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**Quantum transport in 2D materials: Theoretical  
and computational optimisation of large  
heterostructures with spintronics properties**

By

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# Declaration

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## Abstract

Graphene is a monolayer of carbon atoms arranged in a hexagonal lattice, making it the thinnest and strongest material known to man. Its exceptional electronic and thermal properties have generated great interest for its potential use in various applications, particularly in electronics and spintronics. Since its recent isolation, graphene and related 2D materials have been in the scientific spotlight owing to various fundamental discoveries regarding their synthesis and exceptional properties.

In particular, graphene nanoribbons (GNRs) are narrow strips of graphene with widths ranging from a few nanometers to several tens of nanometers. GNRs also have improved charge transport properties compared to graphene, making them attractive for use in electronic applications. GNRs have potential applications in spintronics, a field that exploits the intrinsic spin of electrons for information storage and processing. The two symmetry-breaking edges in GNRs are known for being host to spin-polarized edge states, which can enable the creation of spin-based devices and enable the transport of spin currents. Despite impressive advances in fabrication techniques, it is an ongoing challenge to produce and control the desired transport properties in GNR devices. Therefore, characterising the effects of realistic disorders on device behaviour remains crucially important.

When dealing with a realistic system size, theoretical predictions of spin properties can be intractable in terms of computational resources. Machine learning (ML) techniques have been employed in various fields, such as consumer recommendation systems, protein folding and chemistry, to exploit patterns in data and make predictions. In this thesis, we address ML techniques to accurately estimate the transport properties and magnetic moment profiles for arbitrarily large and disordered systems. Alongside conventional techniques, developing a neural network tool that accurately estimates the magnetic profile for large and disordered GNRs, we have conducted a thorough analysis on how the edge disorder impacts the robustness of spin-currents in GNRs. The robustness of spin-currents in zigzag graphene nanoribbons (ZGNRs) is highly intertwined with the edge roughness profile at low energies. Whereas spin current is persistent in smooth-edged ribbons due to the absence of back-scattering possibilities, short-ranged scatterers in rough-edged profiles curtail the establishment of edge spin-polarised currents. Our results highlight how ML, by predicting quickly and accurately moment profiles for realistic systems, complements conventional transport techniques to study magnetism and spin transport in 2D materials.

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*Les affaires interminables sont celles où il n'y a pas de difficultés.*

- Napoléon Bonaparte

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# Common acronyms

|             |                                  |
|-------------|----------------------------------|
| <b>AC</b>   | Armchair                         |
| <b>AFM</b>  | Antiferromagnetic                |
| <b>AGNR</b> | Armchair Graphene nanoribbon     |
| <b>CNT</b>  | Carbon Nanotube                  |
| <b>CVD</b>  | Chemical Vapour Deposition       |
| <b>DFT</b>  | Density Functional Theory        |
| <b>DOS</b>  | Density Of States                |
| <b>FM</b>   | Ferromagnetic                    |
| <b>GAL</b>  | Graphene Antidot Lattice         |
| <b>GF</b>   | Green's Function                 |
| <b>GNR</b>  | Graphene nanoribbon              |
| <b>KRR</b>  | Kernel Ridge Regression          |
| <b>LDOS</b> | Local Density Of States          |
| <b>MAE</b>  | Mean Absolute Error              |
| <b>MFH</b>  | Mean-field Hubbard               |
| <b>ML</b>   | Machine Learning                 |
| <b>NN</b>   | Neural Network                   |
| <b>SC</b>   | Self-consistent                  |
| <b>SiC</b>  | Silicon Carbide                  |
| <b>STM</b>  | Scanning Tunnelling Microscopy   |
| <b>STS</b>  | Scanning Tunnelling Spectroscopy |
| <b>TB</b>   | Tight-binding                    |
| <b>TMDC</b> | Transition Metal Dichalcogenide  |
| <b>RGF</b>  | Recursive Green's Function       |
| <b>ZZ</b>   | Zigzag                           |
| <b>ZGNR</b> | Zigzag Graphene nanoribbon       |

## Introduction

### 1.1 Moore's law and limitation

The first industrial revolution had a profound impact on humanity in its socio-economic foundations. The predominantly agrarian and artisanal society was abruptly transformed into a commercial and industrial one thanks to the development of steam power and machinery. Since then, each new revolution, driven by a profound change in technology, has deeply marked modern society. Currently at the twilight of the third “digital” industrial revolution, propelled by the creation in 1947 of the transistor [1], we are gradually making a transition towards the fourth revolution where data, automation and artificial intelligence prevail. Our daily lives have transformed as a result of the development of microprocessors during the past 60 years. A smartphone we carry in our pockets today offers the processing capability that was once provided by supercomputers the size of a warehouse.

#### 1.1.1 Limitations of Moore's law and nanoscaling

The processing power of our daily used electronic devices are fueled by our capacity to create more powerful devices on smaller and smaller surfaces. Moore's law [2], which states that the number of transistors, the fundamental component of each microprocessor, doubles every two years, can be used to describe this remarkable progress and shows how miniaturisation evolved in the past 60 years. For instance, silicon MOSFETs (Metal Oxide Semiconductor Field-Effect Transistor) scaling and shrinking at an exponential rate results in the integrated circuit chip's transistor count doubling every two years [3, 4]. This led the fabricated microprocessors and memory chips having increased transistor density, faster performance, and lower power consumption. Although Moore's law has

proven correct until now, it is soon to reach the so-called “atomic wall”. In addition to the impossibility of miniaturising the electronic components any further, an arising problem is also the consideration of quantum effects at these scales. Furthermore, “smaller and faster” is no longer sufficient for nanodevices. The two major problems using these devices in products like computers and cell phones are power and heat. The majority of the computing power in modern computer chips comes from operations switching at ever-higher frequency. The hegemonic era and development of big data, machine-to-machine communication and artificial intelligence, by increasing demand on our computational and energetic capacities, is putting today’s information technology under high pressure. As every industrial revolution requires, there is an absolute need for modern electronics to change its paradigm beyond Moore’s law with consideration and respect towards the protection of our limited energetic resources.

## 1.2 Alternatives to Moore’s law

Fortunately, there are alternatives for our current technology to overcome its limitations. The awareness of the looming limits has sparked a global initiative to create alternate device technologies. There are indeed concrete solutions and paths of scientific innovation to have more efficient and less-energy consuming nanodevices. Conventional semiconductor devices use exclusively the charge of electrons to generate, transmit and process information. The electron is a fundamental particle that plays a crucial role in many physical phenomena, including electricity and magnetism. In the field of spintronics, researchers strive to exploit the spin of electrons in order to develop new technologies and devices. For example, by controlling the spin of electrons, it may be possible to create more energy-efficient transistors, memory devices, and sensors [5–7]. The field of spintronics also holds promise for applications in quantum computing, where the spin of an electron can be used to represent a quantum bit, or qubit [5]. In addition to the spin, the electron has other properties that have been used in various technological applications, such as the spin-orbit interaction which causes electrons to change their spin states [8–10] and that can be exploited for use in data storage and logic operations [11, 12] as well as other applications such as quantum computing.

The discovery of graphene [13] and other atomically-thin two-dimensional materials [14] opens the path to effectively control and tune the required properties for disruptive technologies. Two-dimensional materials such as graphene [15] and transition metal dichalcogenides [16] feature another way to control the so-called valley degree of freedom electrons display due to the crystal structure of the material. The valleys are characterized by different electron spin and angular momentum states, and can be used to encode and manipulate quantum infor-

mation [17, 18]. The valley degree of freedom can also be used to create new types of electronic and optoelectronic devices [16], such as valley transistors and valley-based sensors [19]. To exploit these exotic flavours of spin and valley in devices, it is necessary to actively control their electronic and magnetic properties at the nanoscale.

### 1.2.1 Graphene and 2D materials

Recent years have seen significant progress in the study of graphene-related nanoscale materials, which are anticipated to lead to the development of various future technologies [20, 21]. Graphene is a single layer of carbon atoms arranged in a hexagonal lattice (cf. Fig. 1.1-a). The hexagonal lattice can also be seen as two intersecting triangular sublattices. A unit-cell containing two neighbouring atoms, from the two different sublattices, can generate the entire lattice by translation. Graphene is the key building block for a number of other related materials. Graphite, stemming from “ $\gamma\rho\alpha\phi\epsilon\iota\nu$ ”, meaning “to write” in ancient Greek, is the centuries-long lead in our pencils and is composed of stacked monolayers of graphene that hold together via weak van der Waals forces [22]. Carbon nanotubes (CNTs) (cf. Fig. 1.1-c) consist in graphene monolayers being rolled up along a particular direction [23]. CNTs showed a variety of intriguing and potentially usable electronic and physical features [24]. Nanotubes are either metallic or semiconducting, depending on the direction in which they are rolled up and offer sensitive and tunable electronic properties [24, 25]. As surprising as it may be, all of the materials mentioned above derived from graphene, were successfully synthesized and produced before graphene be isolated in 2004 [13, 26]. Before this crucial date where isolation of graphene through the scotch-tape method was realised, this material was not even predicted to exist in the free state [20, 27]. Before going into some of the numerous intriguing features of graphene, let us quickly review its discovery and fabrication and let us see how it can propel innovation in modern electronics.

#### Graphene: discovery and properties

The micromechanical cleavage or the so-called Scotch-tape method led to the successful isolation and observation of graphene in 2004 [13]. This technique, as simple as it seems, involves etching the top layer of a high-quality graphite crystal using adhesive tape and then transferring it onto a substrate. The scotch-tape method is a low-cost and easy method for producing graphene, but it is limited to producing small flakes of graphene and therefore is not suitable for obtaining a high yield of high quality graphene. Since then, additional techniques, such as chemical exfoliation by dispersion in organic solvents, have also been used to create graphene samples [28–30]. Chemical vapor deposition (CVD) [31] and

epitaxial growth [32] are other improved methods for growing graphene monolayers onto metallic or semiconducting crystalline substrates, such as silicon carbide (SiC). More recently, bottom-up techniques for synthesizing graphene-based structures [33, 34] extended the scope for the synthesis and characterization of this type of materials. It involves building up the material from smaller components such as chemical precursors, rather than exfoliating it from bulk graphene.

Following its discovery, graphene has become increasingly interesting from an experimental and theoretical standpoint. Numerous intriguing and distinctive physical features have been postulated and explored. Graphene, which has a breaking strength 200 times greater than steel, is not only the first two-dimensional atomic crystal, but it is also the thinnest and strongest material ever discovered [35]. Graphene appears to be ideal in its usage as a reinforcement in high performance composites because it is an incredibly strong material [36]. It is acknowledged as being a remarkably efficient thermal [37] and electrical [38] conductor. Nonetheless, since graphene's discovery, it's undeniable that its electronic properties have received the most excitement and been the focus of the majority of investigations [8]. The potential use of graphene in computer electronics is the primary area of present attention. The potential of graphene field effect transistors for high-frequency applications has been illustrated by promising results [39–43]. And although graphene was only discovered two decades ago, most of its electronic theory had already been developed [44, 45] from the 1950s and served as the foundation for calculations of the electronic properties of graphite and, later, CNTs [25]. Graphene is a zero-bandgap semi-metal whose valence and conduction bands touch at two discrete points of the Brillouin zone, namely the Dirac points. The electronic band structure of graphene close to the Fermi energy, near the Dirac points, scales the momentum of electron linearly to its energy contrarily to a parabolic relation in conventional semiconductors. The so-called valley flavour that could be used as a way to fine-tune electronics and transport features originates from the existence of these two different Dirac cones in graphene and several 2D materials. In the vicinity of the Fermi energy, electrons lose their effective mass and act like relativistic particles as a result of the linear bands. In fact, the behavior of these electrons mirrors the physics of quantum electrodynamics (QED) for massless fermions and may be explained using a Dirac-like equation rather than the conventional Schroedinger equation [8, 20, 21]. As a result, graphene enables testing of some QED hypotheses in a more straightforward laboratory setting, hardly feasible for really relativistic systems. Klein tunneling [46], where a relativistic particle has an enhanced tunneling probability through a potential barrier, due to a suppression of backscattering, is an example of this type of behavior. Such phenomenon for Dirac fermions in graphene has been theoretically predicted [47] and experimentally demonstrated [48–50]. The fact that

the electrons in graphene are massless provides another benefit in their capacity to travel long distances without scattering, and this high mobility property has been demonstrated experimentally at the micrometer scale [13, 51].

### Graphene-based materials

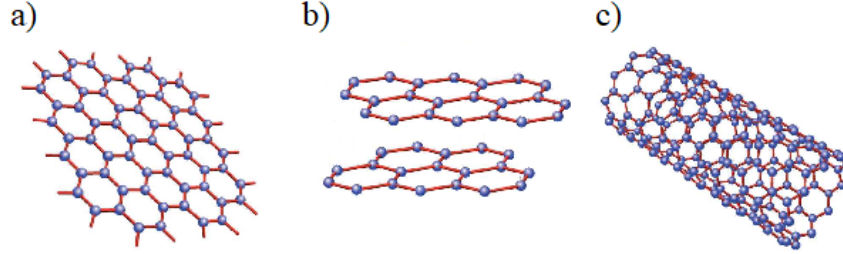


Figure 1.1: Graphene-based nanomaterials: (a)- Graphene monolayer. (b)- Stacked graphene monolayers. (c)- Carbon nanotubes (CNTs). Adapted from [52].

Since its discovery, graphene has not been limited to its monolayer form. Indeed, a vast zoology of new materials derived from graphene such as bilayer systems (cf. Fig. 1.1-b) have emerged and have created a considerable boom in electronic applications [53, 54]. As well as the number of layers involved, the stacking order plays a crucial role in the electronic properties of such systems [55, 56]. Signatures of unconventional superconductivity and other exotic physics are observed in such materials and a whole new domain called *twistronics* has emerged from stacking graphene and 2D materials at particular angles (cf. Fig. 1.3-b)[57–60].

As can be seen in the Fig. 1.2, in addition to stacking graphene layers, a single graphene sheet can be “sliced” into a narrow strip to create a quasi-one-dimensional structure known as a graphene nanoribbon (GNR). GNRs can be experimentally fabricated by numerous ways including top-down approaches like lithography [61], epitaxial growth of sidewall GNRs [62] and etching [63]. Driven by recent advancements in chemical synthesis methods, bottom-up fabrication techniques also yield on-surface narrow GNRs with atomically precise edges [33, 34]. Considering that nanoribbons can be obtained by “unzipping” CNTs [64], the same way nanotubes electronic characteristics depend on their rolling direction and circumference, the electronic properties of GNRs are highly dependent on their edge orientations and widths [65–69]. Armchair and zigzag directions, two common nanoribbon edge geometries, are extensively studied and shown to have significantly different electronic properties. Nanoribbons are expected to be metallic or semiconducting depending on their width and edge orientation when electron-electron interactions are considered [70]. For armchair graphene nanoribbons, the gap size is inversely proportional to the ribbon width [70, 71]. Nanoribbons could have useful applications in integrated circuits. The conducting channel has to be completely closed in the off state, which is difficult to

achieve only with the gapless spectrum of graphene. However, as formerly discussed, bandgaps are present in nanoribbons and indeed nanoribbon transistors with large on/off ratios have been demonstrated [72–74]. On the other hand, zigzag-edged graphene nanoribbons are remarkable because they can host localized edge states (cf. Fig. 1.2-e), which give rise to a variety of features not present in armchair-edged ribbons [66, 67]. When electron-electron interactions are taken into consideration, localized states that occur close to the Fermi energy can give rise to spin-polarized edge states.

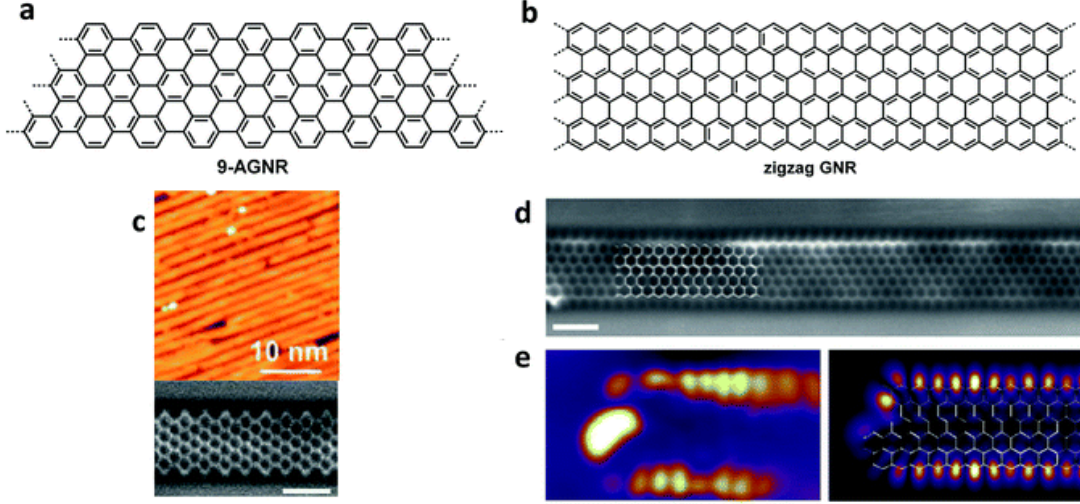


Figure 1.2: (a)- 9-AGNR schematic. (b)- 6-ZGNR schematic. (c)- Top: STM images showing the length of the 9-AGNR obtained from bottom-up techniques. Bottom: High-resolution noncontact atomic force microscopy (nc-AFM) frequency shift image of 9-AGNR. (d)- nc-AFM high-resolution image of a 6-ZGNR. (e)- Left- Differential conductance maps of filled edge states taken at a sample bias of 0.3V. Right- DFT-based LDOS at a tip-sample distance of 4Å, showing the spatial position of localised edge states. Adapted from [75].

### Van-der-Waals heterostructures

In contrast with graphene and its discovery, other two-dimensional materials such as transition metal dichalcogenides (TMDC) offer interesting opportunities due to their strong spin-orbit coupling [76, 77]. The spin-orbit coupling (SOC), via spin Hall and inverse spin Hall effect, is gauging the efficiency with which a charge current can be converted into a spin current and *vice versa* [78]. Whereas a very weak SOC, as in graphene, allows the conservation of spin properties over long distances, a very strong SOC, mainly due to the transition-metal counterparts of TMDCs, could enhance charge-to-spin conversion and exert better spin control. Unfortunately, a strong SOC is also responsible of spin relaxation hence making it difficult for these materials to be used as a platform for spin-based information transport [79]. As irreconcilable as these different materials seem due to their respective electronic properties, it is possible to combine them in

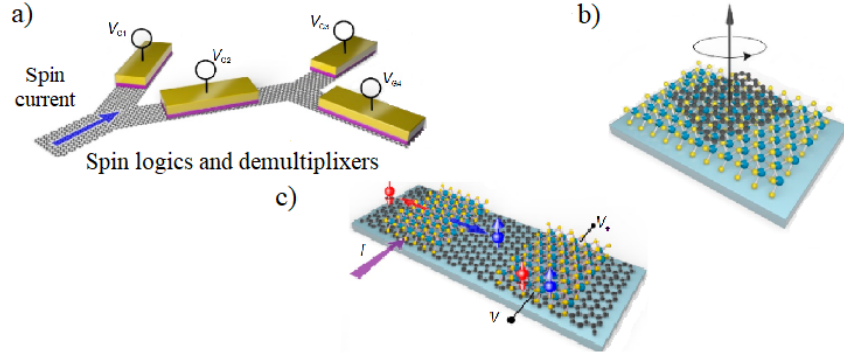


Figure 1.3: Spintronics devices schematics: (a)- Spin logic gates schematics: A spin-current is injected through a multibranch ZGNR system and by application of gate voltages, one can create spin-logic gates. (b)- Graphene monolayer on top of TMDC with a certain angle for proximity-induced twist/spintronics. (c)- Proximity-induced spintronic effects in GNR by depositing some high SOC materials. Adapted from [80].

Van-der-Waals heterostructures by stacking them on top of each other. According to prior research, stacked systems enable one layer to affect the electronic and spin behaviours of electrons in a different layer by proximity effects [76, 77]. Spin currents may be produced and transported over long distances by designing a device with areas of high and low proximity-induced SOC in the graphene layer (cf. Fig. 1.3-c).

### 1.2.2 Spintronics

Some strategies require abandoning conventional electron-based transport, to consider instead the development of spin-based transport in nanodevices. Compared to conventional electronics, spintronics has become a promising alternative. The central concept behind spintronics is to utilize both the charge and the spin degree of freedom associated with an electron's intrinsic angular momentum. Since spintronics enables information storage, processing, and communication with less energy usage than is now possible with conventional electronics, this field is anticipated to play a significant role in the development of the electronic industry [81–83]. The Giant Magnetoresistance (GMR) effect, which has applications in hard drives, is a perfect example of a significant technological advancement in this area [84, 85]. This effect demonstrates how a material's electrical resistance can be significantly changed by the parallel or anti-parallel magnetic alignment of adjacent ferromagnetic layers. All magnetic materials employed in today's technology currently belong to the d- or f-blocks of the periodic table [86, 87]. Although ferromagnetic materials are suited for generating spin currents, they are not suited for spin transport due to the high spin-orbit coupling present in these materials, being a source of spin relaxation [79]. While graphene is essentially non-magnetic, nanostructures tailor-made from it such as graphene nanoribbons display suitable spin-transport properties [6, 88]. Spin-polarized edge states, hosted in zigzag edge

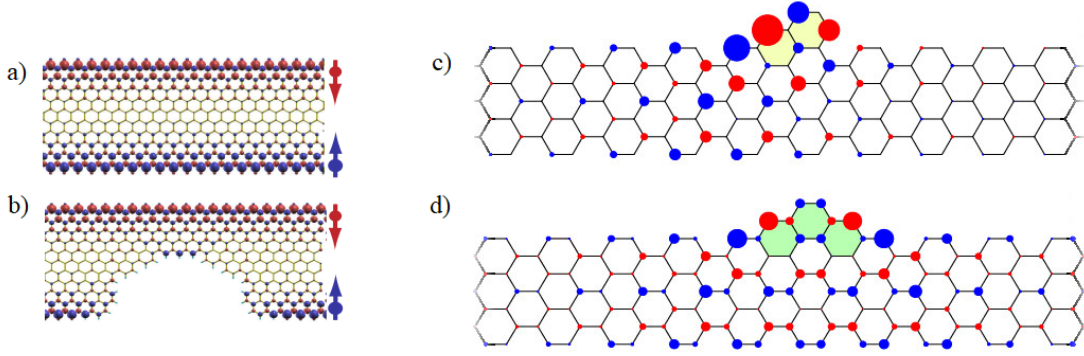


Figure 1.4: Adapted from [90]: (a)- ZGNRs host anti-ferromagnetically coupled spin-polarised transmission channels on their edges. The two contributions cancel out leading to no net spin-current. (b)- Purposeful asymmetrical disorder, here shown by rough disorder on the bottom edge, is one way to induce spin transport functionalities in nanoribbons. Adapted from [103]: (c) and (d)- Nanoribbons with chiral edges (portion of ZZ-like edge structure) present localised edge states

shaped ribbons, serve as the foundation for many of the proposed graphene-based spintronic devices. It is expected that the parallel zigzag edges exhibit opposing spin currents. A system like that would offer the opportunity to tune its spin-transport features [65, 66, 70, 89, 90]. Several theoretical ways to induce spin functionalities in ZGNRs among which transverse electric fields [67] and gate voltage [89, 91] have been investigated. A various amount of spintronic devices based upon these functionalities such as spin-filters [67, 92–94], spin-polarised beam splitter [95, 96], spin qubits [97, 98] and logic gates [99, 100] (cf. Fig. 1.3-a) have been proposed. Graphene edges can hold spin polarization, but this is not sufficient for using graphene as a source of spin-polarized electrons. The reason is that the spins at the edges are not quantized in a fixed direction and are not fixed in time [101]. This is because graphene has no intrinsic magnetic anisotropy. This means that the spins at the edges will be easily flipped by external magnetic fields, or even by thermal fluctuations [102]. Therefore, graphene has limits as a standalone source of spin-polarized electrons.

### Disorder and impurity in graphene-based materials

Although some of these edge state signatures have been observed in experiments [34, 104, 105], there are uncertainties about their stability, and any magnetic properties that do emerge are not expected to be very robust when edge disorder is present [106, 107]. Numerous research groups have studied extended edge defects in the form of vacancies or other deformations [108–113]. It is widely agreed from these studies that the presence of edge-disorder induces Anderson-type localization [114, 115] in the ribbons, which suppresses conductive paths through the ribbons for specific energies.

Pristine ZGNRs are known to host spin-polarized transport channels near their edges (cf. Fig. 1.4(a)), but opposite contributions from each of their antiferromagnetic edges tend to cancel any net spin-current. Thus the asymmetry [90] that could arise from disorder as seen on Fig. 1.4(b) or the presence of junctions [116], shown in as seen on Fig. 1.4(c)-(d) on the edges could induce spin-filtering functionalities in these structures. Another topic that has received a considerable amount of attention in the literature, particularly in the areas of transport and magnetism, is the purposeful introduction of disorder into graphene systems, whether in the form of vacancies or impurity atoms [117–122]. This is owing to the fact that doping a material can be a useful tool for modifying or fine-tuning its electronic properties [123]. Nevertheless, there is an important distinction between the situation involving a graphene sheet and nanoribbons. Due to the presence of two symmetry-breaking edges, several of the electronic characteristics of the nanoribbon are predicted to depend on the position of the impurity. Numerous studies that looked at the conductance through a nanoribbon system when the impurity position or distribution was modified have noticed this dependence [108, 110, 119, 124].

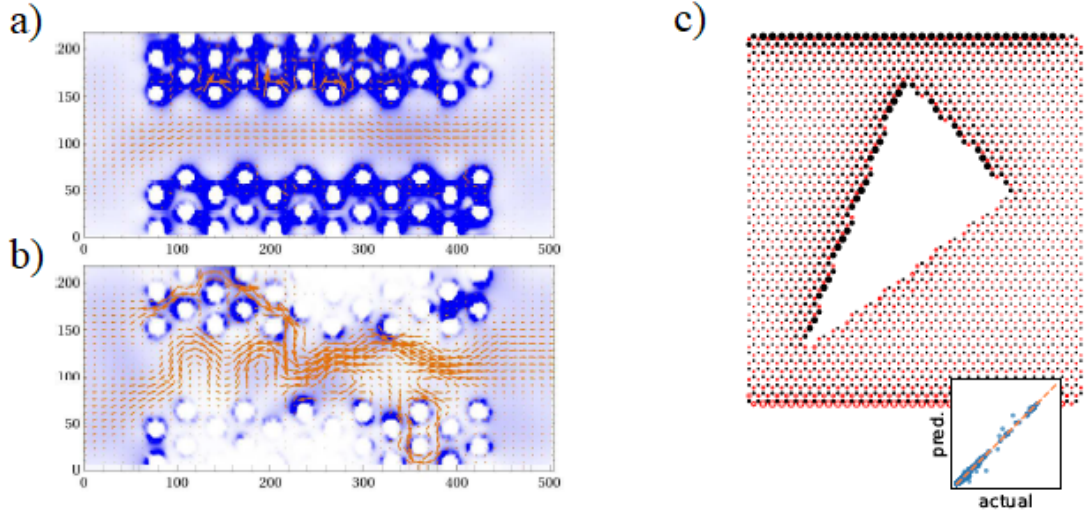


Figure 1.5: Adapted from [125]: (a)- GAL waveguide with pristine circular antidots on both top and bottom edges. The blue-shaded color and the arrows respectively show the LDOS and the current flow for a particular energy. (b)- An edge roughness and a random fluctuation of position of the antidots breaking the periodic pattern is considered. One can appreciate how the introduction of disorder severely changes the LDOS and current map. Adapted from [126]. (c)- Randomly generated subtractive antidot magnetic profile obtained with ML in a ZGNR with electron-electron interactions. Localised magnetic moments can be observed on the zigzag portions of the antidot. The inset shows how ML can accurately predict magnetic profiles when compared to conventional Hubbard SC procedure.

Recent research has focused on graphene antidot lattice (GAL) systems [127, 128], where it is also predicted that imposing a periodic perturbation on the graphene

sheet will open up a bandgap. According to theoretical investigations of GAL-based systems [98, 125, 129], the bandgap behavior frequently conforms with a basic scaling equation between the period of the perturbation and the antidot size [98]. Fig. 1.5(a) shows a waveguide for electrons made of graphene with macroscale circular antidots on top and bottom edges. Here we see the potential for nanopatterned graphene for suitable transport applications. But the electronic structure features predicted for periodically nanopatterned GAL system can be very sensitive to atomic scale imperfections and defects [125]. Fig. 1.5(b) shows the same waveguide at the same energy but now the presence of positional disorder disrupting the periodicity and edge roughness on the antidots is completely changing the transport profile of this device. Subtractive antidot systems [130, 131], where triangular ZZ-edged perforations support the emergence of half-metallic [93] and anisotropic transport [132].

The impact of disorder on electronic transport, either in the form of edge roughness, extended edge disorder, dopants in the bulk or nanopatterned macroscale disorder typically require the study of a vast amount of different configurations. Configurational-averaging is an essential component of disorder studies, particularly in one-dimensional systems like GNRs, in order to remove configuration-specific features and determine the main trends as the parameters of disorder are varied [90, 109, 125]. For spin-based transport, magnetic ribbons subject to disorder are even harder to study as the procurement of their preliminary magnetic profiles are constrained by the limitations of conventional techniques. Spin-polarised density functional theory (DFT) has a limited field of action when it comes to simulate magnetic profiles as it is constrained to small-scaled or periodic systems. Tight-binding (TB) simulations with a Hubbard mean-field approach has a broader power as the technique is resilient for larger and systems exempt of periodicity. Yet, the self-consistent Hubbard procedure can be costly in terms of computational resources as it requires the inversion of the full Hamiltonian of the system thus scaling with the system size [89, 133]. This usually hinders the consideration of disordered zigzag-edge magnetism at mesoscopic scales.

### 1.2.3 Machine-learning

As we have seen previously, the disorder in graphene nanostructures, whether it is extrinsic and arises from their synthesis and over which it is difficult to have control or intentionally induced to control their electronic and transport properties require the treatment of a very large number of configurations. Conventional techniques must be supplemented with tools to generate and process a large amount of data efficiently and at lower computational cost. Machine learning may be the answer to pave the way towards novel powerful devices. Significant

improvements in computational science skills have created new areas of study and massively increased the scope of the work of the material science community [134–136]. The relentless effort towards routinely generating huge data sets via atomistic simulation is driving great interest [134]. Machine Learning (ML), the capacity of computer algorithms to interpret data and extrapolate novel inferences for novel scenarios, is becoming more important as a tool of choice to evaluate the expanding and complicated data generated in numerous scientific and technical contexts [137–139]. In materials science, it has been estimated that the space of stable organic molecules is over  $10^{60}$  [140]. Among this gigantic space is probably found chemicals that could potentially solve our society’s most crucial questions like drugs in response to orphan diseases or even alloys with suitable properties. An emerging field in materials science is high-throughput computational materials design [141, 142]. Conventional methods of discovering novel materials, such as (DFT)-based methods, are currently unable to keep up with the ever-growing needs for novel materials. Machine learning, which combines powerful data processing, excellent prediction performance, and low computational cost, is therefore widely employed in material identification, material analysis, and material design [135, 141–143]. ML alongside conventional transport techniques can create a new way of designing nanostructures for charge, spin and valley applications. Firstly, it will allow to understand how the intentional introduction of disorder through several forms could help to control electronic, spin and valleys properties. Also, how extrinsic and non-controllable sources of disorder that can emerge from the edges or antidots during synthesis processes would impact realistic mesoscopic devices. Aside from comprehending how to design such devices, ML will also be helpful in order to optimise such graphene-based nanostructures. Indeed, due to the interplay and competition of several complex flavour effects, it is cumbersome to design an optimised device that will ensure to deliver the required properties. Non-intuitive geometries mixing different sources of disorder like nanomeshes, superposed finite regions of TMDCs with high SOC on GNRs could be obtained through reverse engineering ML-acquired knowledge for powerful, robust and powerful spintronic devices.

### 1.3 Thesis layout

The work in this thesis focuses on tackling the problem of design and optimisation for graphene-based nanostructures that will gather the desired electronic and spin-transport properties as discussed in the earlier section. The presentation is sequential in the sense that each chapter is built and enriched gradually by the studies realised in the previous ones. The thesis is organised as follows:

- Chapter 2 details the general theoretical and computational framework employed throughout this thesis. The electronic band structure of graphene

and graphene nanoribbons, calculated using the nearest-neighbour tight-binding formalism are introduced. Green’s function, a central mathematical quantity in our work, is introduced and heavily discussed as it provides direct access to the density of states which underpins many of the electronic and transport properties of nanomaterials. An added layer of complexity is necessary in order to account for electronic interactions in nanostructures. Magnetic properties are investigated within the scope of the Hubbard model and the Hartree-Fock approximation. The methodology for quantum transport is presented alongside many different algorithms and techniques, provided for efficient and accurate calculations. Finally, a broad overview of machine learning techniques expands the scope of the chapter and provides a perspective on how this tool can be used to tackle optimisation problems in nanoelectronics.

- Chapter 3 focuses on how to predict quantum transport in disordered graphene nanoribbons (GNRs) with machine learning (ML). By first discussing previous works relating the effects different types of disorder have on the transport properties for GNRs, we study the effect impurities have on quantum transport through different straightforward scenarios. We infer that crucial informations such as the distance to an edge or the sublattice play a major role to relate quantum transport and structural properties in the presence of impurities. Based on this preliminary work, we have developed ML-techniques capable of accurately predicting transport properties in disordered GNRs with only geometrical considerations. This is followed with an analysis of our results where we detail the importance of the description on the predictive performance of our models. This chapter serves as a proof-of-concept and highlight the ability of machine learning techniques to capture the complexity of disordered nanostructures, and suggest that they can be used to complement conventional techniques to better understand a wider array of systems.
- Chapter 4 provides a detailed overview on how to use neural networks for quick and accurate prediction of magnetism in carbon-based nanostructures at half-filling. We first discuss the origin of magnetism in carbon-based structures and introduce the effort to observe magnetic properties by experimental groups. Local magnetic properties in graphene-based structures are heavily dependent on the edge structure of such materials when electronic interactions are considered. Based on the incentives from chapter 3 and motivated by the necessity of circumventing prohibitive conventional methods for realistic systems, we have trained a neural network with only geometric considerations. This trained model allows the prediction of magnetic properties of carbon-based structures at a moderate computational cost when

compared to conventional techniques. The comparative results between our ML model and conventional methods are discussed for a wide array of different nanostructures such as nanoflakes and nanoribbons. Advantages and limitations of our model are finally discussed alongside various promising applications.

- Chapter 5 gives a complete and detailed perspective of spin-transport in the context of edge-disordered ZGNRs. By first discussing the implication that edge disorder causes on quantum transport, we introduce the different types of edge disorder in ZGNRs based on experimental observations and theoretical works. Afterwards, we assess and benchmark how the trained neural network from chapter 4 can predict magnetic profiles of disordered ribbons. This offers quick and accurate access to spin-transport properties that are scaled-up for arbitrarily large and disordered ribbons, so far infeasible with conventional techniques. We then conduct a detailed and systematic analysis of spin-transport in edge-disordered GNRs for rough and smooth types of disorder. We show how robustness of spin-currents depends on the disorder profile present at the edges and envisage how asymmetry can avail the observation of spin-polarised transport properties in such materials.
- Finally, chapter 6 gives a summary of our work and extends discussions towards perspectives and prospects we can envision for the future.

## Methods

In this chapter, an overview of the general methodology used for this work is presented. To characterise the electronic structure of 2D materials, the tight-binding model is presented and applied to carbon-based nanostructures such as GNRs. The band structure of 2D materials such as graphene and derived nanostructures can be represented by this straightforward model, yet encompassing the important features. Then, we turn our attention to the Green's function, a key-stone quantity from which electronic and transport properties can be extracted. Green's functions are computed directly from the Hamiltonian and intertwined with the physical system's density of states. With the use of Dyson's equation, one may determine how perturbations will affect the electronic structure of a system subject to disorder. Without the need to diagonalise a new Hamiltonian, the Green's function of the perturbed system is directly obtained from that of the unperturbed one. The recursive Green Function (RGF) method can be used to determine the Green's function of very large systems based on Dyson's equation. The following section will introduce Landauer-Büttiker formalism for two- and multiterminal systems to calculate the transport signatures of quantum devices. We will finally conclude by explaining the fundamentals of machine and supervised learning. Various algorithms are described, with neural networks receiving the most attention, as they were the algorithm of choice for a major part of my research. Finally, the chapter ends with a brief exploration of unsupervised learning.

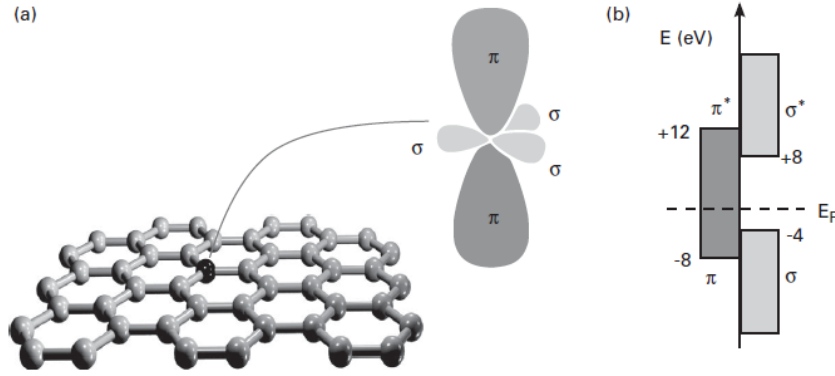


Figure 2.1: (a)- Graphene is made of hybridized  $sp^2$  carbon atoms. The doubly-occupied  $\sigma$  bonds, represented in grey-shaded orbitals for a single atom, are in-plane and responsible for the superlative strength and structural properties of graphene. The out-of-plane  $2p_z$  orbital, shown in dark grey orbitals, is half-filled with one  $\pi$  electron. (b)- The  $\pi$  and  $\pi^*$  bands, responsible for the conduction and valence bands in graphene lies near the Fermi energy describing the low-energy physics. The  $\sigma$  and  $\sigma^*$  bands present a big bandgap around  $E_F$ . Adapted from [144].

