Persistence of Edge-State in Stacked Graphene and Nano-Graphene Materials

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Abstract
Nano-carbon materials are investigated intensively. In this paper, the edge-state in nanographene materials with zigzag edges is studied theoretically. In particular, while the inter-layer interactions are considered, we prove that edge states exist at the energy of the Dirac point in the doubly stacked nanographene, and in the case of the infinitely-wide lower layer case. This property applies both for the A-B and A-C stackings.

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1. Introduction

The graphite and single layer graphene materials have been studied intensively, since the electric field effect has been found in atomically thin graphene films [1]. These materials can be regarded as bulk systems. On the other hand, nanographenes with controlled edge structures have been predicted to have localized states along the zigzag edges [2]. The presence of the edge states have been observed by experiments of scanning tunneling spectroscopy [3,4]. Thus, the studies of the edge states are one of the interesting topic of the field.

Previously, the magnetic switching effect has been found in the process of insertion and extraction of molecules in activated carbon fibers [5]. The inserted molecules remain in nanometer size pores, and give effective pressure to the nanographite clusters. The Pauli susceptibility decreases due to the decrease of the magnetic moment magnitude. We have studied the magnetism of the nanographite using the tight binding model including the interlayer interaction between neighboring nanographene layers [6-8]. We have found that open shell nature of each layer might explain the experimental observations. Recently, interlayer hopping interaction effects in stacked graphite have been investigated theoretically [9]. The electronic structures change dramatically including the massless Dirac cone and parabolic dispersions, depending on the layer numbers from a single graphene, bilayer graphene, to multi layers.

In this paper, we will study the edge-state in nanographene materials with zigzag edges including the inter-layer interactions, extending the work of a single layer [2]. We will prove that edge states exist at the energy of the Dirac point in the doubly stacked nanographene, and in the case of the infinitely-wide lower layer case. This property can be shown both for the A-B and A-C stackings.

2. Edge states of one graphene layer

In this section, we review the idea of the edge state which appears along the zigzag line of a graphene [2]. Figure 1 shows a graphene sheet which has one zigzag line at the top most edge
of the figure. The graphene extends infinitely in the left, right, and down directions. We will constitute a wavefunction of the edge state at the energy \( E = 0 \) as follows. The lattice sites are divided in A and B sublattices. The edge atoms belong to the A sublattice. The edge state has the amplitude zero at all the sites of the B sublattice. The wavenumber in the one dimensional direction is denoted as \( k \), and \( a \) is the lattice constant of the unit cell, which is the length between the neighboring edge atoms. The condition that the amplitude becomes zero at the atom between \((n - 1)\)th and \( n \)th edge sites, when the nearest neighbor hopping interaction \( t \) is considered, is

\[
e^{ik(n-1)a} + e^{ika} + x = 0,
\]

and this gives the amplitude

\[
x = [-2\cos(ka/2)]e^{ik(n-1/2)a}.
\]

The similar condition,

\[
e^{ika} + e^{ik(n+1)a} + y = 0,
\]

gives

\[
y = [-2\cos(ka/2)]e^{ik(n+1/2)a}.
\]

The condition that the amplitude becomes zero at the sites surrounded by the amplitudes \( x \), \( y \), and \( z \) is

\[
x + y + z = 0.
\]

Therefore, we obtain the amplitude at the third zigzag line

\[
z = [-2\cos(ka/2)]^2e^{ika}.
\]

Iterating this process, we can prove that the amplitude at the \( n \)th unit cell along the \( m \)th is proportional to \([-2\cos(ka/2)]^{m-1}\). The absolute value is smaller than unity if the wavenumber satisfies \( 2\pi/3 < ka \leq \pi/2 \). Therefore, the edge state at the energy \( E = 0 \) extends into the bulk
of the graphene with exponentially damping amplitude with respect to the distance from the edge. The edge state locates near the boundary of the first Brillouin zone in the wavenumber space.

3. Edge states in bilayer graphene with parallel zigzag lines

Figure 2(a) shows the A-B stacked bilayer graphene with zigzag edges at the top of the figure. The system extends infinitely in the other directions. The upper layer is shown by the solid lines, and the lower layer (dotted line) is shift downward by the bond length $b$. The number $n$ ravels the $n$th unit cell shown by the dashed line. The other label $m$ indicates each zigzag line. For the convention, the upper layer begins with $m = 0$, and the lower layer starts with $m = 1$. At the circles, two carbon atoms overlap completely, and weak hopping interaction $t_1$ is assigned here. The same $m$ indicates the zigzag lines in the upper and lower layers.

