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ENERGY STATES OF ELECTRONS IN LAYERED GRAPHENE

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Abstract: In this paper, the quantum Green's function method was used to find the electron energy spectra and determine their density of states for single and bilayer graphene. On this basis, the electronic contribution to the thermodynamic properties of these layered graphenes is analysed below and compared with experimental data.
Key words: Graphene, electrons, quantum Green's functions, energy spectra, specific heat.

INTRODUCTION

Carbon - one of the most common chemical elements in nature - is characterised by a large number of its allotropic modifications, which result from the ability of carbon atoms to form various *sp*-hybridized bonds: tetrahedral (sp^3 - diamond), trigonal (sp^2 - graphite, fullerene), and/or linear (*sp* - carbyne). The most common form of carbon - graphite - is a layered structure in which the interaction between the layers occurs through weak van der Waals bonds, in which the binding energy between the atoms in the layer is more than ten times greater than the interaction energy between the layers, which essentially determines the basic (physical and chemical) properties of graphite, but also the possibilities for separation into individual layers, each of which is graphene. Graphene can therefore be considered as a monolayer of graphite in which the carbon atoms are assembled into an ideal hexagonal crystal structure, as shown in Figure 1 (defined in [1]).
This structure consists of two equivalent triangular sublattices - in one atom of "type" A and in the other atom of "type" B, the atom type being a conditional feature, since both A and B is carbon atoms that do not differ from each other. Different symbols for them are only introduced to indicate the affiliation to "their" sublattice. The carbon atoms B form two triangular sublattices that interpenetrate each other.

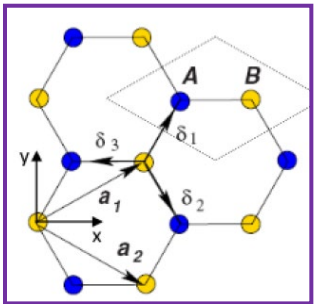

Fig. 1. *Graphene crystal structure*

Figure 1 shows two elementary translation vectors $\vec{a}_1$ and $\vec{a}_2$ and a primitive cell constructed on these vectors (rhomb - dashed line). Also shown in this figure are the vectors $\vec{\delta}_{1,2,3}$ connecting a particular carbon atom from one sublattice to its three nearest neighbours from another sublattice. Each of the two vectors transforms sublattice B into sublattice A.

The elementary translation vectors from Fig. 1 are given as:

$$\vec{a}_1 = a\left(\frac{3}{2}, \frac{\sqrt{3}}{2}\right); \quad \vec{a}_2 = a\left(\frac{3}{2}, -\frac{\sqrt{3}}{2}\right), \tag{1}$$

where the parameter $a = 0{,}142\ \mathrm{nm}$ - represents the side of the hexagon, i.e.,the distance between the nearest neighbors. The vectors from (1) have a length $a\sqrt{3}$ over which a primitive cell can be constructed – a rhombus connecting four "yellow" atoms. Within the rhombus, there must be a "blue" atom, so that the primitive cell contains two atoms.

The coordinates of the vector $\vec{\delta}_i,\ i = 1{,}2$, calculated from the selected atom of the sublattice B are then:

$$\vec{\delta}_1 = a\left(\frac{1}{2}, \frac{\sqrt{3}}{2}\right); \quad \vec{\delta}_2 = a\left(\frac{1}{2}, -\frac{\sqrt{3}}{2}\right); \quad \vec{\delta}_3 = a(1{,}0), \tag{2}$$

and the reciprocal lattice vectors are equal to:

$$\vec{b}_1 = \frac{2\pi}{3a}(1, \sqrt{3}); \quad \vec{b}_2 = \frac{2\pi}{3a}(1, -\sqrt{3}). \tag{3}$$

These vectors and the vectors $\vec{a}_{1,2}$ form a primitive cell in the form of a rhombus, and the Brillouin zone can be chosen in the form of a regular hexagon, as in Fig. 2 (defined in [1]).

