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Effect of impurities ordering in the electronic spectrum and conductivity of graphene

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ABSTRACT

By carrying out a computation in the Lifshitz tight-binding one-electron model, we obtain the energy spectrum and electrical conductance of graphene, in the presence of substitutional impurity atoms, thus assessing the influence of the latter. In the weak-scattering approximation, we study specific features of the electron energy spectrum in the gap region having width $\eta|\delta|$ and centered at the point $y\delta$, arising because of the ordering of substitutional impurity atoms on nodes of the crystal lattice. Here η is the parameter of ordering, δ is the difference of the scattering potentials of impurity atoms and carbon atoms, and y is the impurity concentration. It is shown that if the ordering parameter η is close to $\eta_{\max} = 2y$, $y < 1/2$, the plot of the density of electron states has peaks on the edges of the energy gap. Those peaks correspond to impurity levels. As the ordering parameter η decreases, the impurity levels split into the impurity bands. The regions of localization of electron impurity states, which arise at the edges of the spectrum and edges of the energy gap, are investigated.

1. Introduction

Most studies of the energy spectrum of graphene are based on the density functional theory [1] and are limited to numerical calculations, with the undoubted merit of showing the opening of a gap in the energy spectrum of graphene caused by the presence of an impurity [2–7]. It is obvious, though, that it is insufficient to restrict the analysis to numerical calculations only, in order to understand the nature of this effect. Instead, the influence of impurities on the energy spectrum and properties of graphene should be also described within a simple, but adequate model presenting the exact analytical solutions.

In the Lifshitz tight-binding one-electron model, the theory of reconstruction of the spectrum of graphene caused by an increase in the concentration of point impurities was developed in works [8–11]. Moreover, the possibility of the metal-dielectric transition in such system was predicted. Results of the analytical consideration of a reconstruction of the spectrum were confirmed with the help of a numerical experiment. It allowed one to verify the existence of a quasigap filled by localized states and showed its dominant role in the localization of the scattering by pairs and triples of impurity centers.

The numerical calculations within the Kubo–Greenwood quantum-mechanical formalism in the Lifshitz tight-binding one-electron model were performed in [12,13] to study the influence of impurity atoms or atoms adsorbed on the surface on the electronic structure and electrical conductance of graphene. In those works, the method of reduction of the Hamiltonian to the three-diagonal form was developed to study the influence of completely ordered impurity atoms on the energy spectrum and electrical conductance of graphene in the ballistic and diffusive modes of conductance. In work [13] in the Lifshitz tight-binding one-electron model, it was found that the gap 0.45 eV in width appears in the energy spectrum of electrons of graphene deposited on a potassium substrate. There, it was assumed that the appearance of this gap is associated with a change in the symmetry of the crystal. This assumption was corroborated in works [15–17]. Within the Lifshitz tight-binding one-electron model, the influence of the ordering of impurities on the energy spectrum and electrical conductance of graphene was considered in work [18]. It was established that the ordering of substitutional atoms on nodes of the crystal lattice [also] causes the appearance of a gap $\eta|\delta|$ in width in the energy spectrum of graphene centered at the point $y\delta$, where η is the ordering pa-

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rameter, δ is the difference of the scattering potentials of impurity atoms and carbon, and y is the impurity concentration. We note that the conclusions in work [18] were based on the results of analytic studies of the energy spectrum and electrical conductance of graphene performed in the approximation of coherent potential. However, the domain of convergence of the cluster expansion used in [18] for Green's function and the domain of validity of the approximation of coherent potential, as well as the specific features of the electron energy spectrum near the gap arising at the ordering of impurity atoms, were not analyzed. These themes will be considered in the present work.

2. Theoretical model

The Hamiltonian in the Lifshitz tight-binding one-electron model describing the one-electron states of graphene with substitutional impurity atoms can be written in the form

$$H = \sum_{in} |in\rangle v_{in} \langle in| + \sum_{in, i'n' \neq in} |in\rangle h_{in,i'n'} \langle i'n'|, \tag{1}$$

where $h_{in,i'n'}$ is a matrix element (hopping integral) of the Hamiltonian that is nondiagonal in the Wannier representation and is independent of the random distribution of atoms in the accepted approximation of diagonal disorder; v_{in} is a diagonal matrix element taking the value v^A or v^B if atom A or B is located, respectively, at node in; i is the number of a sublattice, and n is the number of a node of the sublattice.