## 2.1 Electronic structure: Tight-binding model

### 2.1.1 Introduction

Since there are four valence electrons in the second shell of a carbon atom, four single bonds are able to form. One  $2s$  and two  $2p_x$ - $2p_y$  carbon orbitals can hybridize to form  $sp^2$  carbon (cf. Fig. 2.1-a), creating a strong trigonal structure in planar carbon materials like graphene, which forms doubly-occupied  $\sigma$  bonds with its three neighbours. The remaining electron finds itself in the out-of-plane  $2p_z$  orbital, and forms the half-filled  $\pi$  band, which is the source of graphene's unusual electronic properties [8]. Using the orthogonality between  $\sigma$  and  $\pi$  electrons and focusing on the low-energy region (cf. Fig. 2.1-b), it is possible to neglect the  $\sigma$  bands to investigate the electronic properties of graphene. The tight-binding (TB) model allows a simple description of the electronic structure of a physical system [145]. A solid is described as a lattice made up of atoms that are separated by lattice parameters. Each atom in the system has an associated localised atomic orbital, which together makes up the electronic wavefunction. By including the overlap between the wavefunctions of adjacent atoms, the tight binding approximation gives an accurate description of the electronic properties for a particular material. When the overlap is minimal, the approximation can be quite accurate and produce results that are well-concordant with experimental observations or with more sophisticated approaches for studying the electronic structure of solids. In order to simplify the Hamiltonian and describe the molecular orbital as the linear sum of all atomic orbitals, we use the linear combination of atomic orbitals (LCAO) in the following derivation.

We will employ the nearest-neighbour tight-binding approach throughout this

study to characterize the electronic band structure of graphene. The Hamiltonian describing the system is of the form

$$\hat{\mathcal{H}} = \sum_{\langle i,j \rangle} t_{ij} |i\rangle \langle j| + \sum_i \varepsilon_i |i\rangle \langle i|, \quad (2.1)$$

where  $t_{ij}$  is the hopping parameter to a neighbouring site  $j$  and  $\varepsilon_i$ , the onsite energy of site  $i$ . The Hamiltonian matrix's eigenvalues are then used to determine the band structure. The matrices used in this equation typically have a dimension equal to the number of orbitals being employed to characterize the system. For systems that display translational invariance, moving into the  $k$ -space and using the Bloch theorem allows to study the system in a sub-region, *i.e* the first Brillouin zone (BZ) [145, 146]. Consequently, the eigenvectors of the system are simply periodic Bloch wavevectors; however, nonperiodic or extended systems require a different strategy. The Bloch's theorem allows to express the electronic eigenfunction  $|\mathbf{k}\rangle$  as a linear combination of localised atomic orbitals with coefficients  $\phi^{\mathbf{k}}$  in the given form:

$$|\mathbf{k}\rangle = \frac{1}{\sqrt{N}} \sum_j e^{i\mathbf{k} \cdot \mathbf{R}_j} \phi^{\mathbf{k}} |j\rangle, \quad (2.2)$$

where  $\mathbf{k}$  is the wave vector,  $\mathbf{R}_j$  is the position vector of lattice site  $j$  and  $\frac{1}{\sqrt{N}}$  is a normalisation factor. The electronic states of the system can be found by solving the time-independent Schrodinger equation

$$\hat{\mathcal{H}} |\mathbf{k}\rangle = \varepsilon(\mathbf{k}) |\mathbf{k}\rangle$$

$$\varepsilon(\mathbf{k}) \sum_j e^{i\mathbf{k} \cdot \mathbf{R}_j} \phi^{\mathbf{k}} |j\rangle = \sum_j e^{i\mathbf{k} \cdot \mathbf{R}_j} \phi^{\mathbf{k}} \hat{\mathcal{H}} |j\rangle$$

after which  $\langle m|$  should be projected to obtain the secular equation :

$$\varepsilon(\mathbf{k}) \phi^{\mathbf{k}} \sum_j e^{i\mathbf{k} \cdot \mathbf{R}_j} \langle m|j\rangle = \sum_j \phi^{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{R}_j} \langle m| \hat{\mathcal{H}} |j\rangle. \quad (2.3)$$

Assuming that there is no overlap between orbitals of different sites, as we assume for graphene  $p_z$  orbitals, the basis set for atomic orbitals is fully orthogonal, so that  $\langle m|j\rangle$  simplifies to  $\delta_{m,j}$ . Hence, we obtain the following relation

$$\varepsilon(\mathbf{k}) \phi^{\mathbf{k}} = \sum_j \phi^{\mathbf{k}} e^{i\mathbf{k} \cdot (\mathbf{R}_j - \mathbf{R}_m)} \langle m| \hat{\mathcal{H}} |j\rangle. \quad (2.4)$$

In the nearest-neighbour tight-binding approach, the Hamiltonian matrix ele-

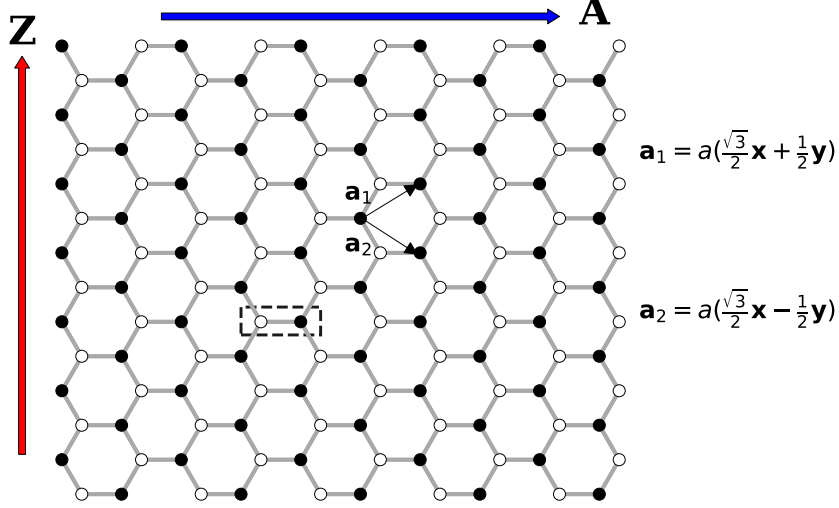


Figure 2.2: A slab of graphene lattice where sites from the two intersecting triangular sublattices are represented at the lattice sites by filled or hollow symbols. A unit cell containing one site from each sublattice is enclosed by the dashed rectangle. This lattice can be entirely spanned by translation around the two primitive vectors  $\mathbf{a}_1$  and  $\mathbf{a}_2$ . The main armchair (AC) and zigzag (ZZ) directions in the lattice are respectively marked with large blue and red-colored arrows.

ments are defined as

$$\langle m | \hat{\mathcal{H}} | j \rangle = \begin{cases} \varepsilon_0 & \text{if } m = j \\ t & \text{if } m \text{ \& } j \text{ nearest neighbours} \end{cases} \quad (2.5)$$

where  $\varepsilon_0$  is the onsite energy and  $t$  is the hopping parameter. These parameters are usually found by fitting the results to experimental measurements or *ab-initio* calculations [8]. Using standard matrix operations, one can solve the Eq. 2.4 to obtain the eigenvalues  $\varepsilon(\mathbf{k})$  and the eigenfunctions  $|\mathbf{k}\rangle$ .

### 2.1.2 Graphene: Band structure and electronic properties

The carbon atoms in graphene are arranged in a hexagonal-shaped lattice. Two neighbouring sites constitute the unit cell that generates the entire lattice by translation along two primitive lattice vectors,  $\mathbf{a}_1$  and  $\mathbf{a}_2$ . Thus, graphene could also be regarded as a triangular Bravais lattice with a two-atom unit cell. Any unit cell in the graphene lattice can be located by a linear combination of these vectors with integer coefficients,  $\mathbf{r} = m\mathbf{a}_1 + n\mathbf{a}_2$  (cf. Fig. 2.2). As used to calculate the electronic structure of graphene, the orbital basis set is represented by  $|\mathbf{r}, n\rangle$  where the location of the unit cell is given by  $\mathbf{r}$  and  $n = 1, 2$  refers to the site within the unit cell where the orbital is centered around differentiating each of the sublattices. By moving to reciprocal space, two Bloch functions, one for each

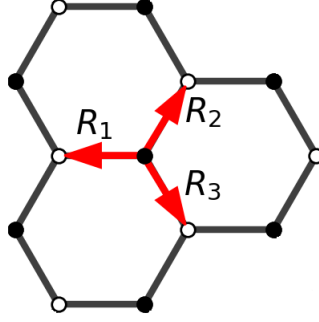


Figure 2.3: Principal vectors defining the nearest neighbours to calculate the dispersion relation in Eq. 2.8.

sublattice, are needed to form the basis set, written as

$$|\mathbf{k}, n\rangle = \frac{1}{\sqrt{N}} \sum_j e^{i\mathbf{k} \cdot \mathbf{r}} |\mathbf{r}, n\rangle. \quad (2.6)$$

Each atom on the lattice has three nearest neighbours, and the hopping parameter for nearest neighbours in graphene is known to be  $t_{ij} \equiv -t \approx -2.7$  eV [8]. This quantity,  $t$ , will be used as a unit of energy throughout this work. The onsite energy,  $\varepsilon_0$ , is the same at each lattice site and defines the center of the energy bands, and is set to zero in these calculations. The  $k$ -dependent Hamiltonian sizes as a  $2 \times 2$  matrix when the Bloch functions' basis set is considered and is of the form

$$H = \begin{pmatrix} 0 & tf(\mathbf{k}) \\ tf^*(\mathbf{k}) & 0 \end{pmatrix} \quad (2.7)$$

where  $f(\mathbf{k})$ , the structure factor is calculated by adding the phase terms coming from each nearest neighbour of a site within the unit cell.

$$\begin{aligned} f(\mathbf{k}) &= \sum_{i=1}^3 e^{i\mathbf{k} \cdot \mathbf{R}_i} \\ &= e^{i\frac{k_x \cdot a}{\sqrt{3}}} + e^{-i\left(\frac{k_x \cdot a}{2\sqrt{3}} - \frac{k_y \cdot a}{2}\right)} + e^{-i\left(\frac{k_x \cdot a}{2\sqrt{3}} + \frac{k_y \cdot a}{2}\right)} \\ &= e^{i\frac{k_x \cdot a}{\sqrt{3}}} + 2 \cos\left(\frac{k_y \cdot a}{2}\right) e^{-i\frac{k_x \cdot a}{2\sqrt{3}}} \end{aligned} \quad (2.8)$$

By solving the matrix secular equation  $|H - E\mathbb{I}| = 0$ , the eigenvalues are written as

$$\begin{aligned} \varepsilon_{\pm}(\mathbf{k}) &= \pm t |f(\mathbf{k})| \\ &= \pm t \sqrt{1 + 4 \cos\left(\frac{k_y \cdot a}{2}\right)^2 + 4 \cos\left(\frac{k_y \cdot a}{2}\right) \cos\left(\frac{\sqrt{3}k_x \cdot a}{2}\right)} \end{aligned} \quad (2.9)$$

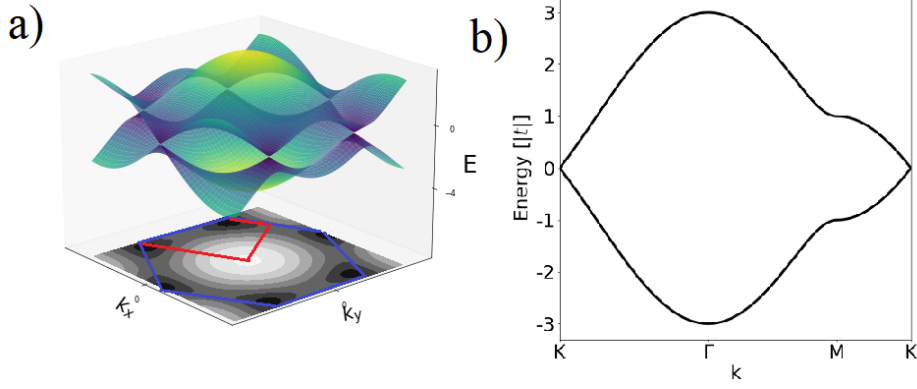


Figure 2.4: **(a)**- Band structure of graphene obtained with the tight-binding model as a function of  $k_x$  and  $k_y$ . The projection onto the  $k_x$ - $k_y$  plane shows the iso-energy surfaces where the darkest shade correspond to  $E = 0$ . The first BZ of graphene, delimited by the blue lines, is a hexagon described by these points. **(b)**- Bands when moving along the high-symmetry points of the first BZ depicted by the red path in the panel **(a)**.

with the associated eigenvectors

$$|\mathbf{k}, \pm\rangle = \frac{1}{\sqrt{2N}} \sum_j e^{-i\mathbf{k} \cdot \mathbf{r}} (|\mathbf{r}, 1\rangle \pm e^{-i\phi(\mathbf{k})} |\mathbf{r}, 2\rangle) \quad \text{where } e^{-i\phi(\mathbf{k})} = \frac{f^*(\mathbf{k})}{|f(\mathbf{k})|} \quad (2.10)$$

The energy band structure in Eq. 2.9 is shown in the Fig. 2.4-**a** as a function of  $k_x$  and  $k_y$ , and along some of the important high symmetry points of the Brillouin zone. The band structure along the red path in Fig. 2.4-**a** for graphene is also shown in the bottom panel (cf. Fig. 2.4-**b**). As the  $2p_z$  orbitals in  $sp^2$  carbon contain a single electron, the  $\pi$  band is half-filled and the Fermi energy of the undoped system is at  $E_F = 0$ . The Fermi surface for undoped graphene is then only constituted of the 6 corners of the hexagonal-shaped first Brillouin zone (cf. blue hexagon in Fig. 2.4-**a**) where the  $\pi$  and  $\pi^*$  bands touch. The DOS vanishes at these so-called Dirac points and makes graphene, a zero-gap semimetal. By translation along the two primitive vectors of the Brillouin zone, two Dirac points, generally called  $K$  and  $K'$  points are unique and are responsible for the so-called valley flavours of the electron in graphene. The shape of the bands close to the Fermi energy is responsible for many of the unusual features of graphene. Graphene's band structure is linear at  $E_F$ , in contrast to the parabolic bands found in ordinary semiconductors. Electrons or holes close to the Dirac points exhibit relativistic behaviours as a consequence of the linear-shaped bands or Dirac cones and have zero effective mass, as indicated by the Dirac equation from quantum electrodynamics [8, 20, 21]. Although the latter approach will not be the main emphasis of this thesis, it is worthwhile to quickly examine how graphene electrons are approximated in the linear regime as it offers a bridge with other fields of physics. This method, useful in the low-energy regime, is particularly adapted when one deals with one single particle approach and desire, for instance,

to investigate scattering effects due to disorder in graphene.

### Linear dispersion regime

In the vicinity of the Fermi energy, the Dirac cones displays a linear relationship between energy and momentum for the electron, directly advocating that the Dirac equation is valid in the low-energy regime. Thus, it is possible to approximate linearly the dispersion relation of graphene (cf. Eq. 2.9) around one of the Dirac cones. Without loss of generality, we will make the linear expansion of the graphene's spectrum around the  $\mathbf{K} = (0, \frac{4\pi}{3a})$  point. By considering the expansion around  $\mathbf{K}$  with an infinitesimal  $\partial\mathbf{k}$  increment of  $f(\mathbf{k})$  in Eq. 2.8 such that  $\mathbf{k} = \mathbf{K} + \partial\mathbf{k}$ , we get :

$$\begin{aligned} f(\mathbf{k}) &= \sum_{i=1}^3 e^{i\mathbf{K} \cdot \mathbf{R}_i} e^{i\partial\mathbf{k} \cdot \mathbf{R}_i} \\ &\approx 1 + \left(-\frac{1}{2} + i\frac{\sqrt{3}}{2}\right) (1 + i\partial\mathbf{k} \cdot \mathbf{R}_2) + \left(-\frac{1}{2} - i\frac{\sqrt{3}}{2}\right) (1 + i\partial\mathbf{k} \cdot \mathbf{R}_3) \\ &\approx \frac{\sqrt{3}a}{2} |\partial\mathbf{k}| e^{i(\frac{\pi}{2}-\theta)} \end{aligned} \quad (2.11)$$

where  $\theta$  is the angle from the  $k_x$  plane. Now that we have expanded the structure factor  $f(\mathbf{k})$ , we just need to calculate the modulus of this quantity and multiply it by  $t$ , the hopping term in graphene to obtain the linear approximation of the dispersion relation :

$$\varepsilon_{\pm}(|\partial\mathbf{k}|) = \pm \frac{\sqrt{3}at}{2} |\partial\mathbf{k}|. \quad (2.12)$$

The pre-factor can also be rewritten in terms of the Fermi velocity,  $v_F \sim 10^6$  m/s, in graphene and we obtain

$$\varepsilon_{\pm}(|\partial\mathbf{k}|) = \pm \hbar v_F |\partial\mathbf{k}|, \quad (2.13)$$

which is a typical description of a relativistic “massless” particle except that the speed of the electron is bounded by  $v_F$ . Once again, this linear expansion around one of the Dirac cones is valid in the near vicinity of the Fermi energy and allows to understand intriguing QED-like effects occurring in graphene such as Klein tunneling [46–48].

### 2.1.3 Graphene Nanoribbons: Band structure and electronic properties

Graphene nanoribbons are quasi one-dimensional structures obtained from trimming graphene along particular directions and widths. The introduction of edges in graphene strongly dictates the electronic structure of such materials. Indeed,

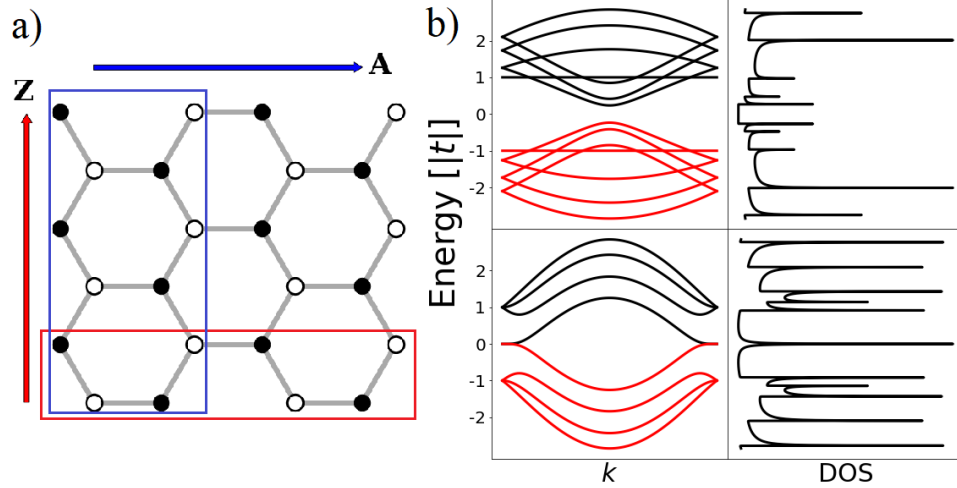


Figure 2.5: (a)- Armchair and zigzag directions are respectively shown by the blue and red arrows. Considered semi-infinite along their periodic direction, graphene nanoribbons are characterised by their widths. The blue rectangle shows the unit-cell of a 6-AGNR whereas the red rectangle is the unit-cell of a 4-ZGNR. (b)- On the top panel are shown the band structure and associated DOS of a pristine 6-AGNR and the bottom panels depict the 4-ZGNR pristine band structure and DOS. The red and black bands in the band structure plots represent respectively the valence and conduction bands of their associated ribbons.

“hard-wall” boundary conditions occur due to the presence of the edges alongside their transversal directions such that the electronic wavefunction vanishes at the boundaries. The two main edge orientations, Zigzag and Armchair are shown in Fig. 2.5 by the red and blue arrows respectively. The quantum confinement of the wave function along the transversal direction due to edges depends on the edge termination of the ribbon as we shall see. As each of these edge orientations have their own subtleties reflecting in the electronic properties of GNRs, let us discuss how these Zigzag-nanoribbons (ZGNRs) and Armchair-nanoribbons (AGNRs) differs from one another.

If we focus on the zigzag-oriented nanoribbon by considering the red arrow in Fig. 2.5 as the periodic direction, we see that the atoms at the edges consist solely in either black or white atoms. The sublattice symmetry breaking occurring for ZGNRs alongside the hard-wall boundary conditions do not yield all the electronic states [69]. The remaining edge state is found by solving a transcendental equation, which produces a complex value for the quantized wavevector [69, 147]. This edge state is a signature of ZGNRs and localised at the edge of the ribbon which contributes in a large peak in the DOS at the Fermi energy (cf. bottom left panel of Fig. 2.5-b). Indeed, when electron-electron interactions are considered, as described in the chapter 4, spin polarised states are found at the edges and decay towards the ribbon centre, with the ground state of the system having the two edges with opposite spin polarisation [66]. The band structure

is obtained numerically by considering a unit cell, shown as a red rectangle in Fig. 2.5-a, containing lattice sites across the width of the ribbon. The standard Bloch theorem is then applied by taking advantage of the periodicity along the length of the ribbon. The band structure, shown in the left bottom panel of Fig. 2.5-b, displays the degeneracy of the valence (red) and conduction (black) bands at  $E_F = 0$ . These bands are largely flat at the Fermi energy and gets flatter as the width of the ribbon is increased.

For AGNRs, the application of hard wall boundary conditions is successful in replicating the tight-binding model's anticipated band structure. We see that unlike ZGNRs, imposing such boundary conditions does not affect the sublattice symmetry as the edge is terminated by both black and white atoms (cf. Fig. 2.2). The width in AGNR determines whether the ribbon is metallic or semiconducting, as tight-binding band structure predicts that only one third of AGNRs are metallic. This is in contradiction with experimental observations and DFT results as AGNRs are predicted to be semiconducting [67]. DFT calculations often yield smaller bandgaps for AGNRs compared to TB predictions. This difference arises because DFT includes more electronic correlations, which can affect the energy levels and bandgaps. The TB model may oversimplify the electronic interactions, leading to an underestimation of the bandgap [148]. Indeed, edge effects in nanometer-sized ribbons must be carefully considered to determine their bandgaps because the bonding between atoms at the edges is not uniform. The nearest-neighbour TB model can be modified to account for edge deformation effects in armchair graphene nanoribbons. This introduces an additional term in the TB model to increase the hopping energy between edge atoms by about 12% [70].

The blue rectangle in Fig. 2.5-a is used as the primary unit-cell for a 6-AGNR and allows us to calculate the band structure in the top panel of Fig. 2.5-a and the associated DOS.

## 2.2 Green's Functions

Undoubtedly one of the most important and useful tools in the arsenal of theoretical physics is the use of Green's function (GF) methods. The GF is a calculational tool used in mathematics to estimate the response to a linear differential equation [149]. GFs are used to explain how a system behaves when subject to an excitation. In physics and in the realm of condensed matter specifically, GF acts as a susceptibility function that relates a response to a perturbation, in this case an electronic excitation [149]. The Schrödinger equation, which describes the electronic energy states of a system, serves as the linear differential equation in

this context.

The GF of a system allows direct access to its density of states (DOS), which is a central and experimentally measurable quantity in solid-state physics [145]. It describes the number of energy states that are available to be occupied at a particular energy. Theoretical predictions and experimental results can be directly compared using techniques such as scanning tunneling microscopy. In addition, a number of electronic transport methods have been developed based on direct application of GF because the GF effectively describe the propagation of electrons across a conducting system. Treating electrons as quantum particles and considering the associated Schrödinger equation, we define the GF to be :

$$\hat{g}^{a/r}(E) = \lim_{\eta \rightarrow 0} \left[ (E \pm i\eta) \hat{I} - \hat{\mathcal{H}} \right]^{-1} \quad (2.14)$$

where  $\hat{g}^{a/r}$  is defined as respectively the *advanced* or *retarded* GF,  $E$  is the energy,  $\hat{\mathcal{H}}$  is the Hamiltonian operator of the considered system and  $\eta$  is a small positive real parameter that ensures the function to be well-defined near the energy eigenvalues. The non-hermicity of GF, due to the presence of  $\eta$ , prevents GF from being an observable. When the limit is taken to zero, however, one could associate a physical meaning to the GF. The retarded GF describes the propagation of the excitation away from the source whereas the advanced one propagates towards the source. In the remaining of the study and if not explicitly mentioned, the term “GF” will refer to the retarded GF.

It is possible to directly demonstrate the relationship between the GF and the DOS. By writing the Hamiltonian in a basis set defined by its eigenstates, we can always express the Hamiltonian operator as

$$\hat{\mathcal{H}} = \sum_a |\psi_a\rangle \epsilon_a \langle \psi_a| \quad (2.15)$$

Inserting the Hamiltonian into the expression of the GF in Eq. 2.14, we obtain

$$\hat{g} = \lim_{\eta \rightarrow 0} \sum_a |\psi_a\rangle \frac{1}{E + i\eta - \epsilon_a} \langle \psi_a| \quad (2.16)$$

Considering an LCAO-type Hamiltonian, one can describe the Hamiltonian in a basis set of atomic orbitals  $|j\rangle$  centered on a site  $j$ . Projecting on two different orbitals  $|j\rangle$  and  $|l\rangle$ , we get

$$g_{jl} = \langle j | \hat{g} | l \rangle = \lim_{\eta \rightarrow 0} \sum_a \langle j | \psi_a \rangle \frac{1}{E + i\eta - \epsilon_a} \langle \psi_a | l \rangle. \quad (2.17)$$

Multiplying this expression by the conjugate of the denominator, we split into

real and imaginary parts the expression of the projected GF  $\hat{g}_{jl}$  as

$$g_{jl} = \lim_{\eta \rightarrow 0} \left[ \sum_a \langle j | \psi_a \rangle \frac{E - \epsilon_a}{(E - \epsilon_a)^2 + \eta^2} \langle \psi_a | l \rangle + i \sum_a \langle j | \psi_a \rangle \frac{-\eta}{(E - \epsilon_a)^2 + \eta^2} \langle \psi_a | l \rangle \right] \quad (2.18)$$

Set  $l = j$  and recall that the Dirac delta function is asymptotically defined by

$$\delta(x) = \frac{1}{\pi} \lim_{a \rightarrow 0} \frac{a}{x^2 + a^2} \quad (2.19)$$

We conclude that

$$-\frac{1}{\pi} \Im(g_{jj}) = \sum_a |\langle j | \psi_a \rangle|^2 \delta(E - \epsilon_a) \quad (2.20)$$

The right-hand side of this equation corresponds by definition to the local density of states (LDOS) for the site  $j$  at energy  $E$ . The LDOS, as will be seen later, is a central quantity from which many physical quantities like the occupation number are computed. Consequently, it is possible to express the DOS, being the sum of the LDOS over all sites in the system, in terms of GF in the following fashion

$$\text{DOS}(E) = -\frac{1}{\pi} \Im \text{Tr}[\hat{g}(E)] \quad (2.21)$$

### 2.2.1 Dyson equation

As shown above, Green's function and the density of states of a physical system are closely related. Though, in the above reasoning, we have assumed prior knowledge of the Hamiltonian's eigenstates allowing one to express the operator in this basis set. When invariances and symmetries are attributes of the physical system considered, one can express Hamiltonian eigenvectors thanks to Bloch's theorem. Translational invariance of the system, in particular, allows one to express eigenvectors of the Hamiltonian in a straightforward way as Bloch wave vectors. Yet, this requirement of having symmetries or invariances restrains drastically the physical systems under study. A single impurity in graphene for instance will disrupt the translational invariance hence making Bloch wave vectors unappropriate as a basis set. The Dyson equation circumvents this issue as one can retrieve the GFs of the perturbed system from the pristine case without explicitly calculating the eigenstates. Let us consider  $\hat{g}$  as being the GF associated with the unperturbed Hamiltonian  $\hat{\mathcal{H}}_0$  and  $\hat{G}$  being the GF associated to the perturbed system, namely with  $\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{V}$  dressed with  $\hat{V}$ , encoding all the perturbation's potential. Then, it is possible to derive from  $\hat{G}$  the following

expression:

$$\begin{aligned}
\hat{G} &= \left[ (E + i\eta) \hat{I} - (\hat{\mathcal{H}}_0 + \hat{V}) \right]^{-1} \\
&= \left[ \hat{g}^{-1} - \hat{V} \right]^{-1} \\
&= \left[ \hat{I} - \hat{g}\hat{V} \right]^{-1} \hat{g}
\end{aligned} \tag{2.22}$$

Then multiplying the equation from left by  $\left[ \hat{I} - \hat{g}\hat{V} \right]$ , we obtain :

$$\left[ \hat{I} - \hat{g}\hat{V} \right] \hat{G} = \left[ \hat{I} - \hat{g}\hat{V} \right] \left[ \hat{I} - \hat{g}\hat{V} \right]^{-1} \hat{g} \tag{2.23}$$

which results in the usual form of the Dyson equation after rearrangement to:

$$\hat{G} = \hat{g} + \hat{g}\hat{V}\hat{G} \tag{2.24}$$

This expression is a powerful tool to compute GFs of disordered systems by the prior knowledge of the perturbations applied. Although the Dyson equation coupled with the tight-binding formalism captures a very large array of complexity such as structural defects, magnetic impurities, applied fields, etc., we will focus our attention on onsite potential modification.

### 2.2.2 Perturbation and disorder

The great majority of the perturbations found in the tight-binding Hamiltonians that we will use in this study will be changes to the onsite energy terms. It should be noted that hopping term modification between two atomic sites is also a way to create perturbation. However, one can address an effective onsite potential modification between two sites that will act as a hopping term change. These types of perturbations may be used to represent substitutional atoms that are injected into the host system, as we will directly explain below. The relevant energy orbital on the impurity atom will be different from that of the orbitals on the graphene host, as shown by the shift in the onsite energy term. We will now demonstrate how the Green's functions for the case of a single substitutional atom attached to host can be calculated. Then we will see how multiple impurities involve a more complex behaviour. For illustration purpose, the host system is represented by a simple linear atomic chain to have scalar quantities when using the Dyson equation. When more complicated models are considered, the Dyson equation will involve matrices and matrix multiplication.

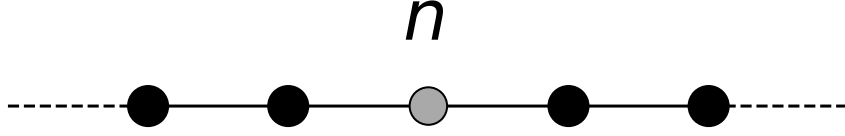


Figure 2.6: A linear chain of a certain host material represented by dark atoms and a substitutional atom in grey. The Dyson equation allows the calculation of the disordered GF just by modifying the pristine GF with the potential corresponding to the substitutional atom.

### Substitutional atom

The simplest kind of impurity is when an atom of another element is substituted for a carbon atom in the lattice. We must alter the onsite energy term(s) characterizing the pertinent orbital(s) at this lattice site, as well as the hopping parameters describing the overlap between these orbitals and those on the nearby carbon atoms, in order to simulate such an impurity. To illustrate in a simple way the effect of the substitutional atom, let us consider a linear chain of atoms as depicted in Fig. 2.6. We can just consider one orbital on the impurity atom and neglect changes in the hopping term. In this case, the onsite potential is written

$$\hat{V} = |n\rangle \delta_n \langle n| \quad (2.25)$$

where  $n$  is the substitutional atom's index and  $\delta_n = \epsilon_n - \epsilon_0$  is the difference between the onsite energies of the impurity atom and the lattice atom it replaced. The Dyson equation is used to transform the unperturbed GF,  $g_{ij}$  into a general matrix element,  $G_{ij}$ , the GF for the perturbed system as

$$G_{ij} = g_{ij} + g_{in} \delta_n G_{nj} \quad (2.26)$$

with  $G_{nj}$  being equal to

$$\begin{aligned} G_{nj} &= g_{nj} + g_{nn} \delta_n G_{nj} \\ &= \frac{g_{nj}}{1 - \delta_n g_{nn}} \end{aligned} \quad (2.27)$$

By substituting the expression of  $G_{nj}$  back into the Eq. 2.26, we obtain

$$\begin{aligned} G_{ij} &= g_{ij} + \frac{g_{in} \delta_n g_{nj}}{1 - \delta_n g_{nn}} \\ &= g_{ij} + g_{in} T_{nn} g_{nj} \end{aligned} \quad (2.28)$$

where

$$T_{nn} = \frac{\delta_n}{1 - \delta_n g_{nn}} \quad (2.29)$$

is the  $\hat{T}$  scattering matrix element describing the scattering caused by the perturbation. In mainstream physics books, the GF is also called a propagator.  $G_{ij}$  indeed describes the electron propagation from site  $i$  to site  $j$  when describing a material. From Eq. 2.28, in its final form,  $G_{ij}$  consists in two terms which can be thought as the contribution of two different paths.  $g_{ij}$  describes the propagation of the electron from site  $i$  to site  $j$  as if the perturbation has no effect on its displacement. The other contribution,  $g_{in}T_{nn}g_{nj}$ , corresponds to indirect propagation between  $i$  and  $j$  via the perturbation, where the scattering introduces a factor of  $T_{nn}$ .

The local density of states (LDOS), being a central quantity involved for finding physical quantities, is the diagonal element of the GF matrix at a particular site. At the impurity site which we find by setting  $i = j = n$  in Eq. 2.28, the expression for the GF is

$$G_{nn} = \frac{g_{nn}}{1 - g_{nn}\delta_n}$$

Now suppose we are interested in a site away from the impurity. The expression for the GF is found in Eq. 2.28, by setting  $i = j \neq n$  and thus, we get

$$G_{ii} = g_{ii} + \frac{g_{in}T_{nn}g_{ni}}{1 - g_{nn}\delta_n}$$

The importance of the off-diagonal matrix elements that are  $g_{in}$  and  $g_{ni}$  is crucial to grasp a physical meaning out of the GF. These variables serve as correlation functions between the various lattice sites and are used to determine how a system will react to a perturbation at one site with respect to another. These terms are frequently encountered as they provide the foundation for many results in the following chapters.

### Multiple impurities

We will now broaden our discussion to include systems with several impurities and examine how this affects the earlier expressions. We take into account substitutional atoms of the type mentioned in the section above.

For an ensemble  $N$  of such impurities, we have

$$\hat{V} = \sum_{a \in N} |a\rangle \delta_a \langle a| \quad (2.30)$$

Using the Dyson equation, we get

$$G_{ij} = g_{ij} + \sum_{a \in N} g_{ia}\delta_a G_{aj} \quad (2.31)$$

with  $G_{aj}$  expressed as

$$G_{aj} = g_{aj} + \sum_{b \neq a \in N} g_{ab} \delta_b G_{bj} \quad (2.32)$$

By substituting the expression of  $G_{aj}$  into Eq. 2.30, we obtain

$$G_{ij} = g_{ij} + \sum_{a \in N} g_{ia} \delta_a g_{aj} + \sum_{a \in N} \sum_{b \neq a \in N} g_{ia} \delta_a g_{ab} \delta_b G_{bj} \quad (2.33)$$

This development has to be done for  $G_{bj}$  and so on for the rest of the  $N - 2$  scatterers until we have an expression in terms of only the unperturbed propagators to start the backsubstitution. This development proves rapidly cumbersome as the number of scatterers increases. A different approach based on the  $\hat{T}$  scattering matrix elements instead seems more adapted. Using the following  $\hat{T}$ -matrix expression

$$\hat{T} = \hat{V} \left[ \hat{I} - \hat{g} \hat{V} \right]^{-1} \quad (2.34)$$

One can always expand  $\left[ \hat{I} - \hat{g} \hat{V} \right]^{-1}$  as a power series of the term  $\hat{g} \hat{V}$  and so  $\hat{T}$  can also be expressed as

$$\hat{T} = \hat{V} + \hat{V} \hat{g} \hat{V} + \hat{V} \hat{g} \hat{V} \hat{g} \hat{V} + \dots \quad (2.35)$$

From the Eq. 2.24, the expression of the Dyson can be written with the  $\hat{T}$  matrix as

$$\hat{G} = \hat{g} + \hat{g} \hat{T} \hat{g} \quad (2.36)$$

Rewriting in terms of single-impurity  $\hat{T}$ -matrices  $\hat{t}_a$ , where

$$\hat{t}_a = |a\rangle t_{aa} \langle a| \quad (2.37)$$

where  $t_{aa} = \delta_a [1 - \delta_a g_{aa}]^{-1}$ , we can rewrite the  $\hat{T}$ -matrix as

$$\hat{T} = \sum_{a \in N} \hat{t}_a + \sum_{a \in N} \sum_{b \neq a} \hat{t}_a \hat{g} \hat{t}_b + \sum_{a \in N} \sum_{b \neq a} \sum_{c \neq b} \hat{t}_a \hat{g} \hat{t}_b \hat{g} \hat{t}_c + \dots \quad (2.38)$$

By combining the expression of the  $\hat{T}$ -matrix above with the Eq. 2.33, the expression for  $G_{ij}$  in the presence of multiple scatterers becomes

$$G_{ij} = g_{ij} + \sum_{a \in N} g_{ia} t_{aa} g_{aj} + \sum_{a \in N} \sum_{b \neq a} g_{ia} t_{aa} g_{ab} t_{bb} g_{bj} + \sum_{a \in N} \sum_{b \neq a} \sum_{c \neq b} g_{ia} t_{aa} g_{ab} t_{bb} g_{bb} t_{cc} g_{cj} + \dots \quad (2.39)$$

Writing the formulas for the  $\hat{T}$  and GF matrix components in terms of the single-scatterer  $\hat{T}$ -matrix elements,  $t_{aa}$ , makes it obvious that the impact of multiple scatterers includes higher order interference terms as well as the effects of single scatterers. These higher order terms describe propagation paths between site  $i$  and  $j$  that go through numerous scattering sites. There are now an endless

number of alternative pathways between the two sites when there are numerous scatterers present in the system, making it conceivable for a pathway to pass by a site more than once. As expected, quantum effects are far from linear and the expression of the GF in the presence of a multitude of impurities is the most obvious example. In this work, several alternative approaches (Chapters 3, 4 and 5) respecting the non-linearity of GFs will replace conventional quantum transport using GFs as key elements.

