Zero-energy states in triangular and trapezoidal graphene structures

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(Received 21 October 2009; published 13 January 2010)

We derive analytical solutions for the zero-energy states of degenerate shell obtained as a singular eigenvalue problem found in tight-binding (TB) Hamiltonian of triangular graphene quantum dots with zigzag edges. These analytical solutions are in agreement with previous TB and density-functional theory results for small graphene triangles and extend to arbitrary size. We also generalize these solutions to trapezoidal structure which allow us to study bowtie graphene devices.

DOI: 10.1103/PhysRevB.81.033403 PACS number(s): 73.22.Dj

Low-dimensional graphene nanostructures are promising candidates as building blocks for future nanoelectronic applications due to their band gaps and magnetic properties tunable with size and shape.[1–6] Remarkable progress has been made in cutting graphene sheets into nanostructures with desired shape and size, significantly influencing their properties.[5–7] In particular, the existence of a band of degenerate states near Fermi level localized at the edges in zigzag ribbons[8–10] and triangular dots[11–17] was predicted by tight-binding model and confirmed by density-functional theory calculations. These zero-energy edge states play important role due to their large contribution to the density of states.[11,14,18] In triangular graphene quantum dots, numerical results show that the degeneracy of the band of zero-energy states is proportional to the edge size and can be made macroscopic. This opens up the possibility to design a strongly correlated electronic system as a function of filling of the shell, in analogy to the fractional quantum Hall effect.[17]

While the existence of zero-energy states was predicted analytically for zigzag ribbons,[8] for triangular structures, the analysis of zero-energy states was limited to numerical techniques such as tight-binding and density-functional theory for specific and small sizes of quantum dots. A size-independent general analytical analysis is therefore desirable. In this work, we present analytical solutions to zero-energy edge states in graphene triangles with zigzag edges. We also show how the results can be generalized to the trapezoidal structures and applied to the bowtie structures.[19] Our method allows the prediction of the number of zero-energy states as a function of the size in all triangular, trapezoidal, and bowtie structures.

Our starting point is the nearest-neighbor tight-binding model. It has been successfully used to describe graphene lattice[20] and applied to other graphene materials such as nanotubes, nanoribbons, and quantum dots.[8,9,11–15,21] The Hamiltonian is written as

$$H = t\sum_{\langle i,j\rangle} a_i^\dagger a_j,$$

where t is hopping integral, $a_i^\dagger$ and a_i are creation and annihilation operators on a site i respectively, and $\langle i,j\rangle$ indicate summation over nearest neighbors. It is important to distinguish between two types of atoms which appear in the unit cell of the honeycomb lattice of graphene sheet. For triangular structures, these atoms form two nonequivalent sublattices (A and B) and they are indicated by red (light gray) and blue (dark gray) circles of the graphene triangle in Fig. 1. Our goal is to find zero-energy solutions to the singular eigenvalue problem,

$$H\Psi = 0.$$

In this case there is no coupling between two sublattices and the solutions can be written separately for A-type and B-type atoms as $\Psi^\mu = \Sigma c_i \phi_i^\mu$ with $\mu = A, B$. The coefficients c_i obey

$$\sum_{\langle i,j\rangle} c_i = 0, \tag{1}$$

where the summation is over ith nearest neighbors of an atom j. In other words, the sum of coefficients around each site must vanish.[8] Let us first focus on the sublattice labeled by A, represented by red (light gray) circles in Fig. 1. We label each atom by two integer numbers n and m (with $0 \le n, m \le N+1$, where N is the number of A-type atoms on the one edge). The dash lines and open circles indicate auxiliary atoms which will later help to introduce boundary conditions. We will now show that coefficients $c_{n,m}$ for all atoms in the triangle can be expressed as a linear combination of coefficients corresponding to atoms on one edge, i.e., $c_{n,0}$. Starting from the first row and using Eq. (1), we can obtain all coefficients corresponding to atoms in the second row. For the first two coefficients from the left we obtain $c_{0,1} = -(c_{0,0} + c_{1,0})$ and $c_{1,1} = -(c_{1,0} + c_{2,0})$. These coefficients are just equal to the sum of two upper-lying coefficients with the minus sign. In analogy, we can write expressions for all coefficients in the second row. In the next step, coefficients in the third row are expressed as a sum of two coefficients in the second row. For first coefficient from the left in the third row we obtain $c_{0,2} = -(c_{0,1} + c_{1,1}) = (c_{0,0} + 2c_{1,0} + c_{2,0})$. The second and third ones will have similar form. By going down rows one by one, we can obtain all coefficients in the structure regardless of the size of the triangle. Similar to the construction of Pascal triangle,[22] these coefficients can be written in a suitable form using binomial coefficients,

