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Edge states of graphene bilayer strip

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Abstract. The electronic structure of the zig-zag bilayer strip is analyzed. The electronic spectra of the bilayer strip is computed. The dependence of the edge state band flatness on the bilayer width is found. The density of states at the Fermi level is analytically computed. It is shown that it has the singularity which depends on the width of the bilayer strip. There is also asymmetry in the density of states below and above the Fermi energy.

1 Introduction

Carbon atoms can create a variety of forms such as graphite, diamond, carbon fibers, fullerenes and carbon nanotubes. A carbon nanotube can be described as a graphene sheet rolled into a cylindrical shape so that the structure is one-dimensional with axial symmetry and in general exhibiting a spiral conformation called chirality. They are interesting because of their unique mechanical and electronic properties [1]. From the pioneering works [2–4], the electronic properties of graphite have attracted interest because of unconventional physical properties of a graphite layer. The development in the fabrication of the single layers of graphite (graphene) [5] caused a striking level of interest in the investigation of the carbon compositions. In addition to the closed carbon molecules [6], systems with boundaries also show interesting features. The nanographite zig-zag ribbon possesses localized edge states near the Fermi level. States like that are absent for ribbons with armchair edges [7]. The graphite sheet is a zero-gap semiconductor with the density of states (DOS) vanishing at the Fermi level, the edge states of the zig-zag ribbons produce a peak in the DOS at the Fermi level. Both the carbon nanotubes and graphite layers have the edge states because of their boundary. The existence of edge states for arbitrarily oriented graphene ribbons with a large class of edge shapes was investigated in reference [8] where a new geometrical understanding of edge state was proposed. The low-energy electronic states of bilayer graphene at its edges and their topological properties was investigate in references [9,10]. There was shown that contribution of edge modes to the linear conductance may dominate over the bulk modes. The topological nature of edge states is also studied in reference [11].

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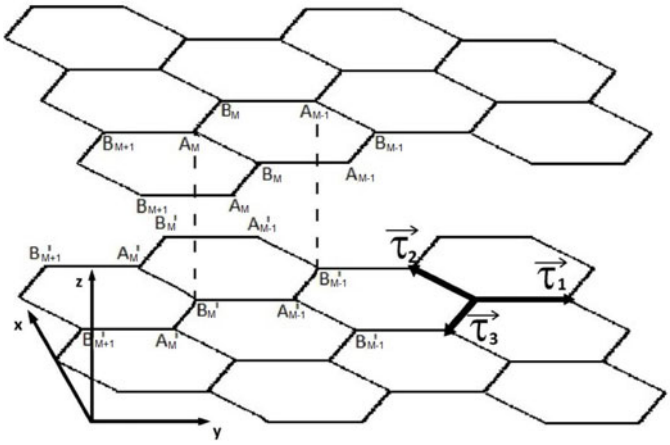

Fig. 1. Structure of finite-width graphene bilayer.

The presence of the edge state results in the relatively important contribution to the density of states (DOS) near the Fermi energy. It was found [12,13] that the HOMO-LUMO (highest occupied molecular orbital and lowest unoccupied molecular orbital, respectively) gap is inversely proportional to the length of the zig-zag carbon nanotube segment. The zig-zag ribbons have partly flat bands at the Fermi level [7,14]. In the presented paper, we focus on the computation of the electronic spectra of the zig-zag bilayer strip and also on the computation of the DOS of the edge states near the Fermi level.

2 Theory

Firstly, we describe the model for the zig-zag bilayer strip. We will study the edge and size effects using the tight-binding model for this strip shown in Figure 1.

