The Brillouin zone, where the Fermi level is located. In graphene sheet the conduction and valence bands consisting of carbon atoms arranged laterally in honeycomb structure.

Recently graphene was successfully fabricated and was shown to depend critically on the difference in binding model and in an effective-mass approximation. In a defect consisting of a single atom, a quasi-bound state like donor or acceptor state emerges near the Dirac point when the potential becomes extremely strong. In the case of AB pair impurities, the quasi-bound state splits into two and the resonance appears near the Dirac point for small scattering potential.

Keywords: impurity scattering, strong and short-range scatterer, lattice vacancy, virtual bound state, resonance scattering, two-dimensional graphite, Dirac point

§1. Introduction

Graphene is atomically thin two-dimensional film of carbon atoms arranged laterally in honeycomb structure. In graphene sheet the conduction and valence bands consisting of π orbitals cross at K and K’ points of the Brillouin zone, where the Fermi level is located.\(^1,2\) Recently graphene was successfully fabricated\(^3\) and the magnetotransport was measured together with the integer quantum Hall effect.\(^4,5\) Several reviews have already been published.\(^6–9\) In this paper effects of impurities with strong and short-range potential are studied in a graphene within a \(k\cdot p\) scheme.

Direct and clear evidences for the presence of atomic defects in graphene layers, such as vacancies consisting of a single atom, two atoms adjacent to each other, etc., were experimentally demonstrated.\(^10,11\) Further, graphene is sensitive to adsorbed atoms partly because of their roles as strong scatterers as well as carrier doping.\(^12–14\) The electron scattering by such localized defects with strong and short-range potential is quite interesting. In fact, the scattering of electrons by vacancies was studied in carbon nanotubes both in a tight-binding model and in an effective-mass approximation and was shown to depend critically on the difference in the number of vacancies at A and B sublattices when the strength of the potential is sufficiently large.\(^15–21\)

In nanotubes, resonance scattering by defects was experimentally observed\(^22–24\) and various theoretical calculations based on first-principles\(^25–28\) and tight-binding models\(^29,30\) were reported.

Electronic states in the vicinity of K and K’ points are known to be well described by effective-mass or \(k\cdot p\) scheme.\(^29–35\) We use this \(k\cdot p\) scheme to discuss effects of scatterers with strong and short-range potential and exactly calculate \(T\) matrix using Green’s function technique. The results show various interesting features associated with formation of virtual bound states, strongly depending on the difference in the number of impurities at two sublattices as in the case of the carbon nanotube.

The paper is organized as follows: In §2, a brief review is given on the effective Hamiltonian in a \(k\cdot p\) scheme and the scattering problem for defects \(A_nB_m\) consisting of \(n\) impurities with short-range potential located at A sublattice points and \(m\) at B sublattice points. In §3, numerical results are presented for some of representative examples. In a defect consisting of a single atom \((n = 1\text{ and } m = 0)\), a quasi-bound state like donor or acceptor state emerges near the Dirac point when the potential becomes extremely strong, where the scattering diverges. In the case of AB pair impurities, the quasi-bound state splits into two and the resonance near the Dirac point appears even for small scattering potential. In Appendix A, explicit formula for the scattering matrix appropriate for numerical calculations are derived, and the dependence of the scattering strength on the potential strength is analytically discussed at the Dirac point.

§2. Formulation

2.1 Effective-mass description

The structure of graphene is shown in Fig. 1(a). A unit cell contains two carbon atoms, which are denoted by A and B. The primitive translation vectors are \(a = (1, 0)a\) and \(b = (−1/2, \sqrt{3}/2)a\) with lattice constant \(a = 2.46\ \)Å. Three vectors connecting neighboring A and B atoms are given by \(\tau_1 = (0, 1/\sqrt{3})a\), \(\tau_2 = (−1/2, −1/2\sqrt{3})a\), and \(\tau_3 = (1/2, −1/2\sqrt{3})a\). Two bands having approximately a linear dispersion cross the Fermi level (chosen at \(\varepsilon = 0\)) at K and K’ points of the first Brillouin zone shown in Fig. 1(b). The wave vectors of the K and K’ points are given by \(K = (2\pi/a)(1/3, 1/\sqrt{3})\) and \(K’ = (2\pi/a)(2/3, 0)\), respectively.

