Analytical study of surface states caused by the edge decoration*

Zhao Yuan-Yuan(赵媛媛)†, Li Wei(李 炜), and Tao Rui-Bao(陶瑞宝)

State Key Laboratory of Surface Physics and Department of Physics, Fudan University, Shanghai 200433, *China*

(Received 1 August 2011; revised manuscript received 18 October 2011)

Analytical studies of the effect of edge decoration on the energy spectrum of semi-infinite one-dimensional (1D) model and zigzag edged graphene (ZEG) are presented by means of transfer matrix method, in the frame of which the conditions for the existence of edge states are determined. For 1D model, the zero-energy surface state occurs regardless of whether the decorations exist or not, while the non-zero-energy surface states can be induced and manipulated through adjusting the edge decoration. On the other hand, the case for the semi-infinite ZEG model with nearest-neighbour interaction is discussed in the analogous way. The non-zero-energy surface states can be induced by the edge decoration and moreover, the ratio between the edge hopping and the bulk hopping amplitudes should be within a certain threshold.

Keywords: surface states, zigzag edged graphene, transfer matrix method

PACS: 73.22.Pr, 73.20.At, 71.15.–m **DOI:** 10.1088/1674-1056/21/2/027302

1. Introduction

It is established that a special class of localized modes can be generated at surfaces, which has been studied for many years, since the pioneering works by Tamm[1] and Shockley.[2] There are many peculiar features of surface states, associated with the formation, density of states and electronic transport.[3] The theory of surface states has been studied in many areas of physics, including surface states in superlattices, surface polaritons,[4] and surface solitons.[5] Some of the specific features of such states have been investigated experimentally as well.[6−8]

On the other hand, with the development of graphene[9,10] in recent years, the surface states of the graphene model[11] have attracted much attention. From the topological view, surface states can be induced in the systems with different structures of edges;[12,13] in experiments, with the help of scanning tunneling microscopy and scanning tunneling spectroscopy, the presence of structure-dependent surface states of graphite can be observed,[14,15] and the transport features can be influenced by the existence of edge states.[16] The results of the surface states are reported in the tight-binding model,[13,17] Dirac equation,[18] and the transfer matrix method (TMM).[19,20]

Besides, the effects of the surface disorder in the graphene system are also reported, such as the surface oscillations, considered as a phonon analogy of Tamm states;[21] staggered potential at the zigzag boundary,[22,23] which can open a gap in the graphene nanoribbon by inversion symmetry breaking; deformation of graphene sheet due to the warping, taking graphene as an elastic membrane and considering two modes of transformation—stretching/contraction and bending, so that the hopping integration and C–C bond length can cause the inhomogeneity:[24] the inhomogeneous magnetic field or strain deformation.[25,26]

It is our purpose, in this paper, to study analytically, the formation of surface states within a simple toy model and make an analogy to the semi-infinite zigzag edged graphene (ZEG) with some appropriate decoration on the edge. Usually, it is widespread that surface Green's function can be computed analytically.[27,28] Here we employ TMM to study the localized surface states, motivated by Ref. [29]. First, we take a semi-infinite 1D toy model and discuss the condition for the existence of localized surface states and then by analogy from the one-dimensional (1D) model, we study localized surface states in zigzag edged graphene (ZEG) with decoration on the edge,

*Project supported by the National Natural Science Foundation of China (Grant No. 10847001) and the National Basic Research Program of China (Grant Nos. 2009CB929204 and 2011CB921803).

†Corresponding author. E-mail: zhaoyuanyuan@fudan.edu.cn

© 2012 Chinese Physical Society and IOP Publishing Ltd

which can be assumed as stretching or deformation on the edge. To simplify our model, we choose that the hopping amplitude on the edge is different from that in the bulk. We find that the zero-energy surface states exist independently of the different hopping energy on the edge, while the non-zero-energy surface states can occur due to the edge decoration; and moreover, the ratio between the edge hopping and the bulk hopping amplitudes should be within a certain threshold.

2. Toy model and formalism

In order to give an analytical description of the energy spectra of the bulk states and the surface states caused by the edge decoration, first we consider here a 1D toy model as shown in Fig. 1. Each unit cell has two atoms, which are labeled as A and B sublattices and the boundary can be chosen in the unit cell $n = 1$. Compared with 1D molecule polyacetylene (dimerized 1D chain), with $n \neq 1$, we can suppose the hopping between unit cells is t_1 and within a unit cell is t_2, except for $n = 1$; in general, we expect that the atom at the boundary can be connected to the bulk atoms with different hoppings, which in the unit cell is t_0; while in our model, the onsite-energy is zero. Then the model Hamiltonian can be written in the form

$$H = t_0\varphi^{\dagger}_{1\mathrm{A}}\varphi_{1\mathrm{B}} + t_1\sum_{i\geqslant 1}\varphi^{\dagger}_{i+1\mathrm{A}}\varphi_{i\,\mathrm{B}} + t_2\sum_{i\geqslant 2}\varphi^{\dagger}_{i\mathrm{A}}\varphi_{i\,\mathrm{B}} + \mathrm{h.c.} \quad (1)$$

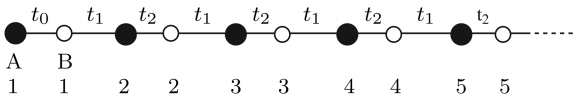


Fig. 1. Schematic illustration of the lattice structure of 1D semi-infinite chain with the closed (black) and the open (white) circles, consisting of A and B sublattices.