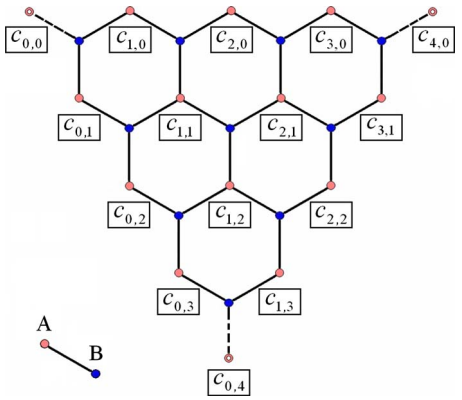

FIG. 1. (Color online) Triangular zigzag graphene structure with $N=3$ atoms on the one edge. Under each A-type atom [indicated by red (light gray) circles] are corresponding coefficients. Dash lines and open circles indicate auxiliary A-type atoms in the three corners, which will help to introduce three boundary conditions. For zero-energy states all coefficients can be expressed as superpositions of coefficients corresponding to atoms from the one edge (upper row of atoms in our case).

$$c_{n,m} = (-1)^m \sum_{k=0}^{m} \binom{m}{k} c_{n+k,0}. \tag{2}$$

Here, it is important to emphasize that the only unknown are the $N+2$ coefficients ($c_{n,0}$'s) from the first row; the rest are expressed as their superpositions, as it is seen from Eq. (2). In addition, we must use the boundary conditions; the construction of the triangle requires vanishing of the coefficients corresponding to auxiliary atoms in each corner (Fig. 1). This gives three boundary conditions ($c_{0,0}=c_{N+1,0}=c_{0,N+1,}$ $=0$), reducing the number of independent coefficients to $N-1$.

The same analysis can be done for B-type atoms indicated by blue (dark gray) circles. In this case, it is convenient to include some of boundary conditions at the beginning as shown in Fig. 2, where we only keep coefficients belonging to auxiliary atoms on the right edge. As a consequence, the coefficient $c_{0,0}$ determines all other coefficients in the triangle. Since there are three auxiliary atoms (equivalently three boundary conditions) but only one independent coefficient, we cannot obtain any nontrivial solution. Hence, zero-energy states can only consist of coefficients of one type atoms—these lying on the edges. Now we can write general form for the eigenvectors for zero-energy states in the triangle,

$$\Psi = \sum_{n=0}^{N+1} \sum_{m=0}^{N+1-n} \left[(-1)^m \sum_{k=0}^{m} \binom{m}{k} c_{n+k,0} \right] \phi^A_{n,m}, \tag{3}$$

where N is the number of atoms on the one edge and $\phi^A_{n,m}$ is p_z orbital on A-type site (n,m). In this expression the only $N-1$ coefficients corresponding to atoms from the first row are independent. Thus, we can construct $N-1$ linearly independent eigenvectors which span the subspace with zero-energy states. This is in agreement with Ref. 14—the number

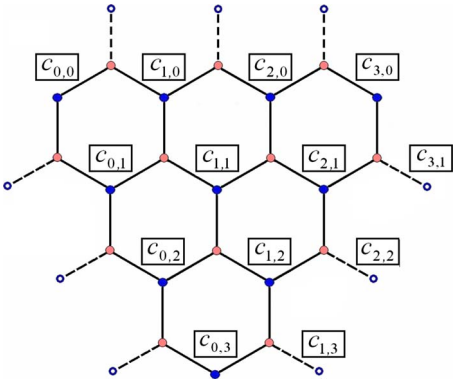

FIG. 2. (Color online) Triangular zigzag graphene structure from Fig. 1. Above each B-type atom [indicated by blue (dark gray) circles] are corresponding coefficients. For convenience, we only left coefficients corresponding to auxiliary B-type atoms on the right edge. For zero-energy states coefficient from upper left corner ($c_{0,0}$) determine all other coefficients in the structure. Introducing three boundary conditions from auxiliary atoms we obtain only trivial solution; zero-energy states consist of only A-type atoms.

of zero-energy states in the triangle is $N-1$, where N is the number of atoms on one edge.

