Electron spectra of graphene with local and extended defects

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Abstract We show theoretically a possibility to increase the superconducting transition temperature \( T_c \) of graphene by introducing defects. Eventually, the peak of local electron densities shifts to the Fermi level with \( T_c \) above ambient temperature in line with recent observations.

1. Introduction

Pronounced hybridization of atomic orbitals in a monolayer of graphene enhances its Debye temperature up to 2500 K, giving rise to the “low-temperature” features in vibrational thermodynamic properties of graphene and its derivatives, nano-tubes and nano-ribbons in a particular, at temperatures above ambient. In the BCS consideration, strongly evidenced for a broad variety of superconductors, the unconventional ones, in particular (see, e.g., [1] and references therein), high temperature of superconducting transition \( T_c \) should be expected then in line with a mean frequency of phonons [2]. Within this approach the absence of superconductivity in conventional graphene materials is explained by a low density of charge carriers in the vicinity of Fermi energy (\( \varepsilon_F \)), together with a lack of phonons for basic contribution to the electron-phonon coupling constant. To enhance the latter, it is necessary to increase the number of conducting electrons and saturate the fraction of phonon spectrum responsible for Cooper pairing. In fact, graphite with intercalated metal layers has manifested a superconducting transition at temperatures increased by a growing number of quasi-flexural phonon modes with frequencies close to the K-point of the first Brillouin zone [3 - 5] in addition to increment of charge carriers number. In the works [6,7] it was demonstrated, that a similar increase of a charge carriers and corresponding phonons number takes place in thin graphene nano-film, i.e. bi- and tri-graphene with a “step-edge” boundary. In present contribution, evolution of the electron and phonon spectra of graphene on insulating substrate gains analytical and numerical analysis when the graphene layer is cut along a zig-zag line (Fig. 1a). It is shown, that such imperfection significantly increases both the population of electrons at Fermi level and the number of quasi-flexural phonons with frequencies about that, corresponding to K-point of first Brillouin zone.

2. Electron spectrum of graphene, cut along zig-zag line

In zero magnetic field, the electron spectrum of graphene is reasonably described within tight-binding approximation (see, e.g.[8 - 10]) and corresponding Hamiltonian, read as:

\[
\hat{H} = \sum_i \varepsilon_i |i\rangle\langle i| - \sum_{i,j} J_{ij} |i\rangle\langle j|.
\]
In the case (see, e.g., [11]) of in-plane electron hopping restricted to the nearest neighbors \( \forall J_{ij} = J = 2.8 \text{ eV} \), and \( \forall \epsilon_i = \epsilon_F = 3J \) (indices \( i \) and \( j \) label sites), the Hamiltonian (1) yields the following dispersion law:

\[
\epsilon_0(k) = \pm J \sqrt{1 + 4 \cos \left( \frac{k \cdot a_i + a_j}{2} \right) \cos \left( \frac{k \cdot a_i - a_j}{2} \right) + \cos \left( \frac{k \cdot a_i}{2} \right) + \cos \left( \frac{k \cdot a_j}{2} \right)}.
\]  

(2)

For high-symmetry directions in \( k \) - space it is illustrated by Fig. 1b with Fermi energy as the reference one.

Due to specific 2D crystal structure of graphene, the spectral branches coincide in a single point of reciprocal space (K-point of 2D first Brillouin zone). The other directions, outgoing from \( \Gamma \) point, are characterized by a finite gap between spectral branches, yielding a linear dispersion of electrons at such point, as \( \epsilon(K) = \epsilon_F \) in graphene, and \( V \)-singularity of DOS at \( \epsilon_v \) (curve 1 in Fig. 1c). The behavior of a real part of Green function \( \text{Re} \, G(\epsilon) \) near the Fermi level, i.e. \( \epsilon(K) = 0 \) (curve 2 in Fig. 1c) demonstrates, that various sorts of defects should localize elementary excitations near this level [5].

