Dirac equation description of the electronic states and magnetic properties of a square graphene quantum dot

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Abstract

Electronic eigenstates of a square graphene quantum dot (GQD) terminated by both zigzag and armchair edges are derived in the theoretical framework of the Dirac equation. We find that the Dirac equation can determine the eigenenergy spectrum of a GQD with high accuracy even if its size is reduced to a few nanometers. More importantly, from the Dirac equation description we can readily work out the number and energy gap of the conjugate surface states, which are intimately associated with the magnetic properties of the GQD. By using the Hartree–Fock mean field approach, we study the size dependence of the magnetic ordering formation in this square GQD. We find that there exists a critical size of the width between the two zigzag edges to indicate the onset of the stable magnetic ordering. On the other hand, when such a width increases further, the magnetic ground state energy of a charge neutral GQD tends to a saturated value. These results coincide with the previous results obtained from the first-principles calculation. Then, based on the Dirac equation solution about the surface state, we establish a simple two-state model which can quantitatively explain the size dependence of the magnetic ordering in the square GQD.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Graphene has become a subject of intense interest since the experimental success in fabricating such an atomically thin layer of graphite [1]. The valence electron dynamics in such a truly two-dimensional material is governed by a massless Dirac equation. As a result, graphene exhibits many unique electronic properties [2, 3], in comparison with conventional semiconductor materials. From an application point of view, graphene possesses very high mobility even at room temperature [4]. Moreover, the planar geometry of graphene is advantageous in tailoring various nanostructures by current experimental means, such as lithographic techniques [5]. So far, the obtainable graphene nanostructures include one-dimensional(1D) nanoribbons [6] and zero-dimensional quantum dots [7]. These nanostructures are viewed as the elemental blocks to construct graphene-based nanodevices.

Accompanying the extensive investigations on the electronic properties in bulk graphene, graphene nanostructures have also attracted much attention in theoretical studies [8]. First of all, some theoretical approaches to produce the effective electron confinement in graphene were proposed [9–12] which is a nontrivial problem due to the Klein tunneling of the carrier in graphene [13, 14]. For example, GQD structures can be formed by patterning gates on a semiconducting graphene nanoribbon [10, 11], or by using inhomogeneous magnetic fields [12]. Then, some device applications of the graphene nanostructures were suggested, such as the spin qubits based on the coupled GQDs [10]. In addition, some electronic properties

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of graphene nanostructures are expected to be different from bulk graphene because of quantum confinement and the edge effect. For instance, spontaneous magnetization is anticipated to emerge in some graphene nanostructures [15, 16], which is attributed to the spin polarized electron occupancy at the zigzag-type edges of the nanostructures. Such a magnetic ordering has been experimentally demonstrated [17, 18]. Quite recently, the possible magnetism of graphene nanostructures with different shapes has been theoretically studied in some detail [19–23]. For example, an infinitely long graphene nanoribbon with zigzag edges can possibly behave as a half-metallic material, in which a spin polarized current can be formed [23]. Such a property is controlled by an external electric field, which can tune the asymmetry of the band structures of the opposite-spin electrons. Apart from the 1D graphene nanoribbon, GQDs with different shapes also exhibit magnetic orderings, such as square quantum dots, and triangular and hexagonal quantum dots terminated by zigzag edges [19–22]. Theoretical calculations indicate that in these zero-dimensional graphene structures the magnetic ordering is so robust that it can be detected at room temperature. In addition, for the square and hexagonal [20, 21] quantum dots, there is a critical size which marks the onset of the spin polarized ground state. In contrast, for a quantum dot with a size smaller than the critical size, the ground state is a paramagnetic state.

The aforementioned results on the magnetic properties of graphene nanostructures are obtained by means of the first-principles calculation [21] as well as the mean field approximation on a Hubbard model of a hexagonal lattice. Although these theoretical approaches can give reliable results about the electronic properties of graphene nanostructures, their applicability is restricted within those structures with relatively small size. Furthermore, in most cases these approaches cannot provide us with a clear physical picture to explain the numerical results. For example, an unambiguous explanation about the critical size for the onset of the magnetic ordering in GQDs is still lacking. On the other hand, the Dirac equation description can just compensate for the disadvantage of the two theoretical approaches mentioned above. As a theoretical model based on the effective mass approximation, a massless Dirac equation can well describe the electron properties of the bulk graphene as well as the graphene nanostructures with relatively large sizes [24, 25]. Usually, such a model can provide analytical results, which are very helpful to explain intuitively the electronic properties associated with the relativistic quantum mechanical features of graphene.

