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Spin-charge order and excitonic effects in sawtooth-like graphene nanoribbons

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ABSTRACT

In this paper we systematically study electronic structures and excitonic effects in one type of the sawtooth-like graphene nanoribbons. A main feature is that the local magnetism is developed for the certain width and changes with the increase of width. A variety of magnetic orders root in the competition of the short range interaction between the same spin-electrons and long range exchange interaction between opposite spin-electrons. For excitonic effects, the binding energy of degenerate spin-triplets T_1 and T_{-1} is higher than that of T_0 for all studied nanoribbons and is size dependent. We reveal the underlying physical mechanism from the charge distributions of excitons and its correlation with the spin-resolved charge density distributions in the ground state. We find that the electrons and holes in degenerate spin-triplets T_1 and T_{-1} are closer together and thus the interaction between them is more strong, while the distribution of electrons and holes is relatively more disperse for T_0, indicating the weaker interaction. We hope that these interesting results are able to be detected in the experiment and these multi-performance samples are better utilized in future device applications.

1. Introduction

Due to reduced dimensionality and enhanced electron–electron interactions, excitonic effects would be dominant for the optical properties of low-dimensional nanostructures. The discovery of graphene has stimulated intense research in this field from the point of view of both fundamental physics and promising applications. Recent theoretical studies, as well as experiments, have shown that the excitonic effects dramatically change the optical response in quasi-one-dimensional structures, such as carbon nanotubes [1–5], armchair graphene nanoribbons [6–12], zigzag graphene nanoribbons [11–14]. On the other hand, more and more graphene nanoribbons (GNRs) with novel structures have been synthesized or fabricated experimentally. For example, segmented GNRs containing lattice-defined junctions have been produced with chemical method [15–20]. These segmented nanoribbons can be tailored together to form a novel structure, which is named the sawtooth-like graphene nanoribbons (SGNRs) [21,22]. Wang et al. have shown by first-principles calculations that one type of SGNRs is a tunable spin-semiconductor under transverse electrical fields [23]. Our recent researches have shown that the another type of SGNRs possess novel magnetic edge states and piezo-antiferromagnetic effect [24]. Research on zigzag GNRs has indicated that the magnetic edge states play an important role in understanding the excitonic effects in those graphene nanostructures [14]. So, in this paper we systematically study electronic structures, magnetic edge states and excitonic effects in the SGNRs. Our studies indicate that the binding energy of excitons is closely correlated with the spin-resolved charge density distributions in the ground state.

A typical SGNR structure is shown in Fig. 1. The basic repeating unit is a butterfly-shaped graphene nanoflake with two zigzag-edged 'wings', which is amplified in the lower panel. The angle between the edges of neighboring 'wings' is 120°. The edge carbon atoms on one 'wing' belong to one sublattice, while those on opposite 'wings' belong to the other sublattice, as distinguished by letters 'A' and 'B' in Fig. 1. The number difference of the atoms of the two sublattices is equal to zero, which leads to zero net magnetic moment according to the Lieb's theorem [25]. This is consistent with our calculated results. The following notation is used in describing an SGNR: m-SGNR is an SGNR with m hexagonal rings in one 'wings' along the directions of $\vec{m}$. A studied representative 4-SGNR is shown in Fig. 1. In this study, we consider seven m-SGNRs with m from 2 to 8. Due to different geometry and sym-

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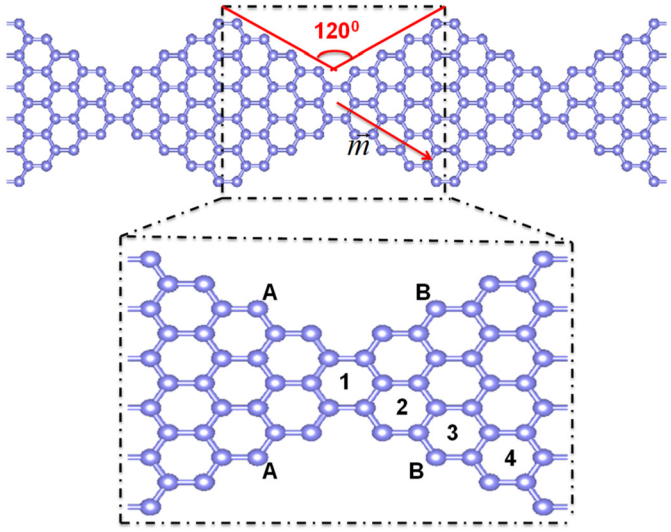

Fig. 1. Atomic structure of a 4-SGNR. The supercell which is shown in dashed-rectangle box is a butterfly-shaped graphene nanoflake. The angle between the edges of neighboring 'wings' in supercell is 120°. The edge carbon atoms on one 'wing' belong to one sublattice, while those on the opposite 'wings' belong to the other sublattice, as distinguished by letters 'A' and 'B'.

metry, we expect the SGNRs to have more abundant and meaningful electronic and optical properties than the straight zigzag GNRs and armchair GNRs.