Without loss of generality, set t_0, t_1, t_2 to be positive. With Eq. (1), we can derive the dynamical equations through defining an elemental excitation with energy E as follows:

$$\begin{aligned} E\varphi_{1\mathrm{A}} &= t_0\varphi_{1\mathrm{B}}, \\ E\varphi_{1\mathrm{B}} &= t_0\varphi_{1\mathrm{A}} + t_1\varphi_{2\mathrm{A}}, \\ E\varphi_{i\mathrm{A}} &= t_2\varphi_{i\,\mathrm{B}} + t_1\varphi_{i-1\mathrm{B}} \quad (i \geqslant 2), \\ E\varphi_{i\,\mathrm{B}} &= t_2\varphi_{i\mathrm{A}} + t_1\varphi_{i+1\mathrm{A}} \quad (i \geqslant 2). \end{aligned} \quad (2)$$

In order to obtain all the states of the toy model, including the bulk states and the physically meaningful localized surface states, we begin with the above equations for the cases $E = 0$ and $E \neq 0$ respectively, of which the equations have different forms.

Under the condition $E = 0$, equation (2) can be reduced to the decoupled ones

$$\begin{aligned} &t_0\varphi_{1\mathrm{B}} = 0, \\ &t_0\varphi_{1\mathrm{A}} + t_1\varphi_{2\mathrm{A}} = 0, \\ &t_2\varphi_{i\,\mathrm{B}} + t_1\varphi_{i-1\mathrm{B}} = 0 \ (i \geqslant 2), \\ &t_2\varphi_{i\mathrm{A}} + t_1\varphi_{i+1\mathrm{A}} = 0 \ (i \geqslant 2). \end{aligned} \quad (3)$$

From Eq. (3), it is easy to know that the wave-functions of B sublattice will vanish $\{\varphi_{i\,\mathrm{B}} = 0 : i = 1, 2, \ldots, \infty\}$; meanwhile the wave-function of A sublattice in the n unit cell will be

$$\varphi_{n\mathrm{A}} = \left(-\frac{t_2}{t_1}\right)^{n-2}\left(-\frac{t_0}{t_1}\right)\varphi_{1\mathrm{A}}, \ n = 2, 3, 4, \ldots. \quad (4)$$

Here $\varphi_{1\mathrm{A}}$ is the initial value of wave excitation with zero energy at the edge site. When $t_1 = t_2$, we can only obtain the extended state satisfying the equations. When $t_1 \neq t_2$, in order to obtain the physically meaningful surface states, we must restrict $t_2/t_1 < 1$, so that when n goes to infinity, the wave-function of A sublattice will approach to 0, showing the state is localized near the edge region. Away from the boundary, the amplitude of the wave-function will decay exponentially as $\mathrm{e}^{-n2a/\lambda_{\mathrm{L}}}$. The localized length λ_{L} of the surface state is $2a/(\ln t_2 - \ln t_1)$, where $2a$ is the periodic constant of the cell. Thus, we can conclude that zero-energy surface state can exist when $t_2 < t_1$, and this result can be obtained by using surface Green's function[30] as well. It is shown that no matter whether the edge decoration exists or not, zero-energy surface state is not affected by edge decoration $t_0(\neq 0)$.

In the following, we will study whether the non-zero-energy surface states can exist or not. After eliminating A and B sublattices in Eq. (2) respectively, we can obtain

$$\begin{aligned} E^2\varphi_{1\mathrm{A}} &= t_0^2\varphi_{1\mathrm{A}} + t_0t_1\varphi_{2\mathrm{A}}, \\ E^2\varphi_{2\mathrm{A}} &= (t_1^2 + t_2^2)\varphi_{2\mathrm{A}} + t_0t_1\varphi_{1\mathrm{A}} + t_1t_2\varphi_{3\mathrm{A}}, \\ E^2\varphi_{i\mathrm{A}} &= (t_1^2 + t_2^2)\varphi_{i\mathrm{A}} + t_1t_2\varphi_{i-1\mathrm{A}} \\ &\quad + t_1t_2\varphi_{i+1\mathrm{A}}, \quad i \geq 3; \end{aligned} \quad (5)$$

and

$$\begin{aligned} E^2\varphi_{1\mathrm{B}} &= (t_0^2 + t_1^2)\varphi_{1\mathrm{B}} + t_1t_2\varphi_{2\mathrm{B}}, \\ E^2\varphi_{i\,\mathrm{B}} &= (t_1^2 + t_2^2)\varphi_{i\,\mathrm{B}} + t_1t_2\varphi_{i-1\mathrm{B}} \\ &\quad + t_1t_2\varphi_{i+1\mathrm{B}}, \quad i \geq 2. \end{aligned} \quad (6)$$

