}_M$ does not show a clear change.

Electrons in the AAB-TLG are assumed to be excited from the occupied states to the unoccupied states by an EM field with polarization $\vec{E}$. The spectral function is given by

$$A(\omega) \propto \sum_{\hbar,\varepsilon} \int_{1\text{stBZ}} \frac{d^2k}{(2\pi)^2} |\langle \Phi^{\varepsilon}(k) | \hat{E} \cdot \vec{p}/m_e | \Phi^{\hbar}(k) \rangle|^2 \times \delta \left( |E^{\varepsilon}(k)| - |E^{\hbar}(k)| - \omega \right) + \delta^2,$$

where $\Phi^{\varepsilon}(k)$ and $\Phi^{\hbar}(k)$ [$|E^{\varepsilon}(k)|$ and $|E^{\hbar}(k)|$] are the wave functions (state energies) of the final and initial states, with $\hbar$ ($\varepsilon$) representing either conduction or valence bands. $\delta = 0.01$\,\text{eV} is the energy width due to various de-excitation mechanisms, and $\delta E(k)$ is the Fermi–Dirac distribution function. The dipole matrix element, $M^{\varepsilon \hbar}(k) = \langle \Phi^{\varepsilon}(k) | \hat{E} \cdot \vec{p}/m_e | \Phi^{\hbar}(k) \rangle$, could be evaluated using the gradient approximation. This element is anisotropic for $\hat{E}$; however, the integral of $|M^{\varepsilon \hbar}(k)|^2$ presents the isotropic properties.

Figure 3 shows the joint density of states ($D_\omega$), which is defined by setting the velocity matrix elements $|M^{\varepsilon \hbar}(k)|$ in Eq. (1) to 1, under different electric fields. It is proportional to the number of optical excitation states. When there exists a large number of states with very similar excitation energies, $D_\omega$ has a prominent structure. The $3 \times 3$ excitation channels in both low and middle frequencies caused by the saddle points or band edge states of the three pairs of the energy bands lead to rich structures spreading out in $D_\omega$. The frequencies of those structures correspond to the energy spacings between the conduction bands and the valence bands for specific states. For the low frequency case (upper inset), a shoulder
(s₁), a weak-peak (s₂), and a sharp-peak structure (s₃) are located at ω ∼ 0.011, 0.09, and 0.32 eV, respectively, corresponding to \( E_{1b₁}^{(s₁)} \rightarrow E_{1b₁}^{(s₁)} \) and \( E_{1b₁}^{(s₁)} \rightarrow E_{1b₁}^{(s₁)} \), \( E_{1b₁}^{(s₃)} \rightarrow E_{1b₁}^{(s₃)} \), \( E_{1b₁}^{(s₃)} \rightarrow E_{1b₁}^{(s₃)} \), and \( E_{1b₁}^{(s₃)} \rightarrow E_{1b₁}^{(s₃)} \), respectively, at zero field (black curve). Furthermore, there are three broad peaks (s₄, s₅, and s₆) and two weak shoulders (s₇ and s₈) at ω ∼ (0.525, 0.61, and 0.65 eV) and (0.75 and 0.78 eV). These structures are associated with the transitions of \( E_{1b₁}^{(s₄)} \rightarrow E_{1b₁}^{(s₁)} \) and \( E_{1b₁}^{(s₁)} \rightarrow E_{1s₁}^{(s₁)} \) and \( E_{1b₁}^{(s₅)} \rightarrow E_{1s₁}^{(s₃)} \) and \( E_{1b₁}^{(s₃)} \rightarrow E_{1s₁}^{(s₃)} \) and \( E_{1s₁}^{(s₃)} \rightarrow E_{1s₁}^{(s₃)} \). Specifically, the transition \( E_{1s₁}^{(s₄)} \rightarrow E_{1s₁}^{(s₁)} \) does not exhibit a special structure, because of the sharp edge states of the parabolic bands. Under the influence of different electric fields, the forms and frequencies of these structures exhibit significant variations.

