Electron states near graphene edge

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Abstract. The band structure of graphene near the Fermi surface is often well described by the effective mass approximation. In this approach electron wave function obeys the Dirac-type equation. To describe a number of effects it is necessary to supplement the equation with boundary conditions. Using the Hermiticity and the time reversal symmetry we derive the phenomenological boundary conditions for a multicomponent effective wave function. The boundary conditions in the case of smooth crystalline potential near the edge are parameterized in terms of a real phenomenological constant that describes a general type edge. The edge states spectra (i.e. Tamm states spectra) for semi-infinite graphene are analyzed.

1. Introduction
Graphene, a monoatomic plane layer of carbon atoms at sites of a 2D hexagonal lattice, is a building block for the formation of 3D graphite, 1D nanotubes, and 0D fullerenes. Its unique properties attract increasing interest of physical community [1].

An electron in graphene has an ultrarelativistic spectrum near each corner of the hexagonal Brillouin zone. A charged two-dimensional (2D) massless Weyl neutrino would have had the same spectrum, if it existed. This spectrum is twice valley-degenerated. The centers of valleys \( K \) and \( K' \) are being spaced by vector \( 2\mathbf{p}_0 \) in Brillouin zone. Such band structure is described in the effective mass approximation by the four-component Dirac-type equation for bispinor \( (\psi, \psi')^T \):

\[
\begin{pmatrix}
\sigma(\hat{p} - p_0) & 0 \\
0 & -\sigma(\hat{p} + p_0)
\end{pmatrix}
\begin{pmatrix}
\psi \\
\psi'
\end{pmatrix}
= E
\begin{pmatrix}
\psi \\
\psi'
\end{pmatrix} .
\]

Here \( \hat{p} = (\hat{p}_x, \hat{p}_y, 0) \) is the momentum operator in 2D system, \( \sigma = (\sigma_1, \sigma_2, \sigma_3) \) are Pauli matrices in the standard representation, \( v = 10^6 \) m/s is effective speed of light. The Hamiltonian acts on the four-component effective wave function \( (\psi_A, \psi_B, \psi'_A, \psi'_B)^T \) [2], [3]. The difference of the Hamiltonian (1) from the traditionally used one is the shift by the quasi-momentum \( p_0 \) been included in (1). This is necessary in order to take into account intervalley scattering of electrons.

To describe a number of effects, including the abnormal quantum Hall effect, size quantization in nanoribbons and quantum dots, it is necessary to understand the behavior of electrons or holes near the graphene edge. To do this, one should derive boundary conditions (BCs) for envelope wave functions. In general case the BCs have rather complicated form [4]. That is why the model BCs [1], [3] are often in use. In the tight-binding approximation armchair and zigzag edges are usually considered [5], [6] and the BCs are taken from the simplest consideration, that is however not well-founded. The model of infinitely-massive wall is also in use [7], [8]. To find edge states (ESs) spectra (an analog of Tamm states) one should solve the pseudorelativistic
equations for the envelope wave functions with the derived BCs. It was found that the ESs spectra are sensitive to the choice of the model of an edge [7], [9]-[11].

The goal of this paper is to derive the BCs for the equation (1) satisfying general physical requirements without any assumptions about microscopic structure of an edge of graphene. Peculiarity of the boundary problem is the following: though there are no intervalley terms in the equation (1) such terms could be in BCs. It is because the equation (1) is applicable only for slowly varying potential. Crystalline potential at the edge may be sharp that leads to intervalley scattering.

To derive the BCs we assume that the Hamiltonian is Hermitian in restricted area, i.e. we construct self-adjoint extension of the Hamiltonian. We restrict ourselves to BCs that do not break time reversal symmetry. Similar approach was used before [4], [8], [12]-[14]. We concentrate on the simplest case when the intervalley scattering is absent. In this case the Dirac-type equation (1) is reduced to a couple of Weyl equations.

The outline of this paper is as follows. In Sec. 2 we consider BCs for the Weyl equation and find the ESs for Weyl neutrino on half-plane. In Sec. 3 the problem of possible boundary conditions for the equation (1) in the case of absence of intervalley scattering at the boundary is reduced to the problem of finding boundary conditions for the Weyl equation. Then, using symmetry arguments we can find ESs spectra for semi-infinite graphene sample from ESs spectra for the Weyl neutrino on semi-infinite plane. Finally, we discuss effects of intervalley scattering qualitatively.

2. The edge states for the Weyl equation on semi-infinite plane

We start with finding BCs for the 2D Weyl equation for two-component wave function $(\psi_1, \psi_2)^T$:

$$v\sigma\hat{p}\psi = E\psi. \quad (2)$$

We assume only the Hermiticity of the equation (2) in restricted area $S$. Performing partial integrations of $<\psi|\sigma\hat{p}|\phi>$ and equating the surface term to zero for a restricted domain in the $(x, y)$ plane we obtain the BCs:

$$\left. \left( \psi_1 + i\cot(w/2) e^{-i\alpha}\psi_2 \right) \right|_S = 0. \quad (3)$$

$w$ is a phenomenological real parameter, that characterizes the edge of the domain, $\alpha$ is the angle between the normal $\mathbf{n}$ and $X$-axis.

