# Solution of the mean-field Hubbard model of graphene rectangulenes

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We present a complete analytical solution of the mean-field Hubbard model of undoped and doped graphene rectangulenes. These are non-chiral ribbons of arbitrary length and width, whose dimensions range from simple short acene molecules all the way up to the bulk limit. We rewrite the Hubbard model in the basis of bulk and edge non-interacting eigen-states, and provide explicit expressions for the Coulomb matrix elements. We present a general mean-field decoupling of the Hamiltonian, and discuss in detail the paramagnetic, ferromagnetic and antiferromagnetic meanfield solutions. We calculate the eigen-energies, occupations, spin densities and addition energies of rectangulenes with lengths and widths ranging from a nanometer to several hundreds of them. We rewrite the exact mean-field tight-binding Hamiltonian back in the site-occupation basis, that can be used to model electronic, thermo-electric, transport and optical properties of experimental-size graphene flakes.

# I. INTRODUCTION

The experimental demonstration of the ability to isolate single graphene sheets [1] promoted the vision that atomic-scale two-dimensional nanoelectronics and nanooptics could be a viable future technology [2]. Elementary units of the graphene lego would then range from simple graphenoid molecules such as acenes [3, 4], graphene nanoribbons (GNR) and all the way up to graphene flakes.

Part of the interest in graphene nanostructures stems from the old prediction by Dresselhaus and coworkers that GNRs having zigzag terminations could host edge states[5]. GNRs' peculiar electronic and magnetic structure were the subject of intense theoretical work for the first years after the discovery of graphene [6–14].

Parallel efforts to fabricate GNRs by unzipping carbon nanotubes were only partially successful because the graphene edges were quite defective [15]. However, GNRs having atomically-precise edges were finally synthesized by bottom-up techniques [16]. This breakthrough opened the door to a plethora of subsequent developments in GNR fabrication and characterization [17–21].

The topological nature of edge states [22] and the connection between GNRs and the Schrieffer-Heeger-Su (SSH) model [23, 24] has also been uncovered and analyzed both theoretically [25] and experimentally [26, 27]. GNR edge states are predicted to be magnetic [10, 28, 29], so that magnetism at the edge has been paid attention throughout these years [30, 31]. GNRs have been explored in optics for their potential utility as plasmon waveguides [32, 33]. Recently, single armchair GNRs of precise width have been deposited onto ultra-clean graphene gaps, therefore creating all-carbon single electron transistors displaying quantum dot behavior [34–36].

GNRs are theoretically well-described by both Density Functional Theory (DFT) [10, 11] and the mean-field (MF) Hubbard model [12, 37]. These two approaches estimate successfully many of the electronic, magnetic and optical properties of GNRs. However, both approaches are numerically costly for large-size GNRs, which limits the ability to simulate them to narrow widths and short lengths, which are usually much smaller than the size of the experimental samples.

We view in this article finite-length GNRs rather as graphene rectangles, so that we have named them *rect*angulenes. We have recently been able to solve analytically the tight-binding model of non-chiral rectangulenes of arbitrary length and width by mapping the model to a wave-guide of finite-length SSH chains [38]. This solution has allowed us to unveil explicitly the bulk-boundary correspondence [39] in graphene. We have also provided a detailed mapping between DFT-simulated rectangulenes and a simple two-site Hubbard model of the edge states of narrow ribbons.

We expand here our previous development to a full analytical solution of the MF Hubbard model of graphene rectangulenes. This new development allows us to simulate undoped and doped rectangulenes of any given size, ranging from graphenoid molecules all the way to lengths and widths of several hundreds of nanometers or even micrometers, that we regard as the bulk limit.

Our solution is relevant because it addresses current issues in different fields of physics, chemistry and materials science. It is also important because it allows us to address theoretically the typical graphene sizes happening in experimental samples. The solution therefore opens the way to accurate and realistic theoretical descriptions of an array of electronic, magnetic, transport, thermoelectric and optical phenomena of real-life graphene devices. The solution can also be extended in the future to more sophisticated descriptions of strong correlations like the GW approximation [40] or Dynamical Mean Field theory [41].

We perform a basis change from site creation and de-

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struction operators to the basis of bulk and edge eigenstates. One of the central results of this article concerns the Coulomb integrals, because they can all be determined analytically. The resulting Hamiltonian is therefor fully known with explicit expressions in terms of U/t. Former DFT and MF calculations were numerically very costly for sizes of about 50 nm, while simulations for sizes larger than 100-200 nm were beyond the power of today's computers. However, we demonstrate that our analytical MF solution delivers all the physics that had to be previously computed numerically. We illustrate this by performing the popular MF paramagnetic, ferromagnetic and antiferromagnetic solutions (PM, FM and AFM, respectively). The figures shown in this article have been plotted with the aid of a simple matlab script running in a laptop. Site occupation calculations lasted the longest, with rectangulenes of size 200  $nm \times 400$  nm taking four to five minutes.

The layout of this article is as follows. Section II summarizes the key results of our previous solution on the non-interacting tight-binding model [38], and introduces the notation and terminology needed henceforth. Section III explains the change from the original site creation and destruction operators to the basis of bulk and edge eigenstates, and determines all the Coulomb integrals. The final result in the section is the complete reformulation of the Hubbard model in the eigen-state basis. Section IV develops the generic MF decomposition and then shows the PM, FM and AFM solutions. We compute eigenenergies, addition energies and site charge and spin occupations. These occupations allow us to rewrite the MF Hamiltonian in the site-basis. We introduce the *edge-only doping* regime and use it to analyse the impact of doping the rectangulenes. We also discuss how to release this approximation to address larger doping regimes. Section V summarizes our results and closes this article.

### II. SOLUTION OF THE TIGHT-BINDING MODEL OF A GRAPHENE RECTANGULENE

We summarize below key results of our solution of the tight-binding Hamiltonian of the rectangulene drawn in figure (1) (a). The figure shows that the rectangulene is pierced by small rectangles that constitute the different unit cells. Cell coordinates are  $\mathbf{R} = (R_x, R_y)$ , where  $R_x$  and  $R_y$  are integer numbers running from 1 to  $M_x$  and from 1 to  $M_y$ , respectively. The width along the Y-axis can also be characterized by the number of horizontal bonds  $N = 2M_y - 1$ . The unit cell, depicted in Figure (1) (b), contains two  $\mathcal{A}$ -atoms and two  $\mathcal{B}$ -atoms, that we label  $\mathcal{A}_1, \mathcal{A}_2, \mathcal{B}_1$  and  $\mathcal{B}_2$ , respectively. We measure lengths along the X- and Y-axes in units of  $\sqrt{3}c$  and c, respectively, where c = 2.46 Å is graphene's lattice constant. The atoms' coordinates are then



FIG. 1. (a) Rectangulene with dimensions  $M_x \times M_y$ .  $\mathcal{A}/\mathcal{B}$  atoms are indicated by dark/bright red circles. Fake atoms are indicated by blue circles. Each unit cell is surrounded with a grey dotted box. (b) Each unit cell contains two  $\mathcal{A}$  and two  $\mathcal{B}$  atoms, whose internal coordinates are written in Eq. (1).

$$\mathbf{r}_{\mathcal{A}_{1}} = \begin{pmatrix} 0\\0 \end{pmatrix}, \ \mathbf{r}_{\mathcal{B}_{1}} = \begin{pmatrix} -2/3\\0 \end{pmatrix}$$
$$\mathbf{r}_{\mathcal{A}_{2}} = \begin{pmatrix} -1/2\\-1/2 \end{pmatrix}, \ \mathbf{r}_{\mathcal{B}_{2}} = \begin{pmatrix} -1/6\\-1/2 \end{pmatrix}$$
(1)

We introduce for later use the unit cell basis states

$$|\mathbf{R}_{i}\rangle = (|\mathbf{R}, \mathcal{A}_{i}\rangle, |\mathbf{R}, \mathcal{B}_{i}\rangle), \ i = 1, 2$$
 (2)

