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Zone-boundary phonon induced mini band gap formation in graphene

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ABSTRACT

We investigate the effect of electron–A_{1g} phonon coupling on the gapless electronic band dispersion of the pristine graphene. The electron–phonon interaction is introduced through a Kekulé-type distortion giving rise to inter-valley scattering between K and K′ points in graphene. We develop a Fröhlich type Hamiltonian within the continuum model in the long-wave length limit. By presenting a fully theoretical analysis, we show that the interaction of charge carriers with the highest frequency zone-boundary phonon mode of A_{1g}−symmetry induces a mini band gap at the corners of the two-dimensional Brillouin zone of the graphene in the THz region. Since electron–electron interactions favor this type of lattice distortion, it is expected to be enhanced, and thus its quantitative implications might be measurable in graphene.

1. Introduction

Since the discovery of graphene [1,2] and its unconventional physical properties, the investigation of electronic properties of both graphene and graphene-based nanostructures have become one of the active areas in condensed matter physics experimentally as well as theoretically,in past few years. Theoretically, in the low-energy limit charge carries of graphene have linear dispersion relation around the so-called Dirac points [3] having Fermi velocity [4] $v_F \simeq 10^6$ m/s, and the Dirac–Weyl equation can be safely used within the framework of continuum description of the electronic band structure of the graphene [5].

It is also well-known that both in-plane and out-of-plane phonon modes play an important role in charge carriers dynamics of the graphene [6–31]. On the one hand the Fermi velocity is reduced by interaction of charge carriers with doubly degenerate in-plane E_{2g} phonon [27,28]. On the other hand, though the electron-highest frequency zone-boundary phonon interaction, i.e., Kekulé-type distortion of the graphene lattice is one of the possible mechanisms among the gap generations, except that the work of Samsonidze et al. [16], there are no theoretical works on its influence on the graphene band dispersion. This first theoretical prediction of dynamical mini band gap formation in graphene due to the highest frequency phonon mode with A_{1g}−symmetry is reported by Samsonidze et al. [16]. They showed that, based on a simple tight-binding model at room temperature, such as an electron–phonon coupling mechanism induces a mini gap at around 10 meV, and it is also responsible for the Kohn anomalies [32] in graphene. The Kekulé structure consists of a network of hexagons with the alternating short and long bonds like in the classical benzene molecule. This pattern was studied for the 1D simple model, finite size carbon nanotubes [33,34]. Investigation of the gap formation, in particular, its control, in both graphene and graphene-based nanostructures is itself one of the hot topics of the current research in graphene, and such a gap generation can be created by strain [35–37] or by substrate induced effects [10,38,39].

In this paper, to investigate the effect of interaction of graphene charge carriers with the highest frequency optical phonon mode of A_{1g} symmetry near the zone boundary K (K′), we performed an analytical study based on Lee–Low and Pines (LLP) theory [40]. The carrier–phonon interaction is described through a Kekulé-type distortion giving rise to inter-valley scattering between K and K′ points in graphene [41–45]. Based on this interaction, we first construct a Fröhlich type Dirac–Weyl Hamiltonian which is non-diagonal in phonon creation and annihilation operators. Secondly, we present a simple analytical model to diagonalize it by just introducing two successive unitary transformations. Finally, we show that the interaction of charge carriers with highest zone boundary phonon mode opens a mini band gap at the corners of the Brillouin zone.

2. Theory

In the long-wave length regime, the Hamiltonian of the graphene electron (hole) interacting with A_{1g}−phonon mode can be written as

$$\mathcal{H} = \mathcal{H}_0 + \sum_{\boldsymbol{q},\mu} \hbar\omega_\mu(\boldsymbol{q}) b^\dagger_{\mu,\boldsymbol{q}} b_{\mu,\boldsymbol{q}} + \mathcal{H}_{e-p} \quad (1)$$

