Low-frequency Magneto-optical Spectra of Bilayer Bernal Graphene

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August 6, 2009

Abstract

The low-frequency magneto-optical absorption spectra of bilayer Bernal graphene are studied within the tight-binding model and gradient approximation. The interlayer interactions strongly affect the electronic properties of the Landau levels (LL’s), and thus enrich the optical absorption spectra. According to the characteristics of the wave functions, the low-energy LL’s can be divided into two groups. This division results in four kinds of optical absorption peaks with complex optical selection rules. Observing the experimental convergent absorption frequencies close to zero magnetic field might be useful and reliable in determining the values of several hopping integrals. The dependence of the optical absorption spectra on the field strength is investigated in detail, and the results differ considerably from those of monolayer graphene.

PACS numbers: 78.20.Ls, 78.67.Pt, 73.20.At, 71.15.Dx
Since few-layer graphenes were produced by the mechanical friction\textsuperscript{1,2} and thermal decomposition,\textsuperscript{3,4} they have attracted considerable experimental and theoretical studies. Monolayer graphene (MG) and bilayer Bernal graphene (BBG; AB-stacked bilayer graphene), two of the simplest few-layer graphenes, display very different electronic features. MG exhibits linear energy dispersions near the Fermi level $E_F = 0$ owing to the hexagonal structure. However, BBG possesses two pairs of parabolic bands\textsuperscript{5,6} owing to the interlayer interactions and stacking configurations.\textsuperscript{7−9} These unusual electronic structures of few-layer graphenes have been experimentally verified through angular-resolved photoemission spectroscopy.\textsuperscript{10,11}

In the presence of a uniform perpendicular magnetic field $\mathbf{B} = B_0 \hat{z}$, the magneto-electronic properties of few-layer graphenes have been obtained by measurements of the quantum Hall conductivity,\textsuperscript{2,12,13} scanning tunneling spectroscopy,\textsuperscript{14,15} and cyclotron resonance.\textsuperscript{16,17} The theoretical results show that the linear bands of MG become the Landau levels (LL’s) characterized by $E_{c,v}^{c,v} \propto \sqrt{n_{c,v} B_0}$,\textsuperscript{18,19} where $c$ ($v$) is the index of the conduction (valence) LL’s. $E_{c,v}^{c,v}$ and $n_{c,v}$ are the energy and the integer quantum number of the $n$th energy band, respectively. The optical absorption peaks possess the selection rule $|\Delta n| = |n_c - n_v| = 1$ and their frequency is proportional to $\sqrt{B_0}$,\textsuperscript{20} which has been confirmed by magnetotransmission measurements.\textsuperscript{16,21,22} For BBG, the effective-mass approximation, which neglects some interlayer interactions, predicts that the magnetic field changes the parabolic bands into LL’s following $E_{n}^{c,v} \propto \sqrt{n_{c,v}(n_{c,v} - 1)} B_0$.\textsuperscript{20,23,24} The optical absorption frequencies obey a linear function of $B_0$ in weak fields, and depend linearly on $\sqrt{B_0}$ as the corresponding energy leaves the parabolic band region.\textsuperscript{20} The optical selection rule related to low-lying LL’s is $|\Delta n| = 1$,\textsuperscript{23} the same rule that is applied to MG. However, the calculations of Peierls tight-binding model including more important interlayer interactions indicate that the low-energy LL’s should exhibit more complex features,\textsuperscript{24} i.e., there exists an energy gap, asymmetry of LL’s, two groups of LL’s ($1^{st}$LL’s and $2^{nd}$LL’s), and composite relations between $E_{n}^{c,v}$ and $B_0$. The varied electronic features are reflected in the magneto-optical properties.