The rectangulene boundary conditions determine the set of eigen-states of the rectangulene. These correspond to the allowed  $\mathbf{\bar{k}} = (\bar{k}_x, \bar{k}_y) = (\sqrt{3} k_x c, k_y c)$  wavevectors. Notice that we have introduced here dimensionless units for consistency with our choice of real-space unit lengths, as well as because the algebraic expressions are simpler. Figure (2) summarizes the **k**-vector grid, that covers a rectangular area in reciprocal space, where  $\bar{k}_x \in (0, 2\pi]$  and  $\bar{k}_y \in (0, \pi]$ . The segment  $\bar{k}_x \in (\pi, 2\pi]$  with  $\bar{k}_y = \pi$  is excluded to avoid state double-counting. The  $\bar{k}_y$  quantization condition is seen in the figure as horizontal red lines at values given by

$$\bar{k}_y = \bar{k}_m = \pi \frac{m}{M_y}, \ m = 1, 2, ..., M_y$$
 (3)

For a given  $\bar{k}_m$ , there exist a set of  $2M_x \bar{k}_x$  wave-vectors that we denote  $\bar{k}_{m\alpha}$  where  $\alpha = 1, 2, ..., 2M_x$ . These



FIG. 2. Two-dimensional plot of the mesh of allowed **k**-vectors for a rectangulene with dimensions  $(M_x, M_y) = (10, 11)$ . The red lines correspond to the  $\bar{k}_y$  quantized values. Blue lines correspond to solving Eq. (7) for  $\bar{k}_y$  as a function of  $\bar{k}_x$ . Black dots at the intersections between blue and red lines correspond to bulk states. Green dots correspond to edge states.

occur at the intersections of the red and blue lines in Figure (2). The resulting black and green dots in the figure mark the allowed  $(\bar{k}_x, \bar{k}_y) = (\bar{k}_{m\alpha}, \bar{k}_m)$  that define the eigen-states of the rectangulene. We find a critical *y*-wavevector

$$\bar{k}_m^c = 2 \cos^{-1} \frac{M_x}{2M_x + 1} \gtrsim \frac{2}{3}\pi$$
 (4)

so that all  $\bar{k}_m$  smaller or larger than  $k_m^c$  have either  $2M_x$ or  $2M_x - 1 \bar{k}_{m\alpha}$  real wave-vectors, respectively. These corresponds to bulk rectangulene states, and are marked by black dots in Figure (2). The missing  $\bar{k}_{m\alpha=2M_x}$  wavevector whenever  $\bar{k}_m > \bar{k}_m^c$  is sketched as a green dot in the figure and is found by letting  $\bar{k}_{m\alpha=2M_x} = 2\pi - i q_m$ become complex. The corresponding eigen-state is an edge state at the zigzag edges whose decay length is  $q_m^{-1}$ . As a consequence, the number of allowed **k**-vectors is equal to the number of unit cells in the rectangulene,  $2M_x \times (M_y - 1/2) = M_x \times N$ , and the number of edge states is

$$N^{\text{edge}} = \text{Floor}\left(\left(1 - \frac{2}{\pi}\cos^{-1}\frac{M_x}{2M_x + 1}\right)M_y\right) \quad (5)$$

The explicit values of the bulk  $\bar{k}_{m\alpha}$  wave-vectors are found by replacing  $\bar{k}_y$  by  $\bar{k}_m$  in the equations for graphene's order parameter, Bloch Hamiltonian component and Bloch phase:

t

$$\Delta_y = 2 \cos(\bar{k}_y/2)$$

$$f_{xy} = f_{xy}^R + i f_{xy}^I = 1 + \Delta_y e^{i\frac{\bar{k}_x}{2}}$$

$$an \theta_{xy} = \frac{f^I}{f^R} = \frac{\Delta_y \sin(\bar{k}_x/2)}{1 + \Delta_y \cos(\bar{k}_x/2)}$$
(6)

and solving for  $\bar{k}_x$  the equation

$$M_x \,\bar{k}_x + \theta_{xy} = \alpha \pi \tag{7}$$

where  $\bar{k}_x \in (0, 2\pi)$  and  $\alpha$  is an integer number. Alternatively, Equation (7) can be seen as an implicit equation for  $\bar{k}_y$  as a function of  $\bar{k}_x$ , that we plot as blue lines in Figure (2). Then, the grid of allowed  $(\bar{k}_{m\alpha}, \bar{k}_m)$  is given by the all the intersections of the red and blue lines. The remaining edge wave-vector is the solution of the equation

$$\tanh\left(M_x q_m\right) = \frac{\Delta_m \sinh\left(q_m/2\right)}{1 - \Delta_m \cosh\left(q_m/2\right)} \tag{8}$$

where  $\Delta_m = 2 \cos(\bar{k}_m/2)$ .

The rectangulene bulk and edge eigen-energies are found by inserting the grid of allowed wave-vectors into graphene's bulk dispersion relation. We find

$$\epsilon_{m\alpha\tau}^{B} = \tau \epsilon_{m\alpha}^{B} = \tau \sqrt{1 + \Delta_{m}^{2} + 2\Delta_{m} \cos\left(\bar{k}_{m\alpha}/2\right)}(9)$$
  
$$\epsilon_{m\tau}^{E} = \tau \epsilon_{m}^{E} = \sqrt{1 + \Delta_{m}^{2} - 2\Delta_{m} \cosh\left(q_{m}/2\right)}$$

The band index  $\tau = \pm 1$  labels the two eigen-states existing for each wave-vector, so that the number of eigenstates is equal to the number of atoms  $2 M_x N$ .

The explicit expressions for the rectangulene bulk and edge states are

$$|\phi_{m\alpha\tau}\rangle = \sum_{R_{x,y}=1}^{M_{x,y}} \sum_{i=1,2} |\mathbf{R}^{i}\rangle \frac{2f_{m,i}(R_{y}) \phi_{m\alpha,i}(R_{x})}{(\mathcal{M}_{x} M_{y} \Lambda_{m\alpha}^{\phi})^{1/2}}$$
(10)  
$$|\psi_{m\tau}\rangle = \sum_{R_{x,y}=1}^{M_{x,y}} \sum_{i=1,2} |\mathbf{R}^{i}\rangle \frac{2f_{m,i}(R_{y}) \psi_{m,i}(R_{x})}{(\mathcal{M}_{x} M_{y} \Lambda_{m}^{\psi})^{1/2}}$$

with

$$\mathcal{M}_{x} = 4M_{x} + 1 \tag{11}$$

$$f_{m,i}(R_{y}) = \sin\left(\bar{k}_{m}\left(R_{y} - d_{i}\right)\right)$$

$$\phi_{m\alpha,i}(R_{x}) = \begin{pmatrix}\phi_{m\alpha,i}^{A}\\\phi_{m\alpha,i}^{B}\end{pmatrix} = \begin{pmatrix}-\tau\left(-1\right)^{\alpha}\sin\left(\bar{k}_{m\alpha}\left(R_{x} - d_{i}\right)\right)\\\sin\left(\bar{k}_{m\alpha}\left(M_{x} + 1 - \left(R_{x} + d_{i}\right)\right)\right)\end{pmatrix}$$

$$\psi_{m,i}(R_{x}) = \begin{pmatrix}\psi_{m,i}^{A}\\\psi_{m,i}^{B}\end{pmatrix} = (-1)^{2d_{i}}\begin{pmatrix}-\tau\sinh\left(q_{m}\left(R_{x} - d_{i}\right)\right)\\\sinh\left(q_{m}\left(M_{x} + 1 - \left(R_{x} + d_{i}\right)\right)\right)\end{pmatrix}$$

where  $d_1 = 0$  and  $d_2 = 1/2$ , and the normalization factors are

$$\Lambda_{m\alpha}^{\phi} = F_{m\alpha}^{1} - \delta_{\bar{k}_{m},\pi} F_{m\alpha}^{2} / \mathcal{M}_{x}$$
(12)  
$$\Lambda_{m}^{\psi} = G_{m}^{1} \sinh\left(\mathcal{M}_{x} q_{m} / 2\right)$$

We have introduced here the following functions

$$F^{1}(k) = 1 - \frac{\sin(\mathcal{M}_{x} k/2)}{\mathcal{M}_{x} \sin(k/2)}$$
(13)  

$$F^{2}(k) = 1 - \frac{\cos(\mathcal{M}_{x} k/2)}{\mathcal{M}_{x} \cos(k/2)}$$
  

$$G^{1}(q) = \frac{1}{\mathcal{M}_{x} \sinh(q/2)} - \frac{1}{\sinh(\mathcal{M}_{x} q/2)}$$
  

$$G^{2}(q) = \frac{1}{\mathcal{M}_{x} \cosh(q/2)} - \frac{1}{\cosh(\mathcal{M}_{x} q/2)}$$

where  $F_{m\alpha}^1 = F^1(\bar{k}_{m\alpha}), \ G_m^1 = G^1(q_m)$  and so forth.

