Coulomb Problem for Graphene with Supercritical Impurity

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Abstract. The properties of charge carriers in graphene with dopants with charge $Z$ within two-dimensional effective Dirac equation with non-zero gap between upper and lower continua are analyzed. The closed set of explicit equations determining the spectrum of charge carriers are obtained for the case of the Coulomb potential modified at small distances. The critical values $Z_{cr}$ of the dopant charge at which the energy level with the given quantum numbers crosses the lower continuum boundary are determined. For $Z < Z_{cr}$, the position $E_0$ and width $\gamma$ of the lowest quasidiscrete state are calculated. For such values of $Z$ screening of the impurity charge and resonance scattering of holes are also considered.

1. Introduction

In the presence of multiply charged impurity the electronic characteristics of graphene are described by the effective two-dimensional Dirac equation with the gap in electronic spectrum [1–11]. In this case the energy spectrum of the two-dimensional heterostructure is absolutely similar to one for the three-dimensional Coulomb problem, including the case with the nuclear charge $Z > 137$, e.g. [12, 13]. The screening of the charge for the Coulomb impurity in the gapped graphene was studied in [4, 6–11]. In the last paper, the authors discuss the screening by electrons created together with holes from the Dirac sea (by analogy with the three-dimensional case [13]). In the present work, we demonstrate that such a mechanism of screening cannot be put into effect, see also [14, 15], but resonances in the scattering of the holes by overcritical impurities occur.

According to [4, 5, 11], the electronic properties of graphene doped by atomic nuclei or ions with charge $Z$ can be described by the effective two-dimensional Dirac equation

$$\hbar v_F \left( -i \sigma \frac{\partial}{\partial x} - \frac{q}{\hbar} + \frac{m^* v_F}{\hbar} \sigma_z \right) \Psi_E(x) = E \Psi_E(x)$$ (1)

Here $v_F$ is the velocity at the Fermi surface, $x = (x_1, x_2)$, $\sigma = (\sigma_x, \sigma_y, \sigma_z)$ are the Pauli matrices, $q = Z \alpha_F$, $\alpha_F = e^2/hv_F$ is the effective fine structure constant for graphene, $\Psi_E(x)$ - is the two-component wavefunction for an electron with the effective mass $m^*$ and energy $E$.

Accounting for [3, 11] the gap width $\Delta = 2m^*v_F^2 = 0.26$ eV, the effective constant $\alpha_F = 0.4$ and the distance between carbon nuclei $a_{CC} = 1.42$ Å for graphene deposited onto SiC substrate we have

$$v_F = 5.5 \cdot 10^8 \text{ cm/s}, \quad m^* = 7.6 \cdot 10^{-4} m_e, \quad a_{CC}/l_F = 5.5 \cdot 10^{-3},$$ (2)
where $m_e$ is the mass of the electron, $l_F = \hbar/m_e v_F$ is the "Compton length" in graphene.

Owing to the axial symmetry, the conserving quantum number [16] is the total angular momentum $J = M + 1/2$ (in $\hbar$ units), i.e., the eigenvalue of the generator for the two-dimensional rotations $-i\partial/\partial\varphi + 1/2\sigma_3$. The orbital angular momentum $M$ is the eigenvalue of the self-adjoint operator $-i\partial/\partial\varphi$ acting in the Hilbert space of square integrable functions on the circle $0 < \varphi < 2\pi$, which eigenfunctions are $[18, 19]$:

$$
\Phi_M(\varphi) = \frac{1}{2\pi} e^{iM\varphi}, \quad M = \delta + m; \quad \delta = 0, \frac{1}{2}, m = 0, \pm 1, \pm 2, \ldots
$$

In terms of

$$
E = m_e v_F^2 \varepsilon, \quad x = l_F \rho, \quad \rho = (\rho \cos \varphi, \rho \sin \varphi),
$$

the wavefunction with fixed total angular momentum is represented as:

$$
\Psi_{\varepsilon,J}(\rho) = \frac{1}{\sqrt{2\pi \rho}} e^{iJ\varphi} \left( e^{-i\varepsilon/2} F(\rho) \right) \left( e^{i\varepsilon/2} G(\rho) \right)
$$

2. Boundary conditions

The functions $F(\rho)$ and $G(\rho)$ satisfy the two-dimensional Dirac equation:

$$
H_D \Psi_{\varepsilon,J}(\rho) = \varepsilon \Psi_{\varepsilon,J}(\rho), \quad H_D = \left( \frac{1 - \frac{2}{\rho} \frac{J}{\rho} + \frac{d}{d\rho}}{\frac{J}{\rho} - \frac{d}{d\rho} - 1 - \frac{2}{\rho}} \right), \quad \Psi_{\varepsilon,J} = \left( \begin{array}{c} F(\rho) \\ G(\rho) \end{array} \right), \quad J = M + \frac{1}{2},
$$

which up to the notation coincides with the set of equations for the radial functions for the three-dimensional problem [12]. In the two-dimensional case, however, the value $J = 0$, i.e. $(M = -1/2)$, which corresponds the ground state, and half-integer values $J = m + 1/2, \quad m = 0, \pm 1, \pm 2, \ldots$ are possible.