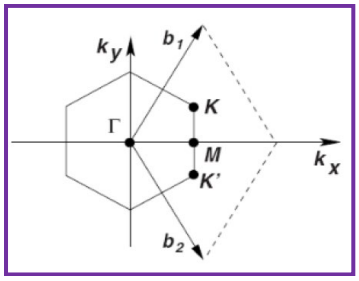

Fig. 2. *Primitive reciprocal lattice cell and Brillouin zone: point Γ is the centre of the zone, points K and K´ are Dirac points at the corners of the Brillouin zone, and point M lies in the centre of the side of the hexagon*

The points K and K´ lie alternately in the vertices of the Brillouin zone. All three points K are connected by reciprocal lattice vectors and are therefore equivalent (analogue all three points K´). No point K can be connected to any point K´ by the reciprocal lattice vector and they are therefore equivalent. Their coordinates are therefore:

$$\mathrm{K}: \frac{2\pi}{3\sqrt{3}a}(\sqrt{3}, 1); \quad \mathrm{K}': \frac{2\pi}{3\sqrt{3}a}(\sqrt{3}, -1). \tag{4}$$

The positions of these points and their surroundings essentially determine the electrical properties of graphene.

It is known [1,2–5] that three of the four valence electrons of each carbon atom in graphene are responsible for the formation of the lattice; each atom binds strongly to its three nearest neighbors via these three electrons in sp_2 hybridized states and forms chemical bonds. This means that the electronic wave functions are a linear combination of the atomic state functions 2*s*, $2p_x$, and $2p_y$. *Sp2-hybridised* electrons form a completely filled deep valence band. The fourth valence electron is therefore practically free. It is in the $2p_z$ state (the *z*-axis is perpendicular to the plane of the graphene) and can participate in elementary charge transport processes and optical transitions.

ELECTRON STATES IN MONOLAYERED GRAPHENE

The Hamiltonian of the graphene monolayer in the nearest neighbor approximation can be written in the form [6]:

$$H = \sum_{i,j} E_0 \left(a_i^+ a_i + b_{i+\delta_j}^+ b_{i+\delta_j}\right) + \sum_{i,j} T \left(a_i^+ b_{i+\delta_j} + b_{i+\delta_j}^+ a_i\right), \tag{5}$$

where E_0 - the energy corresponding to the $2p_z$ orbital of the carbon atom of graphene, a_i^+ and a_i are the operators for the creation and annihilation of the electron of the carbon atom belonging to the i-th atom of sublattice A, b_i^+ and b_i - the operators of the creation and annihilation of the electron of the carbon atom belonging to the i-th atom of sublattice B, T is the jump energy between the nearest neighboring atoms (between the sublattices A and B), δ_j is the distance between the nearest neighboring atoms. The space of the reciprocal lattice is moved by Fourier transformations [7] of the form:

$$\begin{aligned} a_i &= \frac{1}{\sqrt{N}}\sum_{\vec{k}} a_{\vec{k}} \mathrm{e}^{-i\vec{k}\cdot\vec{r}_i}; b_i = \frac{1}{\sqrt{N}}\sum_{\vec{k}} b_{\vec{k}} \mathrm{e}^{-i\vec{k}\cdot\vec{r}_i}; \\ a_i^+ &= \frac{1}{\sqrt{N}}\sum_{\vec{k}} a_{\vec{k}}^+ \mathrm{e}^{i\vec{k}\cdot\vec{r}_i}; b_i^+ = \frac{1}{\sqrt{N}}\sum_{\vec{k}} b_{\vec{k}}^+ \mathrm{e}^{i\vec{k}\cdot\vec{r}_i}. \end{aligned} \tag{6}$$

After the transformations, the Hamiltonian (5) turns into:

$$H = \sum_{\vec{k}} E_0\left(a_{\vec{k}}^+ a_{\vec{k}} + b_{\vec{k}}^+ b_{\vec{k}}\right) + \sum_{\vec{k}}\left[f\left(\vec{k}\right) a_{\vec{k}}^+ b_{\vec{k}} + f^*\left(\vec{k}\right) b_{\vec{k}}^+ a_{\vec{k}}\right], \tag{7}$$

where

$$f\left(\vec{k}\right) = \sum_i T\mathrm{e}^{i\vec{k}\cdot\delta_j} \rightarrow f^*\left(\vec{k}\right) = \sum_i T\mathrm{e}^{-i\vec{k}\cdot\delta_j}, \tag{8}$$

Is the Fourier transform of the „jump" energy.

