Graphene zigzag ribbons, square lattice models and quantum spin chains

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Abstract. We present an extended study of finite-width zigzag graphene ribbons (ZGRs) based on a tight-binding model with hard-wall boundary conditions. We provide an exact analytic solution that clarifies the origin of the predicted width dependence on the conductance through junctions of ribbons with different widths. An analysis of the obtained solutions suggests a new description of ZGRs in terms of coupled chains. We pursue these ideas further by introducing a mapping between the ZGR model and the Hamiltonian for \(N\)-coupled quantum chains as described in terms of \(2N\) Majorana fermions. The proposed mapping preserves the dependence of ribbon properties on its width thus rendering metallic ribbons for \(N\) odd and zero-gap semiconductor ribbons for \(N\) even. Furthermore, it reveals a close connection between the low-energy properties of the ZGR model and a continuous family of square lattice model Hamiltonians with similar width-dependent properties that includes the \(\pi\) flux and the trivial square lattice models. As a further extension, we show that this new description makes it possible to identify various aspects of the physics of graphene ribbons with those predicted by models of quantum spin chains (QSCs).

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Graphene has attracted a lot of interest since its successful synthesis in 2004 [1]. The crystalline structure of the material is given by a triangular Bravais lattice with a two-atom basis, which provides a spinor character to wavefunctions. Calculations of the band structure reveal that conduction and valence bands coincide at six corners of the Brillouin zone (the so-called Dirac points). The linear spectrum around these points makes it possible to describe the low-energy physics by Dirac-type equations. Therefore graphene shows many unique properties not observed in other materials. Among them we should cite the unusual quantum Hall effect and the high conductance of charge carriers through potential barriers, a property that is attributed to the Klein paradox [2].

From the point of view of potential applications, high mobility and stiffness makes graphene an excellent candidate for future electronic devices. Interestingly enough, confined graphene samples (such as ribbons and quantum dots) reveal even more peculiar properties that strongly depend on edge terminations [4]. Thus, cutting through armchair edges renders ribbons that can be metallic or semiconducting depending on the ribbon width, while ZGRs have localized states near the edges with an almost flat band between any two inequivalent Dirac points [3]. Furthermore, numerical [5] and theoretical [15] works predicted a conductance of ZGRs strongly dependent on the ribbon’s width. These works, focused on transport properties through junctions, concluded that junctions between ribbons with even and odd numbers of zigzag lines showed a valley-valve effect.

In this work, we show that this even–odd behavior has a simple explanation based on the presence or absence of zero modes in the spectrum of a finite-width ribbon. This realization leads naturally to a description of ZGRs in terms of coupled chain models that can be extended (in some cases) to models of quantum spin chains (QSCs). This dual description suggests that ZGRs can be viewed as a material realization of many different theoretical models of QSCs. At the same time, the well-known physics of various QSC models can shed light on various properties of graphene ribbons.

1. Model for ZGRs

We first review some results obtained with a tight-binding model for ZGRs with hard-wall boundary conditions. In the absence of magnetic fields and spin–orbit interactions, the
Figure 1. The boundary conditions for ZGR implies that \( u_A = 0 \) on the lower edge and \( u_B = 0 \) on the upper edge (green dotted line). All atoms along each zigzag line are labeled by the same \( y \)-coordinate. The right panel shows a generalized lattice model with interchain hopping term \( t_\perp \) and extra hopping term \( \eta t_\perp \). In graphene \( \eta = 0 \) and \( t_\perp = t \).

Hamiltonian is spin independent and thus it is enough to consider spin up (or down) electrons only. The Hamiltonian and the spinor wavevector in momentum space are given by

\[
H = \begin{pmatrix} 0 & \phi \\ \bar{\phi} & 0 \end{pmatrix}, \quad \Psi_\pm = C \begin{pmatrix} u_A = e^{i\theta/2} \\ u_B = \pm e^{-i\theta/2} \end{pmatrix} e^{i(k_x x + k_y y)}
\]

with \( \phi(k_x, k_y) = t_\perp e^{ik_y} + 2t \cos \frac{k_y a}{2} \) and \( \bar{\phi}(k_x, k_y) = \phi(k_x, -k_y) \). Here \( k_x \) and \( k_y \) are measured from the center of the Brillouin zone (the \( \Gamma \) point) and \( b = a\sqrt{3}/2 \). The angle \( \alpha \) is defined by \( \phi(k_x, k_y) = \sqrt{\phi^2 e^{i\alpha}} \). By an appropriate gauge transformation, all atoms along each zigzag line can be labeled by the same coordinate \( y \). This is equivalent to work with the deformed lattice shown in figure 1. Note that in graphene the inter- and intrachain couplings are equal \((t_\perp = t)\). However, for reasons to be clarified later, we introduce these couplings as independent variables.

Standard hard-wall boundary conditions for ZGRs are given by \( u_A(y = -W/2) = 0 \) and \( u_B(y = W/2) = 0 \) along the lower and upper edges, respectively [3, 4, 13, 14]. It is useful to introduce the variable \( N \) that counts the number of zigzag lines or chains inside the ribbon as \( N = W/b - 1 \). Note that due to translational symmetry along the \( x \)-direction, \( k_x \) is a good quantum number, and for a given \( k_x \) the wavefunction is given by the linear combination of two degenerate states at \( \pm k_y \)

\[
\chi(k_x)_\pm = \begin{pmatrix} \sin(k_y y + \alpha/2 - n\pi/2) \\ \sin(k_y y - \alpha/2 - n\pi/2) \end{pmatrix}
\]

in which \( k_y \) satisfies

\[
\alpha - k_y W = n\pi,
\]

where \( n \) is an integer. The condition imposed by equation (3) can also be written as \( \phi / \bar{\phi} = e^{2i\theta W} \). This also implies that

\[
\phi = e^{ik_y W} \sin k_x b / \sin k_y W.
\]

One peculiar feature of ZGR is the presence of bands with complex wavenumber \( k_y \) (and correspondingly complex \( \alpha \)) between two inequivalent Dirac points \( K = (2\pi/3, 0) \) and \( K' = (4\pi/3, 0) \). Previous works in the limit of semi-infinite ribbons have shown that these bands are flat and correspond to highly localized states at the edge of the ZGR [3, 4, 13, 14]. These results can also be easily obtained from the definition of \( \phi \) and equation (4), which supports a solution with \( e^{ik_y} \approx -2(t/t_\perp)\cos(k_x a/2) \) with zero energy.

