

# Influence of the ordering of impurities on the appearance of an energy gap of graphene

Stefano Bellucci, INFN First Researcher, INFN Graphene Flagship Core 1 Head,  
Director NATO SPS Project «Nanocomposites based Photonic Crystal Sensors»  
Head of NEXT Nanotechnology Laboratory

S.P. Kruchinin, S.P. Repetsky

# Influence of the ordering of impurities on the appearance of an energy gap and on the electrical conductance of graphene //Scientific Reports

*S.P. Repetsky<sup>1</sup>, I.G. Vyshyvana<sup>1</sup>, S.P. Kruchinin<sup>2</sup>, Stefano Bellucci<sup>3</sup>*

<sup>1</sup> Institute of High Technologies, Taras Shevchenko National University of Kiev,

4-g, Academician Glushkov Ave., Kiev 03022, Ukraine

e-mail: srepetsky0208@gmail.com

<sup>2</sup> M.M. Bogolyubov Institute for Theoretical Physics of the NAS of Ukraine,

14-b, Metrolohichna Str., Kiev 03680, Ukraine

<sup>3</sup>INFN-Laboratori Nazionali di Frascati, Via E. Fermi, 40, 00044 Frascati, Italy

# Graphene

In recent times, a special attention has been paid to the possibility of a targeted modification of graphene with the help of purposely introduced impurities, formed defects, and atoms or chemical functional groups deposited on a surface. In this case, wide possibilities to change the physical properties of graphene are opened, due to the controlled introduction of impurities by the method of ion implantation.

The quasirelativistic spectrum of charge carriers determines the unique properties of graphene and, simultaneously, hampers the use of graphene in field-effect transistors due to the absence of a gap in its spectrum. It is known that the impurities can lead to the appearance of such a gap, whose width depends on the type of impurities and their concentration. 3

# Graphene

The numerical calculations The recent investigations of the energy spectrum of graphene are based on the density functional theory. It is worth to note the advantages of this theory related to the self-consistent meta-generalized gradient approximation within the projector-augmented-wave method [1] which is realized with softwares WASP and GAUSSIAN [1]. made within the method have demonstrated the appearance of a gap in the energy spectrum of graphene caused by the presence of an impurity. However, in order to clarify the nature of this effect, it is necessary to supplement the mentioned numerical calculations by analytic studies of the influence of impurities on the energy spectrum and properties of graphene.

# Energy spectrum

1. Sun J., Marsman M., Csonka G. I., Ruzsinszky A., Hao P., Kim Y.-S., Kresse G., and Perdew J.P. Self-consistent meta-generalized gradient approximation within the projector-augmented-wave method, Phys. Rev. B **84**, 035117 (2011).

Works [2-4] present the theory of reconstruction of the spectrum of graphene, which occurs at a growth in the concentration of point-like impurities, and foresee the possibility of the metal--dielectric transition in such a system. The course of the reconstruction of the spectrum, which was predicted on the basis of the analytic calculations, was confirmed with the help of a numerical experiment.

# Energy spectrum

2. Skrypnyk Yu.V., Loktev V.M. Impurity effects in a two-dimensional system with the Dirac spectrum, Phys. Rev. B.V. 73, No. 24.P. 241402(R) (2006).
3. Skrypnyk Yu.V., Loktev V.M. Local spectrum rearrangement in impure graphene, Phys. Rev. B. V. 75. P. 245401 (2007).
4. Pershoguba S.S., Skrypnyk Yu.V., Loktev V.M. Numerical simulation evidence of spectrum rearrangement in impure graphene, Phys. Rev. B. V. 80, No.21. P. 214201 (2009).

# Energy spectrum

In work [5], the influence of the ordering of atoms on the energy spectrum and the electrical conductance of an alloy was studied analytically in the above-mentioned one-band model. It was found [5] that, at the long-range ordering of the alloy, a gap appears in the energy spectrum of electrons. Its width is equal to the difference of the scattering potentials of the components of the alloy.

5. V. F. Los', S. P. Repetsky. A theory for the electrical conductivity of an ordered alloy, *J. Phys.: Condens. Matter*. V. 6: P. 1707–1730 (1994).