We will constitute wavefunctions of the edge state. It is assumed that the edge state has amplitudes at the sites of the A sublattice only. The amplitude becomes zero in the B sublattice. Even if the interactions $t_1$ are present at circles, the alternation of the A and B sites remains in the whole system. So, the bipartite nature remains, too. When we look at the condition of the edge state at the energy $E = 0$ of the upper layer, we find the formula,

$$a_{n,m}e^{-ika/2} + a_{n+1,m}e^{ika/2} + a_{n,m+1} = 0, \quad (7)$$

for even $m$, and

$$a_{n,m}e^{-ika/2} + a_{n+1,m}e^{ika/2} + a_{n+1,m+1} = 0 \quad (8)$$

for odd $m$, where $a_{n,m}$ is the amplitude at the $n$th unit cell of the $m$th zigzag line. Assuming $a_{n,0} = A$, we obtain

$$a_{n,m} = A[-2\cos(ka/2)]^m. \quad (9)$$
The similar condition of the zero energy state gives,
\[ b_{n,m}e^{-ika/2} + b_{n+1,m}e^{ika/2} + b_{n,m+1} + r_1a_{n,m} = 0 \tag{10} \]
for odd \( m \), and
\[ b_{n,m}e^{-ika/2} + b_{n+1,m}e^{ika/2} + b_{n+1,m+1} + r_1a_{n+1,m} = 0 \tag{11} \]
for even \( m \), for the amplitude \( b_{n,m} \) of the lower layer. Here, \( r_1 = t_1/t \) is the ratio of the interlayer hopping integral to the intralayer hoppings. As we know the form of \( a_{n,m} \), we can solve the recurrence formula of the number series to obtain
\[ b_{n,m} = -(m - 1)r_1A[-2\cos(ka/2)]^{m-2} + B[-2\cos(ka/2)]^{m-1} \tag{12} \]
for \( m \geq 2 \), where \( b_{1,m} = B \) is assumed. Therefore, we have found that the edge state persists in the A-B stack case. The magnitudes of \( A \) and \( B \) will be nearly equal \( A \sim B \), so the correction by the interlayer interaction is of the order \( r_1 \) with respect to the intralayer term.

Figure 2(b) shows the A-C stacking case, where the lower layer is moved into the right-down direction with a bond length \( b \). The notations are similar to those of Fig. 2(a). The difference is the fact that the both zigzag edge lines begin with the same index \( m = 1 \). In the A-C stacking case, it is found that the amplitude of the edge state can be constructed in the lower layer, first. The condition of the zero energy state gives,
\[ b_{n,m}e^{-ika/2} + b_{n+1,m}e^{ika/2} + b_{n,m+1} = 0 \tag{13} \]
for even \( m \), and
\[ b_{n,m}e^{-ika/2} + b_{n+1,m}e^{ika/2} + b_{n+1,m+1} = 0 \tag{14} \]
for odd \( m \), for the amplitude \( b_{n,m} \). This sequence is solved as
\[ b_{n,m} = B[-2\cos(ka/2)]^{m-1}, \tag{15} \]
where \( b_{1,1} = B \). The effects of the interlayer interactions give the next relation for the upper layer,
\[ a_{n,m}e^{-ika/2} + a_{n+1,m}e^{ika/2} + a_{n,m+1} + r_1b_{n,m} = 0 \tag{16} \]
for odd \( m \), and

\[
a_{n,m} e^{-ika/2} + a_{n+1,m} e^{ika/2} + a_{n+1,m+1} + r_1 b_{n+1,m} = 0
\]  \hspace{1cm} (17)

for even \( m \). This is solved with the help of the previous solution \( b_{n,m} \) to give

\[
a_{n,m} = A [-2\cos(ka/2)]^{m-1} - (m - 1) r_1 B [-2\cos(ka/2)]^{m-2}
\]  \hspace{1cm} (18)

for \( m \geq 2 \), where \( a_{n,1} = A \). The roles of the upper and lower layers seem to be exchanged from that of the A-B stacking case. The amplitude of the upper layer has correction terms of the order \( r_1 \) owing to the presence of the lower layer.

