Role of electronic excitations in magneto-Raman spectra of graphene

Oleksiy Kashuba¹,³ and Vladimir I Fal’ko²

¹ Institute for Theory of Statistical Physics, RWTH Aachen, 52056 Aachen, Germany
² Department of Physics, Lancaster University, Lancaster LA1 4YB, UK
E-mail: kashuba@physik.rwth-aachen.de

New Journal of Physics 14 (2012) 105016 (19pp)
Received 29 May 2012
Published 16 October 2012
Online at http://www.njp.org/
doi:10.1088/1367-2630/14/10/105016

Abstract. We investigate the signature of the low-energy electronic excitations in the Raman spectrum of monolayer and bilayer graphenes. The dominant contribution to the Raman spectra is due to the interband electron–hole (e–h) pairs, which belong to the irreducible representation $A_2$ of the point group $C_{6v}$ of the graphene lattice, and are characterized by crossed polarization of incoming and outgoing photons. At high magnetic fields, this is manifested by the excitation of e–h inter-Landau-level (LL) transitions with selection rule $n^- \rightarrow n^+$. Weaker Raman-active inter-LL modes also exist. One of those has a selection rule similar to the infrared absorption process, $n^- \rightarrow (n \pm 1)^+$, but the created e–h excitation belongs to the irreducible representation $E_2$ (rather than $E_1$) and couples to the optical phonon mode, thus undergoing an anticrossing with the optical phonon $G$-line in Raman in a strong magnetic field. The fine structure acquired by the $G$-line due to such anticrossing depends on the carrier density, inhomogeneity of doping and presence of inhomogeneous strain in the sample.
1. Introduction

Experimental observation of electronic excitations in graphene is mostly associated with angle-resolved photoemission spectroscopy [1, 2] and optical absorption in monolayers [3–9] and bilayers [5, 6, 10–16] where Raman spectroscopy has been used to study graphene phonons [17], and became the method of choice for determining the number of atomic layers in graphitic flakes [17–23]. In particular, single- and multiple phonon-emission lines in the Raman spectrum of graphene and the influence of the electron–phonon coupling on the phonon spectrum have been investigated in great detail in [24–32].

This paper presents a theory of inelastic light scattering in the visible range of photon energies accompanied by electronic excitations in mono- and bilayer graphene both with and without an external magnetic field. We classify the relevant modes according to their symmetry, analyse peculiar selection rules for the Raman-active excitations of electrons between Landau levels (LLs) in graphene at strong magnetic fields, review the fine structure of the phonon-related Raman under conditions of magneto-phonon resonance (when the inter-LL transition is in resonance with a phonon) and model the dependence of the spectra on the value and homogeneity of carrier density and strain in the sample.

Graphene is a gapless semiconductor [33–36], with an almost linear Dirac-type spectrum \( \varepsilon = \alpha v p \) in the monolayer case and parabolic \( \varepsilon = \alpha p^2/2m \) for bilayer, in the conduction (\( \alpha = + \)) and valence (\( \alpha = - \)) bands, which touch each other in the corners of the hexagonal Brillouin zone (BZ), usually called valleys. In bilayer graphene, there are two additional parabolic bands with the gap \( 2\gamma_1 \). The conduction–valence band degeneracy in the BZ corners of the band structure of graphene is prescribed by the hexagonal symmetry \( C_{6v} \) of its honeycomb lattice, and it is natural to relate Raman-active modes to the irreducible representations of the point group \( C_{6v} \).

References
We argue that the dominant electronic modes generated by inelastic scattering of photons with energy $\Omega$ less than the bandwidth of graphene are superpositions of the interband electron–hole (e–h) pairs which have symmetry of the representation $A_2$ of the group $C_{6v}$ and are odd with respect to the inversion of time. Their excitation process may go in two ways both of which consist of the same steps, but in reversed order. In the first process, the absorption of a photon with energy $\Omega$ transfers an electron from an occupied state in the valence band into a virtual state in the conduction band, followed by emission of the second photon with energy $\tilde{\Omega} = \Omega - \omega$. In the second process the reversed order of events leads to the virtual electron state with large deficit of energy as opposed to the first process with large excess. Net amplitude is determined by the sum of partial amplitudes of the opposite processes. The dominance of such a process over the one involving the contact interaction [37–39] of an electron with two photons is a peculiarity of the Dirac-type electrons in graphene.

A strong magnetic field leads to the quantization of the electronic spectrum into LLs [40]. In graphene, LLs appear symmetrically in the conduction bands $\epsilon_{n,\sigma}^{\alpha}$ ($\alpha = \pm$) with peculiar zero-energy LLs in monolayer ($n = 0$) and bilayer ($n = 0.1$). For the inelastic light scattering in graphene, we find peculiar selection rules, $n^- \rightarrow n^+$ of the dominant Raman-active transitions (solid line in figure 3), in contrast to the $\Delta n = \pm 1$ transitions between LLs, which are dominant in the absorption of left- and right-handed circularly polarized infrared photons [7]. The weaker Raman mode with a similar inter-LL selection rule also differs from the absorption process, having different symmetry properties which allow the interaction with Raman scattering of light on optical phonons creating anticrossings at the $G$-peak line; see figure 4. Raman spectroscopy, therefore, provides data supplementary to that obtained in optical absorption.

The following theory is based on the effective low-energy Hamiltonian derived from the tight-binding model of electron states in graphene. It describes electrons in the conduction and valence bands around the BZ corners $K$ ($\xi = +$) and $K'$ ($\xi = -$) [41, 42]. For monolayer graphene the effective Hamiltonian reads

$$H_m = \xi v \sigma \cdot \mathbf{p} - \frac{v^2}{6\gamma_0}(\sigma^x(p_x^2 - p_y^2) - 2\sigma^y p_x p_y).$$

(1)

Here, $\sigma = (\sigma^x, \sigma^y)$ are Pauli matrices acting on the sublattice components of electronic states on $A$ and $B$ sublattices of graphene honeycomb lattice, and $\mathbf{p}$ being the in-plane momentum counted from the BZ corner. The first term in equation (1) determines Dirac spectrum electrons. The monolayer hopping parameter $\gamma_0 \approx 3$ eV determines the bandwidth, $\sim 6\gamma_0$, and Dirac velocity of electrons $v \approx 10^6$ cm s$^{-1}$ [10, 12, 19, 43]. The second term takes into account weak trigonal warping [41] breaking the continuous rotational symmetry of the Dirac Hamiltonian. The basis is constructed of wavefunctions corresponding to atomic sites $A, B$ in the valley $K$ and $B, A$ in $K'$. Since four-spinors $\{\varphi_{AK}, \varphi_{BK}, \varphi_{BK'}, \varphi_{AK'}\}$ realize four-dimensional (4D) irreducible representation of the full symmetry group of the crystal, matrix operators can be combined into irreducible representations [26, 27, 44] of the group $C_{6v}$; see table 1.

Bilayer graphene, figure 1(b), consists of two coupled sheets of monolayer with $AB$ (Bernal) stacking (as in bulk graphite [45]), and has symmetry $D_{3h}$ which differs from $C_{6v}$ by the accompaniment of a $z \rightarrow -z$ reflection to the rotations by $\pi/3$, comparing to monolayer graphene, but, otherwise, $D_{3h}$ and $C_{6v}$ are isomorphic. Its unit cell contains four inequivalent atoms $A1, B1, A2$ and $B2$ where numbers denote the layer. The conventional Hamiltonian in
**Table 1.** Classification of the Hamiltonian components by $C_{6v}$ irreducible representations.

| $C_{6v}$ rep. | $A_1$ | $A_2$ | $B_1$ | $B_2$ | $E_1$ | $E_2$ |
|---------------|-------|-------|-------|-------|-------|-------|
| Matrix $t ightarrow -t$ | $1$ | $\sigma^z$ | $\xi$ | $\xi\sigma^z$ | $\xi\sigma$ | $e_\xi \times \sigma$ |
| $(1 \cdot \mathbf{l}^*)$ | $(1 \times \mathbf{l}^*)_z$ | $1$, $\mathbf{M}$, $\mathbf{d}$ | $p^2$ | $p$ | $(2p_x p_y, p_x^2 - p_y^2)$ | $u = \frac{1}{\sqrt{2}}(u_A - u_B)$ |

**Figure 1.** Schematic representation of the monolayer (a) and bilayer (b) graphene crystal lattice. (c) The band structure of mono- and bilayer graphene in the vicinity of the $K$ point along the $p_x$-axis. Also shown are some of the two-step processes leading to the creation of an e–h pair in the low-energy bands accompanied by the absorption of a photon followed by emission. Note that the energy of any intermediate state (white circle) is much smaller than photon energy $\Omega$, $\bar{\Omega}$.