We solve the 2D Weyl equation (2) with the BC (3) on a half-plane for a particle with specified momentum $k$ along the boundary. The parameter $w$ is a constant on the edge. At an infinite distance from the boundary we assume that the wave function must be finite. Among the solutions there are those corresponding to the bulk spectrum and solutions corresponding to the ESs. For the latter we obtain the following solutions:

$$E = vk \sin w, \quad k \cos w \geq 0. \quad (4)$$

The ESs band has a linear dependence on the momentum $k$, Fig. 1. Depending on the value of the parameter $w$, it exists in different quadrants of the $(E, k)$ plane. The ESs band is chiral. It is not symmetric about $k = 0$. This is because of the Weyl Hamiltonian is not invariant under space inversion $\mathbf{r} \rightarrow -\mathbf{r}$.

The time reversal operator for the Weyl equation is $\hat{T} = \sigma_2\hat{K}_0$ ($\hat{K}_0$ is the complex conjugation operator). Note that the BC (3) breaks the time reversal symmetry. If we assume that the BC does not break time reversal symmetry, we will obtain only zeros BC.
3. The edge states for semi-infinite graphene without intervalley scattering

We are now ready to consider BCs for the equation (1). If the crystalline potential near the edge of graphene is smooth enough we can neglect the intervalley scattering. It means that the BCs have no intervalley terms, i.e. components of the spinors from different valleys do not mix. In this case electron in graphene can be considered as a couple of the left and the right Weyl neutrino that is massless limit of the Dirac electron:

\[ v \begin{pmatrix} \sigma \hat{p} & 0 \\ 0 & -\sigma \hat{p} \end{pmatrix} \begin{pmatrix} \psi \\ \psi' \end{pmatrix} = E \begin{pmatrix} \psi \\ \psi' \end{pmatrix}. \]

(5)

The time reversal operator (corresponding to complex conjugation of the total wave function) in our representation is [3]:

\[ \hat{T} = \begin{pmatrix} 0 & \sigma_1 \\ \sigma_1 & 0 \end{pmatrix} \hat{K}_0, \]

(6)

where \( \hat{K}_0 \) is the complex conjugation operator. Following the procedure described in Sec. 2 and using \( T \)-invariance in addition to the Hermiticity of the problem we find the following BCs:

\[ (\psi_A + i \cot(a/2)e^{-ia}\psi_B)|_S = 0, \quad (\psi'_A + i \tan(a/2)e^{-ia}\psi'_B)|_S = 0, \]

(7)

here \( \alpha \) is the angle between armchair orientation and the edge of graphene. These BCs depend on a real parameter \( a \) as for the Weyl case (2), (3).

We solve the equation (1) with derived BCs on a graphene half-plane the lateral boundary of which is specified by a 2D vector normal \( (\cos \alpha, \sin \alpha) \) for a particle with specified momentum \( k_y \) along the boundary \( (x = 0) \). As in Sec. 2, among the solutions there are solutions corresponding to the bulk spectrum and solutions corresponding to the ESs, see Fig. 2. We find that the ESs bands in \( E(k_y) \) plane are rays starting in the projection of the valley centers on the edge, \( \pm p_{0y} \), where \( p_{0y} = p_0 \sin \alpha \). The ESs bands are described by the dispersion equations:

\[ E_s(k_y) = sv(k_y + sp_{0y}) \sin a, \quad s(k_y + sp_{0y}) \cos a > 0. \]

(8)

\( s = +1 \) in the left valley and \( s = -1 \) in the right valley.

Solution for the ES envelope wave function is:

\[ \psi(x) \sim e^{-x(k_y+p_{0y}) \cos a}, \quad \psi'(x) \sim e^{x(k_y-p_{0y}) \cos a}. \]

(9)

The ESs band is not symmetric about the center of the valleys \( k_y = \pm p_{0y} \), but it is symmetric about the center of the Brillouin zone \( k_y = 0 \).
Figure 2. Electron spectrum $E(k_y)$ for a graphene half-plane (boundary $x = 0$) for two meaning of the parameter $a$. $p_{0y} = p_{0} \sin \alpha$ is the projection of the valley centers on the $y$-axis. The shaded region corresponds to the continuous spectrum, and the lines to the edge states. The slope of the spectrum of the edge states with respect to the $x$-axis is determined by the boundary parameter $a$: (a) $\sin a = 0$, (b) $\sin a = 0.2$

4. Discussion
In this paper we have studied the edge states of graphene in the case of smooth crystalline potential near the edge. We found that a continuum description of electron wave function in the form of the Dirac equation must be supplemented with certain BCs. The BCs were derived from general physical requirements: the Hermiticity and the time-reversal invariance of the boundary problem. In this simplest case the graphene edge appears to be described by a real parameter $a$. We revealed that without intervalley scattering the Tamm band of the edge states for semi-infinite sample of graphene was easily obtained from Tamm states for Weyl neutrino.

The ESs band is represented with the rays, Fig. 2, beginning at the projection of the valley centers on the edge and located in one of the quadrants of $(E, k_y)$ plane, depending on the parameter $a$. For the value $a = 0$ the known dispersionless spectrum for zigzag edge is obtained [6], [5]. For $\sin a \approx 0.2$ the result, Fig. 2b, agrees with the next-nearest-neighbors tight-binding calculations [9], [11].

In the case of arbitrary crystalline potential near the edge of graphene we derived more complicated BCs taking the intervalley edge scattering into account. The same phenomenological approach was used. We found that in this case left and right ESs rays instead of crossing near $k_y = 0$ have an anticrossing with a gap depending on the intervalley edge scattering.

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