Magnetic and thermolectric properties of topological graphene heterostructures

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Universidade Federal de Uberlândia Instituto de Física - INFIS Programa de Pós-Graduação em Física Patrícia de Assis Almeida

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To my friends and family. I am nothing without them.

"Honest people don't hide their deeds." (Emily Brontë, Wuthering Heights)

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Resumo

Nesta dissertação, apresentaremos um estudo dos sistemas eletrônicos, magnéticos, de transporte e propriedades termoelétricas de heteroestruturas unidimensionais recentemente sintetizadas que são construídas sobre um 'backbone' constituído por uma nanofita de grafeno de base (AGNR). Tais heteroestruturas foram sintetizadas com sucesso, em superfícies de ouro, através processos químicos. O interesse por essas heteroestruturas aumentou depois que foi previsto que eles deveriam ter bandas topologicamente não triviais perto da energia de Fermi. Esta previsão teórica foi confirmada experimentalmente nos últimos dois anos. Suas propriedades topológicas derivam de estados localizados (eles próprios de natureza topológica) que podem aparecer nas diferentes junções que formam a heteroestrutura. A hibridização desses estados simula, próximo à energia de Fermi, um modelo Su-Schrieffer-Heeger (ou seja, uma cadeia dimerizada), dotando a física de baixa energia do sistema com propriedades topológicas. Aqui, não estudamos suas propriedades topológicas. Em vez disso, usando o formalismo de Landauer, primeiro analisamos suas propriedades termoelétricas, por exemplo, condutâncias eletrônicas e térmicas, bem como o coeficiente de Seebeck, denotados como $G, K_e \in S$, respectivamente. Isso nos permite calcular a termocorrente de resposta linear $I_{th}\Delta T = GS$, bem como a figura de mérito $ZT = GS^2TK_e$ (T significa temperatura), que estima a eficiência de um material na transformação de energia térmica em energia elétrica. Nossos resultados indicam que algumas das heteroestruturas (semicondutoras) analisadas têm uma figura de mérito consideravelmente maior do que a do backbone AGNR sobre os quais são construídas. Em seguida, usando o formalismo tight-binding, mostramos que essas heteroestruturas apresentam uma infinidade de bandas planas, reminiscentes da banda plana [single] já estudada em AGNRs originais. Essas bandas planas ocorrem devido à formação dos chamados 'estados orbitais Wannier', através de um processo de interferência. Depois de analisar cuidadosamente suas propriedades eletrônicas usando um modelo tight-binding, pudemos mostrar, pela primeira vez, através de uma colaboração com um grupo interno da DFT, que dopa essas heteroestruturas leva a um estado fundamental ferromagnético. Uma futura direção de pesquisa neste assunto poderia ser o estudo da interação entre ferromagnetismo e topologia em alguns desses sistemas interessantes.

Palavras-chave: Nanofitas de grafeno, Isolantes topológicos, Magnetismo, Estrutura Eletrônica, Propriedades de transporte e termoelétricas.

Abstract

In this dissertation, we will present a study of the electronic, magnetic, transport and thermoelectric properties of recently synthesized one-dimensional heterostructures that are built upon a 'backbone' constituted by an armchair graphene nanoribbon (AGNR). Such heterostructures have been successfully synthesized, in gold surfaces, through chemical processes. The interest in these heterostructures has greatly increased after it was predicted that they should have topologically non-trivial bands near the Fermi energy. This theoretical prediction has been experimentally confirmed in the last couple of years. Their topological properties stem from localized states (themselves topological in nature) that may appear at the different junctions forming the heterostructure. The hybridization of those states simulates, close to the Fermi energy, a Su-Schrieffer-Heeger model (i.e., a dimerized chain), endowing the low-energy physics of the system with topological properties. Here, we do not study their topological properties. Rather, using the Landauer formalism, we first analyze their thermoelectric properties, viz., charge and electronic thermal conductances, as well as the Seebeck coefficient, denoted as G, K_e , and S, respectively. This allows us to calculate the linear-response thermocurrent $I_{th}\Delta T = GS$, as well as the figure of merit $ZT = GS^2TK_e$ (T stands for temperature), which estimates the efficiency of a material in transforming thermal into electrical energy. Our results indicate that some of the (semiconducting) heterostructures analyzed have a considerably larger figure of merit than that of the AGNR backbone upon which they are built. Next, using the tight-binding formalism, we show that these heterostructures present a multitude of flat-bands, reminiscent of the *single* flat-band already studied in pristine AGNRs. These flat-bands occur due to the formation of so-called 'Wannier orbital states', through a quantum interference process. After carefully analyzing their electronic properties using a tight-binding model, we were able to show, for the first time, through a collaboration with a DFT in-house group, that hole-doping these heterostructures leads to a ferromagnetic ground state. A future research direction in this subject could be the study of the interplay between ferromagnetism and topology in some of these interesting systems.

Keywords: Graphene Nanoribbons, Topological Insulators, Magnetism, Electronic Structure, Transport and Thermoelectric properties.

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CHAPTER

Introduction

Since its discovery almost two decades ago ^[6], graphene has emerged as a realistic possibility for addressing the scalability challenges of the nanoelectronics industry workhorse, the complementary metal-oxide-semiconductor (CMOS) field-effect transistor (FET). Indeed, since the early 2000s, as the gate length for the Silicon FET crossed into the sub-100 nm range and the traditional gate insulator approached 10-nm thicknesses, we witnessed the end of Dennard Scaling ^[7],¹ and the slowing of Moore's law. Thus, research in new materials has been increasingly necessary to pickup the pace of performance improvement that consumers have been used to in the previous half century. As mentioned above, among the many different new materials, graphene has emerged as a very promising alternative. Be it because of its very unique properties in bulk ^[6], as well as the recently acquired capacity for precisely synthesizing quasi-one-dimensional (quasi-1D) nanostructures based on graphene.

Graphene nanoribbons are quasi-1D systems that hold the promise of being important elements in the future of nanoelectronics and spintronics. It has been long recognized that the band structure engineering that one can accomplish, by designing relatively complex heterostructures, may greatly improve device performance by enhancing desirable properties (like electron mobility) and mitigating undesirable ones (like electronic thermal conductance). Besides, some of these heterostructures may also present emergent behavior, like ferromagnetism, through an increase in the importance, for the ground state, of electronic correlations.

In this dissertation, two main aspects will be analyzed in recently synthesized heterostructures ^[2, 8] that are based on armchair graphene nanoribbons (AGNRs). First, using a Landauer formalism, combined with Green's functions calculations, we numerically obtain the thermoelectric properties of these heterostructures. We observe a marked increase in the figure of merit in relation to the AGNR backbone from which the heterostructure originates. Secondly, by using the tight-binding and the Density Functional

¹ Which posits that as transistors get smaller, and thus their density increases, power consumption stays constant and clock operating frequencies can increase.

Theory (DFT) methods, we obtain that, when doping these heterostructures, they develop a ferromagnetic ground state.

Our results in these two fronts serve as examples of the current trend of using graphene heterostructures to produce devices with improved thermoelectric properties, as well as obtaining rare ground states (1D ferromagnetism) that may be used in information processing devices.

This dissertation is divided into six chapters. In chap. (2), we briefly describe the electronic properties of graphene and graphene nanoribbons. Two important types of graphene nanoribbons are the so-called zigzag and armchair graphene nanoribbons (ZGNR and AGNR, respectively). AGNRs, and related heterostructures, are the primary focus of this dissertation. Thus, in chap. (2) we will present mostly the details of the tight-binding approximation for AGNRs, postponing details of the ZGNRs properties to Appendix (D).

In chap. (3), we introduce the AGNR heterostructures denoted N-AGNR-I(n,m) and N-AGNR-S(n,m) ^[2, 8], where N indicates the width of the AGNR backbone upon which the heterostructure is constructed, while n and m basically define the size of the heterostructure unit cell. The letters I and S mean 'Inline' and 'Staggered', where an Inline heterostructure is more symmetric than a Staggered one (thus, it has a smaller unit cell). In this chapter, we present the band structure and density of states, of both heterostructures, analyzing how they depend on the parameters N, n, and m. At the end of the chapter, we briefly outline their synthesis process. The tight-binding method, used for the majority of the results presented here, is described in Appendix (A).

In chap. (4), we describe the Landauer formalism and present a brief introduction to thermoelectric properties, viz., charge and electronic thermal conductances, as well as the Seebeck coefficient, denoted as G, K_e , and S, respectively. This allows us to calculate the linear-response thermocurrent $I_{th}\Delta T = GS$, as well as the figure of merit $ZT = GS^2TK_e$ (T stands for temperature), which estimates the efficiency of a material in transforming thermal into electrical energy. We also present results for these quantities for AGNRs of varying widths. We finish chap. (4) with a detailed analysis, for the Inline and Staggered heterostructures, of the thermoelectric properties introduced at the beginning of chap. (4). We carefully analyze their dependence on the parameters N, n, and m, showing that, for some cases, the figure of merit greatly increases in relation to what was obtained, earlier in chap. (4), for the pristine AGNRs.

In chap. (5), we present a detailed tight binding and DFT analysis of the Inline heterostructures. Our tight-binding results indicate the presence of a multitude of perfectly flat-bands. One of the flat-bands is reminiscent of the one that appears in pristine armchair nanoribbons and has its origin in a quantum mechanical destructive interference effect, dubbed 'Wannier orbital states' by Lin *et al.* ^[9]. The additional flat-bands found in these heterostructures, some reasonably closer to the Fermi level, seem to be generated by a similar interference process. After doing a thorough tight-binding analysis of the band structures of the different kinds of heterostructures, focusing in the properties of the flat-bands, we use DFT to study the possibility of magnetic ground states when placing, through doping, the Fermi energy close to the different flat-bands. Our DFT results confirmed the expectation that these heterostructures, after being appropriately hole-doped, develop a ferromagnetic ground state that seems to require, as in the case of pristine armchair nanoribbons, the presence of a dispersive band crossing the flat-band. In addition, we found a remarkable agreement between the tight-binding and DFT results for the charge density distribution of the so-called Wannier orbital states.

In chap. (6), we present a brief summary of the analyzes carried out, and the conclusions obtained, in this dissertation.

In the Appendices, we briefly present (in this order) the tight-binding method, the Su-Schrieffer-Heeger (SSH) model, details of an analytic solution to the tight-binding method for AGNRs, the same for ZGNRs, the tight-binding Hamiltonian for an N-AGNR(1,3) heterostructure, in real and reciprocal spaces, the addition of next-nearest-neighbor hoppings to the Inline heterostructures, DFT results for Staggered heterostructures, and, finally, the numerical codes (in Fortran) used in this dissertation.

CHAPTER 2

Two-dimensional graphene and graphene nanoribbons

2.1 Graphene

Carbon atoms that arrange themselves in a honeycomb-like crystal lattice are responsible for giving rise to graphene. This material is famous for being the first planar (2D) system, which implies that the graphene sheet is a single atom thick, and this was accomplished in the laboratory in 2004 ^[1]. Carbon atoms, in turn, are one of the most abundant chemical elements in nature, being of great importance since it has a great capacity to form chemical bonds with atoms of the same species and with others. Returning to graphene, it can be seen as the basic unit that is responsible for giving rise to several structures, as depicted in Fig. 1, such as graphite, fullerenes, carbon-nanotubes, graphene, etc.

2.1.1 Energy dispersion of Monolayer Graphene

In the following, by using a nearest-neighbor *tight-binding* (TB) model, model, we will determine the energy eigenvalues of the graphene sheet. ^[10]. As previously mentioned, carbon atoms arrange themselves in a honeycomb lattice to create graphene sheets. These atoms, in turn, have atomic number Z = 6, which means that the distribution of electrons in its ground state is $1s^2, 2s^2, 2p^2$. Each one of these atoms presents itself in an sp^2 hybridization state. In sp^2 hybridization, carbon atoms hold three σ bonds and one π bond. Thus, in graphene, the orbitals $2_s, 2p_x$, and $2p_y$ combine to form σ orbitals, while p_z orbitals do not hybridize and are free to produce π orbitals. While σ bonds are responsible for graphene's mechanical properties, p_z orbitals, which point out of the plane, are relevant for its electronic properties ^[11]. It is worth pointing out that bands described by these orbitals are impressive, as they present valleys, with linear dispersion, located at the six



Figure 1 – Carbon allotropes. we know that a carbon atom has in its second shell four electrons, this feature can give rise to many types of different chemical bonds, such as sp, sp2, and sp3. Graphite is a laminar material in which carbon atoms form covalent bonds with orbitals in an sp^2 hybridization, and the layers are weakly bonded by van der Waals bonds. From ^[1].

extremities of the first Brillouin zone (BZ) ^[12, 13]. As we can see in Fig. 2 b), two of these valleys are non-equivalent. The valleys represent an extra degree of freedom, called valley degree of freedom, similar to spin for the charge carriers. The dispersion at the valleys is linear, and, because of that, the bands at those points are known as Dirac cones. Thus, electrons at low energy behave like massless Dirac fermions ^[14]. The graphene lattice, by itself, is not a Bravais lattice. However, we can create a honeycomb lattice by using two distinct (non-equivalent) triangular Bravais lattices, called A and B sublattices. So, the honeycomb lattice is wholly defined if we construct a basis formed by two carbon atoms, one for each sublattice. By convention the two atoms in the graphene unit cell are denoted by A and B and are spatially separated by a_0 distance, as shown in Fig. 2. Furthermore, due to this spatial configuration, its honeycomb lattice produces a bipartite structure which implies a symmetrical energy spectrum about the Γ point (center of the



Figure 2 - (a) The honeycomb lattice in real space. The unit cell is displayed as a yellow parallelogram. (b) First BZ of graphene, along with high-symmetry points. Dirac cones, which approximate the dispersion close to the Fermi energy, are also indicated.

BZ). The graphene crystalline structure, in real space, is described as a function of two primitive lattice vectors ^[5]. According to Fig. 2, they are given by

$$a_1 = \frac{a}{2}(3,\sqrt{3}), \quad a_2 = \frac{a}{2}(3,-\sqrt{3})$$
 (1)

where a is the band length of the real-space unit cell vector and each site has three nearest-neighbors (NN). The 3 vectors connecting an A site to its neighbors are given by

$$\gamma_1 = \frac{a}{2}(1,\sqrt{3}) \quad \gamma_2 = \frac{a}{2}(1,-\sqrt{3}) \quad \gamma_3 = -a(1,0)$$
 (2)

From Eq. (1), it is possible to determine the reciprocal vectors \mathbf{b}_i by using the relation $\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij}$ ^[15], thus we obtain

$$\boldsymbol{b}_1 = \frac{2\pi}{3a}(1,\sqrt{3}), \quad \boldsymbol{b}_2 = \frac{2\pi}{3a}(1,-\sqrt{3}).$$
 (3)

Below, we define the high-symmetry points in the graphene lattice (Eq. 4), commonly used to describe the energy dispersion in k-space. In the center of the BZ, we have the Γ point. Next, we have the M point, located at the center of the honeycomb edge. Finally, there are the two special points K and K', located at the corners of the first BZ. Their components are given by

Wave vector	Γ	\mathbf{M}	Κ	\mathbf{K}'	
k_x	0	$(2\pi/\sqrt{3}a)$	$(2\pi/\sqrt{3}a)$	$(2\pi/\sqrt{3}a)$	(4)
k_y	0	0	$(2\pi/3a)$	$(-2\pi/3a)$	

The graphene TB Hamiltonian, in real space, is written as

$$\mathcal{H} = -t \sum_{\langle ij \rangle} a_i^{\dagger} b_j + \text{ h.c..}$$
(5)

In Eq. (5), a_i and a_i^{\dagger} (b_i and b_i^{\dagger}) are the annihilation and creation operators for electrons on a site *i* located in the *A* (*B*) sublattice, respectively, and $\langle ij \rangle$ means that we are performing a sum only for nearest neighbors. The hopping energy is defined as t = 1 (unit of energy). The Hamiltonian diagonalization in momentum space is straightforward. Thus, to find the energy dispersion, we will expand the creation/annihilation operators in momentum space by using Fourier Transform Equations

$$a_{i} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}_{i}} \alpha_{k}$$

$$a_{i}^{\dagger} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{r}_{i}} \alpha_{k}^{\dagger}$$

$$b_{j} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}'} e^{i\mathbf{k}'\cdot\mathbf{r}_{j}} \beta_{k'}$$

$$b_{j}^{\dagger} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}'} e^{i\mathbf{k}'\cdot\mathbf{r}_{j}} \beta_{k'}^{\dagger},$$
(6)

where β_k , α_k are operators that create electrons with momentum **k**. By replacing Eqs. (6) into Eq. (5), we get

$$\mathcal{H}(k) = \frac{-t}{N} \sum_{i,j} \sum_{\mathbf{k},\mathbf{k}'} \left[e^{i\mathbf{k}\cdot\mathbf{r}_i} e^{-i\mathbf{k}'\cdot(\mathbf{r}_i+\gamma_j)} \alpha(\mathbf{k})\beta^{\dagger}(\mathbf{k}') + e^{-i\mathbf{k}\cdot\mathbf{r}_i} e^{i\mathbf{k}'\cdot(\mathbf{r}_i+\gamma_j)} \alpha^{\dagger}(\mathbf{k})\beta(\mathbf{k}') \right]$$

$$= \frac{-t}{N} \sum_{i,j} \sum_{\mathbf{k},\mathbf{k}'} \left[e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_i} e^{-i\mathbf{k}'\cdot\gamma_j} \alpha(\mathbf{k})\beta^{\dagger}(\mathbf{k}') + e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_i} e^{i\mathbf{k}'\cdot\gamma_j} \alpha^{\dagger}(\mathbf{k})\beta(\mathbf{k}') \right]$$

$$= \frac{-t}{N} \sum_j \sum_{\mathbf{k},\mathbf{k}'} \left[\delta_{\mathbf{k}\mathbf{k}'} e^{-i\mathbf{k}'\cdot\gamma_j} \alpha(\mathbf{k})\beta^{\dagger}(\mathbf{k}') + \delta_{\mathbf{k}\mathbf{k}'} e^{i\mathbf{k}'\cdot\gamma_j} \alpha^{\dagger}(\mathbf{k})\beta(\mathbf{k}') \right]$$

$$= -t \sum_j \sum_{\mathbf{k}} \left[e^{-i\mathbf{k}\cdot\gamma_j} \alpha(\mathbf{k})\beta^{\dagger}(\mathbf{k}) + e^{i\mathbf{k}\cdot\gamma_j} \alpha^{\dagger}(\mathbf{k})\beta(\mathbf{k}) \right],$$
(7)

from where we define

$$v_{\mathbf{k}} = \sum_{j} e^{-\mathbf{i}\mathbf{k}\cdot\gamma_{j}} = e^{-\mathbf{i}\mathbf{k}\cdot\gamma_{1}} + e^{-\mathbf{i}\mathbf{k}\cdot\gamma_{2}} + e^{-\mathbf{i}\mathbf{k}\cdot\gamma_{3}},\tag{8}$$

which, using Eqs. (2), can be rewritten as

$$\begin{aligned}
\psi_{\mathbf{k}} &= e^{i\mathbf{k}\cdot\gamma_{1}} + e^{i\mathbf{k}\cdot\gamma_{2}} + e^{i\mathbf{k}\cdot\gamma_{3}} \\
&= e^{i\mathbf{k}\cdot\delta_{3}} \left[1 + e^{i\mathbf{k}\cdot(\gamma_{1}-\gamma_{3})} + e^{i\mathbf{k}\cdot(\gamma_{2}-\gamma_{3})} \right] \\
&= e^{-ik_{x}a} \left[1 + e^{i3k_{x}a/2} e^{i\sqrt{3}k_{y}a/2} + e^{i3k_{x}a/2} e^{-i\sqrt{3}k_{y}a/2} \right] \\
&= e^{-ik_{x}a} \left[1 + e^{i3k_{x}a/2} \left(e^{i\sqrt{3}k_{y}a/2} + e^{-i\sqrt{3}k_{y}a/2} \right) \right] \\
&= e^{-ik_{x}a} \left[1 + 2e^{i3k_{x}a/2} \cos \left(\frac{\sqrt{3}}{2} k_{y}a \right) \right].
\end{aligned}$$
(9)

Replacing Eq. (9) into Eq. (8), we obtain

$$\mathcal{H}(k) = -\sum_{\mathbf{k}} \left(\begin{array}{cc} \alpha^{\dagger}(\mathbf{k}) & \beta^{\dagger}(\mathbf{k}) \end{array} \right) \left(\begin{array}{cc} 0 & tv_{\mathbf{k}} \\ tv_{\mathbf{k}}^{*} & 0 \end{array} \right) \left(\begin{array}{c} \alpha(\mathbf{k}) \\ \beta(\mathbf{k}) \end{array} \right).$$
(10)

From Eq. (10), we get the graphene dispersion relation

$$E_{\pm}(\mathbf{k}) = \pm t\sqrt{3 + f(\mathbf{k})},\tag{11}$$

where

$$f(\mathbf{k}) = 2\cos\left(\sqrt{3}k_ya\right) + 4\cos\left(\frac{3}{2}k_xa\right)\cos\left(\frac{\sqrt{3}}{2}k_ya\right).$$
 (12)

In Fig. 3(a), we depict the graphene energy dispersion along high symmetry lines. As we can see, the graphene spectrum consists of two dispersive bands that meet at the K and K' points. Thus, graphene is a gapless semiconductor (a semi-metal). In Fig. 2(b) the 3D graphene band structure is shown as a function of $\mathbf{k} = (k_x, k_y)$. Note that, at the six borders of the first BZ the energy dispersion is linear and resembles a cone (see Fig. 2). To see this explicitly, we can expand Eq. (12) near to a **K**-point, for small $\mathbf{q} = \mathbf{k} - \mathbf{K}$ values, i.e.

$$\mathbf{k} = \mathbf{K} + \mathbf{q},\tag{13}$$

Now, by expanding Eq. (12) in a Taylor series about **K**, we get

$$\theta_{(\mathbf{K}+\mathbf{q})} = f_{(\mathbf{K}+\mathbf{q})} = e^{-iK_x a} e^{-iq_x a} \left[1 + 2e^{i3a/2(K_x+q_x)} \cos\left(\frac{\sqrt{3}(K_y+q_y)a}{2}\right) \right]$$

= $e^{-iK_x a} e^{-iq_x a} \left[1 - 2e^{3iaq_x/2} \cos\left(\frac{\pi}{3} + \frac{\sqrt{3}a}{2}q_y\right) \right].$ (14)

thus

$$\theta_{\mathbf{K}+\mathbf{q}} = -\frac{3\mathbf{i}a}{2} \left(q_x + \mathbf{i}q_y \right) e^{-\mathbf{i}K_x a} \approx -\frac{3\mathbf{i}a}{2} \left(q_x + \mathbf{i}q_y \right) \tag{15}$$

So, close to a \mathbf{K} -point [low energy regime], it is possible to express the graphene Hamiltonian as

$$H_{(\mathbf{K}+\mathbf{q})} = \begin{pmatrix} 0 & \Theta \\ \Theta^* & 0 \end{pmatrix} = v_F \begin{pmatrix} 0 & q_x + iq_y \\ q_x - iq_y & 0 \end{pmatrix}$$
(16)

where

$$v_F = \frac{3at}{2} \tag{17}$$

is the Fermi velocity. We can express Eq.(16) by using Pauli matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{18}$$

resulting in

$$\mathcal{H}(\mathbf{K} + \mathbf{q}) = v_F \left(q_x \sigma_x - q_y \sigma_y \right) = v_F \mathbf{q} \cdot \boldsymbol{\sigma}$$
(19)

where

$$\mathbf{q} = (q_x, -q_y) \tag{20}$$



Figure 3 – (a) 2D dispersion relation for graphene along a high symmetry line passing by the K, Γ , and M points in the first BZ, (b) Graphene density of states, (c) 3D graphene band structure (d) Dispersion relation at the corners of the first BZ.