The π electronic structures are calculated from the tight-binding Hamiltonian

$$H = \sum_i \epsilon_i |\varphi_i^u\rangle\langle\varphi_i^u| + \sum_{i,j} \gamma_{ij} \left(|\varphi_i^u\rangle\langle\varphi_j^u| + h.c\right) + \sum_i \widetilde{\epsilon_i} |\varphi_i^d\rangle\langle\varphi_i^d| + \sum_{i,j} \widetilde{\gamma}_{ij} \left(|\varphi_i^d\rangle\langle\varphi_j^d| + h.c\right) + \sum_{l,n} W_{ln} \left(|\varphi_l^d\rangle\langle\varphi_n^u| + h.c\right), \quad (1)$$

ϵ_i and $\widetilde{\epsilon_i}$ are the site energies of the upside and down layer; $|\varphi_i^u\rangle$, $|\varphi_i^d\rangle$ are the π orbitals on site i at the upside and down layer; γ_{ij}, $\widetilde{\gamma}_{ij}$ are the intralayer hopping integrals; W_{ij} are the interlayer hoping integrals which depend on the distance d_{ij} and angle θ_{ij} between the π_i and π_j orbitals.

To describe the parameter which characterizes the zig-zag bilayer strip, we start from the graphene layer where we can define the vectors connecting the nearest neighbor carbon atoms in the form:

$$\overrightarrow{\tau_1} = a\left(0; \frac{1}{\sqrt{3}}\right),$$
$$\overrightarrow{\tau_2} = a\left(\frac{1}{2}; -\frac{1}{2\sqrt{3}}\right),$$
$$\overrightarrow{\tau_3} = a\left(-\frac{1}{2}; -\frac{1}{2\sqrt{3}}\right). \quad (2)$$

The distance between atoms in the unit cell is $d = |\overrightarrow{\tau_i}| = \frac{a}{\sqrt{3}}$. We want to find a solution to the double-layer graphene strip in the form:

$$\psi(\overrightarrow{r}) = \psi^u(\overrightarrow{r}) + \psi^d(\overrightarrow{r}) \quad (3)$$

where

$$\psi^u(\overrightarrow{r}) = \sum_{i=0}^{M+1} (C_{A_i}\psi_{A_i} + C_{B_i}\psi_{B_i}), \quad (4)$$

and

$$\psi^d(\overrightarrow{r}) = \sum_{i=0}^{M+1} \left(C_{A_i'}\psi_{A_i'} + C_{B_i'}\psi_{B_i'}\right). \quad (5)$$

Here M describes the width of the graphene bilayer. We want to find a solution to the above equation in the form of the Bloch function

$$\psi_\alpha(\overrightarrow{k}, \overrightarrow{r}) = \frac{1}{\sqrt{N}} \sum_n e^{i\overrightarrow{k}\cdot\overrightarrow{r_n}} |\varphi(\overrightarrow{r} - \overrightarrow{r}_n)\rangle, \quad (6)$$

where α denotes A or B atoms. Here $\overrightarrow{k} = (k, 0)$, $\overrightarrow{r_n}$ is the position of a unit cell and N is the number of unit cells; $|\varphi(\boldsymbol{r})\rangle$ is a π orbital. We denote

$$\epsilon_i = \Delta = \left\langle \varphi^{out}(r - A_i) |H| \varphi^{out}(r - A_i) \right\rangle = \left\langle \varphi^{out}\left(r - B_i^{'}\right) |H| \varphi^{out}\left(r - B_i^{'}\right) \right\rangle, \quad (7)$$

$$\widetilde{\epsilon}_i = -\Delta = \left\langle \varphi^{out}(r - B_i) |H| \varphi^{out}(r - B_i) \right\rangle = \left\langle \varphi^{out}\left(r - A_i^{'}\right) |H| \varphi^{out}\left(r - A_i^{'}\right) \right\rangle. \quad (8)$$

Now we define the hopping integrals within each layer as $\gamma_{ij} = \tilde{\gamma}_{ij} = \gamma_0$. We take into account only the interaction between nearest-neighbors also in the case of interlayer interaction

$$\left\langle \varphi(r - A_i) |H| \varphi\left(r - B_i^{'}\right) \right\rangle = \gamma_1. \quad (9)$$

We neglect the terms corresponding to the hopping between atoms $B_i^{'}$ and atoms B_i with the hopping energy γ_4 and the terms γ_3, corresponding to the hopping between atoms $A_i^{'}$ and atoms B_{i-1}.

