Edge states and sublattice imbalance of rectangular graphene nanoflakes

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Abstract
The energy states of $\pi$-electrons in a rectangular graphene flake with a pair of zigzag edges and a pair of armchair edges were studied using a tight-binding method. It is demonstrated that the known exact solution can be interpreted as the results derived from the analytical solutions for graphene nanoribbons on a brick-type lattice by considering the wavefunctions and sublattice imbalance. Edge states in rectangular graphene flakes with a symmetric structure, whose energies are not exactly zero but approach zero as the size increases, are characterized by discrete allowed modes, whereas the zero-energy state appears in rectangular graphene flakes with an asymmetric structure. By applying the edges states of rectangular graphene flakes, zero-energy states were examined in Y-shaped graphene flakes, which involve the same three zigzag edges as in the triangular graphene flakes. Sublattice imbalance in the model was found to force the edge states, including the undamped mode, into zero energy. Configurations of the allowed modes in the zero-energy state are revealed.

1. Introduction

The experimental discovery of graphene [1], which can be extracted from graphite, has attracted much attention because of its fundamental research and potential applications in the fields of condensed matter physics and materials science. Graphene, a two-dimensional crystal of carbon atoms arranged in a honeycomb lattice, has distinct electronic properties [2, 3] owing to $\pi$-electron behavior near the Fermi energy. Edge boundaries in graphene, which can be classified into two types: armchair edges and zigzag edges, have been investigated in graphene nanoribbons [4–10]. Edge states that occur at zigzag edges are particularly interesting, along with topological insulators [11, 12] that form a new category of materials. Starting with graphene nanoribbons, there has been growing interest in graphene flakes (GFs) cut out of a graphene sheet (often called by different names, e.g., graphene nanodisks, graphene nanoislands, and graphene quantum dots). The characteristics of electronic states in GFs have been reported in terms of various shapes: rectangle [8, 13, 14], triangle [15–23], hexagon [15, 18, 19, 22], parallelogram [15], trapezoid [16], round [22], and ring-shaped [18, 24]. There are also interesting reports of graphene and graphene nanoribbons about thermal and topological properties [25–29].

In this study, we deal with rectangular GFs, which is one of systems discussed by Ryu and Hatsugai [8] in their investigation of the edge states in particle-hole symmetric Hamiltonians. Following an analytical study of the spectrum of $\pi$-electrons in rectangular GFs by Malyshova and Onipko [13], we considered the wavefunctions and energy levels on the basis of the analytical solutions of two types of graphene nanoribbons by Wakabayashi et al [7] to investigate the relationship between edge states and structural asymmetry. Then, we treated a model derived from zigzag-edged triangular GFs attached to a distinguished sublattice imbalance, and clarified the characteristics of edge states.

We employed the simplest tight-binding Hamiltonian defined by

\[ H = \epsilon \sum_i c_i^\dagger c_i + t \sum_{\langle i,j \rangle} c_i^\dagger c_j, \] (1)
Figure 1. A rectangular GF consisting of $N_x \times N_y$ hexagons ($N_x = 5$ and $N_y = 4$) can be represented by $M_x = 11$ and $M_y = 8$. The zigzag and armchair edges are arranged along the $x$- and $y$-direction, respectively. Each carbon site is assigned by a pair of indices $(m_x, m_y)$, and is indicated by an open circle (A-site) or a closed circle (B-site). $a_0$ is the graphene lattice constant. See text for details.

Figure 2. The Brillouin zone (BZ) of a rectangular GF with $N_x = 5$ and $N_y = 4$ ($M_x = 11$ and $M_y = 8$). The allowed wave vectors $(k_x, k_y)$ corresponding to the ordinary states are indicated by circles. The independent wave vectors are depicted by red closed circles. Numerals inside the BZ are the values of $j_y$, while the ones outside are those of $j_x$ in equation (7). Imaginary wavenumbers $\imath k_y$ are created at $p^{(j)}$ for $j_y = 5$ and $j_x = 7$ in the yellow region. K and K' are the Dirac points where the energy is zero. Thin lines indicate constant energy lines with $E = \pm 1$. 
where $c_i^\dagger$ and $c_i$ are the creation and annihilation operators for a $\pi$-electron at site $i$, respectively; $t$ is the hopping integral between the nearest-neighbor sites $(i,j)$; and $\epsilon$ is the site energy. Hereafter, the energies will be measured from the value of $\epsilon$ in units of $|t|$. In this study, zero energy corresponds to $\epsilon = 0$ for the Fermi energy. This is a common approach to study the behavior of $\pi$-electrons near the Fermi energy in graphene. Bery and Fertig [10] demonstrated that the results obtained from tight-binding calculations are comparable to the solutions of Dirac equations for graphene nanoribbons. However, a report by Zarenia et al. [19] on triangular and hexagonal GFs showed that the results of both approaches are qualitatively similar but quantitatively different in some cases.

2. Results and discussion

2.1. Rectangular graphene flakes

A rectangular GF consisting of $N_x \times N_y$ hexagons [13, 14] is shown in figure 1. Each site of carbon atoms is assigned by a pair of indices $(m_x, m_y)$ in a brick-type lattice, where $m_x = 1, 2, \cdots, M_x$ and $m_y = 1, 2, \cdots, M_y$, in the same manner as [6, 7]. The rectangular GF can also be specified by

$$M_x = 2N_x + 1,$$

$$M_y = 2N_y.$$  

The total number of sites is

$$N = M_x M_y.$$  

We define two independent sublattices, A and B, for $m_x + m_y = \text{odd}$ and $m_x + m_y = \text{even}$, respectively.