2. Method and theory

Our studies are based on the tight-binding Pariser–Parr–Pople (TB-PPP) model [26,27], which has been successfully used to study the electronic structures and excitonic effects in π-conjugated polymers [28–30], single-walled carbon nanotubes (SWNTs) [31–33], armchair GNRs [8–12] and zigzag GNRs [11,12,14,34,35]. The Hamiltonian of the TB-PPP model describes

$$H = H_0 + H_{e\text{-}e} \tag{1}$$

$$H_0 = \sum_{\langle i,j\rangle,\sigma} t c_{i\sigma}^{+} c_{j\sigma} + \sum_{i,\sigma} U\left(\langle n_{i\bar{\sigma}}\rangle - \frac{1}{2}\right) n_{i\sigma}, \tag{2}$$

$$H_{e\text{-}e} = U\sum_{i}\left(n_{i\uparrow} - \langle n_{i\uparrow}\rangle\right)\left(n_{i\downarrow} - \langle n_{i\downarrow}\rangle\right) + \frac{1}{2}\sum_{i,j(i\neq j)}\sum_{\sigma,\sigma'} V_{ij}\left(n_{i\sigma} - \langle n_{i\sigma}\rangle\right)\left(n_{j\sigma'} - \langle n_{j\sigma'}\rangle\right), \tag{3}$$

where H_0 is the spin-resolved one-electron Hamiltonian, and $H_{e\text{-}e}$ is the electron–electron interaction Hamiltonian. $n_{i\sigma} = c_{i\sigma}^{+} c_{i\sigma}$ is the spin-resolved number operator, $c_{i\sigma}^{+}(c_{i\sigma})$ is the electron creation (annihilation) operator with spin σ on site i, t is the nearest-neighbor transition integral, U is the on-site Hubbard interaction parameter and $\langle n_{i\sigma}\rangle$ is the average occupation probability of spin σ electron on site i. V_{ij} is the long range Coulomb interaction between the site i and site j, which is modeled by the Ohno's potential [36,37]

$$V_{ij} = \frac{U}{\kappa\sqrt{1 + (\frac{4\pi\varepsilon_0}{e^2} U r_{ij})^2}}.$$

The dielectric function parameter $\kappa = 4.2$ is used to describe the vacuum environment or free standing SGNRs, ε_0 is the permittivity of vacuum, e is the magnitude of the electron charge and r_{ij} is the distance between site i and site j in units of Å.

A exciton state, $|ex\rangle$, is constructed by a linear combination of single electron–hole (e–h) pair states, i.e. $|ex\rangle = \sum_{k_c,k_v} \rho(k_c,k_v) \times |k_c,k_v\rangle$, where $\rho(k_c,k_v)$ is the weight coefficient and $|k_c,k_v\rangle$ is excited state of the single e–h pair. k_c and k_v denote the wave vector of electrons in conduction bands and valence bands, respectively. When considering spin freedom of electron, each e–h pair generates a total of four spin-states, including one spin-singlet (S) and three spin-triplets (T_0 for $S_z = 0$, T_{-1} for $S_z = -1$, T_1 for $S_z = 1$). The four spin-states are respectively expressed as

$$\begin{aligned} S&: |k_c k_v\rangle = \frac{1}{\sqrt{2}}\left(c_{kc\uparrow}^{+} c_{kv\uparrow} + c_{kc\downarrow}^{+} c_{kv\downarrow}\right)|g\rangle \\ T_0&: |k_c k_v\rangle = \frac{1}{\sqrt{2}}\left(c_{kc\uparrow}^{+} c_{kv\uparrow} - c_{kc\downarrow}^{+} c_{kv\downarrow}\right)|g\rangle \\ T_{-1}&: |k_c k_v\rangle = c_{kc\downarrow}^{+} c_{kv\uparrow}|g\rangle \\ T_1&: |k_c k_v\rangle = c_{kc\uparrow}^{+} c_{kv\downarrow}|g\rangle \end{aligned} \tag{4}$$

where $|g\rangle$ denotes the ground state where the electrons are not excited from valence bands to conduction bands. Then, the exciton eigenvalue equation can be indicated as

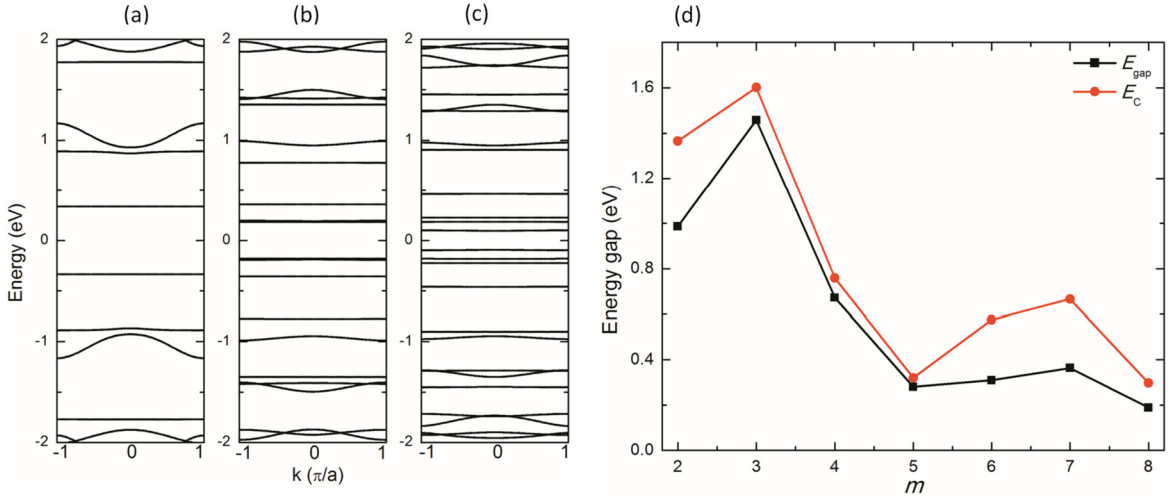

Fig. 2. Band structures of m-SGNRs with $m = 4$ (a), $m = 7$ (b) and $m = 8$ (c). (d) The variation of the energy gap with m.