The electronic dispersions around the $K$ point for mono- and bilayer are compared in figure 1. Two low-energy bands touch each other at the centre of the valley, which is also the position of the Fermi energy in the neutral structure (a neutrality point), and are described by the effective two-band low-energy Hamiltonian written in the basis of orbitals

$$H_b = \begin{pmatrix} \frac{v_3}{v} \sigma^x & H_m \sigma^x & H_m \\ H_m & \gamma_1 \sigma^x \end{pmatrix}, \tag{2}$$

where $v_3 \sim 0.1v$ is related to the weak direct $A1 \rightarrow B2$ interlayer hops [19, 36, 43], and $\gamma_1 \sim 0.4\text{eV}$ is the direct interlayer coupling [1, 5, 6, 10, 12, 19, 31, 43, 46]. The basis is constructed using components corresponding to atomic sites $A1$, $B2$, $A2$, $B1$ in the valley $K$ and $B2$, $A1$, $B1$, $A2$ in $K'$. The electronic dispersions around the $K$ point for mono- and bilayer are compared in figure 1. Two low-energy bands touch each other at the centre of the valley, which is also the position of the Fermi energy in the neutral structure (a neutrality point), and are described by the effective two-band low-energy Hamiltonian written in the basis of orbitals

$$H_b = \begin{pmatrix} \frac{v_3}{v} \sigma^x & H_m \sigma^x & H_m \\ H_m & \gamma_1 \sigma^x \end{pmatrix}, \tag{2}$$

where $v_3 \sim 0.1v$ is related to the weak direct $A1 \rightarrow B2$ interlayer hops [19, 36, 43], and $\gamma_1 \sim 0.4\text{eV}$ is the direct interlayer coupling [1, 5, 6, 10, 12, 19, 31, 43, 46]. The basis is constructed using components corresponding to atomic sites $A1$, $B2$, $A2$, $B1$ in the valley $K$ and $B2$, $A1$, $B1$, $A2$ in $K'$. The electronic dispersions around the $K$ point for mono- and bilayer are compared in figure 1. Two low-energy bands touch each other at the centre of the valley, which is also the position of the Fermi energy in the neutral structure (a neutrality point), and are described by the effective two-band low-energy Hamiltonian written in the basis of orbitals

$$H_b = \begin{pmatrix} \frac{v_3}{v} \sigma^x & H_m \sigma^x & H_m \\ H_m & \gamma_1 \sigma^x \end{pmatrix}, \tag{2}$$

where $v_3 \sim 0.1v$ is related to the weak direct $A1 \rightarrow B2$ interlayer hops [19, 36, 43], and $\gamma_1 \sim 0.4\text{eV}$ is the direct interlayer coupling [1, 5, 6, 10, 12, 19, 31, 43, 46]. The basis is constructed using components corresponding to atomic sites $A1$, $B2$, $A2$, $B1$ in the valley $K$ and $B2$, $A1$, $B1$, $A2$ in $K'$. The electronic dispersions around the $K$ point for mono- and bilayer are compared in figure 1. Two low-energy bands touch each other at the centre of the valley, which is also the position of the Fermi energy in the neutral structure (a neutrality point), and are described by the effective two-band low-energy Hamiltonian written in the basis of orbitals

$$H_b = \begin{pmatrix} \frac{v_3}{v} \sigma^x & H_m \sigma^x & H_m \\ H_m & \gamma_1 \sigma^x \end{pmatrix}, \tag{2}$$

where $v_3 \sim 0.1v$ is related to the weak direct $A1 \rightarrow B2$ interlayer hops [19, 36, 43], and $\gamma_1 \sim 0.4\text{eV}$ is the direct interlayer coupling [1, 5, 6, 10, 12, 19, 31, 43, 46]. The basis is constructed using components corresponding to atomic sites $A1$, $B2$, $A2$, $B1$ in the valley $K$ and $B2$, $A1$, $B1$, $A2$ in $K'$.
on sites A1 and B2 [36],
\[ \hat{H}_{\text{eff}} = -\frac{v^2}{\gamma_1}(\sigma^x(p_{x}^2 - p_{y}^2) + 2\sigma^y p_x p_y). \] (3)
Two others, referred to as high-energy bands, are split by the interlayer coupling \( \gamma_1 \) from the
neutrality point.

Figure 2. Feynman diagrams for Raman scattering amplitude \( R \) from the ground
state to the final state with e–h excitation.

2. Inelastic light scattering in graphene at zero magnetic field

To include the interaction of the electrons with photons in the effective Hamiltonians (1) and (2),
we construct the canonical momentum \( p - \frac{e}{c} A \), where the vector potential of light
\[ A = \sum_{l,q,q_z} \frac{\hbar c}{\sqrt{2\Omega}} (1e^{i(qr - \Omega t)}/h b_{q,q_z,l} + \text{h.c.}) \] (4)
includes an annihilation operator \( b_{q,q_z,l} \) for a photon with in-plane momentum \( q \), energy
\( \Omega \) (which determines its out-of-plane momentum component \( q_z = \sqrt{\Omega^2/c^2 - q^2} \)) and
polarization \( l \). Expanding the Hamiltonians up to the second order in the vector potential, one
obtains the interaction part
\[ H_{\text{int}} = -\frac{ev}{c} J \cdot A + \frac{e^2}{2c^2} \sum_{i,j} (\partial^2_{p_i p_j} H) A_i A_j, \] (5)
where \( (ev/c) J_i = (e/c) \partial_{p_i} \hat{H} \) is the current vertex and \( \frac{e^2}{2c^2} \partial^2_{p_i p_j} H \) is the two-photon contact-
interaction tensor.

The full amplitude \( R = R_D + R_w \) of inelastic Raman scattering of the photon on electrons
changing its energy \( \Omega \) to \( \tilde{\Omega} = \Omega - \omega \) (\( \omega = \epsilon_f - \epsilon_i \) is the Raman shift) and momentum and
polarization from \( q, l \) to \( \tilde{q}, \tilde{l} \) is described by the Feynman diagrams shown in figure 2.

The building blocks of the diagrams include Green’s functions for the electrons and the
electron–photon interaction vertices:
\[ = G^{(A)}_{\epsilon} = (\epsilon - H + i0)^{-1},\]
\[ = \frac{ev\hbar}{\sqrt{2\Omega}} J_q \cdot l, \quad = \frac{ev\hbar}{\sqrt{2\Omega}} J_{-q} \cdot \tilde{l}^*, \] (6)
\[ = R_w = \frac{e^2\hbar^2}{2\sqrt{\Omega^2}} (\partial^2_{p_i p_j} H) l_i \tilde{l}_j^* \delta_{p,\tilde{p} + q, -\tilde{q}}. \]
Thus, the inelastic light scattering amplitude is contributed by a one-step process $R_w$ (contact interaction [38]) and a two-step process $R_q$ involving an intermediate virtual state. The two-step process, such as shown in figure 2, consists of an absorption (emission) of a photon with energy $\Omega$ ($\tilde{\Omega}$) transferring an electron with momentum $p$ from an occupied state in the valence band into a virtual intermediate state, followed by another electron emission (absorption) of the second photon with energy $\tilde{\Omega}$ ($\Omega$), which moves the electron to the final state with momentum $p + q - \tilde{q}$.