In this work, the influence of the important interlayer interactions on the magneto-optical absorption spectra of BBG is investigated in detail by gradient approximation\textsuperscript{25,26} and Peierls tight-binding model (see the geometry and detailed electronic properties in Ref. 24). The band-like matrix\textsuperscript{24,27−31} is designed to solve a very huge Hamiltonian matrix. In this way, the wave functions\textsuperscript{24} are obtained and can be used to divide the LL’s of BBG into
two groups $1^{st}$LL’s and $2^{nd}$LL’s. For the magneto-optical excitations at a small magnetic field, the matrix will be larger and more complicated in the calculations, which makes the computation time very long. By utilizing the band-like matrix and obtaining the localized feature of wave functions, we can efficiently reduce the calculation time and thus evaluate the magneto-optical absorption spectra. The absorption peaks exhibit complex selection rules and composite field-dependent absorption frequencies. What deserves to be mentioned is that our study is more comprehensive than other studies in optical properties. The previous experimental and theoretical works mainly focused on the optical properties owing to $1^{st}$LL’s. However, in our work, all of the possible optical absorption peaks resulting from the two groups are discussed in detail, and could be clearly distinguished from each other. Furthermore, a comparison of magneto-optical absorption spectra of MG and BBG is also made.

The dispersionless LL’s of BBG at $B_0 = 40$ T are shown in Fig. 1(a). The interlayer interactions strongly influence the main features of LL’s. The conduction and valence bands are asymmetric. There is an energy gap between the lowest unoccupied LL and the highest occupied LL. Based on the characteristics of wave functions, LL’s can be classified into two groups, $1^{st}$LL’s (black curves) and $2^{nd}$LL’s (red curves). $1^{st}$LL’s appears at $|E_{c,v}^n| > 0$, and $2^{nd}$LL’s begins at $E_{c}^n \gtrsim \gamma_1 + \gamma_6 (0.34 \text{ eV})$ and $E_{v}^n \lesssim -\gamma_1 + \gamma_6 (-0.39 \text{ eV})$. $\gamma_i$’s $^{6,24,32}$ are the most important hopping integrals. The energies of these LL’s exhibit the composite relationship of $E_{c,v}^n \propto B_0$ and $E_{c,v}^n \propto \sqrt{B_0}$. $^{24}$

The characteristics of wave functions deserve a closer investigation because they strongly dominate the optical properties. Each LL is composed of fourfold degenerate states with similar characteristics. At $k_x = k_y = 0$, the wave functions mainly consist of four localized subenvelope functions centered at positions $x_1 = 1/6$, $x_2 = 1/3$, $x_3 = 2/3$, and $x_4 = 5/6$. $x_j = 1-4 = A_{i,N}/2R_B$ or $= B_{i,N}/2R_B$, where $i$ is the index of the $i$th layer and $N$ represents the $N$th $A_i$ or $B_i$ atoms. $R_B^{24,27}$ defines the dimensionality of the Hamiltonian matrix. The feature of wave functions resulting from the atoms with an even number ($A_{i,e}$ and $B_{i,e}$) is similar to that with an odd ($A_{i,o}$ and $B_{i,o}$) number. Because of this, only odd atoms are discussed in following calculations, where $e$ ($o$) is an even (odd) integer. For convenience, one of the fourfold degenerate states at $x_1 = 1/6$ is selected to be examined, as shown in Figs. 1(b)-1(e). Through appropriate fitting, the wave functions of the $n_1$th $1^{st}$LL (black
(2) and (2). Optical absorption peaks can easily be obtained by the definition of wave functions in Eqs. (2a) and (2b).

\[ A_{1,o}^c \propto \varphi_0(x), A_{2,o}^c \propto \varphi_2(x), B_{1,o}^c \propto \varphi_1(x), n_{1,eff}^c = 0 \text{ for } n_1 = 1; \] (1a)

\[ A_{1,o}^v \propto \varphi_0(x), A_{2,o}^v \propto \varphi_2(x), B_{1,o}^v \propto \varphi_1(x), n_{1,eff}^v = 1 \text{ for } n_1 = 1; \] (1b)

\[ A_{1,o}^{c,v} \propto \varphi_{n_1-1}(x), B_{1,o}^{c,v} \propto \varphi_{n_1-2}(x), B_{2,o}^{c,v} \propto \varphi_{n_1}(x) \text{ for } n_1 (= n_{1,eff}^{c,v}) \geq 2. \] (1c)

\[ A_{1,o}^{c,v} \propto \varphi_0(x), A_{2,o}^{c,v} \propto \varphi_0(x), B_{1,o}^{c,v} \propto \varphi_2(x), B_{2,o}^{c,v} \propto \varphi_1(x), n_{2,eff}^{c,v} = 0 \text{ for } n_2 = 1; \] (2a)

\[ A_{1,o}^{c,v} \propto \varphi_{n_2-1}(x), B_{1,o}^{c,v} \propto \varphi_{n_2-2}(x), B_{2,o}^{c,v} \propto \varphi_{n_2}(x) \text{ for } n_2 (= n_{2,eff}^{c,v} + 1) \geq 2. \] (2b)