In the vicinity of the Fermi level, therefore, electronic states are described by the Schrödinger equation given by

\[
\mathcal{H}\mathbf{F}(\mathbf{r}) = \varepsilon\mathbf{F}(\mathbf{r}),
\]  

with

\[
\mathcal{H} = \mathcal{H}_0 + V,
\]

where \(V\) represents impurity potential. The Hamiltonian

\[
\mathcal{H} = \mathcal{H}_0 + V,
\]
of the ideal graphene is given by

\[ \mathcal{H}_0 = \begin{pmatrix} KA & K' A & KB & K' B \\ 0 & \gamma(\hat{k}_x - i\hat{k}_y) & 0 & 0 \\ 0 & 0 & 0 & \gamma(\hat{k}_x + i\hat{k}_y) \\ 0 & 0 & \gamma(\hat{k}_x - i\hat{k}_y) & 0 \end{pmatrix}, \tag{2.3} \]

with \( \gamma \) being a band parameter, and the wave function is written as

\[ \mathbf{F}(r) = \begin{pmatrix} F^K(r) \\ F^{K'}(r) \end{pmatrix}, \tag{2.4} \]

with

\[ F^K(r) = \begin{pmatrix} F^{KA}(r) \\ F^{KB}(r) \end{pmatrix}, \quad F^{K'}(r) = \begin{pmatrix} F'^{KA}(r) \\ F'^{KB}(r) \end{pmatrix}. \tag{2.5} \]

Here, \( F^{KA} \) and \( F^{KB} \) describe the amplitude at an A and B site, respectively, for the wave-function component at the \( K \) point, and \( F'^{KA} \) and \( F'^{KB} \) describe that for the \( K' \) point.

For the discussion of scattering by short-range scatterers localized at several lattice points, it is more convenient to choose the representation in which the \( (4 \times 4) \) matrix Hamiltonian is rewritten as

\[ \mathcal{H}_0 = \begin{pmatrix} KA & K' A & KB & K' B \\ 0 & 0 & \gamma(\hat{k}_x - i\hat{k}_y) & 0 \\ 0 & 0 & 0 & \gamma(\hat{k}_x + i\hat{k}_y) \\ 0 & \gamma(\hat{k}_x - i\hat{k}_y) & 0 & 0 \end{pmatrix}, \tag{2.6} \]

and the wave function is rewritten as

\[ \mathbf{F}(r) = \begin{pmatrix} F^A(r) \\ F^B(r) \end{pmatrix}, \tag{2.7} \]

with

\[ F^A(r) = \begin{pmatrix} F^{KA}(r) \\ F'^{KA}(r) \end{pmatrix}, \quad F^B(r) = \begin{pmatrix} F^{KB}(r) \\ F'^{KB}(r) \end{pmatrix}. \tag{2.8} \]

The eigen-states and energies are written as

\[ \mathbf{F}_\alpha(r) = f_\alpha e^{ik \cdot r}, \quad \varepsilon_\alpha = s\gamma k, \tag{2.9} \]

\[ f_\alpha = \begin{pmatrix} \Phi^A_\alpha \\ \Phi^B_\alpha \end{pmatrix}, \tag{2.10} \]

with \( \alpha = (v, s, k) \), where \( v = K \) or \( K' \), \( k = |k| \), and \( s = +1 \) and \(-1 \) for the conduction and valence bands, respectively.

For an impurity localized with potential strength \( u \) at a carbon A site \( r_j = n_a a + n_b b + \tau_1 \) with integers \( n_a \) and \( n_b \), we have \(36) \)

\[ V_j(r) = V_j \delta(r - r_j), \]

\[ V_j = u \begin{pmatrix} \Phi^A_\alpha \\ 0 \end{pmatrix}, \quad \Phi^A_\alpha = \begin{pmatrix} 1 \\ e^{-i\phi^A_\alpha} \end{pmatrix}, \quad \phi^A_\alpha = (K' - K) \cdot r_j \tag{2.11} \]

For an impurity localized at a carbon B site \( r_j = n_a a + n_b b + \tau_1 \), we have

\[ V_j(r) = V_j \delta(r - r_j), \quad V_j = u \begin{pmatrix} 0 \\ \Phi^B_\alpha \end{pmatrix}, \quad \Phi^B_\alpha = \begin{pmatrix} 1 \\ e^{-i\phi^B_\alpha} \end{pmatrix}, \quad \phi^B_\alpha = (K' - K) \cdot r_j \tag{2.12} \]

Within a tight-binding model, a short-range impurity gives local site energy \( u_0 \) measured from that of a carbon atom. Then, we have

\[ u = u_0 \Omega_0, \tag{2.13} \]

where \( \Omega_0 = \sqrt{3}a^2/2 \) is the area of a unit cell.