$$R_D = \frac{e^2 \hbar^2 v^2}{2 \sqrt{\Omega \tilde{\Omega}}} \left( (J_q \cdot \hat{I}) G^A_{\Omega+\epsilon_i} (J_{-\tilde{q}} \cdot \hat{I}^*) + (J_{-\tilde{q}} \cdot \hat{I}^*) G^A_{\Omega+\epsilon_i} (J_q \cdot \hat{I}) \right).$$  (7)

In graphene, the two-step process via the virtual state and the contact interaction process have different properties and polarization selection rules, which reflects their intricate relation with the irreducible representations of the symmetry group of the crystal. Generally, the components of the scattering amplitude $R^{ij}$ realize a representation of the symmetry group $C_{6v}$. Since vectors $I, \hat{I}^*$ belong to $E_1$ representation, the $R$ representation can be expanded into irreducible ones

$$E_1 \otimes E_1 = A_1 \oplus A_2 \oplus E_2.$$  (8)

Forming the corresponding combinations from the components of the polarization vector, see table 1,

$$\Xi_s = |I \times \hat{I}|^2, \quad \Xi_{s2} = |I \cdot \hat{I}|^2, \quad \Xi_o = |d|^2 = 1 + (I \times \hat{I}^*)(\hat{I} \times \hat{I}^*),$$  (9)

where $d = (l_x \hat{I}^x + l_y \hat{I}^y, l_x \hat{I}^x - l_y \hat{I}^y)$ and $\Xi_s + \Xi_{s2} + \Xi_o = 2,$  (10)

we can write the scattering probability in the most general form

$$w = w_s \Xi_s + w_{s2} \Xi_{s2} + w_o \Xi_o.$$  (11)

The first two terms with polarization factors $\Xi_s$ and $\Xi_{s2}$, corresponding to $A_2$ and $A_1$ representations, respectively, describe the contribution of photons scattered with the same circular polarization as the incoming beam. The third term, with polarization factor $\Xi_o$, corresponding to $E_2$ representation, represents the scattered photons with circular polarization opposite to the incoming beam.

Microscopically, the probability for a photon to undergo inelastic scattering from the state $(q, q_e)$ with energy $\Omega$ into a state $(\tilde{q}, \tilde{q}_e)$ with energy $\tilde{\Omega}$, by exciting an e–h pair in graphene, is

$$w = \frac{2}{\pi \hbar^2} \sum_{\alpha_i, \alpha_f} \int d^2\mathbf{p} |\langle f | R | i \rangle|^2 \times f_i (1 - f_i) \delta (\epsilon_i + \omega - \epsilon_f),$$  (12)

where $f_i$ and $f_f$ are filling factors of the initial and final electronic states, respectively, the spin and valley degeneracies have already been taken into account, and the initial and final states are defined by the momentum $p$ and (sub)band index $\alpha_i/\alpha_f$: $|i (f)\rangle = |p (p + q - \tilde{q}, \alpha_i/\alpha_f)\rangle$. The angle-integrated spectral density of Raman scattering $g(\omega)$ is

$$g(\omega) = \frac{1}{c} \int \int d^2\mathbf{q} \, d\tilde{q} \frac{w}{(2\pi \hbar)} \delta \left( \tilde{\Omega} - \sqrt{\tilde{q}^2 + \tilde{q}_e^2} \right),$$  (13)

and quantum efficiency $I = \int g \, d\omega$ expresses the total probability for a single incoming photon to scatter inelastically on an electron and excite an e–h pair in the low-energy part of the spectrum.

New Journal of Physics 14 (2012) 105016 (http://www.njp.org/)
2.1. Raman scattering in monolayer graphene

Calculation of the Raman spectrum and intensity of the signal in each of the distinct polarization components, \( w_j \), \( w_{j2} \) and \( w_3 \), requires an explicit expression for the Raman scattering amplitude \( R \). Raman measurements are usually carried out at \( \Omega, \Omega \sim 1-3 \text{ eV} \), which is much smaller than the bandwidth [17]. Raman shift, which measures the electronic excitation energy, is \( \omega \lesssim 0.2 \text{ eV} \), allowing us to expand the Green’s functions over the large \( \Omega \) and to perform summation over the intermediate virtual states of the process.

Both the electron and the hole of the e–h excitation have almost the same momentum \( (p+q-\hat{q} \text{ and } p, \text{ respectively}) \), since \( q, \hat{q} \ll p \) and the momentum transfer from light is negligible \( (v/c \sim 3 \times 10^{-3}) \), so that below we use \( J_q = \xi \sigma \delta_{p,p+q} \). For \( vp \ll \Omega \) the dominant contributions to the Raman scattering amplitude are

\[
R_\Omega \approx \frac{(\hbar v)^2}{\Omega^2} \left( -\frac{i}{\lambda} (I \times \hat{I})_z + \frac{M \cdot d}{\Omega} \right),
\]

where the main order of \( R_\Omega \) has the matrix form of representation \( A_2 \) of \( C_{6v} \). Contact interaction \( R_w \) is responsible for the creation of the excitations with the symmetry of the representation \( E_2 \); see table 1. For the scattering of photons with \( \Omega < \gamma_0, R_w \ll R_\Omega \) [47].

In undoped graphene the inter-band e–h pairs with \( \epsilon_i \approx -\epsilon_i \approx \omega/2 \) are the only allowed electronic excitations. The probability of the creating an electronic excitation by photons with \( \Omega < \gamma_0, q-\hat{q} \ll p (\omega \gg \hbar \Omega) \) in the main order of the expansion in \( \omega/\Omega \ll 1 \) is

\[
w \approx \frac{\hbar e^4 v_0^2}{\Omega^4} \left( \frac{\Omega^2}{2(6\gamma_0)^2} \Xi_\omega \right).
\]

It is dominated by the contribution \( R_\Omega \) of the first two diagrams in figure 2, describing two-step processes involving a virtual intermediate state.

Doping in graphene, with chemical potential \( \mu \gg \Omega v/c \), blocks inter-band electronic excitations with energy transfer \( \omega < 2\mu \). After integrating over all directions of the propagation of scattered photons, we find the spectral density of the angle-integrated Raman signal,

\[
g(\omega) \approx \frac{1}{4} \Xi_\omega \left( \frac{e^2}{\pi \hbar c} \right)^2 \frac{\omega}{\Omega^2} \omega (\omega - 2\mu).
\]

The total contribution of the electronic scattering to the total Raman efficiency is

\[
I_0 = \int_0^{\Omega/2} g(\omega) d\omega \sim \left( \frac{e^2}{2\hbar c} \frac{v}{c} \right)^2 \sim 10^{-10}.
\]

In doped graphene, one may also expect to see some manifestation of the intra-band e–h excitations in the vicinity of the Fermi level and electron energies \( \epsilon_i \approx \epsilon_i \approx \mu \). Their analysis requires taking into account all terms in the expression for \( R_\Omega \), equations (15). Then, we find that, for \( \omega \lesssim (v/c) \Omega \ll \Omega < \gamma_0 \), the yield of this low-energy feature is \( \delta I = \int \delta g(\omega) d\omega \sim 10^{-15} \) for \( \Omega \sim 1 \text{ eV} \).
2.2. Raman scattering in bilayer graphene

For bilayer graphene with the interlayer coupling less than the base photon energy, $\gamma_1 \ll \Omega, \tilde{\Omega}$, we also study the low-energy excitations in the final states, in particular, those with $\omega \ll \gamma_1$. The reason for restricting the following analysis to the low-energy excitations is that the higher-energy excitations decay fast due to electron–electron and electron–phonon processes, leaving very little chance to observe any structure in the Raman signal. As a result, we employ the same expansion $\omega / \Omega \ll 1$ as in section 2.1. Keeping terms up to the $\Omega^{-3}$ order (the latter appears when the virtual state is taken to be in the high-energy bands) in the expansion of the Green’s functions and performing summation over the intermediate states of the process, we obtain the amplitude $R$ in the form of a $4 \times 4$ matrix

$$R \approx \left( \frac{\hbar v}{\Omega^2} \left( \begin{array}{cc} \sigma_z & 0 \\ 0 & \sigma_z \end{array} \right) \left( \mathbf{1} \times \tilde{\mathbf{r}} \right)_z + \frac{\mathbf{M} \cdot \mathbf{d}}{\Omega} \right),$$

$$\mathbf{M} = \left( \begin{array}{ccc} \gamma_1 \sigma_x (\mathbf{e}_z \times \sigma) \sigma_x \\ \mathbf{M} \\ 0 \end{array} \right).$$