\( \varphi_n(x) \) is the product of the nth-order Hermite polynomial and Gaussian function, where \( n \) is the number of zero points in \( \varphi_n(x) \) and chosen to define the quantum number of wave functions. \( n_{1,eff}^{c,v} \) \( (n_{2,eff}^{c,v}) \) is the effective quantum number of the nth 1st LL’s (nth 2nd LL’s) defined by the quantum number of \( B_{2,o}^{c,v} \) \( (A_{1,o}^{c,v}) \). It should be noted that the 1st LL’s and 2nd LL’s could be distinguished by the different features of the wave functions in the mixed region \( (E_c \gtrsim 0.34 \text{ eV} \text{ and } E_v \lesssim -0.39 \text{ eV}) \), which is useful in analyzing the optical excitation channels.

When BBG is subjected to an electromagnetic field at zero temperature, only excitations from the valence to the conduction bands occur. The optical selection rule \( \Delta \mathbf{k} = 0 \) due to the vertical transitions is mainly determined by the zero momentum of the photon. Based on the Fermi’s golden rule, the optical absorption function is given by

\[
A(\omega) \propto \sum_{n_{1,2}^{c,v},n_{1,2}^{v,eff}} \left| \langle \psi^{c}(n_{1,2}^{c,eff}, k) | \hat{E} \cdot \mathbf{P} | \psi^{v}(n_{1,2}^{v,eff}, k) \rangle \right|^2 \int_{1stBZ} \frac{d \mathbf{k}}{(2\pi)^3} \left[ f \left( E^c(k, n_{1,2}^{c,eff}) \right) \right. - \left. f \left( E^v(k, n_{1,2}^{v,eff}) \right) \right] \right|^{2}
\times \operatorname{Im} \left\{ \frac{\left[ \frac{E^c(k, n_{1,2}^{c,eff})}{E^c(k, n_{1,2}^{c,eff}) - E^v(k, n_{1,2}^{v,eff}) - \omega - i\Gamma} \right] - \left[ \frac{E^v(k, n_{1,2}^{v,eff})}{E^c(k, n_{1,2}^{c,eff}) - E^v(k, n_{1,2}^{v,eff}) - \omega - i\Gamma} \right] \right\},
\] (3)

where \( \hat{E} \) is the unit vector of an electric polarization. The velocity matrix element \( M^{c,v} = \langle \psi^{c}(n_{1,2}^{c,eff}, k) | \hat{E} \cdot \mathbf{P} | \psi^{v}(n_{1,2}^{v,eff}, k) \rangle \) is calculated within the gradient approximation. \( M^{c,v} \) strongly depends on the characteristics of wave functions and would dominate the peak intensity. Due to the orthogonality of \( \varphi_n(x) \), \( M^{c,v} \) has nonzero values except one condition when \( A_{i,o}^{c,v} \) \( (A_{i,e}) \) and \( B_{i,o}^{c,v} \) \( (B_{i,e}^{c,v}) \) own the same \( \varphi_n(x) \). Accordingly, the selection rules of optical absorption peaks can easily be obtained by the definition of wave functions in Eqs. (1) and (2).

The low-frequency optical absorption spectrum of BBG at \( B_0 = 40 \text{ T} \) presents many prominent and some inconspicuous (indicated by arrows) peaks, as shown in Fig. 2(a).
The prominent peaks with definite optical selection rules are discussed in the following paragraphs. The peaks can mainly be classified into four kinds of peaks, $\omega_{11}$’s (black dots), $\omega_{22}$’s (red dots), $\omega_{12}$’s (green dots), and $\omega_{21}$’s (blue dots), which originate in the excitations of $1^{st}$LL’s $\rightarrow$ $1^{st}$LL’s, $2^{nd}$LL’s $\rightarrow$ $2^{nd}$LL’s, $1^{st}$LL’s $\rightarrow$ $2^{nd}$LL’s, and $2^{nd}$LL’s $\rightarrow$ $1^{st}$LL’s, respectively. The former (latter) two kinds of peaks result from the transitions between two LL’s in the same (different) groups, as illustrated by the inset of Fig. 2(d). The four kinds of absorption peaks might have different optical selection rules because of the characteristics of wave functions in the two groups of LL’s.