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where $\mathcal{H}_0 = v_F \boldsymbol{\alpha}\cdot\boldsymbol{p}$ is the unperturbed part, whose spectrum describes cone like behavior around the Dirac points with eigenvalues $\varepsilon_{k\lambda} = \lambda v_F k$. λ is the band index, and takes $-1(+1)$ values corresponding to valence (conduction) bands in pristine graphene. These two bands touch each other at the corners of the Brillouin zone, i.e., at the well-known K and K′ points whose coordinates are given by $\mathbf{K} = (2\pi/a)(1/3, 1/\sqrt{3})$ and, $\mathbf{K}' = (2\pi/a)(2/3, 0)$, respectively. We have labeled these points in Eq. (1) by the valley index μ. Here, $\boldsymbol{\alpha}$ is the four component Dirac matrices, and a is the carbon-carbon interdistance bond length, i.e., 1.42 Å. Thus, the corresponding eigenfunctions of the unperturbed part $\mathcal{H}_0$ can easily be constructed in terms of four component pseudospinors

$$\langle r|\mathrm{K}\lambda\boldsymbol{k}\rangle = \frac{\exp(i\boldsymbol{k}\cdot\boldsymbol{r})}{\sqrt{2}L}\begin{pmatrix}\lambda\\ e^{i\theta(\boldsymbol{k})}\\ 0\\ 0\end{pmatrix}$$

$$\langle r|\mathrm{K}'\lambda\boldsymbol{k}\rangle = \frac{\exp(i\boldsymbol{k}\cdot\boldsymbol{r})}{\sqrt{2}L}\begin{pmatrix}0\\ 0\\ e^{i\theta(\boldsymbol{k})}\\ \lambda\end{pmatrix}, \tag{2}$$

where L^2 is the total area of the system. In Eq. (1), the last term represents the electron–phonon couplings [44], and is given by

$$\mathcal{H}_{e-p} = 2\frac{\beta_{\mathrm{K}}\gamma}{a^2}\begin{pmatrix}0 & \omega^{-1}\Delta_{\mathrm{K}'}(\boldsymbol{r})\sigma_y\\ \omega\Delta_{\mathrm{K}}(\boldsymbol{r})\sigma_y & 0\end{pmatrix} \tag{3}$$

where $\beta_{\mathrm{K}} = -d\ln J_0/d\ln a$, $\gamma = (3a/2)J_0$, $\omega = \exp(2\pi i/3)$, J_0 is the resonance integral between nearest neighbor carbon atoms which is of order 2.77 eV, σ_y is the 2×2 Pauli matrix. In Eq. (3), the amplitude of distortions at K and K′ points is defined by

$$\Delta_{\mathrm{K}}(\boldsymbol{r}) = \sum_{\boldsymbol{q}}\sqrt{\frac{\hbar}{2NM_C\omega_{\mathrm{K}}(\boldsymbol{q})}}\left(b_{\mathrm{K},\boldsymbol{q}} + b^{\dagger}_{\mathrm{K}',-\boldsymbol{q}}\right)e^{i\boldsymbol{q}\cdot\boldsymbol{r}}$$

$$\Delta_{\mathrm{K}'}(\boldsymbol{r}) = \sum_{\boldsymbol{q}}\sqrt{\frac{\hbar}{2NM_C\omega_{\mathrm{K}}(\boldsymbol{q})}}(b_{\mathrm{K}',\boldsymbol{q}} + b^{\dagger}_{\mathrm{K},-\boldsymbol{q}})e^{i\boldsymbol{q}\cdot\boldsymbol{r}}, \tag{4}$$

respectively. N is the number of unit cells, M_C is the mass of a carbon atom. In Eq. (4), $b_{\mathrm{K},\boldsymbol{q}}$ ($b_{\mathrm{K}',\boldsymbol{q}}$) and $b^{\dagger}_{\mathrm{K},\boldsymbol{q}}$ ($b^{\dagger}_{\mathrm{K}',\boldsymbol{q}}$) are the phonon creation and annihilation operators at points K (K′) with phonon wave vector $\boldsymbol{q}$ and frequency $\omega_{\mathrm{K}}(\boldsymbol{q})$. The corresponding highest zone-boundary phonon energy is $\hbar\omega_{\mathrm{K}}(0) = 161.2$ meV [44]. Therefore, the electron–phonon interaction Hamiltonian given by Eq. (3) can be conveniently rewritten in the following form:

$$\mathcal{H}_{e-p} = -\sum_{\mu\neq\nu}\sum_{\boldsymbol{q}}[\tilde{\mathrm{M}}_{\mu\nu}b_{\mu,\boldsymbol{q}}e^{i\boldsymbol{q}\cdot\boldsymbol{r}} + \mathrm{h.c.}]. \tag{5}$$

We have defined $\tilde{\mathrm{M}}_{\mu\nu}$ as $\mathrm{M}_0\mathrm{M}_{\mu\nu}$ such that

$$\mathrm{M}_{\mathrm{KK}'} = \frac{\omega}{\sqrt{N}}\begin{pmatrix}\mathbf{0} & \mathbf{0}\\ \sigma_y & \mathbf{0}\end{pmatrix},$$

$$\mathrm{M}_{\mathrm{K}'\mathrm{K}} = \frac{\omega^{-1}}{\sqrt{N}}\begin{pmatrix}\mathbf{0} & \sigma_y\\ \mathbf{0} & \mathbf{0}\end{pmatrix},$$

together with $\mathrm{M}_0 = 3a_0q_0J_0$. Here, $a_0 = (\hbar/2M_C\omega_{\mathrm{K}}(0))^{1/2}$, and $q_0 = (\partial J_0/\partial a)/J_0$ is predicted [47,46] at around 2.0 Å^{-1} and 2.5 Å^{-1}.