From Eq. (20), we can see that when we take a low energy limit, the electrons in graphene actually behave like massless particles [Dirac fermions]. Hence, electrons in graphene effectively behave like "relativistic particles" without mass and are described by a renormalized Dirac equation. That exotic behavior is meaningful, since it allows us to investigate high-energy systems in a condensed matter model.



Figure 4 – Variation of the band-gap width of an AGNR as a function of its width N. Notice that the N = 3p and 3p + 1 are semiconducting (for integer p) while AGNRs with N = 3p + 2 are metallic (vanishing band-gap) in the tight-binding approximation.

2.2 Graphene nanoribbons

Graphene nanoribbons (GNRs) are nanomaterials created by cutting graphene sheets. These cuts can be performed by choosing different directions, which will give rise to ribbons with different edges. Edge-type is a fundamental feature for these systems, since it will determine, in combination with quantum effects, coming from the system low-dimensionality, how the wave functions will be confined in this quasi-1D systems. As previously mentioned, despite the excellent electronic properties of graphene, it is a gapless semiconductor, what causes problems in your use in electronic devices. The gap issue (In the TB approach) has been overcome in recent years by using graphene nanostructures, in particular, the so-called GNRs. Given the quantum confinement of electronic states (wave functions) in the ribbon, it may provoke the emergence of a gap in the graphene strip [^[16]]. Whether or not this forbidden region occurs, and what is its magnitude, will be for the most part determined by the ribbon width. There are the two special crystallographic directions types of GNRs, known as zig-zag, and armchair nanoribbons. These names are related to the type of edges of each ribbon. Here we will focus only on armchair ribbons [a derivation of the tight-binding model for a ZGNR ribbon is presented in Appendix C.

GNRs with armchair edges, by convention, are classified according to the number of dimers $N_{\rm a}$ across its width $W_{\rm a}$. Following this nomenclature, we will refer to an armchair

nanoribbon as $N_{\rm a}$ -AGNR, where $N_{\rm a}$ is the number of dimers in the system and 'A' comes from "armchair". The width of an armchair nanoribbon (See Fig. 5) is defined as

$$W_{\rm a} = (N_{\rm a} - 1) \frac{\sqrt{3}}{2} a$$
, with $a = 1.42$ Å (21)

Unlike what happens for zig-zag nanoribbons, armchair nanoribbons may present different electronic behavior, since they can have either metallic or semiconducting electronic structures. Thus, AGNRs are classified into three distinct families, according to their respective bandgap $E_{\rm gap}$, as

$$E_{\text{gap}} = t \left[4 \cos \left(\frac{p\pi}{3p+1} \right) - 2 \right] \qquad (N_{\text{a}} = 3p)$$

$$E_{\text{gap}} = t \left[2 - 4 \cos \left(\frac{(p+1)\pi}{3p+2} \right) \right] \qquad (N_{\text{a}} = 3p+1)$$

$$E_{\text{gap}} = 0 \qquad (N_{\text{a}} = 3p+2)$$

$$(22)$$

An N_a -AGNR is metallic for $N_a = 3p+2$ and semiconducting if $N_a = 3p$ or $N_a = 3p+1$, where p is positive and integer ^[2]. We can also notice that the gap of an N_a -AGNR is inversely proportional to its width, as can be seen in Fig. 4. Thus, they can be grouped according to gap size

$$E_{3p}^{gap} \gtrsim E_{3p+1}^{gap} > E_{3p+2}^{gap} \ (=0)$$
 for all values of p . (23)

It is possible to notice a significant reduction in the gap when we increase the width of the ribbon, which allows us to conclude that from a certain very large width, all the AGNRs will show a metallic behavior. However, it is important to point out that this treatment for armchair ribbons is only in agreement with the literature when compared with results obtained from the tight-binding method. First-principles calculations show, however, that there are no metallic AGNRs. In what follows, to simplify the notation, we will refer to $N_a = N$.

2.2.1 Tight-binding model for Armchair nanoribbons

Fig. 5 shows the lattice structure of an armchair graphene nanoribbon. The yellow rectangle displays the system unit cell. The width of an AGNR is given by $a/2\sqrt{3}N$, where a is the lattice constant, and 2N gives us the total amount of atoms in the unit cell, as illustrated in Fig. 5. In addition a_T specifies the ribbon length.

In appendix C, we present a complete derivation of the eigen-energies and wave functions of armchair nanoribbons. Here, in a nutshell, we have that the senergy eigenvalues are given by

$$E = s\sqrt{1 + 2\epsilon_p \cos\frac{k}{2} + \epsilon_p^2},\tag{24}$$



Figure 5 – Real space structure of an N = 12 AGNR. The dashed lines indicate its unit cell.

and their respective wave functions

$$\begin{pmatrix} \psi_{m,A} \\ \psi_{m,B} \end{pmatrix} = N_{\rm c} \begin{pmatrix} -s\sqrt{\epsilon_p + {\rm e}^{-{\rm i}k/2}} \\ \sqrt{\epsilon_p + {\rm e}^{{\rm i}k/2}} \end{pmatrix} \sin(mp).$$
(25)

In Fig. 6, we show the band structures for AGNRs with different widths. What we can notice is that the AGNRs present different electronic behaviors [both metallic and semiconductor families]. In addition, we also observe a tendency of decreasing gap with increasing N as shown in Fig. 4

2.2.1.1 AGNR Density of states

In panels (a) to (d) of Fig 7, we present the density of states (DOS) for AGNRs with different widths (N = 4, N = 5, N = 12, and N = 30). From the DOS, it is possible to verify the electronic behavior presented by these materials (semiconductor or metallic behavior), as well as it is easy to verify a dimensionality signature of those systems. This signature is apparent in the singularities, named Van Hove singularities, present in the DOS results shown in all for panels, which are characteristic of one-dimensional (1D), or quasi-1D, materials. Furthermore, it is verified that when the number of sites within the unit cell of the armchair ribbon increases, the DOS begins to approach the graphene DOS, presented above, as can be seen in Fig. 7, for an AGNR with N = 30 (60 sites).



Figure 6 – Panels (a) to (d) show the AGNR energy dispersion for N = 4, N = 5, N = 12, and N = 30, respectively.



Figure 7 – Panels (a) to (d) show the AGNR DOS for N = 4, N = 5, N = 12, and N = 30, respectively.
CHAPTER 3

Topological graphene heterostructures

Among the numerous advances in the study of graphene-based nanostructures, we may state that perhaps one of the most important/exciting was the discovery of the topological properties of AGNRs. The topology of AGNRs was theoretically predicted in 2017 by Steven Louie's group ^[17]. Soon after, the experimental confirmation took place ^[17]. Briefly, each topological system has associated with it a topological invariant (which, in short, serves to designate what topological class the structure belongs to, trivial or nontrivial). In the case of AGNRs, the associated invariant is called Z_2 . On one hand, if a given AGNR has a $Z_2 = 0$, it will be called trivial (like the vacuum). On the other hand, if $Z_2 = 1$, the AGNR will be in its topologically non-trivial phase. As will be shown below, these AGNR properties can be used to simulate a Su-Schrieffer-Heeger (SSH) $^{[18]}$ dimerized chain. An effective SSH model can be simulated by intercalating AGNR segments with alternating Z_2 values. The resulting system could be seen as analogous to a 1D topological insulator, a 1D topological insulator, something still negligibly investigated. Similar to both 3D (with their well-known 2D edge states) and 2D (with 1D edge states) counterparts, these heterostructures will be able to support edge states, presenting all the peculiarities associated with a 0D metallic state. To simulate a low energy model (an effective model) equivalent to the SSH model, based on AGNRs, we must 'construct' the fundamental component of the SSH chain, namely, a dimerized chain. For this, we must create the dimers, composed of two localized states, with energy equal to zero, and that also overlap (hybridize). This can be achieved as long as these localized states are close to each other. To obtain the localized states, it is necessary to connect different AGNR segments with different Z_2 values. By doing this, an edge state is expected to occur on the boundary between the two strands.

As an illustration of what was discussed above, consider Fig. 8. It shows a periodic heterostructure formed by intercalating short strands of AGNRs with N = 5 between longer strands of AGNRS with N = 9. Since both ribbons have different Z_2 values, localized edge states (at zero energy) should appear at the region between both strands. In Fig. 8, such edge states are indicated by the larger red circles. If the distance between these



Figure 8 – Representation of an 'SSH chain' built from graphene nanoribbons ('Staggered' case). The parameter t_m represents a hopping (overlap integral) between different unit cells, and t_n represents hopping inside a unit cell. ^[2]

localized states is not too large, they will hybridize. This hybridization is indicated by the overlap integrals t_n (horizontal oval, with solid contour) and t_m (diagonal oval, dashed contour). Thus, the resulting low energy effective model is that of the SSH model ^[18]. If one engineers correctly the heterostructure, the values of t_n and t_m obtained are such that one may end up in the non-trivial side of the SSH phase diagram ^[4]. It should be noted that a comprehensive theory describing the formation of the edge states between the different AGNR strands has only recently been developed. For details, please see Ref. ^[19], and references therein.

In terms of the overlap integrals t_n and t_m , the band structure close to the Fermi level can be described using the SSH model, where the system obeys the following dispersion relation (see Appendix B)

$$E(k) = \pm \sqrt{t_n^2 + t_m^2 + 2t_n t_m \cos(k)}.$$
(26)

In the rest of this chapter, we will deal with the two types of heterostructures first introduced in Refs. $^{[2, 8]}$.

3.1 Inline heterostructure

To explore the AGNR heterostructure features, we need first to set the nomenclature defined in Ref. ^[2]. Let us first describe the so-called Inline type (see Fig. 9). We denote it as N-AGNR-I(n,m), where N specifies the backbone width and I refers to the 'Inline' type, while n is the number of adjacent extended segments (N+4), and, finally, m specifies the distance between two n-segments (see Fig. 9). It is worth saying as well that the [m] and [n] quantities are measured in a_{cc} (carbon distance in hexagonal lattice) units.

Bellow, we will present the results for DOS and energy dispersion for the heterostructures above defined. A full description of the Hamiltonino TB used here can be found in Appendix E.



Figure 9 – Schematic representation of a 5-AGNR-I(3,3) heterostructure. Where N = 5 (i.e., a 5-AGNR backbone, in cyan), n = 3, and m = 3.

3.1.1 Band structure as a function of the parameter N

Now, we show the results for the energy dispersion and density of states for the Inline heterostructures. For each of the results shown in Fig. 10, we fix (n, m) = (1, 3) and vary the parameter N = 3, 5, 7, 9 (width of the back-bone, see Fig. 10). An important point to be highlighted is that our results agree semi-quantitatively with the results found from ab-initio calculations. It is possible to note that when we increase N value there is a tendency towards SSH behavior for the dispersion close to the Fermi level.

3.1.2 Band structure as a function of the parameter n

Figure 11 shows the same results as in Fig. 10, but now we fix N = 5 and m = 3, and vary n = 2, 3, 4, 5. What can be immediately noticed, by comparing the four panels, is that the increase in n is responsible for a significant reduction in the system's bandgap. This behavior can be observed if we consider, for example, that for n = 2 the band gap is $E_g = 0.958$ eV and for n = 5 the band gap is $E_g = 0.292$ eV. It is important to point out that this behavior is in contrast to what happens with the Staggered heterostructures, analyzed in the next section, in which it is verified that an increase of n implies a notable enlargement in the band gap.

3.1.3 Band structure as a function of the parameter m

The Fig. 12 shows the results for a heterostructure with N = 5, but now we fix N = 5and n = 1, and vary m = 2, 3, 4, 5. For m = 2, the dispersion near to the Fermi level resembles what is expected for the SSH model. However, it is noticed that for m > 2, the system starts to have its topological properties suppressed.

3.2 Staggered heterostructure

A Staggered heterostructure, denoted N-AGNR-S(n,m), is the asymmetric counterpart of the Inline heterostructure. The 'staggered' system is made of $n \ge 1$ segments, where n measures the number of (N + 2)-AGNR 'extensions', as can be seen in Fig. 13 (in red).



Figure 10 – Energy spectrum and density of states (DOS) for n = 1, m = 3, and N varying from 3 to 9. (a) 3-AGNR-I(1,3), (b) 5-AGNR-I(1,3), (c) 7-AGNR-I(1,3), (d) 9-AGNR-I(1,3). On top of each panel, we show a sketch of the corresponding heterostructure.

As shown there, the difference with the Inline hetrostructure is that the (N+2) pieces are distributed in an 'staggered' way on opposite sides of the bare nanoribbon backbone, in order to create a more asymmetric system. This configuration is then repeated regularly to create a periodic system, which will then have unit cell sizes that are considerably larger than an Inline heterostructure with the same n and m parameters. The separation between the segments is given by m, which serves to measure the distance between the n parts on opposite sides of the backbone (see Fig. 13). In the same way as for the case shown in the earlier section, N is the number of dimers in the unit cell of an AGNR without any extensions (the so-called backbone) and S comes from 'Staggered'. Note that $m \ge 1$, thus m can also be equal to 1, which is not possible for Inline heterostructures, since this would result just in an (N + 4) - AGNR.



Figure 11 – Energy spectrum and density of states (DOS) for N = 5, m = 3, and n varying from 2 to 5. (a) 5-AGNR-I(2,3), (b) 5-AGNR-I(3,3), (c) 5-AGNR-I(4,3), (d) 5-AGNR-I(5,3). On top of each panel, we show a sketch of the corresponding heterostructure.

3.2.1 Band structure as a function of the parameter N

In Fig. 14, we present several results for energy spectrum and DOS for N-AGNR-S(1,3), where we have set m = 3 and n = 1, and we vary N. We should should note that, contrary to what happens for Inline heterostructures, which will exhibit boundary states for any value of N, for the Staggered case this will be valid only for N = 3p + 1, with p = 2^[2]. The most interesting result is the 7-AGNR-S(1,3) heterostructure, which was recently synthesized, and shows a low energy dispersion for the SSH model in a trivial phase ^[20].

3.2.2 Band structure as a function of the parameter n

In Fig. 15, we present several results for energy spectrum and DOS for 5-AGNR-S(n,3), where we have set N = 5 and m = 3, and we vary n. The general effect caused by the



Figure 12 – Energy spectrum and density of states (DOS) for N = 5, n = 1, and m varying from 2 to 5.(a) 5-AGNR-I(1,2), (b) 5-AGNR-I(1,3), (c) 5-AGNR-I(1,4), (d) 5-AGNR-I(1,5). On top of each panel, we show a sketch of the corresponding heterostructure.



Figure 13 – Schematic representation of a 5-AGNR-S(2,2) heterostructure. Where N = 5 (5-AGNR, backbone in cyan), n = 2, and m = 2.



Figure 14 – Energy spectrum and density of states (DOS) for N = 5, m = 3, and n varying from 2 to 5.(a) 3-AGNR-S(1,3), (b) (1,3), (c) 7-AGNR-S(1,3), (d) 9-AGNR-S(1,3). On top of each panel, we show a sketch of the corresponding heterostructure.

increase of n, for fixed m and N, is to cause a separation of the bands near to the Fermi level. This effect is more pronounced for N>5 (not shown).

3.2.3 Band structure tion of the parameter m

In Fig. 16, we present several results for energy spectrum and DOS for 5-AGNR-S(1,m), where we have set N = 5 and n = 1, and we vary m. The variation of the band structure with m is dramatic. We even see a flat-band at the Fermi energy for the 5-AGNR-S(1,4) heterostructure.

3.3 Bottom-up graphene nanoribbon synthesis

The first step in creating AGNRs, with atomically precise edges in a laboratory, is the choice of the type of monomer to be used, which consists of each one of the molecules that, following some conditions, join together (polymerization), building large chains of molecules (polymers)^[3]. After the monomers are selected, they are synthesized and purified [see first panel in Fig. 17(a)]. Afterwards, the precursor monomer is deposited



Figure 15 – Energy spectrum and density of states (DOS) for N = 5, m = 3, and n varying from 2 to 5. (a) 5-AGNR-S(1,3), (b) 5-AGNR-S(2,3), (c) 5-AGNR-S(3,3), (d) 5-AGNR-S(4,3). On top of each panel, we show a sketch of the corresponding heterostructure.

on a metallic surface, usually Au(111), in an ultra-high-vaccum chamber (UHV) [second panel in Fig. 17(a)]. Then, there is the evaporation and annealing processes, which gives rise to a dehalogenation process, which consists in replacing halogen atoms (Group 17 of the periodic table) in a molecule [third panel in Fig. 17(a)]. At this moment, the monomers diffuse across the metal surface and form the polymers. The polymer still needs to go through the processes of annealing and cyclodehydration, Fig. 17(b). Then, the polymer takes its planar form with the new benzene rings. Fig. 17(c). See Ref. ^[3] for details.

3.3.1 Bottom-up AGNR-heterostructure synthesis

The synthesis of heterostructures from AGNRs, through a bottom-up approach, is achieved via a procedure in which it is necessary to make use of more than one precursor monomer, through the fusion of different monomers (which, in isolation, would give rise to different segments of the pristine AGNR). In Figs. 18 and 19, we can see a representation



Figure 16 – Energy spectrum and density of states (DOS) with N = 5, n = 1, and m varying from 2 to 5. (a) 5-AGNR-S(1,1), (b) 5-AGNR-S(1,2), (c) 5-AGNR-S(1,3), (d) 5-AGNR-S(1,4). On top of each panel, we show a sketch of the corresponding heterostructure.

of what was said above, we have two individual monomers that when merging will be responsible for creating a new system (heterojunction) $^{[2]}$.

To obtain a 7-AGNR-S(1,3) (Fig. 18), first, the samples were synthesized via a stepwise annealing process. After, the BADMT molecular precursor (monomer 1, 6,11-bis(10bromoanthracene-9-yl)-1,4-dimethyltetracene) was placed on Au(111) at room temperature. In sequence, the sample was annealed at 200° C, and 400° C. This process leads to a monomer activation, polymerization, and finally, the cylcodehydrogenation process originates the 7-AGNR-S(1,3) heterostructure. For the synthesis of a 7-AGNR-I(1,3) the same procedure was used, with the only difference being the substitution of the of the precursor monomers as can be seen in Fig. 19.



Figure 17 – Schematic representation of the synthesis of an AGNR. From Ref. ^[3].



Figure 18 – Schematic representation of the fabrication of a 7-AGNR-S(1,3) heterostructure and an AFM image of the synthesized material. From Ref. ^[2].



Figure 19 – Schematic representation of the fabrication of a 7-AGNR-S(1,3) heterostructure and an AFM image of the synthesized material. From Ref. ^[2].

CHAPTER 4

Thermoelectric properties of AGNR heterostructures

4.1 Landauer formalism

A powerful approach when there is coherent transport through a mesoscopic conductor is the Landauer-Buttiker Theory. Created by Landauer and further generalized by Buttiker, this approach relates the current through a conductor to the electron transmission probability ^[21].

In Fig. 20, we show the system to be analyzed, a quasi-one-dimensional conductor. Here, we assume that transport is ballistic and, besides that, the conductor is sandwiched by two reservoirs (considered semi-infinite), at chemical potentials μ_1 and μ_2 (see Fig. 47). The source and drain have many allowed states, a much larger number than the system between them. The electron distribution in each reservoir is given by the Fermi distribution f(E), which is a step-like function at T = 0 K and varies smoothly at temperatures T > 0 K. This is equivalent to saying that, at zero temperature, the electronic levels in the reservoirs are filled until an energy E equal to the chemical potential μ . The Fermi distribution is given by

$$f^{\alpha}(E) = \frac{1}{1 + \exp\left[\left(E - \mu_{1,2}\right)/k_B T\right]},$$
(27)

where α represent the Fermi distribution indexes \pm . T and K_B are the temperature and the Boltzmann constant.