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To get further insight into the properties of finite-width ribbons, we derive below the expressions for wavefunctions and energies of these quasi-degenerate bands.

First, we consider the case where \( k_x > \pi \) that renders \( \cos(k_x a/2) < 0 \). For a zero-energy solution to exist \((\varphi = 0)\), it is necessary that \( e^{ik_y} > 0 \). This implies that \( k_y \) should be imaginary and we can write \( k_y = iq \) where \( q \) is a positive real number. By returning to equation (4), we obtain \( e^{\alpha} > 0 \), which implies that \( \alpha \) is imaginary. Therefore the condition set in equation (3) can be satisfied by setting \( n = N = W/b - 1 \), which results in

\[
\chi_{\pm}(k_x a > \pi) = C \left( \sinh q(y + W/2) \pm \sinh q(y - W/2) \right).
\]  

(5)

Now consider the case for \( k_x < \pi \) for which \( \cos(k_x a/2) > 0 \). The zero-energy condition now requires that \( e^{ik_y}b \approx -2 \cos(k_x a/2) t/t_L < 0 \) and thus \( k_y \) must be a complex number: \( k_y = \pi + iq \) where \( q \) is a positive real number. In this case, equation (3) can be satisfied by \( n = N = W/b - 1 \), which results in

\[
\chi_{\pm}(k_x a < \pi) = C \left( \sinh[(q + i\pi)(y + W/2)] \pm \sinh[(q + i\pi)(y - W/2) - iN\pi] \right).
\]  

(6)

The energy dispersion for all bands is given by \( E = \pm t_L \sin(k_y b)/\sin(k_y W) \). In particular, the edge state dispersion near \( k_x a = \pi \) can be approximated as

\[
E \approx \pm t_L (k/t_L)^N,
\]  

(7)

where \( k \) is the dimensionless momentum measured from the center of the band \( k_x a = \pi \) (located between two inequivalent Dirac points).

Equation (7) reveals an important feature of ZGR: ribbons with an odd number of chains possess different transport properties than those with an even number of chains [5, 7]. This feature is reflected in the phase factor of \( N\pi \) that appears in equation (6), which changes the relative sign of the spinor components in the wavefunction. A clear picture of this feature emerges when considering wavefunctions at three different \( y \)-points (one at the center of the ribbon \( y = 0 \) and two points on opposite edges \( y = \pm W/2 \)) and finding their asymptotic form when approaching \( k_x a = \pi \).

The argument proceeds as follows: first, evaluate the wavefunctions at \( k_x a > \pi \) and obtain their limiting expression as \( k_x a \to \pi \).

At \( y = 0 \) as \( q \to \infty \) the spiner is

\[
\chi_{\pm}(k_x a > \pi) \approx C \left( e^{iqW/2} \mp e^{-iqW/2} \right) \approx Ce^{iqW/2} \left( 1 \mp 1 \right).
\]  

(8)

Here \( C \sim e^{-qW} \) and the wavefunction inside the ribbon goes to zero at \( k_x a = \pi \). Note the relative sign of \( u_A/u_B \).

At the left edge \( y = -W/2 \) as \( q \to \infty \) the expression reduces to

\[
\chi_{\pm} \approx C \left( \begin{array}{c} 0 \\ \mp e^{iqW} \end{array} \right) \approx Ce^{iqW} \left( \begin{array}{c} 0 \\ 1 \end{array} \right)
\]  

(9)

and finally, at the right edge \( y = W/2 \), as \( q \to \infty \) we obtain

\[
\chi_{\pm} \approx C \left( \begin{array}{c} e^{iqW} \\ 0 \end{array} \right) \approx Ce^{iqW} \left( \begin{array}{c} 1 \\ 0 \end{array} \right).
\]  

(10)
Note that for each band (conduction or valence) the signs of the spinor components are consistent when we start from the left (equation (9)), go through the middle (equation (8)) and then to the right (equation (10)).

Now let us approach \( \pi \) from the left, i.e. with \( k_x a < \pi \). At \( y = 0 \) as \( q \to \infty \) the expression for the spinor is

\[
\chi_{\pm}(k_x a < \pi) \approx C \left( e^{i q W/2} \pm e^{-i q W/2} \right)
\]

\[
\approx C e^{i q W/2} \left( \pm e^{-i q W/2} \right). \tag{11}
\]

At the left edge \( y = -W/2 \) and as \( q \to \infty \)

\[
\chi_{\pm} \approx C \left( 0 \pm e^{i q W} \right) \approx C e^{i q W} \left( 0 \pm 1 \right). \tag{13}
\]

Similarly, at the right edge \( y = W/2 \) and as \( q \to \infty \)

\[
\chi_{\pm} \approx C \left( e^{i q W} \pm e^{-i q W} \right) \approx C e^{i q W} \left( e^{i q W} \pm 0 \right). \tag{14}
\]

For \( W \) odd (\( N \) even) any two conduction bands \( \chi_{+} \) and \( \chi_{-} \) have the same asymptotic wavefunction (note that the ratio of \( u_A / u_B = -1 \)). The same results hold for any two valence band wavefunctions with a ratio \( u_A / u_B = 1 \). This means that as \( k_x \) moves continuously through the band center, the conduction band does not cross the zero-energy (Fermi energy) point (the same holds for the valence band). In contrast, for ribbons of \( W \) even (\( N \) odd), two bands \( \chi_{+} \) and \( \chi_{-} \) with different energies are the ones that have the same asymptotic wavefunction (note that the ratio of \( u_A / u_B = -1 \)). Similarly, the two other bands \( \chi_{+} \) and \( \chi_{-} \) have their wavefunctions with the ratio \( u_A / u_B = 1 \) as the center of the band is approached. This means that if we change \( k_x \) from left to right we go from conducting band to valence band or from valence band to conducting band, i.e. the bands cross.

