Competition of edge effects on the electronic properties and excitonic effects in short graphene nanoribbons

Yan Lu, Sheng Wei, Jing Jin, Wengang Lu, and Li Wang

1 Department of Physics, Nanchang University, Nanchang, 330031, People’s Republic of China
2 Institute of Physics, Chinese Academy of Sciences, Beijing, 100190, People’s Republic of China
3 Beijing Key Laboratory for Nanomaterials and Nanodevices, Beijing, 100190, People’s Republic of China
4 Authors to whom any correspondence should be addressed.

E-mail: wglu@iphy.ac.cn and liwang@ncu.edu.cn

Abstract
We explore the electronic properties and exciton effects in short graphene nanoribbons (SGNRs), which have two armchair edges and two zigzag edges. Our results show that both of these two types of edges have profound effects on the electronic properties and exciton effects. Both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) states are not totally energy degenerate in SGNRs due to the spin-polarized states on the zigzag edges.

1. Introduction
Graphene is considered a promising material for future electronic applications due to its high mobility and low-dimensional structure [1–3]. Unfortunately, its zero–energy–gap property hinders its use in photonic applications [4]. To open an energy gap in graphene, we can further lower its dimension to one-dimensional nanoribbons [5–14]. Armchair-edged graphene nanoribbons (AGNRs) and zigzag-edged graphene nanoribbons (ZGNRs) are two typical graphene nanoribbons (GNRs) having energy gaps. Importantly, these two GNRs represent two different mechanisms of opening energy gaps in graphene. In AGNRs, it is the dimensional confinement between the two armchair edges that opens the gaps, which are divided into three families (one is nearly metallic and other two are semiconducting) depending on their widths [7, 13–17]. While in ZGNRs, it is the spin–polarization of the edge states on the two zigzag edges that opens gaps [6–8, 13, 18, 19]. An interesting issue is to investigate the competition between these two mechanisms of opening gaps in one system.

Recently, short GNRs (SGNRs) have received a great deal of attention because they can be fabricated with precise edges by bottom-up method [20–30]. An SGNR has four edges, two of them are armchair edges and the other two are zigzag edges. Thus SGNRs may have mixed electronic properties of AGNRs and ZGNRs [29, 30]. Kimouche et al observed an ultra-narrow SGNR having very small energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which means this SGNR belongs to the metallic family of AGNRs [29]. On the other hand, Wang et al observed a series of SGNRs that have spin–polarized HOMO and LUMO at the two zigzag edges, which verifies the spin–polarization on the zigzag edges [30]. These two experiments showed plenty and interesting electronic properties of SGNRs. However, the roles of the two kinds of edges and how they work together to determine physical properties are still unclear. In this paper, by using the spin–polarized tight-binding (TB) method, we will investigate the electronic properties of SGNRs with various sizes. We will also show that the HOMO and LUMO states are
alternatively changed between the bulk and the edge states when increase the width between the two armchair edges. Then, we will take into account the electron–electron interactions in the TB model to calculated the exciton effects of SGNRs, and show that there are two kinds of exciton energies and exciton binding energies in SGNRs due to the two types of edges.

2. Theoretical method

To investigate the excitonic effects in SGNRs, we apply the TB Pariser-Parr-Pople (PPP) model [31], which has been successfully used to describe excitons in π-conjugated polymers [32, 33], carbon nanotubes [34], and graphene nanoribbons (ZGNRs) [35]. The PPP Hamiltonian is given by

\[ H = H_0 + H_{e-e} \]  

where \( H_0 \) is the TB Hamiltonian with on-site Hubbard interaction and is taken the form as [36]

\[ H_0 = t \sum_{\langle i,j \rangle, \sigma} c_{i\sigma}^\dagger c_{j\sigma} + \sum_{i, \sigma} [\langle n_{i\uparrow} \rangle - \frac{1}{2}] n_{i\sigma}, \]  

where \( \langle i, j \rangle \) means \( i \) and \( j \) are nearest neighbors; \( c_{i\sigma}^\dagger \), \( c_{i\sigma} \), and \( n_{i\sigma} \) are the creation, annihilation, and number operators on site \( i \) with spin \( \sigma \), respectively; \( \langle n_{i\sigma} \rangle \) is the average occupation probability of spin \( \sigma \) electrons on site \( i \); \( t \) and \( U \) are the nearest-neighbor hopping and on-site Hubbard interaction, respectively. \( H_{e-e} \) in equation (1) denotes the e–e interactions and is described as [34]