Malyshova and Onipko [13] proved that the energy states of rectangular GFs can be described by two wavenumbers perpendicular to each other, $k_x$ and $k_y$. For simplicity, these are made dimensionless as follows:

$$p_x = \frac{1}{2} k_x a_0,$$

$$p_y = \frac{1}{2} \sqrt{3} k_y a_0,$$

where $a_0$ is the graphene lattice constant. The Brillouin zone of a rectangular GF is in the shape of a rectangle ($0 < k_x < \frac{2\pi}{a_x}$, $0 < k_y < \frac{2\pi}{\sqrt{3}a_y}$), as shown in figure 2. The allowed wavenumbers in the $x$-direction along a zigzag-shaped boundary are discrete.

$$p_x^{(j_x)} = \left( \frac{j_x}{N_x + 1} \right) \frac{\pi}{2} = \frac{j_x}{M_x + 1} \pi$$

where integer $j_x = 1, 2, \cdots, M_x$, within $0 < p_x < \pi$. For each $p_x^{(j_x)}$, the wavenumbers $p_y$ in the $y$-direction along an armchair-shaped boundary are obtained by solving the following equation [7, 13, 14]:

$$F(p_y) = \sin(M_y p_y) + 2 \cos(p_x^{(j_x)}) \sin((M_y + 1)p_y) = 0 \quad (8)$$

or

$$E(p_y) = \sinh(M_y p_y') - 2 \cos(p_x^{(j_x)}) \sinh((M_y + 1)p_y') = 0 \quad (9)$$

When $0 < p_x^{(j_x)} \leq \pi/3$ or $2\pi/3 \leq p_x^{(j_x)} < \pi$, equation (8) has $M_y$ real solutions: $p_y^{(1)} = p_y^{(j_x)}$ ($p_y^{(1)} < p_y^{(2)} < \cdots < p_y^{(M_y)}$) within the range from 0 to $\pi$. However, when $\pi/3 < p_x^{(j_x)} < 2\pi/3$, except for $p_x^{(j_x)} = \pi/2$, equation (8) has $M_y - 1$ solutions. The other one in the latter case is an imaginary solution $p_y = ip_y'$ satisfying equation (9), which corresponds to an edge state. Although $N$ wave vectors, including the ordinary states and edge states, are allowed in the Brillouin zone, they are reduced to half their number because one wave vector can describe both energy states in the valence and conduction bands. Consequently, we have only to consider that

$$0 < p_x^{(j_x)} \leq \frac{\pi}{2} \left( j_x = 1, 2, \cdots, \frac{M_x + 1}{2} \right)$$

and

$$0 < p_y^{(j_x)} \leq \frac{\pi}{2} \quad (0 < p_x^{(j_x)} < \pi/2)$$

$$0 < p_y^{(j_x)} \leq \frac{\pi}{2} \quad (p_x^{(j_x)} = \pi/2). \quad (11)$$

The existence of the edge states (or imaginary wavenumbers $p_y'$) depends on the existence of integer $j_x$, to satisfy
\[ 0 < 2 \cos \left( p^{(k)}_x \right) < g(\pi) \]  

where

\[ g(p) = - \frac{M_y}{M_y + 1} \cos \left( (M_y + 1)p \right) \]

which is derived from \( \frac{dE}{dp} = 0 \) according to [7]. Equation (12) can be rewritten as

\[ \frac{M_x + 1}{\pi} \arccos \left( \frac{M_y}{2M_x + 1} \right) < \frac{\pi}{2} < \frac{M_x + 1}{2} \]  

Clearly, the number of edge states increase with increasing \( M_x \). For example, those in the rectangular GF with \( M_x = 11 \) and \( M_y = 8 \) appear only when \( j_x = 5 \) as 4.2408 < \( j_x < 6 \) from equation (14). Those with \( M_x = 21 \) and \( M_y = 10 \) appear when \( j_x = 8, 9, 10 \) as 7.6956 < \( j_x < 11 \). When \( M_y \to \infty \), equation (14) becomes \( (M_x + 1)/3 < j_x < (M_x + 1)/2 \), that is, simply

\[ \frac{\pi}{3} < p^{(k)}_x < \frac{\pi}{2} \]

which corresponds to the left half of the yellow region in figure 2. The number of \( j_x \) satisfying equation (15) is

\[ N_R = \text{Int} \left[ \frac{N_x}{3} \right] \]

It should be noted that an edge state corresponding to \( p^{(k)}_x \) closer to \( \pi/2 \) (or \( j_x \) closer to \( (M_x + 1)/2 \)) appears preferentially when \( M_y \) or \( M_x \) increase.