### 2.2 Scattering matrix

Let us consider \( T \) matrix

\[ T = V + \frac{1}{\varepsilon - H_0 + i0}T, \tag{2.14} \]

and the Green’s function

\[ G_{iji'} = G(r_j - r_{i'}, \varepsilon) = \sum_\alpha f_\alpha \frac{1}{\varepsilon - \varepsilon_\alpha + i0}f_\alpha^* e^{ik_{\alpha}(r_j - r_{i'})}. \tag{2.15} \]

Then, the scattering amplitude for incident state \( \alpha \) and outgoing state \( \alpha' \) is given by

\[ \langle \alpha' | T | \alpha \rangle = \sum_i f_\alpha^* T_{ij} f_\alpha e^{-ik_{\alpha'} \cdot r_{i'}} e^{ik_{\alpha} \cdot r_j}, \tag{2.16} \]

where \( T_{ij} \) is a \( (4 \times 4) \) matrix satisfying

\[ T_{ij} = V_i \delta_{ij} + V_i \sum_l G_{il} T_{lj}. \tag{2.17} \]

Effects of multiple scattering from a single impurity can exactly be taken into account by replacing eq. (2.17) by

\[ T_{ij} = \tilde{V}_i \delta_{ij} + \tilde{V}_i \sum_{l \neq i} G_{il} T_{lj}, \tag{2.18} \]

with

\[ \tilde{V}_i = [1 - V_i G(0, \varepsilon)]^{-1} V_i. \tag{2.19} \]

When all impurities are localized in a region smaller than the electron wavelength, eq. (2.16) can be replaced by

\[ \langle \alpha' | T | \alpha \rangle = f_\alpha^* T_{S} f_\alpha e^{ik_{\alpha'} \cdot r_{0}} e^{-ik_{\alpha} \cdot r_0}, \tag{2.20} \]

where \( r_0 \) is the center-of-mass of all the impurities and

\[ T_{S} = \sum_{i,j} T_{ij}. \tag{2.21} \]

We shall confine ourselves to the case of such scatterers...
and energy region satisfying this condition.

### 2.3 Green’s function

The Green’s function is explicitly written as

\[
G(r, \varepsilon) = \frac{ik}{\gamma(2\pi)^2} \int \frac{d^3k}{(\varepsilon + \gamma k^2)^2 - \gamma^2 k^2} f_c(k)e^{i\bar{k} \cdot \bar{r}}
\]

\[
\times \begin{pmatrix}
\varepsilon & 0 & \gamma(k_x - ik_y) \\
0 & \varepsilon & 0 \\
\gamma(k_x + ik_y) & 0 & \varepsilon \\
\end{pmatrix},
\]

(2.22)

where \( f_c(k) \) is the cutoff function defined by

\[
f_c(k) = \frac{k^2}{\varepsilon^2 + k^2}.
\]

(2.23)

The cutoff wave number, \( k_c \), is chosen in such a way that contributions come from the region corresponding to the first Brillouin zone, i.e.,

\[
\gamma k_c = \varepsilon_c \sim 3\gamma_0,
\]

where \( \gamma_0 \) is the nearest-neighbor hopping integral in a tight-binding model and \( \varepsilon_c = 3\gamma_0 \sim 9 \text{ eV} \) is a half of the \( \pi \)-band width. We have \( \gamma = (\sqrt{3}/2)\varepsilon_0 \gamma_0 \).

The Green’s function is written as

\[
G(r, \varepsilon) = \begin{pmatrix}
g_0(r) & g_1(r) & 0 \\
g_0(r) & 0 & \bar{g}_1(r) \\
0 & g_1(r) & 0 \\
\end{pmatrix}.
\]

(2.24)

The diagonal element becomes \( g_0(r) = g_0(|r|) \), with

\[
g_0(r) = \frac{1}{4\gamma^2} \left\{ \varepsilon [Y_0(kr) + \frac{2}{\pi} K_0(kr)] - i\varepsilon J_0(kr) \right\},
\]

(2.25)

where \( k = |\varepsilon|/\gamma \), \( J_0 \) and \( Y_0 \) are the Bessel function of the first and second kind, respectively, and \( K_0 \) is the modified Bessel function of the second kind. The Green’s functions \( g_1(r) \) and \( \bar{g}_1(r) \) connecting different sublattice points satisfy

\[
g_1(-r) = -g_1(r), \quad \bar{g}_1(-r) = -\bar{g}_1(r),
\]