4. **Edge states in bilayer graphene with infinitely-wide lower layer**

In this section, we will consider the bilayer graphene, where the lower layer has infinite spatial extent. So, the nanographene with one zigzag edge is placed upon one infinite graphene. We consider both of the A-B and A-C stackings. They are shown in Figs. 3(a) and (b), respectively. As the convention of the choice of the starting point of the initial amplitudes, \( A \) and \( B \), is different, we would like to formulate again for the both cases.

Figure 3(a) shows the A-B stacking case. As the upper layer A-site \((n, m = 1)\) interacts directly with the lower layer site as denoted by the circles, the starting points are indexed differently from those of the previous section. Here, the zigzag lines of the upper and lower layers in the down direction are indexed by \( m \). And, the zigzag lines of the lower layer in the up direction are indexed by \( l \) with \( l = m = 1 \). In the upper layer, the amplitude is

\[
a_{n,m} = A [-2\cos(ka/2)]^{m-1}
\]  \hspace{1cm} (19)

with \( a_{n,1} = A \). In the lower layer, the condition of the zero energy state is the relations,

\[
b_{n,m} e^{-ika/2} + b_{n+1,m} e^{ika/2} + b_{n,m+1} + r_1 a_{n,m} = 0
\]  \hspace{1cm} (20)
for even $m$,
\[ b_{n,m}e^{-ika/2} + b_{n+1,m}e^{ika/2} + b_{n+1,m+1} + r_1a_{n+1,m} = 0 \] (21)

for odd $m$,
\[ c_{n,m}e^{-ika/2} + c_{n+1,m}e^{ika/2} + c_{n,m+1} = 0 \] (22)

for even $l$ and $l \geq 2$, and
\[ c_{n,m}e^{-ika/2} + c_{n+1,m}e^{ika/2} + c_{n+1,m+1} = 0 \] (23)

for odd $l$. We obtain,
\[ b_{n,m} = -mr_1A[-2\cos(ka/2)]^{m-1} + B[-2\cos(ka/2)]^{m-1} \] (24)

and
\[ c_{n,l} = B[-2\cos(ka/2)]^{l-1} \] (25)

for $l \geq 2$, where $b_{n,1} = c_{n,1} = B$.

Figure 3(b) is the A-C stacking case. In the lower layer, the amplitude of the edge state is calculated as
\[ b_{n,m} = B[-2\cos(ka/2)]^m \] (26)

and
\[ c_{n,l} = B[-2\cos(ka/2)]^l, \] (27)

where $b_{n,0} = c_{n,0} = B$. In the upper layer, the effect of the interaction appears. The amplitude can be derived by the relation
\[ a_{n,m}e^{-ika/2} + a_{n+1,m}e^{ika/2} + a_{n,m+1} + r_1b_{n,m} = 0 \] (28)

for odd $m$ and $m \geq 1$, and
\[ a_{n,m}e^{-ika/2} + a_{n+1,m}e^{ika/2} + a_{n+1,m+1} + r_1b_{n+1,m} = 0 \] (29)
for even \( m \). This is solved with the help of above solution \( b_{n,m} \) to give

\[
a_{n,m} = A[-2\cos(ka/2)]^{m-1} - mr_1 B[-2\cos(ka/2)]^m
\]

for \( m \geq 2 \), where \( a_{n,1} = A \). Therefore, we have constructed the wavefunction of the zero energy state for the infinitely-wide lower layer cases.

5. Summary

We have studied the edge-state in nanographene materials with zigzag edges including the inter-layer hopping interactions. We have shown that edge states are present at the energy of the Dirac point in the doubly stacked nanographene, and in the case of the infinitely-wide lower layer case. This property has been found both for the A-B and A-C stackings.
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Figure Captions

Fig. 1. The edge states along the zigzag edge of a graphene. See the text for the notations.

Fig. 2. Bilayer graphene with parallel zigzag lines. (a) A-B stacking and (b) A-C stacking are shown. See the text for the notations.

Fig. 3. Bilayer graphene with the infinitely-wide lower layer. (a) A-B stacking and (b) A-C stacking are shown. See the text for the notations.
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