The energies and wavefunctions of the ordinary or edge states can be obtained directly by applying the wave vectors \((p^{(k)}_x, p^{(k)}_y)\) or \((p^{(k)}_x, p'_y)\) to the \( \pi \)-electron band energy of graphene. The energy and wavefunctions of the ordinary states can be expressed as

\[ E(p^{(k)}_x, p^{(k)}_y) = \sigma \sqrt{1 + 4 \cos(p^{(k)}_x) \cos(p^{(k)}_y) + 4 \cos^2(p^{(k)}_y)} \]  

and

\[ \psi^{(A)}(m_x, m_y) = (-1)^m \sigma C \sin(m_y p^{(k)}_y) \sin\left\{(M_y + 1 - m_y)p^{(k)}_y \right\} \]

\[ \psi^{(B)}(m_x, m_y) = C \sin(m_y p^{(k)}_y) \sin(m_y p'_y) \]

Those of the edge states are

\[ E_e(p^{(k)}_x, p'_y) = \sigma \sqrt{1 - 4 \cos(p^{(k)}_x) \cosh(p'_y) + 4 \cosh^2(p'_y)} \]  

and

\[ \psi^{(A)}(m_x, m_y) = (-1)^m+1 \sigma C_e \sin(m_y p^{(k)}_y) \sinh\left\{(M_y + 1 - m_y)p'_y \right\} \]

\[ \psi^{(B)}(m_x, m_y) = C \sin(m_y p^{(k)}_y) \sinh(m_y p'_y) \]

where \( C_e \) and \( C \) are the normalization factors, and \( \sigma = -1 \) and +1 distinguish between the valence and conduction bands, respectively. \( C \) and \( C_e \) are expressed as follows:

\[ C = \left( \frac{1}{S_x(p^{(k)}_x)S'_y(p'_y)} \right)^{-1} \]

and

\[ C_e = \left( \frac{1}{S_x(p^{(k)}_x)S'_y(p'_y)} \right)^{-1} \]

where formally

\[ S_x(p^{(k)}_x) = \sum_{m_x=1}^{M_x} \sin^2(m_x p^{(k)}_x) = \frac{1}{2} \left[ M_x - \frac{\sin(M_x p^{(k)}_x)}{\sin(p^{(k)}_x)} \cos\left\{(M_x + 1)p^{(k)}_x \right\} \right] \]

\[ S_y(p^{(k)}_y) = \sum_{m_y=1}^{M_y} \sin^2(m_y p^{(k)}_y) = \frac{1}{2} \left[ M_y - \frac{\sin(M_y p^{(k)}_y)}{\sin(p^{(k)}_y)} \cos\left\{(M_y + 1)p^{(k)}_y \right\} \right] \]
and
\[
S'_x(p'_x) = \sum_{m_y=1}^{M_y} \sinh^2(m_y p'_y) = \frac{1}{4} \left[ \frac{\sinh((2M_y + 1)p'_y)}{\sinh(p'_y)} - (2M_y + 1) \right],
\]
with the exception that
\[
C = \left( \frac{1}{\sqrt{2}} (M_x + 1)M_y \right)^{-1} = \sqrt{2}(N_x + 1)N_y^{-1}
\]
when \( p_y^{(l,h)} = p_x^{(l,h)} = \pi/2 \), corresponding to the M-point in figure 2. In fact, it can be demonstrated that \( S_x(p_y^{(l,h)}) \) is always constant
\[
S_x = \frac{1}{2} (M_x + 1) = N_x + 1
\]
by taking into account equation (7). On the other hand, the summations of \( j \)-components are not always reduced to simple constants because \( p_y^{(l,h)} \) and \( p_y \) are solutions that satisfy equations (8) and (9), respectively.

Furthermore, we can demonstrate that \( S_x \) is divided into two halves for sublattices A and B regardless of whether \( M_x \) is even or odd. To distinguish between sublattices A and B, the sites at \( m_y \) are divided into two groups with \( m_y = \text{even} \) and \( m_y = \text{odd} \), whose numbers are \( N \) and \( N' \), respectively. Therefore, \( N = N' = M_x/2 \) when \( M_x \) is even, while \( N = (M_x - 1)/2 \) and \( N' = (M_x + 1)/2 \) when \( M_x \) is odd.
\[
S_x = S_x^{(m_y=\text{even})} + S_x^{(m_y=\text{odd})},
\]
where
\[
S_x^{(m_y=\text{even})} = \sum_{n=1}^{N} \sin^2(2np_y^{(l,h)}) = \frac{S_x}{2}
\]
and
\[
S_x^{(m_y=\text{odd})} = \sum_{n=1}^{N'} \sin^2(2n - 1) p_y^{(l,h)} = \frac{S_x}{2}
\]

The contribution from A-sites to \( S_x \) is the same as that from B-sites despite the sublattice imbalance in a row of sites with any \( m_y \).

From the above, we can derive the various characteristics of the energy spectrum of rectangular GFs. It is significant that there is no wave vector satisfying \( E = 0 \) or \( E_c = 0 \) within the region of equations (10) and (11), as pointed out by Ryu and Hatsugai [8]. Moreover, the existence of peaks at \( E = \pm 1 \) is considered as one of the characteristics of the energy spectrum of clusters made from a graphene sheet [15, 30]. The degeneracy at \( E = \pm 1 \) is also evident in a \( N_x \times N_y \) rectangular GF, which can be interpreted as the number of wave vectors \((p_x^{(l,h)}, p_y^{(l,h)})\), on the line \( QM \) or \( MM' \) in figure 2. This is because when \( p_y = \pi/2 \) or \( p_y = \pi - p_{y_{\text{ext}}} \), then \( E = \pm 1 \) from equation (17). Therefore, we can predict that the degree of degeneracy is \( N_y + \text{GCF} - 1 \), which is \( N_y \) at a minimum, or \( 2N_y \) at a maximum for \( N_x = N_{y_{\text{ext}}} \), where \( \text{GCF} \) is the greatest common factor of \( N_x + 1 \) and \( N_y \).