### 2.2.3 Integrating over Green's functions

The GF is the key element from which most of the properties of a physical system are extracted. The physical quantities of interest are functions containing GFs and a very large number of physical observables depend on their integrals. A simple example is the calculation of the occupation of an orbital at site  $i$ . It is given by an integral over the LDOS,  $\rho$ , at this site as follows

$$n_i = \int_{-\infty}^{E_F} dE \rho_i(E) = -\frac{1}{\pi} \lim_{\eta \rightarrow 0} \Im \left[ \int_{-\infty}^{E_F} dE G_{ii}(E + i\eta) \right] \quad (2.40)$$

There are a number of challenges involved in calculating this integral as shown along the real energy axis. First of all, at certain energies, low-dimensional systems can show Van Hove singularities. Although they are prevented from sitting on the axis of integration by the inclusion of a non-zero imaginary energy component,  $\eta$ , in the formulation of the GF, they can still cause issues for a numerical integration in the form of sharp, narrow peaks in the integrand. Another issue is that bound states typically have abrupt peaks in the DOS of perturbed systems that are beyond the bulk system's energy band. This may make choosing an acceptable lower bound for the integral in Eq. 2.40 challenging. By using complex analysis properties, it is possible to perform integration despite the presence of singularities over the integrand axis. These issues can be resolved by realizing that the retarded GF is analytical in the upper half of the energy plane, i.e., that the function  $G(z)$ , where  $z$  is a point in the complex energy plane with the coordinates  $z = E + iy$ , has no singularities for  $y > 0$ . Additionally, we observe that the function  $G(z)$  is smoother and easier to integrate along the imaginary axis than the real energy axis. Let us focus on the contour of the Fig. 2.7. The integral of  $G(z)$  around this contour is 0 according to Cauchy's theorem, as the function  $G$  is analytical over  $C$ , i.e no singularities are enclosed by  $C$ . The contour  $C$  can be split into three component parts:

- $r$  - A line parallel to the real axis, from  $E_F - R$  to  $E_F$ , with constant imaginary part  $\eta$ . When  $R \rightarrow \infty$ , this path integral is giving the integral of interest in the Eq. 2.40.
- $i$  - A line parallel to the imaginary axis, from  $i\eta$  to  $iR$ , with constant real

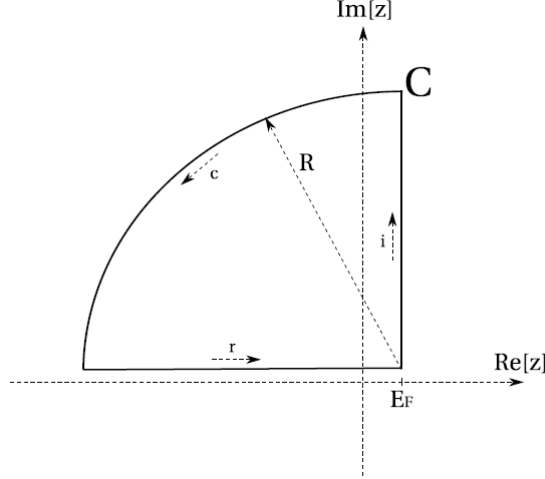


Figure 2.7: Integration contour in the energy plane.

part  $E_F$  ,

- $c$  - An arc of radius  $R$  connecting the top of  $i$  with the end of  $r$ .

Because  $G(z)$  is analytic over  $C$ , we can write according to Cauchy's theorem [150] :

$$\begin{aligned} I_C &= I_c + I_r + I_i = 0 \\ \rightarrow I_r &= -I_c - I_i \end{aligned} \quad (2.41)$$

By considering our GF as  $G(z) \sim \frac{1}{z}$  and  $R \rightarrow \infty$ , the integrand over the arc  $c$  vanishes except that the integral is not necessarily zero because of the branching points (cf. junctions between the arc  $c$  and the linear paths  $i$  and  $r$ ). The integral over  $c$  becomes

$$\begin{aligned} \lim_{R \rightarrow \infty} I_c &= \lim_{R \rightarrow \infty} \int_c \frac{1}{z} dz \\ &= \lim_{R \rightarrow \infty} \int_{\frac{\pi}{2}}^{\pi} \frac{1}{Re^{i\theta}} (iRe^{i\theta} d\theta) \\ &= \int_{\frac{\pi}{2}}^{\pi} i d\theta \\ &= \frac{i\pi}{2} \end{aligned} \quad (2.42)$$

It has to be noted that in virtue of Jordan's theorem [150], in the limit  $R \rightarrow \infty$ , the above calculated integral is 0 if  $G(z) \sim R^{-\alpha}$  for  $\alpha \geq 2$ . This scenario happens when the physical quantity of interest depends on the product of GFs.

Consequently, the local occupation number at site  $i$  can be written as

$$\begin{aligned}
n_i &= -\frac{1}{\pi} \lim_{\eta \rightarrow 0} \Im [I_r] = -\frac{1}{\pi} \lim_{\eta \rightarrow 0} \Im [-I_c - I_i] \\
&= -\frac{1}{\pi} \Im \left[ -i \lim_{\eta \rightarrow 0} \int_{\eta}^{\infty} dy G_{ii}(E_F + iy) - \frac{i\pi}{2} \right] \\
&= \frac{1}{2} + \frac{1}{\pi} \lim_{\eta \rightarrow 0} \int_{\eta}^{\infty} dy \Re [G_{ii}(E_F + iy)] \\
n_i &= \frac{1}{2} + \lim_{\eta \rightarrow 0} \frac{1+\eta}{2} \int_0^1 dt \frac{1}{t^2} \Re \left[ G_{ii}(E_F + i \frac{1+\eta-t}{2}) \right]
\end{aligned} \tag{2.43}$$

where we substitute  $y$  by  $\frac{1+\eta-t}{2}$  in the last line to make the integration boundaries simpler. Hence by virtue of complex analysis, we manage to transform a real axis integral where singularities are more frequent into an imaginary axis one where the integrand is much smoother and easier to integrate.

#### 2.2.4 Spintronics - Electron-electron interactions:

As formerly introduced, the tight-binding Hamiltonian is appropriate to describe graphene. Although the tight-binding formalism is an efficient tool in describing many different systems, it does not consider electron-electron interactions, required in order to describe magnetic materials. To account for these interactions it is necessary to include a many body term to the Hamiltonian called a Hubbard term. This section will focus on the description of the Hubbard Model approach laying the many body term that accounts for short-ranged electronic interactions. Details about mean-field approximation alongside the self-consistent procedure will be presented to see how to tackle the resulting many-body Hamiltonian from the Hubbard model.

#### Hubbard Model

As electrons are considered indistinguishable particles and because the Hubbard term is a many-body term, the second quantisation formalism is introduced as it describes quantum many-body physics in a more appropriate manner. Instead of describing only a physical system by indexation of atomic sites, in the tight-binding fashion like

$$\mathcal{H}_{\text{TB}} = \sum_{i,j} |i\rangle \gamma_{ij} \langle j| \quad \text{with} \quad \gamma_{ij} = \begin{cases} \varepsilon_0 & \text{if } i = j \\ t & \text{if } i = j \pm 1 \end{cases}, \tag{2.44}$$

one can rewrite this Hamiltonian by including the spin degree of freedom and the usage of the creation and annihilation operator

$$\mathcal{H}_{\text{TB}} = \sum_{i,j,\sigma} \gamma_{ij} \hat{c}_{j\sigma}^\dagger \hat{c}_{i\sigma}. \quad (2.45)$$

Here  $c_{j\sigma}^\dagger$  creates an electronic state with spin  $\sigma$  on site  $j$  whereas  $c_{i\sigma}$  annihilates an electron with spin  $\sigma$  on site  $i$ . As magnetic moment arises when a local imbalance between spin-up and spin-down electrons is created, the spin degeneracy of this Hamiltonian will not lead to any magnetic signature. An exchange term resulting from the Coulomb repulsion of the electrons causes magnetic moments in materials. This term causes the production of a moment by ending the degeneracy between up and down spin electrons. The Coulomb interaction term for a system made of  $N$  electrons is written as

$$V_{\text{C}} = \sum_{i,j=1}^N \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \quad (2.46)$$

In the second quantisation formalism and with the appropriate creation and annihilation operators, this Coulomb repulsion term, written in an operator form is given by

$$V_{ab} = \frac{1}{2} \sum_{i,j,k,l} \langle i,j | \frac{e^2}{\mathbf{r}_{ab}} | k,l \rangle \sum_{\sigma,\sigma'} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma'}^\dagger \hat{c}_{k\sigma'} \hat{c}_{l\sigma} \quad (2.47)$$

where the  $\frac{1}{2}$  term prevents the double counting of indices and  $\langle i,j | \frac{e^2}{\mathbf{r}_{ab}} | k,l \rangle$  is the expectation value of the Coulomb term, which is addressed as

$$\langle i,j | \frac{e^2}{\mathbf{r}_{ab}} | k,l \rangle = \int d\vec{r}_a \int d\vec{r}_b \psi_i^*(\vec{r}_a) \psi_j^*(\vec{r}_b) \frac{e^2}{r_{ab}} \psi_k(\vec{r}_b) \psi_l(\vec{r}_a) \quad (2.48)$$

where  $\psi_i$  is the localised wavefunction centred around site  $i$ . The suitability of a Hubbard model for characterizing the physical properties of graphene remains a topic of ongoing discussion and is contingent upon the specific observable in question [151]. Our findings indicate that a Hubbard model can effectively assess the presence of edge magnetism and antiferromagnetic insulator phases. Research highlights that non-local Coulomb interactions tend to noticeably diminish local correlation effects in sp-electron materials across a broad doping range. Therefore, the effect of this can be incorporated in a  $U$  only model by renormalising the value of  $U$  [151]. According to the Hubbard model, screening limits interaction to a single site, hence only the term corresponding to  $i = j = k = l$  has to be taken into account. Thus, considering the restriction on electrons sharing the same orbital from the screening and by virtue of the Pauli exclusion principle, the Coulomb term is restricted to the case where  $\sigma \neq \sigma'$ . Consequently, the resulting

Hamiltonian reads

$$\mathcal{H}_{\text{Hub}} = \frac{U}{2} \sum_{i,\sigma} \hat{n}_{i\sigma} \hat{n}_{i\bar{\sigma}} \quad (2.49)$$

where  $U$  is the diagonal Coulomb integral and the number operator  $\hat{n}_{i\sigma} = \hat{c}_{i\sigma}^\dagger \hat{c}_{i\sigma}$  gives the occupation of the state at site  $i$  with spin  $\sigma$ . Since the Hubbard Hamiltonian is still a many-body Hamiltonian, we are unable to use the prior methods taking advantage of LDOS to find magnetic properties for graphene based-materials. A technique to handle this interaction as a single particle effect will be investigated in the following section.

### Mean-field Hartree-Fock approximation

By combining the many-body Hubbard term and the tight-binding component written in accordance to the second quantisation formalism, we obtain the following general Hamiltonian

$$\mathcal{H} = \sum_{i,j,\sigma} \gamma_{ij} \hat{c}_{j\sigma}^\dagger \hat{c}_{i\sigma} + \frac{U}{2} \sum_{i,\sigma} \hat{n}_{i\sigma} \hat{n}_{i\bar{\sigma}} \quad (2.50)$$

To study local signature of magnetism within a device, a single particle Hamiltonian is necessary in order to compute site-dependent properties. Consequently, it is necessary to perform an approximation on the Hubbard many-body term that will allow to manipulate the Hamiltonian as a single particle one. In this work, the Hubbard term will be considered through the Hartree-Fock field approximation which consists in trivially substituting the number operator  $\hat{n}_{i\sigma}$  by

$$\hat{n}_{i\sigma} = \langle \hat{n}_{i\sigma} \rangle + (\hat{n}_{i\sigma} - \langle \hat{n}_{i\sigma} \rangle) \quad (2.51)$$

where  $\langle \hat{n}_{i\sigma} \rangle$  is the expectation value for the occupation number. By neglecting terms of order  $(\hat{n} - \langle \hat{n} \rangle)^2$  and higher, we can now write

$$\hat{n}_{i\sigma} \hat{n}_{i\bar{\sigma}} \approx \hat{n}_{i\sigma} \langle \hat{n}_{i\bar{\sigma}} \rangle + \hat{n}_{i\bar{\sigma}} \langle \hat{n}_{i\sigma} \rangle - \langle \hat{n}_{i\sigma} \rangle \langle \hat{n}_{i\bar{\sigma}} \rangle \quad (2.52)$$

As the many-body term is now a sum of single particle terms, we notice that the last term in the Eq. 2.52 applies a spin-independent shift in the band centre of magnetic atoms. To better comprehend how the Hubbard term in the Eq. 2.50 after the Hartree-Fock approximation has spin-dependent and spin-independent terms, let us define the average occupation number at site  $i$

$$n_i = \langle \hat{n}_{i\downarrow} \rangle + \langle \hat{n}_{i\uparrow} \rangle \quad (2.53)$$

and the dimensionless magnetic moment at site  $i$  as

$$m_i = \langle \hat{n}_{i\downarrow} \rangle - \langle \hat{n}_{i\uparrow} \rangle \quad (2.54)$$

With these new quantities introduced, the approximated Hubbard term is now written

$$\frac{U}{2} \sum_{i,\sigma} \hat{n}_{i\sigma} \hat{n}_{i\bar{\sigma}} = \sum_i \left( \frac{U}{2} (n_i \mp m_i) - U \langle \hat{n}_{i\sigma} \rangle \langle \hat{n}_{i\bar{\sigma}} \rangle \right) \hat{n}_{i\sigma} \quad (2.55)$$

where  $\mp$  is  $-$  when  $\sigma = \uparrow$  and  $+$  when  $\sigma = \downarrow$ . Now that is discarded the Hubbard many-body term into single particle terms, the contributions of spin-dependent and independent terms is made visible by the usage of the average occupation number and magnetic moments. The spin-independent contribution,  $\delta_i$ , gives the bandcentre shift for the magnetic site  $i$  such that

$$\delta_i = U \left( \frac{n_i}{2} - \langle \hat{n}_{i\sigma} \rangle \langle \hat{n}_{i\bar{\sigma}} \rangle \right) \quad (2.56)$$

whereas the spin-dependent contribution,  $\Delta$ , is proportional to the magnetic moment

$$\Delta = U m_i \quad (2.57)$$

The splitting,  $\Delta$ , between the bands leads to an imbalance in occupation for spin-polarised electrons at a site  $i$ . The local onsite potential applied at magnetic sites to account for the electron-electron interactions can be written in terms of the bandcentre shift and splitting as

$$V_{ii}^\sigma = \delta \mp \frac{\Delta}{2} \quad (2.58)$$

once more, the spin direction determining the sign option.

The Coulomb repulsion parameter  $U$  in graphene has a significant impact on its electronic and magnetic properties [152]. When  $U$  is relatively small compared to other energy scales, such as the hopping parameter  $t$  that describes electron motion between lattice sites, graphene remains in a metallic state. In this regime, the electronic behavior is primarily governed by Dirac fermions, and the system does not exhibit long-range magnetic order.

However, as the Coulomb repulsion  $U$  increases, graphene can undergo a transition to a Mott insulating state. In this state, the strong electron-electron interactions lead to the localization of electrons, resulting in a gap in the electronic spectrum. The system becomes non-metallic and can exhibit antiferromagnetic order, where the spins of neighboring electrons align in an alternating fashion. The competition between the kinetic energy  $t$  and the Coulomb repulsion  $U$  determines the nature of the ground state, and varying  $U$  can drive the system through different phases. Studies have shown that the bands of graphene are highly sensitive to the Coulomb repulsion, leading to a phase transition from a semi-metal to a Mott insulator even at low repulsion values compared to the graphene bandwidth.

## Self-consistent procedure

By using the above-mentioned Hartree-Fock approximation and the Dyson equation to apply a spin dependent perturbation at the magnetic sites, we may determine the GF of a system containing magnetic moments. We see that the GF representing the system's electrons is no longer spin degenerate since the potential to be applied is spin-dependent. As the applied perturbation is now writable in terms of  $\delta$  and  $\Delta$ , the bandcentre shift and splitting of the magnetic orbitals, a simple model embedding those parameters offers a great versatility to determine the behaviour of magnetic materials. The magnetic moment must often be parameterized more precisely, particularly if we wish to study how the moment itself evolves under various circumstances. Electron-electron interactions often need to be taken into consideration in two situations while studying graphene. The first case is when the graphene-based system is doped with atoms which already possess a magnetic moment themselves, for example *d*-band transition metals. The other case that will be frequently encountered in this work is when magnetic moments arise in graphene in the presence of edges or vacancies. Magnetic moments are formed in carbon atoms of graphene itself and are caused by the localized states that are created as a result of the system's specific geometry. For undoped graphene systems the  $p_z$  orbital is half-full, corresponding to  $n_i = 1$ , where each orbital can hold at most two electrons - one of each spin orientation. But for the most part, instead of arbitrarily selecting values for  $\Delta$ , one can calculate them using a self-consistent procedure that assumes knowledge of the occupation,  $n_i$ , for the relevant orbitals. The self-consistent procedure to find the onsite potential  $V_{ii}^\sigma$  for a particular site  $i$  across a system is the following :

1. Initialisation step: Advised initial guesses are made for the magnetic moments,  $\vec{m}^0$ , used to compute the onsite potentials.
2. The occupation of the up and down spin bands,  $n_{i\uparrow}$  and  $n_{i\downarrow}$ , are calculated by integrating the LDOS at each site. The LDOS is obtained by GF taken into account application of the onsite potential.
3. New estimates for the magnetic moments,  $\vec{m}^1$ , are found at each site through the relation  $m_i^1 = n_{i\uparrow}(\vec{\delta}^1) - n_{i\downarrow}(\vec{\delta}^1)$ .
4. Steps 2 and 3 are repeated with the new estimates for magnetic moments until convergence is reached.

## 2.3 Quantum transport

### 2.3.1 Landauer-Büttiker formalism

When the size of electronic devices are comparable or even less than the electron's mean-free path and phase coherence length, the electron quantum nature requires

to consider electronic transport differently from the classical perspective. At macroscopic scale, the conductance is continuously proportional to the diameter of the device whereas in mesoscale devices, a quantisation of the conductance channels appears. Quantum confinement effects due to the nanoscale size of the structures dictates the electron's energy spectrum to be discrete hence forcing the transport characteristics to be discrete as well. To describe these new effects, such as the violation of Ohm's law, a new tool is necessary: the Landauer-Büttiker formalism of quantum transport [153]. In linear response theory and at zero temperature, the multiterminal Landauer-Büttiker formula for the conductance  $G$  in a two terminal system reads

$$G = G_0 \sum_{n=1}^N T_n(E_F),$$

where  $G_0 = \frac{2e^2}{h}$  is the quantum of conductance and where the transmission coefficients  $T_n(E_F)$  are expressed as a sum over all possible  $N$  transmitting modes at a given energy  $E_F$ . The transmission coefficient expresses the possible paths an electron has to be transmitted from one terminal to another given the quantum scattering processes that could occur in the central region. In the case of transmission from a left to right electrode, the Caroli formula for transmission [154] is given by

$$T_{RL}(E) = \text{Tr} [\Gamma^L G_{LR}^r \Gamma^R G_{RL}^a], \quad (2.59)$$

where  $\Gamma^{L/R} = i(\Sigma_{L/R} - \Sigma_{L/R}^\dagger)$  are the level width matrices describing the coupling of the device region to the left and right leads and  $\Sigma_{L/R}$  are the related self-energy matrices.  $G_{LR}^r = (G_{RL}^a)^\dagger$  are the retarded (advanced) GF matrices of the entire connected system in direct contact with the leads. Calculating the transmission requires two main tasks: the electrode calculations (self-energies), in which infinite but periodic problems must be dealt with, and the inversion problem of the central region to find the necessary GFs.

### 2.3.2 Recursive Green's function methods

Despite the efficiency provided by the Dyson equation, the computation of GFs relies on matrix inversion, which scales approximately as  $N^{2.373}$  [155] with  $N$  being the number of orbitals in the considered system. Consequently, one faces some computational bottleneck as the size of realistic mesoscopic structures is very large, e.g., experimental systems with hundreds of thousand of atoms. To reduce the scaling effect associated with matrix inversion, one must provide a way of reducing, in an efficient way, the system size. Recursive methods based on the Dyson equation circumvent such a computationally demanding process. It allows to construct the system in a piecewise fashion, to compute and save the

GFs of sites of interest and update all the relevant stored GFs on the fly. The deconstruction of the system in a sliced fashion and reconnection thanks to the Dyson equation makes the computation of GFs more tractable. For the most part, it seems relevant to proceed in a slicing scheme when the studied system is quasi-one-dimensional as are graphene nanoribbons. As each sliced cell of the system does not need to be the same, recursive approaches avail great versatility. More efficient methods such as the decimation procedure proposed by Rubio and Sancho [156] are extremely powerful when the added cells are identical typically when building the electrodes that connects a central region.

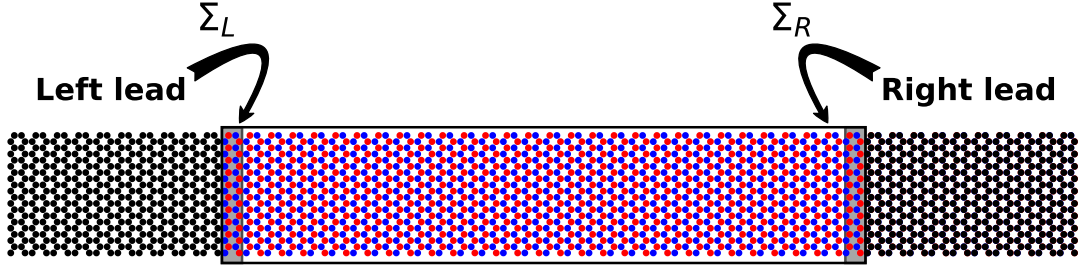


Figure 2.8: Schematic representation of the downfolding of semi-infinite leads into the device region: The black atoms corresponding to the leads can be added to the device region by simply adding the corresponding self-energies. Thus, representing an infinite system with theoretically infinite long matrices goes down to a finite-size matricial problem when the corresponding self-energies are computed upstream.

### Standard recursive approach

The procedure in recursive algorithm is the following : slicing a system under study into pieces and using the Dyson equation repeatedly to connect the system back altogether. The applied potential that acts as the perturbation in the Dyson equation in this approach corresponds to the added new slice. The way the slicing is realised in the first place is taking advantage of the geometry or the symmetries inherent to the studied system. For instance in GNRs, there is a benefit in slicing the ribbon in a transversal way where the sliced pieces will have the same number of atoms per slice. To create the central device region or the leads, it is necessary to have access to the Hamiltonian matrices of each slice  $H_{n_i \times n_i}$  with  $n_i$ , the number of atoms in the  $i$ -th slice and to the connection matrices between two different slices. For the  $i$ -th slice of the system:

- The Hamiltonian matrix  $H_{i,i}$  is the matrix representing all the interactions taking place between the atoms **within** the unit-cell. Thus, for very trivial systems, the diagonal elements represent the on-site energies of each atom and the off-diagonal elements represent the hopping terms between each atom in a slice. Each of these Hamiltonian matrices are associated with a

GF  $\hat{g}_{i,i}$  given by:

$$\hat{g}_{i,i}(E) = \lim_{\eta \rightarrow 0} \left[ (E - i\eta) \hat{I} - \hat{\mathcal{H}}_{i,i} \right]^{-1}$$

- The connecting matrix  $V_{i,i+1}$  is the matrix representing all the interactions taking place **between** the  $i$ -th and  $(i+1)$ -th slices of our system. As the number of atoms in each slice is not necessarily the same, these connecting matrices need not to be square matrices. To get the connection between the  $(i+1)$ -th and  $i$ -th slices, simply take the hermitian conjugate matrix:

$$V_{i+1,i} = (V_{i,i+1})^\dagger$$

When using the recursive algorithm, it is sometimes necessary to keep information about GFs only from the new slice that has been added to the system. This is typically the case when constructing electrodes that are semi-infinite. Furthermore, it is useful to keep the GFs of slices that have been added during the process. This is the case when studying the transport properties of a central region. Here are depicted the two different processes :

**Lead creating process** For illustration, here is presented the creation of the left lead where slices are added from left to right. The right lead creation process is redundantly equivalent where slices are added from right to left. The GFs of interest are only the ones that are added the last to the entire semi-infinite lead, i.e the rightmost slice. In the left lead building process, the little  $\hat{g}$ 's will refer to the unconnected GFs associated for each slice and the big  $\hat{G}$ 's will correspond to the connected GF of the whole lead up to a certain slice.

The general recurrence relation is to connect the  $i^{th}$  slice with GF  $\hat{g}_{i,i}$  to the left lead connected GF  $\hat{G}_{i-1,i-1}$  such that :

$$\hat{G}_{i,i} = \hat{g}_{i,i} + \hat{g}_{i,i} V_{i,i-1} \hat{G}_{i-1,i}$$

with

$$\hat{G}_{i-1,i} = \hat{G}_{i-1,i-1} V_{i-1,i} \hat{g}_{i,i}$$

that can be rewritten such as :

$$\hat{G}_{i,i} = \left[ \hat{I} - \hat{g}_{i,i} V_{i,i-1} \hat{G}_{i-1,i-1} V_{i-1,i} \right]^{-1} \hat{g}_{i,i}$$

At the end of this calculation, it is necessary only to store the last connected GF  $\hat{G}_{i,i}$  and continue this recursion relation till the lead “converges”.

From the previous recursion relation, one has to define a proper convergence criterion. As a reminder, the leads attached to the device region are considered

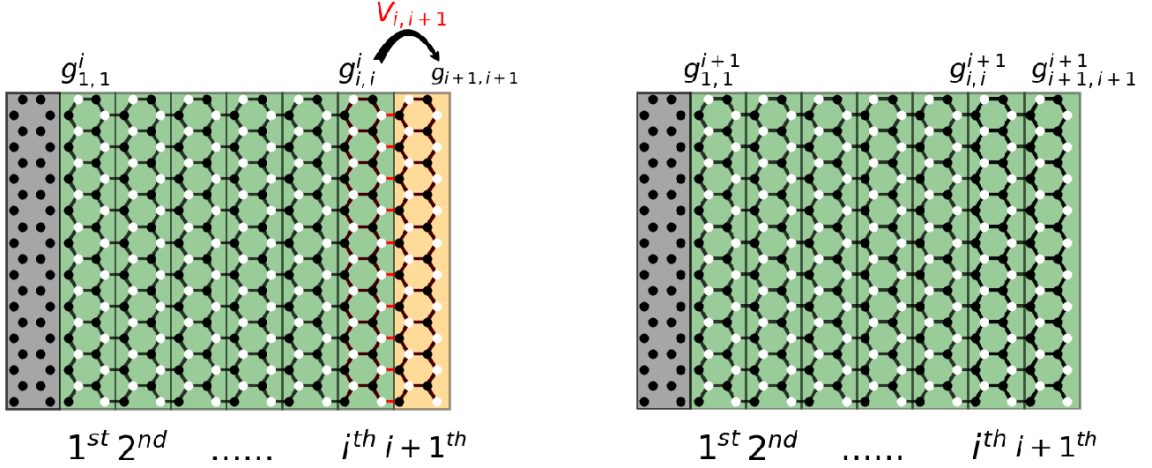


Figure 2.9: Schematic representation of the recursive connection process.

as being “semi-infinite” in a direction. From a computational perspective, the semi-infinite criterion for a lead is occurring when a newly attached slice does not change the overall connected GF, *i.e.*  $\hat{G}_{N,N} \approx \hat{G}_{N+1,N+1}$ . Concretely, for each energy, the following identity  $\hat{G}_{N,N} = \hat{G}_{N+1,N+1}$  is never reachable because of its intrinsic mathematical nature so one sets as criterion the following relation when the  $a^{th}$  iteration gives:

$$\sum_{i,j} |\hat{G}_{i,j}^{a+1,a+1} - \hat{G}_{i,j}^{a,a}| < \epsilon$$

where  $\epsilon > 0$  is a precision threshold that can be set as small as required. When the convergence criterion is reached, one obtains a finite matrix representing a semi-infinite object,  $\hat{G}_{LL}^{N,N}$  (or  $\hat{G}_{RR}^{N,N}$ ), is the so-called surface GF for the left (or right) lead. In order to find the useful self-energy for a lead, we just have to multiply the surface GF  $\hat{G}^{N,N}$  by the connecting matrices such as :

$$\Sigma^R(E) = V_{LR} \hat{G}_{RR}^{N,N}(E) V_{RL} \quad \Sigma^L(E) = V_{RL} \hat{G}_{LL}^{N,N}(E) V_{LR} \quad (2.60)$$

To summarize, leads’ self-energy matrices, which are finite objects, represent semi-infinite leads. It is then possible to down-fold those matrices into the device connecting slices to account for an infinitely long system (cf. Fig. 2.8).

**Central device creation process** This technique is similar to the lead creation process except that it engages an additional bookkeeping process. Indeed, the connection between the central device region and the leads through the self-energies needs two components. If we consider the central device region constituted with  $M$  slices, we need to have :

1. the first slice  $\hat{G}_{11}^M$ .
2. the last slice  $\hat{G}_{MM}^M$ .

3. the crossed GFs  $\hat{G}_{1M}^M$  and  $\hat{G}_{M1}^M$  that are required for transport calculations.

A major difference in comparison with the lead creation method is the requirement to update at each recursion step the value of all the mentioned previous quantities. Obviously, adding a slice to a non-local function such as the GF has an impact and must be taken in account in this region. Then, the recursion step to update all the quantities is the following when it comes to add the  $k^{th}$  slice ( $k \in \{1, \dots, M\}$ ):

- $\hat{G}_{kk}^k = \left[ \hat{I} - \hat{g}_{kk} V_{k,k-1} \hat{G}_{k-1,k-1}^{k-1} V_{k-1,k} \right]^{-1} \hat{g}_{kk}$
- $\hat{G}_{k1}^k = \hat{G}_{kk}^k V_{k,k-1} \hat{G}_{k-1,1}^{k-1}$
- $\hat{G}_{11}^k = \hat{g}_{11} + \hat{g}_{11} V_{1,k-1} \hat{G}_{k-1,k-1}^{k-1} V_{k-1,1}$
- $\hat{G}_{1k}^k = \hat{G}_{1,k-1} V_{k-1,k} \hat{G}_{kk}^k$

The GFs listed above should be computed in the order provided in each iteration since many of them depend on the quantities calculated before them in the same iteration. Furthermore, even though we have calculated the GF here for a single system cell, it is simple to apply this method to any collection of system sites. The necessary GFs, i.e., the matrix elements of interest and the off-diagonal components connecting it to the current edge cell, are simply updated on each iteration after the cell containing the site of interest has been added to the system. Once we have created the device region and updated at each step these GFs, we can connect the three different regions altogether and obtain back our complete system. The connection process can be written in a block-matricial identity such as :

$$G^c = \left[ \begin{pmatrix} I & 0 \\ 0 & I \end{pmatrix} - \begin{pmatrix} G_{11} & G_{1M} \\ G_{M1} & G_{MM} \end{pmatrix} \begin{pmatrix} \Sigma^L & 0 \\ 0 & \Sigma^R \end{pmatrix} \right]^{-1} \begin{pmatrix} G_{11} & G_{1M} \\ G_{M1} & G_{MM} \end{pmatrix}$$

The purpose of using recursive methods is two-fold : In a multi-terminal system, motivated by the need to only store the latest added slices' GF, it allows to efficiently create the leads surface GFs. It should be noted that decimation methods such as the Rubio Sancho [157] one are even more computationally efficient for creating leads. On the other hand, the central device region's GF subject to all kind of disorder are efficiently computed thanks to recursive algorithms.

### TBtrans/Sisl

Even though we develop some in-house codes and routines to compute quantum transport properties of various materials in a multiterminal context, it happens that the use of a highly-optimised quantum transport code is convenient for large systems or large numbers of configurations. As the system size of the studied devices gets unwieldy and computationally prohibitive, one has no choice but to

use properly optimised code that are able to handle devices with hundreds of thousands atoms and many other parameters. Among many other capabilities, TBtrans [158], (**T**ight-**B**inding **trans**port), a free and open-source code, enables the calculation of electronic transport and bond-currents in multiterminal setups with a great versatility. A very welcomed effort by the developers of TBtrans yielded a Python package, Sisl<sup>1</sup>, offering users a great ease and versatility to feed in large-scale tight-binding models with arbitrary geometries to do electronic transport. The ease of use, flexibility and numerous ways to alter the Hamiltonian matrix elements after having created a particular system offer the possibility to conduct high-throughput studies particularly useful in the context of machine learning. For instance, it is very easy to create a pristine GNR which will later be randomly altered and subject to a particular kind of disorder and generate thousands of different configurations and calculate their transport features.

Firstly, when it comes to create the electrodes that will be attached to the central device region, the surface GF of electrodes are calculated by the use of Bloch theorem. By using electrodes' unit-cell that expand in a periodic direction, the  $k$ - and energy  $E$ - resolved Hamiltonian matrix is inverted to obtain the surface GF of the leads. Surface GFs (cf. Eq. 2.60) are then multiplied by the relevant connecting matrices to attach the leads to the central device region.

For the device region, the real advantage in using TBtrans stems from its Block-Tri-Diagonal matrix method (BTD). In a two-terminal setup, classically when calculating electronic transport in nanoribbons attached to left and right leads, the BTD method is essentially the same as the RGF method as discussed in the “device creation” paragraph 2.3.2. Indeed, only few atomic sites of interest in the device region have to be considered when doing electronic transport and these sites are the ones that directly connect the device region to the leads. TBtrans is optimised in the sense that it efficiently propagates the leads' self-energies through the specified atoms of interest. This will then serve to calculate the transmission from left to right with the Caroli formula (cf. Eq. 2.59).

The real strength of TBtrans appears when one deals with multiterminal electronic transport. When performing RGF, one of the way to optimise the computational resources relies on the minimisation of the BTD matrix bandwidth. Typically, it means to ensure to have the same number of atoms/orbitals per slices. The intuitive way of having equally sized slices in a GNR for instance is by slicing transversely the ribbon. These non-intuitive slicing schemes also called orbital pivoting methods are shown for different multiterminal setups in Fig. 2.10. When the number of leads attached to a central region exceeds two, the knitting/slicing algorithm readapts the slicing process in order to obtain blocks of atoms of optimised sizes. Indeed, the optimisation of the slicing scheme via

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<sup>1</sup>named after Nick Papior's wife.

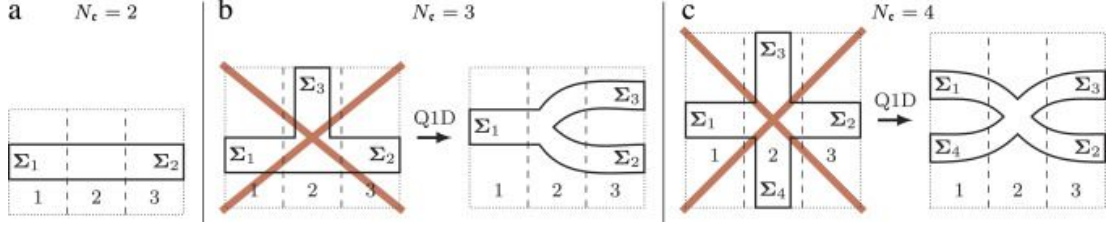


Figure 2.10: Slicing schemes for different multiterminal setups: (a)- For a quasi 1D system as shown here and when only two leads are attached, shown by the self-energy block  $\Sigma$ 's, the naive slicing geometry is already optimised as blocks have already equal sizes. (b) and (c) When the leads are exceeding two, the orbital pivoting scheme rearranges in a non-intuitive geometry the slicing scheme inside the device region driven by the requirement of having equally sized blocks. The naive partitionings shown by red crossed figures here have a central block which has much more atoms compared to other blocks. Adapted from [158].

non-intuitive geometries is taken care by the code in order to have equally-sized slices from which is operated the RGF procedure. This greatly reduces the computational resources needed to perform multiterminal electronic transport.

Aside from the general and non-local quantum transport scope, local properties of nanostructures are easily accessible with TBtrans. The energy-resolved spectral function of a lead  $\alpha$ ,  $\mathbf{A}^\alpha(E) \equiv \mathbf{G}(E)\mathbf{\Gamma}_\alpha(E)\mathbf{G}^\dagger(E)$  is a central quantity in TBtrans and allows a direct access to the local electronic properties such as the bond-current [159] between site  $i$  and  $j$

$$J_{ij}^\alpha(E) = -\frac{1}{\hbar}H_{ij} [\mathbf{G}(E)\mathbf{\Gamma}_\alpha(E)\mathbf{G}^\dagger(E)]_{ij}, \quad (2.61)$$

where  $H_{ij}$  is the relevant matrix element of the general tight-binding Hamiltonian in Eq. 2.1. This quantity is particularly useful to map the local currents of disordered structures and to see how disorder impacts locally the establishment of currents. Some in-house routines that I have coded give me access to this quantity to map the spin-current through a device at relevant energies.

## 2.4 Machine learning

### 2.4.1 Introduction

Given the many successes over the last decades in various fields such as image recognition [160], user recommendation [161], game AI or even translation [162], it is hardly surprising that artificial intelligence (AI) started to be employed in physics. The use of computer algorithms to extract knowledge from prior data is a branch of AI and a science called machine learning (ML). Given some data, the ultimate goal is to find a function that can reliably predict unseen data with prior training based on valuable information. The high versatility of ML has enabled,

in this study, to bypass computationally prohibitive routines by accurate and efficient approximations, providing depth to our understanding of the physics behind phenomena and consequently allowing new discoveries.

In this chapter, the foundations of machine learning starting with the notion of supervised learning are discussed. Then we describe specific algorithms with a focus on neural networks, since these were the most frequently used in this work. Finally, a discussion on how to assess the models' level of uncertainty is presented.