According to the first equation in Eq. (5), we introduce a fictitious $\varphi_{0\mathrm{A}} = 0$ into our discussion. Then we can turn Eq. (5) into matrix forms

$$\begin{aligned}
\begin{pmatrix} \varphi_{i+1\mathrm{A}} \\ \varphi_{i\mathrm{A}} \end{pmatrix} &= T^{i-2} \begin{pmatrix} \varphi_{3\mathrm{A}} \\ \varphi_{2\mathrm{A}} \end{pmatrix}, \quad (i \geqslant 3), \\
\begin{pmatrix} \varphi_{3A} \\ \varphi_{2\mathrm{A}} \end{pmatrix} &= T_1 \begin{pmatrix} \varphi_{2\mathrm{A}} \\ \varphi_{1\mathrm{A}} \end{pmatrix}, \\
\begin{pmatrix} \varphi_{2\mathrm{A}} \\ \varphi_{1\mathrm{A}} \end{pmatrix} &= T_2 \begin{pmatrix} \varphi_{1\mathrm{A}} \\ \varphi_{0\mathrm{A}} \end{pmatrix},
\end{aligned} \tag{7}$$

where T, T_1, and T_2 are defined as

$$\begin{aligned}
T &= \begin{pmatrix} \alpha & -1 \\ 1 & 0 \end{pmatrix}, \\
T_1 &= \begin{pmatrix} \alpha & -t_0/t_2 \\ 1 & 0 \end{pmatrix}, \\
T_2 &= \begin{pmatrix} \beta & -1 \\ 1 & 0 \end{pmatrix},
\end{aligned} \tag{8}$$

with $\alpha = (E^2 - t_1^2 - t_2^2)/t_1t_2$ and $\beta = (E^2 - t_0^2)/t_0t_1$. Meanwhile, the wave-functions of B sublattice satisfy the relations

$$\begin{aligned}
&\begin{pmatrix} \varphi_{i+1\mathrm{B}} \\ \varphi_{i\,\mathrm{B}} \end{pmatrix} = T^{i-1} \begin{pmatrix} \varphi_{2\mathrm{B}} \\ \varphi_{1\mathrm{B}} \end{pmatrix}, \quad (i \geq 2); \\
&\varphi_{2\mathrm{B}} = \gamma\varphi_{1\mathrm{B}}; \quad \varphi_{1\mathrm{B}} = \frac{E}{t_0}\varphi_{1\mathrm{A}},
\end{aligned} \tag{9}$$

with $\gamma = (E^2 - t_0^2 - t_1^2)/t_1t_2$. Energy E must be real for the physical quantity and all α, β and γ are real numbers as well. Diagonalize the transfer matrix T in the form of $D = U^{-1}TU$ and we have

$$\begin{aligned}
\begin{pmatrix} \varphi_{i+1\mathrm{A}} \\ \varphi_{i\mathrm{A}} \end{pmatrix} &= UD^{i-2}U^{-1}T_1T_2 \begin{pmatrix} \varphi_{1\mathrm{A}} \\ \varphi_{0\mathrm{A}} \end{pmatrix}, \\
\begin{pmatrix} \varphi_{i+1\mathrm{B}} \\ \varphi_{i\,\mathrm{B}} \end{pmatrix} &= UD^{i-1}U^{-1} \begin{pmatrix} \gamma \\ 1 \end{pmatrix} \frac{E}{t_0}\varphi_{1\mathrm{A}},
\end{aligned} \tag{10}$$

with

$$D = \begin{pmatrix} \lambda_- & 0 \\ 0 & \lambda_+ \end{pmatrix}, \qquad U = \begin{pmatrix} \lambda_- & \lambda_+ \\ 1 & 1 \end{pmatrix}, \tag{11}$$

$$U^{-1} = \frac{1}{\sqrt{\alpha^2 - 4}} \begin{pmatrix} -1 & \lambda_+ \\ 1 & -\lambda_- \end{pmatrix}, \tag{12}$$

where $\lambda_- = (\alpha - \sqrt{\alpha^2 - 4})/2$ and $\lambda_+ = (\alpha + \sqrt{\alpha^2 - 4})/2$. Equation (10) can be rewritten as

$$\begin{aligned}
\begin{pmatrix} \varphi_{n+3\mathrm{A}} \\ \varphi_{n+2\mathrm{A}} \end{pmatrix} &= U \begin{pmatrix} \Gamma_1\lambda_-^n \\ \Gamma_2\lambda_+^n \end{pmatrix} \varphi_{1\mathrm{A}}, \\
\begin{pmatrix} \varphi_{n+3\mathrm{B}} \\ \varphi_{n+2\mathrm{B}} \end{pmatrix} &= U \begin{pmatrix} \Theta_1\lambda_-^n \\ \Theta_2\lambda_+^n \end{pmatrix} \frac{E}{t_0}\varphi_{1\mathrm{A}},
\end{aligned} \tag{13}$$

where $\Gamma_1 = U_{11}^{-1}(\alpha\beta - t_0/t_2) + U_{12}^{-1}\beta$, $\Gamma_2 = U_{21}^{-1}(\alpha\beta - t_0/t_2) + U_{22}^{-1}\beta$, $\Theta_1 = U_{11}^{-1}\gamma + U_{12}^{-1}$, $\Theta_2 = U_{21}^{-1}\gamma + U_{22}^{-1}$. We must request $\varphi_{1\mathrm{A}} \neq 0$, otherwise the wave function vanishes $\{\varphi_{i\mathrm{A}} = \varphi_{i\,\mathrm{B}} = 0 : i = 1, 2, \ldots, \infty\}$.