Since the electronic modes with the excitation energies $\omega < \gamma_1 / 2$ result from the e–h pairs in the low-energy bands described by the low-energy Hamiltonian $H_{\text{eff}}$ in equation (3), we take only the part of $R$ that acts in that 2D Hilbert space, leaving the terms in the lowest relevant order in $v p / \gamma_1 \ll 1$ and $\gamma_1 / \Omega \ll 1$. This projection results in the effective amplitude of the inelastic two-phonon process,

$$R_{\text{eff}} \approx \frac{\hbar v^2}{\Omega^2} \left\{ -i \sigma_z (\mathbf{1} \times \tilde{\mathbf{r}})_z + \frac{\gamma_1}{\Omega} \left[ \sigma_x d_y + \sigma_y d_x \right] \right\}. \quad (19)$$

It is important to stress that for $\Omega \gg \gamma_1$, $R_{\text{eff}}$ cannot be correctly obtained within an effective two-band theory, equation (3), without the above-described intermediate steps, although for $\Omega < \gamma_1$ one could formally use $H_{\text{eff}}$ and equations (4)–(7) to describe inelastic scattering of far-infrared (FIR) light. Within these approximations the scattering probability

$$w \approx e^4 \hbar^2 v^2 \frac{\gamma_1}{\Omega^2} \left\{ \mathcal{E}_s + \frac{\gamma_1^2}{2 \Omega^2} \mathcal{E}_o \right\}. \quad (20)$$

retains the characteristics of monolayer graphene—the crossed polarization of in/out photons in the dominant mode [48]. The angle-integrated spectral density of Raman scattering

$$g(\omega) = \frac{1}{4} \left( \frac{e^2}{\pi \hbar c} \right)^2 \frac{\gamma_1}{\Omega^2} \left\{ \mathcal{E}_s + \frac{\gamma_1^2}{2 \Omega^2} \mathcal{E}_o \right\} \theta(\omega - 2\mu) \quad (21)$$

reflects the constant density of states characteristic of the parabolic spectrum of the bilayers. This is different from monolayer graphene, where $g(\omega) \propto \omega$, reflecting the linear energy dependence of the density of states [47].

3. Inter-Landau-level transitions in the Raman spectrum of graphene

Upon quantization of electron states into LLSs, Raman scattering inevitably causes inter-LL transitions, which, having fixed energies, manifest themselves in the electronic contribution to the Raman plot as a pronounced structure that can be used to detect their contribution experimentally [49, 50].
3.1. Monolayer graphene

The electronic spectrum of monolayer graphene in a strong magnetic field can be described as a sequence \( n^\alpha \) of LLs, corresponding to the states \([7, 40]\)

\[
|n^\alpha\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} \Phi_n \\ i\alpha\Phi_{n-1} \end{pmatrix} \quad \text{for } n \geq 1, \quad |0\rangle = \begin{pmatrix} \Phi_0 \\ 0 \end{pmatrix}, \quad (22)
\]

with energy \( \alpha \varepsilon_n, \quad \varepsilon_n = \sqrt{2n} \hbar v_0 / \lambda_B, \)

where \( \lambda_B = \sqrt{\hbar c / eB} \) is the magnetic length, \( n \) enumerates the LLs, \( \alpha = \pm \) denotes the conduction band and \( \alpha = - \) the valence band and \( \Phi_n \) are the normalized envelopes of LL wavefunctions. Then, the corresponding elements of Feynman diagrams in figure 2 are

\[
\begin{align*}
\delta_{aa'} &= G^{R/A} = \frac{\delta_{nn'}\delta_{aa'}}{\varepsilon - \alpha \varepsilon_n \pm i0^+}, \\
\gamma &= \frac{ev\hbar}{2\sqrt{\Omega}} J \cdot \mathbf{l}, \quad \gamma' = \frac{ev\hbar}{2\sqrt{\Omega}} J \cdot \mathbf{i}^*, \\
J_{n^\alpha n'^\alpha} &= \alpha \varepsilon_n \varepsilon_{n'} \mathbf{l}_\pm - \alpha^* \varepsilon_{n'} \varepsilon_n \mathbf{e}_\pm, \\
R_w &= \frac{e^2 v^2 \hbar^2}{6\gamma_0^2} \varepsilon J \cdot \sum \pm \mathbf{e}_\pm (\mathbf{le}_\mp) (\mathbf{i}^* \mathbf{e}_\mp).
\end{align*}
\]

Here \( \mathbf{e}_\pm = \frac{1}{\sqrt{2}}(\mathbf{e}_x \pm i\mathbf{e}_y) \) is used to stress that a circularly polarized photon carries angular momentum \( m = \pm 1 \). The matrix structure of the interaction terms allows the following selection rules for optically active inter-LL excitations in monolayer graphene:

\[
\begin{align*}
(i) & \quad n^- \to n^+, \\
(ii) & \quad (n \mp 1)^- \to (n \pm 1)^+, \\
(iii) & \quad n^- \to (n + 1)^+, \\
(iv) & \quad (n + 1)^- \to n^+.
\end{align*}
\]

The excitation of the e–h pairs by Raman scattering in graphene at strong magnetic fields produces the electronic transition (i) between LLs, with angular momentum transfer \( \Delta m = 0 \) and excitation energy \( \omega = 2\varepsilon_n \), see figure 3, and transitions (ii), with \( \Delta m = \pm 2 \) and \( \omega = \varepsilon_{n-1} + \varepsilon_{n+1} \). The amplitudes of these two processes,

\[
\begin{align*}
R_{n^- \to n^+} &= \frac{1}{4} \frac{(ev\hbar)^2}{c^2 \Omega} \sum_{a=\pm} \left[ (\mathbf{le}_a) (\mathbf{i}^* \mathbf{e}_-) \frac{\varepsilon_{n-1} - \alpha \varepsilon_{n+1}}{\Omega - \varepsilon_n - \alpha \varepsilon_{n+1}} - (\mathbf{le}_a) (\mathbf{i}^* \mathbf{e}_-) \frac{\alpha}{\Omega - \varepsilon_n - \alpha \varepsilon_{n+1}} + (\mathbf{le}_a) (\mathbf{i}^* \mathbf{e}_+) \frac{\varepsilon_{n-1} - \alpha \varepsilon_n}{\Omega - \varepsilon_{n-1} - \alpha \varepsilon_n} \right], \\
R_{(n \mp 1)^- \to (n \mp 1)^+} &= \pm \frac{1}{4} \frac{(ev\hbar)^2}{c^2 \Omega} \sum_{a=\pm} \left[ \frac{\alpha}{\Omega - \varepsilon_{n+1} - \alpha \varepsilon_n} + \frac{\alpha}{\varepsilon_{n-1} - \alpha \varepsilon_n} \right],
\end{align*}
\]

are such that \( R_{n^- \to n^+} \gg R_{(n \mp 1)^- \to (n \mp 1)^+} \) for \( \omega \ll \Omega \). The latter relation is determined by a partial cancellation of the two diagrams constituting \( R_{\Omega} \). Note that the inter-LL modes \( n^- \to n^+ \) have the symmetry of the representation \( A_2 \) in table 2 and the same circular polarization of ‘in’ and ‘out’ photons involved in its excitation. Finally, the contact term \( R_w \) in figure 2 allows for a weak transition (iii) \( n^- \to (n + 1)^+ \), with the amplitude \( R_w \ll R_{n^- \to n^+} \). This transition, together with selection rules \( \Delta m = \pm 1 \), resembles the inter-LL transition involved in the FIR absorption [3, 7]. However, the FIR-active excitation is ‘valley-symmetric’ [7, 51] and belongs to the representation \( E_1 \), whereas the Raman-active \( n^- \to (n \pm 1)^+ \) mode belongs...
Table 2. Raman-active inter-LL excitations in graphene.