Hamiltonian (1) describes the states of an electron with its energy, which belongs to the $2p_z$-energy band corresponding to the $(pp\pi)$-coupling [19].

Like work [18], the opening of a gap in the energy spectrum of graphene at the ordering of the impurity will be studied with the use of the theory of multiple scattering. This theory allows one to leave the framework of Born's approximation and to consider a change in the energy spectrum at the scattering of electrons by impurity atoms. Such approach is based on the method of Green's functions and the cluster expansion of the scattering matrix T. As the zero approximation, we choose the coherent potential approximation

Neglecting the small contribution of the processes of scattering on clusters composed of three and more atoms, we present the density of one-electron states of graphene as

$$\begin{aligned} g(\varepsilon) &= \frac{1}{\nu} \sum_{i,\lambda} P^{\lambda 0i} g^{\lambda 0i}(\varepsilon), \\ g^{\lambda 0i}(\varepsilon) &= -\frac{2}{\pi} \operatorname{Im} \Bigg\{ \tilde{G} + \tilde{G} t^{\lambda 0i} \tilde{G} + \sum_{\substack{(lj) \neq (0i) \\ \lambda'}} P^{\lambda' lj/\lambda 0i} \times \\ &\quad \times \tilde{G} \big[t^{\lambda' lj} + T^{(2)\lambda 0i, \lambda' lj} \big] \tilde{G} \Bigg\}_{0i,0i}, \end{aligned} \tag{2}$$

where $\nu = 2$ is the number of sublattices in graphene. The first sum in formula (2) describes the density of electron states in graphene in the coherent potential approximation. Here,

$$T^{(2)n_1 i_1, n_2 i_2} = \big[I - t^{n_1 i_1} \tilde{G} t^{n_2 i_2} \tilde{G} \big]^{-1} t^{n_1 i_1} \tilde{G} t^{n_2 i_2} \big[I + \tilde{G} t^{n_1 i_1} \big], \tag{3}$$

where

$$t^{n_1 i_1} = [I - \tilde{v}_{in} \tilde{G}]^{-1} \tilde{v}_{in} \tag{4}$$

is the operator of scattering on one node, I is the identity operator, and $\tilde{G}(\varepsilon)$ is retarded Green's function of the effective medium described by the coherent potentials σ_i $(i = 1, 2)$.

In formula (2), $P^{\lambda 0i}$ is the probability for atoms of sort $\lambda = A, B$ to fill the node $0i$ of the crystal sublattice $i = 1, 2$;

$$P^{B01} = y_1 = y + \frac{1}{2}\eta, \quad P^{B02} = y_2 = y - \frac{1}{2}\eta, \quad P^{A01} = 1 - P^{B01}, \tag{5}$$

y is the concentration of impurity atoms, and $P^{\lambda' lj/\lambda 0i}$ is the probability for an atom of sort λ' to fill node lj under the condition that an atom of sort λ fills node $0i$ (parameter of binary interatomic correlations in the filling of nodes of the crystal lattice by atoms).

The matrix elements of Green's function of the effective medium $\tilde{G}_{0i,0i}(\varepsilon)$ can be presented in the form

$$\begin{aligned} \tilde{G}_{0i,0i}(\varepsilon) &= \frac{1}{N} \sum_{\mathbf{k}} \tilde{G}_{ii}(\mathbf{k}, \varepsilon), \\ \tilde{G}_{11}(\mathbf{k}, \varepsilon) &= \frac{\varepsilon - \sigma_2}{D(\mathbf{k}, \varepsilon)}, \\ \tilde{G}_{22}(\mathbf{k}, \varepsilon) &= \frac{\varepsilon - \sigma_1}{\varepsilon - \sigma_2} \tilde{G}_{11}(\mathbf{k}, \varepsilon), \\ D(\mathbf{k}, \varepsilon) &= (\varepsilon - \sigma_1)(\varepsilon - \sigma_2) - h_{12}(\mathbf{k}) h_{21}(\mathbf{k}), \end{aligned} \tag{6}$$

where $h_{ii'}(\mathbf{k})$ is the Fourier-transform of the hopping integral. Relations (6) are obtained in the nearest-neighbors approximation by the Fourier transformation of the hopping integral. The wave vector in formulas (6) varies in the limits of the Brillouin zone of graphene.