An important assumption which will be relaxed later for the future development of our theoretical model is that contacts are reflectionless. It means that an electron that propagates through the system will be completely transmitted when it finds the interface between the contacts.





4.1.1 Landauer Formula

Now, we will derive a general expression for the electronic conductance that an arbitrary conductor carries. To do this, we first need to define some really important concepts. First of all, any state in the conductor have different transverse modes [subbands] associated with them. Next, each mode follows a dispersion relation E(N, k) and it has a cut-off energy given by

$$\varepsilon_N = E(N, k = 0) \tag{28}$$

The number of transverse modes M(E) with energy E is found by counting states with cut-off energies $\epsilon_N < E$, where N is any mode. For a complete description, we recommend the Ref. ^[21], as

$$M(E) \equiv \sum_{N} \vartheta \left(E - \varepsilon_{N} \right) \tag{29}$$

where ϑ is a Heaviside function. From Eq. (29), it is possible to find the current related to each one of the transversal modes [M(E)]. Then, to find the complete current, we only need to sum over all of them.

To obtain a general expression for current, we will start by considering a transverse mode $+k_x$, coming from left and with chemical potential equal to μ_1 , that obeys $f^+(E)$. From elementary Physics courses, we learned that for an electron gas, composed of nelectrons [per unit of length], moving with a velocity v, the current can be expressed by I = env. Hence, we are able to say that the current flowing through a single mode, due to +k, can be written as

$$I^{+} = \frac{e}{L} \sum_{k,\sigma} v f^{+}(E) = \frac{e}{L} \sum_{k,\sigma} \frac{1}{\hbar} \frac{\partial E}{\partial k} f^{+}(E)$$
(30)

the sum in Eq. (30) can be converted into an integral by using the following relation

$$\sum_{k,\sigma} \to 2(\text{ for spin}) \times \frac{L}{2\pi} \int \mathrm{d}k \tag{31}$$

we come at

$$I^{+} = \frac{2e}{h} \int_{\epsilon}^{\infty} f^{+}(E) \mathrm{d}E$$
(32)

where ϵ is the threshold energy. And so forth, the current carried by all states +k (M(E) modes) are

$$I^{+} = \frac{2e}{h} \int_{-\infty}^{+\infty} f^{+}(E)M(E)dE$$
(33)

By comparison, the current carried by electrons $-k_x$ moving in the opposite direction (-x direction) with a chemical potential μ_2 is given by

$$I^{-} = \frac{2e}{h} \int_{-\infty}^{+\infty} M(E) f^{-}(E) dE.$$
 (34)

thus, the net current is

$$I = I^{+} - I^{-} = \frac{2e}{h} \int_{-\infty}^{+\infty} M(E) \left(f^{+}(E) - f^{-}(E) \right) dE.$$
(35)

if we impose that the number of modes M(E) does not change in the interval $[\mu_1 > E > \mu_2]$ and T = 0 K, we arrive at

$$I = I^{+} - I^{-} = \frac{2eM}{h} \int_{-\infty}^{+\infty} \left(f^{+}(E) - f^{-}(E) \right) dE.$$

= $\frac{2eM}{h} (\mu_{1} - \mu_{2}).$ (36)

but $\mu = e \times V$

$$I = M(E)\frac{2e^2}{h}(V_1 - V_2)$$
(37)

where the conductance can be written as

$$G = \frac{2e^2}{h}M(E) \tag{38}$$

The expression in Eq. (38) is the expected result for a ballistic conductor. Hereafter, we will derive a more general result that takes electronic transmission into account, that is, for which the transmission probability is not always 100 %. In short, we know that for

an ordinary conductor [that obeys Ohm's law well] the electrical conductance must obey the following expression

$$G \propto \frac{W \quad [\text{width}]}{L \quad [\text{length}]}$$
 (39)

however, when we decrease the conductor dimensions, the Eq. (39) is no longer valid. An important assumption that we must make is that there will be a resistance in the system with such characteristics [reduced dimensions] and that it is independent of the device length L. Another significant point that we must pay attention to is the number of transversal modes will be quantized. Systems for which the two previous statements are valid are well described within the Landauer formalism, which we will show below

$$G = \frac{2e^2}{h}MT\tag{40}$$

to find the Landauer formula for conductance, we will start from Fig. 20. We assume that the Leads are ballistic conductors, each containing M traverse modes and \mathcal{T} represents the transmission function [which is the probability of transmission of electrons through the conductor]. At *lead* 1, the $+k_x$ states will be occupied by electrons coming from the left up to a chemical potential μ_1 . In contact 2, the $-k_x$ states in lead 2 originate from the right contact and have a chemical potential μ_2 . At T = 0 K, the electron flow from lead 1 is written as

$$I_1^+ = (2e/h)M\left[\mu_1 - \mu_2\right] \tag{41}$$

The current from lead 2 is the current I_1^+ times the transmission probability \mathcal{T}

$$I_2^+ = (2e/h)M\mathcal{T}[\mu_1 - \mu_2]$$
(42)

the reflected flow in contact 1 is given by

$$I_1^- = (2e/h)M(1-\mathcal{T})\left[\mu_1 - \mu_2\right]$$
(43)

so the net current I on the device is given by

$$I = I_1^+ - I_1^- = I_2^+ = (2e/h)M\mathcal{T}[\mu_1 - \mu_2]$$
(44)

finally, electronic conductance can be expressed

$$G = \frac{I}{\left(\mu_1 - \mu_2\right)/|e|} = \frac{2e^2}{h}M\mathcal{T}$$
(45)

where \mathcal{T} is transmission function and $2e^2/h$ is a Quantum of Conductance.

4.1.2 Green's function and transmission coefficient

In the Landauer approach, the system under study is connected to contacts and all the electronic transport information can be obtained from the transmission coefficient. Given a Hamiltonian (in the tight-binding method), we can obtain, in a simple way, its coefficients through the Green's function method. In the single-particle approximation the Green's function $\mathcal{G}(E)$ of a system with Hamiltonian H is given by

$$\mathcal{G}(E) = (E - H)^{-1}$$
 (46)

as we can see in Eq. (46), the Green's function has poles at the eigenvalues of the Hamiltonian. We commonly sum or subtract an infinitesimal imaginary part to the energy and express the Green's functions as

$$\mathcal{G}^{\pm}(E) = \lim_{\eta \to 0^+} \mathcal{G}(E \pm i\eta), \tag{47}$$

where the symbols \mathcal{G}^+ and \mathcal{G}^- refer to the retarded and advanced Green's function, respectively. Thus, Eq. (46) can be rewritten as

$$\mathcal{G}^{\pm}(E) = \lim_{\eta \to 0^+} (E \pm i\eta - H)^{-1}.$$
(48)

Now, consider a system whose transport properties we want to investigate and that is sandwiched between two contacts at left and right, denoted p and q. The transmission T_{pq} between them, known as Fisher-Lee relation ^[22], will be given by

$$T_{pq} = \operatorname{Tr}\left[\Gamma_p \mathcal{G}_{pq} \Gamma_q \mathcal{G}_{pq}^{\dagger}\right],\tag{49}$$

where \mathcal{G}_{pq} is the submatrix of the \mathcal{G} matrix with the rows coming from contact p and the columns from contact q, while the $\Gamma_{p/q}$ function carries all contact information that matter for the Transmittance and is related to the self-energy Σ_p by

$$\Gamma_p = i \left(\Sigma_p - \Sigma_p^{\dagger} \right) \tag{50}$$

The Self-energy is actually a way of taking into account the influence of contacts and, can be obtained from the contact's Green's function g_p through

$$\Sigma_p = V g_p V^{\dagger},\tag{51}$$

where V is the coupling (with hopping matrix elements, in the tight-binding approximation) between the leads and central part and the contact. Although g_p is an infinitedimensional matrix, when we use the tight-binding approach, the matrix V has only non-zero matrix elements between sites located at the contact-conductor junction. Thus, we only need to use what is called the surface Green's function ^[23].



Figure 21 – Right side: Transmission curves for AGNRs with N = 3, N = 4, N = 5, N = 6, N = 7, N = 8, and N = 15. Left side: Density of states for AGNRs with N = 3, N = 4, N = 5, N = 6, N = 7, N = 8, and N = 15.

In Fig. 21, we show some results for transmission function and DOS, obtained from Green's function formalism.

4.2 Thermoelectric effects

By applying a small voltage $\Delta V = V_L - V_R$ and a not very large temperature gradient to our system, we can calculate the thermoelectric transport through a nanodevice [quasiequilibrium regime]. Left and right contacts are then at different chemical potentials μ_L and μ_R , and temperatures T_L and T_R ^[24], with

$$\Delta V = \frac{\mu_L - \mu_R}{e},\tag{52}$$

and

$$\Delta T = T_L - T_R. \tag{53}$$

The thermoelectric properties are obtained from the L_n coefficients, obtained from the following equation ^[25]

$$L_n = \int_{-\infty}^{\infty} (E - \mu)^n \,\mathcal{T}(E) \left(-\frac{\partial f(E, T)}{\partial E}\right) \mathrm{d}E \tag{54}$$

in Eq. (54), $\mathcal{T}(E)$ is the transmission probability of electrons of energy E being transmitted through the device, and f(E,T) is the Fermi distribution, as defined above. The derivative of the Fermi distribution is given by



Figure 22 – Derivatives of the Fermi-Dirac fermi dirac distribution. For T = 600K, T = 150K, and T = 20K.

$$\frac{\partial f(E,T)}{\partial E} = -\frac{1}{K_B T} e^{\frac{E-\mu}{E,T}} \left(1 + e^{\frac{E-\mu}{K_B T}}\right)^{-2} \\
= \frac{-\frac{1}{K_B T}}{\left(e^{-\frac{E-\mu}{2K_s,T}} + e^{\frac{E-\mu}{2R,T}}\right)^2} \\
= \frac{-1}{4K_B T \cosh^2\left(\frac{E-\mu}{2K_B T}\right)}.$$
(55)

From eq. (55), we notice that, for T = 0K, the derivative f'(E, T) is a Dirac delta function

$$-\frac{\partial f(E-\mu)}{\partial E} = \delta(\mu), \tag{56}$$

In n Fig. 22, we show the behavior of the derivative of the Fermi function for T = 600K, 150K, and 20K. When the temperature decreases we observe also a decrease in width of the f'(E,T) curves, which shows the tendency to a Dirac delta behavior, which will be confirmed at T = 0 K.

When there is no temperature gradient in the system, that is $\Delta T = 0$, the electrical conductance is given by

$$G = \left(\frac{I}{\Delta V}\right),\tag{57}$$

or

$$G = \frac{2e^2}{h}L_0.$$
(58)

Similarly, if the electric current I in the system vanishes, the so-called Seebeck coefficient S is defined as

$$S = -\left(\frac{\Delta V}{\Delta T}\right)_{I=0},\tag{59}$$

or

$$S = \frac{-1}{|e|T} \frac{L_1}{L_0}.$$
 (60)

The Seebeck coefficient, or thermopower, is the capacity of the material to convert the gradient temperature ΔT to voltage difference ΔV , when no current flows through the device. Other important thermoelectric properties are the Peltier coefficient (Π), and the electronic thermal conductance K_e

$$\Pi = \frac{-1}{|e|} \frac{L_1}{L_0}$$

$$\kappa_e = \frac{2}{hT} \left(L_2 - \frac{\left(L_1\right)^2}{L_0} \right)$$
(61)

Finally, it is possible to derive a relation that tells us the thermal efficiency of a material. This efficiency is expressed through the so-called ZT figure of merit (a dimensionless quantity). The ZT can be obtained from the Seebeck coefficient, electrical conductance, and thermal conductance, as

$$ZT = \frac{GS^2}{K_e}T = \frac{PF}{K_e}T \tag{62}$$

where $PF = GS^2$ is so-called power factor.

$$ZT = \frac{(L_1)^2}{L_0 L_2 - (L_1)^2}.$$
(63)

all thermal proprieties that we have defined above can also described in function of the L_n in the following way

$$G = \frac{2e^{2}}{h}L_{0}$$

$$S = \frac{k_{\rm B}}{e}\frac{L_{1}}{L_{0}}$$

$$K_{\rm e} = \frac{2\left(k_{\rm B}\right)^{2}}{h}\left(L_{2} - \frac{L_{1}^{2}}{L_{0}}\right)$$

$$ZT_{\rm e} = \left[\frac{L_{1}^{2}}{L_{0}^{2}}\right] / \left[\frac{L_{2}}{I_{0}} - \frac{L_{1}^{2}}{L_{0}^{2}}\right].$$
(64)

These equations show that the typical units of thermal properties are

$$\frac{2e^2}{h} = 77\mu S \tag{65}$$

$$\frac{k_{\rm B}}{e} = 86\mu {\rm V/K} \tag{66}$$

$$\frac{2(k_{\rm B})^2 T}{h} = 173 {\rm pW/K} \quad \text{at} \quad T = 300 K \tag{67}$$



Figure 23 – (a) Thermal coefficient relevant for electrical conductance. Contribution to conduction comes from only near the Fermi-level μ .(b) Thermal coefficient relevant for the Seebeck coefficient. Contribution comes from only near μ . (c) Thermal coefficient relevant for the electronic thermal conductance. Contribution comes from both above and below μ , with the same sign, and vanishes at μ .

Below, we will look at the physics of thermoelectric properties. It is important to point out that they are expressed in terms of the product of physical constants(e, h, k_B , etc) and the convolution of two functions ^[26], expressed as

$$\mathcal{I}_n = (E - \mu)^n \left(-\frac{\partial f(E, T)}{\partial E} \right), \quad (n = 0, 1, 2),$$
(68)

thus, the L_n in Eq. (54), at T = 0K (where $E_F = \mu$), may be expressed in terms of the \mathcal{I}_n .

The three thermal integrals as a function of chemical potential μ are shown in Fig. 23. These functions are important since they are responsible for determining the sign the thermoelectric properties may have, since, as can be seen from Eq. (54), the other relevant quantity in the L_n integrals is the transmittance, which is always a positive quantity. For the electrical conductance, L_0 [Fig. 23(a)] selects charge carriers that live at the Fermi level. ($\mu = E$). L_1 and L_2 tell about the transport of Entropy. L_1 [seebeck coefficient] selects particle that has an energy ($E > \mu$) or ($E < \mu$). The same is true for L_2 [Thermal conductance].

4.2.1 Thermoelectric properties of graphene AGNRs

In Fig. 23 we present the properties of a pristine semiconducting armchair nanoribbon (N = 13), as a function of chemical potential μ , at T = 300K. Panel (a) shows a schematic description of the system being studied. In Fig. 24(b), we notice a large Seebeck coefficient, which is mainly due to the system's large band-gap [which may be inferred from panels (c) and (d)]. The Seebeck coefficient is a central quantity in the description of the thermoelectric properties. In short, the Seebeck coefficient is an odd function that is positive for $\mu > 0$ and negative for negative $\mu < 0$ [see Fig. 23(b)]. As can be seen in Fig. 24, it is easy to note that both the electrical and the thermal integrals]. The finite temperature is responsible to cause the degradation of well-defined plateaus. Fig. 23(d) shows the thermocurrent GS, defined as a product of the Seebeck coefficient and the electronic conductance for a 13-AGNR. This is a property of great importance, as together with ZT, it will define the efficiency ranges of the material.

4.3 Thermoelectric transport properties of armchair graphene nanoribbon heterostructures

4.4 Introduction

The discovery of the Seebeck and Peltier effects, in 1821 and 1834, respectively, marked the beginning of thermoelectricity research, i.e., the study of phenomena related to the direct conversion of heat into electrical energy (Seebeck effect), or the reverse, the conversion of electrical current into a cooling heat flow (Peltier effect). Briefly, in the first, heat drives an electrical current, which can be used to perform work (see Fig. B1 in Ref. ^[27]), while, in the second, an electrical current drives a heat flow that can refrigerate something ^[28]. In contrast to a traditional mechanical thermal engine, a thermoelectric (TE) device has no macroscopic moving parts. Quantitatively, the electric potential difference created by a temperature gradient is measured by the Seebeck coefficient S (also called thermopower), while the amount of heat carried by an electrical current is measured by the Peltier coefficient II. Both, together with the thermal conductance $K = K_e + K_{ph}$ (where K_e and K_{ph} are the thermal conductance due to electrons and phonons, respectively), are material specific TE properties ^[29].

More than a century ago, in 1914, Edmund Altenkirch obtained a patent for a TE cooling and heating device ^[30, 31], i.e., a 'solid-state heat engine'. Further commercial progress was hindered by the lack of efficiency—measured by the (dimensionless) TE figure of merit $ZT = \frac{GS^2T}{K}$ in the TE energy conversion effects (G is the electrical conductance, T the absolute temperature, and GS^2 is called power factor). Indeed, a ZT > 3



Figure 24 – Top: Schematic representation of a 13-AGNR transport device. The two contacts are attached to the finite central part and have the same geometry as the central region, being however considered infinite sources of electrons. (a) Seebeck coefficient, (b) Electrical conductance, (c) Thermal conductance, (d) Thermocurrent. All results for a pristine 13-AGNR, at T = 300K.

is required for a commercially competitive refrigerator, while a ZT > 2 is necessary for a power generator to replace conventional technologies ^[32, 33]. However, it was only in 1950 that A. F. Ioffé discovered that doped semiconductors could have ZT values close to 1 (corresponding to about a sixth of Carnot efficiency ^[34]). New developments only occurred in the 1990s, after the U. S. Department of Defense stimulated, through funding, the scientific community involved in TE research to look for new ways to improve ZT values ^[35]. As a consequence, two new lines of research followed: (i) the search for the next generation of advanced bulk TE materials ^[36]; (ii) the exploration of low dimensional systems. Successes of the first line of research may be exemplified by the discovery that skutterudites ^[37], like Cerium- and Lanthanum-filled Fe_3CoSb_{12} , could reach $ZT \simeq 1.4$ ^[36], and, more recently, that doped Cu_2Se may reach $ZT \simeq 2.5$ ^[38] (see also Refs. ^[39, 40], and references therein). The second line of research was inaugurated by a seminal paper by Hicks and Dresselhaus ^[41] proposing the use of quantum-well superlattices to increase ZT(see Refs. ^[42, 43, 35, 44, 45, 46] for details) ¹.

More recently, along the lines of the second proposal mentioned above, much TE research has centered directly in studying the TE properties of so-called hierarchically nanostructured materials ^[48, 49], in addition to nanostructures like quantum dots ^[50, 51], quantum wires ^[52], and nanoribbons, especially graphene nanoribbons (GNR) ^[53, 54]. Regarding the latter, important aspects that have been studied are: (i) mixed edge GNRs, where electron resonant tunneling, originating from the multibarrier structure created by the alternation of zigzag and armchair edges, is exploited to increase the thermoreover S and decrease phonon thermal conductance K_{ph} ^[55], leading to a maximum ZT = 0.79 ^[56]; (ii) drilling nanopore arrays in chiral and zigzag GNRs, where the presence of the nanopores decreases K_{ph} , without impacting G, which is determined by edge currents, leading to an increase in efficiency to $ZT \simeq 2.0$ at room temperature ^[57]; (iii) synthesizing nanoribbons with a supercell structure composed of a hybrid of hexagonal boron nitride and graphene resulted in an increase in ZT of the order of 10 to 20 times ^[58]; (iv) the synthesis of graphene nanoribbons modulated with 'stub' structures (forming heterojunctions), in both zigzag GNRs (ZGNRs) and armchair GNRs (AGNRs) lead to a strong increase in ZT, by boosting S and suppressing K_{ph} ^[59]; (v) finally, a series of strategies have been used to introduce defects in both AGNRs and ZGNRs, leading to disorder, which results in the increase of ZT by enhancing S and decreasing K_{ph} (see Ref. ^[53] for details). A comprehensive review of these aspects can be found in Ref. ^[60] and in the special issue prefaced by the editorial in Ref. $^{[61]}$.

Motivated by those five GNR-related research lines just described, we will study the TE properties of a recently developed AGNR heterostructure that has recently been characterized In Ref.^[2], two types of AGNR heterostructures were introduced, the so-

¹ It should be also noted that TE properties of Topological Insulators have attracted much interest recently (see Refs. ^[47??] for details).



Figure 25 – (Color online) (a) Description of an N-AGNR-I(n,m) (Inline) heterostructure with N = 5 and n = m = 3. (b) Same as in panel (a), but for an N-AGNR-S(n,m) (Staggered) heterostructure, with N = 5 and n = m = 2. The resulting unit cells are indicated by horizontal solid lines and the unit cells of the AGNR backbone are indicated by vertical dashed lines in panel (a).

called 'Inline' and 'Staggered' heterostructures, denoted N-AGNR-I(n,m) and N-AGNR-S(n,m), respectively. In Fig. 47(a), we schematically show how the unit cell of an N-AGNR-I(n=3,m=3) heterostructure is built. On the top panel, the parameter n indicates how many adjacent unit cells (separated by vertical dashed lines) of the so-called backbone (colored in cyan), containing N = 5 dimension in each unit cell, as indicated in the right, will be extended into unit cells containing N + 4 dimers. As indicated in Fig. 47(a), this is done, for the first of the n unit cells, by adding six carbons to the top and bottom of the unit cell. This adds three extra benzene rings (colored in light-green) to the top and bottom of the unit cell. To extend the next unit cell (adjacent to the right), just four extra carbon atoms are needed to add two more benzene rings (colored in red). This second step is repeated until all n adjacent unit cells are extended. Fig. 47(a) shows the result for n = 3. Finally, m indicates at how many unit cells away from the last extended unit cell we will repeat the process of extending n unit cells. There is an important detail here: we are counting m from the *center* of the last extended unit cell to the center of the first extended unit cell of the next n-group to the right (see Fig. S2 in Ref. ^[2]). Therefore, the unit cell of an N-AGNR-I(n,m) heterostructure will contain n + m - 1 unit cells of the original backbone. It is clear that $m \geq 2$, since m = 1 produces an uniform AGNR with a width equal to N+4. In Fig. 47(b), we show the same process, but for a Staggered N-AGNR-S(n=2,m=2) heterostructure. The process for generating the heterostructure, and the definitions of n and m, is similar to the one in Fig. 47(a), with the exception that the *n*-long extensions alternate, separated by m, between opposite edges (notice that now

 $m \geq 1$).