We close this section by noting that the solution outlined above can also be understood by realizing that we have decomposed the rectangulene as a wave-guide of open-ended SSH chains having  $2M_x$  sites each and topological order parameter  $\Delta_m$ . Those chains having  $\Delta_m < 1$  or  $\Delta_m > 1$  are topological or trivial because their winding number is 1 or 0, respectively [24]. The bulkboundary correspondence [39] is explicitly established by noting that the winding number condition enters into the  $\bar{k}_{m\alpha}$  and  $q_m$  quantization equations (7) and (8).

# III. HUBBARD MODEL OF A GRAPHENE RECTANGULENE

# A. Transformation to the eigen-state basis

The mean-field solution to the Hubbard model of a rectangulene is initiated by expanding site-creation and annihilation operators in the basis of rectangulene eigenstates

$$\begin{pmatrix} \hat{a}_{\mathbf{R}i\sigma} \\ \hat{b}_{\mathbf{R}i\sigma} \end{pmatrix} = \sum_{m\alpha\tau} \begin{pmatrix} \langle \mathbf{R}, \mathcal{A}_i | \phi_{m\alpha\tau} \rangle \\ \langle \mathbf{R}, \mathcal{B}_i | \phi_{m\alpha\tau} \rangle \end{pmatrix} \hat{\phi}_{m\alpha\tau\sigma} + (14)$$
$$+ \sum_{m\tau} \begin{pmatrix} \langle \mathbf{R}, \mathcal{A}_i | \psi_{m\tau} \rangle \\ \langle \mathbf{R}, \mathcal{B}_i | \psi_{m\tau} \rangle \end{pmatrix} \hat{\psi}_{m\tau\sigma}$$

We split the site number operators into bulk and edge pieces,

$$\hat{n}_{\mathbf{R}i\sigma} = \hat{n}_{\mathbf{R}i\sigma}^{B} + \hat{n}_{\mathbf{R}i\sigma}^{E}$$

$$\hat{n}_{\mathbf{R}i\sigma}^{B} = \sum_{m\alpha} \frac{4 f_{m,i}^{2}}{\mathcal{M}_{x} M_{y} \Lambda_{m\alpha}^{\phi}} \begin{pmatrix} (\phi_{m\alpha,i}^{\mathcal{A}})^{2} \\ (\phi_{m\alpha,i}^{\mathcal{B}})^{2} \end{pmatrix} \hat{n}_{m\alpha\sigma}^{B}$$

$$\hat{n}_{\mathbf{R}i\sigma}^{E} = \sum_{m} \frac{4 f_{m,i}^{2}}{\mathcal{M}_{x} M_{y} \Lambda_{m}^{\psi}} \begin{pmatrix} (\psi_{m,i}^{\mathcal{A}})^{2} (\hat{n}_{m\sigma}^{E} - \hat{P}_{m\sigma}) \\ (\psi_{m,i}^{\mathcal{B}})^{2} (\hat{n}_{m\sigma}^{E} + \hat{P}_{m\sigma}) \end{pmatrix}$$
(15)

where we have dropped cross bulk-edge, bulk  $(m, \alpha) \leftrightarrow (m', \alpha')$ , bulk  $(m, \alpha, \tau) \leftrightarrow (m, \alpha, \tau')$  and edge  $m \leftrightarrow m'$  terms, but have kept interband edge states  $(m, \tau) \leftrightarrow (m, \tau')$  because they are degenerate. Furthermore, we have introduced the following band-summed and band-

mixing operators

$$\hat{n}^{B}_{m\alpha\sigma} = \sum_{\tau=\pm} \hat{n}_{m\alpha\tau\sigma} = \sum_{\tau=\pm} \hat{\phi}^{\dagger}_{m\alpha\tau\sigma} \hat{\phi}_{m\alpha\tau\sigma} \quad (16)$$
$$\hat{n}^{E}_{m\sigma} = \sum_{\tau=\pm} \hat{n}_{m\tau\sigma} = \sum_{\tau=\pm} \hat{\psi}^{\dagger}_{m\tau\sigma} \hat{\psi}_{m\tau\sigma}$$
$$\hat{P}_{m\sigma} = \sum_{\tau=\pm} \hat{P}_{m\tau\sigma} = \sum_{\tau=\pm} \hat{\psi}^{\dagger}_{m\tau\sigma} \hat{\psi}_{m\bar{\tau}\sigma}$$

where  $\bar{\tau} = -\tau$ .

The second-quantized version of the rectangulene noninteracting tight-binding Hamiltonian is simply

$$\hat{H}^{0} = \sum_{m\alpha\tau\sigma} \tau \,\epsilon^{B}_{m\alpha} \,\hat{n}^{B}_{m\alpha\tau\sigma} + \sum_{m\tau\sigma} \tau \,\epsilon^{E}_{m} \,\hat{n}^{E}_{m\tau\sigma} \quad (17)$$

The full rectangulene's Hubbard Hamiltonian is:

$$\hat{H} = \hat{H}^0 + \hat{V}^{ee} = \hat{H}^0 + U \sum_{\mathbf{R}i} \hat{n}_{\mathbf{R}i\uparrow} \hat{n}_{\mathbf{R}i\downarrow} \quad (18)$$

#### B. Coulomb integrals

Using Eq. (15), we decompose the interacting term in the Hamiltonian into bulk, edge and crossed contributions as follows:

$$\hat{V}^{ee} = \hat{V}^{B} + \hat{V}^{E} + \hat{V}^{BE}$$
(19)
$$\hat{V}^{B} = \sum_{mm'\alpha\alpha'} U^{B}_{m\alpha,m'\alpha'} \hat{n}^{B}_{m\alpha\uparrow} \hat{n}^{B}_{m'\alpha'\downarrow}$$

$$\hat{V}^{E} = \sum_{mm'} U^{E}_{m,m'} \left( \hat{n}^{E}_{m\uparrow} \hat{n}^{E}_{m'\downarrow} + \hat{P}_{m\uparrow} \hat{P}_{m'\downarrow} \right)$$

$$\hat{V}^{BE} = \sum_{mm'\alpha\sigma} U^{BE}_{m\alpha,m'} \hat{n}^{B}_{m\alpha\sigma} \hat{n}^{E}_{m'\bar{\sigma}}$$

with  $\bar{\sigma} = -\sigma$ . The Coulomb matrix elements are

$$U^{B}_{m\alpha,m'\alpha'} = \frac{\mathcal{C}}{\Lambda^{\phi}_{m\alpha}\Lambda^{\phi}_{m'\alpha'}} \sum_{i=1,2} U^{y}_{m,m',i} U^{B,x}_{m\alpha,m'\alpha',i} (20)$$
$$U^{E}_{m,m'} = \frac{\mathcal{C}}{\Lambda^{\psi}_{m}\Lambda^{\psi}_{m'}} \sum_{i=1,2} U^{y}_{m,m',i} U^{E,x}_{m,m',i}$$
$$U^{BE}_{m\alpha,m'} = \frac{\mathcal{C}}{\Lambda^{\phi}_{m\alpha}\Lambda^{\psi}_{m'}} \sum_{i=1,2} U^{y}_{m,m',i} U^{BE,x}_{m\alpha,m',i}$$

where

$$\mathcal{C} = \frac{32 U}{\mathcal{M}_x^2 \mathcal{M}_y^2}$$

$$U_{m\alpha,m'\alpha',i}^{B,x} = \sum_{R_x} \left( \phi_{m\alpha,i}^{\mathcal{A}}(R_x) \ \phi_{m'\alpha',i}^{\mathcal{A}}(R_x) \right)^2$$

$$U_{m,m',i}^{E,x} = \sum_{R_x} \left( \psi_{m,i}^{\mathcal{A}}(R_x) \ \psi_{m',i}^{\mathcal{A}}(R_x) \right)^2$$

$$U_{m\alpha,m',i}^{BE,x} = \sum_{R_x} \left( \phi_{m\alpha,i}^{\mathcal{A}}(R_x) \ \psi_{m',i}^{\mathcal{A}}(R_x) \right)^2$$

$$U_{m,m',i}^{Y} = \sum_{R_y} \left( f_{m,i}(R_y) \ f_{m',i}(R_y) \right)^2$$
(21)

