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Research paper

Model study of the electron-phonon coupling in graphene; relative importance of intraband and interband scattering

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ABSTRACT

The aim of this model study of the electron-phonon coupling in graphene was to find out about the relative importance of the inter- and intraband scattering and which phonon modes are the most active. This was achieved by analyzing the electron-phonon matrix element of the carbon dimer in the unit cell. We found that for the intra molecular orbital matrix elements the longitudinal optical phonon mode is the active phonon mode. The matrix element corresponding to $\sigma \rightarrow \sigma$ is greater than the matrix element for $\pi \rightarrow \pi$. The inter molecular orbital scattering $\pi \rightarrow \sigma$ is driven by the out-of-plane acoustic phonon mode, while the out-of-plane optical mode does not contribute for symmetry reasons. We found the unexpected result that the magnitude of matrix element of the inter molecular orbital scattering $\pi \rightarrow \sigma$ exceeds the intra molecular orbital scattering $\pi \rightarrow \pi$. These results indicate that the in general not considered inter-band scattering has to be taken into account when analyzing e.g. photo-hole lifetimes and the electron-phonon coupling constant λ from photoemission data of graphene.

1. Introduction

Several experimental and theoretical studies of graphene have been presented during the last decade [1,2]. These investigations have revealed remarkable mechanical [3], electronic [4], optical [5] and thermal [6] properties. However, unstrained pristine graphene is not considered to be a good superconductor due to a weak electron-phonon coupling (EPC). The presented simple model study confirms the weak EPC in the π bands while the coupling should be considerably stronger in the occupied part of the σ band.

Our investigation is inspired by the recently reported experimental work by Mazzola et al. [7]. The evidence of a strong EPC in the σ-band was revealed in angle-resolved photoemission spectroscopy (ARPES) measurements with a substantial lifetime broadening and a pronounced characteristic kink in the band dispersion. The EPC constant λ was determined to be approximately 1 near the top of the σ band [7]. This is about a factor 3–4 larger than what have been found in the π band.

The aim of this tight-binding model study has been to sort out, (1) the relative importance of the interband and intraband scattering and, (2) which phonon mode contributes the most in theses scattering processes. The study is focused on calculations and analysis of the electron-phonon (e-ph) matrix element M_{e-ph}, which is the core of the EPC. Approximately we have that $\lambda \sim |M_{e-ph}|/\Omega_0$, where Ω_0 is the dominant phonon mode frequency.

2. Theory

The EPC constant λ can be examined in ARPES measurements. The created photo-hole yields a non-equilibrium which drives electron scattering in order to fill the hole. According to the Heisenberg uncertainty relation the energy width of the detected photo-electron kinetic energy - the lifetime broadening - is inversely proportional to the hole lifetime. At low temperatures, electron scattering is assisted by phonon emission. Theoretical modeling in order to calculate the phonon induced lifetime broadening enables estimation of the strength of the EPC determined by λ. Experiments indicate that the high energy optical phonon modes are the most active modes in the EPC in graphene [7,8].

The strength of the EPC is determined by the e-ph matrix element

$$M^{\nu}_{e-ph} = \langle \Phi_{n'\mathbf{k}'}(\mathbf{r})|\delta V^{\nu\mathbf{q}}(\mathbf{r})|\Phi_{n\mathbf{k}}(\mathbf{r})\rangle, \qquad (1)$$

where $\Phi_{n\mathbf{k}}$ and $\Phi_{n'\mathbf{k}'}$ are initial and final state wave functions of bands n and n', respectively. $\delta V^{\nu\mathbf{q}}$ is the phonon-induced deformation potential where ν and $\mathbf{q}$ labels phonon mode and momentum, respectively.

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2.1. Tight-binding model

In the tight-binding approximation the valence wave functions of graphene are formed by superposition of the atomic $2s$ and $2p$ orbitals. The σ band ($n = \sigma$) states are built by $2s$, $2p_x$ and $2p_y$ orbitals and the π band ($n = \pi$) by the $2p_z$ orbital. The tight-binding wave functions is given by

$$\Phi_{n\mathbf{k}}(\mathbf{r}) = \sum_{usj} c_{nsj}(\mathbf{k})\phi_{nsj}(\mathbf{r} - \mathbf{R}_{us})e^{i\mathbf{k}\mathbf{R}_{us}}, \tag{2}$$

where u labels the unit cells hosting the two different carbon atom sites, $s = A, B$ and $\mathbf{R}_{us}$ denote the equilibrium atom positions (see Fig. 1). The index j labels the atomic site orbital. The orbital ϕ_{nsj} then refers to the orbital j of atom type s of the band n. In the case of the occupied bonding π band the site orbital is the same at all sites ϕ_{2p_z} while for the σ band we have the three differently oriented sp^2 orbitals.