The optical excitations of each prominent peak can clearly be identified, as shown in Fig. 2(a). For convenience, the excitations of $\omega_{11}$’s, $\omega_{22}$’s, $\omega_{12}$’s, and $\omega_{21}$’s are, respectively, represented as $n_{11}^{v,ef} \rightarrow n_{11}^{c,ef}$, $n_{22}^{v,ef} \rightarrow n_{22}^{c,ef}$, $n_{12}^{v,ef} \rightarrow n_{22}^{c,ef}$, and $n_{21}^{v,ef} \rightarrow n_{21}^{c,ef}$ in the following. The selection rule of $\omega_{ij}$’s is denoted by $\Delta n_{ii'} (= n_{ij}^{c,ef} - n_{ij}^{v,ef})$. As to $\omega_{11}$’s and $\omega_{22}$’s, only the first peak ($\omega_{11}^{1}$) of $\omega_{11}$’s originates in single channel, $1 \rightarrow 2$. The other $m$th peak $\omega_{11}^{m}$ ($\omega_{22}^{m}$) consists of the pair $\omega_{11}^{m,L}$ and $\omega_{11}^{m,H}$ ($\omega_{22}^{m,L}$ and $\omega_{22}^{m,H}$) corresponding to $m - 1$ ($m - 1 \rightarrow m$) and $m + 1$ ($m \rightarrow m - 1$), respectively. The superscript $L$ ($H$) indicates the lower (higher) energy of the pair. For example, $\omega_{11}^{1}$ ($\omega_{22}^{1}$) is composed of $\omega_{11}^{1,L}$ and $\omega_{11}^{1,H}$ ($\omega_{22}^{1,L}$ and $\omega_{22}^{1,H}$) owing to $2 \rightarrow 3$ and $3 \rightarrow 2$ ($0 \rightarrow 1$ and $1 \rightarrow 0$), respectively. The reason for this is that the energies of $m - 1$ ($m - 1 \rightarrow m$) and $m + 1$ ($m \rightarrow m - 1$) in $\omega_{11}$’s ($\omega_{22}$’s) are slightly different owing to the asymmetry of the conduction and valence LL’s. In short, the optical selection rules of $\omega_{11}$’s and $\omega_{22}$’s can be represented by $\Delta n_{11} = \Delta n_{22} = \pm 1$, which is the same for the LL’s in MG.

As for the transitions between two different groups, the $m$th peak of $\omega_{12}$’s is formed with the pair, $\omega_{12}^{m,L}$ originating in $m - m$ and $\omega_{12}^{m,H}$ resulting from $m + 1 \rightarrow m - 1$. For instance, the first pair is indicated by $\omega_{12}^{1,L}$ and $\omega_{12}^{1,H}$ in Fig. 2(a), which correspond to $1 \rightarrow 1$ and $2 \rightarrow 0$, respectively. That is to say, $\omega_{12}^{m,L}$ owns the optical selection rule $\Delta n_{12} = 0$ and $\omega_{12}^{m,H}$ possesses $\Delta n_{12} = -2$. For $\omega_{21}$’s, the excitations $0 \rightarrow 0$ and $0 \rightarrow 2$ lead to the peaks $\omega_{21}^{0,L}$ and $\omega_{21}^{0,H}$ of the first pair in Fig. 2(a), respectively. The other channels $m - 1 \rightarrow m + 1$ and $m \rightarrow m$ result in the pair $\omega_{21}^{m,L}$ and $\omega_{21}^{m,H}$, respectively. In other words, the selection rules of $\omega_{21}$’s are $\Delta n_{21} = 0$ and $\Delta n_{21} = 2$. Obviously, the optical selection rules of $\omega_{12}$’s and $\omega_{21}$’s are different from those of $\omega_{11}$’s and $\omega_{22}$’s, which is not clearly discussed in the previous theoretical works.