Most structures are shifted to higher frequencies with an increase in F (red arrows). The s₁ (s₃) structure, because of the split of \( E_{1b₁}^{(s₄)} \rightarrow E_{1b₁}^{(s₁)} \) and \( E_{1b₁}^{(s₁)} \rightarrow E_{1b₁}^{(s₄)} \) \( E_{1b₁}^{(s₃)} \rightarrow E_{1b₁}^{(s₃)} \) and \( E_{1b₁}^{(s₄)} \rightarrow E_{1b₁}^{(s₄)} \), is separated into s₁ and s₁’ (s₃ and s₃’) components. As for the middle frequency, there are nine peaks \( (p_1, \ldots, p_9) \) induced from the M point. These peaks correspond to \( E_{1s₁}^{(s₁)} \rightarrow E_{1s₁}^{(s₁)} \), \( E_{1s₁}^{(s₁)} \rightarrow E_{1s₁}^{(s₁)} \), \( E_{1s₁}^{(s₁)} \rightarrow E_{1s₁}^{(s₁)} \), \( E_{1s₁}^{(s₁)} \rightarrow E_{1s₁}^{(s₁)} \), \( E_{1s₁}^{(s₁)} \rightarrow E_{1s₁}^{(s₁)} \), \( E_{1s₁}^{(s₁)} \rightarrow E_{1s₁}^{(s₁)} \), \( E_{1s₁}^{(s₁)} \rightarrow E_{1s₁}^{(s₁)} \), \( E_{1s₁}^{(s₁)} \rightarrow E_{1s₁}^{(s₁)} \), \( E_{1s₁}^{(s₁)} \rightarrow E_{1s₁}^{(s₁)} \) (lower inset). The range of these peak frequencies broadens quickly as F increases; however, the three peaks of \( p_1 \), \( p_3 \), and \( p_6 \) in the center of the nine peaks show a smaller shift. Several peaks with the same frequency overlap at certain F values, such as \( p_1 \) and \( p_3 \) at F = 0.2. The relatively high D₁ structures might make larger contributions to the optical excitations.

The optical absorption spectra A(ω) for AAB-TLG at different F values are shown in Fig. 4. Because of the different contributions of \( |M^2(k)|^2 \) among the states, the features of D₁ might not be completely reflected in A(ω), e.g., the strength and the form of the structures. The spectra exhibit complex structures in the low \( (ω < 1.65 eV) \) and middle \( (4.4 < ω < 6.5 eV) \) frequency range; otherwise, they are identical among different F values. A(ω) in the low frequency range reflects the optical excitations in the vicinity of the K points (or at the band-edge states); A(ω) in the middle frequency range reflects the excitations at the M points. In the former range (upper inset), the two asymmetric peak structures (s₁ and s₃) in the square-root form appear at ω ∼ 0.011 and 0.09 eV. This phenomenon occurs mainly because each oscillatory subband has two circular constant-energy contours in the energy-wave-vector space, which are related to concave and convex dispersions. The s₁ frequency corresponds to the optical threshold frequency determined by the narrow energy gap; the s₂ frequency corresponds to the oscillation bandwidth of the first pair of energy subbands near the K point. A very sharp dominant peak (s₃), which arises from the band-edge states within the first- and second-band energy subbands, is found at ω ∼ 0.32 eV; its strong intensity is due to the very high D₁ associated with the two valleys in each oscillatory subband. The weak peak at ω ∼ 0.525 eV (s₄) is contributed by the \( E_{1b₁}^{(s₄)} \rightarrow E_{1b₁}^{(s₄)} \) excitation channels. Additionally, the frequency difference between the optical transitions of \( E_{1s₁}^{(s₁)} \rightarrow E_{1s₁}^{(s₁)} \) \( E_{1s₁}^{(s₄)} \rightarrow E_{1s₁}^{(s₄)} \) \( E_{1s₁}^{(s₃)} \rightarrow E_{1s₁}^{(s₃)} \) \( E_{1s₁}^{(s₃)} \rightarrow E_{1s₁}^{(s₃)} \) in the asymmetric band structures should lead to two distinguishable peaks at ω ∼ 0.61 and 0.65 eV (0.75 and 0.78 eV), respectively. However, the structures of s₅ and s₇ do not remain in the absorption spectra because of the extremely small velocity matrix elements. On the other hand, seven logarithmic peaks are spread out in the middle frequency range (lower inset). Not all nine of the excitation channels create obvious spectral structures. The s₃ and s₇ peaks of the D₁ disappear at zero F. The absorption spectrum of the AAB stacking presents more spectral structures at the low- and middle-frequency A(ω), unlike the other stacking systems. The nine interlayer atomic interactions can account for the configuration-created spectral structures.