\[ H_{e-e} = U \sum_i (n_{i\uparrow} - \langle n_{i\uparrow} \rangle) (n_{i\downarrow} - \langle n_{i\downarrow} \rangle) \]  

\[ + \frac{1}{2} \sum_{i, \langle i,j \rangle} \sum_{\sigma, \sigma'} V_0 (n_{i\sigma} - \langle n_{i\sigma} \rangle) (n_{j\sigma'} - \langle n_{j\sigma'} \rangle), \]  

where \( V_0 \) is the long-range Coulomb interaction, and takes the Ohno’s formula [37],

\[ V_0 = \frac{U}{\kappa \sqrt{1 + \left( \frac{\mu \rho_{\sigma \sigma'}}{e^2} \right)^2}}, \]  

where \( \kappa \) is the vacuum permittivity and the magnitude of the electron charge, respectively; and \( r_{ij} \) is the distance between sites \( i \) and \( j \) in unit of Å. The dielectric function \( \kappa \) is introduced to incorporate the screening effects from the environment and the \( \sigma \) electrons in SGNRs.

An exciton state, denoted as \( |\psi\rangle \), can be constructed as a combination of single e–h pair states, i.e.,

\[ |\psi\rangle = \sum_{l_U, l_O} \rho(l_U, l_O) |l_U, l_O\rangle, \]  

where \( |l_U, l_O\rangle \) denotes a single e–h pair state formed by an electron in an unoccupied energy level \( l_U \) and a hole in an occupied energy level \( l_O \), and \( \rho(l_U, l_O) \) is the weight coefficient. If spins are taken into account, there are a total of four kinds of e–h pairs: \( |l_U \uparrow, l_O \uparrow\rangle, |l_U \uparrow, l_O \downarrow\rangle, |l_U \downarrow, l_O \uparrow\rangle, \) and \( |l_U \downarrow, l_O \downarrow\rangle \). Note that the spin of a hole state corresponds to the spin of the electron that originally occupies the state. These four kinds of e–h pairs can be combined to form four exciton states: one singlet (S) and three triplets (\( T_0, T_1, \) and \( T_{-1} \)). Specifically, we have [33, 38]

\[ |l_U, l_O\rangle = \begin{cases} \frac{1}{\sqrt{2}}(|l_U \uparrow, l_O \uparrow\rangle + |l_U \downarrow, l_O \downarrow\rangle), & S; \\
\frac{1}{\sqrt{2}}(|l_U \uparrow, l_O \uparrow\rangle - |l_U \downarrow, l_O \downarrow\rangle), & T_0; \\
|l_U \uparrow, l_O \downarrow\rangle, & T_1; \\
|l_U \downarrow, l_O \uparrow\rangle, & T_{-1}. \end{cases} \]  

Having constructed the Hamiltonian and exciton states, one can calculated the energies and binding energies of excitons in SGNRs by solving their excitonic eigenvalue equations. In this paper, the value of the three independent parameters of \( t, U \), and \( \kappa \) are chosen as \( t = -2.7 \) eV, \( U = 3.6 \) eV, and \( \kappa = 1.4 \), with which the calculated renormalized energy gaps are excellently consistent with the existing measurements for some SGNRs [30]. Other parameters have also been tested and only quantitatively but not qualitatively change of our results. The energetically lowest 900 e–h pairs are selected in the combination of excitonic states.

3. Results and discussion

In figure 1 we plot the structure of a specific SGNR. Each of the dangling edge bond is saturated by one hydrogen atom. There are four edges for an SGNR. Two opposite edges of them are zigzag edges and the other two are armchair edges. We use a pair of integer numbers, \( (n, m) \), to denote the structure of an SGNR, where \( n (n = 0, 1, \)
2, …) stands for the number of units along the zigzag chains and \(m \ (m = 1, 2, 3, \ldots)\) the number of the zigzag chains along the armchair edge direction. Since an SGNR can be seen as both a short AGNR and a short ZGNR, the electronic properties of an SGNR should inherit both the properties of an AGNR and a ZGNR.