The coherent potential σ_i $(i = 1, 2)$ satisfies the equation

$$\begin{aligned} &\sigma_i = \langle v_i \rangle - (v_A - \sigma_i) \tilde{G}_{0i,0i}(\varepsilon)(v_B - \sigma_i); \\ &\langle v_i \rangle = (1 - y_i) v_A + y_i v_B. \end{aligned} \tag{7}$$

Setting $v_A = 0$ in formula (8), we get

$$\langle v_i \rangle = y_i \delta, \tag{8}$$

where

$$\delta = v_B - v_A \tag{9}$$

is the difference of the scattering potentials of components of graphene.

The analytic description of the influence of the ordering of impurity atoms on the energy spectrum of graphene will be carried on in the limiting case of weak scattering $|\delta/w| \ll 1$. Here, $w = 3|\gamma_1|$ is a half-width of the energy band of pure graphene, and $\gamma_1 = (pp\pi)$ is the hopping integral [19].

Green's function of the effective medium for the electron energies close to the Dirac point takes the form

$$\begin{aligned} \tilde{G}_{01,01}(\varepsilon) &= -\frac{S_1(\varepsilon - \sigma_2)}{\pi \hbar^2 v_F^2} \ln \sqrt{1 - \frac{w^2}{(\varepsilon - \sigma_1)(\varepsilon - \sigma_2)}}, \\ \tilde{G}_{02,02}(\varepsilon) &= -\frac{S_1(\varepsilon - \sigma_1)}{\pi \hbar^2 v_F^2} \ln \sqrt{1 - \frac{w^2}{(\varepsilon - \sigma_1)(\varepsilon - \sigma_2)}}, \end{aligned} \tag{10}$$

where $v_F = \frac{3|\gamma_1| a_0}{2\hbar}$ is the velocity of an electron on the Fermi level; and a_0 is the distance between the nearest neighbors, and $S_1 = 3\sqrt{3} a_0^2/2$ is the area of an elementary cell of graphene, and $\hbar$ is Planck's constant.

The solution of the system of equations (7), (10) under the condition $|\delta/w| \ll 1$ is as follows:

$$\tilde{G}_{01,01}(\varepsilon) = -\frac{S_1(\varepsilon-\sigma_2')}{\pi\hbar^2\upsilon_F^2}\ln\sqrt{1-\frac{w^2}{(\varepsilon-\sigma_1')(\varepsilon-\sigma_2')}},$$
$$\tilde{G}_{02,02}(\varepsilon) = -\frac{S_1(\varepsilon-\sigma_1')}{\pi\hbar^2\upsilon_F^2}\ln\sqrt{1-\frac{w^2}{(\varepsilon-\sigma_1')(\varepsilon-\sigma_2')}},$$
$$\sigma_1' = y_1\delta - y_1(1-y_1)\delta^2\frac{S_1(\varepsilon-y_2\delta)}{\pi\hbar^2\upsilon_F^2} \times \ln\sqrt{1-\frac{w^2}{(\varepsilon-y_1\delta)(\varepsilon-y_2\delta)}}, \quad (11)$$
$$\sigma_2' = y_2\delta - y_2(1-y_2)\delta^2\frac{S_1(\varepsilon-y_1\delta)}{\pi\hbar^2\upsilon_F^2} \times \ln\sqrt{1-\frac{w^2}{(\varepsilon-y_1\delta)(\varepsilon-y_2\delta)}},$$

for $sign(\varepsilon-\sigma_1') = -sign(\varepsilon-\sigma_2')$ and

$$\tilde{G}_{01,01}(\varepsilon) = -\frac{S_1(\varepsilon-\sigma_2')}{\pi\hbar^2\upsilon_F^2}\ln\sqrt{\frac{w^2}{(\varepsilon-\sigma_1')(\varepsilon-\sigma_2')}-1} - i\frac{S_1|\varepsilon-\sigma_2'|}{2\hbar^2\upsilon_F^2},$$
$$\tilde{G}_{02,02}(\varepsilon) = -\frac{S_1(\varepsilon-\sigma_1')}{\pi\hbar^2\upsilon_F^2}\ln\sqrt{\frac{w^2}{(\varepsilon-\sigma_1')(\varepsilon-\sigma_2')}-1} - i\frac{S_1|\varepsilon-\sigma_1'|}{2\hbar^2\upsilon_F^2},$$
$$\sigma_1' = y_1\delta - y_1(1-y_1)\delta^2\frac{S_1(\varepsilon-y_2\delta)}{\pi\hbar^2\upsilon_F^2} \times \ln\sqrt{\left|\frac{w^2}{(\varepsilon-y_1\delta)(\varepsilon-y_2\delta)}-1\right|}, \quad (12)$$
$$\sigma_1'' = -y_1(1-y_1)\delta^2\frac{S_1|\varepsilon-y_2\delta|}{2\hbar^2\upsilon_F^2},$$
$$\sigma_2' = y_2\delta - y_2(1-y_2)\delta^2\frac{S_1(\varepsilon-y_1\delta)}{\pi\hbar^2\upsilon_F^2} \times \ln\sqrt{\left|\frac{w^2}{(\varepsilon-y_1\delta)(\varepsilon-y_2\delta)}-1\right|},$$
$$\sigma_2'' = -y_2(1-y_2)\delta^2\frac{S_1|\varepsilon-y_1\delta|}{2\hbar^2\upsilon_F^2},$$