### 2.4.2 Supervised learning

In supervised ML, the goal is to find a function  $f$  that will map an input  $\mathbf{x}$  to an output  $\mathbf{y}$

$$f : x \rightarrow y. \quad (2.62)$$

The input,  $\mathbf{x}$ , is called the feature vector and contains information that is relevant to the prediction of  $\mathbf{y}$ , called the target vector. In fact, we will see later how the structure of  $\mathbf{x}$  is of capital importance in the predictive power of the function  $f$ . Given what the target vector is, supervised learning is divided into two categories: regression or classification.

In classification, the target vector  $\mathbf{y}$  represents a class. A binary classification consists in having two classes for the target vector, for instance email spam detection with classes "Spam/No-spam" with the feature vector being words contained in the emails. One-hot encoding, which is commonly used when there are more than two classes, denotes the  $i^{th}$  class by placing a 1 at position  $i$  and placing zeros everywhere else in the vector  $\mathbf{y}$ . We may use a group of photographs with either a dog, cat, or bird in each one as an example of classification. Then, using the one-hot encoding format, we could encode the classes as Bird=(1,0,0), Dog=(0,1,0), and cat=(0,0,1), where  $\mathbf{x}$  would be the grid of pixels that constitutes the photographs.

In regression,  $\mathbf{y}$  is a real-valued scalar or vector. An example of regression would be the prediction of stock prices. Here,  $x$  would encode the attributes of the stock prices given the attributes of the stock like the current price, the highest price at which a stock traded during a period, the lowest price of the period and so forth...

### General concepts and introduction

The power of an algorithm after being trained on a dataset is assessed via how accurately it predicts the outcome of some unseen data. However, the low predictive error is not exclusively attributed to good performance. In fact, a low predictive error, naively considered a good predictive performance, could be a

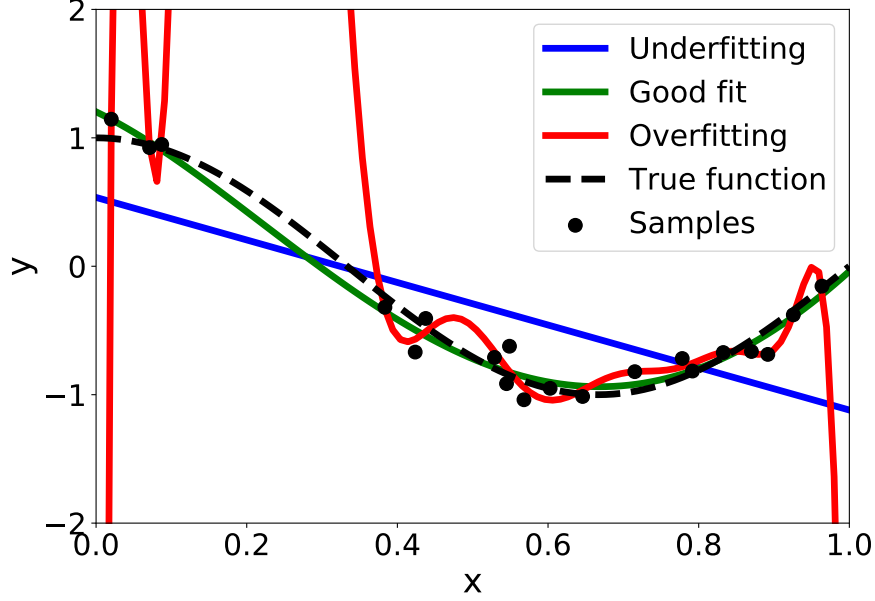


Figure 2.11: Example of overfitting and underfitting : The training data points, shown with black dots, originate from the black dashed curve representing the true function to predict. A Gaussian noise has been applied for the data points on their  $y$ -coordinates for realism. The blue line is underfitting and is not sufficiently complex to represent the true function. While the red line is overfitting and differs widely from the true function, we see the green line's model that approximates well the true function.

sign of overfitting. Overfitting occurs when the model learns the correlations between the data points when trained without actually reaching the true function  $f$ . Underfitting, related to low predictive performance and being the opposite of overfitting, arises when the model does not capture the complexity of data used to train the model. These concepts are explicitly shown when trying to approximate the distribution of data points in Fig. 2.11.

To better grasp the concepts of overfitting and underfitting, let us suppose we are in presence of a scalar ML model  $f(\mathbf{x}, \theta)$ . The ML model, defined by  $\theta$ , parameters learned from some given random set of data, has a resulting squared error when compared to the true value  $y$  that reads

$$\begin{aligned} E_{\theta} [(y - f(\mathbf{x}, \theta))^2] &= (y - E_{\theta} [f(\mathbf{x}, \theta)])^2 + E_{\theta} [(E_{\theta} [f(\mathbf{x}, \theta)] - f(\mathbf{x}, \theta))^2] \\ &= \text{bias} [f(\mathbf{x}, \theta)]^2 + \text{var} [f(\mathbf{x}, \theta)] \end{aligned} \quad (2.63)$$

As one can expect, the goal in building ML models is to minimise the expected error thus keeping the two positive terms present here at their minimum. On the right-hand side of this equation, two different terms are obtained: The squared bias term represents the square of the error of the prediction on average whereas the variance shows the disagreement between the models.

To prevent overfitting and to get a non-biased evaluation of the performance of the model, the dataset is randomly subdivided into three mutually exclusive subsets: a training set, a validation set and a test set. The training set is used to find the values of the model parameters  $\theta$  by minimizing the error by some performance or loss function that dictates how the model performs. The validation set is employed to find the values of hyperparameters, usually denoted  $\lambda$ . The best collection of hyperparameters and the best model—we may have several distinct model choices—are then selected using the validation set by determining which choice has the lowest performance measure compared to the validation set. Ultimately, the test set is used to estimate the generalization error of the model. Keeping the test set exclusive to estimate the generalization error prevents embedding additional bias, as the training and validation sets were used to fit parameters. There is no consensual or theoretical support on how to precisely divide the dataset into training, validation, and set tests. Better model parameters will arise from a larger training set, better hyperparameter estimates will come from a larger validation set, and the size of the test set will determine how accurate the generalization error is. A common split used is 70% – 20% – 10% without being theoretically supported as already mentioned. Considerations such as stratified sampling, temporal splits, and cross-validation techniques [163] are driving the decision on how to operate the split such that overfitting is prevented and robustness is ensured.

### Ridge regression

In order to understand the concepts previously introduced, we will study the simple concrete model of the ridge regression. For a feature vector with components  $n$ ,  $\mathbf{x} = (x_1, x_2, \dots, x_n)$ , a linear regression model predicts

$$f(\mathbf{x}) = b + \sum_{i=1}^n w_i x_i = b + \mathbf{w} \cdot \mathbf{x} \quad (2.64)$$

where we have the bias,  $b$  and the weights,  $\mathbf{w}$ , which together are included in the model parameter set  $\theta = (b, \mathbf{w})$ . It is convenient to use the mean squared error as our performance or loss function.

$$J(\theta) = \frac{1}{N} \sum_{i=1}^N (y^{(i)} - \mathbf{w} \cdot \mathbf{x}^{(i)} - b)^2 \quad (2.65)$$

where  $N$  is the number of data points in the training set. This loss function has the merit to be solved analytically by minimizing  $J(\theta)$  with respect to  $\theta$ . The

optimum value for the bias  $b$  is given by

$$\frac{\partial}{\partial b} J(\theta) = 0 \quad \rightarrow \quad b = \frac{1}{N} \sum_{i=1}^N y^{(i)} \quad (2.66)$$

To find the optimal values for the weights  $\mathbf{w}$ , we rewrite  $J(\theta)$  in a more compact form by defining the  $N \times n$  matrix  $X$ , whose  $i$ -th row is  $x^{(i)}$ ,  $X = (x^{(1)}, x^{(2)}, \dots, x^{(n)})^T$  and letting  $\bar{\mathbf{y}} = \mathbf{y} - b$ . Then we have  $J(\theta) = \frac{1}{N} (\bar{\mathbf{y}} - X \cdot \mathbf{w})^T (\bar{\mathbf{y}} - X \cdot \mathbf{w})$ . The optimum value for  $\mathbf{w}$  is then

$$\nabla_{\mathbf{w}} J(\theta) = 0 \quad \rightarrow \quad \mathbf{w} = (X^T X)^{-1} X \bar{\mathbf{y}} \quad (2.67)$$

Here, the  $n \times n$  matrix  $(X^T X)_{ij} = \sum_{k=1}^n x_i^{(k)} x_j^{(k)}$  gives a quantitative sense of how correlated the features are due to its resemblance to the covariance matrix. This model on its own is highly sensitive to the presence of outliers. Henceforth, it is necessary to have a regularization term that will penalize outliers by giving them less weight. By adding the regularization term parameterised by  $\lambda$  to the loss function,

$$J(\theta, \lambda) = \frac{1}{N} \sum_{i=1}^N (y^{(i)} - \mathbf{w} \cdot \mathbf{x}^{(i)} - b)^2 + \lambda \sum_{j=1}^n w_j^2 \quad (2.68)$$

$$= \frac{1}{N} (\bar{\mathbf{y}} - X \cdot \mathbf{w})^T (\bar{\mathbf{y}} - X \cdot \mathbf{w}) + \lambda \mathbf{w}^T \mathbf{w} \quad (2.69)$$

we obtain what is called a “ridge” regression model. By solving the Eq. 2.67, we get the optimal value for the weights  $\mathbf{w}$  as the following.

$$\mathbf{w} = (X^T X + \lambda \mathbb{I})^{-1} X \bar{\mathbf{y}} \quad (2.70)$$

The term “ridge” originates from the diagonal ridge provided by the regularization term in the parenthesis. The reason why the regularisation term prevents overfitting is made obvious : All values are penalized by the same amount  $\lambda$  as seen in the parenthesis that will be inverted. Highly correlated terms will tend to get more penalized, as once inverted they will have fewer weights. It is also easy to notice that if  $\lambda$  is too large, all the weights of the linear regression will go to zero, which will cause an underfitting. Therefore, it is necessary to carefully gauge the value given to  $\lambda$  to increase the bias without causing underfitting.

Although the ridge regression model is a powerful predictive tool,  $f(\mathbf{x})$  being equal to  $\mathbf{x}^T \cdot \mathbf{w}$  is, in essence, constrained to the linear functions set. This limitation to linear functions massively reduces the predictive possibility in particular when we intend to predict quantum properties, dependent on highly non-linear functions, particularly in the presence of disorder, as discussed in Fig. 2.2.2. To sidestep this constraint, the next chapters are introducing Kernel ridge regression (KRR) and

Neural Networks (NN) where non-linearity between features and target vectors becomes predictable.

### Kernel ridge regression

Working within the quantum realm, we expect the relationship between the feature and the target vectors to be highly non-linear. Based on this assumption, the model function  $f$  that fits the input feature vector  $\mathbf{x}$  to the target output  $y$  should inherently reveal the same non-linearity. Kernel approaches work by learning a similarity metric from the training set without explicitly describing the basis set of functions used to define the metric. Then, a kernel-defined metric is employed to return a weighted sum for prediction. For a given feature vector  $\mathbf{x}$ , the model function in the kernel-based approach is written as

$$f(\mathbf{x}) = b + \sum_{m=1}^M w_m g_m(\mathbf{x}) \quad (2.71)$$

with bias  $b$ , weights  $w_m$  and  $g_m$  a set of  $M$  basis functions. Kernel Ridge Regression (KRR) extrapolates the ridge regression model towards the set of nonlinear functions and the loss function associated with this model is expressed as the following.

$$J = \sum_{i=1}^N \left( y^{(i)} - b - \sum_{m=1}^M w_m g_m(\mathbf{x}^{(i)}) \right)^2 + \lambda \sum_{m=1}^M w_m^2 \quad (2.72)$$

where is used a squared error loss with a regularization penalty. As previously seen for the ridge regression, we know the optimal value for the bias to be  $b = \frac{1}{N} \sum_{i=1}^N y^{(i)}$ . By defining  $\bar{\mathbf{y}}^{(i)} = \mathbf{y}^{(i)} - b$  and the matrix  $H_{ij} = w_j(\mathbf{x}^{(i)})$ , the loss function is written in the following matricial form

$$J = (\bar{\mathbf{y}} - H \cdot \mathbf{w})^T (\bar{\mathbf{y}} - H \cdot \mathbf{w}) + \lambda \mathbf{w}^T \mathbf{w} \quad (2.73)$$

with the optimal value for the weights being

$$\mathbf{w} = (H^T H + \lambda \mathbb{I})^{-1} H^T \bar{\mathbf{y}} \quad (2.74)$$

Using the identity  $(H^T H + \lambda \mathbb{I})^{-1} H = H^T (H H^T + \lambda \mathbb{I})^{-1}$ , we can rewrite the expression for the weights as

$$\mathbf{w} = H^T (K + \lambda \mathbb{I})^{-1} \bar{\mathbf{y}} \quad (2.75)$$

where  $K = H H^T$  is named as the kernel matrix. This expression differs from the classical ridge regression model by introducing the so-called kernel matrix. The kernel matrix  $K$  is defined as a  $N \times N$  positive definite matrix such that  $K_{ij} = (H H^T)_{ij} = \sum_{m=1}^M g_m(\mathbf{x}^{(i)}) g_m(\mathbf{x}^{(j)})$ , i.e. the elements are the inner products

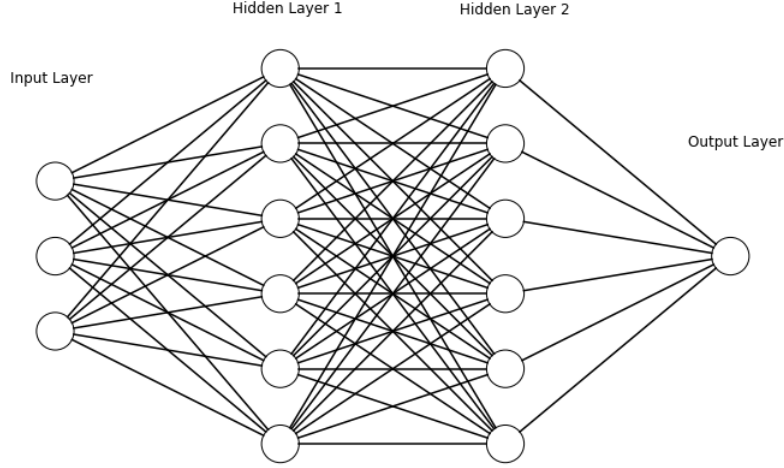


Figure 2.12: A neural network with one input layer, two hidden layers and one output node, typical for a regression task. The connections between the nodes of different layers correspond to the so-called weight matrix  $W$ .

of the basis functions computed over the training set. This is called the “kernel trick”, and the central idea behind relies on the absence of need to concretely know what the basis set functions are. Instead, the inner product obeying certain properties is the only needed requirement. Among the different functions that can be used as a kernel, the Laplacian kernel is defined as  $K_{ij} = \mathbf{D}(\mathbf{x}^{(i)}, \mathbf{x}^{(j)})$  where

$$\mathbf{D}(\mathbf{x}, \mathbf{y}) = \exp \left( -\frac{|\mathbf{x} - \mathbf{y}|}{\sigma} \right) \quad (2.76)$$

The kernel regression model is consequently written as

$$f(\mathbf{x}) = b + \sum_{i=1}^N a_i \mathbf{D}(\mathbf{x}, \mathbf{x}^{(i)}) \quad (2.77)$$

where  $a_i = (K + \lambda \mathbb{I})^{-1} \bar{\mathbf{y}}$ . Other functions such as polynomials, gaussian or other radial basis functions can define a kernel. A kernel function must satisfy symmetry, i.e  $\mathbf{D}(\mathbf{x}, \mathbf{y}) = \mathbf{D}(\mathbf{y}, \mathbf{x})$  and positivity  $\mathbf{q} H H^T \mathbf{q} = (H^T \mathbf{q})^T (H^T \mathbf{q}) \geq 0 \rightarrow \sum_{i,j} q_i \mathbf{D}(\mathbf{x}^{(i)}, \mathbf{x}^{(j)}) q_j \geq 0$ . It is straightforward to see  $\mathbf{D}(\mathbf{x}, \mathbf{y})$  as a way to define a metric and gives a quantitative measure about how close samples are to each other in the dataset. Although being an exactly solvable and powerful predictive regression technique, KRR is constrained by the size of the training set. Indeed, optimal weight calculation implies matrix inversion which has a complexity that scales like  $N^\alpha$  where  $N$  is the size of the training set and  $2 < \alpha \leq 3$  depending on the optimization of the inversion techniques. The limitation on the size of the data set despite the removal of the constraint on nonlinearity brings us to the neural networks.

## Neural networks

Unlike shallow learning models such as linear regression or kernel ridge regression, the neural network is classified as a deep learning model. Indeed, the neural network as we will see by its architecture in successive layers allows a higher level of abstraction. Neural network, as its name implies, is inspired by the brain basic unit cell, the neuron. Mathematical representation of neuron, called formal neuron, have made their way through their 80s and yielded this model, now state of the art for ML. Among many reasons behind its success and of interest for this study, training and prediction time scales linearly with the number of data-points making large-scale training feasible. In addition, neural networks are known to be “universal approximators” because of their ability to learn any function up to an arbitrary error. Their flexibility and versatility to fit any function make them powerful tool for predictive purposes as we shall see in this chapter.

Even if this model is far from being unanimous among deep learning models, we will focus on the classic neural network where neurons are fully connected. They are comprised of three different types of layers: input, hidden and output layers, with each layer containing a certain number of units as seen in Fig. 2.12. By convention, the first layer or input layer is labelled as 0, then the first hidden layer is 1 and so on. The number of units in each layer is  $p^{(i)}$ , with  $p^{(0)} = p$  being the dimension of the feature vector. Units are connected through weight matrices, the weight matrix connecting layer  $i$  and  $i + 1$  is labelled  $W^{(i)}$  with dimension  $p^{(i+1)} \times p^{(i)}$ . There are also bias vectors  $b^{(i)}$  of dimension  $p^{(i+1)}$ . The number of parameters associated with the architecture of the network is given by

$$N_{\text{Params}} = \sum_{i=1}^L (p^{(i)} + 1) p^{(i+1)} \quad (2.78)$$

where  $L$  is the number of hidden layers and  $+1$  is based on the assumption that each unit or node in the neural network has a bias. The output of the  $i^{th}$  hidden layers is given by

$$\mathbf{h}^{(i)} = g(\mathbf{b}^{(i-1)} + W^{(i-1)} \cdot \mathbf{h}^{(i-1)}) \quad (2.79)$$

where  $h^{(0)} = \mathbf{x}$  is the input vector and  $g$  is a non-linear function called the activation function. As a result of the propagation through all the layers, the output is written

$$y = p(\mathbf{b}^{(L)} + W^{(L)} \cdot \mathbf{h}^{(L)}) \quad (2.80)$$

where  $p$  is a function appropriately chosen regarding the task to learn. In the case of regression, there is no restriction on the value the function  $p$  could take so usually, we chose a linear function  $p(z) = z$  for the last layer. The non-linearity of the activation function of each node is to ensure that the neural network is not constrained to the linear function set only. As a fact, the “Universal approximation”

| Activation function          | Mathematical expression             |
|------------------------------|-------------------------------------|
| Logistic (sigmoid)           | $\frac{1}{1+e^{-x}}$                |
| Hyperbolic tangent           | $\frac{e^x - e^{-x}}{e^x + e^{-x}}$ |
| Rectified linear unit (ReLU) | $\max(0, x)$                        |
| Gaussian                     | $e^{-x^2}$                          |

Table 2.1: Table of commonly used activation functions.

theorem states that “*non-linear activation functions used in deep neural network can approximate any measurable function provided sufficiently many hidden units are available*”. Apart from non-linearity, it is also preferable for an activation function to be continuously differentiable. Indeed, we will see later that the optimization of the weights of the network is done by methods based on the gradient. The differentiation criterion of functions is therefore crucial to ensure that we do not have values for which the function has discontinuities. Commonly used activation functions are displayed in the table 2.1. The choice of the activation function, just like the architecture of the network (hidden layers and number of neurons per layer) is generally made during the validation phase.

A neural network can be conceptualized as learning a representation for the decision layer in the hidden layers. When we are mapping  $x$  to  $y$ , applying neural network to the problem is no different from performing a regression task  $f(\mathbf{x}) = b + \sum_{m=1}^M w_m g_m(\mathbf{x})$  where one should think of the hidden layers as good approximators for the  $g_m$  functions. Yet, choosing the neural network’s architecture is more of an art than a science. There is proof, nonetheless, that employing a deeper network results in a more robust approximator. Deeper networks learn features of higher orders which prevents overfitting because they tend to generalise better during the test phase.

## Optimisation

Unlike regression techniques, there is not an optimal solution consisting of inverting a matrix for a neural network. The amount of free parameters such as the architecture, the weights, biases and activation functions makes the optimisation of the neural network an open problem. Although the exact solution does not exist, the key idea remains to find an efficient way to minimise the loss function.

## Gradient-descent algorithm

For a particular neural network architecture, permuting weights and biases between the hidden layers’ neurons should result in a similar output. Consequently, the loss function for neural networks must have as many local minima as we can create equivalent networks by permutation. Assuming that it will be hardly possible to find the global minimum of the loss function, we will see how state of

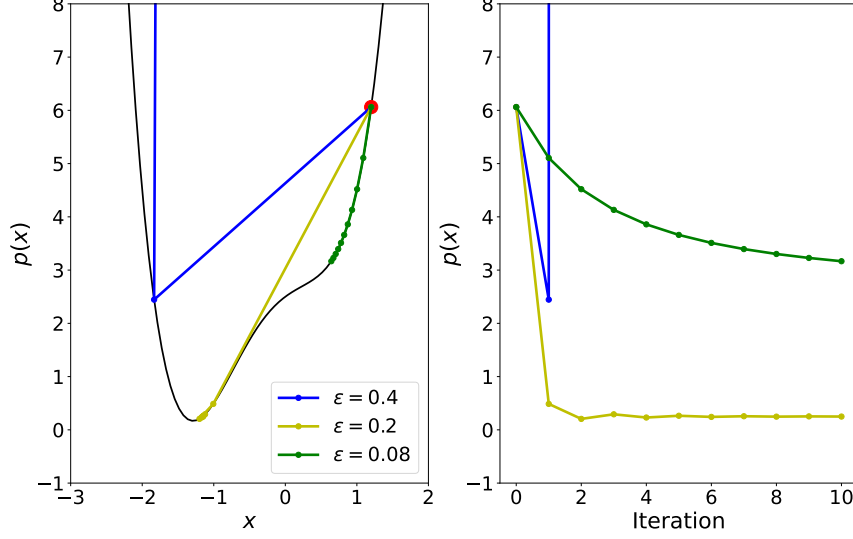


Figure 2.13: Gradient descent method used to find the global minimum of a function. Starting from the initial solution of  $x = 3/2$  (red dot), the right panel shows the courses (coloured curves) of the descent method for different learning rates. The left panel shows the value of the function over the iterations for different the corresponding learning rates. As is shown, a too high valued learning rate can quickly overshoot the minimum in value (blue line) while a low learning rate is inefficient (green line). The optimal learning rate,  $\epsilon = 0.2$  shown in yellow, should be adaptive to the landscape of the function to minimise

the art gradient-based methods still allow for the best compromise in predictive performance.

The gradient of a function  $f$ ,  $\mathbf{g} \equiv \nabla f(\mathbf{x})$  defines how the function or scalar field varies in space. For instance, if  $f$  represents a loss function with a feature vector  $\mathbf{x}$  as an input,  $\mathbf{g}$  will define a vector at point  $\mathbf{x}$  in space giving the direction and rate of fastest increase. Therefore, the progressive minimization of the loss function  $f$  must follow the opposite of the gradient by successive steps. Let  $\epsilon$  be the step size and suppose we calculate the value of the function  $f$  at  $\mathbf{x}' = \mathbf{x} - \epsilon \mathbf{g}$  where we take a step back in the opposite direction to the gradient  $\mathbf{g}$  :

$$f(\mathbf{x}') = f(\mathbf{x} - \epsilon \mathbf{g}) = f(\mathbf{x}) - \epsilon |\mathbf{g}|^2 + \frac{\epsilon^2}{2} \mathbf{g}^T H \mathbf{g} + \dots \quad (2.81)$$

where  $H$  is the Hessian matrix. Assuming the step size or learning rate  $\epsilon$  to be small, we can neglect  $O(\epsilon^2)$  and higher order terms, finally concluding that  $f(\mathbf{x}') < f(\mathbf{x})$  hence minimising the loss function. This is the basis of the so-called gradient descent algorithm which constitutes the groundwork of gradient-based algorithms. Starting from a guess  $\mathbf{x}_0$  and updating with

$$\mathbf{x}_{n+1} = \mathbf{x}_n - \epsilon \nabla f(\mathbf{x}_n), \quad (2.82)$$

the gradient descent algorithm goes through several steps  $n$  until convergence is

reached. Gradient descent is used to train neural networks by first computing the loss function on the training set by forward propagation, and then updating the network's weights in a single gradient descent step until convergence is reached. Therefore, in order to update the network, it is necessary to compute the derivative of the loss function with respect to each network parameter. Back-propagation is a useful algorithm for accomplishing this, which leverages the derivative chain rule to reduce computational and memory needs.

### Forward- and back- propagation

The optimization algorithm updates the weights  $\{\mathbf{W}\}$  and biases  $\{\mathbf{B}\}$  of the training set in order to minimize the loss function. For illustrative purpose and since this algorithm is the basis of most optimizers, we will develop the forward- and back-propagation process:

The weights in the neural network are first initialized with random values. We then consider a training set that will be used for learning. Each sample has its target values, which are those that the neural network must eventually predict. The algorithm follows the following steps:

1. Let be a sample  $\mathbf{x}$  presented as an input of the neural network and  $y$  the desired output for this sample.
2. We propagate the signal forward in the neural network layers:  $x_k^{(n-1)} \mapsto x_j^{(n)}$ , with  $n$  being the hidden layer number.
3. Forward propagation is calculated using the activation function  $\phi$ , the aggregation function  $h$  (corresponding to the scalar product between the weights and the inputs of the neuron) and synaptic weights  $\vec{w}_{jk}$  between neuron  $x_k^{(n-1)}$  and neuron  $x_j^{(n)}$ . The indexing is here reversed :  $\vec{w}_{jk}$  indicate a weight from  $k$  to  $j$ .

$$x_j^{(n)} = \phi^{(n)}(h_j^{(n)}) = \phi^{(n)}\left(\sum_k w_{jk}^{(n)} x_k^{(n-1)}\right)$$

4. When forward propagation is complete, the result at the output is  $y_{\text{pred}}$ . The error between the output given by the network  $y_{\text{pred}}$  and the desired output  $y$  for this sample is then calculated. For the neuron in the output layer, we calculate ( $\phi'$  being the derivative of  $\phi$ ):

$$e^{\text{output}} = \phi'(h^{\text{output}})(y_{\text{pred}} - y)$$

5. The error is propagated backwards  $e^{(n)} = e^{\text{output}} = (y_{\text{pred}} - y) \frac{\partial y}{\partial h_i^{(n)}} \mapsto e_j^{(n-1)}$

by the following formula:

$$e_j^{(n-1)} = \phi'^{(n-1)}(h_j^{(n-1)}) \sum_i w_{ij}^{(n)} e_i^{(n)}$$

6. We update the weights in all layers given :

$$w_{ij}^{(l)} = w_{ij}^{(l)} - \epsilon e_i^{(l)} x_j^{(l-1)}$$

where  $\epsilon$  represents the learning rate, a number in the range  $[0, 1]$

The learning rate represent the step size at each iteration while moving toward a minimum of the loss function. A too high learning rate will overshoot the minima, but a low learning rate will take too long to converge. It can be fixed, to be determined by the user, or vary during execution according to certain heuristics.

### Batch and epoch

Generally when training a neural network, it is common to regroup several data-points in batches to operate the optimisation. Indeed, it will be computationally prohibitive to operate the update in weights and biases for a single data point, as the training set is massive. It is quicker to separate our dataset into batches instead, updating the network using each batch separately. An epoch refers to one cycle of updates through all the batches. As the batch size increases, the accuracy of the estimate of the loss function increases. Considering the gathering of data-points into batches, the update rule becomes

$$\begin{aligned} \mathbf{g}_n &= \nabla_{\theta} \left( \frac{1}{p} \sum_{i=1}^p \mathcal{L}(f(\mathbf{x}^{(i)}), y^{(i)}) \right) \\ \theta_{n+1} &= \theta_n - \epsilon \mathbf{g}_n \end{aligned} \tag{2.83}$$

where  $p$  corresponds to the number of data-points in the batch and  $n = 0, 1, \dots, N$  such that  $N \times p$  is the amount of data-points in the training set or one epoch. Yet, when the batch size is too large, there is a possibility of overfitting. When the batch size is too small, the inherent noise in each batch can also be detrimental with regard to the minimisation of the loss function. An adaptive way of considering batch size and learning rate have to be considered.

### Momentum and ADAM

Momentum in this realm refers simply to the physical concept of momentum applied to optimisation. The same way a golf ball deviates from the hole because it has too much speed, one has to think of momentum has a quantity that over-

shoots shallows local minima but falls in deeper ones. To include the so-called momentum in the update rule, we have

$$\begin{aligned}\mathbf{v}_{\mathbf{n}+1} &= \alpha \mathbf{v}_{\mathbf{n}} - \epsilon \mathbf{g}_{\mathbf{n}} \\ \theta_{n+1} &= \theta_n + \mathbf{v}_{\mathbf{n}+1}\end{aligned}\tag{2.84}$$

where  $\mathbf{v}_{\mathbf{n}}$  is the velocity, which is initialized at zero and  $\alpha$ , a number in the range  $[0, 1]$ . The reasoning behind this is that the velocity term keeps track of the history of the gradient, which leads to a speed up in convergence. The same way momentum is an adaptive technique avoiding the optimisation to get stuck in a local minimum, the ADAM (ADaptive Moment estimation) optimiser is adapting the learning-rate based on some statistical principle. It is one of the most used optimiser and without explicit notice, this is the optimiser used in our neural networks. It adapts the parameter learning rates based on the exponential moving average of the first (mean) and second (variance) moments of the gradients. Calling respectively  $\rho_1$  and  $\rho_2$ , the first and second moments of the gradients, the resulting update procedure is the following

$$\begin{aligned}\mathbf{s}_{\mathbf{n}+1} &= \frac{\rho_1}{1 - \rho_1^{n+1}} \mathbf{s}_{\mathbf{n}} + \frac{1 - \rho_1}{1 - \rho_1^{n+1}} \mathbf{g}_{\mathbf{n}} \\ \mathbf{r}_{\mathbf{n}+1} &= \frac{\rho_2}{1 - \rho_2^{n+1}} \mathbf{r}_{\mathbf{n}} + \frac{1 - \rho_2}{1 - \rho_2^{n+1}} \mathbf{g}_{\mathbf{n}}^2 \\ \theta_{n+1} &= \theta_n - \epsilon \frac{\mathbf{s}_{\mathbf{n}+1}}{\delta + \sqrt{\mathbf{r}_{\mathbf{n}+1}}}\end{aligned}\tag{2.85}$$

where  $\delta$  is a small positive value ensuring no singularities in the formula,  $\mathbf{s}_{\mathbf{n}}$  and  $\mathbf{r}_{\mathbf{n}}$  are initialised at 0.

### Regularisation methods in NN

In addition to conventional regularisation techniques consisting in penalising the large-valued weights in the loss function, there are other methods for neural networks that reveals successful in preventing overfitting.

One of these methods is the dropout. When a neural network is in its training phase, the hidden layers' nodes have their output randomly set to zero with a certain probability  $p$ . If there are  $m$  nodes in total in the hidden layers, there will be  $2^m$  ways of designing the hidden layers architecture by removing hidden layers' nodes. Thus, the dropout method consists in forcing the network to learn to fit inputs to output by averaging over the resulting sub-networks when nodes have been deactivated. This results in making the neural network more robust in the sense that it can generalise better. The other way to prevent overfitting in neural network is through the early stopping method. The longer the training lasts, the most accustomed the neural network becomes to the training set. Indeed, by

|                                              | Kernel Ridge Regression                                                     | Neural Network                                                      |
|----------------------------------------------|-----------------------------------------------------------------------------|---------------------------------------------------------------------|
| Data set size management                     | Kernel Matrix inversion and storage problem for big data sets               | Able to manage big data sets                                        |
| Number of hyperparameters                    | Laplacian kernel width $\sigma$ & regularisation term $\lambda$ ( $N = 2$ ) | Optimiser, . . . , learning rate, batch size, epochs ( $N \geq 5$ ) |
| Data Processing understanding                | Yes                                                                         | "Black box"                                                         |
| Adaptation of learning through optimisation  | No                                                                          | Yes                                                                 |
| Adaptation of learning through data increase | Slight increase until memory issues                                         | Yes                                                                 |

Figure 2.14: Comparative table between Kernel Ridge Regression (KRR) and Neural Networks (NN).

monitoring if the validation error is increasing over time, sign of overfitting, we can halt training.

## Qualitative comparison between KRR & NN

### 2.4.3 Other ML techniques

There are several crucial topics in the field of machine learning that were not addressed in this thesis but are worth mentioning for future work. These include Convolutional Neural Networks (CNNs), and unsupervised learning techniques such as Principal Component Analysis (PCA) and Generative Adversarial Networks (GANs). CNNs are a type of deep learning model widely used in image and video recognition tasks. PCA is a technique for reducing the dimensionality of data while retaining important information, and GANs are a powerful tool for generative modeling, producing new data based on learned patterns in existing data. These topics have a vast potential to extend the discussions and add more value to future work in the field of AI-assisted quantum transport.

### Convolutional neural networks

Convolutional Neural Networks (CNNs) are a type of neural network architecture that was created specifically for inputs with a grid layout, including pictures or time series data [164]. Like a fully-connected NN, a CNN network has an input layer, hidden layers, and an output layer. Any middle layers in a feed-forward NN

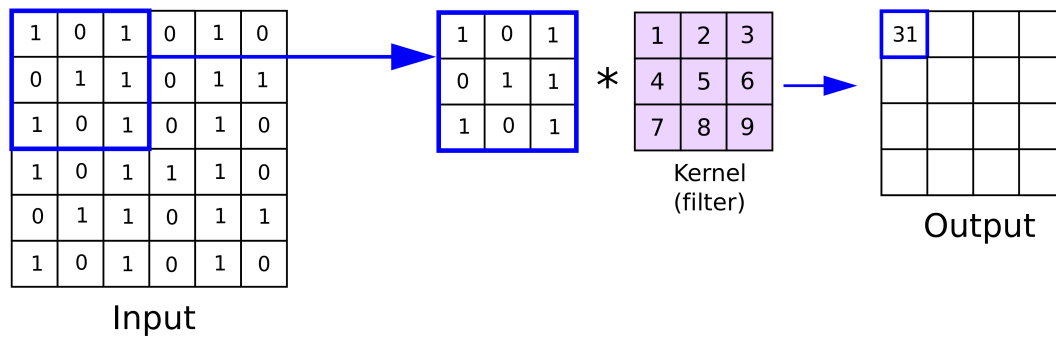


Figure 2.15: An example of a convolution operation in 2 dimensions. Here the input is a  $6 \times 6$  matrix, the kernel a  $3 \times 3$  matrix. The stride in this example being equal to 1, the resulting output is a  $4 \times 4$  matrix

are said to be hidden since the activation function and final convolution hide their inputs and outputs. Fully-connected NNs, albeit effective for processing images, have trouble with huge images because the number of connections between each neuron and every other neuron in the layer, before and after it, grows exponentially with the size of the image. However, with a CNN, convolutional layers are also present in the hidden layers. This typically contains a layer that does a dot product with an input matrix of the layer with a convolution kernel. The number of connections between a neuron and the neurons of the neighboring layers is restricted in convolutional neural networks, whose theory is inspired by the visual cortex of animals. This significantly minimizes the number of parameters that must be learned.

As an example, when a pixelated grey-scale image is processed by a neural network, the dimension of the input vector is equal to the number of pixels present in the image. Thus an image of  $128 \times 128$  pixels will have an input vector of size 16384. Even if the first hidden layer only has 64 units, for example, there will still be over 1 million trainable parameters, making training very computationally expensive and increasing the likelihood of overfitting. Moreover, fully-connected NNs ignore the concept of locality of reference, meaning that 2 different sub-regions of a picture are considered in an equal manner whereas spatially local patterns are important but disregarded. We may try to prevent this by manually developing features, making high-level features pertinent to the issue but hand-engineered filters and general human intervention in feature extraction is a major disadvantage.

The idea behind CNNs is that the network learns filters, called kernels, which are dedicated to find relevant features without a preliminary knowledgeable description of the data.