The problem is posed correctly if (5) is supplemented by physically acceptable boundary conditions for the wavefunctions. In the present case, it is equivalent to the condition that the differential expression $H_D$ is the self-adjoint one and corresponds to the Hamiltonian acting in the Hilbert space of the square integrable functions with the defined Hermitian scalar product

$$
\langle \Psi_1, \Psi_2 \rangle = \int_0^\infty \{ F^*_1(\rho) F_2(\rho) + G^*_1(\rho) G_2(\rho) \} d\rho.
$$

Since the Coulomb potential $V_C(\rho)$ vanishes at large distances, so, as in the three-dimensional problem, the values $\varepsilon \geq 1$ and $\varepsilon \leq -1$ correspond to the upper and lower continua of the solutions of the Dirac equation, respectively, whereas the range $-1 < \varepsilon < 1$ corresponds to the discrete spectrum.

Thus, to ensure the self-adjointness of the Hamiltonian it is essential (as it is shown in [14]) to consider the asymptotic behaviour of the solutions of system (5) at short distances. This behaviour is determined by the value of single parameter $\sigma = \sqrt{J^2 - q^2}$. According to the von Neumann theory of unbounded operators we arrive at conditions [14] which determine a single-parameter family (associated with the differential operator $H_D$) of self-adjoint operators

\footnote{The half-integer quantization of the orbital angular momentum comes into effect for two-dimensional quantum dots with an odd number of electrons [17].}
in the Hilbert space of wavefunctions$^2$:

\[
\frac{u_\sigma}{u_{-\sigma}} = \left( \frac{u_\sigma}{u_{-\sigma}} \right)^* = \tan \theta_\sigma(J), \quad -\frac{\pi}{2} \leq \theta_\sigma(J) \leq \frac{\pi}{2}, \quad 0 < \sigma < 1/2 \\
\frac{u_\tau}{u_{-\tau}} = \left( \frac{u_\tau}{u_{-\tau}} \right)^* = e^{2i\theta_\tau(J)}, \quad \Im \theta_\tau(J) = 0, \quad \tau = \sqrt{q^2 - J^2} > 0, \quad q > |J|, \\
u_{\pm \sigma} = \frac{\Gamma(\mp 2\sigma)(2\lambda)^{\pm \sigma}}{\Gamma(1 \mp \sigma - \frac{\pi}{4} \pm \theta)} \left[ q \sqrt{1 - \varepsilon} - (J \pm \sigma) \sqrt{1 + \varepsilon} \right]
\]

The parameters $\theta_\sigma(J)$ and $\theta_\tau(J)$ define one-parameter families of self-adjoint radial Dirac hamiltonians, which were obtained in a different way in [21–23] in three- and two-dimensional cases respectively. Here $\tau = \sqrt{q^2 - J^2}$, and amplitudes $u_{\pm \tau}$ are obtained from $u_{\pm \sigma}$ by replacement $\sigma \rightarrow i\tau$. Hence, we get, in particular, the equation

\[
\arg \Gamma \left( 2i \sqrt{\left( q_{cr}^{(n)} \right)^2 - J^2} \right) = \sqrt{\left( q_{cr}^{(n)} \right)^2 - J^2} \cdot \ln \left( 2q_{cr}^{(n)} \right) - \theta_\tau(J) + \pi n, \quad n = 0, 1, 2, \ldots
\]

for the critical charge $q_{cr}^{(n)} = Z_{cr} \alpha_F$, at which the $n$-th level with the given quantum number $J$ reaches the boundary of the lower continuum of the solutions of Eq. (5).

3. Short-range Coulomb problem

To fix the parameters $\theta_\sigma(J)$ and $\theta_\tau(J)$ we need additional physical assumptions. According to Pomeranchuk and Smorodinsky [27] we should consider a Coulomb potential modified at small distances $\rho \leq R_0 \ll 1$:

\[
V_R(\rho) = -\frac{q}{R} \begin{cases} R/\rho, & \rho \geq R \\ f(\rho/R), & \rho \leq R \end{cases}
\]

Equation (5) with the replacement $V_C(\rho) \rightarrow V_R(\rho)$ at $J \neq 0$ has an analytical solution for $f(\rho/R) \equiv 1$. Within the framework of this model we have

\[
\tan \theta_\sigma(J; R) = -\frac{(J + \sigma)q J_{\pm 1/2, J}(q) \mp (J - \sigma) J_{\pm 1/2, J}(q) R^{-\sigma}}{(J - \sigma)q J_{\pm 1/2, J}(q) \mp (J + \sigma) J_{\pm 1/2, J}(q) R^{\sigma}},
\]

where $J_{\nu}(q)$ is the Bessel functions with upper (lower) signs corresponding to $J > 0$ ($J < 0$) respectively.