2.1. Decay ratios of edge states

For edge states of graphene ribbons with zigzag edges, the intensity decays at a rate of
\[
D_k = \left| 2 \cos(k x / a_0 / 2) \right|^2 = \left| 2 \cos(p_x) \right|^2 \text{ from the edge [4–7], that is, } I(m_y) \propto D_k^{m_y}. \text{ In rectangular GFs, the rate is discrete}
\]
\[
D_k = \left| 2 \cos(p_x^{(l,h)}) \right|^2
\]
using \( j_x \) in equation (14). However, the decay in rectangular GFs is subjected to \( \sinh^2(\{M_x + 1 - m_y\} m_y) \) in equation (20) for A-sites because the \( x \)-components is constant independently of \( m_y \) according to equations (29) and (30). Although the intensity at \( m_y \) is
\[
W(m_y) = \left| \frac{\sinh(\{M_x + 1 - m_y\} m_y)}{\sinh(m_y)} \right|^2
\]
which is normalized by the value at the edge, the decay rate at each \( m_y \) can be interpreted using equation (9) as follows:
\[
D_{j_x} = G(1) \gtrsim \cdots \gtrsim G(m_y) \gtrsim \cdots \gtrsim G(M_y),
\]
where

\[
G(m_y) = \left( \frac{\sinh ((M_y + 1 - m_y)p_1^l)}{\sinh ((M_y + 2 - m_y)p_1^l)} \right)^2.
\]  

(34)

The decay at the edge of sublattice A or B of a 5 \times 8 rectangular GF is shown in figure 3. \(W(m_y)\) behaves well for the power law of \(D_{jx}\), while \(G(m_y)\) goes against \(D_{jx}\) near the opposite end, where the difference is inconspicuous in \(W(m_y)\). Consequently, the power law of \(D_{jx}\) also holds for the decay of the edge states in rectangular GFs.

\[
I^{(A)}_k(m_y) = \sum_{m_x} |\psi^{(A)}(m_x, m_y)|^2 = cD_{jx}^{m_y}
\]

(35)

\[
I^{(B)}_k(m_y) = \sum_{m_x} |\psi^{(B)}(m_x, m_y)|^2 = cD_{jx}^{M_y+1-m_y}
\]

(36)

where \(c\) is a constant; naturally,

\[
c = \frac{1}{2D_{jx}^{-1}} \frac{1 - D_{jx}}{1 - D_{jx}^{N_y}}
\]

(37)

for normalization.

2.1.2. Size-dependence of edge state energies

The edge states of rectangular GFs are associated with \(j_x\) satisfying equation (14). The energy levels expressed in equation (19) do not appear at zero energy. In the rectangular GF with \(N_x\), the first nearest energies to \(E = 0\) are associated with \(j_x = N_x\); the second nearest ones with \(j_x = N_x - 1\), and so on. That is, the \(n\)-th nearest energies to \(E = 0\), each of which are in the valence and conduction bands, are associated with

\[
j_x = N_x + 1 - n.
\]

(38)

Clearly, the energies approach zero as the size \(N_x \times N_y\) increases. To describe this behavior, we estimated the approximate relation between the energy and size using the energies obtained in numerical calculations for approximately 1500 rectangular GFs, with sizes ranging from \(N_x = 3\) to \(N_x = 50\) and \(N_y = 2\) to \(N_y = 50\). The relation is as follows:

\[
E_n \approx \pm 1.15(1 - D_{jx})D_{jx}^{N_y}
\]

(39)

where \(D_{jx}\) involves \(n\) and \(N_x\) through equations (7) and (38).
For example, a rectangular GF with $N_x = 35$ and $N_y = 20$ has $N_{\text{R}} = 11$ edge states corresponding to $j_x$ from 25 to 35 satisfying equation (14) in the valence or conduction band. Provided that the edge states degenerate substantially when the energy difference is within $10^{-8}$, the rectangular GF is deemed to have seven degenerate edge states at $E = 0$, as seen in figure 4. However, the degeneracy is substantial but not essential, as noted previously. It is more significant that the order of the edge state energies $n$ and $j_x$ are directly connected to equation (38) in rectangular GFs.