From equations (5) and (6), we see that for odd \( N \) the overlap between two spinors in the conduction band at \( k_x a = \pi \pm k \) is equal to zero: \( \int dy \langle \chi_{+}(k_x a = \pi + k)|\chi_{+}(k_x a = \pi - k) \rangle = 0 \). In contrast, for even \( N \) we have \( \int dy \langle \chi_{+}(k_x a = \pi + k)|\chi_{-}(k_x a = \pi - k) \rangle = 0 \).

The analysis of finite-width ribbons presented here clearly shows that the origin of the even–odd dependence found in previous works in the limit of semi-infinite ribbons is given by the nature of the band of the zero-energy mode.

2. Graphene ribbons as coupled quantum chains

The even–odd dependence formalized in the previous section suggests that some physical properties of ZGR should be captured by highly anisotropic models where a ribbon of finite width is viewed as a set of coupled one-dimensional chains. As shown in [16], the Hamiltonian of \( N \) decoupled \((t_\perp = 0)\) chains is

\[
H_N = \sum_{n=1}^{n=N} H_n \quad \text{where} \quad H_n = \int dx [i c_{A_n}(x) \cdot (c_{B_n}(x) + c_{B_n}^\dagger(x - a)) + \text{h.c.}] \quad \text{is the Hamiltonian of the} \ n\text{th chain. The energy of each chain is given by} \ E = 2t \cos k_x a / 2. \quad \text{Near the center of the band} \ k_x a = \pi, \ \text{we can write the lattice creation and annihilation operators by}
\]

\[
c_{A_n}(x) = i(-1)^{y/a}(R_n(x) + L_n(x))/\sqrt{2}, \quad c_{B_n}(x) = (-1)^{y/a}(R_n(x) - L_n(x))/\sqrt{2}. \tag{15}
\]
By introducing the Majorana fermions
\[ R_n = (\xi_{2n-1} + i\xi_{2n}) / \sqrt{2}, \quad L_n = (\xi_{2n-1} + i\xi_{2n}) / \sqrt{2}, \]
the Hamiltonian becomes \( H_N = \int dx [H_0 + \mathcal{H}'] \) with
\[ H_0 = \sum_{n=1}^{2N} i\hbar (\xi_n \partial_x \xi_n - \bar{\xi}_{n} \partial_x \bar{\xi}_{n}), \]
\[ \mathcal{H}' = \sum_{n=1}^{2N-2} -i\hbar (\xi_n \xi_{n+2} - \bar{\xi}_{n} \bar{\xi}_{n+2}) \]
\[ + i\hbar (\xi_n \bar{\xi}_{n+2} - \bar{\xi}_n \xi_{n+2}). \]
In graphene, \( \hbar = m = t_{\perp}/2 = t/2 \). The spectrum of the Hamiltonian can be derived easily and matches well with exact tight-binding results [16].

We emphasize here that the origin of the mass term in (19) is due to the fact that in zigzag ribbons, an \( A \) atom from each chain \( n \) is connected to a \( B \) atom in the next chain \( n + 1 \) but the \( B \) atom in chain \( n \) is not connected to an \( A \) atom in the next chain. In the case of armchair ribbons, on the other hand, the connection between \( A \) and \( B \) atoms of adjacent chains is symmetric. However, this argument does not exclude the presence of the mass term in the effective Hamiltonian of armchair ribbons because the spinor wavefunction of these ribbons has four components and contains two \( A \) and two \( B \) atoms.

### 3. The square lattice model

The generalized form of equation (19) with \( \eta \neq m \), represents the square lattice model in figure 1, which has extra hopping terms between \( B \) atoms in any given chain and \( A \) atoms in the next chain. The \( m \) (mass) term represents the difference between successive rung hopping terms, \( m = t_{\perp} (1 - \eta)/2 \), and the magnetic term \( \hbar \) represents the average \( h = t_{\perp} (1 + \eta)/2 \). Thus, the Hamiltonian in equation (19) describes a continuous family of models that includes the standard square lattice when \( \eta = 1 \) and the \( \pi \)-flux model when \( \eta = -1 \) [17]–[19]. For the particular case of graphene, values of \( \eta \neq 0 \) can represent various hopping terms. In particular, the NNNN hopping term that has been estimated to be of the order of \( t_3 = 0.1–0.3 \text{ eV} \) [20, 21], can be incorporated in the renormalization of the mass and magnetic terms producing \( m = (t_{\perp} - 3t_3)/2 \) and \( h = (t_{\perp} - t_3)/2 \), respectively. Note that this hopping mechanism is also expected to be highly affected by local lattice distortions produced either by ripples or bending of the material.

For the generalized case with \( \eta \neq m \), following the steps outlined in section 1, we can solve the tight-binding Hamiltonian and its wavefunction in a straightforward manner:
\[ H = \left( \begin{array}{cc} 0 & \phi' \\ \phi' & 0 \end{array} \right), \quad \Psi_{\pm} = C \left( \begin{array}{cc} u_A = e^{i\alpha'/2} & 0 \\ u_B = \pm e^{-i\alpha'/2} \end{array} \right) e^{ik_x x + ik_y y}, \]
with \( \phi'(k_x, k_y) = t_{\perp}(e^{ik_x} + \eta e^{ik_y}) + 2t \cos \frac{k_y}{2} \) and \( \phi'(k_x, k_y) = \phi'(k_x, -k_y) \). The angle \( \alpha' \) is defined by \( \phi'(k_x, k_y) = \phi'(k_x, -k_y) \). The energy of the model is given by \( E = \pm \sqrt{(t \cos \frac{k_y}{2} + 2h \cos k_x b)^2 + 4m^2 \sin^2 k_x b} \). As before, \( k_x \) is a good quantum number, while \( k_y \) depends on \( k_x \) and is determined by the boundary conditions, thus it is a function of \( W \) and \( k_x \).
In the presence of the \( \eta t_x \) hopping term, the boundary conditions have to be generalized so that both components of the spinor wavefunction are zero at the edges. The wavefunction inside the ribbon is constructed from the superposition of four degenerate states at \( k_y = (\pm k_1, \pm k_2) \):

\[
\Psi_{\text{ZGR}}(k_y) = \sum_{k_y = \pm k_1, \pm k_2} a(k_y) \begin{pmatrix} e^{i\omega'/2} \\ e^{-i\omega'/2} \end{pmatrix} e^{ik_x x + ik_y y} = C \begin{pmatrix} \varphi(y) \\ -\varphi(-y) \end{pmatrix} e^{ik_x x}.
\]