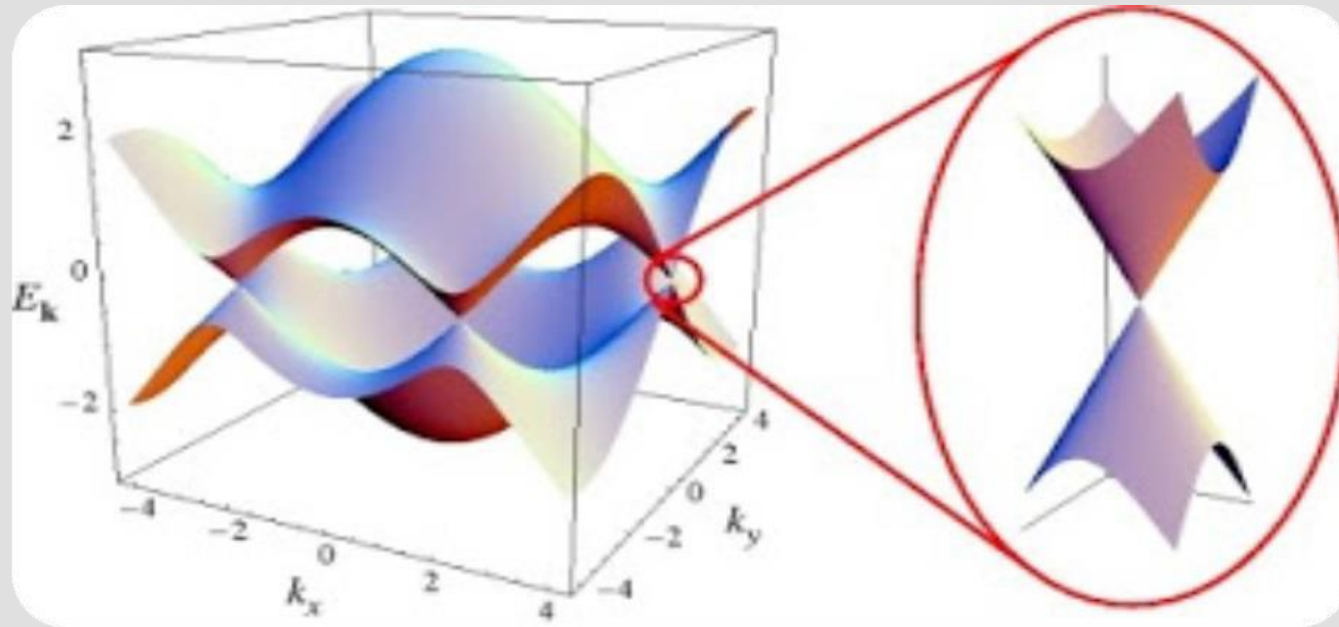
# Energy spectrum

The Hamiltonian describing the one-electron states of graphene with substitutional impurity atoms can be presented in the form [5]

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



# Energy spectrum of pure graphene



# Energy spectrum

The Hamiltonian of graphene can be presented in the form

$$H = \tilde{H} + \tilde{V}$$

$$\tilde{H} = \sum_{in} |in\rangle \sigma_i \langle in| + \sum_{in, i'n' \neq in} |in\rangle h_{in, i'n'} \langle i'n'|$$

$$\tilde{V} = \sum_{in} \tilde{v}_{in}$$

$$\tilde{v}_{in} = |in\rangle (v_{in} - \sigma_i) \langle in|$$

# Energy spectrum

The retarded Green function of graphene, which is an analytic function of the complex energy  $z$  in the upper half-plane, reads

$$G(z) = (z - H)^{-1}$$

The Green function satisfies the Dyson equation

$$G = \tilde{G} + \tilde{G}\tilde{V}G$$

where

$$\tilde{G} = (z - \tilde{H})^{-1}$$

# Energy spectrum

The  $T$ -matrix of the scattering by a random potential is determined by the relation [5]

$$G = \tilde{G} + \tilde{G}T\tilde{G}$$

and satisfies the equation

$$T = \tilde{V} + \tilde{V}\tilde{G}T$$

# Energy spectrum

The  $T$ -matrix as an infinite series [5]:

$$T = \sum_{(n_1 i_1)} t^{n_1 i_1} + \sum_{(n_1 i_1) \neq (n_2 i_2)} T^{(2) n_1 i_1, n_2 i_2} + \dots$$

Here,

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

where

$$t^{ni} = \left[ I - \tilde{v}_{in} \tilde{G} \right]^{-1} \tilde{v}_{in}$$

# Energy spectrum

We present the density of one-electron states of graphene in the form

$$g(\varepsilon) = \frac{1}{\nu} \sum_{i,\lambda} P^{\lambda 0i} g^{\lambda 0i}(\varepsilon)$$

$$g^{\lambda 0i}(\varepsilon) = -\frac{2}{\pi} \operatorname{Im} \left\{ \tilde{G} + \tilde{G} t^{\lambda 0i} \tilde{G} + \sum_{\substack{(lj) \neq (0i) \\ \lambda'}} P^{\lambda'lj/\lambda 0i} \times \right. \\ \left. \times \tilde{G} \left[ t^{\lambda'lj} + T^{(2)\lambda' 0i, \lambda'lj} + T^{(2)\lambda'lj, \lambda' 0i} \right] \tilde{G} \right\}_{0i, 0i}$$

where  $g^{\lambda 0i}(\varepsilon)$  is conditional partial density of states,  $\nu = 2$

is the number of sublattices of graphene.