We will analyze the TE properties $G, S, and K_e$, of these AGNR heterostructures, study how the parameters N, n, and m influence their figure of merit ZT, and find if there is a range of chemical potential values that maximizes ZT and also has a sizable linear-response thermocurrent $\frac{I_{th}}{\Delta T} = GS^{[62, 63]}$ (thermally induced electric current). Although our calculations are done at room temperature T = 300 K, we will disregard heat transport through phonons, that is, we will take $K = K_e$. In Sec. 4.9 we present a justification for that. The rest of the paper is organized as follows: In Sec. 5.2, we introduce the tight-binding Hamiltonian that describes the heterostructures and provide the equations that define the TE coefficients to be calculated. In Sec. 4.6, we present numerical results for the TE properties of pristine (no extensions) N-AGNRs. These results will serve as a benchmark to gauge the improvement (or not) of ZT values for the two heterostructures studied here. In Sec. 4.7, we present results for G, S, K_e, GS , and ZT for Inline N-AGNR-I(n,m) heterostructures, showing how they depend on N, n and m, and, most importantly, how their TE properties compare with those of pristine N-AGNRs (with no extensions), and if there is any improvement in ZT. We do the same in Sec. 4.8, but now for Staggered N-AGNR-S(n,m) heterostructures. In Sec. 4.9 we discuss the results obtained and we end with Sec. 4.10, where we present a summary and our conclusions. Note that despite the interest that the non-trivial topological properties of these heterostructures have generated [2, 8], we do not explore this aspect in particular in this paper.

4.5 Model and thermoelectric coefficients

The electronic structure of these N-AGNR(n,m) heterostructures will be simulated using a tight-binding Hamiltonian

$$H_{\rm tb} = -t \sum_{\langle i,j \rangle \sigma} c^{\dagger}_{i\sigma} c_{j\sigma}, \qquad (69)$$

where $c_{i\sigma}^{\dagger}(c_{i\sigma})$ creates (annihilates) an electron in site *i* with spin σ and $\langle i, j \rangle$ runs over nearest-neighbor sites. This Hamiltonian describes nearest-neighbor hoppings with transfer integral *t*, where a typical value found in the literature for this parameter is $t \sim 3.0 \text{ eV}^{[5]}$. This will be the value used for all our calculations. Reference ^[64], by the current authors, presents an explicit expression for the tight-binding Hamiltonian in reciprocal space for an N-AGNR(1,3) heterostructure.

The temperature dependent electrical and thermal conductances, G and K_e (electronic part only), respectively, as well as the thermopower S (Seebeck coefficient) are given by ^[42, 65, 66]



Figure 26 – (Color online) Thermoelectric properties for semiconducting (left panels, N = 3, 7, and 9) and metallic (right panels, N = 5 and 11) N-AGNRs. Panels (a) to (e) [(f) to (j)] are for electrical conductance G, thermopower S, thermal conductance K_e , thermocurrent GS, and figure of merit ZT, respectively. All TE properties are presented as a function of chemical potential μ .

$$G(T) = -\lim_{\Delta V \to 0} \left(J_e / \Delta V \right)_{|\Delta T=0} = \frac{2e^2}{h} I_0$$
(70)

$$K_e = -\lim_{\Delta T \to 0} \left(J_Q / \Delta T \right)_{|J_e=0} = \frac{2k_B^2}{h} T \left(I_2 - \frac{I_1^2}{I_0} \right)$$
(71)

$$S = -\lim_{\Delta T \to 0} \left(\Delta V / \Delta T \right)_{|_{J_e=0}} = -\frac{k_B}{e} \frac{I_1}{I_0}$$
(72)

where the so-called TE transport coefficients I_{α} (for $\alpha = 0, 1, 2$) are given by

$$I_{\alpha} = \int [\beta(\varepsilon - \mu)]^{\alpha} \beta f(\varepsilon, T) [1 - f(\varepsilon, T)] \mathcal{T}(\varepsilon) d\varepsilon$$
(73)

where $\mathcal{T}(\varepsilon, T)$ is the transmittance for electrons with energy ϵ and temperature T, while $f(\varepsilon, T)$ is the Fermi-Dirac distribution function. The transmittance $\mathcal{T}(\varepsilon, T)$ was calculated

using the Landauer and Green's function formalism, as described elsewhere ^[21, 67]. The calculations for \mathcal{T} were done following a standard Landauer setup, viz., three distinct regions that comprise a central (finite) region, coupled to two semi-infinite reservoirs that serve as source and drain. All three regions are formed by the heterostructure (or the pristine N-AGNR) being analyzed.

As the TE transport coefficients are dimensionless, and since (in SI units) we have that $\frac{2e^2}{h} = 77.48 \times 10^{-6} AV^{-1}$, $\frac{2k_B^2 T}{h} = 0.5753 \times 10^{-12} WK^{-1}$ (for T = 1K), and $\frac{k_B}{e} = 86.16 \times 10^{-6} VK^{-1}$, we will present the results for G, K_e , and S in units of $10^2 \times \mu AV^{-1}$, nWK^{-1} , and mVK^{-1} , respectively. We will present numerical results for these (and derived properties) as a function of chemical potential μ .

Before presenting the results, we wish to make an important remark. One TE property that is usually measured is the so-called linear-response thermocurrent $\frac{I_{th}}{\Delta T} = GS$. Thus, we will present results for this quantity too (in units of nAK^{-1}). We thus consider an improvement in the TE properties of a material if a so-called nanostructure 'band engineering' produces an increase in *both ZT* and *GS* for the same value of chemical potential μ .

4.6 Thermoelectric properties for pristine N-AGNR

AGNRs' electronic properties depend on their width N, since they can present either a metallic (N = 3p + 2) or a semiconducting (N = 3p, 3p + 1), with p an integer) ground state. In Fig. 34, we show a comparison of TE properties (electrical conductance G, Seebeck coefficient S, thermal conductance K_e , thermocurrent GS, and figure of merit ZT) between semiconducting (panels (a) to (e), left column) and metallic (panels (f) to (j), right column) AGNRs for 5 different widths N. In the first row, in Figs. 34(a) and 34(f), we plot the electrical conductance G for semiconducting (N = 3, 7, and 9) and metallic (N = 5 and 11) AGNRs, respectively. In the second row [panels (b) and (g)], we present the thermopower S, while the third row [panels (c) and (h)] shows the thermal conductance K_e . In the fourth row [panels (d) and (i)], we show the thermocurrent GS. Finally, we show the figure of merit ZT in the last row [panels (e) and (j)]. From these results, we see that the metallic systems (right panels) have ZT values that are more than three orders of magnitude lower than the semiconducting systems [compare panels (e) and (j)]. This is easy to understand, since, in a metal, any charge buildup caused by a temperature gradient will be quickly screened by the conduction electrons, resulting in a low Seebeck coefficient S [compare panels (b) and (g)], which, in turn, causes a low thermocurrent GS, a low power factor $PF = GS^2$ (not shown), and thus a low $ZT = \frac{GS^2T}{K_e}$, unless K_e is also small, which is not the case [compare panels (c) and (h)]. In the next Secs., we will present similar results, but for the Inline (Sec. 4.7) and Stag-



Figure 27 – (Color online) Variation of TE properties of N-AGNR-I(1,3) for different values of N: N = 3, 5, 7, and 9, from the first to the fourth column, respectively. All TE properties are presented as a function of chemical potential μ . From top to bottom, in each column: electrical conductance G, thermopower S, thermal conductance K_e , thermocurrent GS, and figure of merit ZT, respectively. The shaded regions in the GS and ZT panels indicate chemical potential ranges where both ZT and GS may take sizable values for the same chemical potential value.

gered (Sec. 4.8) AGNR heterostructures, showing how they vary with geometry (Staggered vs. Inline), and with N, n and m.

Before moving to the next sections, it is important to focus on the following point. Despite the very high ZT values (at room temperature) shown in Fig. 34(e), for the semiconducting AGNRS, some warning comments are necessary. First, obviously, these results do not take thermal conductivity K_{ph} into account. Second, at the chemical potential value where a peak in ZT occurs, we have a vanishing themocurrent GS, meaning that themoelectric efficiency is not accompanied by enough thermocurrent to power up a device. As mentioned in the Introduction, the ideal situation is that where we get sizable values for both quantities, ZT and GS^{-2} . As will be shown in the next few sections, in general, the AGNR ZT maximum values seen in Fig. 34 are much surpassed by those obtained for the heterostructures. However, they suffer from the same problem, viz., they are not accompanied by sizable GS values. Thus, our analysis will focus on searching for smaller peaks in ZT, created by the band engineering afforded by the unit cell extensions that generate the heterostructures. We will see that those 'secondary' peaks appear

² Notice that, a careful analysis indicates the existence of a small chemical potential interval, close to the right-side tail of the ZT peaks in fig. 34(e), where ZT has not vanished yet and GS has already started to rise. However, exploiting that in a device would require fine-tuning of the chemical potential.

around the (much enlarged) 'original' AGNR peaks and that they are associated to larger thermocurrent (GS) values than the 'original' peaks.

4.7 Thermoelectric properties for N-AGNR-I(n,m) heterostructures

4.7.1 Dependence of thermoelectric properties with N

In Fig. 35, in each of the four columns, we show results for all five TE properties we are interested in, i.e., electrical conductance G, thermopower S, thermal conductance K_e , thermocurrent GS, and figure of merit ZT, in this order, from top to bottom. Each column contains results for N-AGNR-I(1,3), for N = 3, 5, 7, and 9, from left to right, respectively. Notice that, since the largest ZT values, ZT_{max} , obtained for most of the heterostructures analyzed (both Inline and Staggered) are substantially higher than those obtained for semiconducting AGNRs, and since we are interested in finding ZT peaks that are accompanied by sizable values of themocurrent GS (which is not the case for the higher ZT peaks), we present the ZT results in a range $0 \leq ZT \leq ZT_i \ll ZT_{max}$, with the objective of finding smaller ZT peaks that are accompanied by sizable GS values. Note that ZT_i , where $i = 1, \ldots, 4$, will have a different value for each of the panels in the bottom row of the four columns in Figs. 35 to 40.

By analyzing the first row in Fig. 35 and comparing it with the results in the first row of Fig. 34, we observe the following: (i) 5-AGNR, which is metallic, has turned into semiconducting when transformed into 5-AGNR-I(1,3) [compare Fig. 34(f) with Fig. 35(b)], which then results in a much improved ZT ($ZT_{max} \approx 230$), as expected [compare Fig. 35(r) with Fig. 34(j)]; (ii) 7- and 9-AGNR (red and green curves in Fig. 34(a), respectively) had their gaps slightly decreased [compare Figs. 35(c) and (d) with Fig. 34(a)], accompanied by a one order of magnitude decrease in their ZT_{max} ; (iii) a zoom-in in the ZT panels shows that all N-AGNR-I(1,3) display the presence of secondary smaller peaks (located around the original N-AGNR peaks) with accompanying structures in GS that make it easier to spot regions of chemical potential where both ZT and GS panels in all four columns. For completeness, we list here the Z_{max} values obtained in Fig. 35: $ZT_{max} \approx 4 \times 10^3$, 2×10^2 , 25, and 25, for N = 3, 5, 7, and 9, respectively.

4.7.2 Dependence of thermoelectric properties with n

In Fig. 36, we show similar results as in Fig. 35, but now for 3-AGNR-I(n,3), for n = 1, 2, 3, and 4. The first column of Fig. 36 reproduces the 3-AGNR-I(1,3) result already shown in Fig. 35 to facilitate the evaluation of any trends with the variation



Figure 28 – (Color online) Variation of TE properties of 3-AGNR-I(n,3) for different values of n: n = 1, 2, 3, and 4, from the first to the fourth column, respectively. From top to bottom, in each column: electrical conductance G, thermopower S, thermal conductance K_e , thermocurrent GS, and figure of merit ZT, respectively. All TE properties are presented as a function of chemical potential μ . Shaded regions have the same meaning as in Fig. 35.

of n. ZT values for n > 1 [panels (r) to (t)] show a steep increase in ZT. Indeed, $ZT_{max} \approx 4 \times 10^3$, 2×10^5 , 6×10^5 , and 2.5×10^8 , for n = 1, 2, 3, and 4, respectively. However, as happened for N-AGNR-I(1,3) in Fig. 35, these large peaks in ZT have very small values of GS associated with them, thus, we searched for smaller peaks that have sizable GS values in their range of variation. We were able to find at least one peak for each heterostructure investigated (see shaded regions in the bottom two rows of panels). In particular, 3-AGNR-I(2,3) has a secondary peak with maximum $ZT \approx 110$, which occurs for a range of chemical potential with sizable GS [see Figs. 36(r) and 36(n)].

4.7.3 Dependence of thermoelectric properties with m

In Fig. 37, we show similar results as in Figs. 35 and 36, but now for 3-AGNR-I(1,m), for m = 2, 3, 4, and 5. Overall, there are increases in ZT (in relation to the ZT values shown for the N-AGNR's in Fig. 34), but they are not as large as the increases obtained with the variation of n, as shown in Fig. 36. In Fig. 37, we have that $ZT_{max} \approx 2.5 \times 10^2$, $4 \times 10^3, 2.5 \times 10^2, \text{ and } 5 \times 10^2, \text{ for } m = 2, 3, 4, \text{ and } 5, \text{ respectively.}$ It is interesting to note that 3-AGNR-I(1,4) and 3-AGNR-I(1,5) have very small values of K_e and GS [see panels (k) and (l), and (o) and (p)]. This is probably associated with the larger gaps seen in these heterostructures [see panels (c) and (d)].



Figure 29 – (Color online) Variation of TE properties of 3-AGNR-I(1,m) for different values of m: m = 2, 3, 4, and 5, from the first to the fourth column, respectively. From top to bottom, in each column: electrical conductance G, thermopower S, thermal conductance K_e , thermocurrent GS, and figure of merit ZT, respectively. All TE properties are presented as a function of chemical potential μ . Shaded regions have the same meaning as in Fig. 35.

4.8 Thermoelectric properties for N-AGNR-S(n,m) heterostructures

In this Section, we will investigate what changes when we pass from the Inline heterostructures [see Fig 47(a)] to the Staggered ones [Fig 47(b)].

4.8.1 Dependence of thermoelectric properties with N

In Fig. 38, we show results for N-AGNR-S(1,3) heterostructures, for N = 3, 5, 7, and 9. For the first Staggered heterostructures analyzed we obtained $ZT_{max} \approx 1 \times 10^4$, 2×10^2 , 6, and 2×10^2 , for N = 3, 5, 7, and 9, respectively. As shown in the bottom two rows of panels, we find promising ZT peaks (with sizable GS) in all heteorstructures investigated.

4.8.2 Dependence of thermoelectric properties with n

In Fig. 39, we show similar results as in Fig. 38, but now for 3-AGNR-S(n,3), for n = 1, 2, 3, and 4. The maxima for ZT obtained in this case were $ZT_{max} \approx 1 \times 10^4$, 2.5×10^4 , 2.5×10^4 , and 4×10^4 , for n = 1, 2, 3, and 4, respectively. As for the case



Figure 30 – (Color online) Variation of TE properties of N-AGNR-S(1,3) for different values of N: N = 3, 5, 7, and 9, from the first to the fourth column, respectively. From top to bottom, in each column: electrical conductance G, thermopower S, thermal conductance K_e , thermocurrent GS, and figure of merit ZT, respectively. All TE properties are presented as a function of chemical potential μ . Shaded regions have the same meaning as in Fig. 35.

just analyzed in the previous subsection, N-AGNR-S(1,3), we obtain promising peaks for all four heterostructures analyzed, in special for 3-AGNR-S(2,3), which has a maximum $ZT \approx 140$.

4.8.3 Dependence of thermoelectric properties with m

In Fig. 40, we show similar results as in Figs. 38 and 39, but now for 3-AGNR-S(1,m), for m = 2, 3, 4, and 5. The maxima for ZT obtained in this case were $ZT_{max} \approx 2 \times 10^2$, 1×10^4 , 1.5×10^4 , and 1.5×10^4 , for m = 2, 3, 4, and 5, respectively. As obtained when checking the variation of the TE properties of N-AGNR-S(n,m) with N and n, in Figs. 38 and 39, the variation in m produces ZT peaks with associated non-vanishing GS values for all heterostructures analyzed, albeit with smaller ZT values.

4.9 Discussion

The positive outcomes we can point to in the results for both types of heterostructures (Inline and Staggered) are as follows. First, although we have not shown these results, all the heterostructures with a metallic N-AGNR (odd N) backbone that we have investigated turned out to become semiconducting, thus with much increased ZT. Second, most of the



Figure 31 – (Color online) Variation of TE properties of 3-AGNR-S(n,3) for different values of n: n = 1, 2, 3, and 4, from the first to the fourth column, respectively. From top to bottom, in each column: electrical conductance G, thermopower S, thermal conductance K_e , thermocurrent GS, and figure of merit ZT, respectively. All TE properties are presented as a function of chemical potential μ . Shaded regions have the same meaning as in Fig. 35.

heterostructures with a semiconducting N-AGNR (odd N) backbone have also seen an increase in ZT values. For some of them, such increase was dramatic. Third, after taking the stringent condition that ZT > 1 peaks should be accompanied by non-vanishing thermocurrent (GS) values, we were able to find a few secondary peaks that fulfill this condition in the majority of the heterostructures studied.

If we take $3 \leq N \leq 15$ (both even and odd), $1 \leq n \leq 7$, and $1 \leq m \leq 7$ we obtain $2 \times 637 = 1,274$ different heterostructures where the factor 2 accounts for Inline and Staggered. Obviously, we recognize that we have just scratched the surface, since we have investigated a total of twenty heterostructures (discounting the repetitions in Figs. 35 to 40). Nonetheless, our results seem to point to the possible existence, in this large amount of different heterostructures, of an optimal combination of parameters, that could be found by some ingenious high-throughput calculation method, guided by some Machine Learning algorithm ^[68, 69, 70].

Despite the fact that we have not done calculations of lattice thermal conductance through phonons (K_{ph}) , which decreases ZT, it is well know that perturbations to the N-AGNR geometry result in smaller values of K_{ph} , when compared to the values obtained for N-AGNRs. Indeed, better TE performance can be achieved via the engineering of carbon allotropes and their derivatives, through a reduction in K_{ph} ^[71] and/or a modification



Figure 32 – (Color online) Variation of TE properties of 3-AGNR-S(1,m) for different values of m: m = 2, 3, 4, and 5, from the first to the fourth column, respectively. From top to bottom, in each column: electrical conductance G, thermopower S, thermal conductance K_e , thermocurrent GS, and figure of merit ZT, respectively. All TE properties are presented as a function of chemical potential μ . Shaded regions have the same meaning as in Fig. 35.

of the electronic band structure, hopefully without degrading the power factor GS^2 . The most important carbon allotrope is graphene, and the engineering strategies involve the production of graphene nanoribbons ^[72], graphene nanomeshs ^[73, 74], graphene nanowiggles ^[75, 76] (for example, Chevron-type GNRs ^[77]), carbon nanotubes ^[78], fullerenes ^[79], graphynes ^[80, 81], and carbon quantum dots ^[82, 83].

Of the strategies mentioned above, the so-called graphene nanowiggles ^[75] are the most relevant in relation to the heterostructures studied here. Connecting types of GNRs, which may be similar or different, into a chain-like, or quasi-1D superlattice, is one of the most studied strategies for achieving a better ZT. For example, a sequence of V-shaped GNR segments (a so-called chevron pattern) can be obtained through a synthesis method that allows the fabrication of perfectly controlled graphene nanostructures ^[84, 85]. A theoretical investigation ^[86] of TE properties of this type of nanoribbons showed a significant reduction in thermal conductance K_{ph} , compared to straight GNRs, resulting in a ZT = 0.6at room temperature. In addition, a study combining density functional theory and the non-equilibrium Green's function formalisms ^[56] has investigated different 'kink' configurations (among them the chevron-type GNRs) and shown that the phonon contribution to the thermal conductance is, in general, dramatically degraded while electronic conduction is preserved. Although, in principle, we do not expect the same degradation level of K_{ph} to occur in our heterostructures, as the one predicted for the chevron-type heterostructures (since our heterostructures are more symmetric), it is certain that some degradation in K_{ph} will occur, when compared to N-AGNRs. Given the very high values of ZT we have shown in the previous sections, when compared to N-AGNRs, it would not be far-fetched to assume that the heterostructures studied here could turn out to have competitive TE properties.