To find the electron dispersion law in the graphene monolayer, quantum Green's functions of the form are sought:

$$\begin{aligned} G_{\mathrm{A}} &= \langle\langle a_{\vec{k}} \left| a_{\vec{k}}^+ \right\rangle\rangle; G_{\mathrm{B}} = \langle\langle b_{\vec{k}} \left| b_{\vec{k}}^+ \right\rangle\rangle; \\ G_{\mathrm{AB}} &= \langle\langle a_{\vec{k}} \left| b_{\vec{k}}^+ \right\rangle\rangle; G_{\mathrm{BA}} = \langle\langle b_{\vec{k}} \left| a_{\vec{k}}^+ \right\rangle\rangle. \end{aligned} \tag{9}$$

The notations $\langle\langle \cdots | \cdots \rangle\rangle$, which were first introduced by Bogolyubov and Tyablikov [8], represent the averaging of operators over the corresponding canonical ensemble. To find the Fourier figure of the corresponding Green's function, Heisenberg's equations of motionare used for the given Green's functions:

$$\varepsilon\langle\langle A|B\rangle\rangle = \langle[A,B]_\eta\rangle + \langle\langle[A,H]_\eta|B\rangle\rangle. \tag{10}$$

Here the designation η indicates whether we are dealing with commutators or anticommu–tators. Since we are talking about electrons (fermions), we are dealing with anticommutators. The labeling $\langle\cdots\rangle$ represents the mean value [9].

Using the commutation relations [7,10,11], the expression for Green's function results from the equations of motion:

$$G_{\mathrm{A}} = \left(\varepsilon - E_0 - \frac{\left|f(\vec{k})\right|^2}{\varepsilon - E_0}\right), \tag{11}$$

and from the theory of quantum Green's functions [7–12] it is known that the pole of the Fourier figure of the Green's function $\mathrm{Re}\, G^{-1} = 0, \varepsilon \equiv \varepsilon + i0$, determines the dispersion law or the energy spectrum of the corresponding particle for which the equation of motion is written, and from (11) follows:

$$\varepsilon_{\vec{k}} = E_0 \pm \left|f\left(\vec{k}\right)\right|. \tag{12}$$

In the vicinity of Dirac points with the coordinates $K = \left(\frac{2\pi}{3a}, \frac{2\pi}{3\sqrt{3}a}\right)$ the following expression results for the Fourier transformation (8) from the energy spectrum (12):

$$f(k) = \hbar v_{\mathrm{F}} q; v_{\mathrm{F}} = \frac{3Ta}{2\hbar}; q = \sqrt{k_x^2 + k_y^2}. \tag{13}$$

where are:

$$v_{\mathrm{F}} = \frac{3Ta}{2\hbar};\ q = \sqrt{k_x^2 + k_y^2}, \tag{14}$$

hopping rate and two-dimensional wave vector.

Expression (12) agrees with the expression obtained by the method of strong bonding [13], and the magnitude of E_0 corresponds to the energy of the Dirac point. If we calculate the

electron energy as the difference to this, we can formally assume it to be $E_0 = 0$. The energy spectrum of the charge carriers then results as follows:

$$\varepsilon = \hbar v_{\mathrm{F}} q. \tag{15}$$

As can be seen, the spectrum of charge carriers in the case of a single-layer graphene is linear in the vicinity of the Dirac points. The surroundings of the points K and K´ are called valleys in accordance with semiconductor physics (Fig. 3, from [1]).

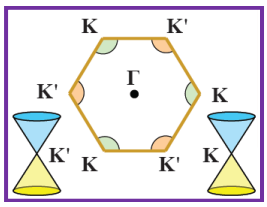

Fig. 3. *Energy spectrum in the vicinity of Dirac points*

The density of states of charge carriers in the graphene monolayer, based on the definition from the theory of Green's functions [7–12], is determined in this case as:

$$\begin{aligned} &g_{\pm}(\varepsilon) = \textstyle\sum_{k,\sigma} \delta(\varepsilon - \varepsilon_{\pm})\,; \varepsilon_{\pm} = \pm\hbar v_F q; \\ &g_{+}(\varepsilon) = 2 \cdot 2 \cdot \frac{A}{(2\pi)^2} \cdot 2\pi \int_0^{\infty} dqq\, \delta(\varepsilon - \hbar v_F q); \\ &g_{+}(\varepsilon) = \frac{2A}{\pi\hbar^2 v_F^2}\varepsilon; g_{-}(\varepsilon) = \frac{2A}{\pi\hbar^2 v_F^2}(-\varepsilon); \Rightarrow g(\varepsilon) = \frac{2A}{\pi\hbar^2 v_F^2}|\varepsilon|. \end{aligned} \tag{16}$$