So far, the Dirac equation succeeds in describing the band structures of graphene nanoribbons with distinct edge types [24, 25]. In the present work, we will employ this model to study the electron states in a square GQD. With an appropriate boundary condition, we can derive an analytical solution of the electron eigenstate in such a GQD. Moreover, by a numerical calculation carried out from the mean field approximation of the Hubbard model, we investigate the size dependence of the magnetic property of the GQD. We find that there is not only the critical size, but also another characteristic size to indicate the saturation of the magnetization. Namely, it is a relatively larger size than the critical size, beyond which the spin polarization energy no longer varies with further increase of the size of the GQD. Then, based on the analytical result obtained from the Dirac equation, we establish a simple theoretical model, which can not only reveal the physical nature of the emergence of the critical and saturated sizes, but also provide an simple way to rapidly create the quantitative result about the critical and saturated sizes, agreeing well with the numerical result of the mean field approximation.

The rest of this paper is organized as follows: starting from the Dirac equation and using appropriate boundary conditions, the wavefunction and the dispersion relation of the electron eigenstate of the square GQD are derived in section 2. Then the eigenenergy spectra calculated from the Dirac equation and the tight-binding model are compared. In section 3, the magnetic property of the GQD is investigated by means of Hartree–Fock mean field theory. By establishing a two-state model, the size dependence of the magnetic ordering is quantitatively explained. Finally, the main conclusion is briefly summarized in section 4.

2. The electronic states of GQD

The honeycomb lattice of the square quantum dot made of graphene monolayers is schematically shown in figure 1. The edges of the square GQD are of two kinds, zigzag edges at the top and bottom, and armchair ones at the left and right sides. We assume that the dangling $\sigma$ bonds at the edges are passivated by hydrogen atoms. Thus, the behavior of the $\pi$ band electron near the Fermi level is not nontrivially affected.
by the truncation of the $\sigma$ bond at the GQD edges. Within the effective mass approximation, the envelope function of the $\pi$ band electron in graphene monolayers obeys the following Dirac-like equation [26]:

$$H\Psi = \gamma = \begin{bmatrix} 0 & -\hat{k}_- & 0 & 0 \\ -\hat{k}_+ & 0 & 0 & 0 \\ 0 & 0 & 0 & \hat{k}_- \\ 0 & 0 & \hat{k}_+ & 0 \end{bmatrix} \begin{bmatrix} \phi_A \\ \phi_B \\ -\phi_A \\ -\phi_B \end{bmatrix},$$

$$= E \begin{bmatrix} \phi_A \\ \phi_B \\ -\phi_A \\ -\phi_B \end{bmatrix},$$

(1)

where $\gamma = \sqrt{3}t_n/2$ with $t$ being the nearest-neighbor hopping energy. In what follows we use units such that $\gamma = h = 1$. $\hat{k}_\pm = \hat{k}_x \pm i\kappa_y$ and $\hat{k}_{x(y)} = -i\partial_{x(y)}$ is an operator to measure the momentum deviation from $K = (-4\pi/3a_0, 0)$ or $K' = (4\pi/3a_0, 0)$ point. The four components of the spinor wavefunction in equation (1) are associated with the total wavefunction $\Psi(r)$ by the following relationship:

$$\psi\mu(R_n) = e^{iKR_\mu} \phi\mu(R_n) + e^{iK'R_\mu} \phi'\mu(R_n), \quad \mu = A, B;$$

and

$$\Psi(r) = \sum_{\mu=A,B} \sum_{R_n} \psi\mu(R_n) \xi(r - R_n)$$

(2)

where $\xi(r - R_n)$ is the carbon atomic wavefunction centered at $R_n$ and $\psi\mu(R_n)$ denotes the probability amplitude of the valence electron appearing in the vicinity of this carbon atom. For the bulk graphene, by solving equation (1) we can obtain the electron eigenstate which has the linear dispersion relation $\epsilon = E/\gamma = sk$, and $s = \pm 1$ denotes the conduction and valence bands, respectively.

As for the present square GQD structure, the $\pi$ band electron obeys the same Dirac equation, but is subject to the following boundary conditions. At the zigzag edges

$$\phi_B(y = 0) = \phi_B'(y = 0) = \phi_A(y = L'_y) = \phi_A'(y = L'_y) = 0,$$

(3)

and at the armchair edges

$$\phi_B(x = 0) = \phi_B'(x = 0),$$

$$\phi_A(x = L'_x) = e^{i\beta L'_x/3} \phi_A'(x = L'_x).$$

(4)