When $|\alpha| \leqslant 2$, $|\lambda_-| = |\lambda_+| = 1$, which corresponds to the extended states in the bulk. Here we can choose k_x along the chain as a good quantum number, after making the Fourier transform of operators in the model hamiltonian, we can have the energy dispersion in the form

$$E^2 = t_1^2 + t_2^2 + 2t_1t_2\cos(k_xa), \ k_xa \in [-\pi, \pi]. \tag{14}$$

Now, we have $\lambda_\pm = \mathrm{e}^{\pm \mathrm{i}k_xa}$. As we know, k_x belonging to $\mathbb{R}$ clearly serves as a wave vector of extended mode propagating along the chain direction.

In the following, we focus on the solution of surface states when the condition $|\alpha| > 2$ is satisfied. In the case of $\alpha > 2$, we obtain $0 < \lambda_- < 1$ and $\lambda_+ > 1$, while $\lambda_- < -1$ and $-1 < \lambda_+ < 0$ for the case of $\alpha < -2$. We will discuss these two cases separately.

In the case of $\alpha > 2$, we have $0 < \lambda_- < 1$, $\lambda_+ > 1$. The necessary conditions for the existence of stable localized surface states must be $\Gamma_2 = 0$ and $\Theta_2 = 0$

$$\begin{aligned}
&U_{21}^{-1}\left(\alpha\beta - \frac{t_0}{t_2}\right) + U_{22}^{-1}\beta = 0, \\
&U_{21}^{-1}\gamma + U_{22}^{-1} = 0.
\end{aligned}$$

With Eq. (12) and definitions of $\lambda_\pm$, the above two equations can be changed to the following

$$\begin{aligned}
&(\alpha + \sqrt{\alpha^2 - 4})\beta - 2\frac{t_0}{t_2} = 0, \\
&\sqrt{\alpha^2 - 4} - \alpha + 2\gamma = 0,
\end{aligned} \tag{15}$$

where α, β, and γ are the functions of energy $E(\neq 0)$. Equation (15) is the necessary condition for the existence of non-zero-energy surface states. Inputting the definitions of α, β, and γ into Eq. (15), we obtain

$$(t_0^2 - t_2^2)(E^2 - t_0^2) = t_0^2t_1^2 \, .$$

When the edge is perfect, $t_0 = t_2(\neq 0)$, there should be no finite value of E for the above equation since

$t_0^2 t_1^2 \neq 0$. Thus we conclude that non-zero-energy surface state does not exist in toy model without edge decoration. When $t_0 \neq t_2$, we have solution

$$E^2 = t_0^2 + t_0^2 t_1^2 / \left(t_0^2 - t_2^2\right). \tag{16}$$

Due to $\alpha > 2$, we obtain $E^2 > (t_1 + t_2)^2 > 0$, which corresponds to a stable surface state. With the definition of γ and α, we obtain $\gamma = \alpha - \left(t_0^2 - t_2^2\right)/t_1 t_2$. Taking it back to Eq. (15), we have

$$\left(t_0^2 - t_2^2\right)/t_1 t_2 = \frac{\alpha}{2} + \frac{\sqrt{\alpha^2 - 4}}{2} > 1.$$

Thus the condition to obtain the non-zero-energy surface state is $t_0^2 > t_2^2 + t_1 t_2$. An appropriate manipulation on the edge decoration t_0 can induce the non-zero-energy surface state, while there is no constraint showing the quantity relation between t_1 and t_2. From previous subsection, it has been known that the zero-energy surface state can exist for $t_2/t_1 < 1$, so the zero mode and the non-zero-energy surface states can appear at the same time with $t_0 (\neq 0) \neq t_2$. However, there will be non-zero-energy surface states only if $t_2 \geqslant t_1$ together with $t_0^2 > t_2^2 + t_1 t_2$.

Similarly we can have constraints for $\alpha < -2$

$$\left(\alpha - \sqrt{\alpha^2 - 4}\right)\beta - 2\frac{t_0}{t_2} = 0,$$
$$\sqrt{\alpha^2 - 4} + \alpha - 2\gamma = 0.$$

They also yield the same energy condition: $E^2 = t_0^2 + t_0^2 t_1^2 / \left(t_0^2 - t_2^2\right)$. And besides $\gamma = \alpha - \left(t_0^2 - t_2^2\right)/t_1 t_2$, when $\alpha < -2$, it is easy to obtain

$$\left(t_0^2 - t_2^2\right)/t_1 t_2 = \frac{\alpha}{2} - \frac{\sqrt{\alpha^2 - 4}}{2} < -1.$$

We can find that the non-zero-energy surface state can also exist under the condition: $t_0^2 < t_2(t_2 - t_1)$ that requests $t_2 > t_1$ and results in zero-energy surface state vanishing.

From the above two cases, we can see that non-zero-energy surface states are tightly related to edge decoration t_0 and can be manipulated by decorating the edge atoms.

We conclude that a zero-energy surface state will exist when $t_2 < t_1$, regardless of edge decoration existing or not. A non-zero-energy surface state can occur due to the edge decoration under the following conditions

$$\begin{aligned} &E^2 = t_0^2 + t_0^2 t_1^2 / \left(t_0^2 - t_2^2\right) \quad (> 0, t_0 \neq t_2), \\ &t_0^2 > t_2^2 + t_1 t_2 > 0; \quad \text{or} \\ &t_0^2 < t_2(t_2 - t_1),\ t_2 > t_1. \end{aligned} \tag{17}$$

Nonzero-energy surface state can be manipulated by decorating the edge.