| $C_{6v}$ rep. Transition | Intensity | Polarization |
|--------------------------|-----------|--------------|
| $E_2$ $n^- \rightarrow (n+1)^+$ | Weak in Raman, strong in magnetophonon resonance | $\sigma^\pm \rightarrow \sigma^\pm$ |
| $(n+1)^- \rightarrow n^+$ | | |
| $A_1$ $(n-1)^- \rightarrow (n+1)^+$ | Weak in Raman | $\sigma^\pm \rightarrow \sigma^\mp$ |
| $(n+1)^- \rightarrow (n-1)^+$ | | |
| $A_2$ $n^- \rightarrow n^+$ | Dominant in Raman | $\sigma^\pm \rightarrow \sigma^\pm$ |

Figure 3. Spectral density $g(\omega)$ of light inelastically scattered from electronic excitations in undoped monolayer (a) and bilayer (b) graphene at quantizing magnetic fields (solid line) and in doped graphene at $B = 0$ (dashed line). Sketch illustrates selection rules for processes corresponding to the visible features in the Raman plot. $\varepsilon_n$ denotes the LL energies in graphene. In addition to dominant $n^- \rightarrow n^+$ processes in both plots, in the bilayer spectrum the feature corresponding to $2^- \rightarrow 0$ and $0 \rightarrow 2^+$ transitions can be recognized.

to $E_2$, allowing the latter to couple to the $\Gamma$-point optical phonon and, thus, leading to the magneto-phonon resonance feature in the Raman spectrum [29]. Also, $R_w$ originates from the trigonal warping term in $\mathcal{H}$, which violates the rotational symmetry of the Dirac Hamiltonian by transferring angular momentum $\pm 3$ from electrons to the lattice, allowing thus a change of angular momentum by $\pm 1$.  

New Journal of Physics 14 (2012) 105016 (http://www.njp.org/)
The dominant inter-LL transitions $n^- \rightarrow n^+$ determine the spectral density of light scattered from electronic excitations in graphene at high magnetic fields:

$$g_{n^-\rightarrow n^+}(\omega) \approx \Xi_s \left( \frac{v^2 e^2 / \lambda_B}{c^2 \pi \Omega} \right)^2 \sum_{n \geq 1} \gamma_n (\omega - 2\epsilon_n).$$

(24)

Here, we use Lorentzian $\gamma_n(x) = \pi^{-1} \Gamma_n / [x^2 + \Gamma_n^2]$, and inelastic LL broadening $\Gamma_n$, which increases with the LL number, and the factor $\Xi_s$ in equation (24) indicates that ‘in’ and ‘out’ photons have the same circular polarization.

3.2. Bilayer graphene

The same as in the non-magnetic case, e–h excitations in bilayer graphene are created in low-energy LLs, as at high energies the LL broadening due to, for example, electron–phonon interaction will smear out the LL spectrum. In strong magnetic fields, low-energy LLs in bilayer graphene can be described [52] by

$$|n^x\rangle = \frac{1}{\sqrt{2}} \left( \begin{array}{c} \Phi_n \\ \alpha \Phi_{n-2} \end{array} \right) \text{ for } n \geq 2, \quad |0/1\rangle = \left( \begin{array}{c} \Phi_{0/1} \\ 0 \end{array} \right),$$

(25)

with energy $\epsilon_{nn} = 2\alpha \frac{\hbar^2 v^2}{\gamma_1 \lambda_B} \sqrt{n(n-1)}$.

In a neutral bilayer, all LLs have additional fourfold degeneracy (two due to the electron spin and two due to the valley). The peculiar $n = 0$ and $n = 1$ LLs are degenerate at $\epsilon = 0$, producing an eightfold degenerate level. Projecting the effective transition amplitude $R_{\text{eff}}$ onto the eigenstates $|n^x\rangle$, we find the electronic Raman spectrum. This procedure leads to the same selection rules as in monolayer graphene; see equations (23). Among these, (i) are the dominant transitions. For an undoped bilayer, the angle-integrated spectral density $g(\omega)$ of Raman scattering in the strong magnetic field is equal to:

$$g(\omega) \approx \left( \frac{v^2 e^2 / \lambda_B}{c^2 \pi \Omega} \right)^2 \left\{ \Xi_s \sum_{n \geq 2} \gamma_n (\omega - 2\epsilon_{nn}) + \Xi_o \left( \frac{\gamma_1}{\Omega} \right)^2 \right\} \times \left\{ \sum_{n=1,2} \gamma (\omega - \epsilon_{(n+1)^+}) + \frac{1}{2} \sum_{n \geq 3} \gamma (\omega - \epsilon_{(n+1)^+} - \epsilon_{(n-1)^{\pm}}) \right\}.$$

(26)

The first term describes the dominant contribution due to the $n^- \rightarrow n^+$ transitions, whereas the last two terms describe the spectral density of the $(n \mp 1)^- \rightarrow (n \pm 1)^+$ transitions.

Low-energy electronic contribution to the Raman plot is shown by a solid line in figure 3(b). The dominant peaks are due to the $n^- \rightarrow n^+$ transitions. The quantum efficiency of a single $n^- \rightarrow n^+$ peak in figure 3(b) is similar to the value $I_1$ in monolayer graphene [47].

A weaker feature in figure 3(b) corresponds to both $2^- \rightarrow 0$ and $0 \rightarrow 2^+$ transitions and is visible, as it is positioned to the left of the first $2^- \rightarrow 2^+$ peak. The quantum efficiencies of the $(n \pm 1)^- \rightarrow (n \mp 1)^+$ transitions are smaller by the factor $(\frac{n}{n+1})^2$ in comparison with the $n^- \rightarrow n^+$ transitions. This is different from the monolayer graphene case, where the corresponding ratio between quantum efficiencies of $(n \pm 1)^- \rightarrow (n \mp 1)^+$ and $n^- \rightarrow n^+$ transitions is $(\frac{n}{n+1})^2$, much smaller than for the bilayer.
4. Magnetophonon resonance in homogeneously and inhomogeneously doped and strained graphene

Single and multiple phonon-emission lines in the Raman spectrum of graphene and the influence of electron–phonon coupling on the phonon spectrum have been investigated in great detail in [24–32, 53]. The coupling of electromagnetic field and phonon excitations is realized via the excitation of the virtual e–h pair, with the same symmetry properties as the Γ-point optical phonon that is created upon recombination of the pair. Analysing all possible combinations of polarization vectors, one may see from table 1 that the amplitude of Raman scattering with excitation of the phonon mode is proportional to

\[ R = R_G \sum \nu u_\nu \cdot d \]  

that describes quantized sublattice displacement

\[ \mathcal{U}(r, t) = (\mathcal{U}_A - \mathcal{U}_B)/\sqrt{2} = \sum_{k, \nu} \frac{\hbar}{\sqrt{2M_0}} \left( u_{c,\nu,k} e^{i(kr-c_0t)/\hbar} + h.c. \right), \]  

where \( M \) is the mass of a single carbon atom, \( u \) is the polarization of the phonon, and the expression for \( R_G \) can be taken from Basko [53]. Raman efficiency then is proportional to

\[ g \propto \sum_{\nu \nu} d_{\nu}^{*} d_{\nu} \text{Im} \tilde{D}_{\nu \nu}^{A}, \]  

where \( \tilde{D} \) is the phonon propagator renormalized by electron–phonon interaction. The latter strongly affects the energy of the phonon under the conditions of its resonance mixing with the inter-LL electronic transitions, an effect known as magnetophonon resonance.