The deformation potential is given by

$$\delta V^{\nu\mathbf{q}}(\mathbf{r}) = -\sum_{us}\mathbf{u}^{\nu\mathbf{q}}_{us} \cdot \nabla_{\mathbf{R}}\, v(\mathbf{r}; \mathbf{R}_{us}), \tag{3}$$

where $\mathbf{q} = \mathbf{k} - \mathbf{k}'$ and

$$\mathbf{u}^{\nu\mathbf{q}}_{us} = \frac{1}{2}A_{\nu\mathbf{q}}\mathbf{e}^{\nu}_{s}(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{R}_{us}}, \tag{4}$$

where $A_{\nu\mathbf{q}} = \sqrt{\hbar/Nm\omega_\nu(\mathbf{q})}$ is the amplitude of phonon mode ν, with N the number of unit cells, m atomic mass and $\mathbf{e}^{\nu\mathbf{q}}_{s}$ the phonon polarization vector. In the case when the temperature is low enough that only phonon emission has to be considered, which is the case in the experiment by Mazzola et al. [7], we have

$$M^{\nu,nn'}_{e-ph} = -\frac{1}{2}A_{\nu\mathbf{q}}D^{\nu}_{nn'}(\mathbf{k},\mathbf{k}')\delta_{\mathbf{k}-\mathbf{k}',\ \mathbf{q}}, \tag{5}$$

where

$$D^{\nu}_{nn'}(\mathbf{k},\mathbf{k}') = \sum_{uu'u''}\sum_{ss's''}\sum_{jj'} c^{*}_{n's'j'}(\mathbf{k}')c_{nsj\mathbf{k}}(\mathbf{k}) \times \mathbf{m}^{nj,n'j'}_{s''}(\mathbf{R}_{u's'},\mathbf{R}_{us}) \cdot \mathbf{e}^{\nu}_{s''}(\mathbf{q}) \times e^{-i\mathbf{k}'\cdot(\mathbf{R}_{u's'}-\mathbf{R}_{u''s''})}e^{i\mathbf{k}\cdot(\mathbf{R}_{us}-\mathbf{R}_{u''s''})}, \tag{6}$$

where the site e-ph matrix element is given by the local site orbitals and the site dependent deformation potential

$$\mathbf{m}^{nj,n'j'}_{s''}(\mathbf{R}_{u's'},\mathbf{R}_{us}) = \int \phi^{*}_{n's'j'}(\mathbf{r}-\mathbf{R}_{u's'}) \times \nabla_{\mathbf{R}}\, v(\mathbf{r};\mathbf{R}_{u''s''})\phi_{nsj}(\mathbf{r}-\mathbf{R}_{us})d\mathbf{r}. \tag{7}$$

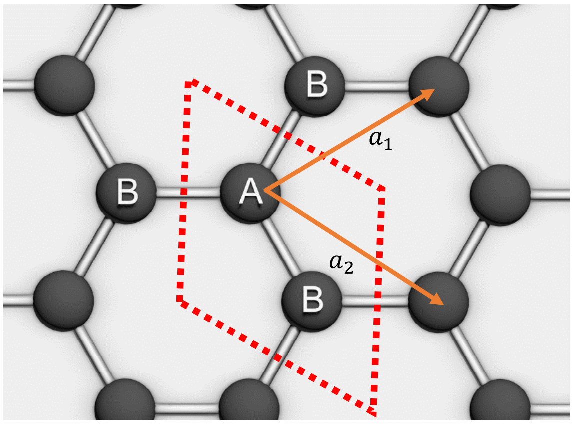

Fig. 1. Schematic drawing of the graphene unit cell with the two carbon atoms denoted by A and B and enclosed by the dashed line. The two lattice vectors a_1 och a_2 are shown.

The vibrational amplitude of the individual carbon atoms is at least an order of magnitude less than the lattice parameter. Thus, the greatest contribution to the three center integral in Eq. (7) is expected for the case when $\mathbf{R}_{u's'}$ and $\mathbf{R}_{us}$ correspond to pairwise nearest neighboring A and B sites and $\mathbf{R}_{u''s''} = \mathbf{R}_{us}$ or $\mathbf{R}_{u''s''} = \mathbf{R}_{u's'}$. The three center integral is then reduced to a two center integral. However, it has been pointed out that for a realistic deformation potential, the convergence with respect to order of neighboring sites is surprisingly slow [9].