3.1. Single-particle properties of the SGNRs

At the beginning, we study the density of states (DOS) of SGNRs by using the TB Hamiltonian \(H_0\) in equation (2). Figure 2 shows the DOS of three SGNRs with a fixed \(n \ (n = 3)\). The red curves are calculated without spin-polarization (\(U = 0\)), while the blue curves are calculated with spin-polarization (\(U = 3.6 \text{ eV}\)). Both of the two types of curves are spin degenerate in energy. Although the two curves are very similar at high energies for an SGNR, there are some differences near the Fermi energy \((E_F = 0 \text{ eV})\). In the absence of spin-polarization, a relatively large peak appears at the Fermi energy when \(m\) is large, and this peak will split slightly as \(m\) decreases due to the dimensional-confinement effects. In the presence of spin-polarization, such a large peak disappears at \(E = 0\), and two new peaks emerge on both sides of the Fermi energy, i.e., an energy gap is opened with spin-polarization in all these SGNRs. This is a typical spin-polarization property of the edge states of ZGNRs [6–8, 13, 19]. So the large peaks at the Fermi energy and the nearby split new peaks are edge states.

Apart from the peaks for edge states, there are also some peaks for bulk states in figure 2. The peaks for the bulk states closest to the Fermi energy in both the occupied and the unoccupied states are indicated with the green dashed lines in figure 2. Unlike the edge states, the positions of the bulk states are almost unchanged no matter if it is with or without spin-polarization. Furthermore, it can be easily seen that these bulk states are further away from the Fermi energy than the two split edge states. Therefore, the HOMOs and LUMOs are edge states for the \(n = 3\) SGNRs, which consistent with previous experiment measurements and calculations of this types of SGNRs [29].

The DOS curves for SGNRs with \(n = 4\), some of which are plotted in figure 3, are very similar to those with \(n = 3\), which implies that the HOMOs and LUMOs are also edge states for the SGNRs with \(n = 4\). However, one must note that, for the two SGNR series, \((3, m)\) and \((4, m)\), the energy differences between the bulk states and the edge states in the \((4, m)\) series are smaller than those of the \((3, m)\) series. This property results from the...
three types of the energy gaps in AGNRs [7, 13–17], which states that the energy gaps of AGNRs can be divided into three types according to their widths described by an integer \( q \): the energy gaps are the largest for the \( q \mod 3 = 1 \) structure group, the smallest for the \( q \mod 3 = 2 \) group, and the middle for the \( q \mod 3 = 0 \) group. From the discussion of the structure of SGNRs in figure 1, the \((n, m)\) SGNR can be regarded as a short AGNR with \( q = 2n+1 \). This means the SGNRs with \( \mod (n, 3) = 0 \) have the largest gaps for bulk states, with \( \mod (n, 3) = 1 \) the mid gaps, and with \( \mod (n, 3) = 2 \) the smallest gaps. Thus the energy differences between the bulk states and the edge states are larger for SGNRs with \( n \mod 3 \) than those with \( n \mod 4 \).

The HOMOs and LUMOs in the above two types of SGNRs are all edge states, and these two types of SGNRs stem from two families of semiconducting AGNRs. In SGNRs corresponding to metallic AGNRs, the HOMO and LUMO states may be bulk states. According to the above discussion, the SGNRs with \( n = 5 \) correspond to the metallic AGNR with \( q = 11 \). And in fact, within the nearest-neighbor TB model, the energy gaps for the bulk states will be zero if the length of the armchair edges are infinite for the \( n = 5 \) SGNRs, but for finite length, the bulk gaps are not zero due to the dimensional-confinement effect. The calculated DOS curves for three SGNRs with \( n = 5 \) are plotted in figure 4. The split edge states are marked by two black dashed lines, which are nearly unchanged for these three SGNRs. However, the energy difference between the occupied and unoccupied bulk states (indicated by green dashed lines) decreases with the increase of \( m \). Therefore, for the \( n = 5 \) SGNRs, the HOMO and LUMO states are edge states when \( m < 12 \), and become bulk states when \( m \geq 12 \).