It should be noted, that in perfect structure of graphene, the atoms of different sublattices (A (●) and B (○) - Fig. 1a) are physically equivalent, which means that their local Green functions, and eventually, local densities of states (LDOS) are coincident. This equivalency should be obviously broken by introduction of defects in one of sublattices. Then electron spectra for the atoms, pertaining to different sublattices should differ. The imperfection, built by atoms of particular sublattice, is represented by a zig-zag boundary. In this case, as is clearly demonstrated by Fig. 1a, similar to vacancy, the atomic bonds are broken in one sublattice only, say the sublattice \( A \), Fig. 1a). In contrast to vacancy, which is the point defect and is breaking translational symmetry along all directions in the crystal [5 – 7], it is conserved along extended defect of zig-zag type. In this direction the one-dimensional vector of reciprocal lattice \( \mathbf{b} = (0, \beta) \), quasi-wave vector \( \mathbf{k} = (0, \kappa) \) can be introduced, and Hamiltonian (1) in a form of Jacobi matrix [11,12] is written as:

\[
\mathbf{H}_{ik} = a_i(\kappa) \delta_{ik} - b_i(\kappa) \left( \delta_{i,k+1} + \delta_{i+1,k} \right) ; \quad i,k = 0,1,2,\ldots,\infty ,
\]  

(3)

where all diagonal matrix elements \( a_i(\kappa) \) with a probable exception of the first one, are zero, while non-diagonal elements \( b_i(\kappa) = a(\kappa) = 2J \cos \frac{\kappa a}{2} \) for even values of \( i \) and \( b_i(\kappa) = \beta = J \) - for odd ones. Construction of 2D first Brillouin zone for perfect graphene and 1D first Brillouin zone for considered problem are presented in Fig. 1a. The non-zero value of a diagonal matrix element (3)
$a_{0}(\kappa)$ can result from relaxation of interactions at the boundary. Assuming these processes to occur on the atoms with dangling bonds only, it is written as

$$\Lambda(\kappa) = 2J \cos \kappa \alpha$$  \hspace{1cm} (4)

The local Green function $G^{(0)}(\epsilon, \kappa, \Lambda)$, corresponding to the row of atoms of sublattice $A$, which lie on zig-zag – boundary (taken as the reference row - $n=0$), can be written in a form of infinite continuous fraction [13, 14], which can be transformed as follows:

$$G^{(0)}(\epsilon, \kappa, \Lambda) = \frac{1}{2} \frac{\epsilon^{2} + 2\Lambda(\kappa)\epsilon + \beta^{2} - \alpha^{2}(\kappa) + Z(\epsilon) \cdot \sqrt{(\epsilon^{2} - \epsilon_{0}^{2})(\epsilon^{2} - \epsilon_{g}^{2})}}{\Lambda(\kappa)\epsilon^{2} + [\Lambda^{2}(\kappa) + \beta^{2}]\epsilon + \Lambda(\kappa)[\beta^{2} - \alpha^{2}(\kappa)\epsilon]}$$  \hspace{1cm} (5)

with the introduced variables: $\epsilon_{0}^{2} = \lbrack \alpha(\kappa) + \beta \rbrack$ and $\epsilon_{g}^{2} = \lbrack \alpha(\kappa) - \beta \rbrack$. The function

$$Z(\epsilon) = \Theta(-\epsilon_{0} - \epsilon) + i \cdot \Theta(\epsilon + \epsilon_{0}) \Theta(\epsilon - \epsilon_{g}) + \Theta(\epsilon + \epsilon_{g}) \Theta(\epsilon_{g} - \epsilon)$$

is determined by a form of Green function both inside and out of double-connected band of quasi-continuous spectrum $\mathcal{D} = \lbrack -\epsilon_{0}(\kappa), -\epsilon_{g}(\kappa) \rbrack \bigcup \lbrack \epsilon_{g}(\kappa), \epsilon_{0}(\kappa) \rbrack$. For $\epsilon \in \mathcal{D}$ function $G^{(0)}(\epsilon, \kappa, \Lambda)$ includes imaginary part, which determines an energy distribution inside the band of quasi-continuous spectrum of the atoms of row $n = 0$.

In the absence of relaxation on the boundary, namely at $\Lambda(\kappa) = 0$, denominator (5) equals $-2\beta^{2}(\kappa)\epsilon$ and function (4) gains pole at $\epsilon = 0$, i.e. on the Fermi level, located in the gap $\lbrack -\epsilon_{g}(\kappa), \epsilon_{g}(\kappa) \rbrack$. Among two roots of denominator (4) at $\Lambda(\kappa) \neq 0$ we should select then the one vanishing at $\Lambda \rightarrow 0$

$$\epsilon_{g}(\kappa, \Lambda) = \frac{\beta^{2} - \Lambda^{2}(\kappa)}{2\Lambda(\kappa)} \rightarrow 0 $$  \hspace{1cm} (7)

determines a dispersion law of the “border” wave, split of the band of quasi-continuous spectrum.