After applying the boundary conditions we obtain

\[
\varphi(y) = \sin \left( \frac{k_2 W - \alpha_2 + \delta}{2} \right) \sin \left( \frac{2k_1 y + \alpha_1 + \delta}{2} \right) - \sin \left( \frac{k_1 W - \alpha_1 + \delta}{2} \right) \sin \left( \frac{2k_2 y + \alpha_2 + \delta}{2} \right)
\]

with \( \delta = 0, \pi \). Here \( k_1 \) and \( k_2 \) are calculated by the degeneracy condition \( E(k_1) = E(k_2) \) and

\[
\sin \left( \frac{k_1 W - \alpha_1 + \delta}{2} \right) \sin \left( \frac{k_2 W + \alpha_2 + \delta}{2} \right) = \sin \left( \frac{k_2 W - \alpha_2 + \delta}{2} \right) \sin \left( \frac{k_1 W + \alpha_1 + \delta}{2} \right).
\]

These two conditions determine \( k_1 \) and \( k_2 \) as functions of \( k_x \) and \( W \). In general, \( k_1 \) and \( k_2 \) are complex numbers.

As mentioned above, the limit \( \eta = -1 \) describes the \( \pi \)-flux phase that in this language implies the case with \( h = 0 \). In this regime, the wavenumbers \( k_1 \) and \( k_2 \) are independent of \( k_x \) and are given by \( k_1 b = \pi / 2 + n \pi b / W \) and \( k_2 b = \pi - k_1 b \). The energy takes the simple form:

\[
E = \pm \sqrt{t^2 \cos \frac{k_1 b}{2} + t^2 \sin^2 k_y b}.
\]

The valence and conduction bands coincide at four points of the Brillouin zone (\( k_x a = \pm \pi, k_x b = \pm \pi \)). At each point there are two gapless modes with \( E = \pm 2t \cos \frac{k_1 b}{2} \approx \pm tk \). Note that for odd \( N \) one of the solutions of \( k_y \) lies exactly at the gapless corner of the Brillouin zone. In contrast, for even \( N \) the zero-energy points are always avoided. By increasing \( \eta \), the wavenumbers \( k_1 \) and \( k_2 \) become complex quantities and acquire a dependence on \( k_x \). However, for odd \( N \), the zero-energy mode survives all along the line \(-1 \leq \eta \leq 1\) with a dispersion that changes from linear at \( \eta = -1 \) to equation (7) at \( \eta = 0 \). As figure 2 shows, the wavefunctions of different modes show incipient localization as \( \eta \) increases and become localized when \( \eta \to 0 \). In the regime with \( \eta > 0 \), the magnetic term dominates and introduces new zero-energy points for both values of \( N \), odd or even. However, for odd \( N \), there is an odd number of zero-energy points, one of them being the existing mode at \( k_x a = \pi \). In contrast, for even \( N \), there is an even number of zero-energy points with no zero modes at \( k_x a = \pi \). Note that the extreme limit \( \eta \to 1 \) represents the simple square lattice where \( k_x b = n \pi b / W \) and energy spectrum \( E = \pm (t \cos \frac{k_x b}{2} + t_\perp \cos k_y b) \). In this case, the mode with linear dispersion at \( k_x a = \pi \) exists only for ribbons with even \( W / b \) (or odd \( N \)).

In order to visualize the evolution of the band structures and wavefunctions of all these different models, it is instructive to study the simplest examples of ZGRs with \( N = 2 \) (even) and \( N = 3 \) (odd) number of chains.
The Hamiltonian of \( N = 2 \) ZGR consists of two independent sets of Majorana pairs, odd and even \((\xi_1, \xi_3)\) and \((\xi_2, \xi_4)\). Consider only one of these sectors
\[
\mathcal{H} = \mathcal{H}_0 - \hbar (\xi_1 \xi_3 - \bar{\xi}_1 \bar{\xi}_3) + im (\xi_1 \bar{\xi}_3 - \bar{\xi}_1 \xi_3).
\]  
By the canonical transformation
\[
\xi_1 = (\chi_1 + \chi_2)/\sqrt{2} \quad \xi_3 = (\chi_1 - \chi_2)/\sqrt{2},
\]
the above Hamiltonian transforms to
\[
\mathcal{H} = \mathcal{H}_0 + im(\chi_1 \bar{\chi}_1 - \chi_2 \bar{\chi}_2) + i\hbar (\chi_1 \chi_2 - \bar{\chi}_1 \bar{\chi}_2).
\]
At \( \eta = -1 (\hbar = 0) \) the spectrum consists of two degenerate massive fermions with \( E = \pm \sqrt{m^2 + k^2} \). For generic \( \eta \) the magnetic term \( \hbar \) lifts the degeneracy and \( E = \pm (\sqrt{m^2 + k^2} \pm \hbar) \).

Graphene ribbons are represented by the critical value \( \hbar = m \) with the particular dispersion of edge states given by \( E \approx k^2/2m \). For \( \eta > 0 \), the bands cut the Fermi energy at two points around \( k_s a = \pi \).