In confining the structure along the width, the edge states are induced by terminating the width dimension with zig-zag shaped edges. The presence of edges in the bilayer strip changes the dimensionality of the system from a two-dimensional to a one-dimensional system. The electronic spectrum of the zig-zag bilayer strip can be described by the following system of equations:

$$(E - \Delta)C_{A_m} = -\gamma_0 C_{B_{m-1}} - g_k C_{B_m} - \gamma_1 C_{B_m'}, \quad (10)$$

$$(E + \Delta)C_{B_m} = -\gamma_0 C_{A_{m+1}} - g_k C_{A_m}, \quad (11)$$

$$(E + \Delta)C_{A_m'} = -\gamma_0 C_{B_{m-1}'} - g_k C_{B_m'}, \quad (12)$$

$$(E - \Delta)C_{B_m'} = -\gamma_0 C_{A_{m+1}'} - g_k C_{A_m'} - \gamma_1 C_{A_m}, \quad (13)$$

where

$$g_k = 2\gamma_0 \cos(ka/2). \quad (14)$$

Here $m = 1, \ldots, M$, are site indices. We assume that the A_0 and B_{M+1} sites are missing. So we have the boundary condition $C_{A_0} = C_{B_{M+1}} = C_{A_0'} = C_{B_{M+1}'} = 0$. The solution is assumed to be [15]:

$$C_{A_m} = Ae^{ipm} + Be^{-ipm}, \quad (15)$$

$$C_{B_m} = Ce^{ipm} + De^{-ipm}. \quad (16)$$

Here A, B, C and D are the coefficients which have to be determined, and p is the transverse wave number. From the boundary condition we have

$$C_{A_0} = A + B = 0, \quad (17)$$

$$C_{B_{M+1}} = Ce^{ip(M+1)} + De^{-ip(M+1)} = 0. \quad (18)$$

And so

$$C_{A_m} = A\left(e^{ipm} - e^{-ipm}\right), \quad (19)$$

$$C_{B_m} = C\left(e^{ipm} - z^2 e^{-ipm}\right), \quad (20)$$

where $z = e^{ip(M+1)}$. And similarly,

$$C_{A_m'} = A'\left(e^{ipm} - e^{-ipm}\right), \quad (21)$$

$$C_{B_m'} = C'\left(e^{ipm} - z^2 e^{-ipm}\right). \quad (22)$$

Substituting equations (19)–(22) into equations (10)–(13) we obtain the energy spectrum

$$E_{1,2} = \frac{\gamma_1}{2} \pm \sqrt{\gamma_0^2 + 2\gamma_0 g_k \cos(p) + g_k^2 + \left(\frac{\gamma_1}{2} + \Delta\right)^2}, \quad (23)$$

$$E_{3,4} = -\frac{\gamma_1}{2} \pm \sqrt{\gamma_0^2 + 2\gamma_0 g_k \cos(p) + g_k^2 + \left(\frac{\gamma_1}{2} - \Delta\right)^2}, \quad (24)$$

and the equation which gives the transverse wave number p is

$$\sin[pM] + \frac{g_k}{\gamma_0} \sin[p(M+1)] = 0. \quad (25)$$

For $M \gg 1$ equation (25) can be written as

$$\sin[pM] = 0. \quad (26)$$

The solution is given by

$$p = \frac{2\pi}{M} l. \quad (27)$$

So for wide enough bilayer the real solution of equation (25) can be expressed in the form given by equation (27). Substituting this solution into equations (23), (24) we get the energy spectrum of extended states of finite bilayer where electrons are delocalized in contrary to the edge states where electrons are localized at the edges of the bilayer. The spectrum of these extended states are similar to the spectrum of infinite bilayer with periodic boundary conditions along the y axis.