Using the Eq. (3) we can then construct an orthonormal basis for zero-energy states. First, with the help of the three boundary conditions, we make a choice for the $N-1$ independent coefficients $c_{n,0}$, from which we obtain $N-1$ linearly independent vectors, for instance, by choosing only one nonzero coefficient for all $N-1$ collections, different one for each eigenvector. Resulting eigenvectors can then be orthogonalized using standard Gram-Schmidt process. The last step is the normalization K_{norm} of the eigenvectors, using expression

$$K_{norm} = \sum_{n=0}^{N+1} \sum_{m=0}^{N+1-n} \left| \sum_{k=0}^{m} \binom{m}{k} c_{n+k,0} \right|^2.$$

The method for obtaining zero-energy eigenfunction coefficients for the triangular structures can also be applied to trapezoidal structures [inset of Fig. 3(b)]. As explained above, the value of the coefficients for atoms in a given row is sufficient to determine the coefficients for atoms in the lower-lying row. If we stop this process of going down the ladder one by one at any row, we then obtain a trapezoidal structure. Equation (3) takes the following form:

$$\Psi = \sum_{n=0}^{N+1} \sum_{m=0}^{M} \left[(-1)^m \sum_{k=0}^{m} \binom{m}{k} c_{n+k,0} \right] \phi^A_{n,m}, \tag{4}$$

where $M=\min(N+1-n, N_{row}-1)$ and N_{row} is the number of rows in the structure [see Fig. 3(b)]. In this case the last row contains $N-N_{row}+2$ auxiliary atoms which increases the number of boundary conditions. The number of zero-energy states is then given by $N_{row}-2$ (for $N_{row}>1$). Here we note that similar to the triangle, zero-energy states consist of only one type of atoms; the only difference is increased number of boundary conditions. In Fig. 3(a) we show tight-binding single-particle states for triangle with $N=5$ atoms on one

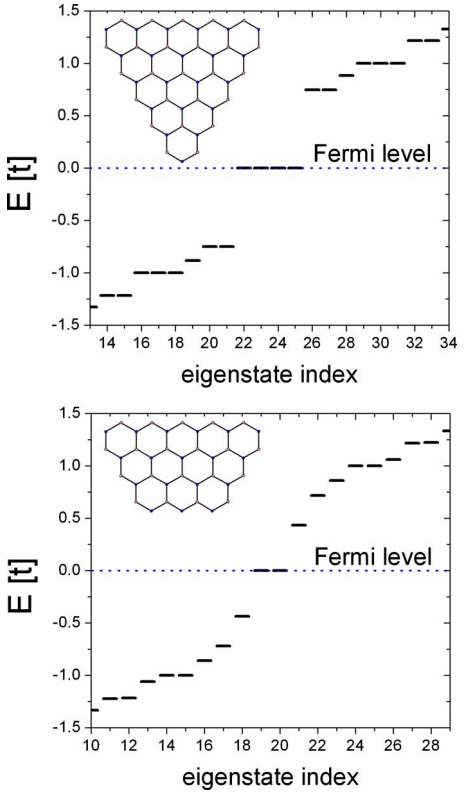

FIG. 3. (Color online) Single-particle spectrum from tight-binding calculations for (a) 46 atoms triangle and (b) 38 atoms trapezoid (with $N_{row}=4$). There are four zero-energy states in the triangle (number of atoms on the one edge $N=5$) and two zero-energy states in the trapezoid in agreement with our analysis. Changing number of rows in the trapezoid we can control number of zero-energy states.

edge. As expected, there are four zero-energy states. For comparison, in Fig. 3(b) we show single-particle states for trapezoid with the same number of atoms in a first row. Here, there are only two zero-energy states in agreement with our analysis—increasing number of boundary conditions decrease number of zero-energy states. We note that the structure which consists of only two rows (the single chain of benzene rings, called acene) does not have zero-energy states while the triangular structure with N atoms on the one edge has maximal number of zero-energy states equal to $N-1$. All intermediate structures (trapezoidal structures) have number of zero-energy states in the range between 1 and $N-2$, depending on the number of rows.