For ZGRs with \( N = 3 \), the Hamiltonian (19) consists of two independent sets of three Majorana fermions (even and odd). Consider one of these sectors
\[
\mathcal{H} = \mathcal{H}_0 + im(\xi_1 \bar{\xi}_1 + \xi_3 \bar{\xi}_3 - \bar{\xi}_1 \xi_3 - \bar{\xi}_3 \xi_1) - i\hbar(\xi_1 \xi_3 + \xi_3 \xi_1 - \bar{\xi}_1 \bar{\xi}_3 - \bar{\xi}_3 \bar{\xi}_1).
\]
It is useful to define linear combinations of the Majorana fields \( \xi_1 \) and \( \xi_5 \) as: \( \eta_1 = (\xi_1 + \xi_5)/\sqrt{2} \) and \( \eta_3 = (\xi_1 - \xi_5)/\sqrt{2} \). Working on the basis \( \eta_1, \eta_3 \) and \( \xi_3 \), it is easy to see that the mass term does not couple \( \eta_3 \) to the two other modes \( \eta_1 \) and \( \xi_3 \) and thus, this mode remains massless. By applying a second transformation
\[
\chi_1 = (\xi_3 + \eta_1)/\sqrt{2}, \quad \bar{\chi}_1 = (\bar{\xi}_3 + \bar{\eta}_1)/\sqrt{2}, \\
\chi_2 = (\xi_3 - \eta_1)/\sqrt{2}, \quad \bar{\chi}_2 = (\bar{\xi}_3 - \bar{\eta}_1)/\sqrt{2}.
\]
The Hamiltonian transforms into
\[
\mathcal{H} = \mathcal{H}_0 + i\hbar \sqrt{2}(\chi_1 \bar{\chi}_1 - \chi_2 \bar{\chi}_2) + i\hbar(\chi_1 \eta_3 + \chi_2 \eta_3 - \bar{\chi}_1 \bar{\eta}_3 - \bar{\chi}_2 \bar{\eta}_3).
\]
At $\eta = -1(h = 0)$ the spectrum has two linear modes $E = \pm k$ and two copies of massive modes with dispersion $E = \pm \sqrt{k^2 + 2m^2}$. The linear modes correspond to the $k, b = \pi$ modes of the $\pi$-flux lattice model. An increase of $\eta$, introduces the magnetic term that couples these modes to the massive modes. As a result, the dispersion of the massless modes changes; however, they remain massless.

Finally, the energy spectrum of the model for a generic value of $\eta$ is given by

$$E (E^2 - k^2 - 2m^2 - 2h^2) = \pm k (E^2 - k^2 - 2m^2 + 2h^2). \quad (29)$$

When $h = m$ (at $\eta = 0$) the massless mode dispersion becomes $E \sim \pm k^3/4m^2$, which describe the edge state of the corresponding ZGR ribbon. In the regime $\eta > 1$, two extra zero-energy points are introduced. As $\eta \to 0$ the dispersion of the massless modes becomes linear again. These linear modes are in fact the solution of the square lattice spectrum near the corners of the Brillouin zone $(k_x a = \pm \pi, k_y b = \pm \pi/2)$.

4. Examples of single-particle interaction terms

Another useful aspect of the coupled chains representation is that it allows us to study the effect of different single-particle terms in the Hamiltonian and to obtain the corresponding band structures in a rather straightforward manner. To exemplify these points, in this section we derive the Majorana representation of three such terms: chemical potential, second neighbor-hopping term and spin–orbit (SO) interactions. We also present the corresponding expressions for terms that involve SO interactions, focusing on the intrinsic spin–orbit (ISO) and Rashba spin–orbit (RSO) terms.

It is interesting to note that the mapping to Majorana fermions preserves the quasi-degenerate features of the edge bands while capturing the main effects of these terms in the model for ZGRs. At the same time, the total Hamiltonian becomes richer and, as we discuss in the next section, some of these terms have direct interpretations in terms of models of QSCs.

From equation (15) we can obtain the relation between the fermion lattice operators $c_{A/B}$ and the Majorana fermions representation as

$$c_{A_n}(x) = (-1)^x \frac{i(\xi_{2n-1} + \bar{\xi}_{2n-1}) - (\xi_{2n} + \bar{\xi}_{2n})}{2},$$

$$c_{A_n}^\dagger(x) = (-1)^x \frac{-i(\xi_{2n-1} + \bar{\xi}_{2n-1}) - (\xi_{2n} + \bar{\xi}_{2n})}{2},$$

$$c_{B_n}(x) = (-1)^x \frac{(\xi_{2n-1} - \bar{\xi}_{2n-1}) + i(\xi_{2n} - \bar{\xi}_{2n})}{2},$$

$$c_{B_n}^\dagger(x) = (-1)^x \frac{(\xi_{2n-1} - \bar{\xi}_{2n-1}) - i(\xi_{2n} - \bar{\xi}_{2n})}{2}. \quad (30)$$

The reverse relations read

$$\xi_{2n-1} + \bar{\xi}_{2n-1} = i(-1)^x (c_{A_n}^\dagger(x) - c_{A_n}(x)), \quad \xi_{2n} + \bar{\xi}_{2n} = -(1)^x (c_{A_n}(x) + c_{A_n}(x)),$$

$$\xi_{2n-1} - \bar{\xi}_{2n-1} = (-1)^x (c_{B_n}^\dagger(x) + c_{B_n}(x)), \quad \xi_{2n} - \bar{\xi}_{2n} = i(-1)^x (c_{B_n}(x) - c_{B_n}(x)). \quad (31)$$
A chemical potential term is given by $\mathcal{H}_\mu(x) = \mu \rho_s(x) = \mu (\rho_{A,s}(x) + \rho_{B,s}(x))$. In the Majorana fermion language, it reads

$$\mathcal{H}_\mu \approx i2\mu(\xi_{2n-1}\xi_{2n} + \bar{\xi}_{2n-1}\bar{\xi}_{2n}).$$  

(32)

The effect of this term is trivial: it shifts the Fermi energy from $E_F = 0$ to $E_F = \mu$ as expected.

A second-neighbor hopping (NN) term is given by: $\mathcal{H}_{\text{NN}} = t_2 \sum \langle ij \rangle (c_{A,i}^\dagger(x)c_{A,j}(x) + c_{B,i}^\dagger(x)c_{B,j}(x)) + \text{h.c.}$ The coupling constant $t_2$ has been estimated to take its value in the range $t_2 = 0.02t - 0.2t$ eV [22]. In terms of Majorana fermions, this term introduces a velocity renormalization (which can be ignored) due to the interchain coupling and an intrachain contribution given by

$$\mathcal{H}_{\text{NN}} \approx -i2t_2(\xi_{2n-1}\xi_{2n} + \bar{\xi}_{2n-1}\bar{\xi}_{2n}).$$  

(33)

This expression suggests that the NN hopping term, in a first approximation, acts as an effective chemical potential, thus breaking particle–hole symmetry [23, 24]. The edge state energy is lowered with the corresponding modes acquiring a finite velocity along the ribbon and becoming more stable (see figure 3).