Degeneracy is accounted for here by spin and by valleys.

ELECTRON STATES IN BILAYERED GRAPHENE

In bilayer graphene, there are transitions of charge carriers both between the atoms in the layer and between the layers. In the general case, there are various transitions between the layers, andthe most important one is$T_{\perp}$, i.e. the transition at an angle of 90º [14], which is marked in Fig. 4.

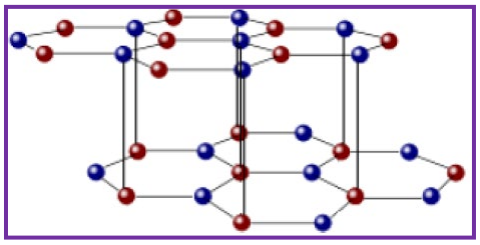

Fig. 4. *Crystal structure of bilayer graphene. The lines connecting the two graphene layers represent the interaction$T_{\perp}$ which is the most important of all coverage integrals (from [14])*

Hamiltonian for bilayer graphene is of the form [6]:

$$\begin{aligned} H = &\textstyle\sum_i E_0\left(a_i^{+(1)}a_i^{(1)} + b_i^{+(1)}b_i^{(1)}\right) + \sum_i E_0\left(a_i^{+(2)}a_i^{(2)} + b_i^{+(2)}b_i^{(2)}\right) + \\ &+ \textstyle\sum_{i,j} T\left(a_i^{+(1)}b_j^{(1)} + b_j^{+(1)}a_i^{(1)}\right) + \sum_{i,j} T\left(a_i^{+(2)}b_j^{(2)} + b_j^{+(2)}a_i^{(2)}\right) + \\ &+ \textstyle\sum_{i,j} T_{\perp}\left(a_i^{+(1)}b_j^{(2)} + b_j^{+(2)}a_i^{(1)}\right). \end{aligned} \tag{17}$$

Here $a_i^{+(1)}a_i^{(1)}$and$b_i^{+(1)}b_i^{(1)}$ are operators of creation and annihilation of electrons of sublattices A and B of the first layer, and $a_i^{+(2)}a_i^{(2)}$ and $b_i^{+(2)}b_i^{(2)}$ are operators of creation and annihilation of electrons of sublattices A and B of the second layer.

If we enter the space of the reciprocal lattice and use the corresponding Fourier transforms as in the expressions (6), we obtain:

$$H = \sum_{\vec{k}} \left[f(\vec{k}) \left(a_{\vec{k}}^{+(1)} b_{\vec{k}}^{(1)} + a_{\vec{k}}^{+(2)} b_{\vec{k}}^{(2)} \right) + \right.$$
$$\left. + f^*(\vec{k}) \left(b_{\vec{k}}^{+(1)} a_{\vec{k}}^{(1)} + b_{\vec{k}}^{+(2)} a_{\vec{k}}^{(2)} \right) \right] +$$
$$+ \sum_{\vec{k}} T_\perp \left(a_{\vec{k}}^{+(1)} b_{\vec{k}}^{(2)} + b_{\vec{k}}^{+(2)} a_{\vec{k}}^{(1)} \right). \quad (18)$$