If $q > |J| > 0$, assuming in (9) $\sigma = i\tau$, we obtain the equality

\[
\exp(2i\theta_\tau(J; R)) = \tan \theta_\tau(J; R), \quad \tau = \sqrt{q^2 - J^2} > 0, \quad J \neq 0
\]

In the case of $J = 0$ the analytical solution is possible for any type of modification of the Coulomb potential

\[
\exp(2i\theta_\tau(R_0)) = \exp \left( 2i q \ln \frac{1}{R_0} \right)
\]

$^2$ At $1/2 < \sigma < |J|$ we arrive at so-called "built-in" boundary condition [20] and the energy is given by a two-dimensional version of the Sommerfeld formula.
Table 1. Critical charge values \( q_{cr}^{(n)}(J) = Z_{cr}^{(n)}(J)\alpha_F \) at which the lowest \( n = 0 \) and first excited \( n = 1 \) levels with \( J = 0 \) reach the boundary of the lower continuum for \( R = 1/20 \) and different cutoffs of the Coulomb potential.

| \( R = 1/20 \) | \( f_0 = 1 \) | \( f_0 = 4/3 \) | \( f_0 = 3/2 \) | \( f_0 = 2 \) |
|-----------------|---------------|---------------|---------------|---------------|
| \( q_{cr}^{(0)} (J = 0) \) | 0.46          | 0.42          | 0.40          | 0.35          |
| \( q_{cr}^{(1)} (J = 0) \) | 1.33          | 1.23          | 1.18          | 1.06          |

Figure 1. Energy of the ground state \( \varepsilon(q, J; R) \) versus the charge \( q = Z\alpha_F \) for the Coulomb potential cutoff radius \( R = 1/20 \) for different values of quantum number \( J \).

where 

\[
R_0 = Re^{-f_0}, \quad f_0 = \int_0^1 f(\xi)d\xi
\]

The value \( f_0 = 1 \) corresponds to rectangular modification of the Coulomb potential and \( f_0 = 4/3 \) – to the uniform distribution of the charge over the impurity volume. The charge dependence of the energy \( \varepsilon_{J=0}(q) \) is determined by the equation:

\[
\frac{(1 - \varepsilon - i\lambda)(2\lambda)^{i\tau}\Gamma(-2iq)\Gamma\left(1 + iq - \frac{\varepsilon}{\lambda}q\right)}{(1 - \varepsilon + i\lambda)(2\lambda)^{-i\tau}\Gamma(2iq)\Gamma\left(1 - iq - \frac{\varepsilon}{\lambda}q\right)} = \exp\left(2iq\ln\frac{1}{R_0}\right)
\]

within the whole range \( 0 < q \leq q_{cr} \).

Equation (7) along with (9)-(11) determines the critical charge \( q_{cr}(J; R) \) as a function of the quantum number \( J \) and the cutoff radius \( R \), see Table 1, whereas conditions (6) with (9) and (10) give the charge dependence of the energy \( \varepsilon_J(q, R) \) at the fixed cutoff radius (see Fig. 1).

The parameters \( \theta_\sigma(J; R) \) and \( \theta_\tau(J; R) \) completely determine the energy spectrum and stationary wavefunctions of (5) at any values of the charge \( q = Z\alpha_F \).

For example, at \( \varepsilon < -1 \) we have, see [14]:

\[
u_\tau = (2k)^{i\tau}\Gamma(-2i\tau)[Aa - Bb], \quad u_{-\tau} = (2k)^{-i\tau}\Gamma(2i\tau)[e^{-i\tau}Ab^* - e^{i\tau}Ba^*],
\]

(13)
where \( k = \sqrt{\varepsilon^2 - 1} \), and
\[
a = \frac{q \sqrt{-\varepsilon + 1} + (iJ - \tau) \sqrt{-\varepsilon - 1}}{\Gamma(1 - i\tau - i\frac{\varepsilon}{k} q)}, \quad b = \frac{q \sqrt{-\varepsilon + 1} - (iJ - \tau) \sqrt{-\varepsilon - 1}}{\Gamma(1 - i\tau + i\frac{\varepsilon}{k} q)}.
\]