3 Edge states of graphene bilayer

Now we are interested in the edge state of the graphene bilayer. This solution can be obtained in the form $p = \pi + i\eta$ [16]. We get the following equation for η:

$$\sinh[\eta M] - \frac{g_k}{\gamma_0} \sinh[\eta(M+1)] = 0. \quad (28)$$

The edge state can exist when the condition

$$|2\cos(ka/2)| < \frac{1}{1+1/M} \quad (29)$$

is fulfilled. The energy spectrum of a state like that is given as:

$$E_{1,2} = \frac{\gamma_1}{2} \pm \sqrt{\gamma_0^2 - 2\gamma_0 g_k \cosh(\eta) + g_k^2 + \left(\frac{\gamma_1}{2} + \Delta\right)^2}, \quad (30)$$

$$E_{3,4} = -\frac{\gamma_1}{2} \pm \sqrt{\gamma_0^2 - 2\gamma_0 g_k \cosh(\eta) + g_k^2 + \left(\frac{\gamma_1}{2} - \Delta\right)^2}. \quad (31)$$

For big enough M the solution of equation (28) can be expressed in the form [16]:

$$\eta = \ln\left[c_k + \frac{1 - c_k^2}{c_k^{2M+1}}\right], \quad (32)$$

where $1/c_k = |2\cos\left(\frac{ka}{2}\right)|$. From equation (32) we have

$$\cosh\eta \approx \frac{1 + c_k^2}{2c_k} - \frac{\left(c_k^2 - 1\right)^2}{2c_k^{2M+3}}, \quad (33)$$

and so

$$E_{1,2} = \frac{\gamma_1}{2} \pm \sqrt{\gamma_0^2 \frac{\left(c_k^2 - 1\right)^2}{c_k^{2M+4}} + \left(\frac{\gamma_1}{2} + \Delta\right)^2}, \quad (34)$$

$$E_{3,4} = -\frac{\gamma_1}{2} \pm \sqrt{\gamma_0^2 \frac{\left(c_k^2 - 1\right)^2}{c_k^{2M+4}} + \left(\frac{\gamma_1}{2} - \Delta\right)^2}. \quad (35)$$

Now we assume, similarly as in reference [17], that $\gamma_1 > 2\Delta$ and also it is assumed that the width of the graphene bilayer is big enough and the following condition is fulfilled:

$$\gamma_1 \gg \gamma_0^2 \frac{\left(c_k^2 - 1\right)^2}{c_k^{2M+4}}. \quad (36)$$

The bands are given by

$$E_1(k) = \gamma_1 + \Delta + \frac{\gamma_0^2}{\gamma_1 + 2\Delta} \frac{\left(c_k^2 - 1\right)^2}{c_k^{2M+4}}, \quad (37)$$

$$E_2(k) = -\Delta - \frac{\gamma_0^2}{\gamma_1 + 2\Delta} \frac{\left(c_k^2 - 1\right)^2}{c_k^{2M+4}}, \quad (38)$$

$$E_3(k) = -\Delta + \frac{\gamma_0^2}{\gamma_1 - 2\Delta} \frac{\left(c_k^2 - 1\right)^2}{c_k^{2M+4}}, \quad (39)$$

$$E_4(k) = -\gamma_1 + \Delta - \frac{\gamma_0^2}{\gamma_1 - 2\Delta} \frac{\left(c_k^2 - 1\right)^2}{c_k^{2M+4}}. \quad (40)$$

We are interested in the $E_2(E_3)$ band which is the valence (conductance) band of the edge states. The minimum of the E_2 band is

$$E_{2,\,min} = -\Delta - \frac{2}{e^2 M} \frac{\gamma_0^2}{\gamma_1 + 2\Delta}, \quad (41)$$

where it was used that $e^x = (1 + x/M)^M$ for $M \to \infty$ and also equation (29). We found $E_{2,\,max} = -\Delta$. Similarly for the E_3 band

$$E_{3,\,max} = -\Delta + \frac{2}{e^2 M} \frac{\gamma_0^2}{\gamma_1 - 2\Delta}, \quad (42)$$

and $E_{3,\,min} = -\Delta$. We can see that the width of the band is inversely proportional to the width of the bilayer.

