NANOSYSTEMS: PHYSICS, CHEMISTRY, MATHEMATICS, 2014, 5 (1), P. 142–147

THE ELECTRON-PHONON MATRIX ELEMENT IN THE DIRAC POINT OF GRAPHENE

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PACS 63.22.Rc,63.20.kd

The chief aim of this paper is to derive the matrix element of electron-phonon interaction in graphene as a function of phonon wave vector. The tight binding model, harmonic crystal approximation, and deformation potential approximation were employed for obtaining the matrix element. Required microscopic parameters are available in the current literature. This technique allows the most precise derivation of the electron-phonon matrix element in graphene based on the semiempirical models. Scattering of electrons from the Dirac point is considered as most important. The 2D plots of the e-ph matrix element absolute value as a function of the phonon wave vector for in-plane modes are given as a result. These plots show the high anisotropy of the e-ph matrix element and singularities in high symmetry points. The results are in agreement with the long-wavelength approximation.

Keywords: graphene, electron-phonon interaction.

1. Introduction

Electron-phonon interaction can affect transport properties of extremely pure graphene [1,2] and consequently its investigation is important for creating electronic devices based on graphene layers, particularly thermoelectric devices [3,4]. Raman spectroscopy is one of the most comprehensive techniques for studies of graphene [5,6] and double resonant Raman peaks are footprints of electronic and vibrational properties of the crystal. This encourages the research of electron-phonon interaction in graphene. The knowledge of vibrational properties, electron wave functions and deformation potential in total can lead to derivation of the electron-phonon matrix element.

2. Harmonic crystal approximation

Graphene is a two dimensional crystal with a honeycomb lattice of carbon atoms. One of the alternatives for the unitary cell is rhombic one. It contains two atoms in basis: A and B types. They have different directions of the chemical bonds, which causes their inequivalence. Reciprocal lattice for the two-dimensional hexagonal crystal is also hexagonal lattice, which is in addition rotated over 60 degrees. Brillouin zone carries symmetrical properties of the crystal and consequently it must be hexagon-shaped. To specify the position of each atom, one can write $\mathbf{R}(u,s) = \mathbf{R}_u + \mathbf{r}_s$, where $\mathbf{R}_u$ is the position of unitary cell in crystal and $\mathbf{r}_s$ is the position of atom of s type in the unitary cell.

The vibrational properties of graphene can be described on the basis of the harmonic crystal approximation [7]. This method starts from the Newton′s second law for each atom in crystal:

$$m\ddot{x}_\alpha\left(u,s\right) = -\sum_{u's'\beta}\Phi_{\alpha\beta}\left(u-u',s,s'\right)x_\beta\left(u',s'\right), \tag{1}$$

where $x_\alpha(u,s)$ is α component of displacement of the s type atom in the u cell, and $\Phi_{\alpha\beta}$ are interatomic force constants. The infinite system of the classical motion equations after substitution are:

$$x_\alpha\left(\mathbf{q},u,s\right) = \frac{1}{\sqrt{m}}w_\alpha(\mathbf{q},s)\exp\left(i\mathbf{q}\mathbf{R}\left(u,s\right)-i\omega(\mathbf{q})t\right) \tag{2}$$

reduces to the eigenvector problem:

$$\omega^2(\mathbf{q})w_\alpha(\mathbf{q},s) = \sum_{s'\beta}C_{\alpha\beta}\begin{pmatrix}\mathbf{q}\\ s\,s'\end{pmatrix}w_\beta(\mathbf{q},s'), \tag{3}$$

for the dynamical matrix $C_{\alpha\beta}$ that is defined as:

$$C_{\alpha\beta}\begin{pmatrix}\mathbf{q}\\ s\,s'\end{pmatrix} = \frac{1}{m}\sum_{u'}\Phi_{\alpha\beta}(u-u',s,s')\cdot\exp(i\mathbf{q}\cdot(\mathbf{R}(u,s)-\mathbf{R}(u',s'))). \tag{4}$$

It is useful to introduce the vector $\mathbf{W}_s(\mathbf{q}) = (w_x(\mathbf{q},s), w_y(\mathbf{q},s))^T$. Eigenvalues for the dynamical matrix give squared frequencies for phonons of different phonon modes and eigenvectors represent corresponding directions and phases of atomic displacements. For a crystal with 2 atoms in its basis, the dynamical matrix dimensions are 6 by 6. But out of plane modes can be separated, and therefore, the in-plane modes can be described by a 4 by 4 dynamical matrix. Interatomic force constants utilized to construct the dynamical matrix are available in current literature [8–12]. The density-functional theory (DFT) is used in [10] to obtain the interatomic force constants for neighbors, up to twentieth, and we use here these data as the most complete.