We use both the phenomenological approach and the tight-binding model to study the interaction of electrons with Γ-point optical phonons in the case of a strong magnetic field. The phenomenology is suitable for describing the low-energy excitations of electrons in the vicinity of Dirac points (K-points), while the tight-binding model is needed to perform the integration over the whole BZ [53] when estimating the intensity of the G-phonon line in Raman. To discuss the electron–phonon interaction it is instructive to trace the electron Hamiltonian

\[ H = H_0 - \mathbf{Q} \cdot \mathbf{U} \]  

back to the tight-binding model

\[ H_0 = \gamma_0 \sum_{s} \begin{pmatrix} 0 & e^{-ikr_s} \\ e^{ikr_s} & 0 \end{pmatrix} \rightarrow \xi \mathbf{v} \mathbf{\sigma} \mathbf{p}, \]  

\[ \mathbf{Q} = \sqrt{6} \frac{d\gamma_0}{dr} \sum_{s} \begin{pmatrix} 0 & e^{-ikr_s} \\ e^{ikr_s} & 0 \end{pmatrix} \frac{\mathbf{r}_s}{a} \rightarrow F \mathbf{\sigma} \times \mathbf{e}_z, \]  

where \( \mathbf{k} \) is a momentum within the BZ, \( \mathbf{K} = (-\frac{4\pi}{3a}, 0), \mathbf{v} = \frac{\sqrt{3}}{2} \gamma_0 a/\hbar \), the vectors \( \mathbf{r}_1 = (-\frac{a}{2}, \frac{a}{2\sqrt{3}}) \), \( \mathbf{r}_2 = (\frac{a}{2}, \frac{a}{2\sqrt{3}}) \) and \( \mathbf{r}_3 = (0, -\frac{a}{\sqrt{3}}) \) are the positions of the nearest ‘B’ atoms with respect to ‘A’ atom, and \( F = \frac{3}{\sqrt{2}} \frac{\partial\gamma_0}{\partial r} \) is the dipole moment of the hopping amplitude to the variation of the bond length.
The renormalization of the phonon energy by its interaction with electrons is taken into account in the random phase approximation. Defining electrons’ bare Green’s functions phonon bare propagator, and electron–phonon interaction vertex,

\[
\begin{align*}
G^R & = (\varepsilon - H \pm i0)^{-1}, \\
G^K & = (1 - 2f)(G^R - G^A), \\
D^A_{\nu \nu} & = \frac{2\omega_0}{(\omega - i\gamma_{ph})^2 - \omega_0^2}\delta_{\nu \nu}, \\
\lambda & = \frac{1}{2}\hbar \sqrt{\frac{3}{M\omega_0}} Q.
\end{align*}
\]

we use the Dyson equation to find the renormalized phonon propagator:

\[
\lambda \Pi^{A}_{\nu \nu} = -\frac{\sqrt{3}\hbar^2 a^2}{4M\omega_0} \int \frac{d\varepsilon}{\pi} \int_{BZ} \frac{d^2p}{(2\pi\hbar)^2} \times \text{Tr}\left\{ Q_{\nu} G^R(\varepsilon) Q_{\nu} G^K(\varepsilon + \omega) + Q_{\nu} G^K(\varepsilon) Q_{\nu} G^A(\varepsilon + \omega) \right\},
\]

\[
\bar{D} = \cdots + \cdots + \cdots + \cdots + \cdots + \cdots.
\]

Here \( \lambda = \sqrt{\frac{\pi}{M\omega_0}} \left( \frac{F_L}{2\nu} \right)^2 = \frac{3\sqrt{3}}{2M\omega_0} \left( \frac{\hbar}{m} \frac{d\nu}{dr} \right)^2 \approx 0.018 \) is dimensionless constant of the electron–phonon coupling [26]. Trace is taken in \( AB \) sites space and a summation over spins is already performed. As the momentum \( k \) of a phonon created by the Raman process is small by parameter \( v/c \), in the following it can be neglected.

The integral for the polarization loop in equation (33) is divergent in the frame of the linear Dirac model, so it can be split into two parts:

\[
\Pi^{A}_{\nu \nu} = \Pi^0_{\nu \nu} + \Delta \Pi_{\nu \nu}, \quad \Pi^0_{\nu \nu} = \Pi^{A}_{\nu \nu}|_{\omega, \mu, B \rightarrow 0} \approx -0.64\gamma_0\delta_{\nu \nu}.
\]

Here \( \Pi^0 \) is calculated numerically within the tight-binding model, and \( \Delta \Pi_{\nu \nu} \) is determined within the effective Dirac model, after subtracting the divergent part from the integrand. For \( B = 0 \) the answer is \( \Delta \Pi^A_{\nu \nu} \propto \delta_{\nu \nu} \) and it repeats the derivation of Raman line shape found in [25, 28–30, 32, 54, 55]:

\[
\gamma_G = \gamma_{ph} - \frac{\lambda}{4}(\ddot{\omega}_0 - \omega_0^2),
\]

\[
\omega_G = \ddot{\omega}_0 - \frac{\mu}{\pi} + \frac{\lambda}{4\pi} \left( \log \left| \frac{\omega_0 + 0.644\lambda\gamma_0}{2\mu} \right| \right)
\]

where \( \ddot{\omega}_0 = \omega_0 + 0.644\lambda\gamma_0 \) (we implied that \( \omega_0 \gg 0.644\lambda\gamma_0 \gg \lambda\varepsilon_F \)), and the expression for \( I_G \) can be taken from Basko [53].

\textit{New Journal of Physics} 14 (2012) 105016 (http://www.njp.org/)
4.1. Magnetophonon resonance in a homogeneously doped monolayer

In the presence of a magnetic field the continuous electronic spectrum splits into the set of discrete LLs. Working in the basis of LL equations (22)–(34) and choosing the circularly polarized basis \( \mathbf{e}_{\psi/\bar{\psi}} = \frac{1}{\sqrt{2}} (\mathbf{e}_z \pm i \mathbf{e}_y) \) for incoming and scattered light, we find that

\[
\Pi_{\psi\bar{\psi}} = (\mathbf{e}_{\psi})_i^* (\mathbf{e}_{\psi})_i^\dagger \Pi_{\psi/\bar{\psi}} + (\mathbf{e}_{\bar{\psi}})_i^* (\mathbf{e}_{\bar{\psi}})_i^\dagger \Pi_{\psi/\bar{\psi}},
\]

where \( \Pi_{\psi/\bar{\psi}} = \Pi_0 + \Delta \Pi_{\psi/\bar{\psi}} \).

For the chemical potential pinned at the zero LL,

\[
\Delta \Pi_{\psi/\bar{\psi}} = \frac{\varepsilon_1^2}{\pi} \left[ \frac{-f_0}{\varepsilon_1 \pm \omega} + \frac{1 - f_0}{\varepsilon_1 \pm \omega} + \frac{1}{\varepsilon_1} - \omega^2 \sum_{n \geq 2} \frac{1}{\Omega_{n,+}(\Omega_{n,+} - \omega^2)} \right],
\]

(38)

where \( f_0 \) is a density-dependent filling factor of the zero level and \( \Omega_{n,\pm} = \varepsilon_n \pm \varepsilon_{n-1} \) are the frequencies of e–h excitations. If \( \mu \) is large enough, so that the \( m \)th level \( (m \geq 1) \) is partially filled, then

\[
\Delta \Pi_{\psi/\bar{\psi}} = \frac{\varepsilon_1^2}{2\pi} \left[ \frac{f_{m^+} - 1}{\Omega_{m^+, \pm} \pm \omega} + \frac{-f_{m^+}}{\Omega_{m^+, \pm} - \omega} + \frac{f_{m^+} - 1}{\Omega_{m^+, \pm} - \omega} \\
+ \frac{1}{\Omega_{m^+, \pm} - \omega} - 2\varepsilon^2 + 2 \sum_{n \geq 2} \frac{1}{\Omega_{n,+}(\Omega_{n,+} - \omega^2)} \right].
\]

(39)

Then, the net Raman efficiency of the \( \Gamma \)-point phonon mode in graphene in a strong magnetic field is

\[
g = \sum_{A=\psi/\bar{\psi}} | \mathbf{d}_A \|^2 \frac{I_{G^{\pm}} \gamma_{ph}}{(\omega - \tilde{\omega}_0 - \lambda \Delta \Pi_A(\omega))^2 + \gamma_{ph}^2},
\]

(40)

where the two terms in the sum correspond to the opposite circular polarizations of the optical phonon, and it is plotted in figure 4 for several doping densities.