2.1.3. Zero-energy state

We have hitherto considered $N_x \times N_y$ rectangular GFs, where $M_x$ is odd and $M_y$ is even from equations (2) and (3). In this section, we deal with an asymmetric structure: rectangular GFs with $M_x = 2N_x + 1 = \text{odd}$ and $M_y = \text{odd}$, where the number of states $N = M_xM_y$ is odd differently from symmetric cases. In other words, we consider the case of $\Delta N = 1$, where the sublattice imbalance $\Delta N = |N_A - N_B|$ using the numbers of A- and B-sites $N_A$ and $N_B$, respectively.
Whereas $N$ states are separated into two halves in the valence and conduction bands when $N = \text{even}$, a zero-energy state must appear inevitably along with two $(N - 1)/2$ states in the valence and conduction bands, when $N = \text{odd}$. The zero-energy state, which cannot be described by equation (17) or (19), is a pure edge state corresponding to

\[ p_x = \frac{\pi}{2} \]  

or $D_{ij} = 0$, the wavefunctions of which form a one-dimensional wave at one end, that is,

\[
\psi_{0}^{(l)}(m_x, m_y) = \begin{cases} 
0 & (m_y = M_y) \\
\frac{1}{\sqrt{S_x}} \sin \left( m_y \frac{\pi}{2} \right) & (m_y = M_y)
\end{cases}
\]  

Figure 6. A Y-shaped GF, where an equilateral triangular GF with zigzag edges connecting three $N_x \times N_y$ rectangular GFs is a model involving three zigzag edges with a size of $N_y$, which are kept away from the sides of the triangular part at a distance of $N_y$.

Figure 7. The intensity distribution at zero energy obtained from a numerical calculation of the Y-shaped GF with $N_x = 5$ and $N_y = 4$, which consists of four-fold degenerate edge states. In (a), the intensity normalized by the maximum value is observed only on sublattice A sites, while every sublattice B site corresponds to a node depicted by transparent circles. The intensity distribution $I(m_y)$ is plotted in (b). The region from $m_y = 1$ to $m_y = M_y = 2N_y = 8$ corresponds to a rectangular part.
from numerical calculations. The rectangular GF with $M_x = 11$ and $M_y = 7$ has a zero-energy edge state, and a non-zero-energy edge state corresponding to $p_x = 5.12$ and $p_y = 0.20957723$, as shown in figure 5.

2.2. Y-shaped graphene flakes

To investigate zero-energy states due to sublattice imbalance or an asymmetric structure, we consider a Y-shaped GF consisting of three $N_x \times N_y$ rectangular GFSs, and an equilateral triangular GF with a zigzag edge length of $N_x$, as shown in figure 6. This model, which is a triangular GF with three zigzag edges when $N_y = 0$, holds the sublattice imbalance $\Delta N = N_x - 1$, and can be proved to have $\Delta N$-fold degenerate states at zero energy, whose wavefunctions produce zero amplitude on sublattice $B$ sites in the same manner as [18]. Therefore, the charge density distribution at zero energy is completely localized on sublattice $A$ sites, and has a tendency to be localized near the zigzag edges. The features can be confirmed in figure 7. Let $\psi(m_x, m_y)$ be a wavefunction of the zero-energy states for $i = 1, 2, \ldots, \Delta N$. Using the probability distribution $\rho_i(m_x, m_y) = |\psi_i(m_x, m_y)|^2$, the intensity distribution

$$I(m_y) = \sum_{m_x} I(m_x, m_y) = \sum_{m_x} \sum_{i=1}^{\Delta N} \rho_i(m_x, m_y)$$

is plotted in figure 7(b). The total intensity is the number of zero-energy states,

$$\sum_{m_y} I(m_y) = \Delta N.$$ 

Figure 8. Intensity distributions $I(m_y)$ on rectangular parts at zero energy in Y-shaped GFSs with $N_y = 16$ obtained from numerical calculations. Those with $N_x = 2, 3, \text{ and } 4$ monotonically decreased corresponding to a single mode $j_x = N_x$. Those with $N_x = 5, 6, \text{ and } 7$ can be decomposed into two components, as depicted by the red line for two modes: $j_x = N_x - 1$ and $N_x$. The cases $N_x = 2$ and $5$ involve an undamped component. The data obtained from decomposition are listed in table 1.
On the other hand, $\Delta N$ can also consist of contributions from three rectangular parts and a triangular part,

$$\Delta N = 3I_{\text{rec}} + I_{\text{tri}}$$  \hfill (44)

where

$$I_{\text{rec}} = \sum_{m_j = 1}^{M_j} I(m_j)$$  \hfill (45)

is the number of zero-energy states for a rectangular part, and $I_{\text{tri}}$ for a triangular part. We can adopt such a large value of $M_j$ to consider $I_{\text{rec}} \gg I_{\text{tri}}$. We can also adapt equation (35) for $I_{\text{rec}}$

$$I_{\text{rec}} = \sum_{j_x} I_{\text{rec}}^{(j_x)}$$  \hfill (46)

where

$$I_{\text{rec}}^{(j_x)} = \sum_{m_j = 1}^{M_j} I_{\text{rec}}^{(A)}(m_j) = \sum_{m_j = 1}^{M_j} c_{j_x} D_{j_x}^{m_j}.$$  \hfill (47)

Therefore, we can compare equations (45) and (46) expressing the edge state decay on sublattice A sites in the rectangular GF:

$$\Delta I_{\text{rec}} = \sum_{m_j = 1}^{M_j} \left( I(m_j) - \sum_{j_x} c_{j_x} D_{j_x}^{m_j} \right)^2.$$  \hfill (48)