These boundary conditions have been successfully used to work out the band structures of the graphene nanoribbons with different edges [24] and the energy spectrum of GQDs [10, 11]. They originate from the requirement that the electron probability amplitude at the hard walls around GQD must vanish. Combining equation (1) with equations (4)–(5), we can derive the eigensolution of electron states in the square GQD. It is given by

$$\Phi = \begin{bmatrix} \phi_A \\ \phi_B \\ -\phi_A \\ -\phi_B \end{bmatrix} = \begin{bmatrix} \frac{1}{\pi} (p_n \sin(qy)e^{ip_n x} + q \cos(qy)e^{ip_n x}) \\ \sin(qy)e^{ip_n x} \\ \frac{1}{\pi} (p_n \sin(qy)e^{-ip_n x} - q \cos(qy)e^{-ip_n x}) \\ -\sin(qy)e^{-ip_n x} \end{bmatrix}.$$  

(5)

The corresponding eigenenergy is given by

$$\epsilon_n = s \sqrt{p_n^2 + q^2}.$$  

(6)

Although it takes the same form as the dispersion relation of the bulk graphene, in the present square GQD the wavevectors $p_n$ and $q$ in the $x$ and $y$ directions are both discrete. $p_n$ is given by

$$p_n = \frac{2n\pi}{(N + 1)a_0} - \frac{2\pi}{3a_0}, \quad n = 0, \pm 1, \pm 2 \cdots$$  

(7)

Corresponding to a given $p_n$, $q$ is determined by a transcendental equation:

$$q = p_n \tan qL'_y.$$  

(8)

By analyzing the above equation we find that the electron state with an imaginary wavevector $q = \imath|q|$ is allowed in the region $p_n > 1/L'_y$. In such a state the electron wavefunction is localized in the vicinity of the zigzag edges. Accordingly, it is called a surface state. In contrast to the surface state, we call a state with a real $q$ the confined state. The normalization coefficient of the spinor wavefunction for the confined state is

$$C = (2L'_y - \sin(2p_n L'_y/L'_x)/p_n)^{-1/2},$$

(9)

whereas for the surface state it is given by

$$C = (2L'_y - \sin(2p_n L'_y/L'_x)/p_n) \times (\sinh(2qL'_y)/q - 2L'_y/2)^{-1/2}.  

(10)

The eigenstate of the GQD shown in equation (6) can be understood in the following way. If the wavefunction is rewritten in a form $\Phi = \Phi^K + \Phi'^K$ with $\Phi^K = [\phi_A, \phi_B, 0, 0]^T$ and $\Phi'^K = [0, 0, \phi_A', \phi_B']^T$, we can immediately find that $\Phi^K$ and $\Phi'^K$ are just the wavefunctions of the eigenstates of an infinitely long zigzag nanoribbon [24] with the free wavevectors $p_n$ and $-p_n$, respectively. Therefore, the eigenstate of the GQD consists of the linear combination of the eigenstates of the zigzag nanoribbon in $K$ and $K'$ valleys. The boundary condition in the armchair direction admisses $K$ and $K'$ valleys. According to such an argument, we should restrict the possible surface states in the wavevector range $1/L'_y < p_n \leq \pi/3a_0$, where $\pi/3a_0$ is just the midpoint between $K$ and $K'$ valleys in the $x$ direction. When $p_n$ is beyond such a value, there is no longer any new surface state due to the valley admixing. Considering such a wavevector limit, we can readily determine the number of the surface states by simply counting the number of the discrete wavevectors $p_n$ in this range. For example, for a GQD of size $N = 13$ and $M = 10$ (denoted as N13M10 in brief), the allowed $p_n$ are $\pi/21a_0$ and $4\pi/21a_0$. Therefore, the total number of the surface states in valence and conduction bands are $2N_L = 4$, where $N_L$ is the number of allowed $p_n$ in the range of $1/L'_y < p_n \leq \pi/3a_0$. Moreover, from this method we can infer that, when $N < 7$, no surface state survives, independent of the value of $M$. We will see below that the surface states are responsible for the magnetic property of the GQD. Such a simple way to determine the number and energy of the surface
states is helpful for us to explain intuitively the numerical result about the magnetic property of the GQD. In addition, it should be noted that, in the following discussion, we only consider the GQD without any carbon atoms at the boundary connected to the GQD by a single π bond. Finally, although the Dirac equation can give an analytical description of the electron eigenstate in the square GQD, we have to point out that its applicability should be strictly restricted within the linear dispersion region of the π band of graphene. It is known that the energy scope of the linear dispersion region in the π band is about t/3, away from the Dirac point. Accordingly, in the two-dimensional k space the linear dispersion region forms a circle around the K or K’ point with a radius equal to \(2/(3\sqrt{3a})\). Therefore, if the energy of an eigenstate of the square GQD is much lower than t/3, it can be well described by the Dirac equation. In contrast, when an eigenenergy exceeds t/3, the Dirac equation gets poorer to describe such an eigenstate in the linear dispersion region. When M decreases further, the results calculated by the two models deviate from each other notably, as shown in figures 2(c)–(e). The result shown in figure 2(f) demonstrates that the Dirac equation description fails to give the correct eigenenergy spectrum for the GQD smaller than the one of N7M8. On the other hand, the result shown in figure 2(a) indicates that at least 10 low-lying eigenstates can be safely described by the Dirac equation for a GQD with a size of 4 nm × 5 nm. In conclusion, the numerical comparison made in figure 2 supports our simple criterion given above for the applicable limit of the Dirac equation approach to the GQD.