In general, the HOMO and LUMO are edge states for SGNRs with \( \mod (n, 3) = 0 \) and \( \mod (n, 3) = 1 \), while they can be bulk states for SGNRs with \( \mod (n, 3) = 2 \), owing to the competition between the splitting edge states on zigzag edges and the bulk states induced by dimensional-confinement between the two armchair edges.

In order to show more clearly the differences between the edges states and bulk states, we plot in figures 5 and 6 the distributions of electrons in the bulk states (HOMO-1 and LUMO+1 in figure 4) and the edge states (HOMO and LUMO in figure 4) of the \((5, 8)\) SGNR, respectively. Figure 5 shows that the electrons in bulk states are distributed over the entire area of SGNRs, except for a little larger density on the edges and a tiny spin dependence, because these states are very close to the edge states in energy. In contrast, they are completely
different for the electrons in edge states. Figure 6 shows that the electron distributions are edge-dominated and spin-dependent. For electrons with spin up in the HOMO, they accumulate at the outmost carbon atoms on one zigzag edge, as shown in figure 6(a). However, for electrons with spin down in the HOMO, they accumulate on the other zigzag edge, as shown in figure 6(b). Thus the spins of electrons are ferromagnetically coupled on one zigzag edge but antiferromagnetically coupled between the two zigzag edges [6–8, 13, 18, 19]. For electrons in the LUMO, their distributions are also edge-dominated and spin-dependent. Importantly, they distribute in some different ways from electrons in the HOMO: electrons with spin up in the LUMO do not distribute on the same edge as electrons with spin up in the HOMO, but distribute on opposite edges. This means that electrons with same spins in the HOMO and LUMO are separated to opposite zigzag edges, while electrons with opposite spins in the HOMO and LUMO locate at the same zigzag edges [8, 18].

As discussed in the above paragraphs, the HOMOs and LUMOs are edge states in the SGNRs with $n = 3$ and $n = 4$, while they are bulk states when $m$ is large enough in the SGNRs with $n = 5$. These two types of HOMOs
and LUMOs will result in two different trends of the TB energy gaps ($E_{\text{g}}^{\text{TB}}$, calculated from $H_0$), depending on the number of $n$. For SGNRs with $n = 3$ and $n = 4$, the $E_{\text{g}}^{\text{TB}}$ decrease firstly with increasing $m$ and then converged when $m \geq 12$ and $m \geq 8$, respectively, as shown in figures 7(a) and (b). This is consistent with the property that edge states are mainly located at the edges and exponentially decay away from the edges. Therefore, the edge states will remain unchanged if the two zigzag edges are far enough from each other. However, when the HOMO and LUMO states are bulk states, the corresponding energy gaps will decrease with increasing $m$, due to the decrease of dimensional-confinement effect. This results in the other trend of $E_{\text{g}}^{\text{TB}}$, such as the SGNRs with $n = 5$ shown in figure 7(c).

### 3.2. Exciton properties of the SGNRs

Having discussed the electronic properties, we now investigate excitonic effects in SGNRs. The excitonic effects for triangle and hexagonal graphene nanoflakes have been investigated by some works [39–42], however, the study of excitonic effects in SGNRs is still lacking. By calculating the excitonic eigenvalue equation, we obtain the renormalized energy gaps, exciton energies, and exciton binding energies in SGNRs. The calculated energy levels of the four exciton states ($S$, $T_0$, $T_1$, and $T_{-1}$) for the (3, 8) SGNR are shown in figure 8. The magenta dashed line denotes the position of the renormalized energy gap ($E_{\text{g}}^{\text{H}}$) from $H$, which is 1.91 eV for the (3, 8) SGNR. This energy gap is about 1.33 eV larger than the corresponding $E_{\text{g}}^{\text{TB}}$, which shows strong e-e interactions in the (3, 8) SGNR. In figure 8, there are some exciton energy levels emerge below the dashed line, and the energy of the lowest exciton energy level of the singlet ($E_0$) is 1.05 eV. Therefore, the binding energy of the singlet ($E_{\text{b}}^S$) is 0.86 eV, showing strong exciton effects in the (3, 8) SGNR. As a function of $m$, $E_{\text{g}}^{\text{H}}$ behave as the same way as the $E_{\text{g}}^{\text{TB}}$, as shown by the magenta diamond-dotted line in figures 7(a)–(c). The convergent property of $E_{\text{g}}^{\text{H}}$ for the $n = 3$ SGNRs agrees with previous experimental observations and ab initio GW calculations [30]. And furthermore, the converged energy in our calculation is 1.89 eV, which is excellently consistent with the experimental value of 1.9 eV in the SGNRs with $n = 3$ [30].