Residue of function (5) in this pole, determines intensity of corresponding discrete level, and, eventually, the portion of quasi-particles moved to the split-off wave. It equals to

$$\mu_{e}^{(0)}(\kappa, \Lambda) = \frac{-\beta^{2} - \Lambda^{2}(\kappa)}{\Lambda(\kappa)} \cdot \frac{\epsilon_{g}(\kappa, \Lambda)}{\sqrt{[\beta^{2} - \Lambda^{2}(\kappa)]^{2} + 4\alpha^{2}(\kappa)\Lambda^{2}(\kappa)}} \cdot \Theta\left(\frac{-\beta^{2} - \Lambda^{2}(\kappa)}{\Lambda(\kappa)} \cdot \epsilon_{g}(\kappa, \Lambda)\right).$$  \hspace{1cm} (8)

Condition of existence of the wave is that of positive meaning of the argument of Heaviside Theta function $\frac{-\beta^{2} - \Lambda^{2}(\kappa)}{\Lambda(\kappa)} \cdot \epsilon_{g}(\kappa, \Lambda) < 0$ and coincides with a condition of existence of non-dispersive gap level for the case $\Lambda = 0$, i.e. $\kappa \in [-M_{x}, K] \bigcup [K_{x}, M_{x}]$ (see Fig. 1a). A dispersion law near Fermi level is linear (relativistic) $\epsilon_{g}(K_{x} + x, \Lambda) \approx h\nu_{v_{f}} x$, where Fermi velocity $v_{f}$ equals to group velocity in the point $K_{x}$. The group velocity, corresponding to dispersion (7) as a function of quasi-wave vector $\kappa$, can be written in the following form:

$$v_{g}(\kappa) = \frac{\partial \epsilon(\kappa)}{\partial \kappa} h = -\frac{\partial \Lambda(\kappa)}{\partial \kappa} \frac{\mu_{e}^{(0)}(\kappa, \Lambda)}{h} - \frac{aJ^{2} \sin \alpha \kappa}{h} \cdot \frac{\Lambda(\kappa)}{\sqrt{(\Lambda^{2}(\kappa) - J)^{2} + 16J^{2}\Lambda^{2}(\kappa)\cos^{2} \kappa \alpha/2}}.$$  \hspace{1cm} (9)
Taking into account (4), \( v_{F}^{(g)} = \frac{a}{\hbar} \sqrt{3} \frac{J_{2} \tilde{J}}{J^{2} + \tilde{J}^{2}} = \sqrt{\frac{3}{2}} \frac{v_{F}^{(0)}}{J_{2} + \tilde{J}^{2}} \), where \( v_{F}^{(0)} = 3aJ/2\hbar \) is the Fermi level of perfect graphene with dispersion (2). When the relation (4) is valid, the dispersion law (7) assumes the states density \( g_{g}(\varepsilon) = \frac{a}{\pi \hbar} v_{g}^{-1}(\varepsilon) \), where \( v_{g}(\varepsilon) \) is the group velocity, represented as energy function. Contribution of gap functions into the LDOS of atoms from different rows (with \( n \geq 0 \)) is \( g_{g}^{(n)}(\varepsilon) = g_{g}^{(e)}(\varepsilon) \cdot \mu_{g}^{(n)}(\varepsilon) \), where

\[
\mu_{g}^{(2m+1)} = \mu_{g}^{(0)} \left( -\frac{\beta}{\Lambda} \right)^{2m} \left( \frac{\sqrt{\left( \beta^{2} - \Lambda^{2} \right)^{2} + 4 \alpha^{2} \Lambda^{2} - \left( \beta^{2} - \Lambda^{2} \right)}}{2 \Lambda \alpha} \right)^{2m} \xrightarrow{\Lambda \to 0} 0; \\
\mu_{g}^{(2m)} = \mu_{g}^{(0)} \left( -\frac{\beta}{\Lambda} \right)^{2m} \left( \frac{\sqrt{\left( \beta^{2} - \Lambda^{2} \right)^{2} + 4 \alpha^{2} \Lambda^{2} - \left( \beta^{2} - \Lambda^{2} \right)}}{2 \Lambda \alpha} \right)^{2m} \xrightarrow{\Lambda \to 0} \left( \frac{\alpha}{\beta} \right)^{2m}.
\]

In Fig. 2 the evolution of LDOS with increasing \( n \) is presented for \( \tilde{J} = 0.1J \).