In figure 3 some low-lying eigenenergies versus \(p_n\) are plotted for a GQD of size N13M10, which is compared with the dispersion relation of a zigzag ribbon with width M = 10. Although these energy levels of the GQD are discrete, from this figure we can readily infer that the energy–wavevector relation of a GQD will change into the band structure of a zigzag nanoribbon with the continued increase of the size N. Thus, we can say that the dispersion relation of the zigzag nanoribbon remains in the Dirac equation description of the square GQD. This is one advantage of the Dirac equation over the tight-binding model in describing the electron states of the GQD. In addition, from the Dirac equation solution, we can easily distinguish the surface states from the confined states, because the two kinds of state have distinct forms of wavefunction. This can be viewed as another advantage of the Dirac equation description. In contrast, it is difficult to identify a surface state in the tight-binding model, in particular, for a GQD with small size.

To check the validity of the Dirac equation solution about the electronic eigenstate of the GQD in some detail, we compare the low-lying energy levels calculated by solving equations (7)–(9) to the ones obtained from the tight-binding model. The tight-binding Hamiltonian of the square GQD takes a form as \(H_{\text{tb}} = -t \sum_{\langle i, j \rangle} \sum_{\sigma} (c^\dagger_{i\sigma} c_{j\sigma} + \text{h.c.})\) where \(c^\dagger_{i\sigma}\) is the electron creation operator associated with a local atomic state at lattice point \(i\), and \(\langle i, j \rangle\) denotes any pair of nearest-neighboring carbon atoms. σ = ↑ (↓) corresponds to the up and down spins. In the basis set consisting of the local atomic orbits, the tight-binding Hamiltonian changes into a matrix. By diagonalizing this Hamiltonian matrix we can obtain the electronic eigenenergy spectrum and the eigen wavefunctions. Noting that electronic eigenstates are spin-degenerate, though, we write the spin index explicitly in the above tight-binding Hamiltonian. The electron spin becomes relevant only in the self-consistent calculation of the electron energy spectrum in the next section where the Hubbard interaction is taken into account.

The comparison of the numerical results of the low-lying eigenenergy spectra obtained by the Dirac equation as well as the tight-binding model is visualized in figure 2. For a relatively large GQD, N35M24 as shown in figure 2(a), the Dirac equation result agrees very well with the tight-binding result. Then we reduce the size of the GQD only in the x direction. These results are plotted in figures 2(a)–(c). We can see that the Dirac equation results get poorer with the decrease of N. In figure 2(c), despite N = 7, there are a few low-lying eigenenergies obtained by the Dirac equation solution to be close to the tight-binding result. This is due to that the relatively large M retains these eigenstates in the linear dispersion region. When M decreases further, the results calculated by the two models deviate from each other notably.

3. Magnetic properties of the GQD

Magnetic properties of graphene nanostructures with various shapes have drawn considerable interest. For example, some theoretical investigations indicate that a zigzag nanoribbon has a spin polarized ground state, which is tightly associated
Figure 2. A comparison of the low-lying energy levels calculated from the Dirac equation (triangle, cross) and tight-binding model (square) for GQDs with different sizes. (a) N35M24; (b) N11M24; (c) N7M24; (d) N7M12; (e) N7M8 and (f) N5M4.

with the surface state at the zigzag edges. This implies that a spontaneous magnetization may occur in such a nonferromagnetic material. Motivated by these previous works [15, 20–22], we now study the possible magnetic property of the square GQD. To do this, we adopt a single-band Hubbard model (to incorporate the Hubbard terms into the tight-binding model) and treat it within the Hartree–Fock approximation. It was previously proved that most magnetic properties of graphene nanostructures can be captured by such a simple approach [15, 16, 20].