Finally we note that the solutions of Eq. (4) can also be applied to bowtie structures.[19] These can be treated as two trapezoidal structures connected by their shorter base, shown in Fig. 4. It is important to emphasize that the upper trapezoid has one zero-energy state which consists of A-type atoms [red (light gray) circles] while lower trapezoid has one zero-energy state which consists of B-type atoms [blue (dark gray) circles]. Connecting these two systems does not affect the zero-energy solutions since coefficients belonging to connecting atoms are zeros. Using zero-energy eigenvectors for trapezoids, Eq. (4), we obtain expressions for two groups of zero-energy states in the bowtie structures,

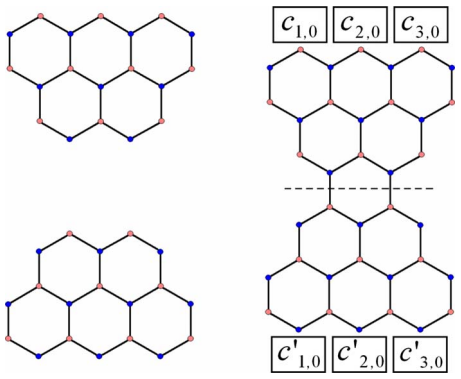

FIG. 4. (Color online) Two trapezoids (left) and bowtie structure (right). Each of two trapezoids has one zero-energy state, consisting of only A-type atoms [indicated by red (light gray) circles] for the upper trapezoid and consisting of only B-type atoms [indicated by blue (dark gray) circles] for the lower trapezoid. Connecting these two systems does not affect the zero-energy solutions since coefficients belonging to connecting atoms are zeros (the four nearest atoms to the dash line). The bowtie structure on the right has two zero-energy states: one which completely lies in upper part and consists of A-type atoms and second one lies in lower part and consists of B-type atoms.

$$\Psi_A = \sum_{n=0}^{N+1} \sum_{m=0}^{M} \left[(-1)^m \sum_{k=0}^{m} \binom{m}{k} c_{n+k,0} \right] \phi_{n,m}^{A} \tag{5}$$

for upper trapezoid, where A indicates A-type atoms from upper part and

$$\Psi_B = \sum_{n=0}^{N'+1} \sum_{m=0}^{M'} \left[(-1)^m \sum_{k=0}^{m} \binom{m}{k} c'_{n+k,0} \right] \phi_{n,m}^{B'} \tag{6}$$

for lower one, where B' indicates B-type atoms from lower part. Two parts of the bowtie structure are separated by the dash line in Fig. 4. Coefficients $c_{n,0}(c'_{n,0})$ correspond to N A-type (N' B-type) atoms from the highest (lowest) row in the bowtie structure from Fig. 4. Note that it is possible to use Eqs. (5) and (6) to asymmetric bowtie structures consisting of two different trapezoids ($N \neq N'$).

In summary, we derived here analytical expression for zero-energy states in triangular and trapezoidal graphene quantum-dot structures. Our method allows prediction of the number of zero-energy states in quantum dots of arbitrary size which can be understood in terms of a competition between the number of independent coefficients and the number of auxiliary atoms (the number of boundary conditions). We also showed that the number of zero-energy states can be controlled by changing the number of rows in the trapezoidal structures but does not depend on the number of atoms in the base of the trapezoid. Finally, we applied our results to bowtie structures and showed that two independent groups of zero-energy states coexist in these systems.

The authors thank NRC-CNRS CRP, Canadian Institute for Advanced Research, Institute for Microstructural Sciences, QuantumWorks and Polish MNiSW under Grant No. N202-071-32/1513 for support.

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