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A Theoretical Study of the Band Structure and the Electronic Edge States in Graphene and Fluorographene

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Abstract. In this work electron transport properties of graphene and fluorographene are investigated. The bandstructure of infinite graphene or fluorographene layer is obtained by using Linear Combination of Atomic Orbitals approach. Non-Equilibrium Green's function method is applied to find density of states in infinite layer as well as at the edge of the semi-infinite layer. The graphene-fluorographene interface problem is studied. It is shown that the interaction between graphene and fluorographene edge eliminates electron states near the Fermi level.

1 Introduction

Graphene is a two-dimensional hexagonal lattice of carbon atoms. Since the first success in deriving graphene layers from graphite [1] there has been a lot of investigations concerning possible applications of this material in nanoelectronics. Graphene-based transistors would be much smaller and effective that the silicon ones [2]. The other point of interest is the graphene-derived 2D-structures. It has been observed that the fluorination changes graphene electronic properties significantly [3] so that it becomes an insulator (pristine graphene is a semimetal). Thus one can use the fluorination to isolate graphene regions, and a point of interest is to study edge states effects in the interfaces between graphene and *fluorographene* (i.e. fully-fluorinated graphene).

In this work we investigate the basic properties of graphene and fluorographene layers such as bandstructure and density of electron states (DOS) per unit cell. Then we consider an interface between semi-infinite layers of graphene and fluorographene and compare the edge DOS with the results for graphene-vacuum and fluorographene-vacuum interfaces.

This study can be continued for the purpose of treating a problem of the finite gap of fluorinated graphene between two semi-infinite graphene layers.

2 Methods

2.1 Linear Combination of Atomic Orbitals

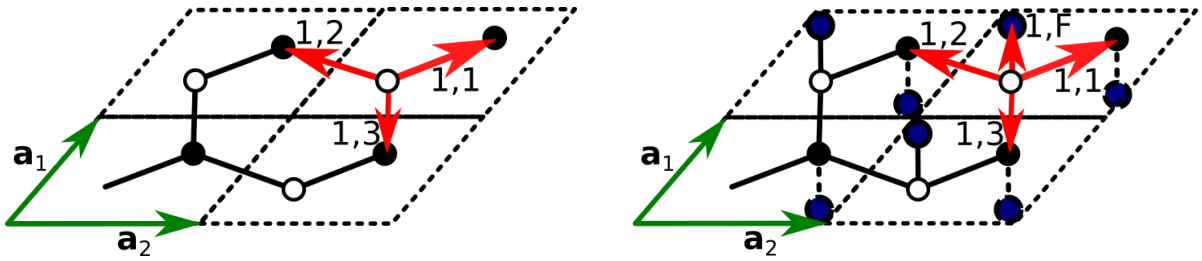
In order to study the bandstructure of an infinite graphene or fluorographene layer we apply Linear Combination of Atomic Orbitals method (LCAO, proposed in [4]). In the single-electron approach one can write the following expression for the wavefunction of the electron in the lattice:

$$\psi_{\mathbf{k}}(\mathbf{x}) = \sum_{\mathbf{r}\in G} e^{i\mathbf{kr}}\phi(\mathbf{x}-\mathbf{r}),$$

where $\mathbf{k}$ is the wave vector corresponding to this Bloch's wave, G is a set of unit cell positions, $\phi(\mathbf{x})$ is the wavefuction of unit cell of the lattice. In the case of a 2D hexagonal structure $G = \{m\mathbf{a}_1 + n\mathbf{a}_2 | m, n \in \mathbb{Z}\}$ ($\mathbf{a}_1, \mathbf{a}_2$ are shown in Figure 1).

In graphene layer each unit cell consists of two carbon atoms, in fluographene there are two carbon atoms and two fluorine atoms per cell. Notice that $\mathbf{k} = (k_x, k_y, 0)^T$ as we deal with 2D structures. The main idea of the LCAO method is that the wavefuction of the unit cell can be expressed as a linear combination of all the orbitals of all the atoms in the unit cell:

$$\phi(\mathbf{x}) = \sum_{i,\alpha} b^{i,\alpha}\phi_{i,\alpha}(\mathbf{x}),$$



(a) graphene (b) fluorographene

Figure 1: four rhombus unit cells of graphene (a) and fluorographene (b) lattices. Green vectors are the primitive vectors $\mathbf{a}_1$ and $\mathbf{a}_2$. Red vectors are directed from the carbon atom number 1 towards its nearest neighbors.

where i indicates atom in the unit cell and α denotes its orbital, $i \in \{1,2\}$, $\alpha \in \{s, p_x, p_y, p_z\}$ for carbons and $i \in \{3,4\}$, $\alpha \in \{p_x, p_y, p_z\}$ for fluorine atoms.