3. Surface states of semi-infinite ZEG

In this section, we will address the existence of the surface states in ZEG, with the help of the formalism shown in the above. Graphene is made up of carbon atoms arranged in hexagonal structure, which can be viewed as a triangular lattice with a basis of two atoms per unit cell. Now the tight-binding Hamiltonian for electrons in graphene, considering the nearest-neighbour hopping interaction, has the form[11]

$$H = t \sum_{\langle i,j \rangle} (\phi_{i,\mathrm{A}}^{\dagger} \phi_{j,\mathrm{B}} + \mathrm{H.c.}), \tag{18}$$

where $\phi_{i,\mathrm{A}}^{\dagger}$ ($\phi_{i,\mathrm{A}}$) creates (annihilates) an electron on site R_i of sublattice A, while in sublattice B, we can use an equivalent definition; t is the nearest-neighbour hopping energy.

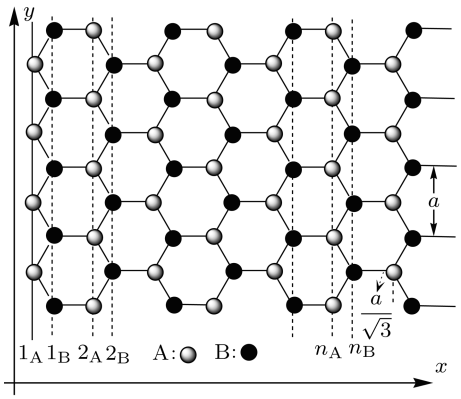


Fig. 2. Schematic illustration of the lattice structure of semi-infinite zigzag edged graphene, the filled circles represent the sublattice B, others are the sublattice A. The left first line 1_A is the zigzag edge of the graphene.

Motivated by Ref. [26], we consider the generation of strain in the graphene lattice through changing the in-plane hopping amplitude at the boundary, by means of appropriate geometrical structure in a substrate, or the weak electric field, thermal field and so on. To simplify our model, within a tight-binding formulation shown above, effects of in-plane strain can be captured by considering the changes in nearest-neighbour hopping amplitude t and write $\tilde{t}_0 \neq 0$ on the edge. The model is of a semi-infinite geometry with zigzag edge, as shown in Fig. 2. It is infinite in the transverse cross section (y direction), while in the longitudinal direction (x direction), there exists a zigzag boundary condition and we assume an integer index n, introduced

in Fig. 2, to label the unit cells, with $n = 1$ representing the cell on the edge. Besides, due to the infinity in the transverse direction, k_y is a good quantum number. From Eq. (18), following the analysis in Ref. [31], we can reduce the system to a one-dimensional model by making a partial Fourier transform and obtain a k_y-dependent series of one-dimensional Hamiltonian

$$\begin{aligned} H = & \sum_{k_y, n\geqslant 2} \Big[t\phi^{\dagger}_{n\mathrm{A}}(k_y)\,\phi_{n-1\mathrm{B}}(k_y) \\ & + 2t\cos(k_y a/2)\phi^{\dagger}_{n\mathrm{A}}(k_y)\,\phi_{n\mathrm{B}}(k_y)\Big] \\ & + \sum_{k_y} 2\tilde{t}_0\cos(k_y a/2)\phi^{\dagger}_{1\mathrm{A}}(k_y)\phi_{1\mathrm{B}}(k_y) \\ & + \text{h.c.} \end{aligned} \tag{19}$$

From Eq. (19), we can derive a series of recursive equations with energy E as follows:

$$\begin{aligned} E\phi_{1\mathrm{A}} &= 2\tilde{t}_0\cos(k_y a/2)\phi_{1\mathrm{B}}, \\ E\phi_{1\mathrm{B}} &= 2\tilde{t}_0\cos(k_y a/2)\phi_{1\mathrm{A}} + t\phi_{2\mathrm{A}}, \\ E\phi_{n\mathrm{A}} &= t\phi_{n-1\mathrm{B}} + 2t\cos(k_y a/2)\phi_{n\mathrm{B}} \quad (n\geqslant 2), \\ E\phi_{n\mathrm{B}} &= t\phi_{n+1\mathrm{A}} + 2t\cos(k_y a/2)\phi_{n\mathrm{A}} \quad (n\geqslant 2). \end{aligned} \tag{20}$$

Comparing Eq. (20) with Eq. (2), we can easily find out that these two equations are the same, if we replace $2\tilde{t}_0\cos(k_y a/2)$, t, $2t\cos(k_y a/2)$ in Eq. (20) with t_0, t_1 and t_2 respectively. First of all, we can obtain the energy for the bulk states, with k_x here a good quantum number,

$$\begin{aligned} E^2 = & t^2[1 + 4\cos^2(k_y a/2) \\ & + 4\cos(k_y a/2)\cos(\sqrt{3}k_x a/2)]. \end{aligned} \tag{21}$$

This is the standard form of the energy spectrum of the infinite bulk graphene, which can be obtained with the analogous discussion of Eq. (14).

Next, we will focus on surface states. In order to obtain the condition for the existence of them, we make the analogous discussion with the toy model in our previous section and take zero-energy surface state and the non-zero-energy surface states respectively.