The above sums can be evaluated analytically. So after some straightforward but lengthy algebra we find that

$$U_{m\alpha,m'\alpha'}^{B} = \mathcal{D} \frac{\delta_{mm'}^{+} C_{m\alpha,m'\alpha'}^{B,+} + \delta_{mm'}^{-} C_{m\alpha,m'\alpha'}^{B,-} / \mathcal{M}_{x}}{\Lambda_{m\alpha}^{\phi} \Lambda_{m'\alpha'}^{\phi}}$$
$$U_{m,m'}^{E} = \mathcal{D} \frac{\delta_{mm'}^{+} C_{m,m'}^{E,+} + \delta_{mm'}^{-} C_{m,m'}^{E,-} / \mathcal{M}_{x}}{G_{m}^{1} G_{m'}^{1}}$$
$$U_{m\alpha,m'}^{BE} = 2\mathcal{D} \frac{\delta_{mm'}^{+} C_{m\alpha,m'}^{BE,+} + \delta_{mm'}^{-} C_{m\alpha,m'}^{BE,-} / \mathcal{M}_{x}}{\Lambda_{m\alpha} G_{m'}^{1}}$$

We have introduced the following short-hand notation to simplify the expressions above

$$\mathcal{D} = \frac{U}{2 \mathcal{M}_x M_y}$$

$$\delta^+_{mm'} = 1 + \frac{1}{2} \left( \delta_{m,m'} + \delta_{m,M_y} \delta_{m',M_y} \right)$$

$$\delta^-_{mm'} = \frac{1}{2} \delta_{m+m',M_y} - \left( \delta_{m,M_y} + \delta_{m',M_y} \right)$$
(22)

The formulae for the coefficients  $C^B$ ,  $C^E$  and  $C^{BE}$  are rather cumbersome and we relegate them to the appendix. We have also found the important sum rules

$$\frac{U}{2} = \mathcal{U}_{m\alpha}^{B} + \mathcal{U}_{m\alpha}^{EB}$$

$$= \mathcal{U}_{m}^{E} + \mathcal{U}_{m}^{BE}$$
(23)

where the summed Coulomb integrals

$$\mathcal{U}_{m\alpha}^{B} = \sum_{m'\alpha'} U_{m\alpha,m'\alpha'}^{B}$$

$$\mathcal{U}_{m\alpha}^{BE} = \sum_{m'} U_{m\alpha,m'}^{BE}$$
(24)

give a measure of the relevance of bulk and edge contributions to the renormalization of the dispersion relation of bulk states. Conversely, the sums

$$\mathcal{U}_{m}^{E} = \sum_{m'} U_{m,m'}^{E} \qquad (25)$$
$$\mathcal{U}_{m}^{EB} = \sum_{m'\alpha'} U_{m'\alpha',m}^{BE}$$

give a measure of the contributions of edge and bulk states to the renormalization of the dispersion relation of edge states. We plot the values of these different Coulomb integrals as a function of  $\bar{k}_m$  in Figure (3), for a rectangulene with dimensions  $(M_x, M_y) = (30, 41)$ , e.g.:  $12.8 \times 10.1$  nm. Interestingly,  $\mathcal{U}^B$  is almost constant and approximately equal to 0.5 U for all  $\bar{k}_y$  wave-numbers. Similarly,  $\mathcal{U}^{EB}$  is rather small but non-zero. In contrast,  $\mathcal{U}^E$  and  $\mathcal{U}^{BE}$  are both different from zero and feature a strong dependence with  $\bar{k}_m$ . We believe that the most important message here however is that bulk states have a much larger contribution to the edge-state dispersion relation than the proper edge states.



FIG. 3. Coulomb integrals  $\mathcal{U}_{m\alpha}^{B}$ ,  $\mathcal{U}_{m\alpha}^{EB}$ ,  $\mathcal{U}_{m}^{BE}$  and  $\mathcal{U}_{m}^{E}$  in units of U (black, blue, red and green dots, respectively) as a function of the wave-number  $\bar{k}_{m}$  for a rectangulene with dimensions  $(M_x, M_y) = (30, 41)$ .

### C. Bulk and edge Hubbard Hamiltonians

We rewrite the Hubbard Hamiltonian is its final form

$$\hat{H} = \hat{H}^B + \hat{H}^E + \hat{V}^{\rm BE} \tag{26}$$

where the bulk and edge Hamiltonians are as follows

$$\hat{H}^{B} = \sum_{m\alpha\tau\sigma} \tau \,\epsilon^{B}_{m\alpha} \,\hat{n}^{B}_{m\alpha\tau\sigma} + \sum_{m\alpha,m'\alpha'} U^{B}_{m\alpha,m'\alpha'} \,\hat{n}^{B}_{m\alpha\uparrow} \hat{n}^{B}_{m'\alpha'\downarrow}$$

$$\hat{H}^{E} = \sum_{m\tau\sigma} \tau \,\epsilon^{E}_{m} \,\hat{n}^{E}_{m\tau\sigma} + \sum_{mm'} U^{E}_{mm'} \left( \hat{n}^{E}_{m\uparrow} \hat{n}^{E}_{m'\downarrow} + \hat{P}_{m\uparrow} \hat{P}_{m'\downarrow} \right)$$
(27)

### D. Occupations and magnetization

The sublattice- and spin-resolved total occupations are

$$\begin{pmatrix} \mathcal{N}_{\sigma}^{\mathcal{A}} \\ \mathcal{N}_{\sigma}^{\mathcal{B}} \end{pmatrix} = \frac{1}{2} \sum_{m\alpha} \begin{pmatrix} \langle \hat{n}_{m\alpha\sigma}^{B} \rangle \\ \langle \hat{n}_{m\alpha\sigma}^{B} \rangle \end{pmatrix} + \frac{1}{2} \sum_{m} \begin{pmatrix} \langle \hat{n}_{m\sigma}^{E} \rangle + \langle \hat{P}_{m\sigma} \rangle \\ \langle \hat{n}_{m\sigma}^{E} \rangle - \langle \hat{P}_{m\sigma} \rangle \end{pmatrix}$$
(28)

where  $\mathcal{N}_{\sigma} = \mathcal{N}_{\sigma}^{\mathcal{A}} + \mathcal{N}_{\sigma}^{\mathcal{B}}$  and  $\mathcal{N} = \mathcal{N}^{B} + \mathcal{N}^{E} = \mathcal{N}_{\uparrow} + \mathcal{N}_{\downarrow}$ . The magnetization per edge state can have contributions from both bulk and edge states

$$m = \frac{\mathcal{N}_{\uparrow} - \mathcal{N}_{\downarrow}}{N^{\text{edge}}} = m^B + m^E \qquad (29)$$
$$m^B = \frac{1}{N^{\text{edge}}} \sum_{m\alpha\sigma} \sigma \langle \hat{n}^B_{m\alpha\sigma} \rangle$$
$$m^E = \frac{1}{N^{\text{edge}}} \sum_{m\sigma} \sigma \langle \hat{n}^E_{m\sigma} \rangle$$

although for low enough doping levels, only edge states contribute. The sublattice-unbalanced magnetization

$$m^{\rm st} = \frac{1}{N^{\rm edge}} \sum_{\sigma} \sigma \left( \mathcal{N}_{\sigma}^{\mathcal{B}} - \mathcal{N}_{\sigma}^{\mathcal{A}} \right) = \frac{1}{N^{\rm edge}} \sum_{m\sigma} \sigma \left\langle \hat{P}_{m\sigma} \right\rangle$$
(30)

is a measure of the staggered magnetization across edges. Fernandez-Rossier introduced [12] a spin dipole operator which is in essence the band-mixing operator  $\hat{P}_{m\sigma}$  defined in the present article.