(2.26)

and are given in terms of polar coordinates \((r, \varphi)\) by

\[
g_1(r) = ie^{-i\varepsilon} g_1(r) , \quad \bar{g}_1(r) = ie^{i\varepsilon} g_1(r),
\]

(2.27)

with

\[
g_1(r) = \frac{1}{4\gamma^2} \left\{ \varepsilon [Y_1(kr) + \frac{2\gamma k_c}{\pi} K_1(kr)] - i\varepsilon J_1(kr) \right\}.
\]

(2.28)

For \( \varepsilon = 0 \), therefore, \( g_1(r) \) is real, giving relations

\[
\bar{g}_1(r) = -g_1(r) = g_1(-r),
\]

\[
g_1(r) = -\bar{g}_1(r) = g_1(-r),
\]

(2.29)

which will be used in discussion of resonances at \( \varepsilon = 0 \) in Appendix A.

For \( kr \ll 1 \) as in the present case, we have

\[
g_0(r) \approx \frac{1}{2\pi^2} \left[ \varepsilon \ln \left( \frac{kr}{2} \right) + \varepsilon K_0(kr) \right] - i\varepsilon^2, \quad (2.30)
\]

\[
g_1(r) \approx \frac{1}{2\pi^2} \left[ - \frac{\gamma}{r} + \gamma k_c K_1(kr) \right] \quad (2.31)
\]

For \( t \ll 1 \), further, we have

\[
K_n(t) = \begin{cases}
-\eta - \ln \frac{t}{2} & (n=0); \\
(n-1)! \left( \frac{t}{2} \right)^{-n} & (n>0),
\end{cases}
\]

(2.32)

with \( \eta \) being Euler’s constant given by \( \eta = 0.57722 \cdots \). At \( r = 0 \), therefore, we have

\[
g_0 \approx g_0(0) = \frac{\varepsilon}{2\pi^2} \ln \frac{\varepsilon}{\varepsilon_c} - i\varepsilon^2, \quad (2.33)
\]

The off-diagonal element is roughly

\[
g_1(r) \approx \frac{1}{2\pi^2} \frac{1}{r},
\]

(2.34)

and is much larger than \( g_0 \) for \( r \sim a \). This large off-diagonal Green’s function for \( r \approx a \) causes characteristic behavior of resonance scattering depending on the number of impurities at different sublattice points.15 This singularity is cutoff only in the extreme vicinity of \( r = 0 \), i.e., when \( r \ll k_c^{-1} \sim a \), and we have \( g_1(0) = 0 \).

### 2.4 Virtual bound states and resonance scattering

As shown in eq. (2.19), the potential of a single impurity is renormalized into

\[
\bar{u} = \frac{u}{1 - 2ug_0}.
\]

(2.35)

This shows that a virtual bound state appears at energy satisfying \( \text{Re}(1 - 2ug_0) = 0 \), which gives the energy

\[
1 = \frac{3\varepsilon u}{2\pi^2}\ln \left| \frac{\varepsilon}{\varepsilon_c} \right|.
\]

(2.36)

Because of the presence of nonzero imaginary part of \( g_0 \), the state is considerably broadened except at \( \varepsilon = 0 \) where \( g_0 = 0 \). The resonance energy is positive for \( u < 0 \) and negative for \( u > 0 \), and approaches the Dirac point with increasing \( |u| \).

When potential asymmetry is introduced between the A and B sublattices, the graphene turns into a semiconductor with nonzero gap. In this case a shallow donor state is formed below the bottom of the conduction band for \( u < 0 \) and a shallow acceptor state above the top of the valence band for \( u > 0 \). In the limit of the vanishing gap, these donor and acceptor states turn into virtual bound states because of the presence of nonzero density of states.

The maximum electron or hole concentrations achievable in graphene is typically of the order of \( n_a = 10^{13} \text{ cm}^{-2} \). This roughly corresponds to Fermi energy \( |\varepsilon_F|/\gamma_0 \lesssim 0.1 \). According to eq. (2.36), the virtual bound state falls into this energy range only for \( |u|/\gamma_0 \gtrsim 8 \). The energy of atomic \( p \) states of B and N atoms are given
by 2.3 eV and −2.50 eV, respectively, if being measured from the carbon p energy,37 showing that the impurity potential is |u|/γ0Ω0 ≲ 1. For graphene hydrogenated or fluorinated, the effective local potential energy may become larger but certainly not much larger. Therefore, virtual bound states are likely to be outside of the Fermi level in actual graphenes.