# The parameter of atomic ordering

In these formulas,  $p_{\lambda 0i}$  is the probability of the occupation of node  $0i$  of the crystal lattice ( $i = 1, 2$ ) by atoms of the sort  $\lambda = A, B$ :

$$p^{B01} = y_1 = y + \frac{1}{2}\eta, \quad p^{B02} = y_2 = y - \frac{1}{2}\eta, \quad p^{A0i} = 1 - p^{B0i},$$

where  $y$  is the concentration of impurity atoms, and  $\eta$  is the parameter of atomic ordering.

# The electrical conductance of graphene

Using the Kubo—Greenwood formula and neglecting the contribution of the processes of scattering by clusters composed of at least three atoms, we get the static electrical conductance of graphene in the form ( $T=0$ ) [5]:





where  $\tilde{K}_{ss'}(v_\alpha, \varepsilon) = \tilde{G}_s(\varepsilon)v_\alpha\tilde{G}_{s'}(\varepsilon)$ ,

$\tilde{G}_r(\varepsilon)$  and  $\tilde{G}_a(\varepsilon)$  are the retarded and advanced Green functions,

$t_s^{\lambda'lj}(\varepsilon)$  and  $T_s^{(2)\lambda'lj,\lambda 0i}(\varepsilon)$  are scattering operators determined by the Green function  $\tilde{G}_s(\varepsilon)$ ,  $\delta_{ss'}$  is Kronecker's symbol,  $\Omega_1 = v\Omega_0$  is the volume of an elementary cell of graphene, and  $\Omega_0$  is the volume per atom.

# The coherent potential

The coherent potential is determined from the condition  $\langle t^{n_i i} \rangle = 0$ .

$$\sigma_i = \langle v_i \rangle - (v_A - \sigma_i) \tilde{G}_{0i,0i}(\varepsilon) (v_B - \sigma_i); \quad \langle v_i \rangle = (1 - y_i) v_A + y_i v_B.$$

Setting  $v_A = 0$ , we get

$$\langle v_i \rangle = y_i \delta,$$

where

$$\delta = v_B - v_A$$

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

# The coherent potential approximation

$$g(\varepsilon) = -\frac{2}{\pi\nu} \text{Im} \sum_i \tilde{G}_{0i,0i}(\varepsilon) = -\frac{2}{\pi\nu N} \text{Im} \sum_{i,\mathbf{k}} \tilde{G}_{ii}(\mathbf{k}, \varepsilon),$$

$$\begin{aligned} \sigma_{\alpha\alpha} &= -\frac{e^2\hbar}{2\pi\Omega_1} \sum_i \left[ v_\alpha \left( \tilde{G}(\varepsilon) - \tilde{G}^*(\varepsilon) \right) v_\alpha \left( \tilde{G}(\varepsilon) - \tilde{G}^*(\varepsilon) \right) \right]_{0i,0i} = \\ &= -\frac{e^2\hbar}{2\pi\Omega_1 N} \sum_{i,\mathbf{k}} \left[ v_\alpha(\mathbf{k}) \left( \tilde{G}(\mathbf{k}, \varepsilon) - \tilde{G}^*(\mathbf{k}, \varepsilon) \right) v_\alpha(\mathbf{k}) \left( \tilde{G}(\mathbf{k}, \varepsilon) - \tilde{G}^*(\mathbf{k}, \varepsilon) \right) \right]_{0i,0i}. \end{aligned}$$