In this expression it is already substituted that $E_0 = 0$.
If you now set up the equations of motion for the corresponding Green's functions, as in the case of single-layer graphene, and then solve the system of equations for the Green's functions, we find:

$$G_{\mathrm{AA}}^{(11)} = \left[\varepsilon - \frac{|f(\vec{k})|^2}{\varepsilon} - T_\perp^2 \left(\varepsilon - \frac{|f(\vec{k})|^2}{\varepsilon} \right)^{-1} \right]^{-1}, \quad (19)$$

for the electronic energy spectrum in the vicinity of the Dirac points, the dispersion law of two-layer graphene thus results in the following form:

$$\varepsilon = \pm \sqrt{v_{\mathrm{F}}^2 \hbar^2 k^2 + \frac{T_\perp^2}{2} \pm \sqrt{v_{\mathrm{F}}^2 \hbar^2 k^2 T_\perp^2 + \frac{T_\perp^4}{4}}}. \quad (20)$$

In contrast to a monolayer, bilayer graphene has an energy spectrum without a gap and a parabolic shape (as in Fig. 5 from [14]). Near the Dirac points, the energy spectrum of bilayer graphene can be described as follows:

$$\varepsilon \approx \pm \frac{\hbar^2 q^2}{2m^*}; m^* = \frac{|T_\perp|}{2v_{\mathrm{F}}^2} = 0{,}054\, m_{\mathrm{e}}, \quad (21)$$

where m^* is the effective mass of charge carriers, and m_{e} is the mass of electrons at rest.

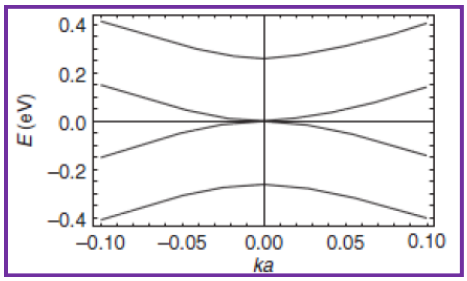

***Fig. 5**. Energy spectrum of electrons in bilayer graphene*

The density of charge carrier states, using the same procedure as in the graphene monolayer [15,16], was determined in the following form:

$$g(\varepsilon) = \sum_{\vec{k},\sigma} \delta\left(\varepsilon - \frac{\hbar^2 q^2}{2m^*} \right) = 2 \frac{A}{(2\pi)^2} \cdot 2\pi \int_0^\infty q dq\, \delta\left(\varepsilon - \frac{\hbar^2 q^2}{2m^*} \right);$$
$$\varepsilon < 0: \quad g(\varepsilon) = 0; \quad (22)$$
$$\varepsilon > 0: \quad \delta\left(\varepsilon - \frac{\hbar^2 q^2}{2m^*} \right) = \sum_{k_*} \frac{\delta(k-q)}{\left| \frac{d}{dq} \left(\varepsilon - \frac{\hbar^2 q^2}{2m^*} \right) \right|_{k=k_*}}; \quad \varepsilon = \frac{\hbar^2 q^2}{2m^*};$$

$$\delta\left(\varepsilon-\frac{\hbar^2q^2}{2m^*}\right)=\frac{\delta\left(k-\sqrt{2m^*\varepsilon/\hbar^2}\right)}{\frac{\hbar^2}{m}\sqrt{\frac{2m^*\varepsilon}{\hbar^2}}}+\frac{\delta\left(k+\sqrt{2m^*\varepsilon/\hbar^2}\right)}{\frac{\hbar^2}{m}\sqrt{\frac{2m^*\varepsilon}{\hbar^2}}}$$

$$g(\varepsilon)=\frac{A}{\pi}\cdot\sqrt{\frac{2m^*\varepsilon}{\hbar^2}}\frac{1}{\frac{\hbar^2}{m^*}\sqrt{\frac{2m^*\varepsilon}{\hbar^2}}}=\frac{A}{\pi}\frac{m^*}{\hbar^2}\theta(\varepsilon)$$

CONCLUSION

In this paper, the quantum Green's function method was used to determine the energy spectra of single and bilayer graphene. It is common to use the strong bond method (developed in [13]) in the late 1940s to determine the energy spectra of graphene. Quantum Green functions originates from quantum field theory and was used in condensed matter physics in the 1960s [18]. It should be noted that this field of science is expanding and is far from complete, as new areas of application are constantly being found. In this sense, this method is increasingly applied to new materials such as graphene and other low-dimensional systems. In this work, the energy spectra of single and bilayer graphene as well as the density of states for these structures were determined. All results are in agreement with the experimental data available to us [19–21].

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