Taking into account second condition from (6) and the wavefunction normalization to \( \delta(k - k') \) we obtain
\[
\varepsilon^{2i\delta_J} = \frac{f_f(k; q)}{f_J(k; q)}, \quad B = e^{-\pi \tau} e^{\frac{\pi(\varepsilon - i\tau)}{2k}} e^{-i\delta_J} \sqrt{2\pi(-\varepsilon)},
\]
where \( \delta_J(k; q) \) is the scattering phase,
\[
f_J(k; q) = -i(e^{\frac{\pi}{2} - i\varphi_J}a - e^{-\frac{\pi}{2} + i\varphi_J}b^*)
\]
is the Jost function, where we introduced the notation
\[
e^{2i\varphi} = \frac{(2k)^{-i\tau} \Gamma(2i\tau)}{(2k)^{-it} \Gamma(-2i\tau)} e^{2i\theta_r(J)}.
\]

The condition \( B = 0 \) leads to the equation for the spectrum of complex energies of quasistationary states of holes corresponding to the poles of the scattering matrix \( S_J(k; q) = \exp(2i\delta_J(k; q)) \),
\[
\frac{(-2ik)^{i\tau}[q \sqrt{-\varepsilon + 1} + (iJ - \tau) \sqrt{-\varepsilon - 1}] \Gamma(-2i\tau) \Gamma(1 + i\tau - i\frac{\varepsilon}{k} q)}{(-2ik)^{i\tau}[q \sqrt{-\varepsilon + 1} + (iJ + \tau) \sqrt{-\varepsilon - 1}] \Gamma(2i\tau) \Gamma(1 - i\tau - i\frac{\varepsilon}{k} q)} = e^{2i\delta_J(q; R)}.
\]
The solutions of this equation determine both the position of a quasidiscrete level \( \varepsilon_0 \) and its width \( \gamma \):
\[
\varepsilon_{qs} = -\varepsilon_p = \varepsilon_0 = \frac{i}{2}\gamma, \quad \varepsilon_0 > 0, \quad \gamma > 0,
\]
Due to the Coulomb barrier in the lower continuum the width \( \gamma \ll 1 \)
\[
k = k_0' - ik_0'', \quad k_0' = \sqrt{\varepsilon_0^2 - 1} > 0, \quad k_0'' = \frac{\gamma}{2k_0'} > 0,
\]
and these poles are located on the second (unphysical) sheet [28], in accordance with the unitarity of the partial scattering matrix.

The scattering phase \( \delta_J(k; q) \) as a function of hole energy \( \varepsilon_{\text{hole}} = -\varepsilon > 1 \) for \( J = 0 \) and \( q > q_{cr} \) is shown in Fig. 3. For \( J = 1/2 \) and \( J = -1/2 \) the behaviour of the phases is the same.

The poles of scattering matrix determine the complex energies \( \varepsilon_{qs} \) of quasistationary states of holes (16). Figure 2 shows the position of the lowest quasidiscrete level \( \varepsilon_0 \) and its width \( \gamma \) as a function of \( q - q_{cr} \). If the hole energy \( \varepsilon_{\text{hole}} \) is in the range of dramatic change of scattering phase, such a states are evident as resonances in the hole-impurity scattering and the partial cross-section \( \sigma_J = \sin^2 \delta_J(k; q) \) have the resonant form, see Fig. 4.

4. Conclusions

Thus, the "cutoff" i.e., the regularization of the Coulomb potential at small distances, ensures that the Dirac Hamiltonian is self-adjoint both for two-dimensional and for three-dimensional problems. This implies that the one-particle approximation for the Dirac equation is consistent at any values of the Coulomb charge, including the overcritical range. It means that there is no spontaneous creation of electron-hole pairs. At the same time, owing to the presence of low permeable effective Coulomb barrier, the continuum states near the boundary of lower continuum form quasistationary states which may appear as resonances in the scattering of holes on supercritical impurity.
Figure 2. Position of the lowest quasidiscrete level $\varepsilon_0$ and its width $\gamma$ versus the difference $q - q_{cr}$ at the cutoff radius $R = 1/20$. $\varepsilon^*$, $\gamma^*$ are the position and width of the pole of $S$-matrix corresponding to the resonance for $q = 0.52$.

Figure 3. Scattering phase $\delta_J$ for $J = 0$ as a function of the hole energy for $q = 0.52$ which is close to $q_{cr}$ for $R = 1/20$, the hole energy $\varepsilon_{hole} \simeq \varepsilon^*$ is in the range of dramatic change of scattering phase with width $\gamma^*$.

Figure 4. The partial scattering cross-section $\sigma_J$.

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