The line described by equation (40) displays two types of typical behaviour depending on the range of parameters. Far from the resonance only a slight shift of the electron and phonon excitations exists,

\[
\omega_{\psi/\bar{\psi}} \approx \tilde{\omega}_0 + \lambda \Delta \Pi_{\psi/\bar{\psi}}(\tilde{\omega}_0).
\]

(41)

Since the line shift may differ for the opposite circular polarizations of the phonon, this leads to a small splitting of the \( G \)-line in Raman. In the vicinity of the intersection of the phonon line with the e–h excitation line for several doping densities, the polarization operator becomes large and causes significant change in the spectra, forming an anticrossing, in addition to the line splitting. The form of the line is determined by four solutions \( \omega_{\psi/\bar{\psi}} \)

\[
\omega - \tilde{\omega}_0 - \lambda \Delta \Pi_{\psi/\bar{\psi}}(\omega) = 0,
\]

(42)

two for each polarization with energies above (+) or below (−) the bare phonon line. The form of such anticrossings in undoped graphene is shown in figure 4. The resonance takes a more sophisticated form in the case of the doped graphene. With increasing the electron density (and correspondingly the filling factor), the transition \( 1^- \rightarrow 0^+ \) invoked by anticlockwise polarized light is weakened by Pauli blocking (see the first anticrossing in figure 5(a)), while the \( 0^- \rightarrow 1^+ \) transition remains. When the \( n = 0 \) LL is fully occupied \( (n_e = 1/\pi \lambda_{ph}^2 \approx 1.4 \times 10^{12} \text{cm}^{-2}) \), in anticlockwise polarization the anticrossing is completely blocked (see figure 5(b)), which coincides with the experimentally observed features [49].

New Journal of Physics 14 (2012) 105016 (http://www.njp.org/)
**4.2. Influence of inhomogeneous doping and strain on the magnetophonon resonance line shape**

In the graphene deposited on the substrate, the density of the electrons is very often not the same everywhere in the sample but varies, forming puddles at the length of 100–500 nm [56]. Also, ripples of the graphene sheet induce inhomogeneous strain. At weak magnetic fields the the electron density and strain disorder leads to the scattering of the charge carriers. The situation changes when an external magnetic field (∼25 T) is applied. At such a strong field, the magnetic length is about 5 nm, which is much smaller than the typical size of the spatial fluctuations of both carriers density and strain. In this case, the Raman response of the graphene flake is the average of the locally defined spectra. Below, we discuss how such averaging changes the fine structure of the magnetophonon resonance.

**4.3. Inhomogeneous density**

The spatial distribution of the electron densities results in the summing up of the local spectra contributions from the various parts of the graphene flake. The net picture is the overlay of the
Figure 5. Anticrossing of $1^- \rightarrow 0^+$ and $0^- \rightarrow 1^+$ transitions with the optical phonon for various levels of graphene doping. (a) Homogeneous graphene, electron density $n_e = 1 \times 10^{12}$ cm$^{-2}$: transitions in both circular polarizations are active, but $1^- \rightarrow 0^+$ is suppressed; (b) graphene with a homogeneous doping with electron density $n_e = 2 \times 10^{12}$ cm$^{-2}$: only the $0^- \rightarrow 1^+$ transition is active; (c) graphene with inhomogeneous electron density, such that the average density is $\bar{n}_e = 1.5 \times 10^{12}$ cm$^{-2}$ and distribution with the variance $\delta n_e = 0.4 \times 10^{12}$ cm$^{-2}$. (d) The same as in (c), but with $\bar{n}_e = 2.3 \times 10^{12}$ cm$^{-2}$ and $\delta n_e = 0.4 \times 10^{12}$ cm$^{-2}$.

anticrossings at different filling factors (like the one shown in figures 5(a) and (b)) weighted with the normal distribution factor, which we use mostly for illustration purposes.

As shown in figures 5(c) and (d), this leads to the inhomogeneous broadening of the side lines related to the variation of the size of the anticrossing gaps between the $0^- \rightarrow 1^+$ transition and the phonon, and it blurs out the much weaker splitting/anticrossing of the phonon and $1^- \rightarrow 0^+$ transition.

4.4. Inhomogeneously strained graphene

Inhomogeneous strain in graphene is often associated with magnetic field, $B_{\text{strain}}$ for electrons in $K$ valley and $-B_{\text{strain}}$ in $K'$, which is estimated as $B_{\text{strain}} \sim \frac{h e}{a l^2}$, where $a$ is the bond length and $l$ and $h$ are the linear scale and height of a ripple in graphene [34]. In the external magnetic
Figure 6. The $0^- \rightarrow 1^+$ and $1^- \rightarrow 0^+$ anticrossing for strained graphene with electron density $n_e = 2 \times 10^{12}$ cm$^{-2}$. (a) Homogeneously strained graphene with effective $B_{\text{strain}} = 3$ T: one anticrossing splits into two shifted vertically by $2B_{\text{strain}}$; (b) graphene subjected to inhomogeneous strain averaged over the distribution with the variance $\delta B_{\text{strain}} = 3$ T: the peak corresponding to the $0^- \rightarrow 1^+$ transition has a distinctive asymmetric shape.

field $B$, the total effective field acting on electrons in the valleys $K$ and $K'$ is different,

$$B_\xi = B + \xi B_{\text{strain}},$$

where $\xi = +$ for $K$ point and $\xi = -$ for $K'$. The difference in magnetic field leads to different Landau spectra in each valley, thus splitting the values of the external field $B$, for which, e.g., the resonance of $0_K^- \rightarrow 1_K^+$ and $0_{K'}^- \rightarrow 1_{K'}^+$ with the phonon is realized. Formally, this can be taken into account by a substitution $\Delta \Pi(B) \rightarrow \frac{1}{2} \sum_{\xi=\pm} \Delta \Pi(B_\xi)$ in equation (40).

For the local Raman spectrum related to an area with a fixed $B_{\text{strain}}$, this results in a fine structure of the anticrossing shown in figure 6(a), where an additional line appears seemingly crossing the phonon mode without splitting. Such a behaviour occurs due to the fact that instead of an anticrossing/mixing of two modes, now three modes are coupled, forming one phonon–electron mixed excitation with energy pinned in the middle of two strongly split side bands. Here, the central phonon line corresponds to the circular polarization of the phonon for which mixing with electronic modes is suppressed by Pauli blocking, due to the high density of electrons used in the calculation. Averaging out a normal distribution of $B_{\text{strain}}$ with zero average expectation and variance $\delta B_{\text{strain}} = 3$ T, the anticrossing branches become asymmetrically broadened, as shown in figure 6(b).

5. Summary

We have presented a theory of the inelastic scattering of photons in mono- and bilayer graphene accompanied by an excitation of e–h pairs. The dominant scattering processes are characterized by crossed polarization of in/out photons, while the Raman efficiency is proportional to the density of states (a linear increase with Raman shift for monolayer and constant for bilayer) and in the case of doping a gap of width $2\mu$ opens up.

*New Journal of Physics* 14 (2012) 105016 (http://www.njp.org/)
In a strong magnetic field, Raman spectra acquire a pronounced structure with peaks corresponding to the inter-LL transitions. The selection rules for the strongest mode preserve LL number $n$: $n^->n^+$, and the quantum efficiency of the single peak in figure 3 is $I_1 \sim \left(\frac{e^2}{\pi \hbar \omega}\right)^2 \sim 10^{-12}$ per incoming photon for $\Omega \sim 1$ eV photons in the magnetic field $B \sim 10$ T. The theoretical prediction for the intensity of the phonon-induced $G$ peak [53], which is a well-known Raman feature in carbon materials [54], estimates $I_G \sim 10^{-11}$. This result is close in order of magnitude to the intensity of a single $n^->n^+$ peak. Hence, the spectral features of inter-LL transitions in graphene can be observed experimentally [49]. The weaker mode with the same selection rules, similar to the absorption process, $n^->(n \pm 1)^+$, but belonging to different symmetry group representations ($E_2$, while the absorption has $E_1$), is coupled to the phonon mode, creating the anticrossing and the $G$-peak line.