![Fig. 2: Evolution of LDOS with increasing \( n \) for atoms labeled at insets of every fragment at excitation of the gap wave with dispersion (7).](image)

In a conduction band near \( \varepsilon_{F} \), peaks of width \( 2\tilde{J} \) appear in LDOS of atoms, pertained to sublattice A. They coincide with the spectral density \( \rho_{g}^{(e)}(\varepsilon) \) calculations (10) for even \( n \). These functions are presented in fragments of Fig. 2 by dashed lines, which perfectly superimpose on LDOS dependences. It should be noted, that at the same time LDOS keep their relativistic (Dirac) behavior, corresponding to the Fermi velocity of perfect graphene \( v_{F}^{(0)} \) at \( \varepsilon \to -0 \), while at \( \varepsilon \to +0 \) it corresponds to the Fermi velocity \( v_{F}^{(e)} \) in one-dimensional system. It means, that angular coefficient of linear dependence \( \rho_{g}^{(2m)}(\varepsilon \to +0) \) is related to the similar one \( \rho_{g}^{(2m)}(\varepsilon \to -0) \) as \( \sim \left[ v_{F}^{(0)}/v_{F}^{(e)} \right]^{2} \).
In sublattice B only LDOS of the boundary atom \((n = 1)\) reveals a small peak of the width \(2\hat{J}\). It coincides completely with spectral density \(\rho_g^{(1)}(\varepsilon)\). With a distance from the boundary the peaks become vanishingly small. Near Fermi level, the behavior of LDOS of the atoms from sublattice B is non-relativistic and correspondent to the quasi-particles of finite mass.

3. Electron spectrum of graphene with vacancy

Earlier [5 – 7], we have shown that the presence of isolated vacancy in graphene provides the sharp resonance in its electron spectrum at the Fermi level. This peak, similar to the case, considered above, takes place only in the LDOS of atoms from sub-lattice with dangling bonds on the atom, i.e. taking into account only the nearest-neighbor interactions in sublattice without vacancy. Atoms of another sublattice do not manifest such peak at Fermi level. The effect of near-to-nearest neighbor interactions over the whole structure of graphene was studied and demonstrated appearance of asymmetry in the DOS of graphene relative to Fermi level [7].

In Fig. 3, LDOS of the atoms, neighbor to vacancy, are presented for different distances from the vacancy. Relaxation of interactions between the nearest neighbors of vacancy is taken into account here. In consideration of interactions between the rest of the atoms we restricted ourselves to interactions of the nearest neighbors, but took into account interactions between vacancy’s nearest neighbors with a single dangling bond. These atoms are the second neighbors of each other. Their coupling constant is assumed to be \(0.1\hat{J}\). All of the LDOS are calculated using Jacobi matrix technique, with Hamiltonian \(H\) (1) presented in the basis, obtained by orthonormalization of sequence \(\{\mathcal{L}^\nu_{\Psi_0}\}_{\nu=0}^\infty\). For generating function \(\Psi_0\) we have chosen a single excitation of atoms, labeled in inset of each fragment.

![Fig. 3: Evolution of electron LDOS of the neighbors of vacancy with increasing distance from the latter.](image)

It is clearly seen that LDOS of atoms from vacancy-free sublattice have peaks, similar to those in Fig. 2. At \(\varepsilon \to -0\) these functions manifest a pronounced relativistic behavior. In another sublattice, LDOS of near-to-nearest neighbors of vacancy have small peaks, which rapidly decay with the distance from vacancy. This decay is accompanied by “restoration” of relativistic behavior of the considered dependences.
4. Conclusion

It is shown here, that in electron spectra of graphene with zig-zag boundary, there appear the waves, split of the bands of quasi-continuous spectrum, which propagate along the boundary and decay with a distance from it. They, moreover, propagate only via the atoms of sublattice, which contains atoms with dangling bond, appeared with a formation of boundary. Dispersion of these waves is determined by character of relaxation processes during formation of the boundary. Dispersion in electron spectrum is relativistic, but corresponds to the significantly less values of group velocity, compared to infinite monolayer of graphene. The similar behavior is demonstrated by electron spectra of graphene with isolated vacancy. The split gap waves lead to a formation on local densities of state of the sharp resonances, which enrich significantly electron spectrum near Fermi level, as well as phonon spectrum near the point of intersection of acoustic and optical branches, polarized normally to the plane of graphene monolayer [5,6]. These phonons within a considered frequency range do not practically interact with differently polarized phonons, and also possess high group velocities, which there dominant contribution to electron-phonon coupling. The presented results demonstrate a possibility to facilitate superconductivity in a graphene matter by a controlled creation of defects like vacancy or zig-zag boundary, which distort the atomic bonding in a particular sublattice of graphene monolayer.

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