The bandstructure arises from the eigenvalue problem:

$$\tilde{H}|\psi_{\mathbf{k}}\rangle = E_{\mathbf{k}}\psi_{\mathbf{k}},$$

where $\tilde{H}$ is the Hamiltonian.

We can multiply both sides of this equation by $\phi_{i,\alpha}$:

$$\langle\phi_{i,\alpha}|\tilde{H}|\psi_{\mathbf{k}}\rangle = E_{\mathbf{k}}\langle\phi_{i,\alpha}|\psi_{\mathbf{k}}\rangle.$$

Let us neglect all the overlap integrals, so $\langle\phi_{i,\alpha}|\psi_{\mathbf{k}}\rangle = b^{i,\alpha}$ and we obtain a homogeneous system of linear equations on the coefficients $b^{i,\alpha}$:

$$\sum_{j,\beta} H^{i,\alpha}_{j,\beta}(\mathbf{k}) b^{j,\beta} = E_{\mathbf{k}} b^{i,\alpha},$$

where $H^{i,\alpha}_{j,\beta}(\mathbf{k}) = \sum_{\mathbf{r}\in G} e^{i\mathbf{kr}}\langle\phi_{i,\alpha}(\mathbf{x})|\tilde{H}|\phi_{j,\beta}(\mathbf{x}-\mathbf{r})\rangle$.

In this sum we take into account only nearest-neighbors interaction terms. Each carbon atom has three neighboring carbon atoms (and also one fluorine atom in the fluorographene layer). Let us denote the unit direction vectors from the carbon atom to his neighbors as $\delta_{i,1} = (l_{i,1}, m_{i,1}, n_{i,1})^T$, $\delta_{i,2}$, $\delta_{i,3}$,$\delta_{i,F}$, where $i \in \{1,2\}$ is the index of this carbon atom. Also we have the following relation: $\delta_{1,*} = -\delta_{2,*}$.

The matrix elements $H^{i,\alpha}_{j,\beta}(\mathbf{k})$ can be expressed in terms of Slater-Koster parameters [5]:

$$H^{1,\alpha}_{1,\alpha} = H^{2,\alpha}_{2,\alpha} = \varepsilon^C_\alpha; \quad H^{3,\alpha}_{3,\alpha} = H^{4,\alpha}_{4,\alpha} = \varepsilon^F_\alpha; \quad H^{i,\alpha}_{i,\beta} = 0 \text{ for } \alpha \neq \beta; \quad H^{1,s}_{2,s} = V^C_{ss\sigma}\sum_{j=1}^{3} e^{i\mathbf{k}\delta_{1,j}};$$

$$H^{1,s}_{2,p_x} = V^C_{sp\sigma}\sum_{j=1}^{3} l_{1,j}e^{i\mathbf{k}\delta_{1,j}}; \quad H^{1,p_*}_{2,s} = -H^{1,s}_{2,p_*}; \quad H^{1,p_x}_{2,p_y} = \left(V^C_{p_xp_y\sigma} - V^C_{p_xp_y\pi}\right)\sum_{j=1}^{3} l_{1,j}m_{1,j}e^{i\mathbf{k}\delta_{1,j}};$$

$$H^{1,p_x}_{2,p_x} = V^C_{p_xp_x\pi}\sum_{j=1}^{3} e^{i\mathbf{k}\delta_{1,j}} + \left(V^C_{p_xp_x\sigma} - V^C_{p_xp_x\pi}\right)\sum_{j=1}^{3} l^2_{1,j}e^{i\mathbf{k}\delta_{1,j}}; \quad H^{1,p_*}_{2,p_{**}} = H^{1,p_{**}}_{2,p_*};$$