for $sign(\varepsilon-\sigma_1') = sign(\varepsilon-\sigma_2')$.

In Eqs. (11)–(12), σ_i' and σ_i'' are, respectively, the real and imaginary parts of coherent potentials $\sigma_i, i = 1, 2$.

The analysis of formulas (11) and (12) indicates that, at the ordering of impurity atoms, the gap $\eta|\delta|$ in width centered at the point $y\delta$ arises in the energy spectrum of graphene. For $\delta > 0$ or $\delta < 0$, the gap is placed, respectively, to the right or left from the Dirac point on the energy scale. As is seen from formulas (2) and (11), the density of electronic states $g(\varepsilon) = 0$ in the approximation of coherent potential for this energy region.

In this case, formulas (2) and (13) imply that the density of states tends to infinity near the gap edge. This is caused by the presence of other components in the formulas for the coherent potentials σ_1' and σ_2' (12). The width of the given energy region is

$$\left|\frac{\Delta\varepsilon(\eta)}{w}\right| = \frac{w}{\eta|\delta|}\exp\left(-\frac{2y\pi w^2}{3\sqrt{3}\eta\delta^2(1-y+\eta/2)(y-\eta/2)}\right);$$

$$0 < \eta \le 2y. \quad (13)$$

Outside the indicated peak, the density of states increases by a linear rule with the distance from the gap edge:

$$g(\varepsilon) = \frac{S_1(\varepsilon-y\delta)}{\pi\hbar^2\upsilon_F^2}, \quad \left|\frac{\Delta\varepsilon(\eta)}{w}\right| < \left|\frac{\varepsilon-\sigma_i'}{w}\right| \le \left|\frac{\delta}{w}\right|. \quad (14)$$

The estimate of the peak (13) (carried out under the condition that the density of states on the peak slope is twice more than its value at a point of the adjacent minimum.

3. Results

The result is obtained for a small value of the scattering potential $|\delta/w| \ll 1$. The dependence of the density of states on the energy for an arbitrary value of the scattering potential has a more complicated form.

In Fig. 1, we show the results of numerical calculations of the density of states of graphene for the scattering potential $\delta/w = -0.3$, hypothetical value of the substitutional impurity concentration $y = 1/2$, and order parameter $\eta = 1/2$. Numerical calculations are performed according to the formulas (2), (6), and (7). It is seen from Fig. 1 that the gap arises in the energy spectrum of graphene at the ordering of a substitutional impurity, $\eta = 1/2$. The fine structure of the energy dependence of the density of states near the gap is presented in Fig. 1, b, c, d.

For the sake of comparison, Fig. 2 shows the energy dependence of the density of states for the scattering potential $\delta/w = -0.3$, concentration $y = 0.2$, and different values of the order parameter η. It is seen from Fig. 2 that the gap width increases with the order parameter, which agrees qualitatively with the conclusions obtained in the limiting case of weak scattering $|\delta/w| \ll 1$.

For values of the ordering parameter η close to the maximum one $\eta_{max} = 2y$, $y < 1/2$, there exists only a small fraction of impurity atoms that are placed on the sublattice mainly occupied by carbon atoms. In this case, the plot of the density of electron states on the edges of the energy gap arising at the impurity ordering has peaks corresponding to impurity levels (Fig. 1, c, d). As the ordering parameter tends to the maximum value $\eta_{max} = 2y$, the width of region (13) for the energies of electrons in impurity states approaches zero.