The density of states can be expressed in the form

$$N(E) = \frac{L}{2\pi} \frac{1}{\frac{dE}{dk}}, \quad (43)$$

where L is the length of the bilayer in the x direction. We get the density of the state in the region $E_{3,\,min} - E_{3,\,max}$ in the vicinity of the energy $E = -\Delta$ in the form

$$N(E) = \frac{L}{2\pi a M \left(E + \Delta\right)^{\frac{2M+1}{2M+2}} \left(\gamma_0^2/(\gamma_1 - 2\Delta)\right)^{1/2(M+1)}}. \quad (44)$$

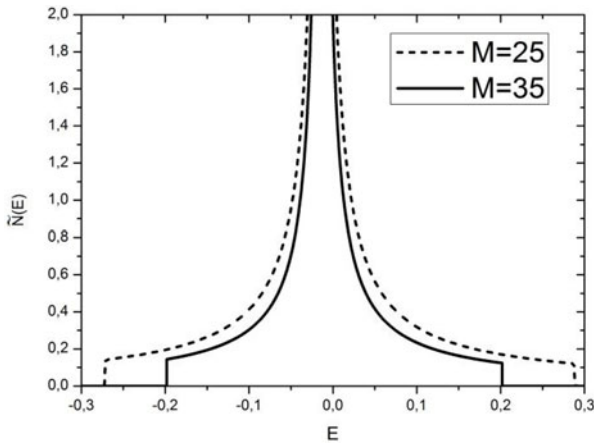

Fig. 2. $\tilde{N}(E) = (2\pi a/L)N(E)$ dependance on E (eV) in the vicinity of $-\Delta$. The following parameters were used: $\gamma_0 = 3$ eV, $\gamma_1 = 0.35$ eV, $\Delta = 0.01$ eV.

The density of the state in the region $E_{2,\,min} - E_{2,\,max}$ in the vicinity of the energy $E = -\Delta$ has the form

$$N(E) = \frac{L}{2\pi a M \left(-E-\Delta\right)^{\frac{2M+1}{2M+2}} \left(\gamma_0^2/(\gamma_1+2\Delta)\right)^{1/2(M+1)}}. \tag{45}$$

Both these densities of the states have a singularity at the energy $E = -\Delta$ (Fig. 2). The strength of the singularity depends also on the width of the bilayer. The width of the bilayer is characterized by the parameter M. The density of the state of the $E_4(k)(E_1(k))$ band is the same as the $E_3(k)(E_2(k))$ band.

4 Conclusion

In the presented paper the electronic spectra of the zig-zag bilayer strip were studied analytically. In contrast to the work [18], the spectral characteristics of the edge states are shown in more details. We get for big enough M that the electronic spectra of the extended states of the graphene bilayer strip are similar to the spectra of the graphene bilayer with the periodic boundary condition. Because of the boundary we also get edge states. It was shown that the width of the edge state band is inversely proportional to the width of the bilayer strip which is characterized by the parameter M. So for big enough M we get partly flat bands of the edge states. The density of states at the Fermi level has a singularity which also depends on the width of the bilayer strip. There is asymmetry in the DOS at the Fermi energy, similarly to the electron-hole asymmetry in the bilayer graphene [19]. This asymmetry is caused by the parameter Δ which describes the difference in the site energy of the atoms at the sites $A_i, B_i^{'}$ and the atoms at the sites $B_i, A_i^{'}$.

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