$$H^{1,\alpha}_{4,\beta} = 0; \quad H^{1,s}_{3,p_x} = V^{C-F}_{sp\sigma}l_{1,F}e^{i\mathbf{k}\delta_{1,F}}; \quad H^{1,p_x}_{3,p_x} = V^{C-F}_{pp\pi}e^{i\mathbf{k}\delta_{1,F}} + \left(V^{C-F}_{pp\sigma} - V^{C-F}_{pp\pi}\right)l^2_{1,F}e^{i\mathbf{k}\delta_{1,F}};$$

$$H^{1,p_x}_{3,p_y} = \left(V^{C-F}_{pp\sigma} - V^{C-F}_{pp\pi}\right) l_{1,F} m_{1,F} e^{i\mathbf{k}\delta_{1,F}}; \quad H^{2,\alpha}_{3,\beta} = 0; \quad H^{2,s}_{4,p_x} = V^{C-F}_{sp\sigma} l_{2,F} e^{i\mathbf{k}\delta_{2,F}};$$

$$H^{2,p_x}_{4,p_x} = V^{C-F}_{pp\pi} e^{i\mathbf{k}\delta_{2,F}} + \left(V^{C-F}_{pp\sigma} - V^{C-F}_{pp\pi}\right) l^2_{2,F} e^{i\mathbf{k}\delta_{2,F}}; \quad H^{2,p_x}_{4,p_y} = \left(V^{C-F}_{pp\sigma} - V^{C-F}_{pp\pi}\right) l_{2,F} m_{2,F} e^{i\mathbf{k}\delta_{2,F}};$$

$$H^{i,\alpha}_{j,\beta} = \bar{H}^{j,\beta}_{i,\alpha}.$$

Other matrix elements can be obtained by simultaneous permutation of (p_x, p_y, p_z) and (l, m, n). The Slater-Koster parameters are taken from [6].

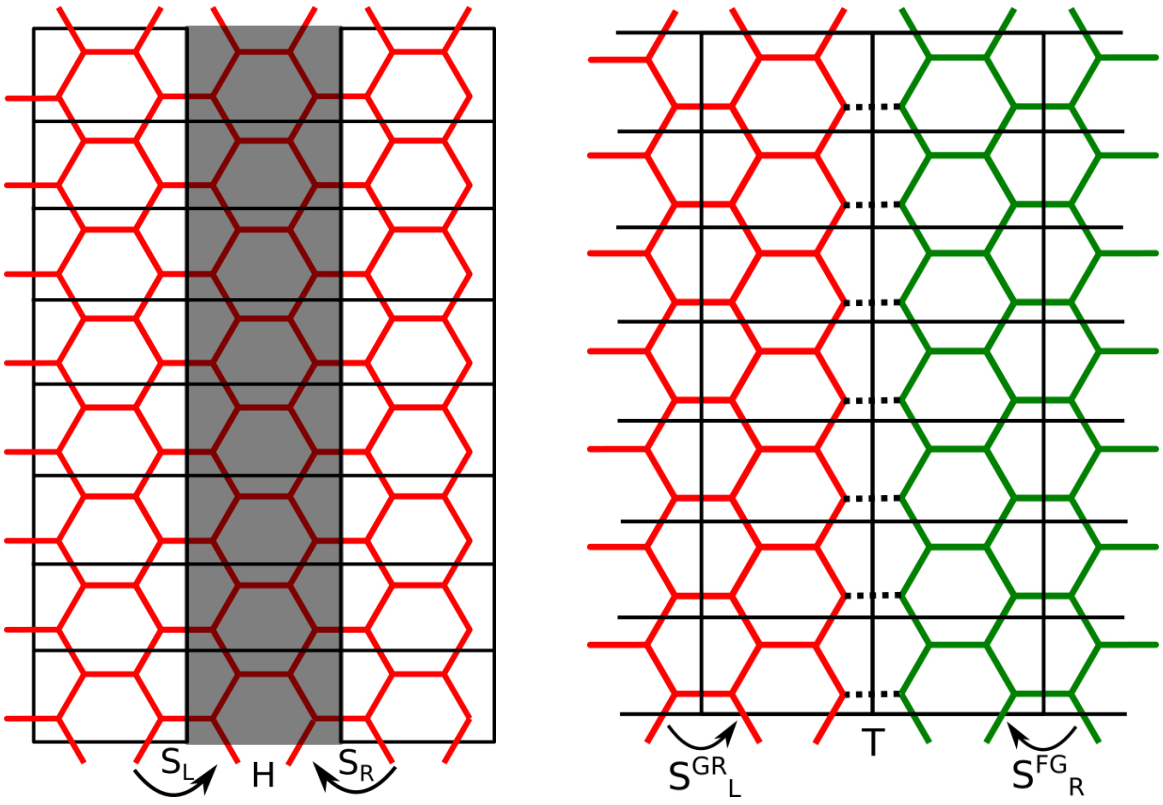
The eigenvalues of the matrix H were found numerically by using the QR algorithm. Let $\{Q_i\}_{i=0}^{\infty}$ be a sequence of unitary matrices, $\{R_i\}_{i=0}^{\infty}$ — a sequence of upper-triangle matrices, $\{H_i\}_{i=0}^{\infty}$ — a sequence of Hermitian matrices with the following relations:

$$H_0 = H; \quad H_i = R_{i-1}Q_{i-1} \text{ for } i > 0; \quad Q_i R_i = H_i.$$

Then $H_i \sim H$ and H_i converges to some upper-triangle matrix while $i \to \infty$ [7].

2.2 Non-Equilibrium Green's Functions

The non-equilibrium Green's function method (NEGF) is a powerful tool to solve the quantum transport problem [8]. Nevertheless we will use this method to obtain edge DOS only.



(a) semi-infinite graphene layer (b) graphene-fluorographene interface

Figure 2: semi-infinite graphene layer divided by unit cells (a), graphene-fluorographene interface (zigzag edge).

Let us consider a semi-infinite lattice that is infinite in the y-direction (Figure 2a). We can divide it into equal unit strips, introduce the $\mathbf{k}$-vector directed along the axis of the strip ($\mathbf{k} = (0, k, 0)^T$) and use the technique that was described in the previous subsection in order to obtain the matrix H. In this case the unit cell consists of four carbons (and also four fluorographenes in the fluorographene layer). Then we have to define matrices S_L and S_R that correspond to the interaction with the left neighbor strip and with the right neighbor strip, respectively:

$$H^{i,\alpha}_{j,\beta}(\mathbf{k}) = \sum_{\mathbf{r}\in G} e^{i\mathbf{kr}} \langle \phi_{i,\alpha}(\mathbf{x}) | \tilde{H} | \phi_{j,\beta}(\mathbf{x}-\mathbf{r}) \rangle;$$
$$S_L{}^{i,\alpha}_{j',\beta'}(\mathbf{k}) = \sum_{\mathbf{r}\in G'} e^{i\mathbf{kr}} \langle \phi_{i,\alpha}(\mathbf{x}) | \tilde{H} | \phi_{j',\beta'}(\mathbf{x}-\mathbf{r}) \rangle;$$
$$S_R{}^{i,\alpha}_{j'',\beta''}(\mathbf{k}) = \sum_{\mathbf{r}\in G''} e^{i\mathbf{kr}} \langle \phi_{i,\alpha}(\mathbf{x}) | \tilde{H} | \phi_{j'',\beta''}(\mathbf{x}-\mathbf{r}) \rangle,$$

where $G' = \{-\Delta_x \mathbf{e}_x + n\Delta_y \mathbf{e}_y | n \in \mathbb{Z}\}$, $G'' = \{+\Delta_x \mathbf{e}_x + n\Delta_y \mathbf{e}_y | n \in \mathbb{Z}\}$, $\Delta_x \times \Delta_y$ is the size of the unit cell. The expressions for the matrix elements have the same form as in the previous subsection. It follows from the definition that $S_L = S_R^\dagger$.