3.1. Zero-energy surface state

The recursive equation (20) can be reduced into decoupled equations for sublattices A and B. Compared with Eq. (4), it is easy to know that the wave-functions of the whole sublattice B will vanish: $\{\phi_{n\mathrm{B}} = 0 : n = 1, 2, \ldots\}$, meanwhile the wave-functions of the sublattice A in the n-th unit cell will be

$$\phi_{n\mathrm{A}} = (-2\cos(k_y a/2))^{n-1}\,\frac{\tilde{t}_0}{t}\phi_{1\mathrm{A}}, \quad n = 2, 3, 4, \ldots.$$

The convergence condition $|-\cos(k_y a/2)| < 1$ is required, otherwise the wave function would diverge in the semi-infinite graphene sheet. Therefore, in the region $k_y a \in (2\pi/3, 4\pi/3)$ the zero-energy surface states can exist.[11] From the above discussion, the existence of the zero-energy surface states is independent of the edge decoration of different hopping energy from that in the bulk.

3.2. Nonzero-energy surface states

From the above discussion, we know that the existence of the zero-energy surface states is determined by its geometrical structure, next we will find the condition for the existence of the non-zero-energy surface states. We will begin with Eq. (20). When $\cos(k_y a/2) = 0$, here we can easily find that $\phi_{1\mathrm{A}} = 0$ and $\phi_{n\mathrm{A}} = \phi_{n-1B}$, $n \geq 2$, just like isolated pairs in oscillation. We take $\cos(k_y a/2) \neq 0$ and rewrite the coupled equations as follows (we assume $t = 1$, $\eta = \tilde{t}_0/t$ and take $\theta = k_y a/2$):

$$\begin{aligned} E^2\phi_{1\mathrm{A}} &= 4\eta^2\cos^2\theta\phi_{1\mathrm{A}} + 2\eta\cos\theta\phi_{2\mathrm{A}}, \\ E^2\phi_{2\mathrm{A}} &= (1 + 4\cos^2\theta)\phi_{2\mathrm{A}} + 2\cos\theta\phi_{3\mathrm{A}} \\ &\quad + 2\eta\cos\theta\phi_{1\mathrm{A}}, \\ E^2\phi_{n\mathrm{A}} &= (1 + 4\cos^2\theta)\phi_{n\mathrm{A}} \\ &\quad + 2\cos\theta(\phi_{n-1\mathrm{A}} + \phi_{n+1\mathrm{A}}), \quad n\geqslant 3; \end{aligned} \tag{22}$$

and

$$\begin{aligned} E^2\phi_{1\mathrm{B}} &= (1 + 4\eta^2\cos^2\theta)\phi_{1\mathrm{B}} + 2\cos\theta\phi_{2\mathrm{B}}, \\ E^2\phi_{n\mathrm{B}} &= (1 + 4\cos^2\theta)\phi_{n\mathrm{B}} \\ &\quad + 2\cos\theta(\phi_{n-1\mathrm{B}} + \phi_{n+1\mathrm{B}}), \quad n\geqslant 2. \end{aligned} \tag{23}$$

Then when $n \geq 3$, the above relations can be expressed in terms of transfer matrix

$$\begin{pmatrix} \phi_{n+1\sigma} \\ \phi_{n\sigma} \end{pmatrix} = T^{n-2}\begin{pmatrix} \phi_{3\sigma} \\ \phi_{2\sigma} \end{pmatrix}, \tag{24}$$

with

$$T = \begin{pmatrix} \alpha & -1 \\ 1 & 0 \end{pmatrix}; \tag{25}$$

and particularly

$$\begin{pmatrix} \phi_{3\sigma} \\ \phi_{2\sigma} \end{pmatrix} = T_{1\sigma}\begin{pmatrix} \phi_{2\sigma} \\ \phi_{1\sigma} \end{pmatrix}, \tag{26}$$

with

$$T_{1\mathrm{A}} = \begin{pmatrix} \alpha & -\eta \\ 1 & 0 \end{pmatrix}, \quad T_{1\mathrm{B}} = T; \tag{27}$$

$$\alpha = \frac{E^2 - 4\cos^2\theta - 1}{2\cos\theta}, \tag{28}$$

where σ represents A (B) sublattice.

From Eq. (25), we can obtain the eigenvalues: $\lambda_- = (\alpha - \sqrt{\alpha^2 - 4})/2$ and $\lambda_+ = (\alpha + \sqrt{\alpha^2 - 4})/2$. When $|\alpha| \leq 2$, it is easy to know that $|\lambda_+| = |\lambda_-| = 1$, which corresponds to the extended states in the bulk, and the bulk energy has been shown in Eq. (21).