When several impurities are present, these virtual bound states interact with each other and split into separate levels. This interaction strength is determined by Green’s function connecting impurity positions and therefore the splitting is particularly important for impurities located in different sublattice points connected via off-diagonal elements \( g_1 \) because \( |g_1| \gg |g_0| \), i.e., for impurities \( A_nB_m \) with \( n > 0 \) and \( m > 0 \). As a result, some of the split virtual bound states can have energy close to the Dirac point for moderately strong impurity potential \( |u|/\gamma_0 \Omega_0 \sim 1 \), as will be demonstrated in the numerical results shown in the next section.

In Appendix A, further simplification appropriate for explicit calculations of the solution of eq. (2.18) for a finite number of impurities is presented and exact formal expression of \( T_S \) is derived at the Dirac point. With the use of this result, we can obtain essential features of resonances in the vicinity of the Dirac point sensitive to the number of A and B impurities as a function of the potential strength.

2.5 Effective scattering potential

A defect with a certain configuration of impurities usually causes almost equal amount of scattering between the K and K' points and exhibit anisotropic scattering explicitly depending on incident and scattered directions. In actual systems, there can be scatterers with three different directions, 0, 2π/3, and −2π/3 around a certain B sublattice point, for a given configuration of scatterers. It is straightforward to show that under +2π/3 and −2π/3 rotation, the effective T matrix, \( T_S \), is transformed into \( U^*T_SU \) and \( UT_SU^* \), respectively, with

\[
U = \begin{pmatrix}
\omega & 0 & 0 & 0 \\
0 & \omega^{-1} & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1 \\
\end{pmatrix}. \tag{2.37}
\]

We shall consider the average \(|\langle \alpha|T_S|\alpha' \rangle|^2\) over these three directions for each kind of configurations.

After the average, scatterers become almost isotropic within each valley and between different valleys. This has been checked through explicit numerical calculations, although results are not shown here. In the following, we consider the effective scattering potential, \( V_S \), giving the transport relaxation time \( \tau_{tr} \), i.e.,

\[
\frac{1}{\tau_{tr}} = \frac{2\pi}{h} \frac{1}{2} \sum_{v,v'} \int \frac{dk'}{(2\pi)^2} n_i |\langle \omega k|T_S|v's'k' \rangle|^2 \times (1 - \cos \theta_{k,k'}) \delta(\varepsilon_{sk} - \varepsilon_{s'k'})
\]

\[
= \frac{2\pi}{h} n_i V_S^2 \frac{1}{2} \sum_{v,v'} \int \frac{dk'}{(2\pi)^2} \delta(\varepsilon_{sk} - \varepsilon_{s'k'}), \tag{2.38}
\]

where \( v \) and \( v' \) denote the K and K' points, \( n_i \) is the defect concentration, and \( \theta_{k,k'} \) is the angle between \( k \) and \( k' \).

3. Numerical Results

Figure 2 shows some examples of effective potential \( V_S \) of a defect consisting of a single A site as a function of energy for \( u > 0 \). Results for \( u < 0 \) are obtained by mirror reflection with respect to \( \varepsilon = 0 \). The energy of a virtual bound state obtained by Eq. (2.36) is denoted by a downward arrow. Actual peaks in the effective potential are slightly shifted to the zero-energy side because of the large energy dependence of the imaginary part of \( g_0 \) as shown in eq. (2.33). In the limit \( u \to \infty \), the potential becomes proportional to \(|g_0|^{-1} \) independent of \( u \) and therefore diverges at \( \varepsilon = 0 \).

Figure 3 shows \( V_S \) of defect A2 consisting of nearest-neighbor sites with distance \( a \). Clear resonance enhancement at bonding and anti-bonding states with small splitting becomes apparent for \( u/\gamma_0 \Omega_0 \gtrsim 10 \). For a pair with small distance, this splitting is determined by \( \text{Re}(g_0) \), which rapidly decreases with decreasing \( |\varepsilon| \) as shown in Eq. (2.33), leading to the reduction of the bonding-antibonding splitting for a pair of impurities at same sublattice points.

Figure 4 shows \( V_S \) of defect A1B1 consisting of a pair of neighboring A and B sites. Because the bonding and anti-bonding splitting of bound states is determined by \( \text{Re}(g_1) \) which is much larger than \( \text{Re}(g_0) \) and nearly independent of energy, the energy of anti-bonding state can lie close to the zero energy even for moderate values of \( u \). Figure 4(a) shows that this state crosses the Dirac point at \( u/\gamma_0 \Omega_0 \approx 2.5 \), where the scattering strength at the Dirac point diverges. With the further increase of \( u \), the bound state goes into the conduction band and the scattering potential approaches a small value independent of \( u \) in the limit of infinitely large \( u \).