Now one can write down equations on the retarded Green's functions:

$$G_L(E, \omega, k) = \left((E + i\omega)\mathbf{1} - H - S_L G_L S_L^\dagger \right)^{-1};$$
$$G_R(E, \omega, k) = \left((E + i\omega)\mathbf{1} - H - S_R G_R S_R^\dagger \right)^{-1};$$
$$G(E, \omega, k) = \left((E + i\omega)\mathbf{1} - H - S_L G_L S_L^\dagger - S_R G_R S_R^\dagger \right)^{-1}.$$

The total density of states in infinite layer per unit cell have the follow expression:

$$\rho_o(E) = \frac{-1}{\pi} \lim_{\omega \to 0+} \frac{\Delta_y}{2\pi} \int_{-\pi/\Delta_y}^{\pi/\Delta_y} \mathrm{Im}\mathrm{Tr} G(E, \omega, k) dk.$$

For the density of states on the left (right) edge of the semi-infinite lattice we have:

$$\rho_L(E) = \frac{-1}{\pi} \lim_{\omega \to 0+} \frac{\Delta_y}{2\pi} \int_{-\pi/\Delta_y}^{\pi/\Delta_y} \mathrm{Im}\mathrm{Tr} G_L(E, \omega, k) dk.$$

Now let us consider an interface between two semi-infinite layers (Figure 2b): graphene on the left side and fluorographene on the right side, so G_L^{FG} and G_R^{GR} for the strips at the interface have already been defined. We need to define the matrices T_{LR} and T_{RL} describing the interaction between the strips, $T_{RL} = T_{LR}^\dagger$. Finally, we have:

$$\tilde{G}_L^{GR}(E, \omega, k) = \left(\mathbf{1} - G_L^{GR} T_{RL}^\dagger G_R^{FG} T_{RL} \right)^{-1} G_L^{GR};$$
$$\tilde{G}_R^{FG}(E, \omega, k) = \left(\mathbf{1} - G_R^{FG} T_{LR}^\dagger G_L^{GR} T_{LR} \right)^{-1} G_R^{FG},$$

so edge DOS $\rho_L^{GR}(E)$ and $\rho_R^{FG}(E)$ are found.

In order to solve the matrix equation on G_L (G_R) we use the Sancho-Rubio iterative method [9]:

$$G_{Ln} = \frac{1}{E + i\omega} \left(\mathbf{1} - D_n^s\right)^{-1};$$

$$D_{n+1}^s = D_n^s + A_n \left(\mathbf{1} - D_n\right)^{-1} B_n; \quad D_{n+1} = D_n + A_n \left(\mathbf{1} - D_n\right)^{-1} B_n + B_n \left(\mathbf{1} - D_n\right)^{-1} A_n;$$

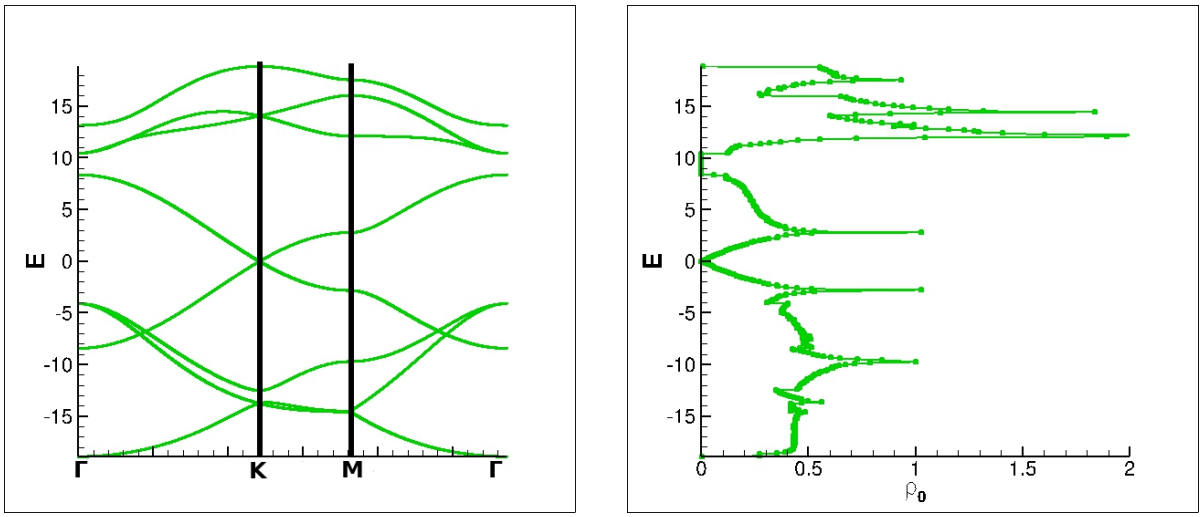
$$A_{n+1} = A_n \left(\mathbf{1} - D_n\right)^{-1} A_n; \quad B_{n+1} = B_n \left(\mathbf{1} - D_n\right)^{-1} B_n;$$

$$A_0 = \frac{1}{E + i\omega} S_L; \quad B_0 = \frac{1}{E + i\omega} S_L^\dagger; \quad D_0 = D_0^s = \frac{1}{E + i\omega} H.$$

We have performed our computations using C++ programming language with implementation of OpenMP parallelization tool.