We now turn to discuss the lowest exciton energies and the corresponding exciton binding energies as a functions of $m$ for the (3, $m$) SGNRs. The lowest exciton states are dominated by the HOMO and LUMO states, which are edge states. To produce a singlet exciton $S$, the spin of an electron does not flip during the excitation from an occupied state to an unoccupied state. And according to the electron distributions in the HOMO and LUMO plotted in figure 6, we can conclude that the electron and hole in an S exciton are distributed on the
opposite zigzag edges in the \( n = 3 \) SGNRs. Then, since the distance between the electron and the hole will increase as \( m \) increases, the binding energies \( (E_{bS}) \) of the \( S \) exciton will decrease. Then the lowest exciton energy, defined as \( E_S = E^{HOMO}_{S} - E^{LUMO}_{S} \), will increase since \( E^{HOMO}_{S} \) is nearly unchanged. The trends of \( E_S \) and \( E_{bS} \) are reflected by the curves within the letters A and B in figure 7(a). After the B point, the calculated exciton energies and binding energies are nearly unchanged, which disagrees with our above discussions. This is because after the B point, the original lowest exciton state has been elevated to be one of the exciton excitation state, and accordingly, the original second lowest exciton excitation state becomes the lowest. And careful investigations show that after the B point the lowest exciton states either consists of an electron in the edge states and a hole in the bulk states, or consists of a hole in the edge states and an electron in the bulk states. In other words, after the B point, the lowest singlet exciton state is formed by the electron excitation between edge states and bulk states.

In figure 9, we plot the energy levels of \( S \) exciton as a function of \( m \) for the \((3, m)\) SGNRs. The pink dashed lines denote the positions of energy levels of excitons formed between edge states, while the cyan dashed lines denote the positions of energy levels of excitons formed between edge states and bulk states. The energy of the pink dashed line is increased as increase the value of \( m \), and it becomes the second lowest energy level when \( m > 16 \), which consist with the position of B point plotted in figure 7(a).

Similarly, the B point also exists for the SGNRs with \( n = 4 \), as shown in figure 7(b). In the discussions for figures 2 and 3, the energy differences between the bulk states and edge states in the SGNRs with \( n = 4 \) are smaller than those with \( n = 3 \). This means the exciton with half edge state and half bulk state will be easier to become the lowest exciton states in SGNRs with \( n = 4 \) than that with \( n = 3 \). This is consistent with the much smaller value of \( m \) of the B point, as shown in figure 7(b).

However, a quite different trend of the exciton energies and exciton binding energies is found for the SGNRs with \( n = 5 \). In these SGNRs, the HOMO and LUMO states are bulk states when the value of \( m \) is large enough,
and the corresponding distributions of the electrons and holes are distributed over the entire structures. Thus the dimensional-confinement effect decreases as the sizes of the SGNRs increase, which results in the exciton energies \( E_b \) and exciton binding energies \( E_b^* \) decreasing with the increase of the sizes, as shown in figure 7(c). This trend agrees with most of the size-dependent excitonic effects in materials [43–45].

It is interesting to investigate the types of the lowest exciton states as a functional of the size of SGNRs. In figure 10 we plotted the calculated information, where the hollow circles denote exciton states formed between edge states; the half hollow circles denote exciton states formed between edge and bulk states; and the solid circles denote exciton states formed between bulk states. And the edges between the hollow circles and half hollow circles correspond to the definitional of B point. For SGNRs with \( \text{mod} (n, 3) = 0 \), the value of \( m \) that corresponding to the B point increase of about 8 when the value of \( n \) is increased to the next value. For example, for SGNRs with \( n = 3 \), the B point corresponds to \( m = 16 \), and for SGNRs with \( n = 6 \), the B point corresponds to \( m = 24 \), and so on. There are no such regular rules for the B point of SGNRs with \( \text{mod} (n, 3) = 1 \) and \( \text{mod} (n, 3) = 2 \). However, the value of \( m \) for B point is generally increased as increase the value of \( n \), as shown in figure 10.