The eigensolution of the Hartree–Fock Hamiltonian for a charge-neutral GQD can be obtained by an iteration method. In analogy with the previous work, our iterative calculation indicates that the spin polarization situation of the obtained eigenstate of the charge-neutral GQD depends on the initial spin configuration to start the iteration procedure. The different initial states will lead to eigenstates with distinct kinds of spin polarization. At first, to begin with an initial spin configuration of Néel order, we will arrive at an eigenstate with spin polarized electron occupation on individual lattice points. In particular, on the lattice points near the two zigzag edges the spin polarization is very strong. The net spin distributions at the two zigzag edges show the anti-ferromagnetic order (AFM) in figure 1. Second, if we start from an initial state with the uniform spin polarization at all the lattice points, the self-consistent calculation converges to an eigenstate with ferromagnetic (FM) ordering. In addition, a paramagnetic state (PM) can be achieved if the initial spin configuration is set to be unpolarized at all lattice points. Herein we adopt the same definition about the magnetic orderings as given in the previous works [15]. The AFM state refers to the spin moments of the electrons. As a result, spin polarized electron occupancy on individual lattice points may occur in the charge-neutral GQD.

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carbon atoms on one zigzag edge being anti-aligned to those on the opposite edge, while the FM state means that the spin moments on both zigzag edges point in the same direction. Moreover, the PM state can be defined alike, which refers to the spin-up and-down electrons being equally occupied at every lattice point. Next we focus on the size dependence of the magnetic orderings. To do this, in figure 4 we compare the total energy difference ($\Delta E$) between the FM (AFM) states and the PM state for the charge-neutral GQD, as a function of the width $M$ between the two zigzag edges, while the width $N$ in the armchair direction takes several typical values. First of all, we can find that there exists a critical size $M_c$, which denotes the onset of the PM–FM (AFM) transition. Namely, only when $M > M_c$ is the magnetic ordering stable. By comparing the results shown in figures 4(a)–(d), we find that $M_c$ depends sensitively on the transverse width $N$ and the Hubbard $U$. With the increase of $N$ and $U$, the critical size $M_c$ decreases notably.

There is one point we have to emphasize herein about the magnetic ordering in the GQD depicted above. The FM or AFM state in the GQD considered by us and the one in an extended honeycomb lattice have distinct underlying mechanisms. It is the surface states localized at the zigzag edges that cause the AFM in the GQD. The surface states in the GQD tend towards dispersionless as the width between the opposite zigzag edges get larger. Thus, a finite density of states forms in the vicinity of the Dirac point (energy zero point), which is responsible for the formation of the magnetic ordering even with a very small Hubbard $U$. However, such a surface state is absent in the extended honeycomb lattice in which there is no zigzag edge. The linear dispersion of the extended honeycomb lattice leads to the vanishing density of states at the Dirac point, which then requires a very large Hubbard $U$ for the PM–AFM transition in such an extended lattice. In fact, a similar comparison was made in [16] where the magnetic ordering in a zigzag ribbon only needs a much smaller (infinitely small, in fact) Hubbard $U$ than in the extended honeycomb lattice. In analogy with the GQD, the zigzag ribbon possesses surface states which form a flat band at the Dirac point, leading to the magnetic ordering even with an infinitely small $U$. In short, we think the magnetic ordering formed by a small $U$ is due to the existence of the surface state in the GQD. The spin polarized electron occupancy is notable only in the regions near the zigzag edges. The value of the Hubbard $U$ we used in our work is too small to show the formation of the AFM state following the mechanism of the extended lattice (from the result shown in [16] we can find out that such a critical $U$ is larger than $2t$).

Another noticeable feature in figure 4 is that the energy difference tends to a saturated value when the width $M$ exceeds a specific value $M_s$. Hereafter we call $M_s$ the saturated size. It is quantitatively determined in the following way: when the size of the GQD increases from $M_s$ to $M_s + 2$, the relative increment of $\Delta E$ should be less than 1%. In addition, from figure 4 we can find that the energy of the AFM state is notably lower than that of the FM state in the region $M_c < M < M_s$. This indicates that the AFM state in the region between the critical size and the saturated size is just the ground state of the charge neutral GQD [21, 27]. On the other hand, when $M$ is sufficiently large, the energy difference between the FM and AFM states becomes indistinguishable. This can be explained in such a way: the surface states in the GQD can be viewed as the bonding or anti-bonding states arising from the interaction between two kinds of surface states located at the opposite zigzag edges. In fact, each of two such surface states belongs to a semi-infinite two-dimensional graphene terminated by a zigzag edge. When $M$ is very large, the interaction between the two kinds of surface states gets weak. As a result, the exchange integral between them, which determines the relative orientations of the net spin moments at two zigzag edges, becomes negligibly small. Thus the energy difference between FM and AMF states tends to zero. Finally, we have to point out that the existence of the critical size for a hexagonal and square graphene quantum dots was previously reported [20–22], based on the first-principles calculation. The result about the square GQD agrees quantitatively with our present result obtained by the mean field approximation [21, 22]. However, a clear explanation about the critical size is yet lacking.