Next $|\alpha| > 2$, due to rank $(T) = 2$ now, we can diagonalize transfer matrix T in the form of $D = U^{-1}TU = \mathrm{diag}\{\lambda_-, \lambda_+\}$, so U matrix and its inverse can be written in terms of $\lambda_\pm$:

$$U = \begin{pmatrix} \lambda_- & \lambda_+ \\ 1 & 1 \end{pmatrix},$$

$$U^{-1} = \frac{1}{\sqrt{\alpha^2 - 4}} \begin{pmatrix} -1 & \lambda_+ \\ 1 & -\lambda_- \end{pmatrix}; \tag{29}$$

for $n \geq 3$, equation (24) is rewritten as

$$\begin{pmatrix} \phi_{n+1\sigma} \\ \phi_{n\sigma} \end{pmatrix} = U \begin{pmatrix} \lambda_-^{n-2} & 0 \\ 0 & \lambda_+^{n-2} \end{pmatrix} U^{-1} T_{1\sigma} \begin{pmatrix} \phi_{2\sigma} \\ \phi_{1\sigma} \end{pmatrix}, \tag{30}$$

while

$$\begin{aligned} &\phi_{2\mathrm{A}} = \beta\phi_{1\mathrm{A}}, \\ &\phi_{2\mathrm{B}} = \gamma\phi_{1\mathrm{B}}, \\ &\beta = \frac{E^2 - 4\eta^2\cos^2\theta}{2\eta\cos\theta}, \\ &\gamma = \frac{E^2 - 4\eta^2\cos^2\theta - 1}{2\cos\theta}. \end{aligned} \tag{31}$$

From the above relations, it is easy to know that all the wave functions can be expressed in terms of wave function $\phi_{1\mathrm{A}}$. In order to obtain the physically meaningful surface states, we have to make sure that the wave functions of both A sublattice and B sublattice are convergent when n goes to infinity. Next, we will consider different values of $\alpha > 2$ and $\alpha < -2$ separately, to find out the condition for the existence of surface states.

(i) $\alpha > 2$: It is natural to have $\lambda_+ > 1$. According to Eqs. (30) and (31), in order to obtain the convergent states when n goes to infinity far away from the edge, we can write down the conditions in terms of the original wave functions at $n = 1, 2$

$$\begin{aligned} &(\alpha - \lambda_-)\phi_{2\mathrm{A}} = \eta\phi_{1\mathrm{A}}, \\ &\phi_{2\mathrm{B}} = \lambda_-\phi_{1\mathrm{B}}. \end{aligned} \tag{32}$$

We can gain the energy of the surface states in the form of

$$E^2 = 4\eta^2\cos^2\theta + \frac{\eta^2}{\eta^2 - 1}, \tag{33}$$

with the definitions of α, β, and γ, we have two inequalities $\alpha > 2$ and $|\lambda_+| > 1$, so that we can obtain the constraints of the inhomogeneous hopping energy for the existence of those states

$$\begin{aligned} &\eta < 1,\ 0 < \frac{1}{2(1-\eta^2)} < |\cos\theta| \leqslant 1 \\ &\Longrightarrow \eta^2 < 1/2; \end{aligned} \tag{34a}$$

$$\begin{aligned} &\eta > 1,\ 0 < \frac{1}{2(\eta^2-1)} < |\cos\theta| \leqslant 1 \\ &\Longrightarrow \eta^2 > 3/2. \end{aligned} \tag{34b}$$

(ii) $\alpha < 2$: It is easy to know $\lambda_- < -1$. With the similar discussion as stated above, we can find the conditions for the existence of the surface states as follows:

$$\begin{aligned} &(\alpha - \lambda_+)\phi_{2\mathrm{A}} = \eta\phi_{1\mathrm{A}}, \\ &\phi_{2\mathrm{B}} = \lambda_+\phi_{1\mathrm{B}}. \end{aligned} \tag{35}$$

The results shown in Eqs. (33) and (34) can be obtained.

Besides, we can directly obtain these results from Eq. (17), by taking $t_0 = 2\tilde{t}_0\cos(k_y a/2)$, $t_1 = t = 1$, $t_2 = 2t\cos(k_y a/2)$, $\eta = \tilde{t}_0/t$, and $\theta = k_y a/2$.

As shown above, we can easily see that the existence of the non-zero-energy surface states depends on the edge decoration. The ratio between the edge hopping and the bulk hopping should be within a certain threshold, so that we can detect the finite-energy surface states. Comparing the results obtained above with those by means of the exact diagonal method on a finite-size zigzag graphene nanoribbon in Fig. 3, we can obtain the analytical expression for the dispersion of the bulk states, so we just compare the dispersion of the surface states through exact diagonal method and TMM. The former is calculated in the numerical way, while the latter is obtained through Eq. (33); from Fig. 3, it is easy to see that these results are in excellent agreement with each other.

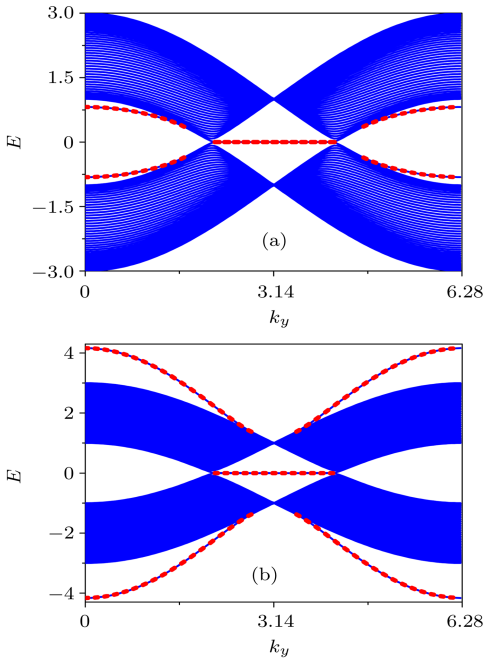


Fig. 3. (colour online) By exact diagonalization method, the dispersion relation of the bulk states and the surface state as depicted by blue line, while the dispersion relation of the edge state obtained through TMM as depicted by the dashed line (red dash-line). Parameters: (panel (a)) $\tilde{t}_0 = 0.5t$, (panel (b)) $\tilde{t}_0 = 2.0t$.