3 Results

3.1 Infinite Layer Properties



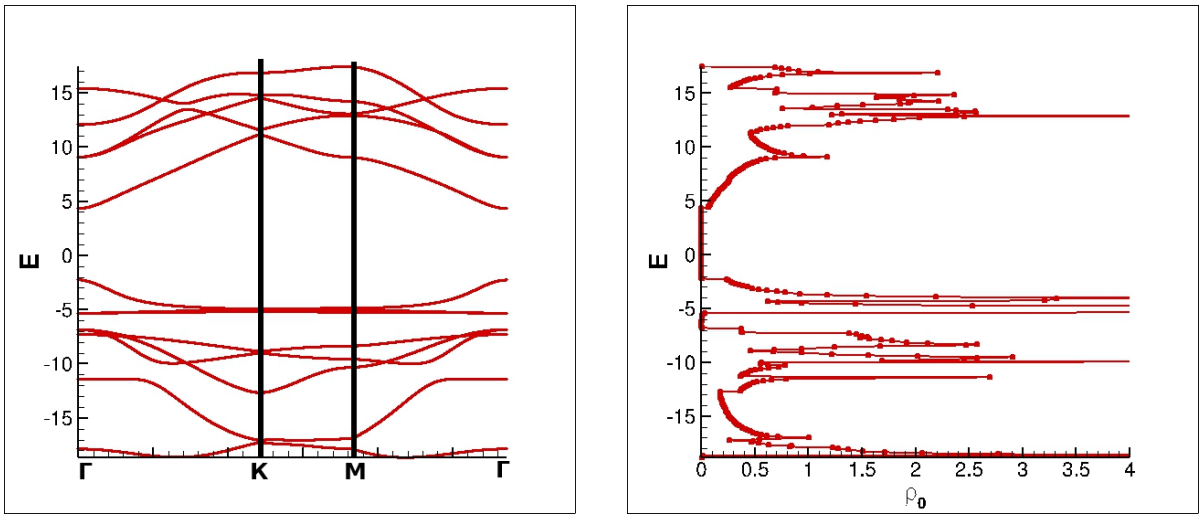
(a) (b)

Figure 3: the bandstructure (a) and DOS (b) of infinite graphene layer. $[E] = 1\text{eV}$

First of all let us consider an infinite graphene layer. In Figure 3a is shown the energy spectrum over the first Brillouin's zone. It is computed using LCAO method (see the previous section). As we take into account all outer orbitals of carbon atom (s, p_x, p_y, p_z) and there are two carbon atoms per unit cell, we obtain eight bands. At the K-point of the first Brillouin's zone one can notice the intersection between the valence band and the conductive band so here we have a zero band gap. In Figure 3b the density of electronic states per unit cell of graphene layer is presented. Each extremum of the bandstructure produce a peak in the DOS plot. At the Fermi level $\rho_0(0) = 0$.

In the case of fluorographene we have additionally two fluorine atom per unit cell. As far as we take into account only outer p-orbitals of fluorine atoms, we have $4 \times 2 + 3 \times 2 = 14$ bands (Figure 4a). DOS distribution shows that fluorographene is an insulator with a band gap $\sim 2.14\text{eV}$, and $\rho_0 = 0$ in this region (Figure 4b).