For our purpose to qualitatively understand the relative importance of the intraband and interband scattering and the most important phonon mode in the two cases, we simplify furthermore and assume that $u = u'$ referring to the unit cells of the atomic site wave functions. Thus we consider only intersite scattering within the unit cell.

We will take the matrix element of D as a measure of the strength of the EPC. According to Eq. (5) we have that $|M^{\nu,nn'}_{e-ph}|^2 \sim |D^{\nu}_{nn'}|^2/\Omega_0$, where Ω_0 is a presumably dominant phonon mode frequency. This connects to the ECP strength measured by λ, which is determined by the reciprocal frequency moment of the Eliashberg function which leads to the additional frequency factor in the denominator, $\lambda \sim (|D^{\nu}_{nn'}|/\Omega_0)^2$.

To simplify the notation to express $D^{\nu}_{nn'}$ in Eq. (6) we introduce the two molecular orbitals corresponding to the binding σ and π orbitals. We refer to a coordinate system with the z axis oriented in the direction of the AB dimer of the unit cell and the x axis in the direction normal to the graphene layer. With B atom in the origin and A atom in the position $z = R_A$ the orbitals are written

$$\Psi_\sigma(\mathbf{r}) = |sp^2_z\rangle_A + |sp^2_z\rangle_B = |2s\rangle_A - |2p_z\rangle_A + |2s\rangle_B + |2p_z\rangle_B, \tag{8}$$

and

$$\Psi_\pi(\mathbf{r}) = |2p_x\rangle_A + |2p_x\rangle_B \tag{9}$$

where the low index A and B refers to the location of the atomic wave functions in the unit cell. The normalized molecular wave functions are then given by

$$\Phi_n(\mathbf{r}) = \frac{\Psi_n(\mathbf{r})}{\langle\Psi_n|\Psi_n\rangle}. \tag{10}$$

For the case $u = u' = u''$ and omitting phase factors, which will be of types $e^{i\mathbf{k}'\cdot\mathbf{R}_A}$ and $e^{i\mathbf{k}\cdot\mathbf{R}_A}$ in Eq. (6), the D matrix takes the form

$$\tilde{D}^{\nu}_{nn'} = \langle\Phi_n|\nabla_{\mathbf{R}}\, v_\nu|\Phi_{n'}\rangle. \tag{11}$$

The diagonal elements of the $\tilde{D}$ matrix corresponds to the intraband scattering $\tilde{D}^{\nu}_{\sigma\sigma}$ and $\tilde{D}^{\nu}_{\pi\pi}$, while the off-diagonal elements $\tilde{D}^{\nu}_{\sigma\pi}$ and $\tilde{D}^{\nu}_{\pi\sigma}$ correspond to interband scattering.

The deformation potential $\nabla_{\mathbf{R}}\, v_\nu$ referring to the three optical phonon modes (ZO, TO and LO) and the three acoustical modes (ZA, TA and LA) are generated by applying the rigid ion approximation (RIA) [10]. In this case we have

$$v(\mathbf{r};\mathbf{R}) \approx v(\mathbf{r} - \mathbf{R}).$$

This means that $\nabla_{\mathbf{R}}\, v \approx -\nabla_{\mathbf{r}}\, v$ and we can take the gradient of the one-electron atomic potential V with respect to the electronic coordinates $\mathbf{r}$ at the A and B sites as follows for the six different vibrational modes

$$\nabla v_{ZO} = -\frac{\partial V}{\partial x}\bigg|_A + \frac{\partial V}{\partial x}\bigg|_B, \quad \nabla v_{ZA} = \frac{\partial V}{\partial x}\bigg|_A + \frac{\partial V}{\partial x}\bigg|_B$$

$$\nabla v_{TO} = -\frac{\partial V}{\partial y}\bigg|_A + \frac{\partial V}{\partial y}\bigg|_B, \quad \nabla v_{TA} = \frac{\partial V}{\partial y}\bigg|_A + \frac{\partial V}{\partial y}\bigg|_B$$

$$\nabla v_{LO} = -\frac{\partial V}{\partial z}\bigg|_A + \frac{\partial V}{\partial z}\bigg|_B, \quad \nabla v_{LA} = \frac{\partial V}{\partial z}\bigg|_A + \frac{\partial V}{\partial z}\bigg|_B.$$