To better comprehend the convolutional aspect of CNN, let us start with a 1-dimensional example. Suppose we have a  $p$ -dimensional feature vector that we

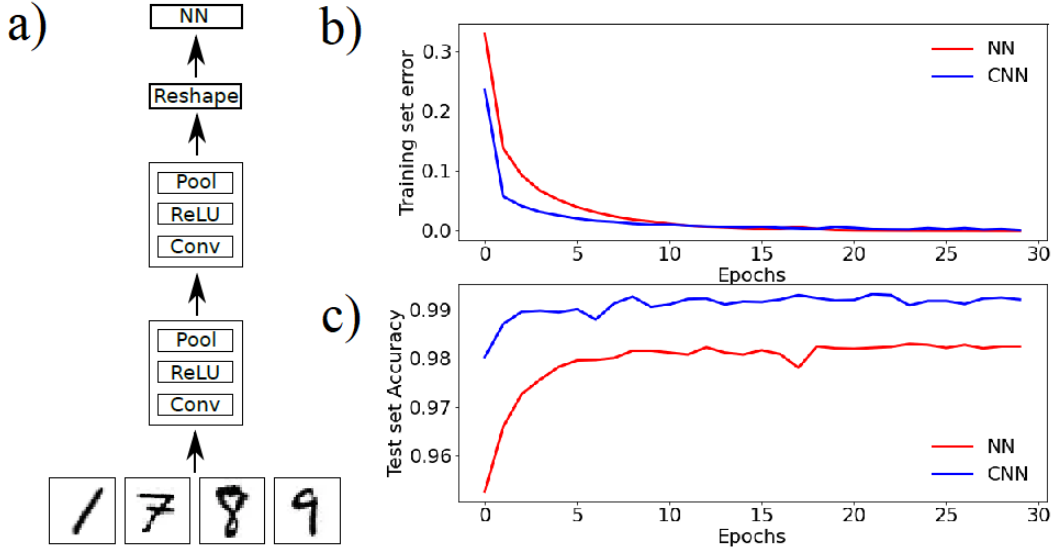


Figure 2.16: (a)- The architecture of the CNN used for comparison with the performance of a fully connected NN. The used data originates from MNIST [165]. The number of parameters of the CNN is over 90 000 whereas the fully connected NN has over 400 000 parameters to be. (b)- The training process is shown for both models

call  $\mathbf{x}$ , and a  $k$ -dimensional kernel vector  $\mathbf{c}$ . Then the convolutional operation results in a new vector,  $\mathbf{s}$ , with

$$s_i = (\mathbf{x} * \mathbf{c})_i = \sum_{j=1}^k x_{(i-1)s+j} c_j \quad (2.86)$$

which has a dimension of  $\frac{p-k}{s} + 1$  where  $s$  is the stride parameter. For an explicit illustrative example, suppose  $\mathbf{c} = (2, -3)$ ,  $s = 1$  and  $p = 3$  then for a given  $\mathbf{x}$ , the resulting convolution vector is equal to

$$(x, y, z) * (2, -3) \longrightarrow (2x - 3y, 2y - 3z, 2z - 3x) \quad (2.87)$$

The weight matrices in CNNs can be thought of as fully connected networks with multiple weights restricted to the same value. A concrete example of 2-dimensional convolution operation is shown in Fig. 2.15.

In most cases, a combination of kernels and convolution layers are utilized, followed by an activation function. We can generalise this concept to higher dimensions by considering a kernel tensor  $A_{ijk}$  and the input to the layer  $C_{ij}$  then the resulting convolution operation will be

$$(C * A)_{ij} = \sum_{lm} C_{l,(j-1)s+m} A_{ilm} \quad (2.88)$$

Often convolution operations via kernels are used in parallel with the pooling

method, where a sub-region of the incoming input layer is reduced to its mean or maximum. Pooling is used to reduce the size of the inputs, so that the feature vector passed to the fully connected network is constrained to workable sizes. The performance of a fully-connected network compared to a CNN are shown in Fig. 2.16 where we trained the models on the MNIST dataset[164]. This dataset, where hand-written digits are gathered on greyscale pixelated images is used to see how well the NN and CNN models are able to correctly assign the hand-written digits to its value.

Unsupervised learning's goal is to identify structure in unlabeled data. This is employed in numerous applications, such as reducing a dataset's dimension for visualization, clustering data samples that have common non-intuitive features, discovering anomalous data, or creating new samples that are similar to those in the dataset for data augmentation. In this section, I present two categories of unsupervised learning: principal component analysis (PCA) and generative adversarial networks (GAN).

### Principal component analysis

Principal component analysis (PCA) [166] is a (pre-processing) method of unsupervised learning that essentially reduces the multi-collinearity, i.e the high correlation between two or more explanatory variables describing data samples in a given data set. The likelihood of overfitting the model in regression analysis increases with the number of explanatory variables allowed, leading to results that cannot be extrapolated. It is then frequently used to obtain lower-dimensional data while retaining the most of the data's variation by projecting each data point onto only the first few principal components. In order to see and handle high-dimensional datasets while preserving as much of the dataset's variation as feasible, such dimensionality reduction can be a very helpful pre-processing step.

Suppose we have a dataset of  $p$ -vectors  $(\mathbf{x}^{(1)}, \mathbf{x}^{(2)}, \dots, \mathbf{x}^{(N)})$  that must be reduced to a  $k$ -dimensional space with  $k < p$ . We assume for illustration that the data have zero mean along the  $p$ -feature dimension such that  $\frac{1}{N} \sum_{i=1}^N x_k^{(i)} = 0$ . The total variance for each feature then correspond to

$$\sigma^2 = \sum_{k=1}^p \frac{1}{N} \sum_{i=1}^N \left(x_k^{(i)}\right)^2 \quad (2.89)$$

As it is difficult to visualise, let us start with the  $k = 1$  case, better to comprehend the mechanism of PCA. The linear mapping  $y_i$  will be  $\mathbf{w}^T \cdot \mathbf{x}^{(i)}$  and consequently,

the variance is equal to

$$\sigma^2 = \sum_{i=1}^N (\mathbf{w}^T \cdot \mathbf{x}^{(i)} - \bar{y})^2 \quad \text{with} \quad \bar{y} = \frac{1}{N} \mathbf{w}^T \cdot \sum_{i=1}^N \mathbf{x}^{(i)} = 0 \quad (2.90)$$

Letting  $X = \sum_{i=1}^N \mathbf{x}^{(i)} \mathbf{x}^{(i)T} = |\mathbf{x}^{(i)}|^2$ , the Lagrangian associated with the variance is equal to

$$L = \mathbf{w}^T X \mathbf{w} - \lambda(|\mathbf{w}|^2 - 1) \quad (2.91)$$

where we have constrained  $\mathbf{w}$  as being a unit vector since making this vector arbitrarily big could result in maximising the variance. By taking the derivative with respect to  $\mathbf{w}$  of the Lagrangian, we get the value of  $\mathbf{w}$  that maximises the variance

$$\nabla_{\mathbf{w}} L = 0 \quad \longrightarrow \quad X \mathbf{w} = \lambda \mathbf{w} \quad (2.92)$$

which turns out to be an eigenvector of  $X$ . The variance in the reduced dimension is the corresponding eigenvalue, and after normalizing it and substituting it into the Lagrangian, we can see that it is the greatest eigenvalue that we could find. If we want to apply the same concept to a  $k$ -dimensional space, we choose the orthogonal  $k$  eigenvectors with the largest eigenvalues. By calling  $U_k$ , the matrix where the columns are the  $k$  eigenvectors and  $H$ , the matrix whose  $i$ -th row is  $\mathbf{x}^{(i)T}$  then the optimal dimensionality reduction is

$$\underbrace{H}_{N \times p} \longrightarrow \underbrace{H \cdot U_k}_{N \times k} \quad (2.93)$$

Given that  $U_p$  is an orthogonal matrix, the reduced space has the same variance as the original data when  $k = p$ . Because of this, the total variance in the reduced space over the overall variance is used as an indicator of how easily the data may be compressed.

## Generative adversarial networks

Generative adversarial networks (GANs) are a class of techniques that can estimate an implicit distribution from a dataset [167]. This algorithm is able to create data that shares common characteristics with the dataset on which it was trained. For example, the site <https://thispersondoesnotexist.com/> [168] generates faces of people who do not exist in reality. After being trained, the generator, as it suggests, is a neural network able to generate new data similar to the ones in the dataset.

The training process is done with the assistance of a second neural network called the discriminator and both NNs play a zero-sum game against each other. The discriminator network takes the output from the generator and predicts if the generated data has been generated or is coming from the real dataset. The

game ends when the generator has learnt the underlying distribution and the discriminator can no longer distinguish between generated and real data. This means that the generator is trained to trick the discriminator rather than to reduce the distance to a particular image. This allows the model to learn without supervision.

Given a sample  $X$ , the discriminator is a binary classifier; its output is  $D(X)$ , which is 1 if it believes the sample to be real and 0 if it believes the sample to be artificially generated. Let us call  $p_{\text{generator}}$  the distribution of the generated samples then the cost function that has to be minimised for the discriminator is simply the binary cross entropy

$$J^D = -\frac{1}{2}E_{X \sim p_{\text{data}}}[\log(D(x))] - \frac{1}{2}E_{X \sim p_{\text{generator}}}[\log(1 - D(x))], \quad (2.94)$$

where  $p_{\text{data}}$  is the original data distribution, the overall  $\frac{1}{2}$  is here in order for the cost functions of the generator and discriminator to match at equilibrium. Indeed, cross entropy, relying on the logarithmic function heavily penalises classifiers that are confident about a wrong classification. Moving from discrete to continuous distributions, we are allowed to write the discriminator's cost function in an integral form

$$J^D = -\frac{1}{2} \int dx [p_{\text{data}}(x)\log(D(x)) + p_{\text{generator}}(x)\log(1 - D(x))] \quad (2.95)$$

and by using the Euler-Lagrange equation to minimise the cost function, we get the optimal discriminator strategy

$$D_{\text{optimal}}(x) = \frac{p_{\text{data}}(x)}{p_{\text{data}}(x) + p_{\text{generator}}(x)} \quad (2.96)$$

Thus the optimally trained discriminator estimates the ratio between  $p_{\text{data}}(x)$  and  $p_{\text{data}}(x) + p_{\text{generator}}(x)$ .

The generator takes a latent vector,  $\mathbf{z}$ , that is randomly selected from a distribution,  $p(\mathbf{z})$ , typically either an uniform or normal distribution. It then attempts to produce a sample,  $G(\mathbf{z}) = X$ , that is as realistic as possible with regard to the original dataset. As a result, the generator may be considered of as turning the latent distribution into the dataset's distribution. The generator has a cost function since it aims to "trick" the discriminator

$$J^G = E_{X \sim p_{\text{generator}}}[\log(1 - D(x))] \quad (2.97)$$

Yet, the function  $\log(1 - x)$  has a small derivative for  $x$  values close to 0, which is why in practice this cost function is not employed. Therefore, there is not a strong enough gradient to update the generator's weights to produce high-quality

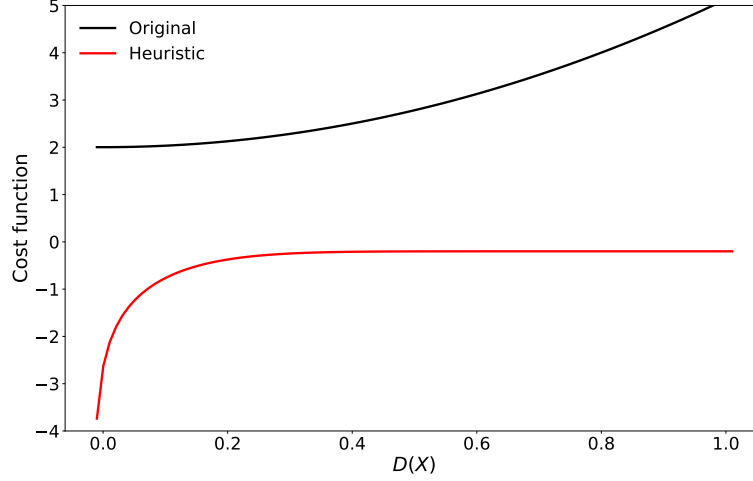


Figure 2.17: Cost functions of the generator  $J^G$  as a function of the output from the discriminator  $D(X)$ . The original cost function is nearly flat for small values of  $X$ , hindering the training process of the generator. The heuristic cost function is used instead, efficiently updating the weights of the generator’s NN particularly at the start of the training or where  $x \sim 0$ .

samples in the beginning of training, when the discriminator can easily distinguish between the generated and real samples. Instead we use a heuristic cost function for the generator

$$J^G = -E_{X \sim p_{\text{generator}}}[\log(D(x))] \quad (2.98)$$

preferred as it has a big derivative for small values of  $x$  as can be observed in Fig. 2.17. We show a little application of in-house GAN routine capable of generating images similar to the MNIST dataset [165]. The MNIST dataset gathers greyscale images of handwritten digits and this dataset have been used when machine learning algorithms’ usage were still slowly blooming. This network’s goal is then to learn how to produce indistinguishable images of handwritten numbers by learning how to trick the discriminator NN. Each of the image constituting of our 6-element long latent vector  $\mathbf{z}$  is a greyscale picture of size  $28 \times 28$  as are the original pictures in the MNIST dataset. The training has been realised on 200 epochs and the latent output vector  $\mathbf{z}$  is shown at different timesteps of the training process in Fig. 2.18. We observe from Fig. 2.18(a) to (c) how the initially noisy greyscale images turn into handwritten digits that could be easily found in MNIST.



Figure 2.18: (a)- The latent vector  $\mathbf{z}$  composed of 6 images at the start of the training process. This 6-images long vector is initialised with noisy pixelated images at the start. (b)- In the middle of the training process, both generator and discriminator are competing to get their image output vector as close as possible to the MNIST data samples. We observe the onset of hand-written appearing as the training goes. (c)- At the end of training, the adversarial training process yield a 6-pictures long output that is very similar to data samples of the MNIST dataset.

## Predicting quantum transport in disordered graphene nanoribbons with machine learning

### 3.1 Introduction

In this chapter, we predict electronic transport in disordered GNRs with machine learning and show how it can be efficiently used to complement conventional transport calculation techniques. GNRs, quasi one-dimensional nanostructures made from graphene, have attracted a lot of attention in the literature, and applications for these materials have been proposed in a large variety of domains, including nanoelectronics and spintronics [6, 8, 88]. The electronic structure for these materials were calculated in chapter 2 where the width and edge geometry properties of GNRs were also introduced. Attention is brought to the two principal edge geometries, namely those corresponding to the armchair and zigzag directions.

Transport properties in GNRs which stem from the electronic properties are highly dependent on the width of the ribbon as much as their edge orientations [65, 89, 91, 169]. The experimental synthesis of GNRs, whether by top-down or bottom-up approaches, is prone to the presence of disorder. Although we are witnessing an improvement in the quality of the samples by innovative synthesis techniques, producing nanoribbons of very high quality and in high volumes, remains a difficult challenge [33, 34, 61, 72, 73, 170]. GNRs transition from a domain where bulk disorder is the main scattering mechanism to a ballistic one where boundary conditions, and particularly edge defects are the main factors determining the transport parameters [113, 118, 171]. The studies mentioned above focused on edge disorder that results from the difficulties of producing atomically precise edges for ribbons.

Yet, as detrimental as edge disorder seems to quantum transport, the purposeful introduction of disorder in GNRs, either at the edges or in the bulk, has opened new fields and perspectives. Defect-engineering and material doping can be effective ways to tune the GNRs electronic and transport properties [117, 118, 170]. As the main difference between bulk graphene and GNRs resides in the presence of two symmetry-breaking edges, we intuitively expect the position of the impurity with regard to edges to play a crucial role in the GNRs' electronic properties. This dependence has been addressed in a number of studies which examined the conductance through a nanoribbon system when the impurity location or distribution was varied [118, 124]. In Section 3.2, the key conclusions of these studies will be presented and explained using a straightforward model of our own.

As far as it is possible to explain the effect of a single impurity and relate its impact onto transport, explaining the resulting effect of several impurities is less clearly understood. Disorder makes it difficult to describe the impurity potential using inverse scattering techniques. Based on the scatterers' positions, multiple scattering is likely to have unpredictable impacts on the electronic dynamics. As quantum transport relates to the electron wave-like nature, we have already seen how non-linear the presence of multiple impurities is when calculating the Green's function in a linear atomic chain (cf. Section 2.2). The existent non-linearity in Green's functions in the presence of multiple scatterers in a quasi one-dimensional structure such as GNRs is no different. One simply can not linearly interpret the effect of two or more impurities as the resultant linear combination of the individual scattering defects. Consequently, the non-linearity brought by the quantum interference effects of several impurities hinders our capacity to extrapolate these effects onto electronic transport.

Machine learning (ML) and in particular, supervised learning techniques could cope with the lack of information arising from these quantum effects which can introduce interference, noise and uncertainty into the data. By making sense of accumulated knowledge, these approaches directly enable the resolution of computationally expensive sets of equations. By an informed description of the impurities positions across the ribbon width, ML techniques allows us to predict the conductance from known patterns and infer new knowledge for unseen disordered configurations.

We present here the role of structure, geometry and disorder in GNRs using advanced machine learning techniques such as kernel ridge regression and neural network to lay the groundwork for investigating and determining the suitable methods for more complex operations. Furthermore, our work serves as a proof-of-concept and starting point for such implementations. We performed simulations for electronic transport through disordered nanoribbons, and show that both kernel ridge regression and neural network techniques can be used to accu-

rately estimate transmission profiles from geometrical details. In both cases, the careful choice of descriptors plays a crucial role in performance to describe the effect of disorder in GNRs on their transport properties. The choice and resulting performance of a descriptor when compared to others is essential to grasp the key features that describes how impurities impact quantum transport. Our results highlight the ability of machine learning techniques to capture the complexity of disordered nanostructures, and suggest that they can be used to complement conventional techniques to better understand a wider array of systems.

Section 3.2 provides an overview of the position-dependent properties in GNRs due to a single impurity or the combined effect of several impurities including their electronic and transport properties.

Section 3.3 will discuss the use of machine learning techniques for the study of transport properties in disordered GNRs. Descriptors, inspired by materials science and previous works are then introduced and provide a crucial representation of the electronic and transport properties of disordered GNRs. By presenting a detailed explanation of the kernel ridge regression method and its implementation for the study of transport properties in disordered GNRs, we compare it to neural networks and discuss their advantages and drawbacks.

After exposing the details of the data set generation, including the number of samples and descriptors used for the machine learning calculations, section 3.4 will present the results obtained from the calculations obtained from machine learning techniques for various disordered nanostructures.

## **3.2 Position-dependent properties in GNRs**

### **3.2.1 Transport properties in the presence of a single impurity in GNRs**

Before addressing the impact of edge or bulk impurity distributions, we will first explore how the conductance of armchair- and zigzag-edged GNRs is impacted by a single impurity when its position is varied across the width of the ribbon.

Previous investigations have focused on the position dependency of transport properties for doped materials. This typically entails an ab-initio analysis of a ribbon with particular impurity species taken into account at various locations along the ribbon’s width [119, 172]. However, these studies are constrained to narrow and periodic ribbons as ab-initio calculations require high computational resources, unadapted for realistically disordered GNRs. Alongside DFT investigations, tight-binding studies have been done on the impact of vacancy defects on GNRs conductance. It has been shown that vacancies at the center of a wide

ZGNR affect the conductance more severely than those on the edge [173]. Much of the studies done so far have concentrated their efforts to express the relationship between edge disorder and quantum transport as it is the type of disorder most frequently seen experimentally. Aside from vacancy defects, tight-binding related investigations focused on impurities at different position across AGNRs and ZGNRs in different energy regimes [124].

To demonstrate how essential are the roles of the relative distance to an edge and sublattice, we now consider the transport in an infinitely-long nanoribbon with a single scatterer at various positions across the ribbon's width. Scatterers like substitutional impurities are the only impurity types considered here. A shift in the onsite potential,  $\epsilon_i$ , at the impurity site is used in a tight-binding description of the ribbons to account for atoms different from the host material. In our case for illustrative purposes, we fix the value at  $\epsilon_i = 2|t|$  where  $t = -2.7$  eV is the hopping parameter between adjacent carbon atoms in graphene.

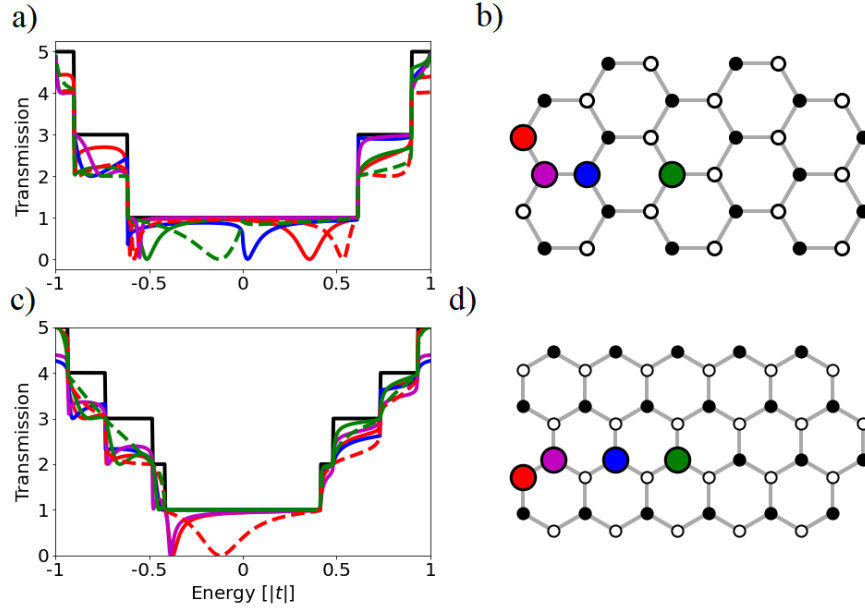


Figure 3.1: (a)-(c) Conductance vs. energy (in units of  $|t|$ ) for an infinite 6-ZGNR and 11-AGNR respectively. The infinite or periodic direction is along the vertical **3.1**. The solid black line represents the pristine case conductance whereas the solid-line curves show the conductance when an impurity is deposited at different locations shown in the adjacent schematics in (b)-(d). The red (green) dashed-lined curves represent the conductance for a vacancy deposited at the red (green) location for both ribbons.

The conductance for energies in the region around  $E_F = 0$  a through a 6-ZGNR (top panels) and 11-AGNR (bottom panels) for four different impurity locations are shown in solid lines in Fig. 3.1. The longitudinal periodic direction for both ribbons is going along the vertical. The impurity locations are varied between the edge and centre of the ribbon, as shown in the schematics (right panels). In

both cases, the dashed green and red lines shows the extreme case scenario where the impurity potential is set to  $10|t|$ , mimicking the transmission profile when a vacancy is present at those two positions.

For the 6-ZGNR shown in Fig. 3.1(a)(b), we first observe that all the atoms on the left edge are from the white sublattice and all the atoms on the opposite edge are from the other sublattice. In the top left panel depicting the transmission at different positions shown in the schematics, if we focus on the single channel region where  $0 < E \lesssim 0.6|t|$ , we see that the presence of a single impurity away from the edge at the center of the ribbon (green curve) has nearly no impact on the transmission. Indeed, the green curve follows scrupulously the pristine black solid quantised conductance for this energy range. Similar behaviour is observed for the transmission curve of the purple impurity. Below  $E \lesssim 0.6|t|$ , we see the presence of two dips for the red and blue curves whereas we note the absence of such dips for the purple and green curves. This suggests that if an atom belongs to the same sublattice as the closest nearby edge, the low-energy behaviour for the conductance displays a dip. Given the largely flat bands in this energy region and the electrons' low velocity, even a weak scatterer can create a quasi-localized state close to the Fermi energy, which will cause the observed conductance dips. As the strength of the scatterer is increased, the conductance dip broadens and shifts away from  $E_F = 0$ . The red dashed lines, representing a vacancy instead of a weak scatterer in this particular case, display the appearance of two dips close to both ends of the first plateau, *i.e.*  $E \approx \pm 0.6|t|$ . Consequently, we see not only the importance of the impurity's position and how it impacts the conductance in such systems but also the role sublattice plays in ZGNRs.

Fig. 3.1(c)(d) depict the single weak scatterers' presence across different positions in the AGNR case. We see that for  $E > 0$ , the transmission is very mildly impacted by the presence of the scatterer. We also note that a vacancy located at the edge (red dashed lines) still impacts the conductance for the low-energy regime whereas the electronic conductance seems blind to disorder when the vacancy is in the centre of the ribbon (green dashed lines). For both edge orientations in the second transmission plateaus and for higher transmission modes where  $E \gtrsim 0.6|t|$ , we see that the presence of the single impurity has a very mild impact on the conductance wherever the impurity is located.

Consequently, we see how the position across the ribbon of a single impurity affects the transmission. In AGNRs, weak disorder affects slightly the conductance regardless of its position. In ZGNRs, an impurity at an edge is responsible for a strong dip in conductance in the first transmission plateau. The breadth and energy at which the dip appears in the conductance gives additional information about the strength of the impurity. Furthermore, the appearance of a dip

is closely related to the distance to the same sublattice edge in the ZGNR case. It is then foreseeable that the conductance in presence of multiple impurities in AGNRs will be difficult to estimate since the effect of a single impurity is difficult to characterize with regard to its position. For ZGNR, except when the impurity lies on the edge or on a position close to the edge with the same edge's sublattice, it seems also difficult to directly relate transport properties to the position of scatterers.

### 3.2.2 Transport properties in the presence of multiple impurities in GNRs

Now that we have seen the different effects that a single impurity can have on the conductance in a nanoribbon depending on the orientation of the edge and its position, we need to understand what happens when a pair of impurities is present in this type of structure. Indeed, we will see that it is not generally possible to predict the effect that a pair of impurities will have on the conductance by considering a simple linear combination of the individual effects of their single equivalents.

One can also notice a certain analogy between the effect of quantum interference on charge transport depending on the impurity positions within the sublattice of a nanoribbon and charge transport in polycyclic molecules. In the field of molecular electronics, when a molecule like anthracene is placed between two electrodes, the constructive or destructive interferences that also manifest in the study of electronic transport show a dependence on where the electrodes are positioned [174]. An analogy of where the electrodes are positioned depending on the so-called Magic number and the sublattice position of the impurities in GNRs regarding constructive or destructive interferences can thus be drawn.

Let us now consider the effect of multiple impurities embedded in nanoribbons and see if their signatures on quantum transport can be explained by considering the effects of their single counterparts. The conductance with respect to energy for a 6-ZGNR (top panels) and 11-AGNR (bottom panels) subject to weak disorder are shown in left and right panels of Fig. 3.2 respectively. The energy range is now constrained to  $E > 0$  as the impurity strength,  $\epsilon_i = 2|t|$ , has been set to account for the weak scatterers' presence across the ribbons. The adjacent panels in the middle of Fig. 3.2 show where the pair of impurities are deposited across the ribbons with different edge orientations. In both panels, the single coloured solid lines represent the transmission for a single impurity present at the locations shown in the adjacent schematics. The combination of the 2 impurities are shown in the corresponding conductance plots as a dotted line in all the different conductance vs. energy plots.

Even if non-exhaustive, the various number of different scenarios are interesting

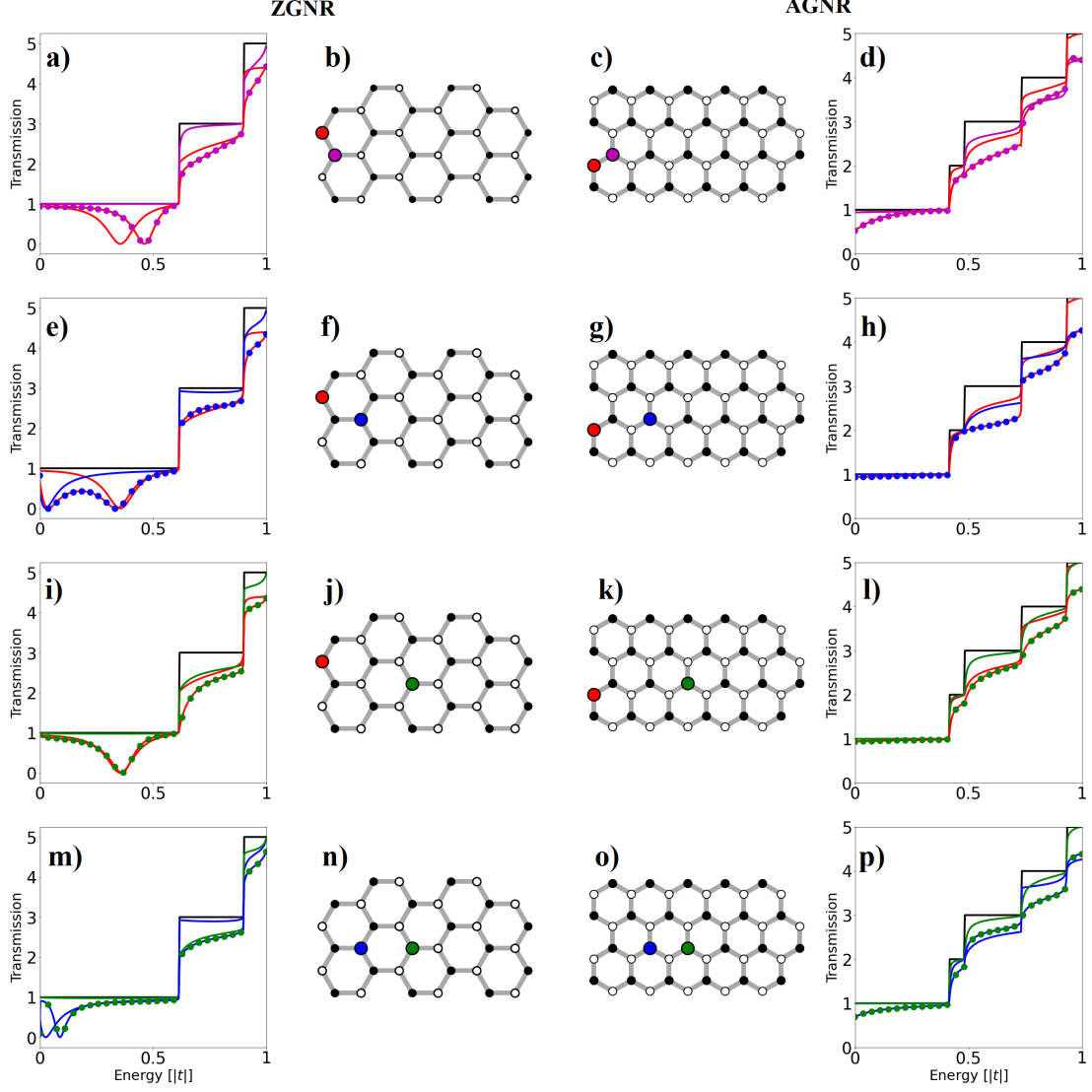


Figure 3.2: Single and combined impurities' conductances shown for different edge-terminated ribbons and for different positions of the weak scatterers. In all the conductance plots, the solid black line represents the pristine quantised transmission, the solid single-coloured lines show the conductance when there is only one impurity shown in the adjacent schematics. The double-coloured dotted lines show the conductance for the combination of the pair of impurities shown in the nearby schematics.

to be scrutinised. For the AGNR case, if we focus on the panel Fig. 3.2(c)(d), we first see that the single red and purple impurity curves are equal to the pristine transmission represented by the solid black line on the first transmission plateau. The combined pair of impurities holds an unexpected signature as we can observe a dip in conductance for  $E_F = 0$ . This is rather interesting as no linear combination of the single impurity cases' conductances can explain this dip, once more underlining the non-linear nature of interference effects in quantum transport. Similar behaviour is observed in Fig. 3.2(o)(p) whereas the central panels i.e Fig. 3.2(g)(h) and Fig. 3.2(k)(l) behaves more conventionally as all the 3 curves

are flat in the first transmission plateau. This suggests that the inter-impurity distance also has a role to play for the low-energy regime in the AGNR case when several impurities are present across the ribbon width. For the higher energy regime, the picture is more complicated as once again, it is difficult to assign the behaviour of the pair of impurities as a combination of their single counterparts. As mentioned in chapter 2, multiple scatterers means the possibility for electrons to experience multiple interference and resonance effects. These effects arising from the quantum nature of electrons and their confinement due to edges makes it difficult to infer straightforward causality.

In the ZGNR cases shown on the left panels with their associated schematics, the picture looks easier to comprehend for the low-energy regime, i.e  $E \lesssim 0.6|t|$ . As one or two of the single impurities' conductances present a dip in conductance, the resulting conductance of the pair of impurities seems to follow the single impurity cases counterparts. This is particularly true when we look at the central panels Fig. 3.2(e)(f) and Fig. 3.2(i)(j). However, this is still non-linear as there are no parameters that fit the 2 single impurity curves over the entire low-energy range that will predict the combined impurity case. Nevertheless, Fig. 3.2(a)(b) and Fig. 3.2(m)(n) are also interesting as we see a certain shift in the appearance of the conductance dip of the pair of impurities' conductance when compared to the single impurities' conductances. Therefore, the energy at which a dip appears is not necessarily indicative of the impurity's location.

For higher-energy modes, the conductances in the AGNRs and ZGNRs, whatever the considered pair of impurities, is strongly impacted by the presence of the pair of impurities. However, the impact impurities have in these scenarios is less sensitive to a particular position distribution. No clear signatures of the different combinations are shown through their respective conductances, making it hard to relate transport and structural properties in the presence of weak disorder. In the top panels, the first energy plateau manifests some conductance dips that are related to the single impurities' cases behaviours. We hardly expect the conductance of combined impurities to be expressed as a linear combination of their respective single conductances. There are no  $\alpha$  and  $\beta$  parameters for the entire energy range such that :

$$T_{\blacksquare} = \alpha T_{\blacksquare} + \beta T_{\blacksquare}$$

Indeed, quantum interferences due to multiple scattering processes cannot be explained in a linear fashion [74]. As discussed in the methods section, the tight-binding Green's function for the linear chain in the presence of multiple impurities was displaying interference terms mirroring the huge amount of possible scattering events an electron can go through. As we increase the number of impurities and we extend the dimensionality by considering a two-dimensional material like GNRs,

the quantum scattering events and their intrinsic non-linearity hinders greatly the perspective of finding a simple relationship between electronic transport and structural properties. Fortunately, destructive interference due to multiple electronic waves' reflections between impurities, a complex quantum behaviour, can be easily captured by ML models due to their high non-linearity.

### 3.3 Machine learning quantum transport in disordered GNRs

Supervised learning techniques rely on labeled training data to learn the mapping between inputs and outputs. This mapping is represented by a function, also known as a model, that can be used to make predictions on new, unseen data. The quality of this function is determined by how well it generalizes to new examples, which is closely related to how well it captures the underlying relationships in the training data. One of the most decisive steps in a ML task is deciding the manner in which the system is described in order to guarantee its uniqueness. Indeed, a knowledgeable description has to be provided such that the description of a random configuration is not mistaken with another one. It is then necessary for the descriptor to meet some conditions like uniqueness, differentiability and to reproduce embedded symmetries of the characterised system. The first rep-

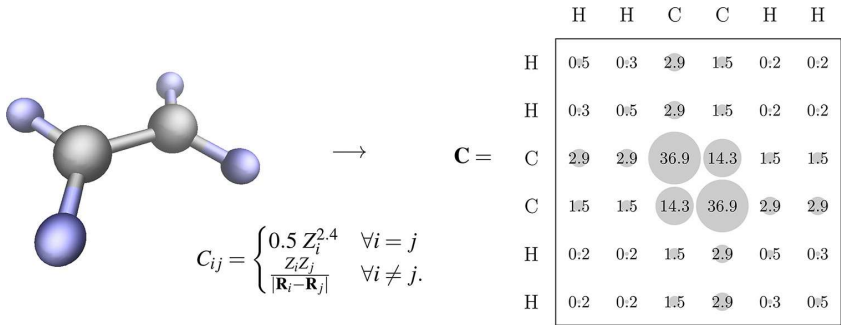


Figure 3.3: Coulomb matrix representation of Ethene. Adapted from [138].

resentation which we consider is that proposed for the description of molecules using the Coulomb matrix [138, 175]. As shown in Fig. 3.3, molecules are represented by a square matrix where the matrix elements encode energetic/repulsion informations via the charges  $Z_i$  and geometric/distance informations via the coordinates  $\mathbf{R}_i$  of each atom. Chemical compound description notably through the

Coulomb matrix representation has inspired some previous work on transport in disordered GNRs done by Lopez-Bezanilla et al. [176]. This work adapted the Coulomb matrix representation to encode the same energetic/distance information between the different atoms constituting molecules for the purpose of studying quantum transport in disordered nanoribbons. This work is the first attempt known to predict quantum transport in disordered GNRs with machine learning. The descriptor used in this work is also a square matrix  $\mathbf{M}$ , that encodes energetic and geometrical features to describe the system defined as follows:

$$\mathbf{M}_{ij} = \begin{cases} \epsilon_i & \forall i = j \\ t_{ij} & \forall i \text{ adjacent } j \\ \sqrt{d_{ij}} & \text{otherwise} \end{cases}$$

where  $\epsilon_i$  is the onsite potential of a site  $i$ ,  $t_{ij}$  is the hopping term between neighbouring sites  $i$  and  $j$  and  $\sqrt{d_{ij}}$  is the square root of the relative distance between two atoms across the system.  $\mathbf{M}$  scales with the number of atoms in the central device region and can be very prohibitive as the system size is increased. This descriptor, that we call **DMAT** (as for Distance MATrix) is an augmented version of the tight-binding Hamiltonian of the central device region where an additional information, namely  $\sqrt{d_{ij}}$  encodes the distance of atoms from one another. Contrary to the Hamiltonian matrix that is rather sparse and can be reduced to a tri-block diagonal matrix,  $\mathbf{M}$  is a full matrix making it difficult if it has to be used as a feature vector. It gives information about the energetic features of the system and the relative distances between impurities but omits important structural details such as distances from the edges and sublattice dependency. Indeed, as seen in the previous section, these features are found to play a critical role in how an impurity impacts the transmission [108, 124]. Nonetheless, the square matrix  $\mathbf{M}$  has a size that directly depends on the number of sites across the central device region. Consequently, this descriptor is computationally unadapted when the system size increases and will be computationally prohibitive even in the context of machine learning. If this study has to ever be employed to characterise transport properties in realistically disordered systems where ribbons easily count hundreds of thousand atoms, this representation will not be tractable as the size of the input vector will be unwieldy. Furthermore, the work conducted by Lopez-Bezanilla [176] is using a particular ML approach, namely kernel ridge regression (KRR). As we will see in the following sections and particularly with Eq. 3.2, this algorithm has advantages but is also known to suffer from the size of the training set. Indeed, as we will see in more details later throughout this chapter, KRR defines a metric in the feature space by essentially doing matrix inversion. The size of the matrix to be inverted scales with the number of samples in the training set. And knowing that each sample or configuration is described by an input vector that scales, in the present case, with the number of atoms in

each configuration indicates how computationally prohibitive this descriptor is. In our work, we give more attention to the distance that impurities have from edges of the ribbon and to their relative sublattice occupancy. By considering the impurities' positions only and removing the background, we seek to find an approach that is firstly tractable in terms of input vector size but also that can be adapted to any polygon-shaped nanostructures as long as it has edges. Accordingly, we have tried to describe the randomly generated configurations by several different descriptors:

1. **D2E** (distance to edge): A sorted vector where each element represents the distance of an impurity from edges. The elements are sorted in ascending order as having non-sorted distances will impede the learning process of structural similarities. Note that this descriptor includes no inter-impurity information, only information about the overall distribution of impurities across the ribbon width. Consequently, this descriptor is not able to capture multiple scattering events, interferences and Fabry-Perot like resonances as these effects depend on inter-impurity distance. A distinction has to be made whether one deals with AGNR or ZGNR systems. In zigzag-shaped GNR, edges are composed of atoms belonging to the same sublattice, and studies have shown that an impurity near an edge of the same sublattice type has a major impact on back-scattering process and therefore on transmission [108, 124]. For this reason, we split in two different cases the first descriptor :
  - For armchair-edged systems, the distance considered is the distance from the closest edge.
  - For zigzag-edged systems, the distance to the same sublattice edge is considered.
2. **D2E + Triup**: The second descriptor is a triangular upper matrix where the diagonal elements correspond to the **D2E** descriptor and the upper off-diagonal terms are the relative distances between the impurities in the system. Since the full matrix is symmetric, the redundancy of information is detrimental in terms of performance. Consequently, this descriptor combines the unique information from the **D2E** and **DMAT** descriptors where both the distance to the edge and the inter-impurity distance are gathered in a vector form. Fig. 3.4 shows how a single random configuration is represented in a matricial form, later transformed as a vector.
3. **D2E + Triup(dx dy)**: The third descriptor is a square matrix where the diagonal elements correspond to the **D2E** descriptor, the upper off-diagonal terms are the longitudinal distances and the lower off-diagonal terms represent the transversal distances between impurities in the system.