The frequency, intensity, and number of spectral structures are very sensitive to changes in the electric-field strength. The intensity of the threshold peak is greatly enhanced (upper inset in Fig. 4), which is a result of the F-enlarged constant-energy loops. The frequency of this peak is largest at F = 0.1 (green curve) because of the maximum \( E_g \) value (upper inset in Fig. 2). Similar results are also revealed for the second peak (s₂). There exists an additional weaker peak (s₁’) between the two prominent peaks, reflecting the distinct band-edge states in the valence and conduction bands at the K point. Moreover, the originally merged absorption peaks \( s₃ \) might be distinct, such as in the splitting of one peak into two that is related to \( E_{1b₁}^{(s₃)} \rightarrow E_{1b₁}^{(s₃)} \) and \( E_{1b₁}^{(s₃)} \rightarrow E_{1b₁}^{(s₃)} \). This phenomenon is caused by the F-enhanced asymmetric energy spectrum. In the middle frequency range, the peak frequency extends, and peaks with a larger shift are less likely to remain, e.g., the s₁, s₂, and s₅ peaks at F = 0.2.

The stacking configurations can diversify the energy dispersions and improve the optical properties of TLGs. For the low-lying band structure, there are critical differences among the four stacking configurations. AAA- and ABA-stacked trilayer graphene possesses special band structures with three pairs of linear bands for the former, and a pair of linear bands and two pairs of parabolic bands for the latter. The AAA and ABA electronic structures can be regarded as the superposition of monolayer graphene, and monolayer and bilayer graphenes, respectively. In contrast, the ABC and AAB
stackings exhibit unique energy bands that are absent in monolayer and bilayer systems. The former has pairs of partially-sombrero-shaped and linear bands, and the latter consists of pairs of oscillatory, sombrero-shaped, and parabolic bands. Notably, only the AAB stacking is a narrow direct-gap semiconductor, whereas the others are gapless 2D semimetals.

The diverse energy dispersions are directly reflected in the rich optical spectrum. For AAA and ABA stackings, only the intra-Dirac-cone optical excitations can remain, as a result of the linearly symmetric or anti-symmetric superposition of the wavefunctions in different layers. There is only a single shoulder structure in the low-frequency absorption spectra. The spectrum of AAA is displayed immediately after the forbidden excitation region under the specific fermion distributions, because of the almost symmetric upper and lower Dirac cones. However, that of ABA derives from the distinct parabolic bands. In the middle-frequency spectrum, these two systems present, respectively, three and five \( \pi \)-electronic absorption peaks derived from the saddle points of the three pairs of subbands. Regarding the ABC and AAB stackings, excitation channels between any valence and conduction bands are available. The threshold frequency of AAA is zero, whereas that of ABA is determined by the narrow energy gap. The low-frequency spectra exhibit peak and shoulder structure in the low-frequency absorption spectra. Whereas that of ABA derives from the distinct bands with oscillatory, sombrero-shaped, and parabolic characterizations for AAA stacking remain similar, whereas they change drastically for the other stackings. ABA stacking has 3 × 3 excitation channels, as observed in the ABC and AAB stacking configurations. More special absorption structures are created in these three systems. Furthermore, an optical gap is opened in the ABC stacking.