### IV. MEAN-FIELD SOLUTIONS OF THE HUBBARD MODEL OF A GRAPHENE RECTANGULENE

### A. Bulk states

We apply first a mean-field approximation to the bulk piece of the Hamiltonian, where  $n^B_{m\alpha\tau\sigma} = \langle \hat{n}^B_{m\alpha\tau\sigma} \rangle$ . We find

$$\hat{H}_{MF}^{B} = \sum_{m\alpha\tau\sigma} \xi_{m\alpha\tau\sigma}^{B} \hat{n}_{m\alpha\tau\sigma}^{B}$$

$$\xi_{m\alpha\tau\sigma}^{B} = \tau \epsilon_{m\alpha}^{B} + \sum_{m'\alpha'} U_{m\alpha,m'\alpha'}^{B} n_{m'\alpha'\bar{\sigma}}^{B} + \sum_{m'} U_{m\alpha,m'}^{BE} n_{m'\bar{\sigma}}^{E}$$
(31)

where the dispersion relation is spin-split because of the bulk-edge cross-terms. The bulk contribution to the total energy is

$$E_T^B = \sum_{m\alpha\tau\sigma} \xi_{m\alpha\tau\sigma}^B n_{m\alpha\tau\sigma} - E_{\rm dc}^B \qquad (32)$$
$$E_{\rm dc}^B = \sum_{mm'\alpha\alpha'} U_{m\alpha,m'\alpha'}^B n_{m\alpha\uparrow}^B n_{m'\alpha'\downarrow}^B$$

We shall assume for now that the rectangulene is in the edge-only doping regime, where doping is low enough that missing/extra electrons only affect edge states. As a consequence, bulk states will always be half-filled,  $n_{m\alpha-\sigma} = 1$  and  $n_{m\alpha+\sigma} = 0$ . Hence the number of electrons residing in bulk states is  $\mathcal{N}^B = 2(M_x N - N^{\text{edge}})$ , where the number of edge states  $N^{\text{edge}}$  is given in Eq. (5). The bulk dispersion relation simplifies to

$$\xi^B_{m\alpha\tau\sigma} = \tau \,\epsilon^B_{m\alpha} + \mathcal{U}^B_{m\alpha} + \sum_{m'} U^{BE}_{m\alpha,m'} \,n^E_{m'\bar{\sigma}} \quad (33)$$

And the contribution of bulk states to the rectangulene total energy is

$$E_T^B = \sum_{m\alpha} \left( \xi_{m\alpha-\uparrow}^B + \xi_{m\alpha-\downarrow}^B - \mathcal{U}_{m\alpha}^B \right) \tag{34}$$

We also have that the bulk contribution to the magnetization is identically zero,  $m^B = 0$ .

The apparently anodyne result in Eq. (33) when paired with the sum rule in Eq. (25) amounts to a huge simplification that enables us to carry out calculations for huge rectangulenes, because the number of Coulomb matrix elements to be calculated and stored is reduced from  $M_x^2 N^2$  to  $M_x NN^{edge}$ .

### B. Edge states

We perform now a mean-field approximation to the edge piece of the Hamiltonian so that  $n_{m\tau\sigma}^E = \langle \hat{n}_{m\tau\sigma}^E \rangle$  and  $P_{m\tau\sigma} = \langle \hat{P}_{m\tau\sigma} \rangle$ . We also have the band-summed relationships  $n_{m\sigma}^E = n_{m-\sigma}^E + n_{m+\sigma}^E$  and  $P_{m\sigma} = P_{m-\sigma} + P_{m+\sigma}$ . The edge mean-field Hamiltonian becomes

$$\hat{H}_{MF}^{E} = \sum_{m\tau\sigma} \xi_{m\tau\sigma}^{E} \hat{n}_{m\tau\sigma}^{E} + \sum_{m\sigma} U_{m,m'}^{E} P_{m'\bar{\sigma}} \hat{P}_{m\sigma} (35)$$
$$\xi_{m\tau\sigma}^{E} = \tau \epsilon_{m}^{E} + \mathcal{U}_{m}^{BE} + \sum_{m'} U_{m,m'}^{E} n_{m'\bar{\sigma}}^{E}$$

Diagonalization of the mean-field edge Hamiltonian provides us with the edge eigen-energies  $\xi^E_{m\tau\sigma}$  and edge eigen-states. The edge states' occupations are determined by the equation of state

$$n_{m\sigma}^E = n_F(\xi_{m+\sigma}^E) + n_F(\xi_{m-\sigma}^E)$$
(36)

where  $n_F$  is the Fermi function. The order parameter  $P_{m\sigma}$  is determined by solving the self-consistency equations adequate to each mean-field solution, as discussed below.

We introduce the edge filling  $\delta^E$  by taking half-filling as a reference:

$$\delta^E = \mathcal{N}^E - 2\,N^{\text{edge}} = \sum_{m\sigma} n^E_{m\sigma} - 2\,N^{\text{edge}} \qquad (37)$$

The edge contribution to the rectangulene total energy is determined by the equation

$$E_T^E = \sum_{m\tau\sigma} \xi_{m\tau\sigma}^E n_{m\tau\sigma}^E - E_{dc}^E$$

$$E_{dc}^E = \sum_{mm'} U_{m,m'}^E \left( n_{m\uparrow}^E n_{m'\downarrow}^E + P_{m\uparrow} P_{m'\downarrow} \right) + \sum_m \mathcal{U}_m^{BE} n_m^E$$
(38)

#### C. Paramagnetic solution

The PM mean-field solution is found by setting  $n_{m\tau\uparrow}^E = n_{m\tau\downarrow}^E = n_{m\tau}^E/2$  and  $P_{m\tau\sigma} = 0$ . Then the edge and bulk dispersion relations do not depend on the spin degree of freedom

$$\xi_{m\tau}^{E} = \tau \epsilon_{m}^{E} + \mathcal{U}_{m}^{BE} + \frac{1}{2} \sum_{m'} U_{mm'}^{E} n_{m'}^{E} \qquad (39)$$
  
$$\xi_{m\alpha\tau}^{B} = \tau \epsilon_{m\alpha}^{B} + \mathcal{U}_{m\alpha}^{B} + \frac{1}{2} \sum_{m'} U_{m\alpham'}^{BE} n_{m'}^{E}$$

Finally, the edge double-counting contribution to the total energy is

$$E_{\rm dc}^E = \frac{1}{4} \sum_{mm'} U_{m,m'}^E n_m^E n_{m'}^E + \sum_m \mathcal{U}_m^{BE} n_m^E \quad (40)$$

### D. Ferromagnetic solution

The FM mean-field solution is found by setting  $n_{m\tau\uparrow}^E \neq n_{m\tau\downarrow}^E$  and  $P_{m\tau\sigma} = 0$ . Then the edge and bulk dispersion relations are

$$\xi^{E}_{m\tau\sigma} = \tau \epsilon^{E}_{m} + \mathcal{U}^{BE}_{m} + \sum_{m'} U^{E}_{mm'} n^{E}_{m'\bar{\sigma}} \qquad (41)$$
  
$$\xi^{B}_{m\alpha\tau\sigma} = \tau \epsilon^{B}_{m\alpha} + \mathcal{U}^{B}_{m\alpha} + \sum_{m'} U^{BE}_{m\alpha m'} n^{E}_{m'\bar{\sigma}}$$

and the edge double-counting term is

$$E_{\rm dc}^E = \sum_{mm'} U_{m,m'}^E n_{m\uparrow}^E n_{m'\downarrow}^E + \sum_m \mathcal{U}_m^{BE} n_m^E \quad (42)$$