Using the least squares method to minimize $\Delta I_{\text{rec}}$,

$$\sum_{j_x} c_{j_x} \sum_{m_j = 1}^{M_j} D_{j_x}^{m_j} D_{j_x}^{m_j} = \sum_{m_j = 1}^{M_j} I(m_j) D_{j_x}^{m_j},$$  \hfill (49)

is obtained. The coefficient $c_{j_x}$ can be determined from a symmetric matrix $\sum_{m_j = 1}^{M_j} D_{j_x}^{m_j} D_{j_x}^{m_j}$ and a vector $\sum_{m_j = 1}^{M_j} I(m_j) D_{j_x}^{m_j}$. The remaining issue is the mode represented by $j_x$ (in equations (7) and (31)). However, this was solved by applying them to the cases with small $N_x$ shown in figure 8, where the intensities $I(m_j)$ for the rectangular parts at zero energy in the Y-shaped GFs with $N_y = 16$ are depicted. It is clear that the cases with $N_x = 2, 3, 4$ have a single mode $j_x$, while the cases with $N_x = 5, 6, 7$ consist of two modes. We have estimated that the allowed modes in the cases with larger $N_x$ satisfy

$$\frac{\pi}{3} \leq p_x^{(j_x)} < \frac{\pi}{2},$$  \hfill (50)

that is,

$$\frac{2}{3}(N_x + 1) \leq j_x \leq N_x.$$  \hfill (51)
and the number of integer $j_x$ satisfying equation (51), or the number of modes is

$$N_T = \text{Int} \left[ \frac{N_e + 1}{3} \right].$$

Consequently, $j_x$ or $j'_x$ in equation (49) ranges from $N_e$. The intensity distribution of the rectangular part $I(m)$ in equation (45) can be decomposed into $I_j(m)$ in equation (47), i.e., $N_T$ components characterized by $D_{j_x}$, one of which is an undamped component with $D_{j_x} = 1$ ($\pi/3$) for $j_x = N_e$ in the case of Y-shaped GFs with $N_e = 3\ell - 1$ ($\ell = 1, 2, 3, \cdots$). The decomposition results in the cases of $N_T = 1, 2, 3$ are shown in figure 8 and table 1. The examples of larger $N_T$ can be confirmed in figure 9 and table 2. In the tables, it can be seen that the value of $I_{tri}$ is mainly occupied by the component of mode $j_x = N_e$ closest to $\Delta = D_{1}$, because the wavefunctions with smaller $D_{j_x}$ are localized.

Table 1. Decomposition of the number of zero-energy states in Y-shaped GFs with small $N_e$ and $N_y = 16$. The size of a rectangular part is denoted by $N_e \times N_y$, and $c_{j_x}$ are the mode and coefficient, respectively, in equation (49). $I_{rec}$ in equations (47) is the number of zero-energy states for a rectangular part, which consists of $N_T$ components corresponding to $j_x$ and $I^{(m)}_{j_x}$ in equation (47). The contribution of a triangular part $I_{tri} = \Delta N - 3\ell^{(m)}$.

| $N_e \times N_y$ | $j_x$ | $c_{j_x}$ | $I^{(m)}_{j_x}$ | $3I_{rec}$ | $I_{tri}$ |
|------------------|-------|----------|----------------|-----------|-----------|
| 2 × 16           | 2     | 1.0101010 x 10^{-2} | 0.969 679 | 0.969 679 | 0.030 303 |
| 3 × 16           | 3     | 0.471 404 53      | 2.000 000 | 2.000 000 | 0.000 000 |
| 4 × 16           | 4     | 1.618 033 99      | 3.000 000 | 3.000 000 | 0.000 000 |
| 5 × 16           | 5     | 9.9502488 x 10^{-3} | 0.955 224 | 3.955 224 | 0.044 776 |
| 6 × 16           | 5     | 2.732 050 8       | 3.000 000 | 0.000 000 |
| 7 × 16           | 6     | 0.218 668 11      | 1.999 874 | 4.999 874 | 0.000 126 |
| 8 × 16           | 6     | 4.048 917 3       | 3.000 000 | 0.000 000 |
| 9 × 16           | 7     | 0.707 106 76      | 3.000 000 | 0.000 000 |
| 10 × 16          | 7     | 5.568 535 6       | 3.000 000 | 0.000 000 |
| 11 × 16          | 8     | 9.8039216 x 10^{-3} | 0.941 176 | 6.941 176 | 0.058 824 |
| 12 × 16          | 8     | 1.137 158 0       | 3.000 000 | 0.000 000 |
| 13 × 16          | 8     | 7.290 859 4       | 3.000 000 | 0.000 000 |
| 14 × 16          | 9     | 0.142 114 62      | 1.997 837 | 7.997 829 | 0.002 171 |
| 15 × 16          | 9     | 1.618 023 9       | 2.999 985 | 0.000 000 |
| 16 × 16          | 9     | 9.215 886 8       | 3.000 000 | 0.000 000 |
| 17 × 16          | 10    | 0.448 687 66      | 2.999 959 | 8.999 959 | 0.000 001 |
| 18 × 16          | 10    | 2.149 675 5       | 2.999 999 | 0.000 000 |
| 19 × 16          | 10    | 11.343 540        | 3.000 000 | 0.000 000 |

Table 2. Decomposition of the number of zero-energy states in Y-shaped GFs with $N_e = 11, 12, 13, \text{and} 20$. $N_e \times N_y$, $c_{j_x}$, etc., are the same as those defined in table 1.