4.10 Summary and Conclusions

In summary, we have (to the best of our knowledge, for the first time) investigated the TE properties of two recently synthesized heterostructures, dubbed Inline and Staggered, denoted N-AGNR-I(n,m) and N-AGNR-S(n,m), respectively, which are obtained via chemical processes, and that can be described as unit cell extensions applied on top of an N-AGNR backbone. We calculated, for both types of heterostructures, using the Landauer formalism, the electrical conductance G, thermopower S, thermal conductance K_e , thermocurrent GS, and figure of merit ZT, at room temperature, and did a careful comparison with the results obtained for the corresponding N-AGNR backbones. Our results allowed us to conclude that (i) all metallic N-AGNR backbones become semiconduncting when transformed in either heterostructure, resulting in the expected increase in ZT; (ii) very large increases in ZT are obtained for some combinations of parameters; (iii) 'secondary' (smaller) ZT peaks are obtained that still present large values of ZT, but that, in addition, are associated to ranges of chemical potential where there is a sizable linear-response thermocurrent $\frac{I_{th}}{\Delta T} = GS$. Despite the fact that our results ignore the degrading effect of phonon thermal conductance K_{ph} over ZT, we argue that a decrease of K_{ph} , when compared to N-AGNR's, should be expected, in view of recent research in quasi-1D supperlattices like the chevron nanoribbons. We hope that our results may spur further research by theory and experimental groups alike.
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Chapter 5

Ferromagnetism in armchair graphene nanoribbon heterostructures

5.1 Introduction

Strong correlations in magic-angle twisted bilayer graphene (TBG), discovered in 2018 ^[87] (see Ref. ^[88] for a review), were associated to the presence of strongly correlated states in flat mini-bands of the hexagonal Moiré superlattice, as previously predicted by band structure calculations ^[89, 90, 91]. Recently, ARPES measurements ^[92] have provided direct evidence for the existence of flat-bands in magic-angle TBG. These developments have greatly increased the interest in the study of low-dimensional systems presenting bands with zero (or quasi-zero) dispersion.

Indeed, in the last one year alone, there has been new flat-band research in many different areas, like their experimental observation in atomically precise one-dimensional (1D) chains ^[93], as well as the study of flat-bands in strongly correlated systems ^[94, 95, 96, 97] ^[98, 99, 100, 101, 102], search for flat-bands in kagome-type lattices ^[103, 104], study of symmetry aspects of flat-band systems ^[105, 106, 107], holographic construction of flat-bands ^[108], flat-bands in pyrochlore lattices ^[109, 110], analysis of randomness in flat-band Hamiltonians ^[111], topological aspects of flat-band systems ^[112, 113, 114, 115, 116, 117], construction of flat-band tight-binding models starting from compact localized states ^[118], and study of flat-bands in graphene and graphene-like lattices ^[119, 120, 121, 122].

For a brief review of the research in flat-bands, describing initial theoretical proposals in the late 1980s ^[123, 124], their association to topological phases ^[125, 126], and their possible realization in superconducting wire networks, cold atoms in optical lattices, and photonic systems, see Ref. ^[127]. For a description of strongly correlated ground states associated to dispersionless bands, see Ref. ^[128].

Following the development of a bottom-up procedure for atomically precise synthesis of semiconducting graphene nanoribbons (GNRs) with different width, edge, and end termination ^[75], a seminal paper by Steven Louie's group in 2017 ^[17] showed that these

synthesized armchair GNRs (AGNRs) strands belonged to different topological phases, protected by spatial symmetries and with a Z_2 topological invariant whose value was dictated by their width and terminating unit cell. Thus, the bulk-boundary correspondence principle ^[129, 130, 131, 132, 133, 134] imposes that at the interface between two finite AGNRs, with different Z_2 values, a topologically protected localized state should exist, with its energy located inside the AGNR gap. This expectation was confirmed by Density Functional Theory (DFT) calculations ^[17]. The following year, two experimental groups, one in Europe^[8] and the other in the USA^[2], published side-by-side Nature papers presenting DFT and tight-binding simulations of Scanning Tunneling Spectroscopy (STS) measurements in superlattices of short AGNR strands, alternating between finite and vanishing Z_2 values, that indicated the presence, inside the (overall) AGNR gap, of a dimerized chain band structure. A Su-Schrieffer-Heeger (SSH) effective model (initially proposed to describe polyacetylene ^[18], and recently revived as a prototypical model for a onedimensional topological insulator ^[4]), was shown to qualitatively describe the experimental results. Thus, in what was described as a hierarchically engineered one-dimensional topological system^[8], the AGNR heterostructure, with topologically non-trivial properties (i.e., a topologically protected end state), is itself composed of alternating topologicallytrivial and non-trivial building blocks. Besides the ability of considerably decreasing the AGNR's spectral gap (with the recent observation of metallicity in an AGNR heterostructure ^[135]-notice that all AGNRs are actually semiconducting ^[16]), the properties of these heterostructures, as implied by the results presented in Refs. ^[2, 8], have generated much attention, as they represent one of the first stable materials (besides polyacetylene) that simulates the SSH model, which up to now had been simulated mainly in cold-atom ^[136], engineered atomic lattices ^[137, 138], photonic ^[139], acoustic ^[140], and mechanical ^[141, 142] experimental configurations. Very recent work, extending the results in Refs. ^[2, 8], may be found in Refs. [143, 144].

A much less studied aspect of these AGNR heterostructures is the presence of dispersionless bands in their band structure. In this work, using the tight-binding method and DFT, we systematically analyze how the presence or not of flat-bands, their proximity to the Fermi energy, their interplay with nearby dispersive bands, as well as if they give origin or not to a ferromagnetic ground state, depends on the parameters that define the AGNR heterostructure. Our results show that, indeed, the majority of the heterostructures studied through tight-binding present several flat-bands that can be associated to 'Wannier orbital' states, as formerly seen in pristine AGNRs ^[9]. By appropriately hole-doping these heterostructures, i.e., bringing the Fermi energy close to a flat-band, a ferromagnetic ground-state is observed through DFT simulations. The ferromagnetic exchange coupling at the flat-band appears to be mediated by a dispersive band that crosses it ^[9].



Figure 33 – Schematic representation of the meaning of the parameters N, n, and m in an N-AGNR(n,m) heterostructure. See text for details.



Figure 34 – Tight-binding band structure of a 3-AGNR(1,3) heterostructure. The flatbands are indicated by labels 1, 2, 3a, 3b, and 4, starting from the Fermi energy at half-filling (E = 0). Note that band 3 is double-degenerate.



Figure 35 – Charge density of the Wannier-like state for the -t flat-band on a pristine 3-AGNR.

5.2 Model for the heterostructures

5.2.1 The geometry of the N-AGNR(n,m) heterostructures

In Ref. ^[2], two types of AGNR heterostructures were introduced, the so-called 'inline' and 'staggered' heterostructures. In this paper, we will analyze the properties just of inline heterostructures (which we will name N-AGNR(n,m) heterostructures), since they present more flat-bands than the staggered heterostructures.

In Fig. 47, we schematically show how the unit cell of an N-AGNR(n,m) heterostructure is built. In the top panel, the parameter n indicates how many adjacent unit cells (delimited by vertical dashed lines) of the so-called backbone (a pristine N-AGNR, depicted in white), containing N = 5 dimens in each unit cell, as indicated in the right, will be extended into unit cells containing N + 4 dimers. As indicated in Fig. 47, this is done, for the first of the n unit cells, by adding six carbons to the top and bottom of the unit cell. This adds three extra benzene rings, colored in cyan, to the top and bottom of the unit cell. To extend the next unit cell (adjacent to the right), just four extra carbon atoms are needed to add two more benzene rings, colored in green. This second step is repeated until all n adjacent unit cells are extended. The top panel in Fig. 47 shows the result for n = 3. Finally, in the bottom panel, m indicates how many unit cells away from the last extended unit cell we will repeat the process of extending n unit cells. There is an important detail here: we count m from the *center* of the last extended unit cell to the center of the first extended unit cell of the next n-group to the right (notice the positioning of the vertical dashed lines in the bottom panel, see Fig. S2 in Ref. ^[2]). Therefore, the unit cell of the N-AGNR(n,m) heterostructure thus obtained will contain n + m - 1 unit cells of the original backbone. It is clear that $m \ge 2$, since m = 1 produces an uniform AGNR with a width equal to N + 4.

5.2.2 Tight-binding Hamiltonian

The band structure of these N-AGNR(n,m) heterostructures will be simulated using a tight-binding Hamiltonian

$$H_{\rm tb} = -t \sum_{\langle i,j \rangle \sigma} c^{\dagger}_{i\sigma} c_{j\sigma}, \qquad (74)$$



Figure 36 – Wannier-like states for all four flat-bands in a 3-AGNR(1,3). From top to bottom, corresponding band energies are $E_1 = -0.56$, $E_2 = -1.61$, $E_{3a} = E_{3b} = -3.00$, and $E_4 = -4.08$ eV.

where $c_{i\sigma}^{\dagger}(c_{i\sigma})$ creates (annihilates) an electron in site *i* with spin σ and $\langle i, j \rangle$ runs over nearest-neighbor sites. This Hamiltonian describes nearest-neighbor hoppings with transfer integral *t*, where a typical value found in the literature for this parameter is $t \sim 3.0 \text{ eV}^{[5]}$. In Appendix E, a specific expression will be given for Eq. (74) for a 3-AGNR(1,3) heterostructure, in real and reciprocal space.

In Sec. 5.6, long-range Coulomb interactions will be added within the DFT framework. A hybrid functional for the exchange-correlation term will be included in the DFT to better describe the Coulomb interactions as well as the Wannier-like states. The calculation methodology will be detailed in Sec. 5.6 as well.

In the next section, we will present tight-binding results for the band structure of a 3-AGNR(1,3) heterostructure. Note that the tight-binding and DFT band structures will be given in units of eV.

5.3 Flat-bands for a 3-AGNR(1,3) heterostructure

In Fig. 34, we show the tight-binding band structure for a 3-AGNR(1,3) heterostructure, for t = 3.00 eV (the nearest-neighbor hopping integral value we will use for all tight-binding calculations). For the energy-interval shown, we label the negative energy flat-bands as 1, 2, 3a, 3b, and 4, starting from the closest one to the Fermi energy (at halffilling). Their respective energies are $E_1 = -0.56$, $E_2 = -1.61$, $E_{3a} = E_{3b} = -3.00 = -t$, and $E_4 = -4.08$ eV, where the band at -t is *double-degenerate*.

It is relatively well known^[9] that N-AGNRs (pristine, with no extensions) with odd-N



Figure 37 – Band structures for N-AGNR(1,3) heterostructures for N = 5, 7, and 9 in panels (a), (b) and (c), respectively. Although it is not so apparent, for N = 9 the only flat-bands left is the pair $\pm t$. Aside from the -t flat-band, the other three flat-bands in panels (a) and (b) have changed their positions in relation to the N = 3 results (see Fig. 34). Note the scale, with only negative energies, to improve readability. The band labeled 4 in panel (a) has acquired dispersion (compare to the corresponding band in Fig. 34.)



Figure 38 – Wannier-like states for three flat-bands in a 5-AGNR(1,3). Numbers 1 to 4 in panel (c) indicate destructive quantum interference sites that prevent a continuous nearest-neighbor path from existing, which would connect all unit cells across the heterostructure, rendering state E_{3b} dispersive.

present two perfectly flat-bands at $\pm t$, and Fig. 34 shows that this also happens for the 3-AGNR(1,3) heterostructure (energy $E_{3a} = E_{3b} = -t$). As a matter of fact, this is true for all odd-N N-AGNR(1,3) heterostructures we have investigated, with the difference that for N = 3, 5 and 7 there are additional flat-bands at higher and lower energies, as shown in Fig. 34. For $N \ge 9$, these additional flat-bands acquire dispersion (see Sec. 5.4). One interesting point is that, in the N-AGNR(1,3) heterostructures, the $\pm t$ bands are double-degenerate for N = 3 and 5, however, this degeneracy is lifted for $N \ge 7$ (see Sec. 5.4).

5.3.1 The Wannier-like states

In Ref. ^[9], a very interesting analysis is done of the magnetism of these $\pm t$ flat-bands that are present in the odd-N AGNR (without extensions, i.e., pristine AGNR). Indeed, the origin of the zero-dispersion is that the Bloch states associated to the $\pm t$ bands are formed by 'isolated' clusters of charge inside each unit cell (the so-called 'Wannier orbital' states, or Wannier-like states), which have zero overlap with the clusters in adjacent unit cells. This happens because of destructive quantum interference ^[9]. This phenomenon is shown in Fig. 35, which shows the integrated charge density (over all k-values) for E = -tin each site of an N = 3 pristine AGNR. Figure 35 simulates the local density of states (LDOS) an Scanning Tunneling Microscope tip would observe in case its parameters were set to capture just the E = -t states of a 3-AGNR. It is remarkable that each and every one of the different Bloch states (for different k-values in the Brillouin zone) at E = -t has the same LDOS profile as the one shown in Fig. 35 (see Ref.^[9] for details). It is worth mentioning that these so-called Wannier-like states are also called 'compact localized states' ^[105], which, as shown in Fig. 35, are localized on a subset of lattice sites, with zero amplitude in the rest of the lattice. As shown in the Introduction, they have recently attracted a great deal of attention. A discussion of their properties and the relevant literature may be found in Ref. $^{[105]}$.

Our tight-binding results for the 3-AGNR(1,3) heterostructure (Fig. 36) show that these Wannier-like -t states, which exist in the odd-N pristine AGNRs, survive (basically unaffected) the (n, m) extensions that give origin to the heterostructure. This can be seen in the LDOS (charge density) profile shown in Fig. 36(c) for state E_{3a} , which shows exactly the same structure as the one in Fig. 35, with the difference that now the extended unit cell is wider, thus it accommodates four occupied dimers along the vertical direction, in contrast to the pristine 3-AGNR, where the Wannier-like state is composed of just two dimers (see Fig. 35). On the other hand, Fig. 36(d) shows the other Wannier-like state, E_{3b} , that is degenerate at E = -t. Interestingly, its charge profile near the edge of the extended unit cell is clearly reminiscent of the pristine 3-AGNR, while, at the center of the unit cell it is a mixture of the E_{3a} state and some charge density occupying the maximally-separated sites that are left empty by the E_{3a} state.



Figure 39 – Wannier-like states for three flat-bands in a 7-AGNR(1,3).

The interesting result shown in the other panels of Fig. 36, for the remaining three flat-bands [panels (a), (b), and (e)], is that they seem to also originate from Wannier-like states with different charge configurations [when compared to panels (c) and (d)] that also do not have overlap between adjacent unit cells. Thus, in principle, they may produce similar magnetic ground states as the one theoretically predicted for the $\pm t$ bands in pristine N-AGNRs ^[9], as long as these flat-bands are crossed by dispersive bands. Section 5.6 presents a DFT analysis of this possibility.



Figure 40 – Band structures for 3-AGNR(n,3) heterostructures for n = 1 to 4, in panels (a) to (d), respectively.

5.4 Wannier-like states for $N \ge 5$

In panels (a), (b), and (c) in Fig. 37, we see the band structure for N-AGNR(1,3) heterostructures, for N = 5, 7, and 9, respectively. Despite the fact that the complexity of the band structures increases with N, we¹

¹ Note that, to improve readability, we show just the negative energies. In addition, to facilitate comparison with Fig. 34, in panel (a) we label bands 1 to 4 accordingly, although they have obviously

: (i) flat-band 1, seen in Fig. 34, remains *perfectly* flat for N = 5 and 7, although at a different energy position, while flat-band 2 has acquired a tiny dispersion; (ii) for all three values of N the -t flat-band is present. In reality, as far as we can tell, the $\pm t$ flat-bands occur for any odd value of N; (iii) for N = 5 and 7, flat-band 4 has already acquired some dispersion; (iv) likewise, for $N \ge 9$, except for -t flat-band, the other three flat-bands (1, 2 and 4) have acquired dispersion; (v) finally, the -t flat-band for N = 5is still double-degenerate, while it is not anymore for N = 7. It is possible that farther from the Fermi level (E = 0, at half-filling) there are additional flat-bands (besides the $\pm t$ ones) for $N \ge 9$, but we have not investigated this possibility.

In Figs. 38 and 39, we show the flat-band Wannier-like states corresponding to bands 1, 2 and 3 presented in Figs. 37(a) and 37(b), for a 5-AGNR(1,3) and a 7-AGNR(1,3) heterostructure, respectively. A careful comparison of Figs. 36, 38, and 39 shows that the Wannier-like states for the same band at different values of N are semi-quantitatively the same, indicating that the maximum N for which we can look for these interesting states is N = 7, which is an N-AGNR(n,m) heterostructure size that can be faithfully obtained in the laboratory ^[8, 75, 145], suggesting that the results obtained here can be tested experimentally.

As mentioned above, there is an interesting point regarding the -t flat-band Wannierlike states E_{3a} and E_{3b} as we vary N in an N-AGNR(1,3) heterostructure: they are still degenerate for N = 5, as can be seen in Fig. 38(c), where we show the combined charge density for both bands E_{3a} and E_{3b} , however, for N = 7, it is not degenerate anymore. Notice that in Fig. 39 we show, in panel (c), the charge density just for the E_{3a} band, since band E_{3b} does not exist anymore. We speculate that, as may be inferred from the charge density distribution in Fig. 38(c), the Wannier-like state E_{3b} for N = 5 seems on the verge of losing its Wannier-like character. This occurs because there are only 4 sites (indicated by numbers 1 to 4, and showing perfect destructive quantum interference) preventing the existence of a continuous nearest-neighbor path that connects all unit cells with each other, which would result in a dispersive state.

5.5 Dependence on parameters n and m.

5.5.1 Band structure dependence with n

In Fig. 40, we see tight-binding band-structure results for 3-AGNR(n,3), for n = 1 to 4, in panels (a) to (d), respectively. In panel (a), we repeat the results shown in Fig. 34 [for 3-AGNR(1,3)] to facilitate comparison. A trend with increasing n (size of the extended region of the heterostructure) can be clearly discerned. Indeed, we see that the $\pm t$ flat-bands survive the increase in the unit cell, and a cluster of flat-bands (and

changed their positions (except for band 3) in relation to Fig. 34.



Figure 41 – Band structures for 3-AGNR(1,m) heterostructures for m = 2 to 5, in panels (a) to (d), respectively.

some bands with very little dispersion) develops in the energy range $-2.0 \leq E \leq -1.0$. It is also interesting to remark that flat-band E_1 (the one closest to the Fermi energy) tends to approach the Fermi energy as n increases. We also did an analysis for larger values of n. For example, for n = 10 (not shown), bands at higher energies seem to become less dispersive. In addition, the flat-band closest to the Fermi energy remains flat and approaches the Fermi energy even more, sitting basically at the Fermi energy for a 3-AGNR(10,3) heterostructure. Finally, for n = 10, the cluster of flat-bands mentioned above becomes more dense and somewhat closer to the Fermi energy.

We also investigated the band structure dependence with n for 5-AGNR(n,3) heterostructures (not shown) and obtained qualitatively the same results as the ones shown in Fig. 40 for N = 3, which may be considered reasonable, since we can intuitively expect a lesser dependence of the electronic structure on N than on n and m.

5.5.2 Band structure dependence with m

In Fig. 41, we see the band structures for 3-AGNR(1,m) heterostructures for m = 2 to 5 in panels (a) to (d), respectively. Here, we also reproduced Fig. 34, in panel (b), to facilitate comparison. As seen with the variation of n (but to a lesser degree), we see in Fig. 41, for 3-AGNR(1,m), that increasing m from 2 to 5 results in an accumulation of flatbands close to the Fermi energy. In addition, as observed for the n-variation, the results for the m-variation of the 5-AGNR(1,m) heterostructures (not shown) are qualitatively similar to the trend seen in Fig. 41 for 3-AGNR(1,m).

We wish to call attention to the band structure in Fig. 41(a), for 3-AGNR(1,2). In it, we see that the flat-band closest to the Fermi energy is crossed by a dispersive band that may be topologically non-trivial [2, 8]. In case this dispersive band is indeed topologically non-trivial, it would be very interesting to study the interplay of topology and ferromagnetism once this system is doped.

Before presenting the DFT results, we compile below the results presented in Figs. 36 to 41. This may serve as a guide to the reader to relate the presence (or absence) and

behavior of flat-bands with the variation of parameters N, n and m:

- 1. The $\pm t$ flat-bands, present in the pristine AGNRs, are also present for *all* values of N, n, and m investigated here, and they are associated to the *same* Wannier-like states identified in the pristine AGNRs ^[9].
- 2. For N-AGNR(1,3) (N = 3 and 5), the $\pm t$ bands are double degenerate (in contrast to the pristine AGNRs) and the partner state is also a Wannier-like state, similar to the one mentioned in the item above. This degeneracy is lifted for N > 5.
- 3. Additional flat-bands appear around the $\pm t$ flat-bands for all heterostructures analyzed, and to each different flat-band it was possible to associate a Wannier-like state that seems like a variant of the $\pm t$ Wannier-like state.
- 4. Regarding the variation of these additional flat-bands with N, we see that they survive (i.e., have zero-dispersion) up to N = 7 for all heterostructures studied here.
- 5. With increasing n, we see that the overall number of flat-bands increases, with a cluster of them forming gradually closer to the Fermi-energy, with one of them seating almost at the Fermi energy already for the 3-AGNR(10,3) heterostructure. This description of the n dependence applies to all prime values $3 \leq N \leq 7$.
- 6. Similar to the *n*-dependence, there is an increase in the number of flat-bands with m, with a similar accumulation close to the Fermi energy. As well, this description qualitatively applies to all prime values $3 \leq N \leq 7$.

We should also mention that a brief study of the so-called 'Staggered' heterostructures, which are less symmetric than the ones analyzed here (see Refs. ^[2, 8]), has shown a tendency to form considerably less flat-bands, indicating that the hetrostructures discussed here are the ones that should receive more attention in the quest for quasi-1D ferromagnetism.