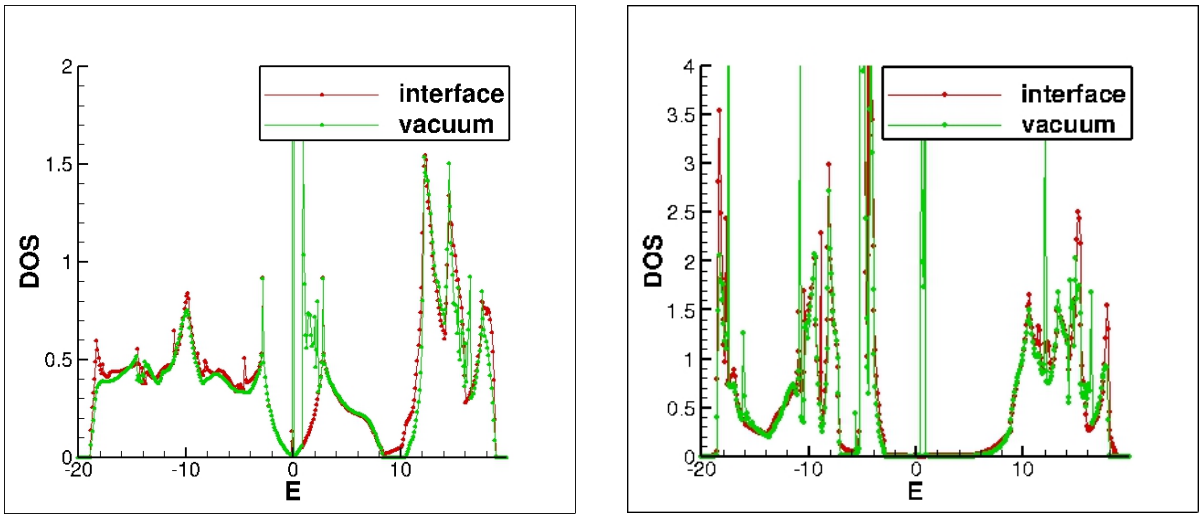
This results are consistent with [6] and this fact proves the validity of our computations.



(a) (b)

Figure 4: the bandstructure (a) and DOS (b) of infinite fluorographene layer. $[E] = 1\text{eV}$

3.2 Interface Problem



a) graphene b) fluorographene

Figure 5: DOS at the edge of semi-infinite layer in the interface (green line) and in the vacuum case (red line). $[E] = 1\text{eV}$.

Let us study the following interfaces: graphene-vacuum, fluorographene-vacuum, graphene-fluorographene. We consider the zigzag edge only. DOS per unit cell at the edge of semi-infinite layer are shown in Figure 5. For the graphene-vacuum interface (green line in Figure 5a) we have several peaks in DOS distribution near the Fermi level. The left peak was also detected when only p_z orbital was taken into account, and this pecularity appears due to configuration of the first Brilloin's zone [10]. The other peaks could correspond to other orbitals, and their presence requires further investigations.

For the fluorographene-vacuum interface (green line in Figure 5b) we see the same peak near the Fermi level. The importance of such a peak is that it is located in the band gap, so

it can be a possible channel of the edge electron transport.

In the case of the graphene-fluorographene interface there is no peaks in the band gap of fluographene (red line in Figure 5b). At the graphene side (red line in Figure 5a), there is only one peak at the Fermi level (which corresponds to configuration of the first Brilloin's zone).

4 Summary

In our work we have achieved the following results:

1. We have replicated previously obtained bandstructure and DOS of infinite graphene and fluorographene.

2. We have calculated DOS on the zigzag edge of graphene and fluorographene semi-infinite layers taking into account $\{s, p_x, p_y, p_z\}$ outer orbitals of carbon atom and $\{p_x, p_y, p_z\}$ outer orbitals of fluorine atom. There we have found several localized energy states near the Fermi's energy level both on the graphene edge and the fluorographene edge.

3. We have studied the graphene-fluorographene interface problem. Although fluorographene is an insulator, it affects electronic states on the graphene edge so there is only one peak of graphene edge DOS near the Fermi level.

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I am grateful to my supervisor Dr. V.L. Katkov who helped me to learn about basic ideas of the condensed matter physics and put me in touch with the front-line investigations on the graphene. Also I would like to bring my acknowledgments to Dr. S.V. Mikhailov who woke my interest on the quantum field theory and gave some fruitful advices, to N.A. Rybakov for his financial support. Finally I thank the organizing committee and especially E. Karpova for inviting me to this program and letting me feel the breath of such a great and respectable scientific organization as JINR is.

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