3. Derivation of electron-phonon matrix element

The wave functions of electron with wave vector $\mathbf{k}$ in graphene can be written as

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}}\sum_{u,s}C_s(\mathbf{k})\varphi(\mathbf{r}-\mathbf{R}_u-\mathbf{r}_s)\cdot\exp(i\mathbf{k}(\mathbf{R}_u+\mathbf{r}_s)). \tag{5}$$

Coefficients $C_s(\mathbf{k})$ define the true Hamiltonian eigenstates with wave vector $\mathbf{k}$, and $\varphi(\mathbf{r})$ is the atomic wave function. Most of important optical and electronic properties of graphene are defined by the bands that appear as a result of interaction between electrons from π orbitals of carbon atoms. Consequently, $\varphi(\mathbf{r})$ here is close to the π orbitals.

The phonon is a wave of atomic displacements from their equilibrium positions and consequently it causes a deviation potential from the potential of unperturbed crystal. It leads to the possibility of electron scattering on corresponding perturbation. For small atomic displacements, the perturbation potential is directly proportional to these displacements. Thereby, one can write the scalar product of atomic displacement and gradient of the certain potential in the following expression:

$$\delta V_{\mathbf{q}}(\mathbf{r}) = \sum_{u'',s''} (\mathbf{W}_{s''}(\mathbf{q}) \cdot \nabla V(\mathbf{r} - \mathbf{R}_{u''} - \mathbf{r}_{s''})) \cdot \exp(i\mathbf{q}(\mathbf{R}_{u''} + \mathbf{r}_{s''})). \quad (6)$$

In the hard ion approach the potential of an atom is assumed to be rigid and consequently in relation (6) V is directly the potential of the atom that is used to calculate band structure in the material, e.g. to construct tight-binding matrix elements in the tight binding model. Indeed, the form of atomic potential changes when the atom is displaced and it leads to the concept of deformation potential. In [13], the deformation potentials in nanotubes and graphene were studied on the basis of *ab initio* calculations.

The Electron-phonon matrix element defines the process of electron scattering with wavevector $\mathbf{k}$ into the state with wavevector $\mathbf{k}'$ on introduced potential:

$$M_{e-ph}(\mathbf{k} \to \mathbf{k}' = \mathbf{k} + \mathbf{q}) \equiv M_{e-ph}(\mathbf{k}, \mathbf{q}) = \int \mathbf{dr}\, \psi^{\dagger}_{\mathbf{k}'}(\mathbf{r}) \delta \hat{V}_{\mathbf{q}}(r) \psi_{\mathbf{k}}(\mathbf{r}). \quad (7)$$

Basic formulae for calculation of the electron-phonon matrix element are given in [13] in clear form, and where possible, designations from [13] are used. However, in [13], the authors mainly investigate nanotube transport properties and do not give the electron-phonon matrix element as a function of the wave vector or represent 2D plots of M_{e-ph} . For instance, the precise Raman spectra calculation requires such information.

After substitution of relations (2), (5), and (6) to (7) one obtains:

$$M_{e-ph}(\mathbf{k}, \mathbf{q}) = \sum_{u,s} \sum_{s'} \sum_{u'',s''} {C_{s'}}^{\dagger}(\mathbf{k}') C_s(\mathbf{k}) \times$$
$$\exp(i\mathbf{k}(\mathbf{R}_{\Delta u} + \mathbf{r}_s) - i(\mathbf{k} + \mathbf{q})\mathbf{R}_{u'} + i\mathbf{q}(\mathbf{R}_{\Delta u''} + \mathbf{r}_{s''})) \cdot (\mathbf{W}_{s''}(\mathbf{q}) \cdot \mathbf{g}(s'; \Delta u, s; \Delta u'', s'')), \quad (8)$$

where

$$\mathbf{g}(u'; \Delta u, s; \Delta u'', s'') =$$
$$\int d\mathbf{r} \left[\varphi^{\dagger}(\mathbf{r}) \nabla V(\mathbf{r} - (\mathbf{R}_{\Delta u''} + \mathbf{r}_{s''} - r_{s'})) \varphi(\mathbf{r} - (\mathbf{R}_{\Delta u} + \mathbf{r}_s - \mathbf{R}_{s'}))\right]. \quad (9)$$

Fig. 1 represents relative positions of atoms that figures in the integral in relation (9).