Next, we try to give a reasonable explanation about the occurrence of the critical and saturated sizes. At the first step, we discuss the relation between the magnetic order formation and the electron occupancy on the surface states. Accordingly, we can work out a simple criterion which can qualitatively explain the numerical result about the critical size obtained above by the Hartree–Fock mean field theory. Then, we establish a two-state model which can give a quantitative explanation of the numerical result about the critical and saturated sizes. All these arguments benefit from the Dirac equation solution about the single-particle surface states. As analyzed in the preceding section, the number of surface states in the range $1/L < p_s < \pi/3a_0$ is finite. Corresponding to a specific $p_s$, there are two conjugate surface states, belonging
Energy differences versus $M$ between AFM (circle) and PM as well as FM (triangle) and PM states for charge-neutral GQDs with different sizes and on-site energies. (a) N7U0.1t; (b) N7U0.5t; (c) N11U0.1t and (d) N11U0.5t. The critical size $M_c$ and the saturated size $M_s$ are labeled on the curves.

Figure 4. Energy differences versus $M$ between AFM (circle) and PM as well as FM (triangle) and PM states for charge-neutral GQDs with different sizes and on-site energies. (a) N7U0.1t; (b) N7U0.5t; (c) N11U0.1t and (d) N11U0.5t. The critical size $M_c$ and the saturated size $M_s$ are labeled on the curves.

to the conduction and valence bands, respectively. The energy gap between them depends on $p_n$ and the size of the GQD. We consider especially the two conjugate surface states with the maximal $p_n$. In comparison with other surface states, this pair of surface states has the smallest energy gap. The finite Hubbard $U$ alters the single-electron energy spectrum since it affords an on-site Coulomb repulsive potential. For example, in a presumed paramagnetic state, the surface state with a specific spin $\sigma$ in the valence band will increase by $U\langle n_{i\sigma}\rangle = U/2$ due to Coulomb repulsion. When such a shift makes the surface state in the valence band align with the surface state in the conduction band, the system is likely to show spontaneous magnetization. Following such an analysis, we obtain a simple criterion to determine the critical size. $M_c$ is the size at which the inequality

$$E_g < U/2$$

begins to hold true, where $E_g$ is the energy gap between the pair of surface states corresponding to the maximal $p_n$. By calculating $E_g$, we can obtain the critical size $M_c$. Using such a simple criterion, we estimate the critical size $M_c$, varying with the size $N$ as well as the Hubbard $U$. These results are shown in figure 5. In comparison with the Hartree–Fock mean field result, we find that the criterion given by equation (13) can roughly account for the dependence of the critical size on $N$ as well as $U$.

Although the above criterion is not too bad, we will show that a more quantitative explanation of the critical size is available. Now that the onset of the magnetic ordering is controlled by the pair of surface states with the minimal energy gap, we establish a simple two-state model by retaining only this pair of surface states in the mean field Hamiltonian. Thus, the Hartree–Fock Hamiltonian for this two-state model takes a form as

$$H^{ts} = \sum_{i\sigma} \epsilon_i c_i^\dagger c_i + U \sum_{i\mu\sigma} \langle \hat{m}_{i\mu\sigma} \rangle \hat{m}_{i\mu\sigma}$$

where $s = \pm$ denotes the two surface states belonging to the conduction and valence bands, respectively. $c_i^\dagger (c_i)$ is the electron annihilation (creation) operator of the surface state of quantum index $i\sigma$. The electron number operator $\hat{m}_{i\mu\sigma}$ counts only the contributions of the two surface states to the electron occupancy on the individual carbon atoms. According to such a meaning, it is associated with the electron number operator of the two surface states via a relation

$$\hat{m}_{i\mu\sigma} = \sum_s \langle \psi_{s}(i) |^2 \Omega c_{i\sigma}^\dagger c_{i\sigma}$$

where $\Omega = \sqrt{3}a_0^2/2$ is the area of the unit cell and $\langle \psi_{s}(i) |^2$ is just the probability of the electron in the surface state(s).
The former is the result that the parameters cross symbols are for the results obtained from the two-state model. 