To diagonalize the phonon subsystem of Eqs. (1)– (5) we employ a unitary transformation scheme within the LLP theory. This includes two successive transformations each of which eliminates the electron coordinates from Eq. (1), and shifts phonon coordinates by an amount of the interaction strength, respectively. To do this we follow the method developed for the investigation of the interaction of electron (hole) with doubly degenerate optical phonon modes of E_{2g} symmetry near the zone center [27], wherein an ansatz was made so as to take into account the chiral nature of the pristine graphene due to its gapless electronic band structure. However, besides the chiral nature of the problem, it should be considered that the zone boundary phonon gives rise to inter-valley scattering between K and K′. Therefore, to be compatible with these properties of the problem, we make an ansatz for the ground-state of the whole system.

$$|\boldsymbol{\Phi}\rangle = \sum_{\mu'\neq\nu'}\sum_{\lambda'}\alpha^{\mu'\lambda'}_{\pm}|\mu'\lambda'\boldsymbol{k}\rangle\otimes U_1U_2|\mathbf{0}\rangle_{\mathrm{ph}} \tag{6}$$

such that $\mathcal{H}|\boldsymbol{\Phi}\rangle = E_{\pm}|\boldsymbol{\Phi}\rangle$. Here, $|\mathbf{0}\rangle_{\mathrm{ph}}$ stands for the phonon vacuum, and $\alpha^{\mu'\lambda'}_{\pm}|\mu'\lambda'\boldsymbol{k}\rangle$ corresponds to electronic state vector defined through the appropriate fractional amplitudes, $\alpha^{\mu'\lambda'}_{\pm}$, due to the fact that total wave function of the system must be the linear combination of $|\mu'+\boldsymbol{k}\rangle$ and $|\mu'-\boldsymbol{k}\rangle$, respectively.

On the one hand, the first unitary transformation

$$U_1 = \exp\left[-i\boldsymbol{r}\cdot\sum_{\boldsymbol{q}}\boldsymbol{q}b^{\dagger}_{\mu,\boldsymbol{q}}b_{\mu,\boldsymbol{q}}\right] \tag{7}$$

eliminates electron coordinates from Eq. (1), since the transformed operators are given by the relations, $\tilde{b}_{\mu,\boldsymbol{q}} = b_{\mu,\boldsymbol{q}}\exp[-i\boldsymbol{q}\cdot\boldsymbol{r}]$ and $\tilde{\boldsymbol{p}} = \boldsymbol{p} - \sum_{\boldsymbol{q},\mu}\hbar\boldsymbol{q}b^{\dagger}_{\mu,\boldsymbol{q}}b_{\mu,\boldsymbol{q}}$. Therefore, the transformed Hamiltonian takes the form,

$$\tilde{\mathcal{H}} = v_F\boldsymbol{\alpha}\cdot\left(\boldsymbol{p} - \hbar\sum_{\boldsymbol{q},\mu}\boldsymbol{q}b^{\dagger}_{\mu,\boldsymbol{q}}b_{\mu,\boldsymbol{q}}\right) + \sum_{\boldsymbol{q},\mu}\hbar\omega_{\mathrm{K}}b^{\dagger}_{\mu,\boldsymbol{q}}b_{\mu,\boldsymbol{q}} - \sum_{\boldsymbol{q},\mu}(\tilde{\mathrm{M}}_{\mu\nu}b_{\mu,\boldsymbol{q}} + \mathrm{h.c.}). \tag{8}$$