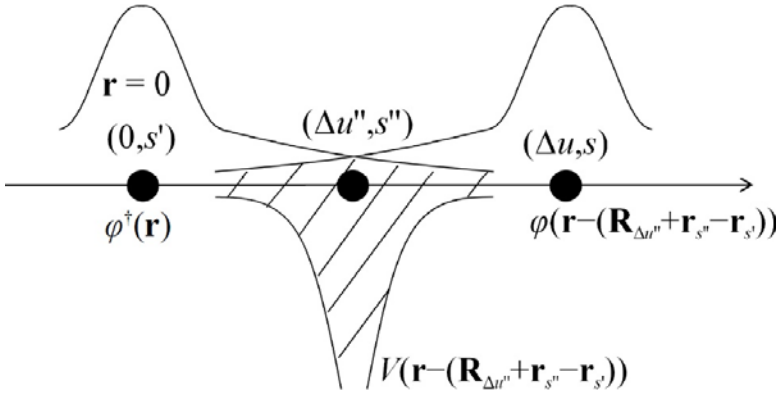

FIG. 1. Diagram illustrating the structure of terms in the expression for the deformation potential.

As was mentioned previously, the relevant electron states in graphene are the result of π orbital interactions. Due to the geometry of the π-π bond, the energy of interaction

between carbon atoms changes significantly only if atoms are displaced along the bond axis. Mathematically it means that the direction of the potential gradient lies along vectors between atom s' and its neighbors. Also, only interactions between nearest neighbors are dominant. Consequently, the two types of terms appear. The first one is so-called off-site term, where $\Delta u = 0$, $s = s'$:

$$\mathbf{g}(s'; 0, s'; \Delta u'', s'') = \frac{\mathbf{R}_{\Delta u''} + \mathbf{r}_{s''} - \mathbf{r}_{s'}}{|\mathbf{R}_{\Delta u''} + \mathbf{r}_{s''} - \mathbf{r}_{s'}|} \cdot \lambda(|\mathbf{R}_{\Delta u''} + \mathbf{r}_{s''} - \mathbf{r}_{s'}|), \tag{10}$$

This corresponds to perturbation of the diagonal terms of Hamiltonian. The second type are on-site terms, where $\Delta u'' = 0$, $s'' = s'$ or $\Delta u'' = \Delta u$, $s'' = s'$:

$$\begin{aligned} \mathbf{g}(s'; \Delta u, s; 0, s') &= \tfrac{\mathbf{R}_{\Delta u} + \mathbf{r}_s - \mathbf{r}_{s'}}{|\mathbf{R}_{\Delta u} + \mathbf{r}_s - \mathbf{r}_{s'}|} \cdot \alpha(|\mathbf{R}_{\Delta u} + \mathbf{r}_s - \mathbf{r}_{s'}|), \\ \mathbf{g}(s'; \Delta u, s; \Delta u, s) &= -\tfrac{\mathbf{R}_{\Delta u} + \mathbf{r}_s - \mathbf{r}_{s'}}{|\mathbf{R}_{\Delta u} + \mathbf{r}_s - \mathbf{r}_{s'}|} \cdot \alpha(|\mathbf{R}_{\Delta u} + \mathbf{r}_s - \mathbf{r}_{s'}|). \end{aligned} \tag{11}$$

They define the off-diagonal perturbation of the Hamiltonian. Numeric values of α and λ are given in [13].

4. Results and discussion

Electrons near the Fermi level make the main contribution to the transport phenomena in graphene. Due to the shape of electron dispersion, these electrons have a wave vector lying near the Dirac point (K point or conical point) of the Brilloiun zone. Visible light can excite electron hole pairs also in the region of the Dirac point only. Consequently, scattering of electrons from the Dirac point of the Brillouin zone attracts most interest.