4. **D2E + Triup(Subpol)**: It corresponds to another version of the **D2E + Triup** descriptor. The main difference is if two impurities do not belong to the same sublattice, the relative distance accounted between them will be negative. Thus, this descriptor highlights the relative sublattice occupancy as an important feature in addition to impurities relative distances.

Once the descriptor is chosen, the corresponding input vector is simply a flattening of the descriptor matrix into a list of elements, with the distinction that descriptors in the form of an upper triangular matrix only consider the diagonal and the elements in the upper part.

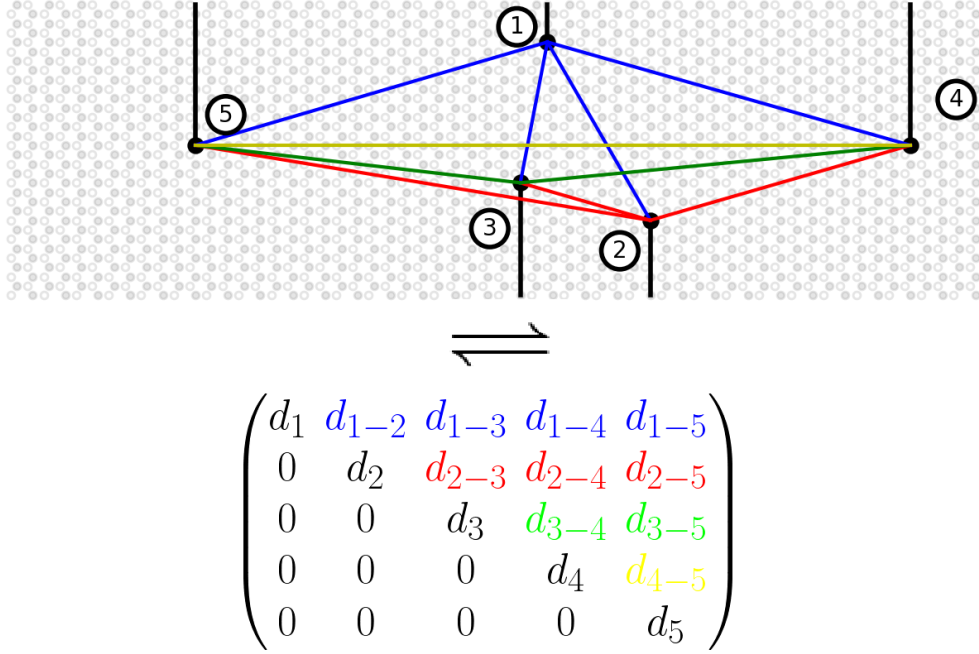


Figure 3.4: Example of the **D2E + Triup** descriptor for a random configuration: The diagonal elements encode the distance of the impurities to the closest edge whereas the upper off-diagonal elements carry information on relative distance between impurities.

To shed light on the symmetries considered in our approach, we account for rotational and translational symmetries by incorporating relative distances rather than coordinates [177]. Additionally, we sometimes address sublattice and inversion symmetries by carefully ordering the descriptors based on the proximity of impurity sites within the same sublattice. Still, the descriptors we have designed in our work are non-invertible, which means that they cannot precisely recreate the entire system from the descriptor alone. It is true that certain descriptors, like the D2E descriptor, primarily capture the distribution of impurities, resulting in multiple systems corresponding to the same descriptor. This inherent non-invertibility is a limitation that was considered. Suggestions to explore potential extensions of our methods, such as those commonly applied to molecules, is intriguing and could serve as a valuable avenue for future work and research [177].

Given that our systems typically have fixed lattices with impurity sites incorporated into the descriptor, investigating techniques for incorporating symmetries in a more comprehensive manner would indeed add depth to our approach.

### 3.3.1 Kernel ridge regression vs. neural networks

With the different descriptors provided, our goal is to accurately predict the transmission of an unseen disordered configuration given information about its geometrical properties. Two different models, namely kernel ridge regression (KRR) and neural networks (NN) have been used throughout this chapter. These two methods have their own properties and subtleties which offer advantages and drawbacks but proven successful in many other scientific contexts [138].

#### Kernel ridge regression

Following the work conducted by Lopez-Bezanilla [176] and many successes in predicting molecule properties in a chemistry context [138, 175], we have decided to use this model to predict quantum transport. Because the relationship between our input vector which describes the impurities' positions and the transmission at a certain energy is highly non-linear, we need to find a method that will be robust in estimating the output despite the inherent non-linearity. By using the so-called kernel trick, KRR is a form of regression where a preliminary mapping into feature space allows to predict an output by linear ridge regression techniques (cf. Section 2.4). The Laplacian kernel model where  $k(x, x') = \exp(-\frac{1}{\sigma} |x - x'|)$  has been used, yielding promising results in a large array of applications [138, 175]. The kernel function is essentially assigning a conceptual distance value for two configurations described respectively by  $x$  and  $x'$ . Particularly, in our concern, this model predicts the transmission  $T^{\text{pred}}$  at an energy  $E$  for a certain descriptor  $\mathbf{D}_j$ , as a sum of weighted exponential functions such as:

$$T^{\text{pred}}(E, \mathbf{D}_j) = \sum_{I=1}^{N_t} \alpha_I(E) e^{(-\frac{1}{\sigma} |\mathbf{D}_i - \mathbf{D}_j|)} \quad (3.1)$$

where  $N_t$  is the number of samples in the training set. The solution to find the coefficient vector  $\alpha$  are directly related to the inversion of the kernel matrix :

$$\alpha = [\mathbf{K} + \lambda \mathbf{I}]^{-1} T^{\text{ref}}(E) \quad (3.2)$$

where  $\mathbf{K}_{ij} = e^{(-\frac{1}{\sigma} |\mathbf{D}_i - \mathbf{D}_j|)}$  is the kernel matrix and  $T^{\text{ref}}(E)$  is the output transmission vector from the training set for a particular energy  $E$ . It should be mentioned that the learning from the output labels is realised on the variation of transmission  $\Delta G(E) = T(E) - T_{\text{pristine}}(E)$  and not on the transmission itself. The variation of transmission, by removing the general trend encoded in

the pristine transmission, ensures to grasp more information about the transport properties induced by a specific impurity configuration. Moreover, transmission alone gives inconclusive results because the effect of the impurities is concealed in the general opening modes' scheme whilst the variation in transmission bears signatures of more heterogeneous effects due to disorder. An important remark is that the kernel matrix  $\mathbf{K}$  depends only on the descriptors  $\mathbf{D}_j$  that encode the structural properties of disordered GNRs. No energy information is encoded in the inputs thus the Kernel Matrix  $\mathbf{K}$  is the same for all energies. The training set allows for an estimation of the best hyperparameters such as the regularisation parameter  $\lambda$  and the width of the Laplacian kernel  $\sigma$  by performing a fine-grained grid-search for each of the descriptors. The best parameters defining the optimal overall MAE for each different data set and their corresponding descriptors are addressed in the KRR column of table 3.1.

### Neural networks

Here in addition to the KRR method, we have also implemented a neural network learning task. There is a major advantage in the usage of a NN compared to KRR. The KRR method faces issues when the data set size is getting too big. Indeed, as the matrix  $\mathbf{K}$  directly scales with the training set size in Eq. 3.2, one faces memory issues if the training set size is extended by more data. This goes against our primary use of machine learning that inspires this work since we seek to optimize and complement techniques that are computationally expensive. The accumulation of knowledge by increasing the data set size is limited when KRR is used. An alternative is to use neural network which are resilient to very huge data set as they are not bounded by similar memory issues, as the memory required here depends on the complexity of the network, not on the size of the data set it trains on. However, a neural network acts like a black box when it comes to comprehend the way it predicts an output with regard to an input. It is a near-to-impossible task to fully understand the relationships that a NN builds between input vector elements and their higher order combinations through the sequential hidden layers.

The descriptors for the neural network are the same as the aforementioned ones in the descriptor section except that the energy is now added as an input value. Thereby, the learning is global here and the energetic aspect is directly encoded in the input values. The neuron architecture for the hidden layer has been intensely studied and fine-tuned by a thorough examination of the best performance from the test set. The selected parameters are summarised in the NN column of table 3.1. All the weights are initialised with different weight initialisation function that depends on the number of incoming neurons from the former layer (cf. weights initialiser column in table 3.1). The batches to train our NN model are

| Systems    |              | Hyperparameters |           | KRR    |                | Neural Network |             |                     |            |        |
|------------|--------------|-----------------|-----------|--------|----------------|----------------|-------------|---------------------|------------|--------|
|            |              | $\sigma$        | $\alpha$  | MAE    | Topology       | Activation     | Dropout (%) | Weights initialiser | Batch size | MAE    |
| 16-AGNR-5  | D2E          | 100             | $10^{-8}$ | 0.068  | $5 \times 135$ | SeLU           | 1           | lecun_uniform       | 1024       | 0.0676 |
|            | DMAT         | 100             | $10^{-5}$ | 0.08   | $5 \times 135$ | SeLU           | 1           | lecun_uniform       | 1024       | 0.0862 |
|            | TRIUP        | 50              | $10^{-5}$ | 0.0597 | $5 \times 110$ | SeLU           | 2           | lecun_uniform       | 1024       | 0.0679 |
|            | TRIUP_subpol | 250             | $10^{-5}$ | 0.0509 | $5 \times 125$ | SeLU           | 2           | lecun_uniform       | 1024       | 0.0598 |
|            | TRIUP_dxdy   | 50              | $10^{-5}$ | 0.0615 | $5 \times 135$ | SeLU           | 2           | lecun_uniform       | 1024       | 0.0682 |
| 32-AGNR-30 | D2E          | 700             | $10^{-7}$ | 0.0579 | $5 \times 135$ | SeLU           | 1           | lecun_uniform       | 1024       | 0.0710 |
|            | DMAT         | 850             | $10^{-5}$ | 0.0898 | $5 \times 135$ | SeLU           | 1           | lecun_uniform       | 1024       | 0.0902 |
|            | TRIUP        | 650             | $10^{-6}$ | 0.0564 | $5 \times 135$ | SeLU           | 1           | lecun_uniform       | 1024       | 0.0752 |
|            | TRIUP_subpol | 700             | $10^{-6}$ | 0.0549 | $5 \times 135$ | SeLU           | 1           | lecun_uniform       | 1024       | 0.0747 |
|            | TRIUP_dxdy   | 300             | $10^{-5}$ | 0.0557 | $5 \times 125$ | SeLU           | 2           | lecun_uniform       | 1024       | 0.0755 |
| 10-ZGNR-10 | D2E          | 100             | $10^{-8}$ | 0.1138 | $5 \times 110$ | SeLU           | 4           | lecun_uniform       | 1024       | 0.1106 |
|            | DMAT         | 50              | $10^{-6}$ | 0.1778 | $5 \times 110$ | SeLU           | 4           | lecun_uniform       | 1024       | 0.1903 |
|            | TRIUP        | 50              | $10^{-7}$ | 0.108  | $5 \times 110$ | SeLU           | 4           | lecun_uniform       | 1024       | 0.0965 |
|            | TRIUP_subpol | 100             | $10^{-8}$ | 0.1124 | $5 \times 110$ | SeLU           | 2           | lecun_uniform       | 1024       | 0.1019 |
|            | TRIUP_dxdy   | 250             | $10^{-9}$ | 0.1045 | $6 \times 120$ | SeLU           | 2           | lecun_uniform       | 1024       | 0.0893 |
| 18-ZGNR-52 | D2E          | 200             | $10^{-9}$ | 0.061  | $4 \times 100$ | ReLU           | 0           | he_normal           | 256        | 0.0605 |
|            | DMAT         | 250             | $10^{-4}$ | 0.1562 | $4 \times 100$ | ReLU           | 0           | he_normal           | 256        | 0.1409 |
|            | TRIUP        | 800             | $10^{-6}$ | 0.063  | $5 \times 100$ | ReLU           | 0           | he_normal           | 256        | 0.0608 |
|            | TRIUP_subpol | 250             | $10^{-5}$ | 0.0627 | $5 \times 135$ | SeLU           | 1           | lecun_uniform       | 1024       | 0.0607 |
|            | TRIUP_dxdy   | 900             | $10^{-6}$ | 0.0617 | $5 \times 110$ | SeLU           | 2           | lecun_uniform       | 1024       | 0.0619 |

Table 3.1: An overview table of the different ML models and descriptors applied to different types of nanoribbons. The KRR subcolumns summarise the optimal hyperparameters to get to the lowest energy-range averaged MAEs. The NN subcolumns gives the details of the topology: for instance ' $5 \times 135$ ' means 5 hidden layers of 135 nodes each. The energy-range averaged MAEs on the last column gives the overall performance for the different NNs alongside the used description.

addressed in table 3.1 and the neural networks have been trained using an early-stopping scheme whenever the learning curve is flat or there is no decrease in the loss function. One observation to be made regarding the size of the parameters in our neural network models is that it appears to be quite large in comparison to the amount of input data available. Whilst this could lead to overfitting, it should be noted that we have tackled this problem by using various dropout rates over the hidden layers and early stopping callback. This preliminary work serves more as a proof of concept, and fully-connected neural network architectures have indeed been attempted on our dataset. However, achieving convergence to an optimized solution has proven to be more challenging with fewer nodes per hidden layer. As a result, we have chosen to retain a large number of nodes per hidden layer to converge more rapidly towards more optimal predictive performance.

### 3.3.2 Data set generation

Primarily, each configuration consists in an either zigzag or armchair-edged nanoribbon where five impurities are randomly dispersed. The disorder strength of these impurities consists in an increase of the onsite energy to  $\epsilon_{\text{impurity}} = 2|t|$  with  $t = -2.7$  eV being the hopping parameter. The onsite energies of the remaining carbon atoms are set to 0 eV. The hopping term between neighbouring sites across the ribbon is kept as  $t$  whether the neighbouring sites are carbon or impurity atoms. A realistic tight-binding model would account for the hopping term to be different between impurity and carbon atoms as the hopping parameter is related to the bond length between neighbouring atoms, their atomic species and

orbital types for instance. However, we keep  $t$  constant as tuning an effective onsite potential could account for the impurity’s specific nature. In both cases, the armchair-edged and zigzag-edged GNRs have comparable sizes and one can evaluate the importance of the edge nature both on the learning process and transport properties. For each configuration, we save in a configuration file the following elements :

- The  $(x, y)$  coordinates of each impurity with respect to the origin taken as the lowest carbon atom in the leftmost part of the central device region.
- The sublattice to which an impurity belongs.

This information is sufficient in order to create the different descriptors discussed previously. The output label is obtained via electronic transport calculations, using TBtrans [158]. For each configuration, an optimised version of the recursive GF method is applied to obtain the GF of interest for the entire device [158]. Semi-infinite left and right leads are attached to the central device region subject to disorder and thanks to the Caroli Formula, we obtain the transmission as a function of energy  $T(E)$ . The energy range considered here depends on the size, precisely on the width of the different ribbons and there are 50 energy points onto which we perform the transmission’s calculation. When the KRR method was used, the prediction of the transmission was carried for each energy point. Unlike KRR, the energy  $E$  is an additional input in our feature vector for the NN method. Therefore the model for one particular system (in terms of width and length) finally retained in the NN case makes a global prediction without considering a single energy point but the full energy range. . All the energy range are expressed in terms of unit of  $|t|$ . 10000 configurations are implemented and split between a training set of 7000 samples, a validation set of 1000 samples to find hyperparameters and a test set of 2000 samples. The test set samples are unseen data for our ML models. After preliminary training, it allows to see how accurate our prediction of transmission is with respect to the given descriptors. This will serve as a way to assess how the trained models are performing.

### 3.4 Results

This section gives an overview of the different results for various ribbons with different edge orientations and sizes. In all the different scenarios, the number of impurities being fixed and sizes of the ribbons being varied, we study the impact of disorder for different values of impurity concentration. For low-concentration regime, the predictive performance of our ML models depends on the width of the ribbon. Indeed, as the ribbon’s width is narrow, quantum effects are more prone to give configuration-specific features due to the presence of impurities. Because all our descriptors encode the distance of an impurity to the edge through

**D2E**, the wider the ribbon, the harder it is to train our ML models. Indeed, as the ribbon's edges are further apart, the transversal quantum confinement of electrons is less pronounced, leading to self-averaging effects. The electronic properties in wide ribbons are less sensitive to the edge's nature. Consequently, if our descriptors are essentially giving information with respect to the edge, the description will fail as the ribbon's width is increased. Regardless of the edge orientation, small and narrow systems have their transport properties very accurately predicted given out the information of the impurity's distance to the edge. Complementary informations are also beneficial to enhance the predictive power of our ML models. As we move to longer but more importantly wider ribbons, the predictive performance suffers from self-averaging effect as we lose the quantum nature of electron confinement by the edges being further apart. Yet, **D2E** is the most crucial information and performs the best for both wide AGNRs and ZGNRs.

### 3.4.1 AGNR

Here are shown the results of our ML models transport properties' prediction for two kinds of ribbons with armchair edge terminations. Apart from the varying length, the width is varied between the two presented ribbons. Both of these ribbons are studied and the specificity of their data set's respective transmission distribution are addressed and discussed with regard to the ML models performance. The most important information to describe such systems is the distance of the impurity to the closest edge, i.e **D2E**. Supplemental informations such as the inter-impurity distance or the sublattice belonging seems to be relevant only when the ribbon's width is narrow enough. Indeed, as the ribbon's width is increased, the quantum confinement of the electrons does not provide configuration-specific feature due to the presence of impurities. This hinders the training of both ML models employed here. NN are particularly difficult to be optimally trained for the long and wide AGNR case.

#### Small and narrow AGNR

We start our investigation with a system consisting of a 16-AGNR unit-cell repeated 5 times over the longitudinal direction (cf. Fig. 3.5(a)). The transmissions that serve as labels for the entire data set are calculated over 50 energy points in the range  $E = [0, 0.5]|t|$ . As there are 160 atoms in the central device region which could potentially be replaced by five impurities, the concentration of impurities in this system is 3.125% and the total number of possible ribbons that could be generated is approximately  $8 \times 10^8$ . The usage of ML techniques circumvents the need to generate all the possible combinations and only a small fraction (one thousandth of a percent) of the entire space of possibilities is sufficient to

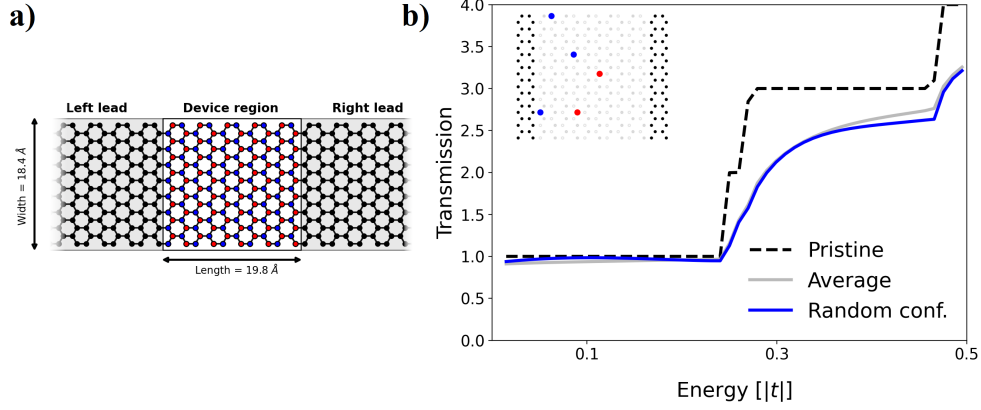


Figure 3.5: **(a)**- Mapping of a small armchair-edged nanoribbon with a repeated 16-AGNR pattern. The central region, where blue and red atoms encode the sublattice dependency, can host disorder whereas the grey shaded areas represent left and right pristine semi-infinite leads. **(b)**- Conductance vs. energy for a random configuration from the data set. The blue line shows the disordered transmission whereas the pristine and the configurational average transmission are respectively shown by the dashed black and grey lines. The inset provides the location and sublattice of the impurities across the ribbon.

get enough data for prediction. Fig. 3.5(a) shows the considered nanoribbon with the attached left and right leads consisting of semi-infinite pristine ribbons. Fig. 3.5(b) shows the conductance as a function of energy (in units of  $|t|$ ) in blue for a configuration from the data set. The pristine transmission is shown by a black dashed curve.

The quality and performance of the KRR and NN techniques coupled with the different descriptors are presented in Fig. 3.6. Fig. 3.6(a) gives an overview of the transmissions for the different configurations from the data set. The pristine transmission represented by the black dashed line correspond to the natural upper limit for all the configurations' transmissions. The green filled region correspond to the spread in values for the entire training set samples whereas the red solid curve represent the configurational average transmission. The blue error bars present over the configurational average represent the standard deviation,  $\sigma(G(E))$ , of the training set transmission's distribution and indicates another measure, apart from the shaded area.

The first detail that we observe is the distribution of the transmission for different configurations within the first plateau. Although the configurational average, hence a majority of configurations, seems to be very close to the pristine transmission along this energy range, there are still many configurations featuring conductance dips. These dips are uniformly distributed all along the first transmission plateau. When just a single impurity was considered in the bottom panels of Fig. 3.1, no signature of conductance dips in the first transmission plateau was

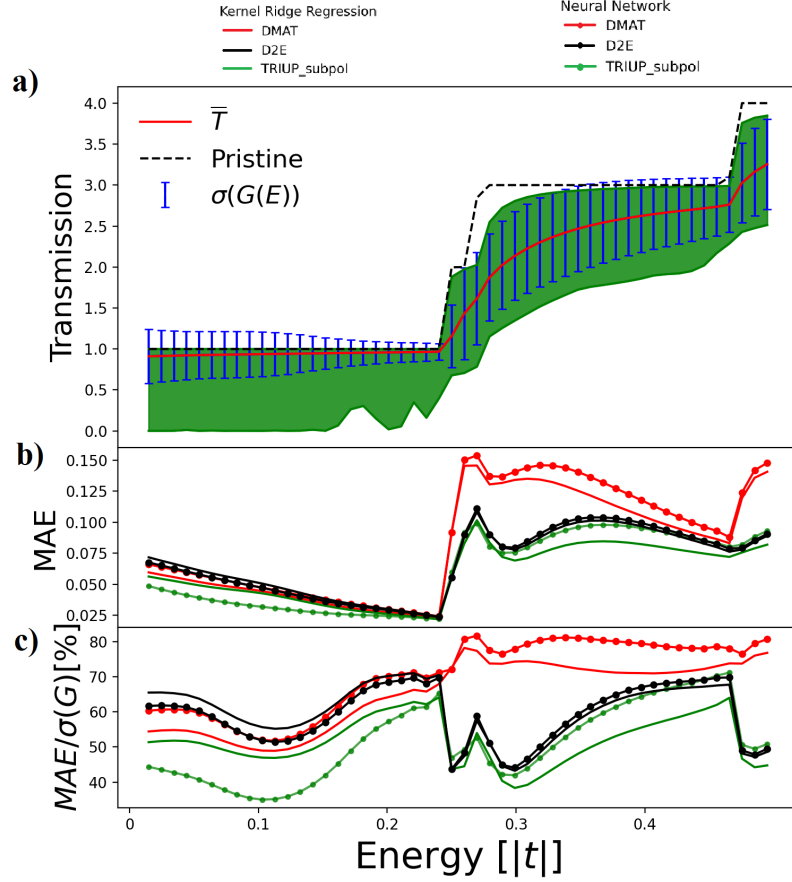


Figure 3.6: **a)** Transmission with respect to energy for the training set generated with the disordered 16-AGNR in Fig. 3.5. The dashed black line represent the pristine AGNR transmission. The red curve represent the configurational average transmission for the training set whereas the green shaded region shows the distribution of the different configurations' transmissions. **b)** Mean absolute error (MAE) with respect to energy for the different descriptors. **c)** Normalised  $\text{MAE}/\sigma(G)$  with respect to energy. In both central and lower panels, the energy averaged MAEs for the different descriptors and normalisation are given in table 3.1.

observed. This phenomenon arises from the quantum nature of electron waves interferences with the multiple weak scatterers present in the AGNR. Even though this conductance dip is not the signature of a single impurity onto transmission whatever its position, we see once again how non-linear and complex is the presence of multiple scatterers in the study of electronic transport. Moreover, we observe that  $\sigma(G(E))$  has not a uniform behaviour along the first transmission plateau. Indeed as we approach the onset of the second transmission channel, the standard deviation in transmission reduces and then increases drastically when we access the second plateau. Indeed, the opening of a new mode in transmission is allowing more electronic states to be available. These electronic states, lying in flat bands of the band structure are high effective-mass electrons. Thus, they have an increased probability to interact with the present impurities in the

system which reflects in high variability in transmission.

The Mean Absolute Error (MAE) for the different descriptors and different ML models with respect to energy are shown in Fig. 3.6(b). The descriptors have their own respective colours whereas the two used different ML models, namely KRR and NN are respectively shown by solid or dotted lines. We see that the performance of both ML techniques are closely related to how spread and diverse the training set samples are (cf. the error bars in Fig. 3.6(a)). The overall performances over the energy range for both KRR and NN techniques and for the different descriptors are gathered in table 3.1 and give a more quantitative insight. On the entire energy range, the descriptor **TRIUP-subpol** with NN is performing the best whereas the NN trained with the **DMAT** descriptor performs the worst. It should be noted that this panel is non-exhaustive as the other descriptors' MAEs have also been calculated but are not shown as they are all situated between these two extreme descriptors. For the first transmission plateau, whether KRR or NN is used, all the descriptors except the NN-trained **TRIUP-subpol** are performing in a similar fashion. Also, it is worth mentioning that all the MAEs for all descriptors and adopted ML models see a decrease in MAE as we get closer to the second transmission channel, directly following the according decrease in  $\sigma(G(E))$  in Fig. 3.6(a). At low energy, because the NN-trained **TRIUP-subpol** include the most complete set of information, we see that the more information we give, the better the performance. This descriptor encodes the distance to the closest edge as well as the inter-impurity distance with an additional sublattice information so it combines the useful information from **DMAT** and **D2E**. The different descriptors perform in a similar fashion with little to no differences between KRR and NN except for the **DMAT** descriptor. Retaining solely the inter-impurity distances does not ensure to accurately predict the transmission. Regarding the slight improvement **TRIUP-subpol** brings compared to the other descriptors, it is difficult to argue if the extra sublattice or inter-impurity distance information play a major role. Thus the low energy regime deserves a more in-depth study as we hardly see how comparatively valuable are the features encoded in the different descriptors.

When we move to the second transmission channel, the increase of variability in the transmission distribution is directly observable in the performance of ML models. The predictive models cope to make correct predictions due to the high degree of diversity related to scattering events occurring in these regions. Furthermore, let us remind that the learning is made with  $\Delta G(E) = T(E) - T_{\text{pristine}}(E)$ , the variation of transmission which emphasizes once more the wide disparity that there are between the training set samples in this region. As the energy is increased though, **DMAT** is globally underperforming compared to other descriptors hence inter-impurity distance on its own does not seem to be the crucial

ingredient in quasi one dimensional structures like GNRs. If we put **DMAT** aside, the **D2E** descriptor (solid black line) being present in all descriptors, one finds evident that it captures the most relevant feature to describe the impact of structural properties on quantum transport. This suggests that inter-impurity or interference effects are not as important as the distribution of the impurities relative to the edges.

The Fig. 3.6(c) essentially shows the same information as the central panel however the MAE is divided by  $\sigma(G(E))$ , the standard deviation of the data set distribution in transmission at each energy point  $E$ . This ensures to see how the learning performs in relation to the distribution's narrowness. One should not interpret a narrow distribution as beneficial for the predictive performance of ML models. In fact, the low variance in transmission at a particular energy has a detrimental effect in the learning process as it means that whatever the effort put in describing two different configurations, they will end up having the same transmission at the same energy due to self-averaging as we move out of quantum regime. This is inherently due to many factors: the intrinsic non-linearity of quantum transport that we are trying to overcome with ML models, the lack of a better description or the lack of optimisation of our models.

In the low energy region of the first plateau, the KRR-based descriptors underperforms globally on average and encourages to find a better description of low-energy backscattering phenomena that occur. It appears that the NN-based **TRIUP-subpol** outperforms all the other descriptors in the low energy region. This suggest that for this particular energy range, the prediction of transport is more sensitive to additional informations such as inter-impurity distance and relative sublattice. Orlof et al. [124] suggests that the low-energy scattering processes in a single impurity case are deeply dependent on intra/intervalley mixing effects in GNRs. Thus, an implementation in future work of valley-related information could give an explanation and extend the discussion towards the multiple scattering effects in AGNR systems. The fact that the NN performs better than its KRR counterparts for **TRIUP-subpol** also suggests that the energy information has an importance in performance. Indeed the KRR method, regardless of the adopted descriptor, is energy independent meaning that each transmission at one energy point has been trained independently from the other energy point.

### Longer and wider AGNR

We now consider a wider and longer armchair-edged ribbon used for the generation of the dataset. It consists in a 32-AGNR wide nanoribbon (cf. Fig. 3.7) repeated 30 times which corresponds to a 4nm wide - 12 nm long ribbon. As five impurities are randomly disposed in this ribbon, the concentration in impurities drops to 0.26% as there are 1920 atoms in this system. The transmission that

labels each configuration of the data set are now calculated over a larger energy window  $E = [0, 0.75]|t|$ .

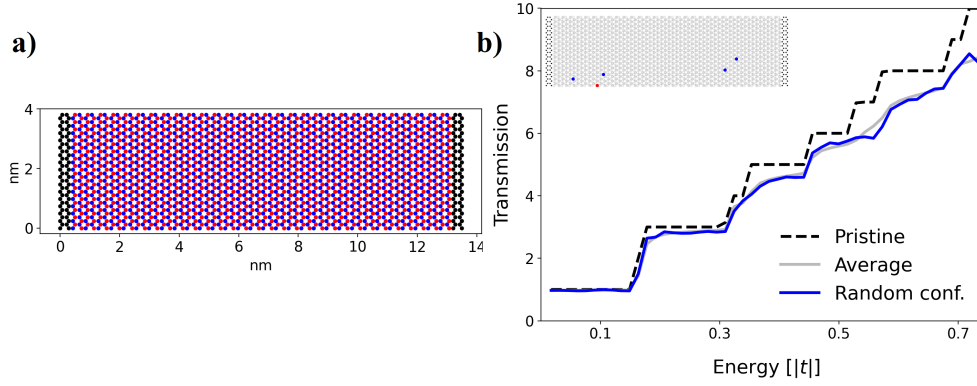


Figure 3.7: **(a)**- Modeled armchair-edged GNR with a 32-AGNR unit-cell repeated 30 times. The black atoms on the side represent the semi-infinite left and right leads attached to the central device region. Blue and red atoms categorise the sublattice dependency. **(b)**- Conductance vs. energy for a random configuration from the data set. The blue line shows the disordered transmission whereas the pristine and the configurational average transmission are respectively shown by the dashed black and grey lines. The inset provides the location and sublattice of the impurities across the ribbon.

Similar to the small AGNR-ribbon, we show the distribution of the different configurations' transmissions for the training set in Fig. 3.8(a). One of the first difference appearing in the wider ribbon is the transmission distribution in the first plateau. The wider the ribbon gets, the smaller the variance in conductance is in particular at low energy. As the distance between the two edges is increased compared to the small AGNR ribbon in Fig. 3.6, we expect that the randomly generated configurations have a higher probability to have more bulk disorder than for the precedent case study. The randomness of the generated configurations due to self-averaging effects result in less pronounced transmissions' signatures and causing the transmissions to be very similar despite varied positions.

A quantitative summary of the overall averaged MAE is shown in table 3.1 for all descriptors and ML techniques. The qualitative behaviour of the MAEs over the energy range are shown in Fig. 3.8(b). When new transmission channels open, we see once again spikes in the MAEs due to the interaction of low-velocity electrons with impurities as expected. Moreover, **DMAT**, on its own, performs poorly for both techniques whereas **TRIUP-subpol** performs the best on the entire energy range particularly for the KRR method. This is again particularly true for the low energy region where **TRIUP-subpol** outperforms all other descriptors. However, as all the descriptor performances are in the same ballpark, additional informations may not be crucial in performance. Thus, the distance to edge is the

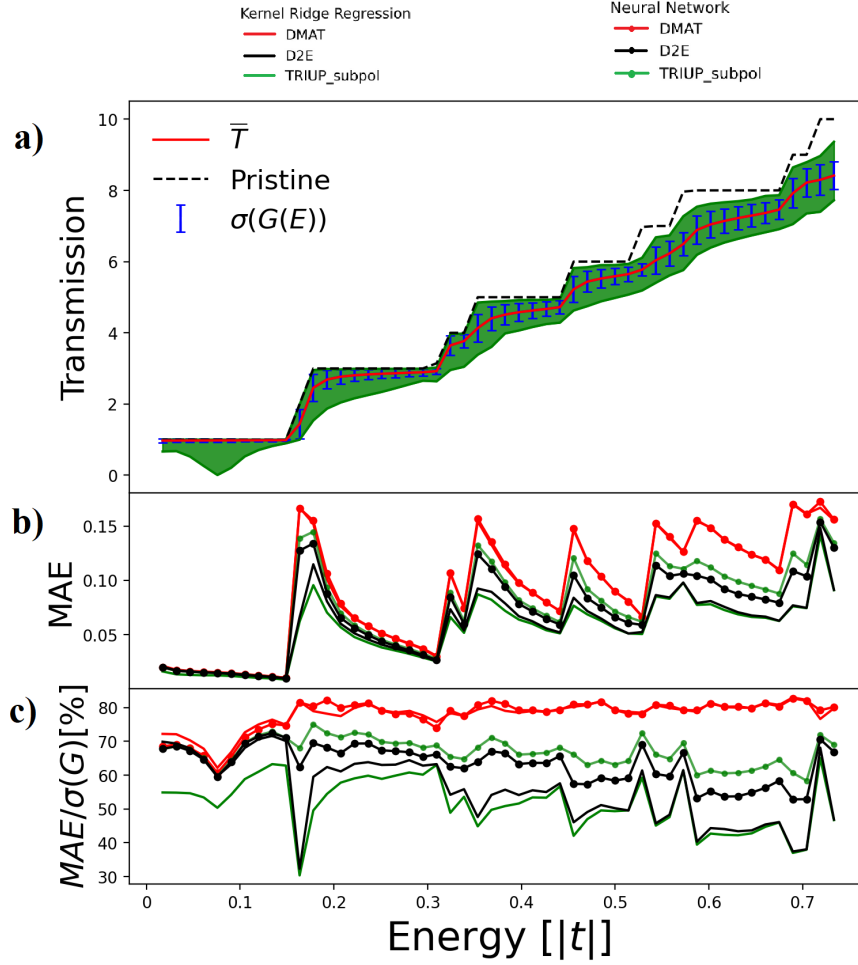


Figure 3.8: **a)** Transmission with respect to energy for 10-ZGNR. The dashed black line represent the pristine AGNR transmission. The red curve represent the configurational average transmission for the training set whereas the green shaded region shows the distribution of the different configurations' transmissions. The error bars in blue represent the standard deviation of the transmission distribution for the entire energy range. **b)** Mean absolute error (MAE) with respect to energy for the different descriptors. **c)** Normalised MAE/ $\sigma(G(E))$  with respect to energy. In both central and lower panels, the energy averaged MAEs for the different descriptors and normalisation are given.

crucial information that relates how disorder impact electronic transport whereas the importance of inter-impurity distance and the sublattice dependency must still be thoroughly investigated.

On the entire energy range, the distribution's transmission has a low variance particularly at the end of the different transmission plateaus. This reduces the MAE, linking performance to the variance of the training, and globally, the dataset. This is rather misleading as the low variance here is carried by the distribution of the transmission itself and not because of an enhanced performance by the ML models. Yet, it also tells that other features are at play and have not been

considered. The most striking observation from the central and bottom panels in this figure is the difference in performance between KRR and NN for all the descriptors except **DMAT**. This difference in performance first addresses how difficult it is to correctly parametrise neural networks compared to the KRR. For one descriptor, finding the best hyperparameters,  $\sigma$  for the laplacian kernel width and  $\alpha$  for the regularisation term for the KRR method can be realised through a grid-search. Yet, it is not straightforward to optimise a neural network as the amount of parameters of the neural network are directly depending on the number of nodes and hidden layers employed. Besides, the activation function, the weights' initialisation scheme, the dropout per layer, the batch size are many of the other hyperparameters that have to be taken into account when trying to optimise a NN.