A staggered sublattice potential is represented by a Hamiltonian $\mathcal{H}_\nu(x) = \nu \rho_{-}(x) = \nu(\rho_{A,s}(x) - \rho_{B,s}(x))$. In the Majorana fermion representation, it takes the form:

$$\mathcal{H}_\nu(x) \approx i2\nu(\xi_{2n-1}\bar{\xi}_{2n} + \bar{\xi}_{2n-1}\xi_{2n}).$$  

(34)

For the ZGR in terms of coupled chains, this term opens a gap in each single chain (even when decoupled from the rest, with $t_\perp = 0$). Thus, every chain making the ribbon is gapped or, equivalently, each pair of Majorana fermions is massive. The total spectrum of the ribbon becomes massive regardless of $N$ being odd or even (see figure 4). Note that this term corresponds to a large momentum transfer between the two inequivalent Dirac points.

Note that, as a consequence, in $N$-odd ribbons, the only term that can open a gap at $k_x a = \pi$ involves intervalley scattering. Although in graphene the staggered chemical potential

Figure 3. Energy bands of the zigzag ribbon with $N = 3$ in the presence (solid lines) and absence (dotted lines) of the next-nearest hopping term $t_2 = 0.1t$. 

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Figure 4. Energy bands of the zigzag ribbon with $N = 3$ in the presence (solid lines) and absence (dotted lines) of the next staggered sublattice potential term $\nu = 0.2t$.

is expected to be zero, recent experimental work on suspended graphene samples suggests the presence of a small energy difference between the two sublattices [25]. Moreover, in nanoribbons made of SiC or BN, there is an intrinsic staggered chemical potential due to the presence of two different atoms in sublattices $A$ and $B$ [26]–[28].

The procedure can also be applied to other single-particle terms in the Hamiltonian. For example, we can also study the expression of SO interaction terms using the Majorana representation. The ISO is $H_{\text{ISO}} = i\tau^s \sum_{ij} v_{ij} c_i^\dagger c_j$ in which $s = \pm$ refers to the $z$-component of the electron spin operator. $v_{ij} = 2(d_{ik} \times d_{kj})/\sqrt{3}$ is the path-dependent number that takes the values $v_{ij} = (\pm 1)$ depending on the shortest path for a hopping process that goes from site $i$ to the next-nearest cite $j$ through an intermediate cite $k$ [29, 30, 33]. For modes with spin up the SO is written as

$$H_{\text{ISO}} \approx t'(\xi_n \xi_{n+2} + \bar{\xi}_n \bar{\xi}_{n+2}).$$

(35)

For spin down the equivalent term corresponds to the transformation $t' \rightarrow -t'$. It has been shown that in the presence of the ISO interaction, the bulk states have a gap of the order of $t'$. The situation is different in ribbons. For ZGRs with $N$ odd, the edge states get exchanged as the conduction and valence bands cross each other at the midgap point $k_xa = \pi$. The ribbon thus remains metallic. In this case the ISO interaction removes the degeneracy of the edge states near $k_xa = \pi$ and renders a pair of linear dispersion bands. Moreover, the edge states become spin-filtered with opposite spin currents at opposite edges of the ribbon. This is the topological insulating or quantum spin Hall phase of graphene [29]. For ZGRs with even $N$ the ISO interaction opens a gap between the edge states at $k_xa = \pi$ [32] and references therein. The gap is very small and scales as $\Delta \sim (t'/\kappa)^N$. Graphene ribbons in this phase are normal insulators (see figure 5).

For graphene samples on a substrate or suspended but subjected to a perpendicular electric field, the RSO interaction becomes quite relevant. The expression for the RSO interaction is $H_{\text{RSO}} = i\lambda \sum u_{ij} c_i^\dagger c_j$ where $u_{ij} \sim d_{ij} \times \mathbf{E}_z$. Here $d_{ij}$ is a vector that connects the
nearest-neighbor cites \( i \) to \( j \). The RSO has two contributions: the intrachain part gives

\[
H_{\text{RSO1}} = -i4\sqrt{3}\lambda (\xi_{2n\uparrow}^\dagger \xi_{2n\downarrow} - \xi_{2n\uparrow}^\dagger \xi_{2n\downarrow} + \xi_{2n-1\uparrow}^\dagger \xi_{2n-1\downarrow} - \xi_{2n-1\uparrow}^\dagger \xi_{2n-1\downarrow}).
\] (36)

The interchain part is

\[
H_{\text{RSO2}} = i2\lambda (\xi_{2n-1\uparrow}^\dagger \xi_{2n+2\downarrow} - \xi_{2n-1\uparrow}^\dagger \xi_{2n+2\downarrow} + \xi_{2n+1\uparrow} \xi_{2n-1\downarrow} - \xi_{2n-1\uparrow}^\dagger \xi_{2n+1\downarrow} + \xi_{2n+1\uparrow} \xi_{2n-1\downarrow} - \xi_{2n+1\uparrow}^\dagger \xi_{2n+1\downarrow} + \xi_{2n\uparrow}^\dagger \xi_{2n+1\downarrow} - \xi_{2n\uparrow}^\dagger \xi_{2n+1\downarrow}).
\] (37)

Note that the RSO does not open a gap in the bulk [31]. The same holds for ZGRs: there is no gap in the ribbon spectrum and the dispersion remains power-law like near the zero-energy point. However, in the presence of RSO interactions, the zero-energy point located at \( k_xa = \pi \) for RSO

Figure 5. Energy bands of the zigzag ribbon with \( N = 2 \) (top) and \( N = 3 \) (bottom) in the presence of the ISO \( t' = 0.1t \). For even \( N \) there is a gap at \( k_xa = \pi \).
zero shifts in opposite directions for opposite spins [31] (see figure 6). For wider ribbons with quasi-flat (and originally spin-degenerate) bands, there is a more pronounced lift of the spin degeneracy. Another interesting point is that the RSO interaction does not remove the even–odd width dependence of the edge states bands for finite-width ZGRs. As a consequence, even in the presence of RSO a ribbon with an odd number of chains remains metallic while one with an even number of chains is insulating. Note that these results also have important consequences for the analysis of the topological insulator phases that can be observed in graphene ribbons as discussed in [30]. This can be readily seen by considering an even \( N \) ribbon: in this case, there is an even number of Kramer pairs at each edge. In contrast, for odd \( N \) ribbons, the number of Kramer pairs is always odd, even in the presence of RSO interactions.