If the ordering parameter η decreases, this fraction of impurity atoms increases, and the impurity levels split into impurity bands (Fig. 2, a). As the ordering parameter η decreases, the width of region (13) for the energies of electrons in impurity states increases. At the full ordering of a substitutional impurity ($\eta = 1$, $y = 1/2$), the indicated peaks on the plot of the density of states are absent. This follows from formula (12), where the second terms in the formulas for the coherent potentials σ_1' and σ_2' become equal to zero.

In Figs. 3–4, we present the dependence of the energy of an electron on the wave vector for graphene with completely ordered substitutional impurity ($\eta = 1$) with the hypothetical concentration $y = 1/2$ in two cases where the scattering potential: $\delta > 0$ (Fig. 3) or $\delta < 0$ (Fig. 4). The dependence of the energy of an electron on the wave vector for the completely ordered arrangement of an impurity is given by the formula following from the equation for poles of Green's function (6):

$$\varepsilon_{1,2}(\mathbf{k}) = \frac{1}{2}\delta \pm \sqrt{\frac{1}{4}\delta^2 + \gamma_1^2\left(1+4\cos\left(\frac{k_x\sqrt{3}a}{2}\right)\cos\left(\frac{k_y a}{2}\right)+4\cos^2\left(\frac{k_y a}{2}\right)\right)}, \quad (15)$$
$$a = \sqrt{3}a_0.$$

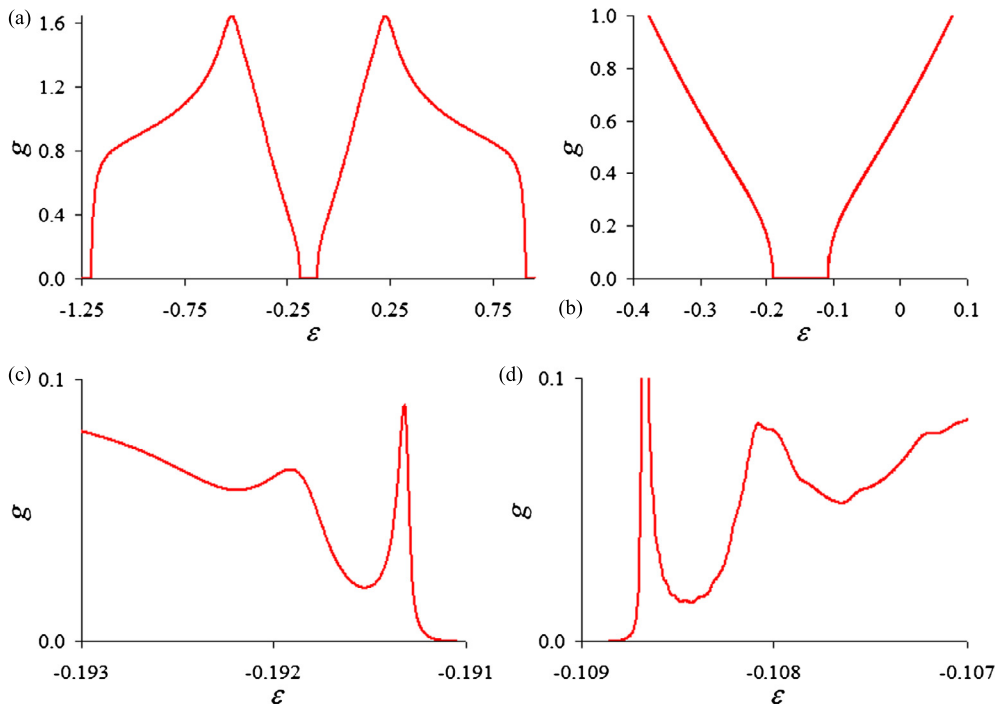

Fig. 1. Dependence of the density of electron states on the energy for graphene with the concentration of the substitutional impurity atoms $y = 1/2$ at values of the scattering potential $\delta/w = -0.3$ and the order parameter $\eta = 1/2$. The whole region of energy values (a), gap region (b), and energy regions in vicinities of the left (c) and right (d) edges of the gap are shown.