As shown in our previous work [38], a FM coupling between edge states only occurs for long enough rectangulenes, that is when the  $\mathcal{U}_m^E$  term dominates over the  $\epsilon_m^E$  term. If this is the case, the equation of state can be solved at zero temperature and arbitrary doping  $\delta^E$ . For positive doping values, the majority spin states  $\uparrow$  are completely filled with  $n_{m\uparrow}^E = 2$ . As  $\mathcal{U}_m^E$ increases with m (see Fig. 3), the minority spinstates  $\downarrow$  are filled following the order of m. As m runs from  $m_{\min}^E = M_y - N^{\text{edge}}$  to  $m_{\max}^E = M_y - 1$ , we define a critical  $m_c^E = m_{\min}^E + \text{floor}(\delta^E/2)$ , so:

$$n_{m_{\min}^E:m_c^E-1,\downarrow}^E = 2 \qquad (43)$$

$$n_{m_c^E,\downarrow}^E = \delta^E - 2 \operatorname{floor}(\delta^E/2)$$

$$n_{m=m_c^E+1:m_{\max}^E,\downarrow}^E = 0$$

The dispersion relations can then be written explicitly as

$$\xi_{m\tau\downarrow}^E = \tau \epsilon_m + \frac{U}{2} + \mathcal{U}_m^E \tag{44}$$

$$\begin{split} \xi^E_{m\tau\uparrow} &= \tau \, \epsilon_m + \frac{U}{2} + \left( \sum_{m'=m_{\min}^E}^{m_c^E - 1} - \sum_{m'=m_c+1}^{m_{\max}^E} \right) \, U^E_{m,m'} + \\ &+ U^E_{m,m_c^E} \left( n_{m_c^E,\downarrow}^E - 1 \right) \\ \xi^B_{m\alpha\tau\downarrow} &= \tau \, \epsilon^B_{m\alpha} + \frac{U}{2} + \mathcal{U}^{BE}_{m\alpha} \\ \xi^B_{m\alpha\tau\uparrow} &= \tau \, \epsilon^B_{m\alpha} + \frac{U}{2} + \left( \sum_{m'=1}^{m_c} - \sum_{m'=m_c+2}^{N^{\text{edge}}} \right) \, U^{BE}_{m\alpha,m'} + \\ &+ U^{BE}_{m\alpha,m_c^E} \left( n_{m_c^E,\downarrow}^E - 1 \right) \end{split}$$

Similarly, the FM total energy has the following analytical expression

$$E_T = \sum_{m\alpha\sigma} \xi^B_{m\alpha-\sigma} + \sum_{m\tau\sigma} \xi^E_{m\tau\sigma} n^E_{m\tau\sigma} - \frac{U}{2} (1+\delta^E) - \sum_{m\alpha} \mathcal{U}^{BE}_{m\alpha} - \sum_{mm'} U^E_{m,m'} n^E_{m'\downarrow}$$
(45)

### E. Antiferromagnetic solution

The AFM solution is selected by letting the order parameter  $P_{m\tau\sigma}$  be different from zero. In this case the edge Hamiltonian looks

$$\hat{H}_{MF}^{E} = \sum_{m\tau\sigma} \left(\tau \,\epsilon_{m}^{E} + H_{m\sigma}\right) \hat{n}_{m\tau\sigma}^{E} + \sum_{m\sigma} \Delta_{m\sigma} \hat{P}_{m\sigma}(46)$$
$$H_{m\sigma} = \mathcal{U}_{m}^{BE} + \sum_{m'} U_{m,m'}^{E} \, n_{m'\bar{\sigma}}^{E}$$
$$\Delta_{m\sigma} = \sum_{m'} U_{m,m'}^{E} \, P_{m'\bar{\sigma}}$$

The above Hamiltonian can be rewritten in the following BCS form

$$\sum_{m\sigma} \left( \hat{\psi}_{m+\sigma}^{\dagger} \, \hat{\psi}_{m-\sigma}^{\dagger} \right) \begin{pmatrix} H_{m\sigma} + \epsilon_m & \Delta_{m\sigma} \\ \Delta_{m\sigma} & H_{m\sigma} - \epsilon_m \end{pmatrix} \begin{pmatrix} \hat{\psi}_{m+\sigma} \\ \hat{\psi}_{m-\sigma} \end{pmatrix}$$
(47)

and can be diagonalized by a Bogoliubov transformation so that

$$\hat{H}_{MF}^{E} = \sum_{m\alpha\sigma} \xi_{m\tau\sigma}^{E} \,\hat{\gamma}_{m\alpha\sigma}^{\dagger} \,\hat{\gamma}_{m\alpha\sigma}$$

$$\xi_{m\tau\sigma}^{E} = \xi_{m\tau}^{E} = H_{m\sigma} + \tau \, R_{m} = H_{m\sigma} + \tau \, \sqrt{\epsilon_{m}^{2} + \Delta_{m}^{2}}$$
(48)

where we have considered  $P_{m\sigma} = \sigma P_m$ , so  $\Delta_{m\sigma}^2 = \Delta_m^2$  independent of the spin. Therefore, the edge eigen-energies are spin-degenerate. The eigen-state operators and Bogoliubov coherence factors are

$$\begin{pmatrix} \hat{\gamma}_{m+\sigma} \\ \hat{\gamma}_{m-\sigma} \end{pmatrix} = \begin{pmatrix} u_{m\sigma}^+ & \operatorname{sign}(\Delta_{m\sigma}) \, u_{m\sigma}^- \\ -\operatorname{sign}(\Delta_{m\sigma}) \, u_{m\sigma}^- & u_{m\sigma}^+ \end{pmatrix} \begin{pmatrix} \hat{\psi}_{m+\sigma} \\ \hat{\psi}_{m-\sigma} \end{pmatrix}$$

$$u_{m\sigma}^{\pm} = \frac{1}{\sqrt{2}} \left( 1 \pm \frac{\epsilon_m^E}{R_m} \right)^{1/2}$$

$$(49)$$

Finally, the order parameter can be determined by the conventional BCS self-consistency equations

$$P_{m\sigma} = \frac{\Delta_{m\sigma}}{R_m} \left( n_F(\xi^E_{m+\sigma}) - n_F(\xi^E_{m-\sigma}) \right)$$
(50)

Just like for the FM solution, the AFM coupling between edge states only occurs for long enough rectangulenes [38]. If this is the case, the equation of state can be solved at zero temperature for the AFM solution similarly to the FM case. We find that the occupations are  $n_{m,-\sigma}^E = 1$  and

$$n_{m_{\rm min}^E:m_c^E-1,+\sigma}^E = 1$$

$$n_{m_c^E,+\sigma}^E = \frac{\delta^E}{2} - \text{floor}(\delta^E/2)$$

$$n_{m_c^E+1:m_{\rm max}^E,+\sigma}^E = 0$$
(51)

As a consequence,

$$H_{m\sigma} = \frac{U}{2} + \sum_{m'=m_{\min}^E}^{m_c-1} U_{m,m'}^E + U_{m,m_c}^E n_{m_c+\bar{\sigma}}^E \qquad (52)$$



FIG. 4. Zero-temperature AFM order parameter  $P_m$  of an undoped rectangulene of width N = 1501, that corresponds to 184,7 nm and hosts 500 states. Black, red and green dots correspond to lengths  $M_x = 10$ , 100 and 1000 (4.26, 42,6 and 426 nm, respectively). Dashed lines show the fitting of the results to  $\tanh^4 \left( \mathcal{M}_x \left( \frac{\bar{k}_m}{\pi} - \frac{2}{3} \right) \right)$ 