5. Graphene ribbons and QSC models

The Hamiltonian (19) can also describe some specific QSC models. Before presenting the connection between the two approaches, it is instructive to briefly review some results of the models of two coupled spin-1/2 chains and a spin-1 chain [34].

5.1. Two coupled spin-1/2 chains

The symmetry of two spin-1/2 Heisenberg antiferromagnetic chains, in the absence of the interchain coupling is \( \text{SU}(2) \times \text{SU}(2) \). In the continuum limit, the spin operator in each chain can be written in terms of current operators and a staggered part as

\[
S_i(x) = J_i(x) + \bar{J}_i(x) + (-1)^{i/a}n_i(x)
\]

where \( i = 1, 2 \) labels chain \( i \). The smooth part of the spin operator corresponds to the sum of right and left mover currents \( (J + \bar{J}) \) of the \( \text{SU}(2) \) Wess–Zumino–Novikov–Witten (WZNW) model, and represents the total magnetization of the chain. The staggered magnetization is represented by \( n \) and generalized models contain a dimerization operator \( \epsilon = (-1)^{i/a}S(x) \cdot S(x+a) \) that represents the time component of the staggered magnetization [35].
The addition of an interchain coupling reduces the symmetry to the generic SU(2) × Z2. In the standard model for two spin-1/2 coupled chains (ladder) [36], the interchain coupling is isotropic: \( H' = J_1 S_1 \cdot S_2 \). The relevant part of this term stems from the staggered magnetization contribution and is given by \( H' \approx J_1 n_1 \cdot n_2 \). The consequence of including such a term is the opening of a gap in the spectrum. In terms of Majorana fermions, the total Hamiltonian can be written in terms of four fermion fields \( \xi_1, \xi_2, \xi_3 \) and \( \xi_4 \). Three of these fields \( \tilde{\xi} = (\xi_1, \xi_2, \xi_3) \) have equal masses \( m \sim J_1 \) and the remaining one (\( \xi_4 \)) has a mass \(-3m\). The classification of Majorana fermion states into triplet and singlet states reflects the underlying global SU(2) symmetry of the ladder.

Majorana fermions \( \tilde{\xi} \) describe the triplet excitations of the two-coupled \( S = 1/2 \) quantum chain [37]. When the model is written in terms of right and left movers, it can be shown that the total currents \( I = J_1 + J_2 \) for each type of mover satisfy the Kac–Moody algebra of the SU\(_{k=2}(2)\) vector currents. Since the central charge of the model is \( C = 3/2 \), the currents can be represented using a triplet of Majorana fermions: \( I^a = \frac{1}{\sqrt{2}} \epsilon^{abc} \xi_b \xi_c \) where \( a, b, c \) refer to 1, 2, 3. The model has two primary fields namely \( \Phi^{(1/2)} \) and \( \Phi^{(1)} \), with the second field given by \( \Phi^{(1)}_{abc} = \xi_a \xi_b \). The other Majorana field \( \xi_4 \) describes the singlet excitations of the model. This field \( \xi_4 \) contributes to the relative (or the so-called wrong [34]) currents \( K = J_1 - J_2 \), which are represented by \( K^a = i\xi_a \xi_4 \). It is convenient at this point to introduce the fields \( Q_a = \xi_a \xi_4 \) and \( Q_a = \tilde{\xi}_a \xi_4 \).

Note that the ferro-antiferromagnetic transformation \( J_2 \rightarrow -J_2 \) (which is reflected in \( m \rightarrow -m \)) does not change the thermodynamics but it interchanges singlet and triplet roles.

### 5.2. Spin \( S = 1 \) chain

The connection to an \( S = 1 \) Heisenberg spin chain is given by considering the biquadratic \( S = 1 \) chain as defined by [38, 39]

\[
H = \sum_x [S(x)S(x + a) + b(S(x)S(x + 1))^2].
\]  

(38)

At \( b = -1 \), the model has gapless modes and is equivalent to a WZW SU(2)\(_{k=2}\) model. The Hamiltonian at this point can be described by the Majorana fermions as

\[
H_0 = \sum_{n=1}^3 i\nu(\xi_n \partial_x \xi_n - \tilde{\xi}_n \partial_x \tilde{\xi}_n).
\]  

(39)

For \( b < -1 \), there are two degenerate massive dimerized phases. For \( -1 < b < 1 \) the spin chain is in the Haldane phase with a gapped singlet ground state [40, 41].

The link between the spin operator and the WZW model is given by

\[
\vec{S}(x) \sim I(x) + \tilde{I}(x) + (-1)^y n(x).
\]  

(40)

Here \( n \) is the staggered part of the spin field. In analogy with the coupled spin-1/2 chains, the smooth (average) magnetization is given by \( M = I + \tilde{I} \).

For \( 0 < b < -1 \), the model has a gap that increases monotonically as a function of \( m = -1 - b \). Close to \( b = -1 \) the model can be described effectively by adding relevant mass terms. The mass term is positive in the dimerized phase and negative in the Haldane phase. These mass terms are expressed in terms of the relevant fields \( \Phi^{1}_{abc} = \xi_a \xi_b \) with a 3 \times 3 matrix representation. For isotropic models, the mass term is written as \( m Tr(\Phi^{1}) \).
5.3. ZGRs and QSCs

To show the connections between these models and graphene ribbons we start with the even $N = 2$ ZGR.