The absorption rate significantly relies on the field strength and the excitation energy. In Figs. 2(a)-2(d), the peak intensity augments with increasing field strength, while the
opposite is true for the peak number. Furthermore, some peaks with commensurate energies are overlapping because the peak spacing declines as the frequency increases, which varies the peak intensity. In contrast to BBG, MG exhibits absorption peaks with uniform intensity (Fig. 2(e)). The interlayer interactions are the main reasons for the difference between BBG and MG. The field-dependent absorption frequencies ($\omega'_a$’s) of $\omega_{11}$’s, $\omega_{22}$’s, $\omega_{12}$’s and $\omega_{21}$’s are shown in Fig. 3(a) by the black, red, green, and blue dots, respectively. $\omega_a$’s rise with increasing $B_0$ and might follow the composite relationship of $\omega_a \propto B_0$ and $\omega_a \propto \sqrt{B_0}$. Apparently, $\omega_a \propto \sqrt{B_0}$ in MG (Fig. 3(b)) is very different from that in BBG. In addition, the convergent frequencies of $\omega_{11}$’s, $\omega_{22}$’s, $\omega_{12}$’s and $\omega_{21}$’s at $B_0 \to 0$ are approximately $0$, $0.73$ eV ($2\gamma_1$), $0.34$ eV ($\gamma_1 + \gamma_6$), and $0.39$ eV ($\gamma_1 - \gamma_6$), respectively. This implies that the optical measurements can reasonably determine the values of $\gamma_1$ and $\gamma_6$ through observing the convergent frequencies of absorption peaks. The predicted result is very useful and reliable for experimental studies.

The tight-binding model is widely applied to tackle the physical problems of semiconductors and carbon-related systems. Through the band-like matrix and the localized feature of wave functions, the huge and complicated Hamiltonian matrix can be further simplified in the calculations of the magneto-optical excitations for small field cases. Thus the computation time is substantially reduced. Moreover, the numerical strategy can be utilized to study not only the electronic and optical properties, but also the Coulomb excitations and transport properties in other crystal materials.

In summary, it can be said that the interlayer interactions strongly affect the magneto-optical properties of BBG in the presence of uniform perpendicular magnetic fields. Based on the characteristics of wave functions, the conduction and valence LL’s are asymmetric and can be divided into $1^{st}$LL’s and $2^{nd}$LL’s leading to four kinds of optical absorption peaks $\omega_{11}$’s, $\omega_{22}$’s, $\omega_{12}$’s, and $\omega_{21}$’s. Their optical selection rules are $\Delta n_{11} = \pm 1$, $\Delta n_{22} = \pm 1$, $\Delta n_{12} = 0, -2$, and $\Delta n_{21} = 0, 2$, respectively, which can again be explained by the characteristics of wave functions. The selection rules and field-dependent absorptions of BBG are more complicated than those of MG. The above-mentioned influences of interlayer interactions on the magneto-optical properties could be confirmed by magnetoabsorption spectroscopy measurements.\textsuperscript{17,21,22} Furthermore, the convergent absorption frequencies at nearly zero field might be helpful and reliable in determining the interlayer atomic interactions $\gamma_1$ and $\gamma_6$ through the magneto-optical measurements.
Acknowledgments

This work was supported by the NSC and NCTS of Taiwan, under the grant No. NSC 95-2112-M-006-028-MY3 and NSC 97-2112-M-110-001-MY2.
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FIG. 1. (a) Landau levels of bilayer Bernal graphene at $B_0=40$ T. The wave functions of (b) $A_{1,o}$, (c) $B_{1,o}$, (d) $A_{2,o}$, (e) $B_{2,o}$ atoms with odd integer indices are shown.

FIG. 2. The optical absorption spectra of bilayer Bernal graphene at (a) 40 T, (b) 30 T, (c) 20 T, and (d) 10 T. The spectrum of monolayer graphene at 40 T is plotted in (e).

FIG. 3. The field-dependent optical absorption frequencies of (a) bilayer Bernal graphene and (b) of monolayer graphene.