Figure 5 shows \( V_S \) of defect A2B1 consisting of neighboring two A sites and a B site lying between them. In this case, bound states split into three due to interaction. The splitting between the highest and lowest states is essentially determined by large \( \text{Re}(g_1) \) and is about the same as in defect A1B1. As a result, the crossing of the highest bound state with the Dirac point occurs around \( u/\gamma_0 \Omega_0 \approx 1.96 \) as in (a). With further increase of \( u \), this bound state goes deeply into the conduction band as shown in (b) and the behavior in the vicinity of the Dirac point becomes similar to the case of defect A1 for sufficiently \( u \) as shown in (c).

Figure 6 shows \( V_S \) of defect A2B2 consisting of neighboring three A sites and a B site located at the center. The behavior is essentially the same as in the case of A2B2 except that the resonance scattering at the Dirac point occurs at smaller value of \( u \), i.e., \( u \approx 1.45 \). Figure 7 shows \( V_S \) of defect A2B2 consisting of neighboring two A and B sites along a zigzag direction. Two bound states cross the Dirac point at \( u/\gamma_0 \Omega_0 \approx 1.58 \) and 3.65 as shown in (a) and (c). In the limit of infinitely large \( u \), the scattering strength approaches a small value independent of \( u \) as in the case of defect A1B1.

These results suggest the following conclusions for defect \( A_nB_m \) (\( n \geq m \geq 0 \)):

(i) The number of bound states which cross the Dirac
point for moderate values of $u$ is given by that of AB pairs, i.e., given by $m$.

(ii) In the limit of sufficiently large $u$, energy of some bound states approaches the Dirac point unless $n = m$. For $n = m$, $V_S$ approaches a small value independent of $u$ and almost independent of energy.

These conclusions can be confirmed in Fig. 8, which shows $V_S$ of various defects as a function of the potential strength at the Dirac point. Further, they can be analytically shown in Appendix A.

§4. Summary and Conclusion

We have studied electron scattering by defects consisting of several strong and short-range impurities at A and B sublattice points lying close to each other within a $k$-$p$ scheme in monolayer graphene. In a defect consisting of a single impurity, a quasi-bound state like donor or acceptor state emerges near the Dirac point when the potential becomes extremely strong. In the case of AB pair impurities, the quasi-bound state splits into two and the resonance appears near the Dirac point for moderately strong scattering potential. In the case of defects consisting of many atoms, the number of resonances crossing $\varepsilon = 0$ when the potential strength is varied is that of AB pairs.

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Appendix A: Scattering Matrix and Resonances at Dirac Point

Let us consider defect $A_nB_m$, consisting of $n$ impurities at A sites and $m$ impurities at B sites. We can assume $n \geq m \geq 0$ without loss of generality. In terms of vectors $a_j$ and $b_j$ defined by

$$a_j = \frac{1}{\sqrt{2}} \left( e^{i\phi_j/2} \right), \quad b_j = \frac{1}{\sqrt{2}} \left( e^{-i\phi_j/2} \right),$$

we can write potential matrix as

$$\Phi_j^A = 2a_ja_j^+, \quad \Phi_j^B = 2b_jb_j^+.$$  \hspace{1cm} (A2)

Then, we can show that $(4,4)$ matrix $T_{ij}$ is expressed by four independent elements such that

$$T_{ij} = \begin{pmatrix} T_{ij}^{AA} & T_{ij}^{AB} \\ T_{ij}^{BA} & T_{ij}^{BB} \end{pmatrix} = \frac{2\bar{u}}{L^2} \begin{pmatrix} t_{ij}^{AA}a_ia_j^+ + t_{ij}^{AB}a_ib_j^+ \\ t_{ij}^{BA}b_ia_j^+ + t_{ij}^{BB}b_ib_j^+ \end{pmatrix},$$

where

$$t_{ij}^{AA} = \delta_{ij} + 2\bar{u} \sum_{l \neq j, l \in A} g_{il}^{AA}t_{ij}^{AA} + 2\bar{u} \sum_{l \in B} g_{il}^{AB}t_{ij}^{AB},$$

$$t_{ij}^{BB} = \delta_{ij} + 2\bar{u} \sum_{l \neq j, l \in B} g_{il}^{BB}t_{ij}^{BB} + 2\bar{u} \sum_{l \in A} g_{il}^{BA}t_{ij}^{BA},$$

$$t_{ij}^{AB} = 2\bar{u} \sum_{l \neq j, l \in A} g_{il}^{AB}t_{ij}^{AB} + 2\bar{u} \sum_{l \in B} g_{il}^{BA}t_{ij}^{BA},$$

$$t_{ij}^{BA} = 2\bar{u} \sum_{l \neq j, l \in B} g_{il}^{BA}t_{ij}^{BA} + 2\bar{u} \sum_{l \in A} g_{il}^{AB}t_{ij}^{AB},$$