The order parameter  $P_m(M_x, M_y)$  must be determined by solving numerically equation (50). We find that the absolute value of the order parameter does not depend on the rectangulene's width  $M_y$ . We plot  $P_m(M_x)$ as a function of  $\bar{k}_m$  in Figure 4 for several undoped rectangulene's lengths  $M_x$ , and at zero temperature. We find that  $P_m$  can be approximated by the function  $\tanh^4\left(\mathcal{M}_x\left(\frac{\bar{k}_m}{\pi}-\frac{2}{3}\right)\right)$  to a high accuracy. Furthermore, for large enough  $M_x > 50 - 100$ , the order parameter of a doped rectangulene can be approximated as follows:

$$P_{m_{\min}^{E}:m_{c}^{E}-1} = 0$$

$$P_{m_{c}^{E}} = 1 + \text{floor}(\delta^{E}/2) - \delta^{E}/2$$

$$P_{m_{c}^{E}+1:m_{\max}^{E}} = 1$$
(53)

so that

$$\Delta_{m\sigma} = -\sigma \left( P_{m_c^E} U_{m,m_c^E}^E + \sum_{m'=m_c^E+1}^{m_{\max}^E} U_{m,m'}^E \right) \quad (54)$$

Fernandez-Rossier proposed a phenomenological BCSlike description of band mixing [12] that is consistent with our results above. Similarly, MacDonald and coworkers developed a phenomenological BCS model of inter-edge mixing that is also consistent with our results [14].

### F. Beyond the edge-only doping regime

The *edge-only doping* regime is too restrictive an approximation in several instances. Examples are gate-



FIG. 5. Electronic structure of a  $(M_x, M_y) = (10, 15)$  rectangulene as a function of the  $k_y$  wave-number at an edge filling (a)  $\delta^E = 0$  and (b)  $\delta^E = 4$  electrons. This rectangulene has dimensions 4.3 nm × 3.7 nm, and hosts 8 edge states. The left column plots the non-interacting (top) and mean-field PM electronic structure. The central/right columns plot the mean-field FM/AFM electronic structure for spin-up (top) and spin-down (bottom).

or voltage-biased finite-length 7-AGNR [36] or bulk-size rectangulenes where the Dirac-point gap is negligible. Fortunately, the approximation can be released to include low-lying bulk states within the self-consistency procedure. This can be achieved by choosing a small energy cutoff  $E_c$  so that occupations of bulk states with energies  $|\xi^B_{m\alpha\tau\sigma} - \mu|$  smaller than  $E_c$  are determined selfconsistently, while those above this energy cutoff are frozen at 0 or 1.

#### G. Dispersion relations

The analysis above opens the door to determine easily the electronic structure on rectangulenes of any size in the edge-only doping regime. We will take below a hopping integral t = 2.7 eV, and a Hubbard-U parame-



FIG. 6. Same as in Figure 5, now for a  $(M_x, M_y) = (950, 901)$  rectangulene whose dimensions are 404.7 nm  $\times$  221.6 nm, and host 600 edge states. This rectangulene is made of about 3.5 million atoms.

ter equal to 0.8t, that we found to fit well our previous Density Functional Theory results [38].

A first simple example of a small nano-structure is shown in Figure 5. This rectangulene hosts 8 edge states, that can be easily spotted in the figure. We find the AFM phase to be more stable at zero doping than the FM phase by 2.42 meV, while they are essentially degenerate when doped with 4 electrons. We find that four-electron doping leaves the rectangulene still in the *edge-only* doping regime. This electronic structure follows the well-known trends of undoped and doped infinite-length zigzag GNRs [14]. However, the states here might be better regarded as molecular orbitals rather than Bloch states, and the figure shows explicitly the discrete spectrum of meanfield eigen-energies.

A second example is shown in Figure 6, that corresponds to a bulk-like graphene sheet *with edges*. Here we show only the undoped-sheet dispersion relation, that features both the bulk Dirac cone as well as the quasicontinuum 1-dimensional spectrum corresponding to the edge branches. We find here that the energy gap at the bulk Dirac point is smaller than the lowest edge eigenenergy, so that the edge-only doping regime does not exist for this rectangulene.

Overall, we find that the edge states are always doubledegenerate. There exist branch-degeneracy ( $\tau = \pm$ ) but spin-degeneracy lifting for the FM solution. In contrast, there is spin-degeneracy but branch-degeneracy lifting for the AFM solution.

### H. Addition energies

Recently, single  $M_x = 5$  rectangulenes have been deposited onto ultraclean graphene nanogaps, and the differential conductance as a function of both bias and gate voltage. has been measured. Neat sequences of Coulomb

blockade diamonds have been observed [34–36], whereby the device addition energies have been extracted.

The addition energy of a rectangulene having a total of  ${\mathcal N}$  electrons is

$$E^{add}(\mathcal{N}) = E_T(\mathcal{N}+1) + E_T(\mathcal{N}-1) - 2E_T(\mathcal{N})$$
 (55)

Our exact solution enables us to compute these addition energies for arbitrary dopings. The *edge-only doping* approximation restricts the validity of the calculations to low dopings and lengths  $M_x$  sufficiently small that bulk states have all higher energies than the edge states to be addressed. This approximation can however be released easily as explained in section IV F above.

We have checked that  $E^{add}$  depends on the rectangulene's width  $M_y$  but not on its length  $M_x$ . Koopman's theorem is verified as follows. The FM/AFM solutions have branch/spin degeneracy meaning that  $E^{add}(\mathcal{N} =$ even) = 0, and we have checked that this is the case. We then find that

$$E^{add}(\delta^E = \text{odd}) = \xi^E_{m+1\tau} - \xi^E_{m\tau}$$
 (56)

(57)

for the AFM solution, while  $\tau$  is replaced by  $\sigma$  for the FM solution. Additionally, we find that  $E^{add}$  is the same for the FM and the AFM solutions. We list in Table I the addition energies of a rectangulene with  $M_y = 13$  (e.g.: width 3.2 nm), that can host up to 8 electrons in edge states. The *edge-only doping* regime restricts in this case the rectangulene's lengths to values  $M_x < 40$ , corresponding to lengths of about 17 nm.

TABLE I. Addition energies of a rectangulene of width  $M_y = 13$ .

$\delta^E$	0	1	2	3	4	5	6	7
$E^{add} (\mathrm{meV})$	82	0	86	0	59	0	37	0



FIG. 7. Energy differences (a)  $E_T^{PM} - E_T^{AFM}$  and (b)  $E_T^{FM} - E_T^{AFM}$  for a mesh of  $M_x$  and  $M_y$  values. Dashed lines indicate the appearance of new edge states. Panel (c) shows  $E_T^{FM} - E_T^{AFM}$  in a smaller mesh with more detail..

### I. Energy differences among phases

Jung and MacDonald analyzed phase stabilities of narrow infinite-length zigzag GNRs as a function of doping[14]. We discuss here energy differences of undoped rectangulenes as a function of width and length (see Fig. 7). Overall, we find that the magnetic energy, measured as the energy difference  $E_T^{PM} - E_T^{AFM}$  is roughly independent of  $M_x$ , especially for  $M_x$  larger than about 20. This is expected because for large enough  $M_x$ , the tails of the edge wavefunctions decay enough that tails at opposite edges do not overlap. It is in contrast roughly proportional to  $M_y$ , e.g.: to the number of edge states. We also find that the energy difference among the FM and AFM phases  $E_T^{FM} - E_T^{AFM}$  decays quickly with  $M_x$  so that the edge states at opposite edges become independent for  $M_x$  larger than about 40-60. For the  $M_y$  dependence, we find that  $E_T^{FM} - E_T^{AFM}$  presents oscillations related to the change in the number of edge states of the system.



FIG. 8. Edge magnetization for a rectangulene with dimensions (a)  $(M_x, M_y) = (5, 46)$  that correspond to a rectangulene with dimensions 2.1 nm × 11.3 nm and hosts 26 edge states; (b)  $(M_x M_y) = (15, 5)$  that correspond to 6.4 nm × 1.2 nm and hosts two edge states.