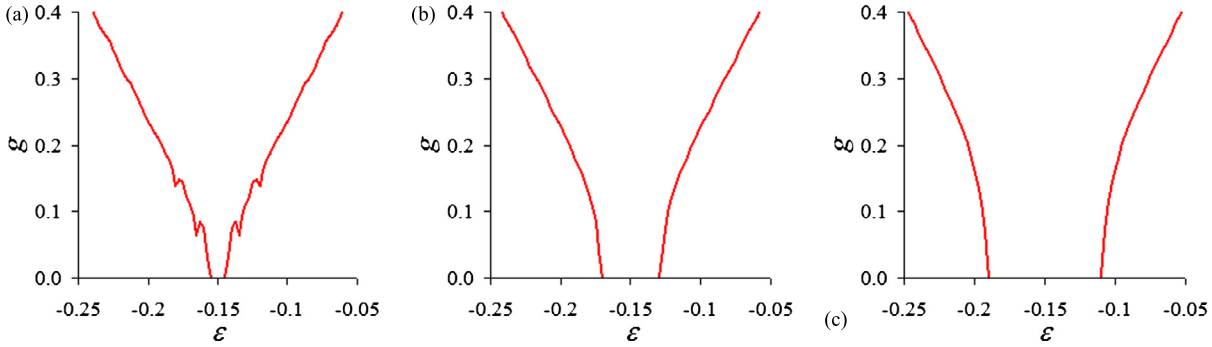

Fig. 2. Dependence of the density of electron states on the energy at values of the scattering potential $\delta/w = -0.3$ and the impurity concentration $y = 0.2$ with different order parameters $\eta = 0.1$ (a), $\eta = 0.25$ (b), $\eta = 0.4$ (c). The energy region in a vicinity of the gap is shown.

In a vicinity of the Dirac point, the dependence of the energy on the wave vector takes the form

$$\varepsilon_{1,2}(\mathbf{k}) = \frac{1}{2}\delta \pm \left(\frac{1}{2}|\delta| + \frac{\hbar^2 v_F^2}{|\delta|}k^2\right). \tag{16}$$

It is seen from Figs. 3–4 that, at the ordering of a substitutional impurity with the stoichiometric concentration $y = 1/2$, the gap appears in the energy spectrum of graphene. For the scattering parameter $\delta > 0$ or $\delta < 0$, the gap is located, respectively, to the right or left from the Dirac point on the energy scale.

If the Fermi level falls in the domain of a gap arising at the ordering, then the electrical conductance $\sigma_{\alpha\alpha} \to 0$, i.e., a metal-dielectric transition appears.

If the Fermi level is located outside the gap, then we see from formula (15) that the electrical conductance increases with the order parameter η.

At the concentration $y = 1/2$, if the order parameter $\eta \to 1$, the electrical conductance of graphene $\sigma_{\alpha\alpha} \to \infty$, i.e., graphene passes to the state with ideal conductance.

Here, the analytical study of the influence of the ordering of an impurity on the energy spectrum and electrical conductance of graphene was executed in the approximation of coherent potential. In order to evaluate the corrections to this approximation caused by the contribution of the processes of scattering of electrons by

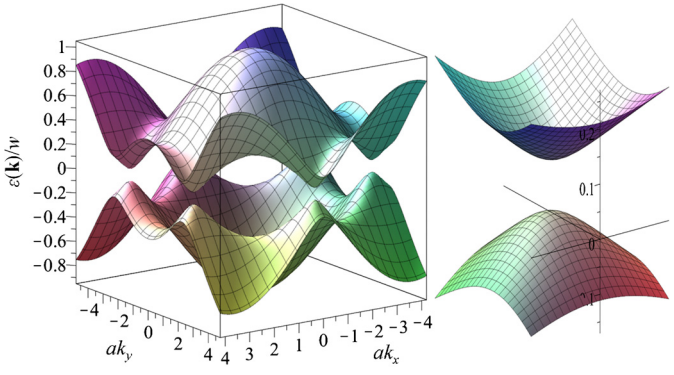

Fig. 3. Dependence of the electron energy on the wave vector for graphene with completely ordered impurity with the concentration $y = 1/2$ and scattering parameter $\delta/w = 0.1$. On the right, the region of the Dirac point is shown.