(A4)

These constitute a set of linear equations, appropriate for explicit analytical and numerical calculations of $T_{ij}$ and then $T_S$.

In the following we shall confine ourselves to the case at the Dirac point $\varepsilon = 0$. Then, we can set $g_0(r_{ij}) = 0$ and have $\bar{u} = u$ and

$$t^{AA} = (1 - 4u^2g^{AB}g^{BA})^{-1}, \quad t^{BA} = 2ug^{BA}t^{AA},$$

$$t^{BB} = (1 - 4u^2g^{BA}g^{AB})^{-1}, \quad t^{AB} = 2ug^{AB}t^{BA}.$$  \hspace{1cm} (A8)

The resonance occurs when a virtual bound state crosses the Dirac point. Therefore, the corresponding value of $u$ is determined by

$$\det(1 - 4u^2g^{AB}g^{BA}) = 0,$$  \hspace{1cm} (A9)

$$\det(1 - 4u^2g^{BA}g^{AB}) = 0.$$  \hspace{1cm} (A10)

These means that $1/4u^2$ is an eigen value of matrices $g^{AB}g^{BA}$ or $g^{BA}g^{AB}$.

With the use of eq. (2.29), we have

$$g^{AB} = g^{BA}, \quad g^{AB} = g^{BA},$$  \hspace{1cm} (A11)

which shows that matrices $g^{AB}g^{BA}$ and $g^{BA}g^{AB}$ are both hermitian. Let us define eigen values and normalized vectors by

$$g^{AB}u_\mu = \mu u_\mu \quad (\mu = 1, \ldots, n).$$  \hspace{1cm} (A12)

We immediately see that

$$\mu (g^{BA}u_\mu)^t g^{BA}u_\mu \geq 0.$$  \hspace{1cm} (A13)

Because $g^{BA}$ is an $(n, m)$ matrix with $n \geq m$, there
are $n-m$ nonzero vectors satisfying $g^{BA}u = 0$. Let $u_\mu, \mu = m+1, \cdots, n$ be such vectors, i.e.,
\[ g^{BA}u_\mu = 0, \quad p_\mu = 0, \quad (\mu = m+1, \cdots, n). \] (A14)

In general, $p_\mu$ is positive for $\mu = 1, \cdots, m$ except in some exceptional cases. By multiplying eq. (A12) by $g^{BA}$ from left for $\mu = 1, \cdots, m$, we have
\[ g^{BA}y^{AB}v_\mu = p_\mu v_\mu, \] (A15)
\[ g^{BA}u_\mu = \alpha_\mu v_\mu, \] (A16)

with $\alpha_\mu = |g^{BA}u_\mu|^{-1}$ for normalization of $v_\mu$. We also have
\[ g^{AB}v_\mu = \alpha_\mu^{-1} p_\mu u_\mu. \]

This shows that $m$ positive eigen values of $g^{AB}g^{BA}$ are the same as those of $g^{BA}g^{AB}$ and therefore the number of the virtual bound states crossing the Dirac point with varying $u$ is $m$, which is the number of AB pairs.

We then have
\[ t^{AA} = \sum_{\mu=1}^{m} u_\mu - u^{\dagger}_\mu + \sum_{\mu=m+1}^{n} u_\mu u_\mu, \] (A17)
\[ t^{BB} = \sum_{\mu=1}^{m} v_\mu - v^{\dagger}_\mu + \sum_{\mu=m+1}^{n} v_\mu v_\mu, \] (A18)
\[ t^{BA} = \sum_{\mu=1}^{m} 2u_\mu a_\mu - u^{\dagger}_\mu a^{\dagger}_\mu, \] (A19)
\[ t^{AB} = \sum_{\mu=1}^{m} 2u_\mu a^{\dagger}_\mu - u^{\dagger}_\mu a^{\dagger}_\mu. \] (A20)