5.6 Ferromagnetic phase obtained with DFT

To address the possible existence of any magnetic phase under hole-doping, we will use DFT, which is a more realistic calculation than tight-binding and that can treat correlations at the mean-field level. We will search for indications of a ferromagnetic ground-state on two heterostructures, viz., 3-AGNR(1,3) and 5-AGNR(1,3). According to Ref. ^[9], the presence of itinerant carriers is important to mediate ferromagnetism between the isolated magnetic moments in each unit cell of the Wannier-like states. The 3-AGNR(1,3) and 5-AGNR(1,3) heterostructures present dispersive bands intercepting



Figure 42 – DFT and tight-binding band structures for a 3-AGNR(1,3) heterostructure, at half-filling, in panels (a) and (b), respectively. As expected, the DFT bands are not particle-hole symmetric, but, other than that, there is a good qualitative agreement between DFT and tight-binding. The numbered bands are discussed in the text.

the flat-bands, as can be seen in Figs. 34 and 37(a), respectively. We will postpone a careful DFT analysis of the ferromagnetic ground-state dependence on the parameters n and m to a future publication.

5.6.1 Details of the DFT calculations

We do a DFT calculation within the projector augmented wave scheme ^[146] for the pseudopotentials. The total energies and electronic structures are self-consistently computed within a plane-wave basis-set with a kinetic energy cut-off of 350 eV. We used the Vienna Ab initio Simulation Package (VASP) ^[147, 148]. For a better description of the exchange-correlation term of the DFT, we use a hybrid functional to improve the description of the many-electron interactions and charge localization ^[149]. The HSE06 hybrid functional has been used ^[150], where the screened functional contains part of the exact Hartree-Fock exchange that has been shown to give accurate results for the exchange splitting, which is crucial to understand the magnetic properties in our system. Interestingly, our results show that the inclusion of the hybrid functional puts the E_{3a} flat-band around 3 eV from the Fermi energy, matching the tight-binding results (see Fig. 42). By suppressing the hybrid functional, using just the generalized gradient approximation ^[151], the E_{3a} band stays around 2.5 eV from the Fermi level. As we are using the periodic supercell approach within the first principles calculations, the exchange interactions between adjacent unit cells are also included.

5.6.2 Band structure for 3-AGNR(1,3): comparison DFT/tightbinding

Panels (a) and (b) in Fig. 42 show a comparison of the DFT and tight-binding band structures for a 3-AGNR(1,3) heterostructure, respectively. Contrary to the tight-binding bands, the DFT bands are not mirror symmetric around E = 0. Note that the tightbinding bands would also lack mirror symmetry if a next-nearest-neighbor hopping had been introduced (breaking chiral symmetry). Some details of the negative energy DFT bands are worthy of mention. First, we see that the DFT band closest to the Fermi energy (numbered 1 in Fig. 42), which is flat in the tight-binding results, has acquired dispersion. Fig. 36(a) shows the tight-binding Wannier-like state for this band. Since its charge density is mostly accumulated at the edges of the unit cell (and it does not completely vanish at its center either), one may argue that small perturbations introduced by the DFT calculations to the tight-binding results may create an overlap between the Wannier-like states in adjacent unit cells and result in dispersion (as discussed above in relation to the E_{3b} tight-binding band for a 5-AGNR(1,3) heterostructure). On the other hand, the Wannier-like states [see panels (b) and (c) in Fig. 36] for the bands denoted 2 and 3a in Fig. 42 are much more concentrated at the center of the unit cell [especially for band 3a, see Fig. 36(c) and thus they should be more robust against perturbations that could create an overlap between adjacent unit cells. Thus, as expected, DFT bands 2 and 3a are *perfectly* flat. Finally, the same reasoning leads us to expect that the DFT bands 3b and 4 should acquire dispersion, as they do indeed, the latter less so than the former.

A final point can be made, along the lines of the qualitative discussion above, if we compare our DFT results with the DFT results in Ref. ^[9]. There, it was obtained, for a pristine (no extensions) 5-AGNR, that the $\pm t$ DFT flat-bands, at zero doping, acquire a dispersion of ≈ 0.4 eV (see Fig. 4(a) in Ref. ^[9]). On the other hand, the DFT $\pm t$ bands for N-AGNR(1,3), for N = 3 [band 3a in Fig. 42(a)] and N = 5 (not shown), are *perfectly* flat. This seems to indicate that in an N-AGNR(n,m) heterostructure, which has a wider unit cell than a pristine AGNR, the charge density of the $\pm t$ Wannier-like states in each unit cell [like the ones shown in Figs. 36(c), 38(c), and 39(c)] is even more insulated from the charge density in adjacent unit cells, and thus can result in a more robust (more massive) DFT flat-band.

5.6.3 DFT bands at finite doping and ferromagnetic groundstate

To bring the Fermi energy close to the flat-bands, and thus investigate their properties, we start hole-doping the 3-AGNR(1,3) heterostructure. We measure the hole-doping x_h from the half-filling point, thus $x_h = 1 - \langle n \rangle$ (therefore, $x_h = 0$ at half-filling), where $\langle n \rangle$ is the electron average site-occupancy.



Figure 43 – DFT band structures for a 3-AGNR(1,3) heterostructure at different holedopings: (a) $x_h = 0.10$, (b) $x_h = 0.0$ (half-filling), and (c) $x_h = 0.23$. In panels (a) and (c), majority-spin bands are in blue and minority-spin bands are in red.

In Fig. 43, we show the DFT bands for $x_h = 0.10$, 0.0 (half-filling), and 0.23, in panels (a) to (c), respectively. The Fermi energy is at E = 0.0 in each panel. In panel (b), we repeat the results shown in Fig. 42(a) to better illustrate the hole-doping effects. In Figs. 43(a) and 43(c), at finite doping, we show the spin-decomposed band structure obtained through a hybrid DFT calculation, where the majority-spin bands are denoted in blue and the minority-spin bands are in red. The cyan arrows connecting the center panel to each one of the adjacent panels indicate the extent of the exchange splitting of each flat-band. The arrows connecting band 2 [in panel (b)] to the corresponding exchangesplit bands in panel (a) indicate the extent of the exchange splitting over band 2 for $x_h = 0.1$, given by $E_{2,0.1} \approx 1.0$ eV. Likewise, the arrows connecting panels (b) and (c) indicate the exchange splitting energy of band 3a for $x_h = 0.23$, corresponding to $E_{3a,0.23} \approx 2.0$ eV.

In Fig. 44, we show the energy difference between the ferromagnetic and paramagnetic states, $\Delta E = E_{FM} - E_{PM}$, for both a 3-AGNR(1,3) (blue circles) and a 5-AGNR(1,3) (purple left-triangles), where $\Delta E < 0$ indicates a ferromagnetic ground-state. The most stable ferromagnetic configuration occurs when the hole-doping reaches the 3*a* flat-band, for both 3- and 5-AGNR(1,3). The inverse dependence of the ferromagnetic stability with N can be attributed to the reduction of the overall band flatness as N increases (see Figs. 34 and 37).

From Ref. ^[9], we obtain that the gain in energy due to ferromagnetic ordering of a pristine 5-AGNR is $\Delta E_p \approx -37.5$ meV (per unit cell). Since the number of occupied Carbon atoms in the ferromagnetic state in each unit cell is $N_{occ} = 6$ (see Fig. 5(b) in Ref. ^[9]), we obtain $\frac{\Delta E_p}{N_{occ}} = -6.25$ meV. The corresponding results for the two heterostructures we analyzed through DFT, i.e., 3-AGNR(1,3) and 5-AGNR(1,3), were $\Delta E_3 = -150$ meV, $N_{occ} = 8$, and $\Delta E_5 = -105$ meV, $N_{occ} = 10$. This results in $\frac{\Delta E_N}{N_{occ}} = -18.8$ meV and -10.5 meV, respectively. This shows that, if we compare the ferromagnetic energy gain for the pristine 5-AGNR and the 5-AGNR(1,3), the heterostructure had almost 70%

more energy gain than that of the pristine AGNR. We believe that to be the case for two main reasons. First, the N-AGNR(n,m) heterostructures studied here through DFT present true flat-bands, contrary to what was seen in the pristine N-AGNRs studied in Ref. ^[9]. Second, the pristine N-AGNRs show a single *low-dispersion* band, while our N-AGNR(n,m) heterostructures show multiple *perfectly* flat-bands [two in the case of 3-AGNR(1,3), bands labeled 2 and 3a in Fig. 42(a)] and multiple *almost* flat-bands [two in the case of 3-AGNR(1,3), bands 3b and 4 in Fig. 42(a)], which should clearly result in a more robust ferromagnetic ground state.



Figure 44 – $\Delta E = E_{FM} - E_{PM}$ as a function of hole-doping x_h for 3-AGNR(1,3) (blue circles) and 5-AGNR(1,3) (purple left-triangles).

5.7 Wannier-like states: comparison between DFT and tight-binding

In this section, we want to highlight the fact that it is not only the DFT and tightbinding band structures that are qualitatively similar (as shown in Fig. 42), but also the Wannier-like states associated with the flat-bands obtained by either method that are qualitatively similar too.

In the top panel of Fig. 45 we reproduce Fig. 36(a), with the tight-binding result for the flat-band E_1 Wannier-like state for a 3-AGNR(1,3) at half-filling. In the bottom panel, we show the corresponding DFT result. Close inspection indicates that there is a semi-quantitative agreement between tight-binding and DFT. Figure 46 makes the same comparison for flat-bands 2, 3a, 3b, and 4, and close inspection of the plots shows that the tight-binding results are surprisingly close to the DFT results in all cases.



Figure 45 – Wannier-like state for flat-band E_1 for a 3-AGNR(1,3) heterostructure. Top panel: tight-binding result; bottom panel: DFT result.



Figure 46 – Wannier-like states for flat-bands E_2 , E_{3a} , E_{3b} , and E_4 for a 3-AGNR(1,3) heterostructure. Top panel: tight-binding result; bottom panel: DFT result, for all pairs of results.

5.8 Summary and conclusions

We have used the tight-binding and DFT- methods to study the electronic properties of recently synthesized N-AGNR(n,m) graphene heterostructures ^[2, 8], which have been shown to present, for specific values of N, n, and m, topological properties at low energy that can be simulated by the SSH model. We found out that the heterostructures show a multiplicity of flat-bands, whose properties can be reasonably well controlled by the parameters N, n, and m. We see flat-bands in our heterostructures up to N = 7. We have strong indications that the quantum interference mechanism that gives origin to the $\pm t$ single flat-band in pristine AGNRs ^[9] is at play in all the flat-bands analyzed in our heterostructures. The pristine AGNR $\pm t$ bands are still present in the heterostructures, but with the interesting presence of a degenerate partner (for N = 3 and 5) in the tightbinding simulations. This degeneracy is slightly lifted in the DFT results for all values of N. Importantly, our DFT results show that a few of the flat-bands observed in the tight-binding simulations remain *perfectly* flat in the DFT simulations as well. Thus, the ferromagnetism observed in our DFT results is considerably stronger than that observed in pristine AGNRs ^[9]. As a bonus, we found that the charge density associated with the flat-bands obtained via tight-binding agree surprisingly well with the corresponding results obtained through DFT.

Given the experimental availability of these heterostructures, our results suggest that it would be interesting to experimentally explore the possibility of ferromagnetism in these systems, which, given the variety of parameters that can be manipulated, opens up the possibility of looking for non-trivial topology in a ferromagnetic quasi-1D system.

Chapter

Conclusion

In this dissertation, our principal objective was to investigate the thermoelectric properties and the possibility of ferromagnetism in heterostructures based on AGNRs. As an extra motivation, to be exploited in future research, these heterostructures display non-trivial topology. We used as basic techniques the tight-binding approach, the Landauer formalism, and the Green's functions method. The former has served as a basis for the band structure analysis and the occurrence of ferromagnetism (obtained through a DFT analysis). The thermoelectric properties were studied by using the Landauer theory, along with Green's functions. The results were substantial, since, concerning the magnetism analysis, we found that the band engineering, obtained by modifying the AGNRs into heterostructures, was responsible for a substantial enhancement of ferromagnetism when compared to the pristine AGNRs, with the exciting benefit that ferromagnetism in a one-dimensional system is still barely explored, even more so in a system with nontrivial topology. We have, also, investigated the thermoelectric properties of two types of heterostructures, Inline and Staggered. We have analyzed, for both types, the electrical conductance G, thermopower S, thermal conductance K_e , thermocurrent GS, and figure of merit ZT, at T = 300 K for different configurations, and did a detailed comparison with the results obtained for the corresponding N-AGNRs. Our results show that the design of heterojunctions from a metallic AGNR is responsible for a significant increase in thermoelectric properties. In addition, some of the heterostructures studied have shown promise, by displaying notable thermoelectric efficiency.

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APPENDIX \mathbf{A}

The tight-binding method

For the model description, we will start by defining an atomic orbital ϕ whose energy is E. Our purpose is to determine the interaction effects of atoms in the crystal. For this, we need to define a proper Bloch wave function. A good guess is the following equation

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} e^{i\mathbf{k}\cdot\mathbf{r}_{j}} \phi\left(\mathbf{r} - \mathbf{r}_{j}\right)$$
(75)

where the summation is performed on all atoms in the lattice. The vector r_j shows the position of the j^{th} atom. The function $\phi(\mathbf{r} - \mathbf{r_j})$ indicates an atomic orbital around j^{th} . A fundamental property of Eq. (75), which guarantees that it satisfies Bloch's theorem, is $(\mathbf{k} + \mathbf{G}) = \mathbf{k}$, where \mathbf{G} is the lattice vector. Starting from Eq. (75), we have

$$e^{\mathbf{i}\mathbf{k}\cdot\mathbf{r_j}} \to e^{\mathbf{i}(\mathbf{k}+\mathbf{G})\cdot\mathbf{r_j}} = e^{\mathbf{i}\mathbf{k}\cdot\mathbf{r_j}}e^{\mathbf{i}\mathbf{G}\cdot\mathbf{r_j}}$$
(76)

from definition of the reciprocal lattice, we now that $\mathbf{G} = 2\pi \mathbf{n}$ (n being an integer).

$$e^{\mathbf{iG}\cdot\mathbf{r_j}} = 1 \tag{77}$$

thus

$$e^{\mathbf{i}(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}_{\mathbf{j}}} = e^{\mathbf{i}\mathbf{k}\cdot\mathbf{r}_{\mathbf{j}}} \tag{78}$$

the above result implies that the significant interval of the wave vector \mathbf{k} is inside the First Brillouin Zone.

One point we should keep in mind is that the method we are dealing with gives us only an approximate result. So the amount we are interested in is the expected value of energy. Remember, the mean value for a generic operator \mathbf{A} in a very large set of identically prepared states ψ is

$$\langle \mathbf{A} \rangle = \langle \psi | \mathbf{A} | \psi \rangle = \int \psi^* \mathbf{A} \psi \mathbf{d}^3 \mathbf{r}$$
(79)

where $\langle \mathbf{A} \rangle$ represents the average of many measurements in the ψ states. The eigen energies will be obtained from the system Hamiltonian operator

$$\mathbf{H} = \frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \tag{80}$$

、

for solve the problem, what we should do is change $\psi \to \psi_k(\mathbf{r})$ and $\mathbf{A} \to \mathbf{H}$ into Eq. (80)

$$\langle \mathbf{H} \rangle = \langle E \rangle = \frac{1}{N} \int \sum_{j}^{\prime} e^{-\mathbf{i}\mathbf{k} \cdot \mathbf{r}_{j}} \phi^{*}(\mathbf{r} - \mathbf{r}_{j}) \mathbf{H} \sum_{j^{\prime}} e^{\mathbf{k} \cdot \mathbf{r}_{j}^{\prime}} \phi(\mathbf{r} - \mathbf{r}_{j}^{\prime}) \mathbf{d}^{3} \mathbf{r}$$
(81)

or

$$\langle E \rangle = \frac{1}{N} \sum_{j,j'} \int e^{-\mathbf{i}\mathbf{k} \cdot \mathbf{r}_j} \phi^* \left(\mathbf{r} - \mathbf{r}_j\right) \mathbf{H} e^{\mathbf{i}\mathbf{k} \cdot \mathbf{r}'_j} \phi \left(\mathbf{r} - \mathbf{r}_j\right) \mathbf{d}^3 \mathbf{r}$$
(82)

For each term $\sum_{j'}$ we will add over all the points \sum_{j} . Since the points are identical, we can change $\sum_{j'} \to N$. Furthermore, we have arbitrarily decided that $r'_j = 0$. Thus

$$\langle E \rangle = \sum_{j} \int e^{-\mathbf{i}\mathbf{k} \cdot \mathbf{r}_{j}} \phi^{*}(\mathbf{r} - \mathbf{r}_{j}) \mathbf{H} \phi(\mathbf{r}) \mathbf{d}^{3} \mathbf{r}$$
(83)

We can simplify our calculations a little more by using the Hückel approximation, in which only the interactions between neighboring sites are considered

$$\langle E \rangle_{\text{Hückel}} = \int \phi^*(\mathbf{r}) \mathbf{H} \phi(\mathbf{r}) \mathbf{d}^3 \mathbf{r} + \sum_{all} e^{\mathbf{i} \mathbf{k} \cdot \mathbf{r}_j} \int_{all} \phi^*(\mathbf{r} - \mathbf{r}_j) \mathbf{H} \phi(\mathbf{r}) \mathbf{d}^3 \mathbf{r}$$
(84)

$$\langle E \rangle_{\text{Hückel}} = \underbrace{\int \phi^*(\mathbf{r}) \mathbf{H} \phi(\vec{r}) d^3 r}_{\equiv \alpha} + \sum_{n,n} e^{-\mathbf{i}\mathbf{k} \cdot \mathbf{r_j}} \underbrace{\int \phi^*(\mathbf{r} - \mathbf{r_j}) \mathbf{H} \phi(\mathbf{r}) d^3 \mathbf{r}}_{\equiv \beta}$$
(85)

The first term α represents the site energy, that is, the mean value to energy for the state $\psi(r)$. The second term is known as the integral, a term that takes into account the interaction between neighboring sites. As an example, we will show how to calculate the auto-energies for "s bands" states from s atomic atoms. As the problem has spherical symmetry, β will be the same for everyone. For a simple cubic lattice with side length a. We get

$$\langle E \rangle_{\text{Hückel}} = \alpha + \beta \sum_{n,n} e^{-\mathbf{i}\mathbf{k}\cdot\mathbf{r_j}}$$
 (86)

and the respective r_j can be written as is

$$\mathbf{r}_{\mathbf{j}} = \pm \mathbf{\hat{x}}a, \pm \mathbf{\hat{y}}a \pm \mathbf{\hat{z}}a \tag{87}$$

Furthermore, the wave vector will be given by

$$\mathbf{k} = \mathbf{\hat{x}}k_x + \mathbf{\hat{y}}k_y + \mathbf{\hat{z}}k_z \tag{88}$$

and by replacing the Eqs. (88) into Eq. (89), we arrive at



Figure 47 – Cubic lattice band structure, with $k_x = k_y = 0$.

$$\langle E \rangle_{\text{Hrckel}} = \alpha + \beta \underbrace{\left(\underbrace{e^{-ik_x a} + e^{+ik_x a}}_{2\cos k_x a} + \underbrace{e^{-ik_y a} + e^{+ik_y a}}_{2\cos k_y a} + \underbrace{e^{-ik_z a} + e^{+ik_z a}}_{2\cos k_z a} \right)}_{= \alpha + 2\beta \left[\cos k_x a + \cos k_y a + \cos k_z a \right]}$$
(89)

In fig. 47, by imposing $k_y = k_z = 0$, we will plot $\langle E \rangle$ vs. k_x
APPENDIX

The SSH model

The Su-Schrieffer-Heeger (SSH) model originally was developed to treat the electrical conductivity in polyacetylene solitons ^[152]. Nowadays, though, it has drawn attention as a simple prototype to investigate topological insulators. This model is described through a one-dimensional chain, Fig 48, of carbon atoms, identified here as A and B sites, in which the atoms periodically organize themselves in a 1D planar system. In Fig. 48, v parameter indicates the hopping strength for electrons inside the unit cell, black dotted rectangle, and w refers to electron hopping between adjacent unit cells. Thus, we can say that the SSH model forms a dimerized chain, where we need to use two different hopping parameters to describe all the relevant physics of the chain.



Figure 48 – Schematic representation of an SSH chain. The model is created using two different lattices, which we will denote as A and B sub-lattices. Because it is a dimerized system, we need to use two hopping parameters, w, and v, to fully describe the system, where the first refers to the electron hop between neighboring unit cells and the second relates to the electron hop inside of each unit cell. The unit cell is shown in a dotted region (rectangle).

B.1 Tight-binding model for SSH chain

We will determine the SSH Hamiltonian by using the nearest neighbor TB approach. In second quantization formalism, it can be written as

$$H = v \sum_{m=1}^{N} (b_m^{\dagger} a_m + \text{H.C.}) + w \sum_{m=1}^{N-1} (a_{m+1}^{\dagger} b_m + \text{H.C.}),$$
(90)

where b_m^{\dagger} is an operator that creates an electron in the *mth* atom of B sublattice and b_m is the operator that annihilates an electron in the *mth* atom of B sublattice, the same is true for A sublattice. The H.C term indicates a hermitian conjugate.