The critical size with $\mu$ Figure 5. (a) The critical size $M_c$ versus $U$. The square symbol denotes the Hartree–Fock mean field result; the star symbol is the result obtained from the simple criterion given by equation (13). The triangle and cross symbols are for the results obtained from the two-state model. The former is the result that the parameters $E_g$ and $U_0$ are evaluated from the Dirac equation. The latter is the result with $E_g$ and $U_0$ calculated from the tight-binding model.

appearing in the vicinity of the carbon atom $\mu$ at lattice point $i$, which can be directly calculated from the analytical wavefunction in equation (2). For the charge-neutral GQD, the two surface states accommodate two electrons with opposite spins. We thus have $\sum_{\sigma} c^\dagger_{\mu \sigma} c_{\mu \sigma} = 2$. In addition, it should be noted that, in such a two-state model, we have ignored the contributions to the average electron occupancy on the individual lattice points from other occupied single-electron eigenstates, except for the two surface states retained in this model. This is because other occupied electron states in the valence band only provide a spin-unpolarized charge background, which influences the opposite-spin electrons in the two surface states on an equal footing. Substituting equation (15) into (14), we obtain the following diagonal Hamiltonian:

$$\begin{align*}
H^B &= \sum_{\sigma} \left( \epsilon_\sigma + \sum_{\sigma'} U_0 \langle c^\dagger_{\sigma',\mu} c_{\sigma',\mu} \rangle \right) c^\dagger_{\sigma\mu} c_{\sigma\mu}, \\
\text{(s')} &= \pm \sigma
\end{align*}$$

with

$$U_0 = \sum_{\mu} U \cdot \Omega \int dr |\psi^0_{\mu}(r)|^2 \cdot |\psi_{\mu}(r)|^2.$$  \hspace{1cm} (17)$$

Here $U_0$ can be calculated analytically by the Dirac equation wavefunction given in equation (2), or numerically by the tight-binding model instead. By a simple derivation from the Dirac equation wavefunction we obtain the analytical form about $U_0$.

It is given by

$$U_0 = \frac{3\sqrt{3}U(\text{sinh} 4gL \sqrt{q} - \text{sinh} 2gL \sqrt{q} + \frac{3L_0}{q})}{L(\text{sinh} 2gL \sqrt{q} - 2L_0)^2}$$  \hspace{1cm} (18)$$

For the PM state, two electrons occupy the valence band surface state ($\epsilon_-$) with opposite spins. From the diagonal Hamiltonian given above, we can immediately obtain that the energy of the two electrons is equal to $E_{PM} = 2\epsilon_- + 2U_0$. On the other hand, for the possible magnetic ordering state, the two electrons occupy two distinct surface states with the same spin. The corresponding energy is then $E_{MO} = \epsilon_- + \epsilon_+$. The critical size for the magnetic ordering to become stable corresponds to $E_{MO} \leq E_{PM}$, namely $E_g \leq 2U_0$.  \hspace{1cm} (19)$$

By means of this criterion we can determine the critical size $M_c$. It should be noted that, although the two-state model is established according to the Dirac equation description of the surface states, the two parameters $E_g$ and $U_0$ can also be calculated from the tight-binding model. Therefore, the two-state model is expected to be still valid even when the conjugate surface states are beyond the linear dispersion region. The critical size obtained from this two-state model is shown in figure 5. In comparison with the mean field result, we find that the two-state model can give a quantitative explanation about the critical size as a function of $U$ and $N$. Besides, in figure 5(a) we also find that the two-state model with the parameters evaluated from the Dirac equation can no longer predict the critical size satisfactorily with the increase of $N$. This can be readily understood. In the two-state model, we consider the pair of surface states with the maximal $p_{x0}$, which gets away from the center of the valley with the increase of $N$. As a result, the Dirac equation becomes poorer to give a quantitative description about the electron probability amplitude. Instead of the Dirac equation solution, if we evaluate the parameters $E_g$ and $U_0$ from the tight-binding model, as shown in figure 5 the two-state model always gives a satisfactory result, which demonstrates that the two-state model has captured the main mechanism dominating the spin polarization in the GQD. Finally, we would like to point out that our numerical result about the critical size shown in figure 5 coincides with those obtained by the first-principles calculation or the mean field method in the previous work [21, 22, 28]. In particular, our calculation indicates that, when $N < 7$, no surface state exists, hence no magnetic ordering occurs. And when $N = 7$ the critical size is $M_c = 8$. These quantitative results were also produced in the relevant work obtained by the first-principles calculation.

In [22] it was stressed that at least three consecutive units along the zigzag edges are required to present spin polarization in the GQD. This agrees exactly with that used by us ($U = t$). Of course, a larger $U$ corresponds to a smaller critical size. If we extrapolate our result shown in figure 4(b) to $U = 2t$, the critical size is expected to be close to $M_c = 6$.  \hspace{1cm} (16)$$

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According to the solution about the surface state given in the previous section, we can predict that the critical size $M_c$ will tend to zero, as the size $N$ becomes sufficiently large. This is because there must be a dispersionless surface state pair when $N$ becomes sufficiently large, regardless of the size $M$. Thus, the GQD becomes an infinitely long zigzag ribbon, which always possesses dispersionless surface states. As a result, the spontaneous magnetization can occur at an arbitrarily small $M$.