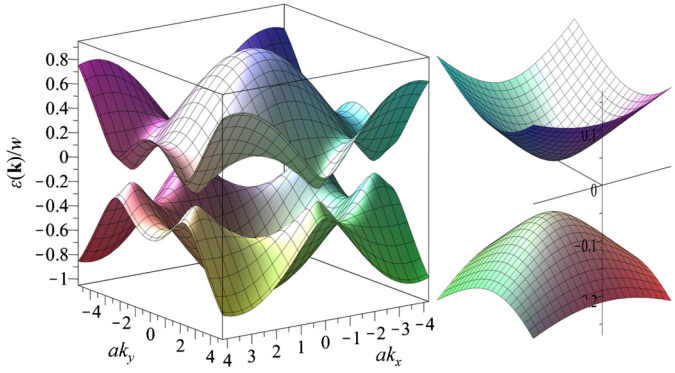

Fig. 4. Dependence of the electron energy on the wave vector for graphene with completely ordered impurity with the concentration $y = 1/2$ and scattering parameter $\delta/w = -0.1$. On the right, the region of the Dirac point is shown.

clusters of two, three, etc. atoms, the following parameter was introduced in [20]:

$$\gamma_i(\varepsilon) = \left| \left\langle \left(t^{oi}(\varepsilon)\right)^2 \right\rangle \sum_{lj \neq 0i} \tilde{G}_{oi,lj}(\varepsilon) \tilde{G}_{lj,oi}(\varepsilon) \right|;$$

$$\left\langle \left(t^{oi}(\varepsilon)\right)^2 \right\rangle = (1 - y_i)\left(t^{Aoi}(\varepsilon)\right)^2 + y_i\left(t^{Boi}(\varepsilon)\right)^2. \tag{17}$$

This parameter was analyzed in [14], where its following representation was given:

$$\gamma_i(\varepsilon) = \left| P_i(\varepsilon)/\left(1 + P_i(\varepsilon)\right) \right|;$$

$$P_i(\varepsilon) = -\frac{\langle (t^{0i}(\varepsilon))^2 \rangle}{1 + \langle (t^{0i}(\varepsilon))^2 \rangle (\tilde{G}_{0i,0i}(\varepsilon))^2} \times \left(\frac{1}{1 + \langle (t^{0i}(\varepsilon))^2 \rangle (\tilde{G}_{0i,0i}(\varepsilon))^2} \frac{d}{d\varepsilon} \tilde{G}_{0i,0i}(\varepsilon) + \left(\tilde{G}_{0i,0i}(\varepsilon)\right)^2 \right) \tag{18}$$

As was shown in work [14], the contributions of the processes of scattering of electrons on clusters to the density of states and the electrical conductance decrease and are guided by some small parameter $\gamma_i(\varepsilon)$, as the number of atoms in a cluster increases. The parameter $\gamma_i(\varepsilon)$ is small in a broad region of changes of characteristics of the crystal, except for narrow energy intervals on the edges of the spectrum and on the edges of the energy gap.

It follows from the formulas (19), (4), and (10) for the order parameter $\gamma_i(\varepsilon)$ that the width of this energy interval on the gap edges is as follows:

$$\left| \frac{\Delta\varepsilon'(\eta)}{w} \right| = \exp\left(-\frac{\pi w^2}{3\sqrt{3}\delta^2(1 - y - \eta/2)(y + \eta/2)} \right). \tag{19}$$

In the energy region (19), the parameter $\gamma_i(\varepsilon)$ takes values $1/2 \leq \gamma_i(\varepsilon) \leq 1$. Thus, the processes of scattering on clusters give a significant contribution to the density of states at the energies of electrons lying in interval (19). We note that formula (15) for the electrical conductance of graphene cannot be used, if the Fermi level falls in interval (19) of energies at the gap edges.

4. Conclusions

It is shown that if the ordering parameter η is close to the maximum value $\eta_{\max} = 2y$, $y < 1/2$, the plot of the density of electron states contains peaks corresponding to impurity levels. These peaks arise at the edges of the energy gap arising at the ordering of impurity atoms (Fig. 1, c, d). As the ordering parameter η decreases, the levels split into impurity bands (Fig. 2, a).

In the approximation of coherent potential, graphene with an impurity is described by the model of effective periodic medium. The above consideration indicates that the approximation of coherent potential cannot be used for the narrow spectral regions due to the appearance of the localized impurity states in graphene. Formula (15) for the electrical conductance of graphene cannot be used as well, if the Fermi level falls in the interval of energies at the gap edges.

The made conclusions on the appearance of a gap in the energy spectrum of graphene at the ordering of an impurity agree with the results of numerical calculations in [21].

Author contributions

All five co-authors, S. P. Repetsky, I. G. Vyshyvana, S. P. Kruchinin, B. Vlahovic, S. Bellucci, contributed equally to the calculations in the work. S. Bellucci and S. Kruchinin jointly supervised the work and wrote the main manuscript text. All authors reviewed the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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