# The Green function

We calculated  $h_{ii'}(\mathbf{k})$  in the approximation of nearest neighbors. The Fourier transform of the Green function in this approximation takes the form

$$\begin{aligned}\tilde{\mathbf{G}}_{11}(\mathbf{k}, \varepsilon) &= \frac{\varepsilon - \sigma_2}{D(\mathbf{k}, \varepsilon)}, & \tilde{\mathbf{G}}_{12}(\mathbf{k}, \varepsilon) &= \frac{h_{21}(\mathbf{k})}{D(\mathbf{k}, \varepsilon)}, \\ \tilde{\mathbf{G}}_{21}(\mathbf{k}, \varepsilon) &= \frac{h_{12}(\mathbf{k})}{D(\mathbf{k}, \varepsilon)}, & \tilde{\mathbf{G}}_{22}(\mathbf{k}, \varepsilon) &= \frac{\varepsilon - \sigma_1}{\varepsilon - \sigma_2} \tilde{\mathbf{G}}_{11}(\mathbf{k}, \varepsilon),\end{aligned}$$

$$D(\mathbf{k}, \varepsilon) = (\varepsilon - \sigma_1)(\varepsilon - \sigma_2) - h_{12}(\mathbf{k})h_{21}(\mathbf{k}).$$

# The Green function

In the used model, the main contribution to the energy spectrum of electrons in the middle of the zone is given by the values of the wave vector  $\mathbf{k}$ , which belong to the domains near Dirac points. The Brillouin zone contains two such domains, where

$$h_{12}(\mathbf{k}) = h_{21}(\mathbf{k}) = \hbar v_F k,$$

$v_F = \frac{3|\gamma_1|a_0}{2\hbar}$  is the velocity of the electron on the Fermi level, and  $\gamma_1 = (pp\pi)$  and  $a_0$  are the hopping integral and the distance between the nearest neighbors, respectively.

# The Green function

$$\tilde{G}_{01,01}(\varepsilon) = -\frac{S_1(\varepsilon - \sigma_2)}{\pi d \hbar^2 v_F^2} \ln \sqrt{1 - \frac{w^2}{(\varepsilon - \sigma_1)(\varepsilon - \sigma_2)}},$$

$$\tilde{G}_{02,02}(\varepsilon) = -\frac{S_1(\varepsilon - \sigma_1)}{\pi d \hbar^2 v_F^2} \ln \sqrt{1 - \frac{w^2}{(\varepsilon - \sigma_1)(\varepsilon - \sigma_2)}},$$

where  $w = 3|\gamma_1|$  is the half-width of the energy band of pure graphene, and  $S_1 = 3\sqrt{3}a_0^2/2$  is the area of an elementary cell of graphene.

# The energy gap

Let us consider the influence of the ordering of atoms on the energy spectrum of electrons of graphene with a substitutional impurity in the limiting case of weak scattering where  $|\delta/w| \ll 1$ .

In this case, the solution of the system of equations is as follows:

$$\tilde{G}_{01,01}(\varepsilon) = -\frac{S_1(\varepsilon - \sigma'_2)}{\pi d \hbar^2 v_F^2} \ln \sqrt{1 - \frac{w^2}{(\varepsilon - \sigma'_1)(\varepsilon - \sigma'_2)}},$$

$$\tilde{G}_{02,02}(\varepsilon) = -\frac{S_1(\varepsilon - \sigma'_1)}{\pi d \hbar^2 v_F^2} \ln \sqrt{1 - \frac{w^2}{(\varepsilon - \sigma'_1)(\varepsilon - \sigma'_2)}},$$



# The energy gap

$$\sigma'_1 = y_1 \delta - y_1(1 - y_1) \delta^2 \frac{\Omega_1(\varepsilon - \sigma'_2)}{\pi \hbar^2 v_F^2} \ln \sqrt{\frac{w^2}{|(\varepsilon - \sigma'_1)(\varepsilon - \sigma'_2)|} + 1},$$
$$\sigma'_2 = y_2 \delta - y_2(1 - y_2) \delta^2 \frac{\Omega_1(\varepsilon - \sigma'_1)}{\pi \hbar^2 v_F^2} \ln \sqrt{\frac{w^2}{|(\varepsilon - \sigma'_1)(\varepsilon - \sigma'_2)|} + 1}.$$

where  $\text{sign}(\varepsilon - \sigma'_1) = -\text{sign}(\varepsilon - \sigma'_2)$ ,

# The energy gap

and

$$\tilde{G}_{01,01}(\varepsilon) = -\frac{S_1(\varepsilon - \sigma'_2)}{\pi d \hbar^2 v_F^2} \ln \sqrt{\frac{w^2}{(\varepsilon - \sigma'_1)(\varepsilon - \sigma'_2)} - 1} - i \frac{S_1(\varepsilon - \sigma'_2)}{2d \hbar^2 v_F^2},$$

$$\tilde{G}_{02,02}(\varepsilon) = -\frac{S_1(\varepsilon - \sigma'_1)}{\pi d \hbar^2 v_F^2} \ln \sqrt{\frac{w^2}{(\varepsilon - \sigma'_1)(\varepsilon - \sigma'_2)} - 1} - i \frac{S_1(\varepsilon - \sigma'_1)}{2d \hbar^2 v_F^2},$$