| $N_e \times N_y$ | $j_x$ | $c_{j_x}$ | $I^{(m)}_{j_x}$ | $3I_{rec}$ | $I_{tri}$ |
|------------------|-------|----------|----------------|-----------|-----------|
| 11 × 20          | 8     | 7.8431373 x 10^{-3} | 0.941 176 | 9.941 176 | 0.058 824 |
| 9                | 0.707 106 78 | 3.000 000 |
| 10               | 2.732 050 8 | 3.000 000 |
| 11               | 13.673 870 | 3.000 000 |
| 12 × 20          | 9     | 0.105 203 93    | 1.997 107 | 10.997 083 | 0.002 917 |
| 10               | 0.988 132 78 | 2.999 928 |
| 11               | 3.365 235 1 | 3.000 089 |
| 12               | 16.206 638 | 2.999 999 |
| 13 × 20          | 10    | 0.327 981 67    | 2.999 932 | 11.999 929 | 0.000 071 |
| 11               | 1.291 803 5 | 2.999 993 |
| 12               | 4.048 928 2 | 3.000 008 |
| 13               | 18.942 472 | 2.999 996 |
| 20 × 30          | 14    | 5.2083348 x 10^{-3} | 0.937 500 | 18.937 500 | 0.062 500 |
| 15               | 0.327 985 24 | 3.000 000 |
| 16               | 0.873 023 12 | 3.000 000 |
| 17               | 1.877 511 6 | 2.999 999 |
| 18               | 4.048 918 6 | 3.000 001 |
| 19               | 10.254 365 | 2.999 999 |
| 20               | 43.766 073 | 3.000 000 |
Table 3. Decomposition of the number of zero-energy states in Y-shaped GFs with $N_{p}$ = 8. The results obtained with smaller $N_{p}$ are listed. $N_{x} \times N_{y}$, $\epsilon_{i}$, $c_{i}$, etc., are the same as those defined in table 1.

| $N_{x} \times N_{y}$ | $j_{x}$ | $\epsilon_{i}$ | $3\bar{\eta}_{i}$ | $3\eta_{y}$ | $I_{m}$ |
|----------------------|---------|----------------|------------------|----------------|--------|
| 8 $\times$ 8          | 6       | 1.8518855 $\times$ 10^{-2} | 0.888905       | 6.888 873     | 0.111 127 |
| 7                   | 1.137 151 6 | 2.999 967 |                      |                |            |
| 8                   | 7.290 860 6 | 3.000 001 |                      |                |            |
| 8 $\times$ 4          | 6       | 3.3514118 $\times$ 10^{-2} | 0.804 339     | 6.792 991     | 0.207 009 |
| 7                   | 1.135 298 3 | 2.988 212 |                      |                |            |
| 8                   | 7.291 931 0 | 3.000 441 |                      |                |            |
| 8 $\times$ 2          | 6       | 6.0655060 $\times$ 10^{-2} | 0.727 861     | 6.522 364     | 0.477 636 |
| 7                   | 1.109 357 91 | 2.786 369 |                      |                |            |
| 8                   | 7.312 175 7 | 3.008 134 |                      |                |            |

nearer the zigzag edges. By compensating the contribution from the triangular part $I_{m}$, we can determine how to distribute the number of zero-energy states $\Delta N$ to $N_{y}$ allowed modes represented by $j_{x}$, ranging from $N_{y}$ to $N_{x}$:

$$\Delta N = \sum_{j_{x} = N_{y}}^{N_{x}} \Delta N_{j_{x}}$$

(54)

where

$$\Delta N_{j_{x}} = \begin{cases} ((N_{x} + 1) \mod 3) + 1 & (j_{x} = N_{y}) \\ 3 & (j_{x} > N_{y}) \end{cases}$$

(55)

The configurations of the allowed modes in the zero-energy states can be represented by the notation: $(j_{x}/(N_{x} + 1))^{\Delta N_{k}}$ $(j_{k} = N_{y}, \cdots, N_{y})$ in descending order) for following the electron configuration of an atom, where numbers of the zero-energy states along with the allowed modes are symbolized by the main part of $I_{y}^{(j)}$ in equation (7). For example, the configurations are $(2/3)^{5}, (3/4)^{4}, (4/5)^{3}$ for $N_{x} = 2, 3, 4 (N_{y} = 1), (5/6)^{5}, (4/6)^{3}, (6/7)^{3}, (5/7)^{2}, (7/8)^{2}, (6/8)^{2}$ for $N_{x} = 5, 6, 7 (N_{y} = 2)$; and $(8/9)^{3}, (7/9)^{2}, (6/9)^{1}, (9/10)^{3}, (8/10)^{2}, (7/10)^{1}$, $(10/11)^{3}, (9/11)^{2}, (8/11)^{1}$ for $N_{x} = 8, 9, 10 (N_{y} = 3)$. It is significant that there is a priority in the distribution of zero-energy states to the modes.

Finally, we turn to the dependence of the decomposition on $N_{y}$. The cases of $N_{x} = 8$ and smaller $N_{p}$ can be compared in table 3. We considered that the configuration of the zero-energy states given by equation (55) holds true independent of $N_{y}$, while the least squares method requires a larger $M_{x}$ to obtain more accurate results— even more so for a Y-shaped GF with larger $N_{y}$. The coefficient $c_{i}$ was affected by $N_{y}$; $c_{i}$ for $D_{i} < 1$ was more dependent than $c_{i}$ for $D_{i} \geq 1$ because the wavefunction extended from the zigzag edges in the rectangular parts to the triangular part. The coefficient can be roughly estimated as $c_{i} \propto \tan^{2}(3\eta_{y})$ in $N_{y} \rightarrow \infty$. Therefore, we consider that the zero-energy states in a triangular GF, which is the case with $N_{y} = 0$, follows the above results other than $c_{i}$ for $D_{i} \geq 1$.