Acknowledgments

We thank A Ferrari, D Smirnov, M Mucha-Kruczynski, K Kechedzhi, M Goerbig, F Guinea, T Ando and D Basko for useful discussions. This reviewed work was supported by the EPSRC, the Royal Society, the EC ERC, the Royal Society’s Wolfson Research Merit Award and the European Research Council’s Advance Investigator grant ‘Graphene and Beyond’.

References

[1] Ohta T, Bostwick A, Seyller T, Horn K and Rotenberg E 2006 Science 313 951
[2] Mucha-Kruczyński M, Tsyplyatyev O, Grishin A, McCann E, Fal’ko V I, Bostwick A and Rotenberg E 2008 Phys. Rev. B 77 195403
[3] Sadowski M L, Martinez G, Potemski M, Berger C and de Heer W A 2006 Phys. Rev. Lett. 97 266405
[4] Jiang Z, Henriksen E A, Tung L C, Wang Y J, Schwartz M E, Han M Y, Kim P and Stormer H L 2007 Phys. Rev. Lett. 98 197403
[5] Kuzmenko A B, van Heumen E, van der Marel D, Lerch P, Blake P, Novoselov K S and Geim A K 2009 Phys. Rev. B 79 115441
[6] Zhang L M, Li Z Q, Basov D N, Fogler M M, Hao Z and Martin M C 2008 Phys. Rev. B 78 235408
[7] Abergel D S L and Fal’ko V I 2007 Phys. Rev. B 75 155430
[8] Blake P, Hill E W, Neto A H C, Novoselov K S, Jiang D, Yang R, Booth T J and Geim A K 2007 Appl. Phys. Lett. 91 063124
[9] Abergel D S L, Russell A and Fal’ko V I 2007 Appl. Phys. Lett. 91 063125
[10] Kuzmenko A B, Crassee I, van der Marel D, Blake P and Novoselov K S 2009 Phys. Rev. B 80 165406
[11] Henriksen E A, Jiang Z, Tung L C, Schwartz M E, Takita M, Wang Y J, Kim P and Stormer H L 2008 Phys. Rev. Lett. 100 087403
[12] Li Z Q, Henriksen E A, Jiang Z, Hao Z, Martin M C, Kim P, Stormer H L and Basov D N 2009 Phys. Rev. Lett. 102 037403
[13] Mak K F, Lui C H, Shan J and Heinz T F 2009 Phys. Rev. Lett. 102 256405
[14] Kuzmenko A B, Benfatto L, Cappelluti E, Crassee I, van der Marel D, Blake P, Novoselov K S and Geim A K 2009 Phys. Rev. Lett. 103 116804
[15] Nair R R, Blake P, Grigorenko A N, Novoselov K S, Booth T J, Stauber T, Peres N M R and Geim A K 2008 Science 320 1308
[16] Gaskell P E, Skulason H S, Rodenchuk C and Szkopek T 2009 Appl. Phys. Lett. 94 143101
[17] Ferrari A C et al 2006 Phys. Rev. Lett. 97 187401
[18] Graf D, Molitor F, Ensslin K, Stampfer C, Jungen A, Hierold C and Wirtz L 2007 Nano Lett. 7 238–42

New Journal of Physics 14 (2012) 105016 (http://www.njp.org/)
[19] Malard L M, Nilsson J, Elias D C, Brant J C, Plentz F, Alves E S, Castro Neto A H and Pimenta M A 2007 Phys. Rev. B 76 201401
[20] Jiang J W, Tang H, Wang B S and Su Z B 2008 Phys. Rev. B 77 235421
[21] Faugeras C, Nerrière A, Potemski M, Mahmood A, Dujardin E, Berger C and de Heer W A 2008 Appl. Phys. Lett. 92 011914
[22] Bercaud S, Ryu S, Brus L E and Heinz T F 2009 Nano Lett. 9 346
[23] Calizo I, Bejenari I, Rahman M, Liu G and Balandin A A 2009 J. Appl. Phys. 106 043509
[24] Pisana S, Lazzeri M, Casiraghi C, Novoselov K S, Geim A K, Ferrari A C and Mauri F 2007 Nature Mater. 6 198–201
[25] Castro Neto A H and Guinea F 2007 Phys. Rev. B 75 198–201
[26] Basko D M 2008 Phys. Rev. B 78 125418
[27] Basko D M 2007 Phys. Rev. B 76 081405
[28] Ando T 2007 J. Phys. Soc. Japan 76 024712
[29] Goerbig M O, Fuchs J N, Kechedzhi K and Fal’ko V I 2007 Phys. Rev. Lett. 99 087402
[30] Yan J, Zhang Y, Kim P and Pinczuk A 2007 Phys. Rev. Lett. 98 166802
[31] Yan J, Henriksen E A, Kim P and Pinczuk A 2008 Phys. Rev. Lett. 101 136804
[32] Basko D M, Piscanec S and Ferrari A C 2009 Phys. Rev. B 80 165413
[33] Wallace P R 1947 Phys. Rev. 71 622–34
[34] Castro Neto A H, Guinea F, Peres N M R, Novoselov K S and Geim A K 2009 Rev. Mod. Phys. 81 109–62
[35] Geim A K and Novoselov K S 2007 Nature Mater. 6 183–91
[36] McCann E and Fal’ko V I 2006 Phys. Rev. Lett. 96 086805
[37] Platzman P M, Wolff P A and Tzoar N 1968 Phys. Rev. 174 489
[38] Platzmann P M and Wolff P A 1973 Waves and Interactions in Solid State Plasmas (New York: Academic)
[39] Hong-Yan L and Qiang-Hua W 2008 Chin. Phys. Lett. 25 3746
[40] McClure J W 1957 Phys. Rev. 108 612–8
[41] Saito R, Dresselhaus G and Dresselhaus M S 1998 Physical Properties of Carbon Nanotubes (London: Imperial College Press)
[42] McCann E, Kechedzhi K, Fal’ko V I, Suzuura H, Ando T and Altshuler B L 2006 Phys. Rev. Lett. 97 146805
[43] Mafra D L, Malard L M, Doorn S K, Htoon H, Nilsson J, Castro Neto A H and Pimenta M A 2009 Phys. Rev. B 80 241414
[44] Kechedzhi K, McCann E, Fal’ko V I, Suzuura H, Ando T and Altshuler B L 2007 Eur. Phys. J. Spec. Top. 148 39–54
[45] Dresselhaus M and Dresselhaus G 1981 Adv. Phys. 30 139–326
[46] Das A, Chakraborty B, Piscanec S, Pisana S, Sood A K and Ferrari A C 2009 Phys. Rev. B 79 155417
[47] Kashuba O and Fal’ko V I 2009 Phys. Rev. B 80 241404
[48] Mucha-Kruczyński M, Kashuba O and Fal’ko V I 2010 Phys. Rev. B 82 045405
[49] Faugeras C, Amado M, Kossacki P, Orlita M, Kühne M, Nicolet A A L, Latyshev Y I and Potemski M 2011 Phys. Rev. Lett. 107 036807
[50] Kossacki P, Faugeras C, Kühne M, Orlita M, Nicolet A A L, Schneider J M, Basko D M, Latyshev Y I and Potemski M 2011 Phys. Rev. B 84 235138
[51] Mucha-Kruczyński M, Abergel D S L, McCann E and Fal’ko V I 2009 J. Phys.: Condens. Matter 21 344206
[52] Abergel D S, McCann E and Fal’ko V I 2007 Eur. Phys. J. Spec. Top. 148 105
[53] Basko D M 2009 New J. Phys. 11 095011
[54] Ferrari A C 2007 Solid State Commun. 143 47–57
[55] Hwang E H and Das Sarma S 2007 Phys. Rev. B 75 205418
[56] Martin J, Akerman N, Ulbricht G, Lohmann T, Smet J H, von Klitzing K and Yacoby A 2008 Nature Phys. 4 144–8