# The energy gap

- $\sigma_1' = y_1 \delta - y_1(1 - y_1) \delta^2 \frac{\Omega_1(\varepsilon - \sigma_2')}{\pi \hbar^2 v_F^2} \ln \sqrt{\frac{w^2}{|(\varepsilon - \sigma_1')(\varepsilon - \sigma_2')|}} - 1,$
- $\sigma_1'' = -y_1(1 - y_1) \delta^2 \frac{\Omega_1(\varepsilon - \sigma_2')}{2 \hbar^2 v_F^2},$
- $\sigma_2' = y_2 \delta - y_2(1 - y_2) \delta^2 \frac{\Omega_1(\varepsilon - \sigma_1')}{\pi \hbar^2 v_F^2} \ln \sqrt{\frac{w^2}{|(\varepsilon - \sigma_1')(\varepsilon - \sigma_2')|}} - 1,$
- $\sigma_2'' = -y_2(1 - y_2) \delta^2 \frac{\Omega_1(\varepsilon - \sigma_1')}{2 \hbar^2 v_F^2},$
- where  $\text{sign}(\varepsilon - \sigma_1') = \text{sign}(\varepsilon - \sigma_2')$ .

# The energy gap

The analysis of formula shows 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. The energies  $\varepsilon$  corresponding to the energy gap edges are determined from the equations:  $\varepsilon - \sigma'_1 = 0$ ,  $\varepsilon - \sigma'_2 = 0$ . In the considered approximation of weak scattering  $|\delta/w| \ll 1$ , the second terms in the formulas for  $\sigma'_1$  and  $\sigma'_2$  can be neglected.

# The energy gap

Relation implies that the maximum value of the parameter of ordering equals  $\eta_{max} = 2y, y \leq 1/2$ . For the complete ordering of impurity atoms, the energy gap width is equal to  $2y|\delta|$ , i.e., it is proportional to the concentration of an impurity  $y$  and to the modulus of the difference of the scattering potentials for components of graphene  $\delta$ . For  $y = 1/2$ , the gap width takes the maximum value equal to  $|\delta|$ . For  $\delta > 0$  and  $\delta < 0$ , the energy gaps lie, respectively, to the right and to the left from the Dirac point on the energy scale.

# Influence of the ordering of impurities on the electrical conductance of graphene

Formulas imply that, at the energies outside the region of the gap, the density of electron states reads

$$g(\varepsilon) = \frac{\Omega_1[\varepsilon - (\sigma'_1 + \sigma'_2)/2]}{\pi \hbar^2 v_F^2}.$$

Let us study the electrical conductance of graphene in the case where the Fermi level is located outside the gap.

$$\sigma_{\alpha\alpha} = \frac{2e^2 \hbar v_F^2}{\pi^2 a_0^2 d \left( y^2 - \frac{1}{4} \eta^2 \right) \delta^2},$$

where  $d$  is the thickness of graphene.

# Energy spectrum of graphene with adsorbed potassium atoms

We study the influence of adsorbed impurities, namely potassium atoms, on the energy spectrum of electrons in graphene [6]. The electron states of the system are described in the frame of the self-consistent multiband strong-coupling model. It is shown that, at the ordered arrangement of potassium atoms corresponding to a minimum of the free energy, the gap arises in the energy spectrum of graphene [7].

The unit cell includes two carbon atoms and one potassium atom, the latter being placed on the graphene surface above a carbon atom at a distance of 0.286 nm, the energy gap is equal to  $\sim 0.25$  eV.

# Energy spectrum of graphene with adsorbed potassium atoms

6. S. P. Repetsky, I. G. Vyshyvana, E. Ya. Kuznetsova, S. P. Kruchinin. Energy spectrum of graphene with adsorbed potassium atoms. International Journal of Modern Physics B Vol. 32 (2018) 1840030 (5 pages).
7. S.P. Kruchinin, S.P. Repetsky, and I.G. Vyshyvana. Spin-Dependent Transport of Carbon Nanotubes with Chromium Atoms. © Springer Science+Business Media Dordrecht 2016 J. Bonca, S. Kruchinin (eds.), ~ Nanomaterials for Security, NATO Science for Peace and Security Series A: Chemistry and Biology, DOI 10.1007/978-94-017-7593-9\_7.



# Energy spectrum of graphene with adsorbed potassium atoms