4. Conclusions

In order to obtain the condition for the existence of the surface states, we have studied the 1D toy model with the help of TMM at first, then we hold a similar discussion with the semi-infinite zigzag edged graphene model. Through the whole analysis, we can obtain the results in the latter model by analogy with the toy model. In the 1D toy model, we conclude that the existence of zero-energy surface state depends on the structure of the model, regardless of whether edge decoration exists or not, while the existence of non-zero-energy surface states can occur due to the edge decoration. In the semi-infinite zigzag edged graphene model, we conclude that the occurrence of the zero-energy surface state depends on the structure of the model, while the non-zero-energy surface states occur due to the edge decoration as well. Particularly, assuming that the electron hopping energy on the edge is $\tilde{t}_0$, different from that t in the bulk, we found that the existence of the zero-energy surface states is independent of the amplitude of $\tilde{t}_0$ and besides, finite energy surface states can exist if $t > \sqrt{2}\tilde{t}_0$ or $t < \sqrt{2/3}\tilde{t}_0$. These surface states occur as pairs with energy $\pm E$ outside the continuum conduction and valence bands.

Acknowledgment

We thank Dr. Yan X. Z. for the helpful comments.

References

[1] Tamm I 1932 *Phys. Z. Sowjetunion* **1** 733
[2] Shockley W 1939 *Phys. Rev.* **56** 317
[3] Davison S G and Stęślicka M 1996 *Basic Theory of Surface States* (Oxford: Oxford University Press)
[4] Agranovich V M and Mills D L 1984 *Surface Polaritons* (Amsterdam: North Holland)
[5] Molina M I, Vicencio R A and Kivshar Yu S 2006 *Opt. Lett.* **31** 1693
[6] Ohno H, Mendez E E, Brum J A, Hong J M, Agulló-Rueda F, Chang L L and Esaki L 1990 *Phys. Rev. Lett.* **64** 2555
[7] Rosberg C R, Neshev D N, Krolikowski W, Mitchell A, Vicencio R A, Molina M I and Kivshar Yu S 2006 *Phys. Rev. Lett.* **97** 083901
[8] Wu Y Y, Chen S, Gao X Y, Andrew Thye Shen Wee and Xu P S 2009 *Acta Phys. Sin.* **58** 4288 (in Chinese)
[9] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 *Science* **306** 666
[10] Novoselov K S, Geim A K, Morozov S V, Jiang D, Katsnelson M I, Grigorieva I V, Dubonos S V and Firsov A A 2005 *Nature* **438** 197
[11] Castro Neto A H, Guinea F, Peres N M R, Novoselov K S and Geim A K 2009 *Rev. Mod. Phys.* **81** 109
[12] Klein D J 1994 *Chem. Phys. Lett.* **217** 261
[13] Fujita M, Wakabayashi K, Nakada K and Kusakabe K 1996 *J. Phys. Soc. Jpn.* **65** 1920
[14] Niimi Y, Matsui T, Kambara H, Tagami K, Tsukada M and Fukuyama H 2005 *Appl. Surf. Sci.* **241** 43
[15] Kobayashi Y, Fukui K I, Enoki T, Kusakabe K and Kaburagi Y 2005 *Phys. Rev.* B **71** 193406
[16] Lin Q, Chen Y H, Wu J B and Kong Z M 2011 *Acta Phys. Sin.* **60** 097103 (in Chinese)
[17] Peres N M R, Guinea F and Castro Neto A H 2006 *Phys. Rev.* B **73** 125411
[18] Brey L and Fertig H A 2006 *Phys. Rev.* B **73** 235411
[19] Jiang L W, Zheng Y S, Yi C S, Li H D and Lu T Q 2009 *Phys. Rev.* B **80** 155454
[20] Li W and Tao R B 2010 *arXiv*: 1001.4168v2
[21] Savin A V and Kivshar Y S 2010 *Phys. Rev.* B **81** 165418
[22] Akhmerov A R and Beenakker C W J 2008 *Phys. Rev.* B **77** 085423
[23] Yao W, Yang S Y A and Niu Q 2009 *Phys. Rev. Lett.* **102** 096801
[24] Klos J W, Shylau A A, Zozoulenko I V, Xu H Y and Heinzel T 2009 *Phys. Rev.* B **80** 245432
[25] Guinea F, Katsnelson M I and Geim A K 2010 *Nat. Phys.* **6** 30
[26] Pereira V M and Castro Neto A H 2009 *Phys. Rev. Lett.* **103** 046801
[27] Lee D H and Joannopoulos J D 1981 *Phys. Rev.* B **23** 4997
[28] López Sancho M P, Lopez Sancho J M, Sancho J M L and Rubio J 1985 *J. Phys.* F: *Met. Phys.* **15** 851
[29] Lee D H and Joannopoulos J D 1981 *Phys. Rev.* B **23** 4988
[30] Peres N M R 2009 *Eur. Phys. J.* B **72** 183
[31] Hatsugai Y 1993 *Phys. Rev. Lett.* **71** 3697