On the other hand, the second unitary transformation

$$U_2 = \exp\left[\sum_{\boldsymbol{q}}\tilde{\mathrm{M}}_0\langle\mu'\lambda'\boldsymbol{k}|\mathrm{M}^{\dagger}_{\mu\nu}|\nu'\lambda\boldsymbol{k}\rangle b^{\dagger}_{\mu,\boldsymbol{q}} - \mathrm{h.c.}\right] \tag{9}$$

is the well-known displaced oscillator transformation which shifts phonon coordinates by an amount of the interaction amplitude, $\tilde{\mathrm{M}}_0 = \mathrm{M}_0/\hbar\omega_{\mathrm{K}}(0)$. It just shifts the phonon coordinates, since it generates the coherent states for the phonon subsystem such that optical phonon operators transform according to the rule $\tilde{b}_{\mu,\boldsymbol{q}} = b_{\mu,\boldsymbol{q}} + \tilde{\mathrm{M}}_0\langle\mu'\lambda'\boldsymbol{k}|\mathrm{M}^{\dagger}_{\mu\nu}|\nu'\lambda\boldsymbol{k}\rangle$. As a result, under the transformation U_2, Eq. (8) can then be written as $\tilde{\mathcal{H}} = \mathcal{H}^0 + \mathcal{H}_1$, where $\mathcal{H}^0$ and $\mathcal{H}_1$ are given by

$$\mathcal{H}^0 = \hbar v_F\boldsymbol{\alpha}\cdot\tilde{\boldsymbol{p}} + \sum_{\boldsymbol{q},\mu}|\tilde{\mathrm{M}}_0|^2\hbar\omega_{\mathrm{K}}|\langle\delta\lambda'\boldsymbol{k}|\mathrm{M}^{\dagger}_{\mu\nu}|\zeta\lambda\boldsymbol{k}\rangle|^2 - \sum_{\boldsymbol{q},\mu}[|\tilde{\mathrm{M}}_0|^2\hbar\omega_{\mathrm{K}}\mathrm{M}_{\mu\nu}|\langle\delta\lambda'\boldsymbol{k}|\mathrm{M}^{\dagger}_{\mu\nu}|\zeta\lambda\boldsymbol{k}\rangle|^2 + \mathrm{h.c.}] \tag{10}$$

and

$$\mathcal{H}_1 = \sum_{\boldsymbol{q},\mu}(\overline{\mathrm{M}}_{\mu\nu}b_{\mu,\boldsymbol{q}} + \mathrm{h.c.}) + \sum_{\boldsymbol{q},\mu}\hbar\tilde{\omega}_{\mu}(\mathbf{q})b^{\dagger}_{\mu,\boldsymbol{q}}b_{\mu,\boldsymbol{q}}, \tag{11}$$

respectively. Here, we have defined

$$\tilde{\boldsymbol{p}} = \boldsymbol{p} - \hbar\sum_{\boldsymbol{q},\mu}\boldsymbol{q}|\tilde{\mathrm{M}}_0|^2|\langle\delta\lambda'\boldsymbol{k}|\mathrm{M}^{\dagger}_{\mu\nu}|\zeta\lambda\boldsymbol{k}\rangle|^2,$$

$$\overline{\mathrm{M}}_{\mu\nu} = \mathrm{M}_{\mu\nu} + \hbar\tilde{\omega}_{\mu}(\mathbf{q})\tilde{\mathrm{M}}_0\langle\mu'\lambda'\boldsymbol{k}|\mathrm{M}_{\mu\nu}|\nu'\lambda\boldsymbol{k}\rangle,$$

and $\tilde{\omega}_{\mu}(\mathbf{q}) = \omega_{\mu}(\mathbf{q}) - v_F\boldsymbol{\alpha}\cdot\mathbf{q}$. Therefore, one applies the phonon vacuum to the sum of Eqs. (10) and (11), only the contribution comes from the diagonalized part, i.e. from $\mathcal{H}^0$. By using the ansatz given by Eq. (6), one first applies Eq. (10) to the term $\alpha^{\mu'\lambda'}_{\pm}|\mu'\lambda'\boldsymbol{k}\rangle$, and then sums over $\boldsymbol{\lambda}'$ to construct the eigenvalue equation $\mathcal{H}|\boldsymbol{\Phi}\rangle^{\mu\nu\lambda} = E_{\pm}|\boldsymbol{\Phi}\rangle^{\mu\nu\lambda}$. Finally, by taking inner products to compare the related coefficients of the states $|\mu'\lambda'\boldsymbol{k}\rangle$ we arrive at four simultaneous equations for $\alpha^{\mathbf{K}+}_{\pm}$, $\alpha^{\mathbf{K}-}_{\pm}$, $\alpha^{\mathbf{K}'+}_{\pm}$ and $\alpha^{\mathbf{K}'-}_{\pm}$ which can be