In conclusion, the tight-binding model and gradient approximation can be used to calculate the band structures and the absorption spectra, respectively, of AAB-stacked trilayer graphene. This system has the lowest symmetry of the geometric structures considered, and induces the ten atomic hopping integrals. There are three pairs of energy bands with oscillatory, sombrero-shaped, and parabolic dispersions at low energy. Saddle points are formed in the middle energy range. At zero electric field, 3 × 3 excitation channels exist in both low and middle frequencies, and cause very rich joint density of states (\( D_J \)). Several low-\( \omega \) peaks or shoulders and nine middle-\( \omega \) peaks exist in \( D_J \); however, these structures are not fully reflected in the absorption spectra because of the relatively small velocity matrix elements. In the presence of an electric field along the stacking direction, the energy dispersions and the energy spacings exhibit significant variations. The field further influences the properties of the spectra, such as the frequency, intensity, separation, and existence of spectral structures. Compared with TLGs in other stacking configurations (i.e., AAA, ABA, and ABC), AAB-TLG has the richest energy dispersions, the richest absorption spectra, and the most complicated electric-field effects.

Acknowledgment This work is supported by the Ministry of Science and Technology, R.O.C., under grant No. MOST 104-2112-M-017-001.

1) K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Science 306, 666 (2004). 2) J. K. Lee, S. C. Lee, J. P. Ahn, S. C. Kim, I. J. B. Wilson, and P. John, J. Chem. Phys. 129, 234709 (2008). 3) Z. Liu, K. Suemana, P. J. F. Harris, and S. Iijima, Phys. Rev. Lett. 102, 015501 (2009). 4) P. Lauffer, K. V. Emets, R. Graupner, Th. Seyller, L. Ley, S. A. Reshanov, and H. B. Weber, Phys. Rev. B 77, 155426 (2008). 5) S. Hattendorf, A. Georgi, M. Liebmann, and M. Morgensen, Surf. Sci. 610, 53 (2013). 6) J. Borysiuk, J. Soltys, and J. Pechota, J. Appl. Phys. 109, 093523 (2011). 7) W. Norimatsu and M. Kusunoki, Phys. Rev. B 81, 161410(R) (2010). 8) J. H. Warner, M. Mukai, and A. I. Kirkland, ACS Nano 6, 5680 (2012). 9) Z. Y. Rong and P. Kuiper, Phys. Rev. B 48, 17427 (1993). 10) J. M. Campanera, G. Savini, I. Suarez-Martinez, and M. I. Heggie, Phys. Rev. B 75, 235449 (2007). 11) L. B. Biedermann, M. L. Bolen, M. A. Capano, D. Zemlyanov, and R. G. Reifenberger, Phys. Rev. B 79, 125411 (2009). 12) C. Y. Lin, Y. J. Wu, Y. J. Ou, Y. H. Chiu, and M. F. Lin, Phys. Chem. Chem. Phys. 17, 26008 (2015). 13) P. Xu, Y. Yang, D. Qi, S. D. Barber, J. K. Schoelz, M. L. Ackerman, L. Bellaiche, and P. M. Thibado, Phys. Rev. B 86, 085428 (2012). 14) W. T. Pong, J. Bendall, and C. Durkan, Surf. Sci. 601, 498 (2007). 15) A. S. Kazemi, S. Crampin, and A. Ilie, Appl. Phys. Lett. 102, 163111 (2013). 16) Y. Que, W. Xiao, H. Chen, D. Wang, S. Du, and H. J. Gao, Appl. Phys. Lett. 107, 263101 (2015). 17) C. P. Chang, J. Wang, C. L. Lu, Y. C. Huang, M. F. Lin, and R. B. Chen, J. Appl. Phys. 103, 101109 (2008). 18) C. L. Lu, C. P. Chang, Y. C. Huang, R. B. Chen, and M. L. Lin, Phys. Rev. B 73, 144427 (2006). 19) Y.-P. Lin, C.-Y. Lin, C.-P. Chang, and M.-F. Lin, RSC Adv. 5, 80410 (2015). 20) C. W. Chiu, Y. H. Ho, F. L. Shyu, and M. F. Lin, Appl. Phys. Express 7, 115102 (2014). 21) C. W. Chiu, S. H. Lee, S. C. Chen, F. L. Shyu, and M. F. Lin, New J. Phys. 12, 083060 (2010).