When the MAE is normalised by  $\sigma(G)$  however as in Fig. 3.8(c), another obvious contrast with the central panel resides in the difference of behaviour of KRR-based MAEs compared to NN-based ones. Indeed, we see that the trend is similar for the central panel where after a spike or a transmission channel opening, there is a decrease for both KRR and NN regardless of the descriptor (except **DMAT**). When normalised by the transmission range, the MAE for NN models appear flattened therefore insensitive to the variation due to  $\sigma(G)$ . This can be explained by the fact that NN-based descriptors have also the energy encoded as an additional information. The difficulty in predicting transport for this particular armchair-edged ribbon and concentration could also be explained by the lack of variety among the generated different configurations. As a matter of fact, the standard deviation  $\sigma(G)$  of the training set is narrower for the big ribbon in comparison to the small AGNR ribbon in Fig. 3.5. The increase in length and more particularly in width combined with how crucial the **D2E** descriptor is suggest that the effect of the weak scatterers is more difficult for our ML models to predict. Most configurations behave quite similarly to the average, with configuration specific features being less pronounced, and giving the ML methods less to work with. A wider dataset could also enhance the performance of the NN however for the **D2E** descriptor. We have investigated wider datasets to train our model without finding any significant improvements. Yet, we note that the results for the NN tend asymptotically towards those of the KRR for high-energy range and a slight improvement is still ongoing towards the low-energy region. This suggests that there are still room for optimisation of our NN-models.

To concretely observe how our models performs when confronted to unseen data, we show in Fig. 3.9 two random configurations from the test set. Fig. 3.9(a)(b) show the transmission with respect to energy. The dashed black line represent the pristine transmission and the grey show the configurational averaged transmission. The insets display the positions of the impurities across the ribbons in

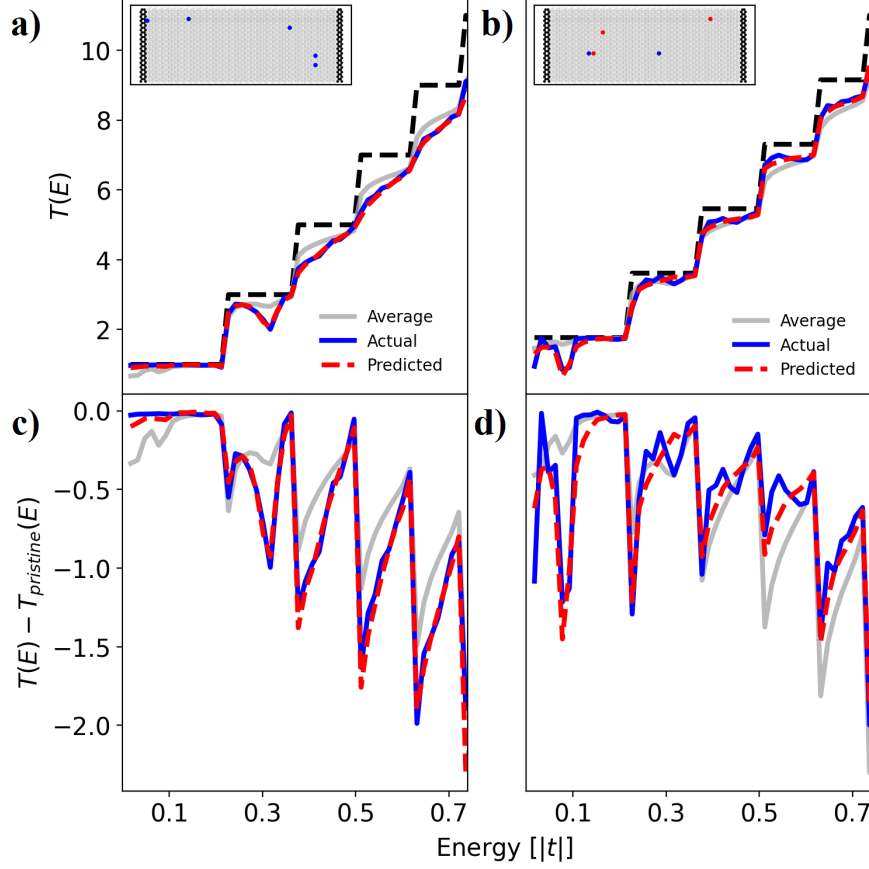


Figure 3.9: (a)(b)- Transmission  $T(E)$  of two random unseen configurations with respect to energy. The pristine transmission is shown by the dashed black line. The light grey curve represent the average training set transmission whereas the dashed red lines correspond to the prediction made by KRR with the **D2E + Triup(Subpol)** descriptor to be compared to the actual curve depicted in blue. Insets display the position and sublattice dependence of the impurities in the system. (c)(d)- Variation of transmission  $T(E) - T_{\text{pristine}}(E)$  with respect to energy.

their respective configurations. The sublattice which the impurities belongs to for the different configurations are shown in the inset by red or blue atoms. The actual transmission for this configuration is shown in solid blue line whereas the predictions of transmission itself, realised with KRR and the **TRIUP-subpol** descriptor is shown with the red-dashed curves. Fig. 3.9(c)(d) are essentially showing the same information except here is shown the variation of transmission  $T(E) - T_{\text{pristine}}(E)$  with respect to energy. The actual transmission's variation (blue solid lines) in Fig. 3.9(d) for this configuration is subject to unstable resonances in the middle of several transmission plateaus. We see that KRR has difficulties in capturing these complex unstabilities and predict smoother transmission values there. The predicted transmission and variation of transmission show good agreement and are closely related to the overall trend of the actual transmission. These results allow us to rule out the possibility that our ML model is only learning the configurational average. Yet, here is shown that the predicted

curves follow the actual transmission instead of the configurational average while observing the variation of transmission curves in Fig. 3.9(c)(d).

### 3.4.2 ZGNR

Here is presented an overview of the results of our ML models regarding transport in disordered ZGNRs. Two ribbons of different widths and lengths are investigated, and the particularity of each data set's transmission distribution is addressed and analyzed in relation to the performance of the ML models. This time, the distance between the impurity and the edge with same sublattice is the most crucial detail to define such systems. The sublattice degree of freedom is indeed known to play a major role as atoms on ZZ-edges all belong to the same sublattice [124]. Only when the ribbon's width is sufficiently small do additional details like the inter-impurity distance or the sublattice belonging appear to be significant. Unlike the wide and long AGNR system studied in the previous section, NN models are trained in a more effective way despite the self-averaging effect occurring with an increased ribbon width. Even if the width is increased, the conductance of the randomly generated configurations still present some configuration-specific transport features, improving the overall predictive performance of our ML models.

#### Small and narrow ZGNR

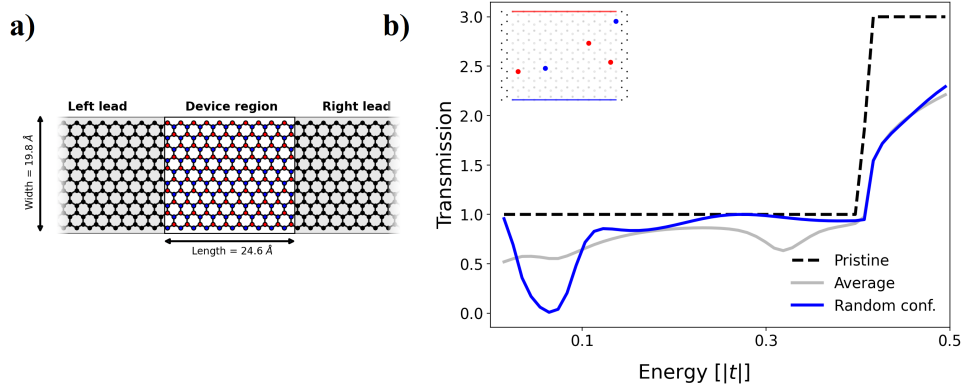


Figure 3.10: (a)- Mapping of a small zigzag-edged nanoribbon with a repeated 10-ZGNR pattern. The edges in ZGNRs are made of atoms from the same sublattice. (b)- Conductance vs. energy for a random configuration from the data set. The blue line shows the disordered transmission whereas the pristine and the configurational average transmission are respectively shown by the dashed black and grey lines. The inset provides the location and sublattice of the impurities across the ribbon. Red and blue lines at the edges are represented in the inset to see the distance of the impurities to the edge with the same sublattice.

In the zigzag-edged system shown above in the Fig. 3.10, consisting in a 10-ZGNR wide nanoribbon repeated 10 times, both KRR and NN methods alongside the commonly-used descriptors were used to predict the conductance of disordered

ZGNRs. The ribbon size for the ZGNR, comparable with its small AGNR counterpart in Fig. 3.5 allows to differentiate the specificity of the edge orientation onto predictive performance. There are 5 impurities randomly dispatched in a 200-atoms system, corresponding to a concentration of 2.5%. As the sublattice dependency plays a more critical role and each edge of the system is now associated with a different sublattice, the **D2E** descriptor takes as feature the distance of the edge having the same sublattice as the impurity. Indeed, several studies showed in the single impurity case, the paramount effect of sublattice dependency in relation to electronic transport [65–67, 69]. The closer an impurity from the same sublattice is present to one edge, the bigger the effect on back-scattering. For this particular reason, as mentioned before, the keystone descriptor, **D2E** from which are built the other descriptors, is encoding this information intrinsically. Indeed, the distance considered for the description is the distance from the same sublattice edge and not necessarily the closest one.

The quantitative and qualitative behaviour of the ML models’ performances are shown in the table 3.1 and in Fig. 3.11 for this particular small ZGNR. With the same convention as for the aforementioned AGNR systems, we observe a wider variance in the spread of transmission in the ZGNR case when looking at Fig. 3.11(a). The variability in transmission at each energy point is an advantage as configuration-specific features are improving the learning ability of our model. Indeed, it means a lower risk of confusion for our ML models as assigning a particular description to a particular transmission is easier in this case.

The MAEs for the different descriptors and the different ML techniques with respect to energy are shown in Fig. 3.11(b). Globally both qualitatively and quantitatively, we observe that the NNs trained with **TRIUP-dxdy** and with **DMAT** perform the best and worst respectively. Again, the best performing descriptors regardless of the employed ML models are all include the **D2E** descriptor and the overall increase is mainly due to additional informations. However, it is not possible to strongly state which of these additional informations, considering the similar performances, are crucial in the description of disorder. All the NN models have better performances than their KRR counterparts. As it is assumed that both of these models have been properly optimised, it means that the additional energy information given for NNs has helped in the overall performance increase. When we move to the MAE normalised by the standard deviation  $\sigma(G(E))$  in Fig. 3.11(c), the same trends are shown. The MAEs in the present case seem to drop for high values of  $\sigma(G(E))$  particularly at  $E \approx 0.32|t|$ . These trends were also present in the central panel but here the dip in MAE, so a better performance, is exaggerated by the normalisation even though the performance is slightly better.

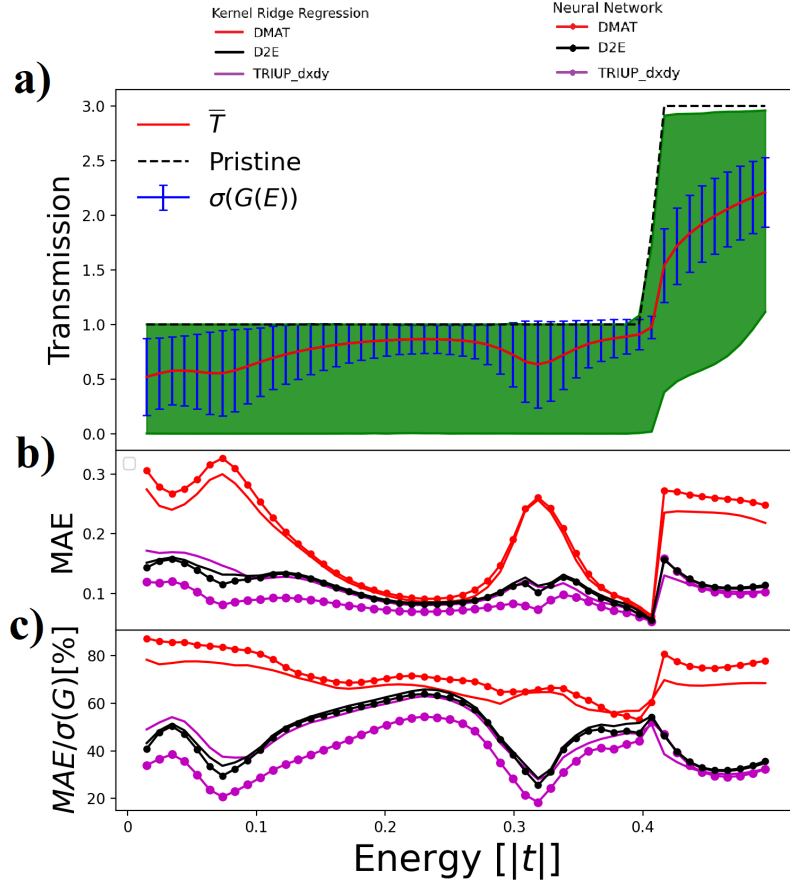


Figure 3.11: (a)- Transmission with respect to energy for 32-AGNR. The dashed black line represent the pristine ZGNR transmission. The red curve represent the configurational average transmission for the training set whereas the green shaded region shows the distribution of the different configurations' transmissions. (b)- Mean absolute error (MAE) with respect to energy for the different descriptors. (c)- Normalised  $MAE/\sigma(G(E))$  with respect to energy with respect to energy. In both central and lower panels, the energy averaged MAEs for the different descriptors and normalisation are given.

### Longer and wider ZGNR

To see how our models evolve as we consider a bigger size ribbon with a similar size as its AGNR counterpart, we have trained our models with a dataset containing randomly disordered ribbon with characteristics shown in Fig. 3.12. As there are 5 impurities randomly dispersed in the central device region made of 2080 atoms, the corresponding concentration of impurities is 0.24%. The width in this ribbon being increased, the generated ribbon have less probability to be on the edges. The resulting self-averaging effect may hinder the beneficial variety in transmission's distribution that helps the ML models to perform better. Following the same methodology, the results of the different ML models with the different descriptors are quantitatively and qualitatively in the table 3.1 and Fig. 3.13.

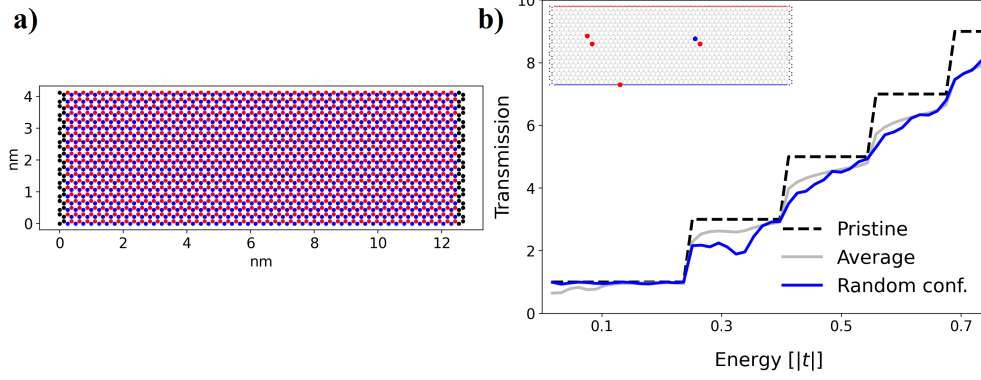


Figure 3.12: **(a)**- 20-ZGNR repeated 52 times across the length corresponding to a 4nm wide and 12.5nm long ribbon. The black atoms on the side represent the semi-infinite left and right leads attached to the central device region. Blue and red atoms categorise the sublattice dependency. **(b)**- Conductance vs. energy for a random configuration from the data set. The blue line shows the disordered transmission whereas the pristine and the configurational average transmission are respectively shown by the dashed black and grey lines. The inset provides the location and sublattice of the impurities across the ribbon. Red and blue lines at the edges are represented in the inset to see the distance of the impurities to the edge with the same sublattice.

As expected,  $\sigma(G(E))$  has decreased all over the energy range as the ribbon's width has been increased due to self-averaging effects in Fig. 3.13(a). At fixed number of impurities, the wider the ribbons, the less diverse the transmission signatures are. Again, the inter-impurity distance, encoded in **DMAT**, is performing poorly when we look at the MAE vs. energy and its normalised version in Fig. 3.13(b)(c). Here, regardless of the employed ML techniques, the performances of the entire descriptor set are shrinking down to the performance of the **D2E** descriptor. With the assumption that the adopted ML models are properly optimised, it means that the most meaningful description of disorder in a wide ZGNR with dilute concentration of impurities is the distance to the edge with the same sublattice. All the other informations, even if not detrimental and confusing, are not as valuable as the distance to the same sublattice edge encoded in **D2E**.

To grasp how accurate is the prediction of our ML models alongside the **D2E** descriptor, we are showing in Fig. 3.14 how the transmission of two unseen random configurations are predicted. We have used the KRR trained with the **D2E** to predict the actual transmission. The positions of the impurities are shown by red and blue atoms in the insets of the top panels. As we deal with ZGNRs that have sublattice polarised edges, we are representing the edges with red and blue bars to appreciate the distance of the impurities with respect to the same sublattice edge. For both panels, the red-dashed lines represent the predicted transmission whereas the blue solid lines are showing the actual transmission

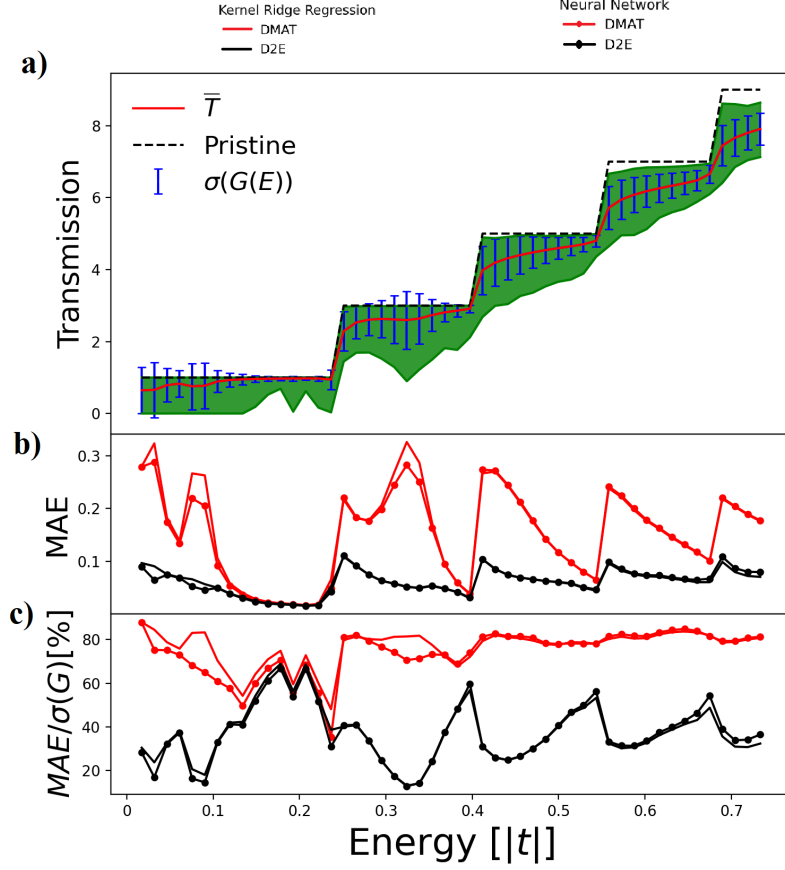


Figure 3.13: **Top:** Transmission with respect to energy for 18-ZGNR. The dashed black line represent the pristine AGNR transmission. The red curve represent the configurational average transmission for the training set whereas the green shaded region shows the distribution of the different configurations' transmissions. **Central:** Mean absolute error (MAE) with respect to energy for the different descriptors. **Lower:** Normalised MAE( $/\sigma(G(E))$ ) with respect to energy. In both central and lower panels, the energy averaged MAEs for the different descriptors and normalisation are given.

or the variation of transmission with respect to the pristine transmission in their respective panels. The predictions are globally accurate even though we see slight difficulties in predicting the transmission values at the energies situated in the middle of transmission plateaus.

### 3.5 Conclusion

This chapter presented the use of advanced machine learning techniques, such as kernel ridge regression and neural networks, to investigate the role of structure, geometry, and disorder in graphene nanoribbons. The simulations performed for electronic transport through disordered nanoribbons show that these techniques can be used to accurately estimate transmission profiles from geometrical details. The choice of descriptors for the machine learning algorithms plays a crucial

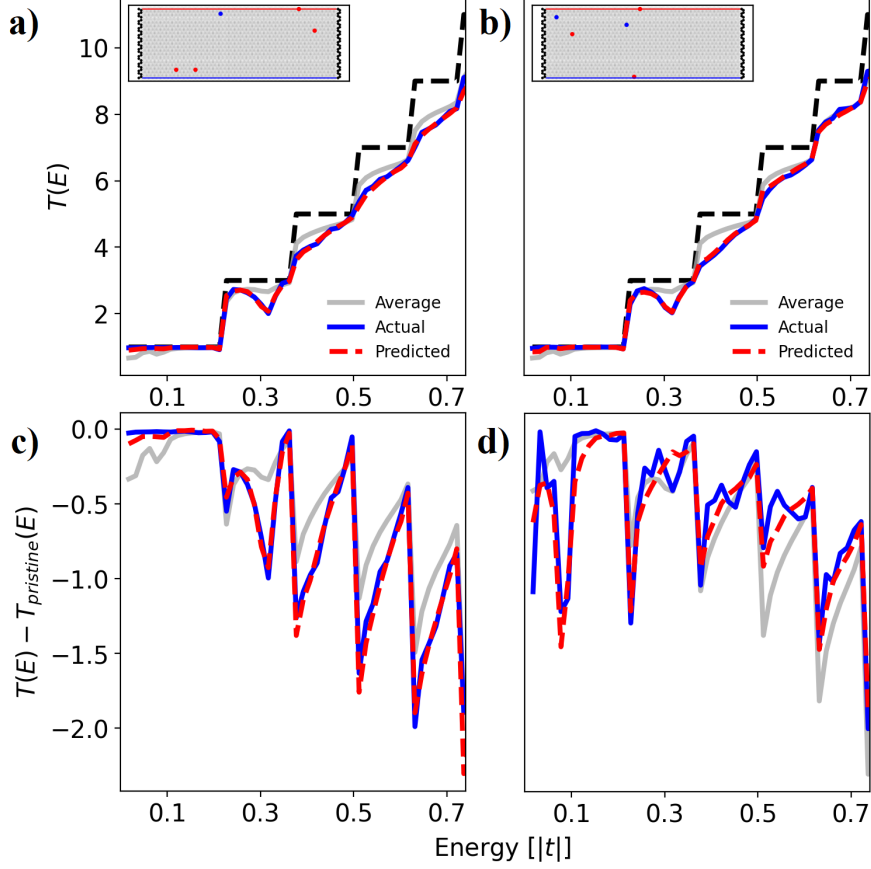


Figure 3.14: (a)(b)- Transmission  $T(E)$  of two random unseen configurations with respect to energy for 32-AGNR. The pristine transmission is shown by the dashed black line. The light grey curve represent the average training set transmission whereas the dashed red lines correspond to the prediction made by KRR with the **D2E** descriptor to be compared to the actual curve depicted in blue. Insets display the position and sublattice dependence of the impurities in the system. (c)(d)- Variation of transmission  $T(E) - T_{\text{pristine}}(E)$  with respect to energy.

role in their performance, and it is essential to understand the key features that describe how impurities impact quantum transport. An important part for the success in the KRR and NN methods lies in the diversity and non-uniformity of the configurations in the training set.

For the small and narrow AGNR system, the distance of the impurity to the closest edge is the most important information as it greatly enhances the predictive performance of our ML models. For the small system with zigzag edges, the distance of the impurity to the edge having the same sublattice is even more relevant as this allows ML models to predict successfully the transport characteristics of such ribbons. Complementary informations such as the inter-impurity distance and the relative sublattice improve the accuracy in predicting quantum transport for small systems with low concentration. As we move to longer and wider ribbons, the predictive performance of ML methods is impacted by self-averaging effects as the width of ribbons are increased. Where additional

informations such as inter-impurity distance and sublattice were beneficial in enhancing the accuracy of prediction for smaller systems, we have proven that the most crucial information for describing disorder in such system remains the distance to the edge only. As the width is increased, quantum effects are self-averaged and configuration-specific features diluted in the configurational average, making it difficult to train our ML models. Further investigations have been performed regarding a higher number of impurities and/or a stronger disorder strength in these systems. An increase in the number of scatterers, in the KRR approach, leads to more complexity for the machine learning process especially with the formerly discussed descriptors. Indeed, self-averaged effects occur with the increase of impurity concentration through the system suggesting alternative descriptors must be provided to grasp those averaging effects. Also, we should note that the tight-binding model simplifications neglect important electronic interactions beyond nearest neighbors, which can lead to limitations in accuracy compared to DFT. The choice to employ a tight-binding model with orthogonal basis sets and nearest-neighbor hopping introduces simplifications that makes the calculations computationally manageable and provide valuable insights into the electronic properties of the system, yet it is important to acknowledge their consequences. For instance in the context of (magnetic) impurities or disorder, such as adatoms or vacancies, this can introduce long-range scattering interactions that affect the transport properties of graphene nanoribbons. We could also mention more complex parameterisations required to fully capture the interaction between an impurity and graphene, which could be benchmarked with DFT. DFT takes into account a broader range of interactions and provides a more accurate description of electronic properties. It considers the electronic density and exchange-correlation effects, which can be crucial for understanding the behavior of graphene [178]. Also in realistic cases, graphene nanoribbons are grown on substrates which can introduce long-range interactions through their influence on the local electronic structure, charge transfer, and the formation of surface states. These are not needed for this proof of principle study, as TB and simple impurity descriptions captures the essential physics of the problem.

Yet, the results highlight the ability of machine learning techniques to capture the complexity of disordered nanostructures and suggest that they can be used to complement conventional techniques to better understand a wider array of systems. The KRR and NN approaches complement conventional techniques' toolkit in order to investigate complex disordered systems. An approach based on ML techniques to predict electronic transport in disordered nanostructures in complement of the usage of conventional techniques has been presented. In addition, this ansatz captures most of the complexity of structural defects on the electronic transport properties by describing the distance of the scatterers to the edge or to the same sublattice edge more specifically for the ZGNR. The systems

here are useful as a case study highlighting the performance of ML, but these types of calculations are not difficult to perform with conventional techniques, and big systems seem to converge towards the average. Whereas there is no major advantage in using ML for this particular scenario of quantum transport in disordered GNRs, we put forward the ability ML can offer for complementing conventional methods. As discussed in the introduction of this thesis, ZGNRs hold magnetic properties due to their localised edge states and were not considered during this preliminary work that serves as a proof of concept on the usage of machine learning for quantum transport. In fact, for certain spatial distribution of disorder such as the one close to the edges, we expect our model to perform even better as turning up the electronic interaction gives more information. As we will see in the next chapters, adding more information through an approximation of the Hubbard model increases our predictive performance. Yet, it should be noted that we restrain our later study to disorder present on the edge when considering the impact this has on spin-polarised quantum transport.

In the next chapter, we will further develop the ideas outlined here, for a calculation that requires a similar description of location within a graphene lattice but where the scaling of the calculation allows the benefits of ML to be fully valued. Overall, while the current case study may not show a significant advantage for using ML, it serves as a starting point for understanding the potential of ML in the field of quantum transport in disordered systems. The next chapter will expand on these ideas and provide a deeper understanding of the strengths and limitations of ML in this area.

## Predicting magnetism in graphene nanostructures with neural networks

### 4.1 Introduction

Modern technology is shaped by the advancements in finding suitable magnetic materials, crucial for data storage and which hold particular prospects for spintronics and quantum computing applications. Indeed, since the discovery of the giant magnetoresistance effect [84], the field of spintronics was mainly investigating ferromagnetic materials and related alloys composed of metallic compounds such as iron, cobalt or nickel to control and manipulate spin currents. This achievement's underlying physics has served as the cornerstone for spin-transport experiments for the last two decades [179]. The discovery of graphene [13, 180] reshuffled the cards as graphene is an emerging material for spintronics because of its high electronic charge mobility, weak spin-orbit coupling, negligible hyperfine interaction, and gate tunability, among other features [181]. While graphene is non-magnetic, carbon-based materials derived from it have a number of benefits like biocompatibility, lighter weight compared to ferromagnetic compounds in addition to promising magnetic properties. However, the main difficulty faced by carbon-based magnetism resides in its poor experimental reproducibility. Indeed, the origin of magnetism in carbon materials is essentially caused by unpaired  $\pi$ -electrons sitting mainly on the edges of such structures. Unfortunately, these graphene-derived structures have a high propensity for being reactive and their magnetic characteristics are particularly vulnerable to minute changes in the bonding configuration around the edges. Overall, the interplay between disorder and spin transport in graphene ribbons is complex, and further research is needed to fully understand the impact of disorder on spin transport in these systems. Until recently, the quality and precise control of the edge topology in

graphene nanoribbons and nanoflakes created by top-down approaches made difficult the observation of magnetism in these materials. However, large effort to obtain cleaner structures experimentally led to one of the most powerful strategies towards a controllable construction of functional nanoarchitectures via bottom-up techniques. These new approach based on chemical precursors have resulted in a surge in magnetic carbon-based nanostructures research during the past few years and recently led to the direct experimental evidence of local magnetism in carbon-based architectures.

To validate and complement the ever-growing experimental findings, several computational approaches can be used to describe the electronic structure of graphene nanostructures and relationships between topology and emergence of spin-polarized states. However, theoretical investigations can often only be performed on small or perfectly periodic systems due to high computational costs. Here, we show how a machine learning approach can quickly and reliably simulate arbitrary large and disordered systems by estimating magnetic moment profiles using only geometric input. The predicted profiles reproduce significant electronic and magnetic properties with excellent agreement with mean-field Hubbard calculations. This method has the potential to dramatically accelerate the identification of suitable geometries for spintronic applications by providing quick and precise prediction of the magnetic moments of experimental-scale systems. This will then serve us to be able to carry out an in-depth study of spin transport in disordered graphene ribbons where the impact of disorder is still an open question (cf. Chapter 5).

This chapter starts by giving an overview of the origin of  $\pi$ -magnetism in carbon-based materials in section 4.2. Different finite-size nanostructures such as nanoflakes and nanoribbons are presented as they are known to theoretically host  $\pi$ -magnetism due to sublattice imbalance, topological frustration or low-energy edge states.

Section 4.3 discusses experimental fabrication and characterisation techniques whether by top-down or bottom-up approaches in the magnetic material context. Although we are witnessing nowadays very decisive success in controlling precisely the edge structures of GNRs, disorder is still present during the synthesis process of such nanomaterials.

We address in section 4.4 the impact that disorder in the form of vacancies could have onto the spin-related properties at half-filling of such materials and how complex these effects can be if several and competing edge disorder sources are observed in such materials.

Section 4.5 motivates the need for a novel approach aside from the conventional theoretical methods. As we seek for a cost-efficient method to obtain the magnetic

profile of realistic sized and disordered materials, it is necessary to adopt a method that does not need systems to present periodicity or does not scale with the system size. Trained neural networks have proven their worth in many different contexts and we argue the advantages of using this method instead of the conventional mean-field ones.

After presenting the generated data set specificities and the descriptor used for our model training, we provide in section 4.5.3 onwards insights about the accurate, time-efficient prediction made by our NN model. An overview of the performance as well as the prediction of unseen data are shown. We finally discuss the limitations of our predictor and its potential applications in various materials science related fields.

## 4.2 $\pi$ -magnetism in carbon-based nanostructures

Following the first isolation of graphene [13], 2D materials and their promising applications raised a growing interest and regarded as the next platform for state-of-the-art spintronics [182, 183]. In contrast to conventional transition metals such as Iron or Cobalt in the  $d$ - and  $f$ -blocks, light elements with  $p$  electrons in their valence shells such as Carbon are not known to host intrinsic magnetism. However, reports of intrinsic magnetism in carbon nanostructures began to emerge at the beginning of this century and frequently made headlines, often being followed by the words “unconventional” [184, 185] or “unexpected” [186]. The first experimental demonstration of spin transport in graphene at the micrometer scale [181] established the reality of a possible observation of magnetic properties and marked the beginning of an intense implication of the scientific community to use graphene as a platform for spintronics [187, 188].

In general, magnetism is related to either spin-orbit coupling or electronic localisation [189, 190]. Graphene, a strongly diamagnetic material, disproves both properties. This material still offers interesting perspectives for spin-related applications as among its diverse and remarkable properties [180], graphene has two major characteristics being essential for spin transport [188], namely high carrier mobility [8] and low spin-orbit coupling [6]. The magnetic properties of the ground state can be used to comprehend the magnetic ordering in graphene. As a bipartite lattice, graphene is composed of hybridised  $sp^2$  carbon atoms that are arranged in two alternating triangular sublattices. In other words, only carbon atoms of one sublattice are covalently bonded to atoms of the other sublattice.  $\pi$ -orbitals, which result from the hybridization of the carbon  $p_z$  electrons, are the low energy electronic states that predominantly control the majority of physics in graphene and its derivative materials. Each  $sp^2$  carbon atom has one  $p_z$  electron corresponding to the half-filled  $\pi$  orbitals in graphene. Each  $p_z$  electron can

only create  $\pi$ -bonds with electrons from atoms on the opposite sublattice in a bipartite arrangement. It follows naturally that some electrons cannot create a  $\pi$ -bond if the two sublattices contain different numbers of atoms. The electrons that are still unpaired transform into  $\pi$ -radicals with associated spin  $S = 1/2$ . The generalisation of this reasoning is known as the Lieb’s theorem [191]. It states that bipartite lattice with repulsive electron-electron interaction ( $U > 0$ ) will have a ground state with net spin  $S = \frac{1}{2}|N_A - N_B|$ , where  $N_A$  and  $N_B$  are the number of atoms belonging to the  $A$  and  $B$  sublattices respectively. The presence of  $\pi$ -radicals can also be understood as the consequence of topological frustration. Topological frustration refers to the fact that molecules like triangulenes cannot be represented by a Kekulé structure (alternation of single and double covalent bonds). Drawings of chemical structures must include explicit radicals to account for the valence four of carbon atoms. This is explicitly shown in the first row of Fig. 4.1 where the black dots showing  $\pi$ -radicals result from the impossibility of drawing Kekule structures. Topological frustration affects all of the molecular structures with sublattice imbalance introduced in the next section but not exclusively.

Indeed, the emergence of magnetism in carbon-based nanostructures is not exclusively driven by sublattice imbalance. Pristine ZGNRs or even the iconic Clar’s goblet (cf. left panels of Fig. 4.1) have the same number of atoms in both sublattices but are still expected to have magnetic moments when electron-electron interactions are included [89, 192, 193]. Whereas these structures have no net spin in accordance with Lieb’s theorem, they host zero-energy states, predicted by tight-binding to be located on their zigzag edge portions [193]. This creates a magnetic instability and according to Lieb’s theorem, these low-energy states, sitting on different sublattices, are antiferromagnetically polarised ensuring  $S = 0$ . In order to enable bonding interactions between electrons with opposite spins in adjacent sites, it is energetically more favorable for them to be antiferromagnetically coupled [133]. This generalisation results in the same spin being shared by atoms on the same sublattice of the bipartite lattice while they are antiferromagnetically aligned to atoms on the opposite sublattice.

#### 4.2.1 Finite dot and regular-shaped nanoislands

While graphene is essentially non-magnetic, many of its derived nanostructures display several tunable spin-related properties for applications [6, 88]. One of the many ways to induce spin-related properties in graphene-based materials is to create sublattice imbalance by introduction of vacancy defects [120, 133, 182, 192, 194]. A sublattice asymmetry resulting in a spin imbalance in the  $\pi$ -electron cloud may be hosted by specific graphene structural forms, leading to graphene nanosystems with net magnetic moment. Since Clar’s proposal of a

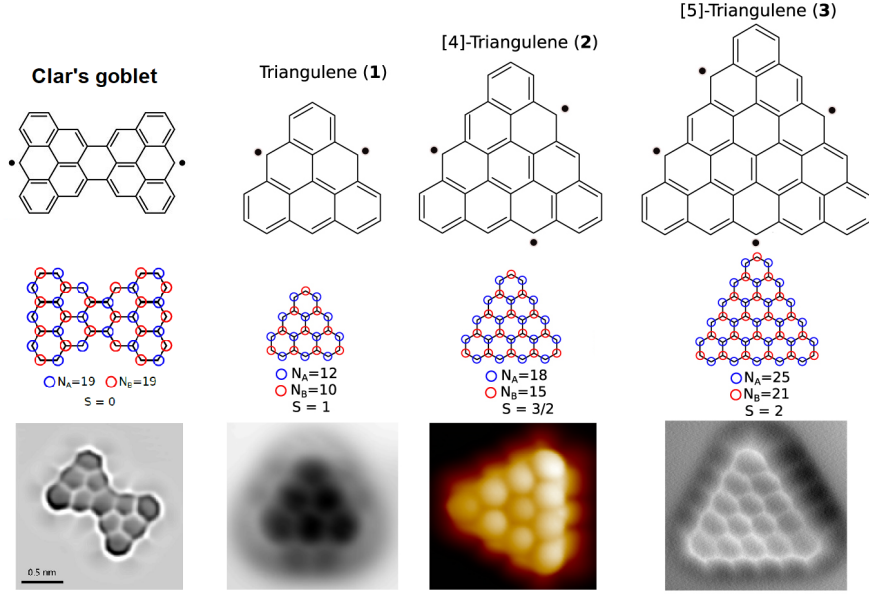


Figure 4.1: **Top-** Molecular structure of different graphene-based nanostructures such as the Clar's goblet and different-sized  $[n]$ -triangulenes. The impossibility of drawing Kekule structures results in the presence of  $\pi$ -radical shown by black dots on some vertices, responsible of magnetic properties for these materials. **Central-** The two alternate sublattices are represented by red and blue circles. Sublattice-imbalanced molecules have a spin-polarised ground state if  $\pi$ -radicals are on the same sublattice as for all  $[n]$ -triangulenes as they each contribute for  $S = 1/2$ . The  $\pi$ -radicals for Clar's goblet sit on different sublattices and are antiferromagnetically polarised resulting in no net spin. **Bottom-** Bond-resolved SPM images of the associated structures. Adapted from [195–198].

particular nanographene structure known as Clar's goblet [199], many studies of finite dot structures, such as  $[n]$ -triangulenes [198, 200],  $n$  denoting the number of hexagons along each molecular edge (cf. Fig. 4.1), and random-shaped graphene nanoislands [201–203] have been reported. Indeed, it was anticipated that nanographenes' magnetic moments and their correlations could be precisely manipulated by chemical doping, edge topology, and size [88, 89, 204]. Many investigations have reported the presence of spin-split states by scanning probe techniques [198, 200, 205, 206]. Direct evidence of carbon magnetism has also been reported [197, 207] bolstering the role of topological frustration to give rise to unconventional magnetism. The use of STM and STS characterization at a sub-molecular scale, combined with various theoretical calculations enabled the direct observation of spin-split frontier orbitals in real space.