Fig 2. shows the absolute value of electron-phonon matrix element as a function of the phonon wave vector $\mathbf{q}$ for TA,LA,TO and LO modes. Initial electron wave vector $\mathbf{k}$ corresponds to the Dirac point ($\mathbf{k} = (4\pi/3a_0, 0)$). High anisotropy of the electron-phonon matrix element is detected. Patterns obey D_{3h} symmetry, which is strictly necessary for the Dirac point of Brillouin zone in graphene. The directions in Brillouin zone and segments of hexagonal Brilloiun zone with high and low values of the electron-phonon matrix element tolerably match to the ones from [14]. In [14], the authors used density-functional perturbation theory (DFPT) to calculate the electron-phonon matrix element, but the details of their calculations are unfortunately very brief.

Next, there are estimations [15] of the matrix element of scattering of electron in Dirac point within the long wave length approximation. For small phonon wave vectors $\mathbf{q}$, the following behavior was indicated:

$$\begin{aligned} M_{e-ph}^{TA,LA} &\sim q, \\ M_{e-ph}^{TO,LO} &\sim const. \end{aligned} \tag{12}$$

It can be seen that the obtained results agree well with estimations from [15].

Introduced derivation of the electron-phonon matrix element is based on the most complete and full sets of microscopic material parameters, and thus, it provides the most precise semiempirical approach at this point. The results obtained can be used for improvement of Raman spectra calculation. Taking into account the high anisotropy of the electron-phonon matrix element is also important for investigation of the electron drag by phonons in graphene.

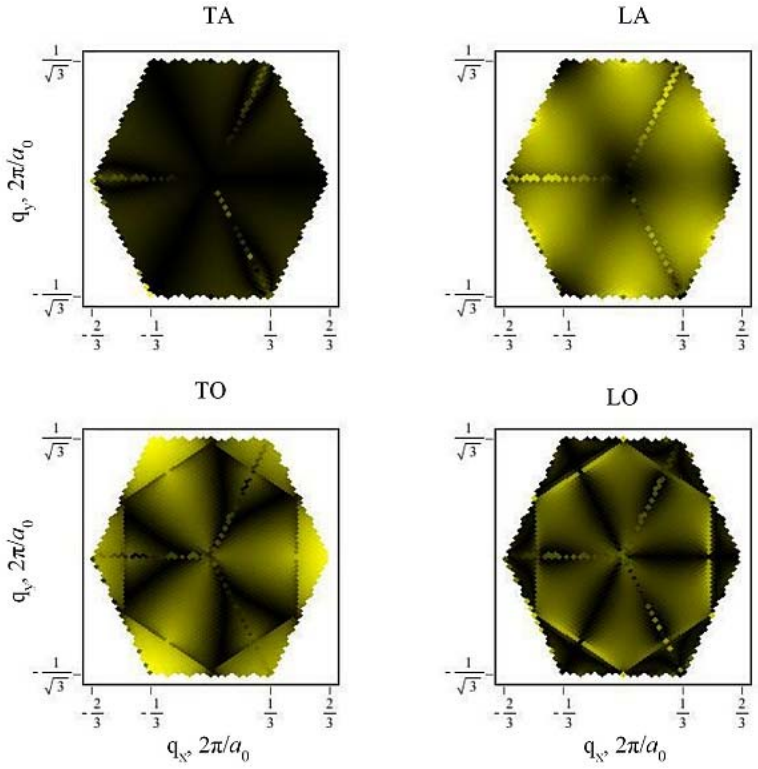

FIG. 2. Absolute value of electron-phonon matrix element for TA,LA,TO, and LO modes as a function of wave vector. The initial state of the electron corresponds to the Dirac point. Lighter areas correspond to larger values of matrix elements.

Acknowledgements

We would like to thank A. Ya. Vul' and A. T. Dideykin for their attention. This work was supported by the Dynasty foundation Grant for PhD students and by the St. Petersburg government grant for PhD students. The work was partly supported by programs of the Presidium of the Russian Academy of Sciences "Fundamental Foundations of the Technologies of Nanostructures and Nanomaterials" and "Quantum Mesoscopic and Unordered Systems".

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