Figure 7(d) plots the energy gaps, renormalized energy gaps, exciton energies, and exciton binding energies of the SGNRs with a fixed \( m \) \((m = 16)\), but changing with \( n \). These energies oscillate with the periods of 3, coming from the three value of \( \text{mod} (n, 3) \). Therefore, these oscillations inherit the three kinds of energy gaps of AGNRs [7, 13–17]. However, we must point out that by increasing the value of \( n \), we also increase the lengths of zigzag edges and the numbers of edge states, all of which will change the exciton effects in SGNRs. These properties will change the period occasionally in SGNRs.

In materials without spin-polarization, the three triplet exciton states are totally energy degenerate. It is interesting to investigate the triplets in SGNRs with spin-polarization. Figure 11 shows the energies and binding energies of \( T_0 \) and \( T_1 \) triplet excitons in various SGNRs. From these four plots, we can see that the energies and binding energies of the \( T_0 \) triplet \((E_{T0} \text{ and } E_{T0}^*)\) are not equal to the energies of the \( T_1 \) triplet \((E_{T1} \text{ and } E_{T1}^*)\). However, the two triplets, \( T_1 \) and \( T_{-1} \), are energy degenerate (not shown). These energy properties of the triplets can be understood by the spin-polarization properties of SGNRs [35]. According to the definition of \( T_0 \), \( T_1 \), and \( T_{-1} \) in equation (6), the spin does not flip when an electron is excited from an occupied state to an unoccupied state to form a \( T_0 \) triplet, but flip to form \( T_1 \) or \( T_{-1} \) triplet. Then, considering the spin-dependent distribution of electrons in the edge states shown in figure 6, we conclude that depending on the spin is flipped or not, it will result in totally different distributions of electrons and holes in the three triplets, and result in the energy splits of the triplets.

Specifically, for the \( n = 3 \) and \( n = 4 \) SGNRs whose HOMO and LUMO states are edge states, the electrons and holes are separated onto the opposite zigzag edges for the lowest exciton states of the \( T_0 \) excitons, similar to those of the S excitons. This means the lowest \( T_0 \) exciton states will also change to the excitons composed of half edge states and half bulk states after the B point, shown in figures 11(a) and (b), where the \( E_{T0} \)'s begin to be flat. However, the electrons and holes are at the same edges for the \( T_1 \) and \( T_{-1} \) excitons. So the distances between the zigzag edges will not change the distance between the electrons and holes in these two excitons. Therefore, the binding energies are nearly unchanged when increasing \( m \), as shown in figures 11(a) and (b). Thus, the lowest exciton states in \( T_1 \) and \( T_{-1} \) are always the edge exciton states and will not change to the exciton states with half edge states and half bulk states. For the \( n = 5 \) SGNRs, the lowest exciton states of \( T_0 \) excitons are bulk exciton states because their HOMO and LUMO states are bulk states, but the lowest of \( T_1 \) and \( T_{-1} \) are edge exciton states.
formed with electrons and holes in the edge states. Because the electrons and holes on same edges will result in very strong exciton binding energies. The binding energies of $T_1$ and $T_{-1}$ excitons are stronger than those of the $T_0$, as shown in Figure 11(c). The energies and binding energies of the triplets will also behave some oscillation properties with the number of $n$, as shown in Figure 11(d).

4. Conclusions

In conclusion, we have calculated the electronic properties of SGNRs by using spin-resolved TB method with Hubbard interaction. We found spin-polarized edge states on the two zigzag edges. However, the HOMO and LUMO states are not always edge states. They alternatively change between bulk states and edge states when extending the zigzag edges. As a result, the energy gaps are divided into two kinds of trends when they are plotted as functions of the lengths of the armchair edges. We have also taken into account the $e-e$ interaction in the TB Hamiltonian to calculated the exciton energies and exciton binding energies of SGNRs, and found strong exciton effects in all these SGNRs. Specifically, we found that there are two kinds of the exciton energies and exciton binding energies, due to the two kinds of HOMO and LUMO states. We also found the break of the energy degeneracy of the three triplet excitons, because of the anti-ferromagnetic couplings between the two zigzag edges.

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