Now we turn to discuss the occurrence of the saturated size $M_s$, based on the Dirac equation description of the surface states. The mean field result of $M_s$ as a function of $N$ is shown in figure 6. It depends on $N$ non-monotonically, in contrast to its insensitive dependence on the Hubbard $U$. For example, when $N$ increases from 7 to 11, $M_s$ decreases notably, followed by an abrupt rise at $N = 13$. Such a situation recurs when $N$ increases further. According to our solution of the surface state, when $N$ increases within a small range, such as from $N = 7$ to 11, the number of surface states does not change. The pair of surface states with the minimal $p_n$ has the maximal energy gap (we denote it as $E_g$ in the inset of figure 3). According to our two-state model, such a gap goes against the formation of spin polarization in the two conjugate surface states. The energy difference between the spin polarized and unpolarized electron occupancies on the two surface states is equal to $E_g - 2U_0$. From equations (7)–(9) we infer that, with the increase of $M$, $q$ goes close to $p_n$. As a result, $E_g$ tends to vanish. Meanwhile, as $q$ goes close to $p_n$, $U_0$ tends towards a constant, because the wavefunction (equation (6)) of surface states near zigzag edges tends towards a constant value. When $E_g$ becomes sufficiently small, such a pair of surface states, hence all pairs of surface states, have a stable contribution to the spin polarization. Thus, the total energy difference shown in figure 4 tends to a saturated value. In comparison to the case of $N = 7$, the GQD with $N = 11$ has a smaller $E_g$ corresponding to the same $M$. Thus the GQD with $N = 11$ corresponds to a smaller $M_s$. However, when $N$ increases further, a new surface state comes into being, with a larger $E_g$ than the case of $N = 7$. Thus a larger $M_s$ is needed. This justifies the abrupt rise of $M_s$ at $N = 13$, as shown in figure 6. In such a spirit, we can establish a simple criterion by which we can estimate the value of $M_s$. This is

$$p_n - q \leq \eta.$$  \hspace{1cm} (20)

where $p_n$ is the smallest wavevector in the surface-state-allowed region. $\eta$ is an appropriate small quantity to characterize the extent that $q$ approaches $p_n$. The energy gap $E_g$ is then sufficiently small and $U_0$ becomes a constant. For the numerical calculation, we choose $\eta = 10^{-4}/a_0$. From figure 6 we can find that such a simple rule creates a saturated size $M_s$ which agrees very well with the Hartree–Fock mean field result. Finally, we have to point out that the result in figure 6 only shows the saturated size $M_s$ in a very finite range of the size $N$, because the self-consistent calculation becomes rather time-consuming as $N$ gets larger. But we can predict that, as $N$ increases further, the oscillation of the $M_s$ will become weak since the discrete wavevector $E_n$ tends to a continuous quantity. Finally the saturated size $M_s$ tends to that of the infinitely long zigzag ribbon.

4. Conclusion and remarks

The electronic eigenstates of a square GQD terminated by both zigzag and armchair edges have been studied analytically in the theoretical framework of the Dirac equation. By comparing with the result of the tight-binding model, we find that the Dirac equation can well describe the electron eigenstates even if the size of a GQD is reduced to a few nanometers. Moreover, the Dirac equation method has advantages over the tight-binding model in two aspects. At first, the Dirac equation solution about the electron eigenstates can tell us not only the energy levels but also the dispersion relation. Then, from the Dirac equation solution, we can readily determine the number of surface states. In addition, by using the Hartree–Fock mean field theory, we have also investigated the magnetic properties of the square GQD. We find that stable magnetic ordering states are allowed for a charge-neutral GQD with an appropriate size. The magnetic ordering depends on the width between two zigzag edges sensitively. Only when the width is larger than a critical size is the magnetic ordering stable. On the other hand, when this width becomes sufficiently large, the magnetic ordering ground state energy tends towards a saturated value. We find that the critical size is dominated by the pair of surface states with the minimal energy gap, while the saturated size is determined by the pair of surface states with the maximal energy gap. Based on the Dirac equation description, we establish a simple model in which only the two dominated surface states are incorporated. Consequently, this two-state model can quantitatively explain the size dependence of the magnetic ordering of the square GQD. Thus, by virtue of such a toy model, we can estimate rapidly the characteristic sizes for the formation of magnetic ordering in the GQD.
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