The energy spectrum of the SSH model is obtained by the H diagonalization. For simplification, we can use the system periodicity to make the diagonalization simpler. We can set periodic boundary conditions (PBC) along one direction, to simulate an infinite lattice. As a result, it is conceivable to admit a basis change, from real space to reciprocal. In this way, by using Fourier transform, we can transform the creation/annihilation operators. For this, we use the following set of equations

$$a_{m} = \frac{1}{\sqrt{N}} \sum_{k} a_{k} e^{ikx_{m}},$$

$$b_{m} = \frac{1}{\sqrt{N}} \sum_{k} b_{k} e^{ikx_{m}},$$

$$a_{m}^{\dagger} = \frac{1}{\sqrt{N}} \sum_{k} a_{k}^{\dagger} e^{-ikx_{m}},$$

$$b_{m}^{\dagger} = \frac{1}{\sqrt{N}} \sum_{k} b_{k}^{\dagger} e^{-ikx_{m}}.$$
(91)

by applying Fourier transform on first term of H, we find

$$\sum_{m=1}^{N} b_{m}^{\dagger} a_{m} = \sum_{m=1}^{N} \frac{1}{\sqrt{N}} \sum_{k} b_{k}^{\dagger} e^{-ikx_{m}} \frac{1}{\sqrt{N}} \sum_{k'} a_{k'} e^{ik'x_{m}}$$

$$= \sum_{kk'} \left(\sum_{m=1}^{N} \frac{1}{N} e^{-i(k-k')x_{m}} \right) b_{k}^{\dagger} a_{k'},$$
(92)

where the above term in parentheses is the Kronecker delta symbol

$$\delta_{kk'} = \sum_{m=1}^{N} \frac{1}{N} e^{-i(k-k')x_m},\tag{93}$$

therefore

$$\sum_{m=1}^{N} b_{m}^{\dagger} a_{m} = \sum_{kk'} \delta_{kk'} b_{k}^{\dagger} a_{k'}.$$

$$= \sum_{k} b_{k}^{\dagger} a_{k}.$$
(94)

Repeating the procedure for the second term, we get

$$\sum_{m=1}^{N-1} a_{m+1}^{\dagger} b_m = \sum_{m=1}^{N-1} \frac{1}{\sqrt{N}} \sum_k a_k e^{-ikx_{(m+1)}} \frac{1}{\sqrt{N}} \sum_{k'} b_{k'} e^{ik'x_m},$$

$$= \sum_{kk'} \left(\sum_{m=1}^{N-1} \frac{1}{N} e^{-ikx_{(m+1)}} e^{ik'x_m} \right) a_k^{\dagger} b_{k'},$$
(95)

but $x_{m+1} = x_m + 1$. This implies that

$$\sum_{m=1}^{N-1} a_{m+1}^{\dagger} b_m = \sum_{kk'} \left(\sum_{m=1}^{N-1} \frac{1}{N} e^{-i(k-k')x_m} \right) e^{-ik} a_k^{\dagger} b_{k'},$$

$$= \sum_{kk'} \delta_{kk'} e^{-ik} a_k^{\dagger} b_{k'},$$

$$= \sum_k e^{-ik} a_k^{\dagger} b_k.$$
 (96)

Thus, the Hamiltonian in k-space is given by

$$H = \sum_{k} \left[v(b_{k}^{\dagger}a_{k} + \text{H.C.}) + w(e^{-ik}a_{k}^{\dagger}b_{k} + \text{H.C.}) \right]$$

=
$$\sum_{k} \left[(b_{k}^{\dagger}a_{k}(v + we^{ik}) + a_{k}^{\dagger}b_{k}(v + we^{-ik}) \right],$$
 (97)

where

$$H(\mathbf{k}) = \begin{pmatrix} 0 & \mathbf{v} + \mathbf{w}e^{-ik} \\ \mathbf{v} + \mathbf{w}e^{ik} & 0 \end{pmatrix}$$
(98)

is a block diagonal Hamiltonian, given for all different k values. Solving $H(\mathbf{k})$, we get the eigenvalues of the SSH chain

$$E = \pm \sqrt{v^2 + w^2 + 2vw\cos(k)}.$$
(99)

where \pm stands for the conduction and valence bands, respectively. The energy dispersion is shown in Fig. 49 as a function of the w and v parameters. It is easy to notice that when w = 0, which corresponds to several isolated dimers, we have just dispersionless energy bands (flat bands, where the group velocity is zero) in the system spectrum. For v = 0, we can observe similar behavior, although, as we will discuss later, the physics presented by it is quite different from that presented by the previous one. When v = w, we have the simple case where there is a single atom per unit cell, similar to a metallic arrangement. For v > w and v < w, we obtain two dispersive bands with *gap* of energy.



Figure 49 – Illustration of band structure of the SSH model. For five distinct hopping parameters. (a) w = 0 and v = 1, with $\nu = 0$, (b) w = 0.6 and v = 1, with $\nu = 0$, (c) w = 1 and v = 1, with ν undefined, (d) v = 0.6 and w = 1, with $\nu = 1$ and (e) v = 0 and w = 1, with $\nu = 1$.

When examining just the energy spectrum, we can erroneously assume that the phase diagram presented in Fig. 49 gives a symmetry relation between results before and after v = w (metallic system). We will see below that the two situations differ in several important physical properties. Thus, it becomes suitable to comprehend in more depth this distinction. In consequence, it is necessary to investigate the system topology, which is hidden not in the band structure, but in its eigenvectors. Here, we will introduce a new quantity designated by *winding number*. For a two-level system, the Hamiltonian can be written according to Pauli matrices, $\vec{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$, as follows

$$H(k) = \begin{pmatrix} 0 & h(k) \\ h^*(k) & 0 \end{pmatrix} = d_x(k)\hat{\sigma}_x + d_y(k)\hat{\sigma}_y + d_z(k)\hat{\sigma}_z,$$
(100)

where, in the SSH model, the vector $\vec{d}(k)$ is given by

$$\vec{d}(k) = \left(v + w\cos(k), w\sin(k), 0 \right)$$
(101)

Since k varies from 0 to 2π , the vector $\vec{d}(k)$ draws a circle on the plane (dx, dy), centered on (v, 0) and with a radius equal to w. The topology of this path is described by a topological invariant, called *winding number* ν , which counts the number of times that $\vec{d}(k)$ winds around the origin.

Given the unit vector

$$\hat{d}(k) = \frac{\vec{d}(k)}{|\vec{d}(k)|},$$
(102)

an analytical expression is obtained for the winding number

$$\nu = \frac{1}{2\pi} \int \left(\hat{d}(k) \times \frac{d}{dk} \hat{d}(k) \right)_z dk.$$
(103)

In Fig. 50 we depict the evolution of the $\vec{d}(k)$ vector, according to the dispersion relation shown in Fig. 49, in the first Brillouin zone.



Figure 50 – (a) w = 0 e v = 1, with $\nu = 0$, (b) w = 0.6 e v = 1, with $\nu = 0$, (c) w = 1 e v = 1, with ν undefined, (d) v = 0.6 e w = 1, with $\nu = 1$ e (e) v = 0 e w = 1, with $\nu = 1$.

 \Box For v > w and w = 0, we have $\nu = 0$, which characterizes a topologically trivial phase.

- \Box In v = w, the circle described by $\vec{d}(k)$, touches the origin and $\nu = 0$ is undefined.
- □ The paths described by $\vec{d}(k)$ for v < w and v = 0 involve the origin, thus $\nu = 1$, which indicates a topologically non-trivial phase.

To summarize, the system just before and after v = w differs in a topological characteristic, which in this example is a topological invariant. As illustrated in Fig. 50, the system exhibits a phase transition from the trivial phase, characterized by $\nu = 0$, to the topological phase, indicated by $\nu = 1$. Therefore, the ν (0 or 1) value defines two topological classes of H (k). Considering that we can not transform one class into another without going through a topological phase transition in v = w, that is, without going through a metallic phase (closing the *gap*).

B.1.1 Edge states for open chain

Until now, we have focused on an infinite model (system without borders). let us now concentrate on a finite part of the system. To illustrate this, consider the slices depicted in Fig. 51 (a) (c) as an example, which consists of four periodic cells. In this situation, there are two extreme limits: w = 0 and v = 0. Furthermore, as the system no longer has a periodicity, we have not to worry about the k wave vector.



Figure 51 – w = 0 and v = 1, with $\nu = 0$, (b) w = 0.6 and v = 1, with $\nu = 0$, (c) w = 1 and v = 1, with ν undefined, (d) v = 0.6 and w = 1, with $\nu = 1$ and (e) v = 0 and w = 1, with $\nu = 1$.

- (a)
- 1. For w = 0 and $v \neq 0$, see Fig. 51 (a), the result suggests that system is formed by decoupled dimers (trivial case). Here, the energy spectrum will be extremely degenerate, as shown in Fig. 51 (b).
- 2. For $w \neq 0$ and v = 0, see Fig 51 (c), the case is somewhat different, since, in addition to the dimers that cannot see each other, there are two isolated sites at the boundaries of the chain. This condition gives rise to zero energy states that

live inside gap, as can be seen in Fig. 52 (d). These states are known as edge states (characteristic of a topological phase).



Figure 52 – (a) Energy spectrum as a function of v with, w = 1, parameter, for 10 unit cells.(b) Energy spectrum as a function of v, with w = 1, parameter, for 50 unit cells.(c) Energy spectrum as a function of v, with w = 1, parameter, for 10 unit cells.(d) Energy spectrum as a function of v, with w = 1 parameter, for 50 unit cells. Source: ^[4].

In Fig. 52, we show the energy dispersion as a function of v and w parameters, for four different configurations. As we can see, for v / w < 1.0 (moving to the limit v / w <= 1.0 for strings far away) there are zero energy states. Precisely two states are located at the ends of the (finite) chain. We will focus now on the wave functions related to those states.

Now, to explain the existence of edge states (E = 0), we can take a finite part of the system. As can be seen from Fig. 53 (c), the state with energy $E \neq 0$ is completely delocalized over the whole system (*bulk* state). On the other hand, states with E = 0, (see Figs. 53 (a) and (b)), are extremely located at the edges of the strips. In addition, it is seen that the edge states survive only until v > w. Beyond this limit, that is, the phase transition, there are no more states with zero energy, as can be seen in Fig. 52.

In summary, the discussion above implies that there is a direct correlation between the system topological properties at bulk (encoded in eigenvectors) and the finite chain



Figure 53 - (a) and (b), show wavefunctions for Edgestates on the SSH chain. (c) Shows wavefunction for a bulk state.

behavior, especially at the edges. For example, in SSH model, there seems to be a connection between a topological invariant ν and the existence or not of edge states. In the SSH mode trivial phase (v > w) we saw that, for $\nu = 0$, it is not show zero-edge states (trivial insulator). On the other hand, for the non-trivial phase (w > v) it is observed that the invariant ν is worth 1, which indicates the existence of edge states (topological insulator).

APPENDIX C

Tight-binding for Armchair

In this section, we will show how to calculate the energy spectrum of an AGNR, considering only p_z orbitals and employing the TB method. The TB Hamiltonian for an AGNR ribbon, as sketched in Fig. 5, in real space, has the following form

$$H = -t \sum_{l} \left[\sum_{m \in \text{odd}} a_{l}^{\dagger}(m) b_{l-1}(m) + \sum_{m \in \text{ even}} a_{l}^{\dagger}(m) b_{l}(m) \right] + \text{H.C.}$$

$$-t \sum_{l} \sum_{m=1}^{N-1} \left[b_{l}^{\dagger}(m+1) a_{l}(m) + a_{l}^{\dagger}(m+1) b_{l}(m) \right] + \text{H.C.},$$
(104)

where $\mu_l^{\dagger}(m)$ and $\mu_l(m)$ ($\mu = a, b$) are creation and annihilation operators for an electron in sub-lattices A and B, in the *m*-th dimer (where m = 1, 2, ..., N) of the *l*-th unit cell, and t is the NN hopping parameter. The system is formed by L_y unit cells and has periodic boundary conditions along the y-axis

$$a_{l+L_y}(m) = a_l(m), \quad b_{l+L_y}(m) = b_l(m).$$
 (105)

Since the ribbon has translational invariance in the y-direction, we can apply a Fourier Transform to Eq. (104). The Fourier relations are given by

$$a_{l}(m) = \frac{1}{\sqrt{L_{y}}} \sum_{k} e^{iky_{l,mA}} \alpha_{k}(m),$$

$$b_{l}(m) = \frac{1}{\sqrt{L_{y}}} \sum_{k} e^{iky_{l,mB}} \beta_{k}(m),$$
(106)

where $y_{l,mA}(y_{l,mB})$ is the coordinate of the mA (mB) site and k is the wave-number. These coordinates are obtained according to

$$y_{l,1A} = y_{l,3A} = y_{l,5A} \dots \equiv y_l,$$
 (107)

$$y_{l,2B} = y_{l,4B} = y_{l,6B} \dots \equiv y_l + a_T/6,$$
 (108)

$$y_{l,2A} = y_{l,4A} = y_{l,6A} \dots \equiv y_l + a_T/2,$$
 (109)

$$y_{l,1B} = y_{l,3B} = y_{l,5B} \dots \equiv y_l + 2a_T/3.$$
 (110)

By setting $a_T = 1$ and replacing Eqs. (107) to (110) into Eq. (104), we finally obtain the Hamiltonian in k-space as

$$\mathcal{H}_{k} = -t \sum_{k} \sum_{m} e^{-ik/3} \alpha_{k}^{\dagger}(m) \beta_{k}(m)$$

$$-t \sum_{k} \sum_{m=1}^{N-1} \left[e^{-ik/6} \beta_{k}^{\dagger}(m+1) \alpha_{k}(m) + e^{ik/6} \alpha_{k}^{\dagger}(m+1) \beta_{k}(m) \right] + \text{H.C.},$$
(111)

or, in matrix form, as

$$\mathcal{H}_{k} = \begin{pmatrix} 0 & -te^{-ik/3} & 0 & 0 & -te^{ik/6} & 0 & \dots \\ -te^{ik/3} & 0 & -te^{ik/6} & 0 & 0 & 0 & \dots \\ 0 & -te^{-ik/6} & 0 & -te^{-ik/3} & 0 & -te^{ik/6} & \dots \\ 0 & 0 & -te^{ik/3} & 0 & -te^{ik/6} & 0 & \dots \\ -te^{-ik/6} & 0 & 0 & -te^{-ik/6} & 0 & 0 & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}.$$
(112)

To find the eigenvalues and eigenfunctions of the Hamiltonian for any k value, we have to numerically diagonalize \mathcal{H}_k . Below, we analytically derive the eigenvalues. To simplify the equations, we define two new operators, a_k and b_k through the relations

$$b_{k} = \beta_{k},$$

$$b_{k}^{\dagger} = \beta_{k}^{\dagger},$$

$$a_{k}^{\dagger} = \alpha_{k}^{\dagger} e^{ik/6} \Longrightarrow \alpha_{k}^{\dagger} = a_{k}^{\dagger} e^{-ik/6},$$

$$a_{k} = \alpha_{k} e^{-ik/6} \Longrightarrow \alpha_{k} = a_{k} e^{ik/6}.$$
(113)

By replacing Eqs. (113) into Eq. (111), we get

$$H = -t \sum_{k} \sum_{m} e^{-ik/2} a_{k}^{\dagger}(m) b_{k}(m)$$

$$-t \sum_{k} \sum_{m=1}^{N-1} \left[b_{k}^{\dagger}(m+1) a_{k}(m) + a_{k}^{\dagger}(m+1) b_{k}(m) \right] + \text{H.C.}.$$
(114)

In order to solve Eq. (114), we assume the following ansatz for a state in this system

$$|\Psi(k)\rangle = \sum_{m} \left(\psi_{m,A}\alpha_k^{\dagger}(m) + \psi_{m,B}\beta_k^{\dagger}(m)\right)|0\rangle, \qquad (115)$$

where $\beta_k(m)|0\rangle = 0$ and $\alpha_k(m)|0\rangle = 0$. By replacing (115) into Schrödinger's equation

$$H|\Psi(k)\rangle = E|\Psi(k)\rangle,$$
 (116)

$$E\psi_{m,A} = -e^{-ik/2}\psi_{m,B} - \psi_{m-1,B} - \psi_{m+1,B},$$

$$E\psi_{m,B} = -e^{+ik/2}\psi_{m,A} - \psi_{m-1,A} - \psi_{m+1,A}.$$
(117)

The periodic boundary conditions are given by

$$\psi_{0,A} = \psi_{0,B} = \psi_{N+1,A} = \psi_{N+1,B} = 0.$$
(118)

To solve the equations of motion, we assume a tentative set of solutions as

$$\psi_{m,A} = A e^{ipm} + B e^{-ipm},$$

$$\psi_{m,B} = C e^{ipm} + D e^{-ipm},$$
(119)

where A, B, C, and D are coefficients that we will find from the boundary conditions, and p is the wave vector in the transversal direction. If we substitute Eqs. (118) into Eq. (119), we arrive at the following equations

I
$$\psi_{0,A} = 0 = A + B \Longrightarrow A = -B,$$

II $\psi_{0,B} = 0 = C + D \Longrightarrow C = -D,$
III $\psi_{N+1,A} = 0 = \left(Ae^{ip(N+1)} + Be^{-ip(N+1)}\right),$
IV $\psi_{N+1,B} = 0 = \left(Ce^{ip(N+1)} + De^{-ip(N+1)}\right).$
(120)

From I, II, III, and IV, we find

$$A\left(e^{ip(N+1)} - e^{-ip(N+1)}\right) = A2i\sin(p(N+1)) = 0,$$

$$C\left(e^{ip(N+1)} - e^{-ip(N+1)}\right) = C2i\sin(p(N+1)) = 0.$$
(121)

From Eq. (121), we determine the allowed values of p, since

$$\sin[p(N+1)] = 0 \tag{122}$$

implies

$$p(N+1) = r\pi,\tag{123}$$

therefore, p takes values

$$p = \frac{r}{N+1}\pi, \quad r = 1, 2, 3, \dots, N.$$
 (124)

Now, by using the boundary conditions and Eq. (121), we find that

$$\psi_{m,A} = A \left(e^{ipm} - e^{-ipm} \right), \qquad (125)$$

and

$$\psi_{m,B} = C \left(e^{ipm} - e^{-ipm} \right).$$
(126)

Then, plugging Eq. (125) into the first equation of motion (Eq. (117)), we get

$$EA\left(e^{ipm} - e^{-ipm}\right) = -te^{-ik/2}C\left(e^{ipm} - e^{-ipm}\right) - tC\left(e^{ip(m-1)} - e^{-ip(m-1)}\right) - tC\left(e^{ip(m+1)} - e^{-ip(m+1)}\right),$$
(127)

which, after an algebraic manipulation, results in

$$EA = -tC \left(2\cos p + \exp\left[-ik/2\right]\right),$$
 (128)

hence

$$A = -tC \frac{(2\cos p + \exp[-ik/2])}{E}.$$
 (129)

Likewise, when we solve for the second equation of motion, we obtain

$$C = -tA \frac{\left(2\cos p + \exp\left[ik/2\right]\right)}{E}.$$
(130)

Solving Eqs. (129) and (130), we determine the AGNR's eigenvalues

$$E^{2} = 4\cos^{2} p + 1 + 2\cos p \left(e^{i\frac{k}{2}} + e^{-i\frac{k}{2}}\right),$$

$$E^{2} = 4\cos^{2} p + 1 + 4\cos p \cos \frac{k}{2},$$

$$E = s\sqrt{1 + 2\epsilon_{p}\cos\frac{k}{2} + \epsilon_{p}^{2}},$$

(131)

where $s = \pm 1$, being s = +1 for the conduction band and s = -1 for the valence band, with $\epsilon_p = 2\cos(p)$.