Let us define two-component vectors
\[ a_\mu = (a_1 \cdots a_n)u_\mu, \quad b_\mu = (b_1 \cdots b_m)v_\mu. \] (A21)

Then, we have
\[ T_S = \left( \begin{array}{cc} T^{AA}_S & T^{AB}_S \\ T^{BA}_S & T^{BB}_S \end{array} \right), \] (A22)

with
\[ T^{AA}_S = \frac{1}{L^2} \sum_{\mu=1}^{m} a_\mu \frac{2u}{1-4u^2 p_\mu} a^{\dagger}_\mu + \sum_{\mu=m+1}^{n} a_\mu a^{\dagger}_\mu, \] (A23)
\[ T^{BB}_S = \frac{1}{L^2} \sum_{\mu=1}^{m} b_\mu \frac{2u}{1-4u^2 p_\mu} b^{\dagger}_\mu, \] (A24)
\[ T^{BA}_S = \frac{1}{L^2} \sum_{\mu=1}^{m} b_\mu \frac{4u^2 a^{\dagger}_\mu}{1-4u^2 p_\mu}, \] (A25)
\[ T^{AB}_S = \frac{1}{L^2} \sum_{\mu=1}^{m} a_\mu \frac{4u^2 a^{\dagger}_\mu}{1-4u^2 p_\mu} b^{\dagger}_\mu, \] (A26)

From the above results, we can deduce the following conclusions:

(i) In the case of weak potential $|u|/\gamma_0 \Omega \ll 1$, the effective scattering potential becomes the sum $n \times u$ of a single A site and $m \times u$ of a single B site, thus reducing to that of the lowest Born approximation.

(ii) The number of divergence at the Dirac point as a function of $u$ is given by $m$, which is the number of AB pairs.

(iii) In the limit of strong potential $|u| \to \infty$, $T^{AA}_S$ increases in proportion to $u$ and the scattering intensity diverges when $n > m$. When $n = m$, on the other hand, both $T^{AA}_S$ and $T^{BB}_S$ vanish, and $T^{BA}_S$ and $T^{AB}_S$ approach matrices independent of $u$, showing that the scattering strength becomes a nonzero value independent of $u$ but possibly dependent on details of the configuration.

References
1) P. R. Wallace, Phys. Rev. 71 (1947) 622.


Figure Captions

Fig. 1 (a) The lattice structure of monolayer graphene together with primitive translation vectors $\mathbf{a}$ and $\mathbf{b}$ and three vectors connecting neighboring atoms $\mathbf{\tau}_l$ ($l = 1, 2, 3$). A unit cell contains two carbon atoms denoted by A and B. (b) The first Brillouin zone and K and K’ points.

Fig. 2 (Color online) Some examples of effective potential $V_S$ of defect $A_1$ as a function of energy for $u > 0$. The values of $u/\gamma_0\Omega_0$ are denoted in the figure. Results for $u < 0$ are obtained by mirror reflection with respect to $\epsilon = 0$. The downward arrows indicate energy of a virtual bound state given by Eq. (2.36). A clear resonance enhancement becomes apparent for $u/\gamma_0\Omega_0 \gtrsim 10$.

Fig. 3 (Color online) Some examples of $V_S$ of defect $A_2$ consisting of nearest-neighbor sites. A clear resonance enhancement at bonding and anti-bonding states with small splitting becomes visible for $u/\gamma_0\Omega_0 \gtrsim 10$.

Fig. 4 (Color online) Some examples of $V_S$ of defect $A_1B_1$ consisting of a pair of neighboring A and B sites. Divergent scattering occurs around $u/\gamma_0\Omega_0 \approx 2.5$ for which the antibonding resonance state crosses the Dirac point.

Fig. 5 (Color online) Some examples of $V_S$ of defect $A_2B_1$ consisting of neighboring two A sites and a B site lying between them. Divergent scattering occurs around $u/\gamma_0\Omega_0 \approx 1.96$ and $\infty$.

Fig. 6 (Color online) Some examples of $V_S$ of defect $A_2B_1$ consisting of neighboring three A sites and a B site located at the center. Divergent scattering occurs around $u/\gamma_0\Omega_0 \approx 1.45$ and $\infty$.

Fig. 7 (Color online) Some examples of $V_S$ of defect $A_2B_2$ consisting of neighboring two A and B sites along a zigzag direction. Divergent scattering occurs around $u/\gamma_0\Omega_0 \approx 1.58$ and 3.65.

Fig. 8 (Color online) Some examples of $V_S$ of various defects as a function of the potential strength at the Dirac point.
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