The Hamiltonian written in terms of right and left movers can be bosonized in a straightforward manner by introducing the bosonic fields $\phi_+ = \exp(\pm i \sqrt{4\pi} \phi_+)$ and $\phi_- = \exp(\pm i \sqrt{4\pi} \phi_-)$ for one set of movers and the corresponding $\phi_+$, $\phi_-$ for the other. The total Hamiltonian density reads

$$\mathcal{H} = \mathcal{H}_0 + \frac{m}{\pi} \sum_{\nu=\pm} \sin \left( \frac{4\pi}{\nu} + \frac{\hbar}{\sqrt{2\pi}} \nu \right) \mathcal{H}_+, \quad \mathcal{H}_+ = \hbar (K^x - \bar{K}^x - I^y - \bar{I}^y)$$

where $\Theta_\nu = \phi_\nu - \bar{\phi}_\nu$ is the dual field of $\Phi_\nu = \phi_\nu + \bar{\phi}_\nu$. Equation (41) describes two decoupled sine-Gordon Hamiltonians with a magnetic field (or chemical potential) applied to the dual sector.

The model for the $N = 2$ ribbon can be mapped to the two-leg ladder Hamiltonian discussed above with an anisotropic interchain coupling and an in-plane applied magnetic field: $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{1h} + \mathcal{H}_{2m} + \mathcal{H}_{3m}$. The magnetic field term is expressed in terms of the current operators as $\mathcal{H}_{1h} = \hbar (K^x - \bar{K}^x + I^y - \bar{I}^y)$ that are written in terms of Majorana fermions as shown above. The operator content of these currents can be given in terms of vector spin-chirality operators as: $I - \bar{I} \sim S_1(x) \times S_1(x + a) + S_2(x) \times S_2(x + a)$ and $K - \bar{K} \sim S_1(x) \times S_1(x + a) - S_2(x) \times S_2(x + a)$. The mass terms are produced by the following two interchain couplings. The first term is $\mathcal{H}_{2m} = \Phi_1 \Phi_2 \sim (S_1 \times S_2) \sim (m_1 n_2 - m_2 n_1)$. The second term is $\mathcal{H}_{3m} = \Phi_2 \Phi_3 \sim (n_1 m_2 + m_1 n_2) \bar{I}$. The analysis can be extended to the next even ZGR ribbon, namely the $N = 4$ ribbon, which can be described by two sets of four Majorana fermions. The Hamiltonian of each sector, separately, can be represented by a two-chain spin-1/2 ladder. To get the equivalent spin-chain model, we just need to add two more terms to the equivalent spin model for the $N = 2$ ZGR discussed above: the first term is $\mathcal{H}_{3m} = \Phi_1 \Phi_2 \sim t_1 (S_1 \times S_2) \bar{I}$. The second term is the magnetic field $\mathcal{H}_{2m} = \hbar (K^x - \bar{K}^x)$.

The mapping between odd ZGR ribbons and spin-chain models is simpler for the $N = 3$ case. The equivalent spin chain describes the anisotropic version of the biquadratic spin $S = 1$ chain [38] with an in-plane magnetic field. The Hamiltonian of one of the sectors is given in (28). This model describes an $S = 1$ model with masses $m_1 = m$, $m_2 = -m$ and $m_3 = 0$ and two magnetic fields $h_1 = h_2$. In the language of ZGR ribbons, we note that the value of the mass terms $m_1$ and $m_2$ can be changed when including the ISO interaction (35). In this case then, the mass terms are given by $m_1 = t_{1/2} + st$ and $m_2 = -t_{1/2} + st$ where $s = \pm$ stands for real spin-up spin-down electron.

For the $N = 5$ ZGR each sector has five Majorana fermions. In principle, the Hamiltonian can be described by the $S = 2$ representation of the SU$_{5/2}$ WZW model. The corresponding primary field has the conformal dimension $(1/2, 1/2)$ which can be written in terms of Majorana fermions bilinears. Furthermore, the central charge of the theory is $C = 5/2$, which is another indication that five Majorana fermions are needed to describe the model.
6. Conclusions

ZGRs show remarkable physical characteristics that are predicted to have important effects in their transport properties. In this work, we have provided a detailed analytic treatment of a tight-binding Hamiltonian with hard-wall boundary conditions that explains the surprising width-dependent properties in terms of the existence of a zero-energy mode that corresponds to localized states along the edges of a finite-width ribbon. As a consequence, ZGRs with even widths (odd number of chains) are metallic, whereas odd width ribbons (even number of chains) are insulating.

The unusual even–odd dependence led us to consider models of ZGR in terms of coupled quantum chains. This particular continuous limit preserves the main features of band structures and spinor wavefunctions while keeping the width dependence.

In the Majorana fermion representation, the model of ZGR in terms of coupled chains can be easily extended to include various single-particle interactions and we have analyzed in detail the effects of adding a chemical potential term, second and third nearest-neighbor hoppings, a staggered chemical potential, ISO and RSO interactions.

Besides the straightforward treatment of these terms, the mapping reveals that ZGRs can be viewed as a member of a continuous family of models in square lattices that range from the standard square lattice to $\pi$-flux models. These models share the same even–odd width dependence first obtained in ZGR models. We have presented a full solution for these models and emphasized their similarities with ZGRs.

As a final application, we have shown that it is possible to treat ZGRs as coupled QSCs. A careful analysis of models in terms of Majorana fermions shows that ZGRs with two chains inside are fully equivalent to two spin-$1/2$ coupled chains with an anisotropic interchain coupling and an external magnetic field. We also analyzed another example of an even-width ribbon ($N = 4$). We applied the mapping to odd-number models and showed that an $N = 3$ ribbon corresponds to the anisotropic biquadratic spin $S = 1$ chain with an in-plane magnetic field. A preliminary analysis of an $N = 5$-chain ribbon suggests a description in terms of a set of five Majorana fields for each Hamiltonian sector. We would like to remark that the mapping proposed here allows us to obtain solutions for all these new QSC models by direct comparison with the known results obtained with ZGRs.

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