Now, we will obtain an analytical expression for the eigenstates. For that, we substitute the simplified form of our ansatz (Eqs. (125) and (126))

$$\psi_{m,A} = A \left(e^{ipm} - e^{-ipm} \right) = 2iA\sin(pm),$$

$$\psi_{m,B} = C \left(e^{ipm} - e^{-ipm} \right) = 2iC\sin(pm),$$
(132)

into the equations of motion, we obtain that the coefficients A and C must satisfy the following matrix equation

$$\begin{pmatrix} E & \epsilon_p + e^{ik/2} \\ \epsilon_p + e^{-ik/2} & E \end{pmatrix} \begin{pmatrix} A \\ C \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix},$$
(133)

or

$$\begin{cases} EA + \left(\epsilon_p + e^{ik/2}\right)C = 0\\ EC + \left(\epsilon_p + e^{-ik/2}\right)A = 0, \end{cases}$$
(134)

thus

$$C = \frac{-\epsilon_p + e^{-ik/2}}{E} A = -\frac{\left(\epsilon_p + e^{-ik/2}\right)A}{s\sqrt{(\epsilon_p + e^{ik/2})(\epsilon_p + e^{-ik/2})}}$$
$$= -\frac{\sqrt{\epsilon_p + e^{-ik/2}}}{s\sqrt{\epsilon_p + e^{ik/2}}} A.$$
(135)

Then, substituting Eq. (135) into Eqs. 132, we have

$$\begin{pmatrix} \psi_{m,A} \\ \psi_{m,B} \end{pmatrix} = 2i \begin{pmatrix} A \\ C \end{pmatrix} \sin(mp) = 2i \begin{pmatrix} -\frac{\sqrt{\epsilon_p + e^{-ik/2}}}{s\sqrt{\epsilon_p + e^{ik/2}}} \end{pmatrix} A \sin(mp)$$
$$= -\frac{2iA}{\underbrace{N\sqrt{\epsilon_p + e^{ik/2}}}_{N_c}} \left(\frac{-s\sqrt{\epsilon_p + e^{ik/2}}}{\sqrt{\epsilon_p + e^{-ik/2}}}\right) \sin(mp),$$
(136)

which implies

$$\begin{pmatrix} \psi_{m,A} \\ \psi_{m,B} \end{pmatrix} = N_c \begin{pmatrix} -s\sqrt{\epsilon_p + e^{ik/2}} \\ \sqrt{\epsilon_p + e^{-ik/2}} \end{pmatrix} \sin(mp).$$
(137)

To find $\mathbf{N}_c,$ we need the normalization condition

$$\sum_{n=1}^{N} \left(|\psi_{m,A}|^2 + |\psi_{m,B}|^2 \right) = 1,$$
(138)

where the terms in Eq. (138) are given by

$$|\psi_{m,A}|^{2} = N_{c}^{2} \sqrt{\epsilon_{p} + e^{ik/2}} . \sqrt{\epsilon_{p} + e^{-ik/2}} \sin^{2}(mp),$$

$$|\psi_{m,B}|^{2} = N_{c}^{2} \sqrt{\epsilon_{p} + e^{-ik/2}} . \sqrt{\epsilon_{p} + e^{ik/2}} \sin^{2}(mp),$$
(139)

which may be written more succinctly as

$$\begin{aligned} |\psi_{m,A}|^2 &= N_c^2 \quad |E|\sin^2(mp), \\ |\psi_{m,B}|^2 &= N_c^2 \quad |E|\sin^2(mp). \end{aligned}$$
(140)

Now, substituting Eq. (140) into Eq. (138), we arrive at the following expression for N_c

$$N_c^2 = \frac{1}{|E|} \left(2\sum_{m=1}^N \sin^2(mp) \right)^{-1}, \tag{141}$$

which may be simplified by using

$$2\sum_{m=1}^{N}\sin^{2}(pm) = \sum_{m=1}^{N}\left(1 - \cos(2pm)\right) = N - \sum_{m=1}^{N}\cos(2pm),$$
(142)

followed by the application of the Lagrange identity:

$$\sum_{m=1}^{N} \cos(2pm) = -\frac{1}{2} + \frac{\sin(2Np+p)}{2\sin(p)}$$

$$= -\frac{1}{2} + \frac{2\sin(Np)\cos(Np)\cos(p) + \sin(p)\cos(2Np)}{2\sin(p)}.$$
(143)

Now, by using the trigonometric identities

$$\cos (Np + p) = \cos(Np)\cos(p) - \sin(Np)\sin(p),$$

$$\cos(Np)\cos(p) = \cos (Np + p) + \sin(Np)\sin(p),$$
(144)

Eq. (143) becomes

$$\sum_{m=1}^{N} \cos(2pm) = -\frac{1}{2} + \frac{2\sin(Np)[\cos(Np+p) + \sin(Np)\sin(p)] + \cos(2Np)\sin(p)}{2\sin(p)}$$

$$= -\frac{1}{2} + \frac{2\sin(Np)\cos(Np+p) + 2\sin^{2}(Np)\sin(p) + [\cos^{2}(Np) - \sin^{2}(Np)]\sin(p)}{2\sin(p)}$$

$$= -\frac{1}{2} + \frac{2\sin(Np)\cos(Np+p) + \sin(p)[\cos^{2}(Np) + \sin^{2}(Np)]}{2\sin(p)}$$

$$= \frac{\sin(Np)\cos(Np+p)}{\sin(p)}.$$
(145)

Replacing Eq. (145) into Eq. (142), we have, after some algebra,

$$\sum_{m=1}^{N} \sum_{m=1}^{N} \sin^2 pm = \frac{N}{2} - \frac{1}{4} \left[\frac{\sin(N_p)\cos(Np+p)}{\sin p} \right],$$
(146)

which, when replaced in Eq. 141, results in

$$N_c = \frac{1}{\sqrt{|E|}} \left(N - \frac{\sin Np \times \cos(Np+p)}{\sin p} \right)^{-1/2}, \tag{147}$$

thus, the eigenstate may be finally written as

$$\begin{pmatrix} \psi_{m,A} \\ \psi_{m,B} \end{pmatrix} = N_{\rm c} \begin{pmatrix} -s\sqrt{\epsilon_p + {\rm e}^{-{\rm i}k/2}} \\ \sqrt{\epsilon_p + {\rm e}^{{\rm i}k/2}} \end{pmatrix} \sin(mp).$$
(148)

APPENDIX **D**

Tight-binding model for zig-zag nanoribbons

If we use a unit cell as shown in Fig. 54, we can write the corresponding Hamiltonian for a Z-NRG, in real space, as

$$H = -t \sum_{\ell} \sum_{m=odd}^{N} \left[a_{\ell}^{\dagger}(m) b_{\ell-1}(m) + b_{\ell}^{\dagger}(m) a_{\ell}(m) + a_{\ell}^{\dagger}(m+1) b_{\ell}(m) \right] + h.c.$$

$$(149)$$

$$-t \sum_{\ell} \sum_{m=\text{ even}}^{N} b_{\ell}^{\dagger}(m) a_{\ell-1}(m) + \text{ h.c.}$$



Figure 54 – Zig-zag nanoribbon.

where $a_{\ell}^{\dagger}(m)/a_{\ell}(m)$ are the creation/annihilation operators as defined when dealing with the AGNRs, which obey the following anticommutation relations

$$\left\{ a_{\ell}(m), a_{\ell'}^{\dagger}(m') \right\} = \delta_{\ell,\ell'} \delta_{m,m'}$$

$$\left\{ b_{\ell}(m), b_{\ell'}^{\dagger}(m') \right\} = \delta_{\ell,\ell'} \delta_{m,m'}.$$

$$(150)$$

Furthermore, just as was done for the AGNRs, we will assume that the system has L_x unit cells, and that it also periodic along the x-axis. Thus, we can employ the following set of Fourier transforms to find the equations of motion

$$a_{l}(m) = \frac{1}{\sqrt{L_{x}}} \sum_{k} e^{ikx_{l,mA}} \alpha_{k}(m)$$

$$b_{l}(m) = \frac{1}{\sqrt{L_{x}}} \sum_{k} e^{ikx_{l,mB}} \beta_{k}(m),$$
(151)

where $x_{l,mA}$ ($x_{l,mB}$) is the x-coordinate of the mA (mB) site in the *l*-th unit cell, and the periodic boundary conditions are expressed as

$$a_{l+L_x}(m) = a_l(m)$$

$$b_{l+L_x}(m) = b_l(m).$$
(152)

The previous equations imply that the wave-number k satisfies

$$k = \frac{2\pi}{L_x}m, \quad m = 0, \pm 1, \pm 2, \dots, \pm \frac{L_x}{2} - 1, \frac{L_x}{2}.$$
 (153)

If we solve Eq. (149) using Eq. (151), we arrive at a matrix Hamiltonian given by

$$H(k) = \begin{pmatrix} -t - te^{ik} & 0 & 0 & \dots & 0 \\ -t & -t - te^{ik} & 0 & 0 & \dots & 0 \\ 0 & -t & -t - te^{ik} & 0 & \dots & 0 \\ \vdots & & \ddots & \ddots & \ddots & \vdots \\ \vdots & & 0 & -t & -t - te^{ik} & 0 \\ 0 & \dots & \dots & 0 & -t & -t - te^{ik} \end{pmatrix}.$$
 (154)

diagonalizing the matrix shown in Eq. 154, we obtain the energy spectrum for any N.

As we have seen before, the one-particle state is given as

$$|\Psi(k)\rangle = \sum_{m} \left(\psi_{m,A}\alpha_{k}^{\dagger}(m) + \psi_{m,B}\beta_{k}^{\dagger}(m)\right)|0\rangle, \qquad (155)$$

thus, by replacing Eq. (155) into Schrödinger's equation

$$H|\Psi(k)\rangle = E|\Psi(k)\rangle,\tag{156}$$

we obtain the following equations of motion

$$E\psi_{m,A} = -\psi_{m-1,B} - g_k \psi_{m,B},$$

$$E\psi_{m,B} = -\psi_{m+1,A} - g_k \psi_{m,A},$$
(157)

where

$$g_k = 2\cos\left(\frac{k}{2}\right), \quad m = 0, 1, 2, \dots, N+1.$$
 (158)

In addition, we must also impose that 0 B and (N + 1) A are not present, as can be seen in Fig. 54. Thus, we have that Eqs. (157), the first for m = 1, and the second for m = N, become

$$E\psi_{1,A} = -g_k\psi_{1,B},$$

$$E\psi_{N,B} = -g_k\psi_{N,A}.$$
(159)

thereby, the open boundary conditions along the transversal direction (y-axis) impose that

$$\psi_{0,B} = \psi_{N+1,A} = 0. \tag{160}$$

As done for the AGNRs, we use the following ansatz

$$\psi_{m,A} = Ae^{ipm} + Be^{-ipm},$$

$$\psi_{m,B} = Ce^{ipm} + De^{-ipm},$$
(161)

where A, B, C, and D are arbitrary coefficients. Furthermore, p is the wavenumber in the transversal direction. Applying the boundary conditions (Eq. 160), we found that

$$\psi_{0,B} = C + D = 0,$$

$$\psi_{N+1,A} = Az + Bz^{-1} = 0,$$
(162)

where

$$z = e^{ip(N+1)}.$$
(163)

Thus, solving for B and D and substituting in Eqs. (161), we get

$$\psi_{m,A} = A \left(e^{ipm} - z^2 e^{-ipm} \right)$$

$$\psi_{m,B} = C \left(e^{ipm} - e^{-ipm} \right).$$
(164)

Substituting Eqs. (164) into the equations of motion (Eqs. (157)), we obtain the relation

$$\mathbf{M}\left(\begin{array}{c}A\\C\end{array}\right) = 0,\tag{165}$$

where the 2×2 matrix **M** is given by

$$\boldsymbol{M} = \begin{pmatrix} E\left(e^{ipm} - z^{2e^{-ipm}}\right) & (g_k + e^{-ip}) e^{ipm} - (g_k + e^{-ip}) e^{ipm} \\ (g_k + e^{ip}) e^{ipm} - (g_k + e^{-ip}) e^{-ipm} z^2 & E\left(e^{ipm} - e^{-ipm}\right) \end{pmatrix}.$$
(166)

It should be noted that p equals to $-\pi$, 0, or π represents a trivial solution (that is, $\psi_{m,A} = \psi_{m,B} = 0$ for any m value), making M a vanishing matrix. We obtain non-trivial solutions by finding what values of p and E that satisfy

$$\det \boldsymbol{M} = 0. \tag{167}$$

It is not so complicated to show that $\det M = 0$ results in

$$v e^{i2pm} + w e^{-i2pm} + x = 0$$
 (168)

where v, w and x are functions of E, g_k and z. By making v = w = 0, we obtain

$$E^{2} = \left(g_{k} + e^{ip}\right)\left(g_{k} + e^{-ip}\right) = 1 + g_{k}^{2} + 2g_{k}\cos(p),$$
(169)

which yields the dispersion relation

$$E_s = s\sqrt{1 + g_k^2 + 2g_k \cos(p)}.$$
(170)

Making x = 0 results in the following condition for the transverse wavenumber p = p(k, N)

$$F(p, N) \equiv \sin[pN] + g_k \sin[p(N+1)] = 0,$$
 (171)

which can only be solved numerically.

Finally, through algebraic manipulations similar to the ones done for the AGNRs, the wavefunction can be written as

$$\begin{pmatrix} \psi_{m,A} \\ \psi_{m,B} \end{pmatrix} = N'_{c} \begin{pmatrix} e^{-ipm}z - e^{ipm}z^{-1} \\ e^{-ipm} - e^{ipm} \end{pmatrix}$$
$$= N_{c} \begin{pmatrix} \sin(p(N+1-m)) \\ \sin(pm) \end{pmatrix},$$
(172)

with $N_{\rm c}$ a normalization constant .

In Figs. 55 and 56, we present the band structure and density of states for zigzag ribbons, for several N. The results presented prove the expected behavior for ZGNRs [in a tight-binding approximation], that is, a metallic behavior. In addition, they also have well-placed edge states.



Figure 55 – Panels (a) to (d) show the ZGNR energy dispersion for N = 4, N = 5, N = 12, and N = 30, respectively.



Figure 56 – Panels (a) to (d) show the ZGNR DOS for N = 4, N = 5, N = 12, and N = 30, respectively.

APPENDIX E

Tight-binding Hamiltonian for an N-AGNR(1,3) heterostructure

In this Appendix, we present explicit expressions for the Hamiltonian of an N-AGNR(1,3) heterostructure, in the real and reciprocal spaces. The modifications necessary to obtain the Hamiltonian for a general N-AGNR(n,m) heterostructure are straightforward. In Fig. 57, we show the *l*-th unit cell of an N-AGNR(1,3) heterostructure, where the A sublattice is represented by blue solid dots and the B sublattice by red solid dots. The sites are labeled $p\alpha_q$, where $\alpha = A/B$, with $1 \leq p \leq N + 4$ and $1 \leq q \leq 3$, where p runs along the y-direction, as indicated in the right-hand side, and q runs along the x-direction (starting at the center of the unit cell and moving to its borders).

Using the labeling defined above, we can write the N-AGNR(1,3) Hamiltonian in real space as

$$H = -t \sum_{l} \left[\sum_{p \in \text{odd}}^{N} b_{l,1}^{\dagger}(p) a_{l,1}(p) + \sum_{p=2}^{N-1} b_{l,1}^{\dagger}(p+1) a_{l,1}(p) + \sum_{p=2}^{N-1} a_{l,1}^{\dagger}(p+1) b_{l,1}(p) + \text{H.C.} \right]$$

$$-t \sum_{l} \left[\sum_{p=2}^{N-2} b_{l,2}^{\dagger}(p+1) a_{l,2}(p) + \sum_{p=2}^{N-2} a_{l,2}^{\dagger}(p+1) b_{l,2}(p) + \text{H.C.} \right]$$

$$-t \sum_{l} \left[\sum_{m \in \text{even}}^{N-1} b_{l,1}^{\dagger}(p) a_{l,2}(p) + \sum_{m \in \text{even}}^{N-1} b_{l,2}^{\dagger}(p) a_{l,1}(p) + \text{H.C.} \right]$$

$$-t \sum_{l} \left[\sum_{p=3}^{N-3} b_{l,3}^{\dagger}(p+1) a_{l,3}(p) + \sum_{p=3}^{N-3} a_{l,3}^{\dagger}(p+1) b_{l,3}(p) + \text{H.C.} \right]$$

$$-t \sum_{l} \left[\sum_{p=3}^{N-2} b_{l,2}^{\dagger}(p) a_{l,3}(p+1) + \sum_{p=3}^{N-2} b_{l,3}^{\dagger}(p+1) a_{l,3}(p) + \sum_{m \in \text{even}}^{N-3} b_{l-1,3}^{\dagger}(p) a_{l,3}(p) + \text{H.C.} \right]$$

$$(173)$$

where $a_{l,q}(p)$ $[b_{l,q}(p)]$ annihilates an electron on site pA_q (pB_q) on the *l*-th unit cell. Assuming periodic boundary conditions along the *x*-direction, we take a Fourier transform along that direction and obtain the reciprocal space Hamiltonian

$$\begin{split} H &= -t \sum_{k} \left[\sum_{m \in \text{odd}}^{N} v_{1} \beta_{k,1}^{\dagger}(p) \alpha_{k,1}(p) + \sum_{p=2}^{N-1} v_{2} \beta_{k,1}^{\dagger}(p+1) \alpha_{k,1}(p) + \sum_{p=2}^{N-1} v_{3} \alpha_{k,1}^{\dagger}(p+1) \beta_{k,1}(p) + \text{H.C.} \right] \\ &- t \sum_{k} \left[\sum_{p=2}^{N-2} v_{2} \beta_{k,2}^{\dagger}(p+1) \alpha_{k,2}(p) + \sum_{p=2}^{N-2} v_{3} \alpha_{k,2}^{\dagger}(p+1) \beta_{2}(p) + \text{H.C.} \right] \\ &- t \sum_{k} \left[\sum_{m \in \text{verem}}^{N-1} v_{1} \beta_{k,1}^{\dagger}(p) \alpha_{k,2}(p) + \sum_{p=2}^{N-1} v_{1} \beta_{k,2}^{\dagger}(p) \alpha_{k,1}(p) + \text{H.C.} \right] \\ &- t \sum_{k} \left[\sum_{p=3}^{N-2} v_{1} \beta_{k,3}^{\dagger}(p+1) \alpha_{k,3}(p) + \sum_{p=3}^{N-2} v_{1} \alpha_{k,3}^{\dagger}(p+1) \beta_{k,3}(p) + \text{H.C.} \right] \\ &- t \sum_{k} \left[\sum_{p=3}^{N-2} v_{2} \beta_{k,2}^{\dagger}(p) \alpha_{k,3}(p+1) + \sum_{p=3}^{N-2} v_{3} \beta_{k,3}^{\dagger}(p+1) \alpha_{k,3}(p) + \sum_{p=4}^{N-3} v_{1} \beta_{k,3}^{\dagger}(p) \alpha_{k,3}(p) + \text{H.C.} \right] \\ &- t \sum_{k} \left[\sum_{p=3}^{N-2} v_{2} \beta_{k,2}^{\dagger}(p) \alpha_{k,3}(p+1) + \sum_{p=3}^{N-2} v_{3} \beta_{k,3}^{\dagger}(p+1) \alpha_{k,3}(p) + \sum_{m \in \text{verem}}^{N-3} v_{1} \beta_{k,3}^{\dagger}(p) \alpha_{k,3}(p) + \text{H.C.} \right], \end{split}$$
(174)

where $\alpha_{k,q}(p)$ and $\beta_{k,q}(p)$ are the Fourier transformed operators, and $v_1 = e^{-ika_T/9}$, $v_2 = e^{ika_T/18}$, and $v_3 = e^{-ika_T/18}$, with $a_T = 1$ the unit cell size.



Figure 57 – Site labelling of a unit cell for an N-AGNR(1,3) heterostructure. The sites are labeled $p\alpha_q$, where $\alpha = A/B$, $1 \le p \le N + 4$ and $1 \le q \le 3$, see text for details.

APPENDIX

Tight-binding with next-nearest-neighbor hopping

In Fig. 58 we present tight-binding and DFT results to asses the stability of the tight-binding flat-bands to the addition of a NNN hopping t_{NNN} to the calculations. In Fig. 58(a) we reproduce the tight-binding bands shown previously in Fig. 42(b) for 3-AGNR(1,3), which included just nearest-neighbor (NN) hoppings. In Fig. 58(b) we add NNN hoppings $t_{NNN} = 0.1$ eV ^[5] to the calculations. As expected, the results are not particle-hole symmetric anymore. However, all the flat-bands (in the interval of energy shown) remain flat. Thus, since the DFT results [in panel (c), reproduced from Fig. 42(a)] show that flat-band 1 (the closest to the Fermi energy) has acquired dispersion, we conclude that longer hoppings than NNN are necessary in the tight-binding calculations to produce dispersion in flat-band 1. This can be understood by looking at the Wannier-like state for this band, shown in Fig. 36(a). There, we clearly see that, to connect two unit cells, it is necessary at least a 3^{rd} NN hopping. This may explain too, why flat-band 3b has acquired a small dispersion, while flat-band 4 has acquired just a slight dispersion.



Figure 58 – (a) Tight-binding band structure for 3-AGNR(1,3) with NN hoppings only [reproduced from Fig. 42(b)]. (b) Same as in panel (a), but adding a NNN hopping t_{NNN} to the calculations, with $t_{NNN} = 0.1$ eV. ^[5] (c) DFT results for 3-AGNR(1,3) [reproduced from Fig. 42(a)].

APPENDIX **G**

Results for 'Staggered' heterostructures

In Refs. ^[??8] a second type of heterostructure has been introduced, less symmetric than the one we analyzed in this work. The reason we did not focus our attention in these so-called 'Staggered' heterostructures is that they show less flat-bands than the socalled 'Inline' heterostructures (which were the focus of this work). To exemplify that, in Fig. 59(a) we compare the tight-binding band structure results for a 5-AGNR-S(1,3)heterostructure [panel (a)] with that for a 5-AGNR-(1,3) one [panel (b)]. Notice the inclusion of an 'S' (in bold, for Staggered) to the label for the heterostructure. On top of Fig. 59(a) we show a single unit cell for the 5-AGNR-S(1,3) heterostructure. By comparing it to the single unit cell on top of panel (b) [for 5-AGNR-(1,3)], which was described in Sec. 5.2A, it is easy to understand the meaning of the (1,3) nomenclature, since the idea is the same as the one introduce in Sec. 5.2A.



Figure 59 – (a) Tight-binding band structure for 5-AGNR-S(1,3). (b) Tight-binding band structure for 5-AGNR(1,3). The unit cell of each heterostructure is shown at the top of each panel.

By comparing the two panels, one notices that only the $\pm t$ flat-bands have survived

in the Staggered heterostructure. We have checked that what appears to be two flatbands (touched by a dispersive band, located, respectively, between energies -1 eV and -2 eV, and below energy -3 eV) are in reality two slightly dispersive bands, and not perfectly flat, like the $\pm t$ flat-bands. Our conclusion also rests in the fact that we could not discern a clear Wannier-like state associated to them. Thus, in the 5-AGNR-S(1,3) heterostructure there are just $\frac{1}{4}$ of the flat-bands present in the (Inline) 5-AGNR(1,3) heterostructure, shown in panel (b).

Finally, for completeness sake, in Fig. 60 we show a comparison of the DFT band structure for 3-AGNR-S(1,3), with the tight-binding band structure, in panels (a) and (b), respectively. Aside from the expected broken particle-hole symmetry in the DFT bands, it is easy to see the very good agreement between the two results. A careful analysis of the DFT results shows that the only flat-band that is perfectly non-dispersive is the $\pm t$ flat-band (located just below -3 eV), reinforcing our claim that the Inline heterostructures have more robust flat-bands.



Figure 60 – (a) DFT band structure for 3-AGNR-S(1,3). (b) Tight-binding band structure for 3-AGNR-S(1,3).