#### J. AFM-phase site-charge and -spin occupations

The site-charge occupation can be split into bulk and edge contributions in the *edge-only doping* regime as follows:

$$n_{\mathbf{R}i} = n_{\mathbf{R}i}^B + n_{\mathbf{R}i}^E \tag{58}$$

$$n_{\mathbf{R}i}^{B} = \sum_{m\alpha} \frac{8 f_{m,i}^{2}}{\mathcal{M}_{x} M_{y} \Lambda_{m\alpha}^{\phi}} \begin{pmatrix} (\phi_{m\alpha,i}^{A})^{2} \\ (\phi_{m\alpha,i}^{B})^{2} \end{pmatrix}$$
(59)

$$n_{\mathbf{R}i}^{E} = \sum_{m} \frac{8 f_{m,i}^{2}}{\mathcal{M}_{x} M_{y} \Lambda_{m}^{\psi}} \begin{pmatrix} (\psi_{m,i}^{\mathcal{A}})^{2} \\ (\psi_{m,i}^{\mathcal{B}})^{2} \end{pmatrix} n_{m}^{E}$$

while the site spin densities are

$$M_{\mathbf{R}i}^{E} = \sum_{m} \frac{8 f_{m,i}^{2}}{\mathcal{M}_{x} M_{y} \Lambda_{m}^{\psi}} \begin{pmatrix} (-\psi_{m,i}^{\mathcal{A}})^{2} \\ (\psi_{m,i}^{\mathcal{B}})^{2} \end{pmatrix} P_{m}$$

These occupations can be computed numerically. Some care must be taken to handle numerical divergencies in the edge summations where hyperbolic sine functions appear. We plot the edge magnetization of two rectangulenes in Figure 8. The first corresponds to a wide but short one, that hosts a sizeable number of edge states. The second one is a long 9-armchair GNR that hosts two edge states.

# K. There and back again: real-space tight-binding Hamiltonian

The real-space mean-field Hubbard Hamiltonian

$$\hat{H}_{MF} = \sum_{\mathbf{R}i\sigma} \sum_{a=A,B} \epsilon^{a}_{\mathbf{R}i\sigma} \hat{n}^{a}_{\mathbf{R}i\sigma} - -t \sum_{\langle \mathbf{R}i\sigma, \mathbf{R}'i'\sigma' \rangle} \left( \hat{a}^{\dagger}_{\mathbf{R}i\sigma} \hat{b}^{\dagger}_{\mathbf{R}'i'\sigma'} + c.c. \right) \quad (60)$$
$$\epsilon^{a}_{\mathbf{R}i\sigma} = \left( \epsilon_{0} + U \, n^{a}_{\mathbf{R}i\sigma} \right)$$

incorporates already electron correlations and edge physics. This Hamiltonian can be used to address more complex phenomena by adding to it additional pieces. Site/hopping disorder can be addressed by replacing  $\epsilon_0$  / t by a random distribution of on-site energies/hopping integrals. Similarly, a Peierls phase can be attached to the hopping integrals to investigate Hall physics. Coupling to a gauge vector can be included to analyse the optical response of the rectangulene to light.

### V. CONCLUSIONS

We have presented in this article a full analytical solution of the mean-field Hubbard model of non-chiral graphene rectangulenes of arbitrary length and width. A central aspect of the article has been the determination of the bulk, edge and cross Coulomb integrals of the rectangulene, that are written here for the first time. This solution is not only an algebraic curiosity, but rather is a powerful and flexible platform that enables us to address a wide range of experimental issues in STM, transport, magnetic, Hall and optical phenomena of real-life graphene rectangulenes. It can also be used to address strong electron correlations, by including GW on top of it, or any other perturbative approach.

### ACKNOWLEDGEMENTS

JF would like to thank Prof. Nazario Martin for confirming him that calling finite-length GNRs by the term *rectangulene* is chemically correct. This research has been funded by MCIN/AEI/10.13039/501100011033/ FEDER, UE via project PID2022-137078NB-100 and by Asturias FICYT under grant AYUD/2021/51185 with the support of FEDER funds.

### APPENDIX

We write in this appendix the explicit expressions for some coefficients appearing in the Coulomb integrals in

$$\begin{split} C^{B,+}_{m\alpha,m'\alpha'} &= 2\,F^{1}_{m\alpha} + 2\,F^{1}_{m'\alpha'} - F^{1}_{+} - F^{1}_{-} \\ C^{B,-}_{m\alpha,m'\alpha'} &= 2\,F^{2}_{m\alpha} + 2\,F^{2}_{m'\alpha'} - F^{2}_{+} - F^{2}_{-} \\ C^{B,-}_{m,m'} &= \left(\coth\left(\mathcal{M}_{x}q_{m}/2\right) + \coth\left(\mathcal{M}_{x}q_{m'}/2\right)\right)G^{1}_{+} + \left(\coth\left(\mathcal{M}_{x}q_{m}/2\right) - \coth\left(\mathcal{M}_{x}q_{m'}/2\right)\right)G^{1}_{-} - \\ &- \frac{2}{\sinh\left(\mathcal{M}_{x}q_{m}/2\right)}G^{1}_{m'} - \frac{2}{\sinh\left(\mathcal{M}_{x}q_{m'}/2\right)}G^{1}_{m} \\ C^{E,-}_{m,m'} &= \left(\coth\left(\mathcal{M}_{x}q_{m}/2\right) \times \coth\left(\mathcal{M}_{x}q_{m'}/2\right) + 1\right)G^{2}_{+} + \left(\coth\left(\mathcal{M}_{x}q_{m}/2\right) \times \coth\left(\mathcal{M}_{x}q_{m'}/2\right) - 1\right)G^{2}_{-} - \\ &- 2\frac{\coth\left(\mathcal{M}_{x}q_{m}/2\right)}{\sinh\left(\mathcal{M}_{x}q_{m'}/2\right)}G^{2}_{m'} \\ C^{BE,+}_{m\alpha,m'} &= G^{1}_{m'} + \frac{1 - F^{1}_{m\alpha}}{\sinh\left(\mathcal{M}_{x}q_{m'}/2\right)} - \\ &- 2\frac{\sinh\left(q_{m'}/2\right)\cos\left(\mathcal{M}_{x}\bar{k}_{m\alpha}/2\right)\cos\left(\bar{k}_{m\alpha}/2\right) + \cosh\left(q_{m'}/2\right)\coth\left(\mathcal{M}_{x}q_{m'}/2\right)\sin\left(\mathcal{M}_{x}\bar{k}_{m\alpha}/2\right)\sin\left(\bar{k}_{m\alpha}/2\right)}{M_{x}\left(\cosh q_{m'} - \cos \bar{k}_{m\alpha}\right)} \\ C^{BE,-}_{m\alpha,m'} &= 1 + \coth\left(\mathcal{M}_{x}q_{m'}/2\right)G^{2}_{m'} - \frac{F^{2}_{m\alpha}}{\sinh\left(\mathcal{M}_{x}q_{m'}\right)} - \\ &- 2\frac{\coth\left(\mathcal{M}_{x}q_{m'}/2\right)G^{2}_{m'} - \frac{F^{2}_{m\alpha}}{\sinh\left(\mathcal{M}_{x}q_{m'}/2\right)} - \\ &- 2\frac{\coth\left(\mathcal{M}_{x}q_{m'}/2\right)G^{2}_{m'} - \frac{F^{2}_{m\alpha}}{\sinh\left(\mathcal{M}_{x}q_{m'}\right)} - \\ &- 2\frac{\coth\left(\mathcal{M}_{x}q_{m'}/2\right)\cosh\left(q_{m'}/2\right)\cos\left(\mathcal{M}_{x}\bar{k}_{m\alpha}/2\right)\cos\left(\bar{k}_{m\alpha}/2\right) + \sinh\left(q_{m'}/2\right)\sin\left(\mathcal{M}_{x}\bar{k}_{m\alpha}/2\right)\sin\left(\bar{k}_{m\alpha}/2\right)}{\cosh\left(q_{m'} + \cos \bar{k}_{m\alpha}\right)} \\ \end{array}$$

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