3. Conclusion

The energy states of $\pi$-electrons in an $N_{x} \times N_{y}$ rectangular GF with a pair of zigzag edges and a pair of armchair edges were studied. We have shown that the exact solutions reported by Malyshova and Onipko [13] can be interpreted as the results derived from the analytical solutions for graphene nanoribbons provided by Wakabayashi et al [7]. In rectangular GFs, the discrete allowed modes $p_{x} = \left( \frac{j_{x}}{N_{x} + 1} \right) \frac{\pi}{2}$, where $j_{x}$ are integers satisfying $\pi/3 < p_{x} < \pi/2$, characterize the edge states whose energies are not exactly zero, but approach zero as the size $N_{x} \times N_{y}$ increases. The sublattice imbalance $\Delta N$ in GFs caused the zero-energy states. In ordinary rectangular GFs with $\Delta N = 0$, the edge states appear in pairs as with graphene nanoribbons. In rectangular GFs with $\Delta N = 1$, a zero-energy state appeared, which is also a pure edge state corresponding to $p_{x} = \pi/2$. By applying the edge states of rectangular GFs, we have probed zero-energy states in a Y-shaped GF involving three zigzag edges, consisting of three $N_{x} \times N_{y}$ rectangular parts at the fringe of an equilateral triangular part with side length $N_{x}$. The sublattice imbalance in the model $\Delta N = N_{x} - 1$ forced the edge states, including the undamped mode $p_{x} = \pi/3$ whose wavefunctions are dependent on only one sublattice, into zero energy. Configurations of the allowed modes in the zero-energy states were determined.
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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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References

[1] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 Science 306 666
[2] Aoki H and Dresselhaus M S (ed) 2014 Physics of Graphene (Berlin: Springer)
[3] Raza H (ed) 2012 Graphene Nanoelectronics: Metrology, Synthesis, Properties and Applications (Berlin: Springer)
[4] Fujita M, Wakabayashi K, Nakada K and Kusakabe K 1996 J. Phys. Soc. Jpn. 65 1920
[5] Nakada K, Fujita M, Dresselhaus G and Dresselhaus M S 1996 Phys. Rev. B 54 17954
[6] Wakabayashi K, Fujita M, Ajiki H and Sigrist M 1999 Phys. Rev. B 59 8271
[7] Wakabayashi K, Sasaki K, Nakanishi T and Enoki T 2010 Sci. Technol. Adv. Mater. 11 054504
[8] Ryu S and Hatsugai Y 2002 Phys. Rev. Lett. 89 077002
[9] Ezawa M 2006 Phys. Rev. B 73 045432
[10] Brey L and Fertig H A 2006 Phys. Rev. B 73 235411
[11] Hasan M Z and Kane C L 2010 Rev. Mod. Phys. 82 3045
[12] Niu C, Wang H, Mao N, Huang B, Mokrousov Y and Dai Y 2020 Phys. Rev. Lett. 124 066401
[13] Malyshkev I and Onipko A 2008 Phys. Rev. Lett. 100 166806
[14] Onipko A 2008 Phys. Rev. B 78 245412
[15] Ezawa M 2007 Phys. Rev. B 76 245415
[16] Potasz P, Guclu A D and Hawrylak P 2010 Phys. Rev. B 81 033403
[17] Guclu A D, Potasz P and Hawrylak P 2013 Phys. Rev. B 88 155429
[18] Guclu A D, Potasz P, Korkusinski M and Hawrylak P 2014 Graphene Quantum Dots (Berlin, Heidelberg: Springer) 63–8
[19] Zarenia M, Chaves A, Farias G A and Peeters F M 2011 Phys. Rev. B 84 245403
[20] Yamamoto T and Watanabe K 2006 Phys. Rev. B 74 121409
[21] Fernández-Rossier J and Palacios J J 2007 Phys. Rev. Lett. 99 177204
[22] Akola J, Heiskanen H P and Manninen M 2008 Phys. Rev. B 77 193410
[23] Heiskanen H P, Manninen M and Akola J 2008 New J. Phys. 10 103015
[24] Yannouleas C, Romanovsky I and Landman U 2014 Phys. Rev. B 89 035432
[25] Kane C L and Mele E J 2005 Phys. Rev. Lett. 95 226801
[26] Qiao Z, Yang S A, Feng W, Tse W, Ding J, Yao Y, Wang J and Niu Q 2010 Phys. Rev. B 82 161414(R)
[27] Zhang H, Guo Z, Zhao W, Gong X and Cao J 2012 J. Phys. Soc. Jpn. 81 114601
[28] Cui Y, Zhang H, Chen W, Yang Z and Cai Q 2017 J. Phys. Chem. C 121 15282
[29] Zhang H, Ning Y, Yang W, Zhang J, Zhang R and Xu X 2019 Phys. Chem. Chem. Phys. 21 17087
[30] Yorikawa H and Muramatsu S 1996 Synth. Met 82 17