#### 4.2.2 Zigzag graphene nanoribbons

ZZ-edged ribbons are of particular interest because, in the absence of electron-electron interactions, they host localised flat bands at Fermi energy as can be observed by the solid-lined curves in the band structure and DOS shown in

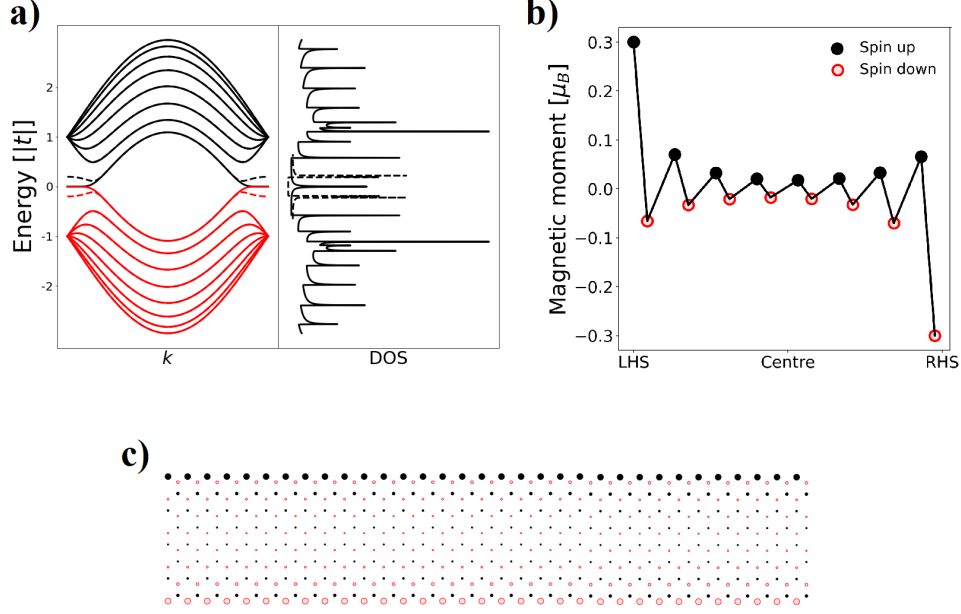


Figure 4.2: (a)- Band structure and DOS for a non-magnetic (solid lines) and magnetic (dashed lines) 8-ZGNR. The valence and conduction bands are respectively shown by red and black colours. (b)- The transversal magnetic moment profile across a 8-ZGNR and (c)- the global magnetic profile for the same system calculated with SC method.

Fig. 4.2(a). These low-energy states decay exponentially away from the edge [65, 169] and are closely connected to a local sublattice symmetry-breaking which occurs at a ZZ edge, consisting solely of sites from a single sublattice, as observed in the band structure shown in Fig. 4.2(a). AC edges contain sites from both sublattices and host no such edge states [67]. The stability of magnetic edge states in ZGNRs is influenced by temperature, and the edge states may become less stable at higher temperatures due to thermal fluctuations. For narrow ZGNRs, there is an estimation that the AFM state can only be stabilized at temperatures  $T \lesssim 10K$  and above, the ZGNRs will show paramagnetic behaviour [106].

The high density of electronic states at low energies at ZZ edges suggests a magnetic instability, and spin-splitting is predicted to occur when electronic interactions are included, giving rise to spin-polarized edge states [67]. For a given graphene-based nanostructure, both local and total magnetic moments depend exclusively on the dimensionless parameter  $U/t$ . Ideally, empirical parameters should be derived from experimental data. However, in the case of magnetic graphene systems, there have been no direct experiments conducted to estimate this parameter. As a result, DFT, particularly with the general-gradient approximation, provides an estimated range for this parameter, typically falling between 1.1 to 1.3 [88, 195]. This range is crucial for achieving accurate results when employing Tight-Binding (TB) models. Beyond a threshold of  $U/t \sim 2.3$ , graphene undergoes a Mott-Hubbard transition, leading to the emergence of an

antiferromagnetically-ordered insulating state. In the rest of our study, we will chose  $U = 1.3|t|$ .

ZGNRs are interesting as the magnetic ordering is ferromagnetic along one edge and antiferromagnetic across the ribbon, as each of the two edges is associated with a different sublattice [67, 88]. The formation of finite magnetic moments near the edges as displayed in Fig. 4.2(b)-(c) changes the band structure of ZGNRs at low energy. The low-energy spin-polarised states have their moments magnitude which decay away from the edges and their spin polarisation is affiliated with the sublattice as can be seen in Fig. 4.2(b)-(c). The spin-splitting makes the flat band dispersive and allows spin currents of opposite polarisation to be carried on each of the edges as observed by the dashed band structure and DOS in Fig. 4.2(a). Also, it should be noted the presence of magnetism in GNRs is not exclusive to these high symmetry directions as in mixed chiral-edged ribbons, ZZ portions can also exhibit magnetic polarization at half-filling [89, 192]. Despite this local spin-polarised current flow, the net spin current in pristine ZGNRs is negligible due to the cancellation of the oppositely-polarised contributions from each edge [67, 191]. Several theoretical ways to induce spin functionalities in ZGNRs among which transverse electric fields [67], gate voltage [89, 91], chemical functionalization [208–210] have been proposed. Away from half-filling, the change in carrier concentration can break the sublattice AFM, but is more complex to calculate. It is the obvious next extension of our work. ZGNRs away from half-filling can be engineered to have a controllable level of conductivity. By introducing external factors like gate voltages, doping, or strain, it is possible to modulate the carrier concentration and, consequently, the polarisation of the current at each edge of the nanoribbon. One of the method that is the most in accordance with Lieb theorem is through defect-engineering [90, 211]. Several spintronic devices based upon these functionalities such as spin-filters [67, 92–94], spin-polarised beam splitter [95, 96], spin qubits [97, 98] and logic gates [99, 100] have been proposed.

### 4.3 State of the art experimental achievements and challenges

The observation of magnetic properties in graphene-based nanostructures is closely linked to the ever-growing success in fabricating devices with well-defined edges. For decades since the rise of graphene as a material with superlative properties [180], experimental fabrication techniques are mainly seeking to improve the precise control and characterisation of the edge structures [212–215].

There are several methods for growing or fabricating graphene and related nanostructures. One of the common fabrication methods include chemical vapor de-

position (CVD) [31]. In this method, graphene can be grown on a metallic substrate, such as copper or nickel. Metallic surfaces can be a problem for graphene nanoribbons characterization because it can interfere with the electronic properties of the deposited structure, leading to measurements difficult to be interpreted [216]. To mitigate this problem, experiments are often realised with insulating or semiconductor substrates such as Silicon Carbide (SiC) for epitaxial growth [32]. This is the process illustrated by Fig. 4.3(b)-(c)-(d) where sidewall GNRs can be isolated via a further etching process (cf. Fig. 4.3(a)-(e)-(f)). This fabrication method allows for the growth of high-quality, single-layer graphene on a substrate that is compatible with existing silicon technology [217], making it a promising material for electronic applications. Transferring graphene to a non-metallic substrate prior to characterization is also another alternative to avoid proximity effects induced by the metallic substrate, detrimental for characterisation with scanning-probe techniques. Generally the transferring process is detrimental to the structural properties of nanoribbons or nanoflakes. Indeed, the  $\pi$ -radicals responsible for the appearance of magnetic properties in such materials are highly reactive [218], making these materials unstable and complicating their synthesis and characterization.

On-surface synthesis of graphene nanostructures is a method for creating finite-size materials on a substrate without the need for transfer or removal from the considered growth surface. As already mentioned, graphene grown on semiconducting substrates like SiC are more beneficial as their characterisation by optoelectronic scanning-probe techniques like scanning tunnelling microscopy (STM) and spectroscopy (STS) reveal easier. From graphene grown on such substrates, top-down approaches as shown in Fig. 4.3(a)-(e)-(f) involve cutting or etching graphene into nanoribbons using techniques such as electron beam lithography [61], scanning probe lithography, or chemical etching [61, 72, 219]. These methods require high precision and can produce GNRs with well-defined widths. The quality of edge structures in such processes are still difficult to control at the atomic scale as rough-edge patterns are observed by STS as seen in Fig. 4.3(f).

One of the most promising techniques is called “mask-assisted growth” where a thin film of a material that can withstand the growth temperature and pressure, such as silicon nitride, is used as a mask [63]. On-surface synthesis of graphene nanostructures has several advantages over other methods, such as the ability to create nanostructures with well-defined shapes, sizes, and the potential for large-scale production. However, some challenges still exist such as controlling the width and edge structure of the GNRs and the potential for defects. There are unfortunately a significant propensity of having edge disordered materials due to the presence of defects or irregularity at the edges of the nanostructures that are created. This can be caused by a number of factors, including the method used

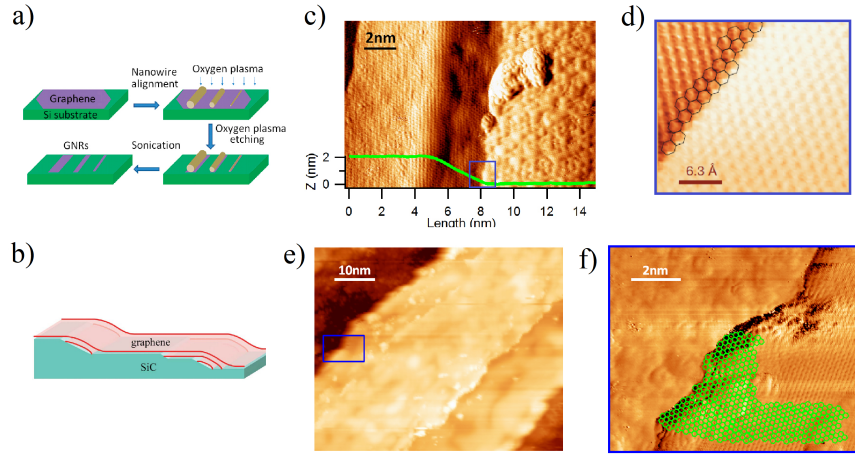


Figure 4.3: (a)- Lithographic method schematics with oxygen plasma beam : protective nanowires are layered on top of graphene that has been deposited on a substrate. The exposed graphene is etched away by an oxygen plasma. When the wires are taken out, nanoribbons are left once the nanowires are removed by sonication. Schematics (b) and STM images (c) of epitaxial growth of graphene sidewall ribbons on Silicon Carbide (SiC). Zooming in to the edge with atomic resolution (d) reveals smooth edge disorder with few nanoconstrictions. However, patterning graphene sidewall nanoribbons on SiC by e-beam lithography as shown by STM images (e) results in a rougher edge profile as seen in the zoomed blue rectangle (f). Adapted from [222].

to cut or etch the graphene material, the presence of impurities in the material, and the specific conditions under which the nanostructures are created. Edge disorder can have a significant impact on the electronic and optical properties of the nanostructures, and can also affect their ability to be used in certain applications. Researchers are actively working to develop methods to reduce or eliminate edge disorder in graphene nanostructures created using top-down methods.

Driven by recent advancements in chemical synthesis methods, bottom-up fabrication techniques also yield on-surface narrow AGNR [33] and ZGNR [34] with atomically precise edges. Impressive achievements with the bottom-up approach resulted in a high degree of tunability to fabricate diverse GNRs with desired widths, edge shapes and topologies [220, 221]. However, although this approach can produce perfect ribbon geometries, it again requires a transfer to a metallic substrate and such process generally alters the quality of the well-defined edges. STM and STS reveal the experimental presence of localised edge states by probing the local electronic structure of ZGNRs edges [34, 104, 105]. Although these promising advances in manufacturing techniques, some degree of extrinsic disorder is inevitable in experiments [33, 105, 223, 224]. In the context of non-magnetic ribbons, top-down approaches consisting in creating edges by etching graphene with oxygen plasma, electron beam or by chemicals do not provide well-defined edges but result in a rough-edge pattern [212–215]. The edge roughness is here

resulting from carbon atoms being torn out from the nanostructure during the etching process. Yet in bottom-up approaches, from chemical precursor methods and epitaxial growth on SiC, the fabricated ZGNRs have a smoother edge profile where random distributions of nanoconstriction as well as chiral edges are observed across the ribbons [74, 105, 223–226].

#### 4.4 Disorder and its local impact on magnetism

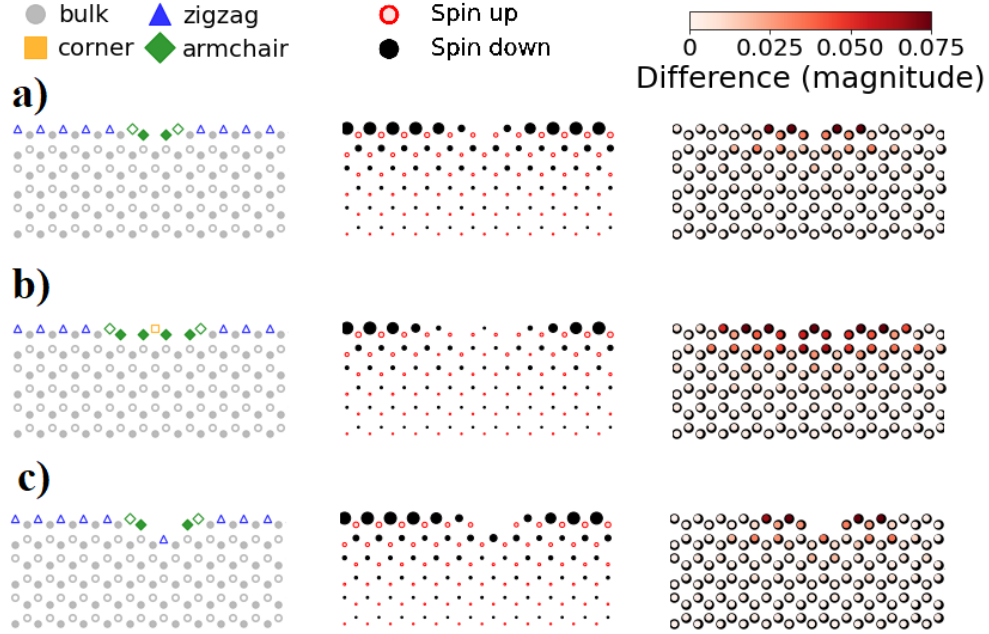


Figure 4.4: 3 different disorder scenarios ((a),(b),(c)) where a varying number of atoms are removed from a pristine ZGNR portion and their impacts on local magnetisation. **Left:** removing atom(s) change(s) the nature of the remaining atoms that are classified according to Fig. 4.5. **Centre:** The magnetic profile of the disordered portions are calculated using SC procedure. The moments and relative spin flavour(following the relative sublattice) are shown by the dot's size and colour respectively. **Right:** The difference in magnitude compared to the pristine magnetic ZGNR case is mapped for each atom in the disordered structure. The colour depth shows the relative variation in magnitude up to 7.5%.

Predicted phenomena in presence of disorder such as Anderson localisation [109, 110] and Coulomb blockade [227] have been observed in GNRs [228–230]. Disorder in graphene-based nanostructures can come in various forms, such as defects, impurities, and variations in the edge structure. Impurities, for example, can also introduce local magnetic moments, which in return locally perturb the electronic structure of the GNR, leading to changes in its magnetic properties. The presence of an edge vacancy is expected to disrupt the local magnetisation on its vicinity [192, 194]. For a sufficient concentration of edge defects, it has been reported that the magnetic characteristic of ZGNRs can be completely quenched [194]. Here specifically, we focus on edge disorder that has also been shown to affect

the formation of local magnetic moments. Fig. 4.4 shows how disorder in the form of vacancies disrupts the local magnetic profile in a nanostructure's edge which can either be a nanoribbon or a nanoflake. Here, the calculations were performed on a sufficiently wide and long ZZ-edged ribbon portion as a prototype system that is purposefully disordered with edge vacancies. Each row of Fig. 4.4 shows a scenario resulting from the removal of one or several atoms. The left column shows how the removal of one or several atoms changes the nature of the remaining edge portion. For instance in Fig. 4.4(a), one atom at the edge has been removed. Consequently, this removal changes the identification of remaining atoms as each site in a nanostructure is classified as either "Bulk" or one of three edge types: "Zigzag", "Corner", or "Armchair" following Ref. [231]. Fig. 4.5 shows the algorithm, based on the number of neighbours and neighbours of the next-nearest neighbouring atoms, used to classify atoms with regard to their types following the work in [231]. Two next-nearest neighbour edge atoms are removed in Fig. 4.4(b) and one edge atom, its neighbour and the remaining dangling atoms have been removed in Fig. 4.4(c). The symbols showing the different edge topologies are depicted as filled or hollow symbols with regard to the sublattice degree of freedom. The removal of atoms shown in the left column results in a different magnetic profile as displayed in the central column of Fig. 4.4. The resulting magnetic profiles are calculated with tight-binding alongside mean-field Hubbard (MFH) SC procedure. As soon as edge atoms are removed and result in the disruption of the ZZ edge, we see a local disruption in magnitude of the local moments. Indeed, magnetic moments are locally maximal in the center of ZZ portions and tend to decay around junctions, corners, toward the bulk and AC portions [192, 201]. The rightmost column shows how these different scenarios act upon the remaining atoms magnetic moments when compared to their values in a pristine ribbon (cf. Fig. 4.2(c)). The depth in colour shows the difference in magnitude with the same pristine portion. It is interesting to concentrate on the subtleties that exist between Fig. 4.2(a) and (b) showing the removal of one and two edge atoms respectively. As already mentioned, it is known that moments magnitude decays away from armchair and corner sites [192, 201]. It seems that the removal of two atoms instead of one disrupts even more the local magnetisation of the remaining disordered portions when we compare the right panels of Fig. 4.2(a) and (b). Yet again, it is not arguable that the resulting removal of a pair of edge atoms is similar to the added effect of removal of one single atom as there are correlation effects that have to be considered. The comparison between Fig. 4.2(b) and (c) has also some interest. Indeed, two and three atoms are removed respectively in these 2 scenarios but the local disruption triggered by the removal of Fig. 4.2(b) has a stronger impact on the local disruption of magnetic features. Even though these scenarios are non-exhaustive, we see how single scenarios of edge vacancies can locally affect

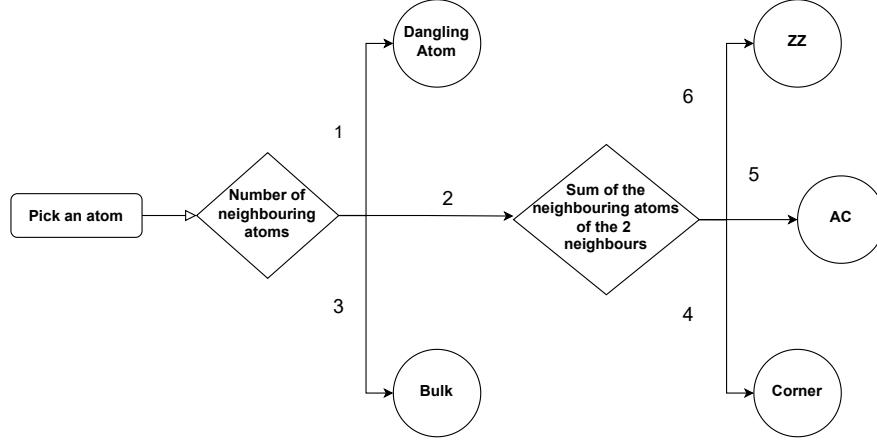


Figure 4.5: Algorithm to classify atoms in graphene-based structures. Based on the coordination number, i.e the number of neighbours and the next-nearest neighbours’ coordinations, it is possible to classify atoms as bulk, armchair, zigzag or corner. Based on the work from [231].

the magnetic profile of disordered edge ZZ-portions. In realistic experimental nanostructures as nanoflakes or nanoribbons, the edge disorder resulting from either top-down or bottom-up approaches can be composed of edges with a mix of rather complex disorder scenarios. As disorder breaks the local sublattice symmetry of ZZ portions, the distance of an atom to various edge structures in addition to its sublattice belonging are key features for accurate magnetic profile prediction [126].

## 4.5 Machine learning the magnetic profile of graphene nanostructures

### 4.5.1 Conventional computational approaches and difficulties

The magnetic moment profile for a graphene structure can be calculated using *ab-initio* calculations [232]. DFT treats electron-electron interactions exactly within the “exchange-correlation” term of the functional [232]. This term takes into account the non-local electron-electron interactions that are difficult to treat accurately with mean-field approaches. DFT is a more accurate method than MFH tight-binding for treating electron-electron interactions, but it is also more computationally expensive. Currently, first-principles electronic structure approaches based on DFT are used in the great majority of computational studies of magnetic carbon nanostructures [120, 194, 198, 200]. Unlike direct recent experimental evidence of local magnetism in graphene-based nanostructures [193], the observed width-dependent bandgaps in the local density of states are compared to theoretical calculations to corroborate the role of electron-electron interactions [233, 234]. DFT’s strength resides in its possibility to study the interactions between the deposited carbon nanostructures under scrutiny and substrates allowing comparison

with experiments [193, 197, 198, 200, 206]. For example, the spin densities for adsorbed atoms, molecules, and extended 2D structures on metal surfaces and interfaces can be successfully calculated [235]. Nevertheless, spin-polarised DFT has a limited field of action when it comes to simulate magnetic profiles as it is constrained to small-scaled or periodic systems.

TB simulations with a MFH approach (cf. Section 2.2) has a broader power as the technique is resilient for larger and systems exempt of periodicity [89, 95, 133, 192]. Although tight-binding simulations are able to handle bigger systems than DFT-based methods, it is still far from managing realistic-sized devices. Theoretical predictions of spin properties, usually calculated using a time-consuming self-consistent (SC) procedure, can be intractable in computational resources required to deal with realistic system size. It can be unwieldy in terms of resources as it requires the inversion of the full Hamiltonian of the system, at each step until convergence, which scales approximately as  $N^{2.373}$  [155] with  $N$  being the number of atomic sites in the considered system [133]. This usually hinders the consideration of zigzag-edge magnetism at mesoscopic scales. It is also a considerable obstacle to averaging over large numbers of similar configurations, as the moment profile for each geometry must be independently calculated. Configurational-averaging is an essential component of disorder studies [90, 93, 96, 109], particularly in one-dimensional systems like GNRs, in order to remove configuration-specific features and determine the main trends as the concentration or the nature of disorder is varied.

#### 4.5.2 Novel approach: Neural network for instantaneous mean-field prediction of magnetism

We demonstrated how neural networks (NN) could be employed to circumvent the self-consistent bottleneck in large-scale studies of edge magnetism in graphene [126]. The following results and discussions are issued from this study. As disorder breaks the local sublattice symmetry of ZZ portions, we have seen in Fig. 4.4 that the distance of an atom in graphene-based nanostructures to the different edge topologies in addition to its sublattice information is crucial if one wants to estimate its magnetic moment.

To train and evaluate the performance of our NN, we need to create a data set full of different nanostructures mimicking the variety occurring in realistic disordered nanoflakes and nanoribbons. The data set, made of 4505 various graphene nanostructures, as shown in Fig. 4.6 presents both irregular (many-sided polygons and edge-disordered dots, cf. Fig. 4.6(a)-(b)) and regular (finite ZGNRs, cf. Fig. 4.6(c)) geometries. The flake sizes, edge lengths, and edge types range from 50 to 9000 atoms in this library. The observation that moment magnitudes depend heavily on their position with respect to surrounding edges, as well as the

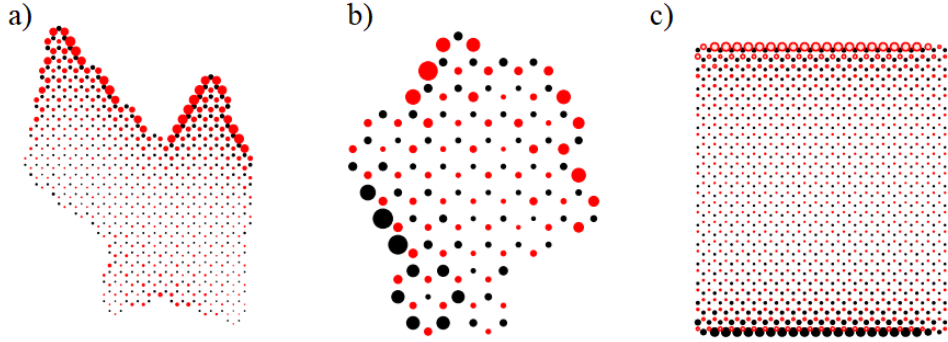


Figure 4.6: Examples of the different nanostructures and SC-obtained magnetic profiles present in our data set : (a) Random many-sided polygon graphene flake, (b) Edge-disordered dot and (c) finite-sized ZGNR. The finite ZGNR portions in the dataset are all extended in their leftmost and rightmost parts by buffer regions that are removed at the end of the SC procedure. Otherwise, the AC edges on the transversal directions of portions will disrupt the magnetic profile of longitudinal pristine ZZ-edge portions.

sublattices of those edges motivates the use of this diverse size range. Indeed, we will see that both large disordered systems and small, simple systems show similar qualitative characteristics because of the adopted description of our systems. For all the generated geometries, the values of magnetic moments  $m_i$  for each site are calculated self-consistently by taking an initial guess for the moment profile and using exact diagonalization to calculate the energy levels. The initial guess for the SC calculation is done by giving the value for the pristine edge moment at zz edge sites and about half this value elsewhere with sign depending on the sublattice. This guess mimics the favourable AFM solution thus we pick moments of opposite sign on different sublattice. The individual occupations of the  $\uparrow$  and  $\downarrow$  states at each site are then calculated, generating a new estimate for the moment profile. This procedure is iterated until the input and output moments at each site are converged to within  $10^{-5}\mu_B$ . We consider only the energetically-favourable antiferromagnetic (AFM) solutions, which are found by choosing an AFM initial guess. We also focus exclusively on undoped graphene, which imposes a half-filling constraint on the occupation. We also note that away from half-filling, the filling fraction of electronic states and the presence of electron-electron interactions changes drastically the electronic topology of graphene [236]. The interplay between electron-electron interactions and the degeneracy of the shell can lead to the destruction of full spin polarization achieved at half-filling [236].

Since local geometrical features have a significant impact on the magnetic moments in random-shaped nanoflakes, we train neural networks to return individual site moments rather than the moment profiles of entire structures. This per-site estimation approach allows trained models to be easily applied to systems of arbitrary sizes regardless of the specificity of their edge topologies.

A careful and informed description of the generated random-shaped nanostruc-

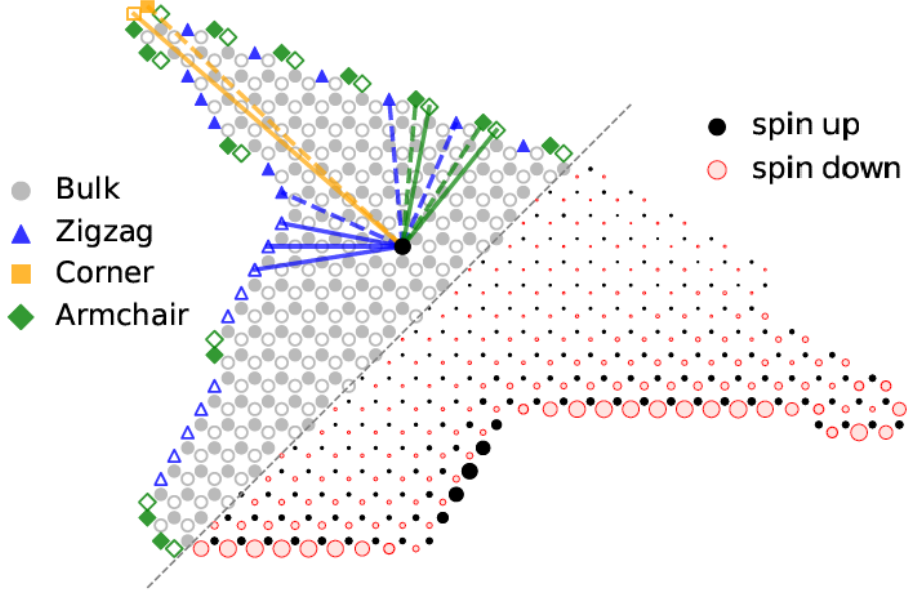


Figure 4.7: **(Left)**: Site types within a disordered graphene flake, with sublattices shown by filled or hollow symbols. Lines show the nearest edge sites (of each type) to the black circle. **(Right)**: SC-calculated moments in the flake, with size (color) denoting the moment magnitude (sign). Adapted from [126].

tures is crucial if the predictive performance of our NN is to match mean-field level of accuracy. The connectivity matrix  $D$  for each flake, where  $D_{ij}$  is the number of carbon-carbon bonds along the shortest path connecting sites  $i$  and  $j$ , is used to construct the feature vector for each site. For each site, we create a reduced connection matrix with dimensions  $2(N_Z + N_C + N_A) + 1$ . This includes the elements of the matrix  $D$  that correspond to the site of interest as well as the  $N_Z$  nearest zigzag,  $N_C$  nearest corner, and  $N_A$  nearest armchair edge locations, each from both sublattices. The classification of edge sites as “Bulk” or one of three edge types: “Zigzag”, “Corner”, or “Armchair” is determined from the connectivity of a site and its neighbours [231] as can be also seen in Fig. 4.5. Fig. 4.7 shows the sites considered for the simple  $(N_Z, N_C, N_A) = (3, 1, 2)$  case, whereas the descriptor used to generate the main results uses  $(N_Z, N_C, N_A) = (11, 3, 5)$ . The descriptor is subject to a finite cut-off radius and overall renormalization of  $r_{\text{cut}} = 15 d_{c-c}$  corresponding to 3.7 nm. Indeed, this distance, being also a hyperparameter of our model, was found to be optimal in the predictive performance of our model.

To create training, validation, and test sets for the training process, the collection of different nanostructures is divided in the 7 : 2 : 1 ratio. TensorFlow [237] and Keras [238] were used to train the neural networks. With the He normal distribution of initial weights, each neuron used rectified linear unit (ReLU) activation, and the networks were trained using an adaptive learning rate method (ADAM). Different networks and descriptors were compared using the mean absolute error

(MAE) (cf. Section 2.4) and mean square error (MSE), with better results being found when optimising with respect to the MAE during training. With the exception of the final layer, which has 200 neurons, the ideal network described in our study has 6 hidden layers each with 1000 neurons in total. Several descriptor definitions and network hyperparameters were taken into consideration, and the model mentioned above produced the best results. The following summarises how the descriptors for this model is created:

- The Euclidean distance matrix for a geometry is generated, and used to identify neighbouring sites, and site types (bulk, zigzag, armchair, corner).
- The shortest path routine from the **scipy.sparse** module was used to generate a shortest-path connectivity matrix  $D$ .
- A maximum distance  $r_{\text{cut}} = 3.7$  nm was chosen, and all distances  $D_{ij}$  adjusted such that  $D_{ij}^{\text{new}} = \max(D_{ij}^{\text{old}}, r_{\text{cut}})$
- For each site in a flake :
  - the indices of the 11 nearest zigzag edge sites, 3 nearest corner sites and 5 nearest armchair edge sites from each *sublattice* were found and ordered by distance, type and sublattice.
  - A reduced matrix obtained from the initial connectivity matrix  $D_{\text{red}}$  is extracted for sites of interest of size  $39 \times 39$  ( $39 = 2(11 + 3 + 5) + 1$ ).
  - The feature vector is composed of the super-diagonal elements of  $D_{\text{red}}$  normalised by  $r_{\text{cut}}$ .

This descriptor was largely inspired by the fundamental concepts governing the creation of descriptors in chapter 3. One can in particular draw a parallel with this descriptor capturing the distance of a site from an edge and the descriptors in section 3.3. However, the descriptor for our NN model here generalises to different types of edges and capture the distance between different edges. Owing to the fact that the distance metric used here is different as the descriptor is based on connectivity (number of  $c$ – $c$  bonds between sites of interest) instead of the regular distance, this descriptor retains more information about the lattice connectivity. Variations on this descriptor: (i) with different numbers of edge sites, (ii) taking just first row of  $D_{\text{red}}$  instead of all super-diagonal elements, (iii) using a Euclidean distance metric, and/or (iv) using different values for  $r_{\text{cut}}$  were also tested, but gave less accurate predictions after training. To prevent overfitting, the learning rate was reduced during training using the **ReduceLROnPlateau** callback in keras. We have also applied a dropout rate of 12% on each hidden layers.

### 4.5.3 Results

#### 4.5.4 Global performance

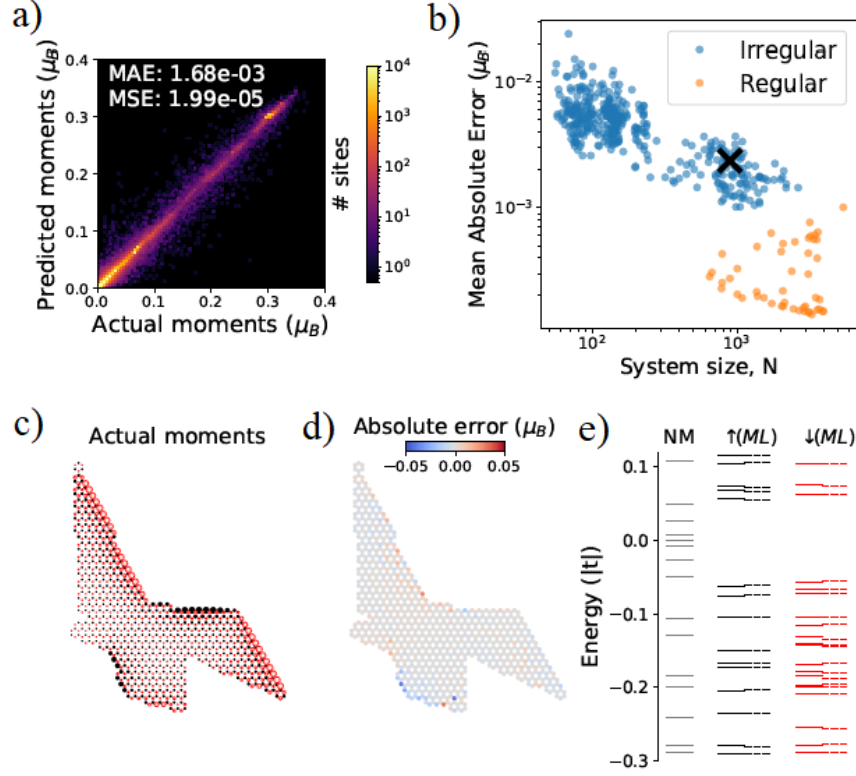


Figure 4.8: (a) Comparison of the moment magnitudes predicted by NN and the actual moment magnitudes for each site and flake in the test set calculated by SC. (b) Mean absolute error (MAE), broken down by flake size and geometry, for each system in the test set. (c)-(d) Actual moment maps and predicted moment deviation maps for a flake in the test set are shown in figures. (e) Comparison of this particular flake’s spin-polarized energy levels computed using the actual (solid lines) or predicted moment values (dashed lines). For a non-magnetic calculation, the energy levels are shown by the grey lines. Adapted from [126].

In Fig. 4.8(a), the actual moments for each of the 271,590 sites from the 451 nanoflakes in the test set are compared with those predicted by a trained neural network. The distribution shows an excellent match between the expected and actual moments since it is maximum along the diagonal and rapidly decays away from it. The mean absolute error (MAE) is a useful metric for comparing networks that were trained on the same set, however the size of the MAE is heavily influenced by the unique flakes in the test set. Since larger systems have proportionally more edge sites with larger moments and prediction errors, the MAE for a single flake depends on its size (cf. Fig. 4.8(b)). The MAE decays as  $\sim 1/\sqrt{N}$  for irregular flakes, where  $N$  is the number of sites in a flake, confirming that the MAE follows the relative edge length of the flake. Regular geometries have a much smaller MAE due to their regular and easily predictable magnetic profiles.

In Fig. 4.8(c)-(d), the actual moments in a polygon flake from the test set are plotted along with the prediction error for each moment. In Fig. 4.8(b), this system is represented by the black “X”. The estimated magnetic moments illustrate the expected trends, such as fading the maximal magnetic moments in the center of long ZZ edge portions fading toward the bulk or other edge types. There are only a few sites where the quantitative match with the actual moments is not excellent as can be seen in Fig. 4.8(d). The network is not aware of the overall size, shape, or length of a flake as it has only been trained with local information about each site. Though several parameters are dependent on the moment profile of the entire flake, if the more-or-less instantaneous ML predictions are accurate enough, we would be able to get over the SC computational limitations. The energy level spectrum of finite magnetic dots is a prime example of an important physical quantity which depends on the the moments throughout the system. The up- and down-spin energy levels determined using ML moments are depicted by dashed black and red lines in the energy spectra of the considered flake in Fig. 4.8(e). They almost exactly match the results obtained using the SC moment profile (solid lines). The spin-splitting of zero-energy states and the general level distribution are among the qualitative and quantitative characteristics of the spectrum that the ML levels accurately represent when compared to the non-magnetic case (grey lines).

#### 4.5.5 Instantaneous and accurate prediction of magnetic profile

Despite the minute prediction errors that the neural network makes once trained, the predictive ability is almost instantaneous when compared to the conventional SC method. Fig. 4.9 shows the difference in prediction time when predicting the magnetic profiles of edge-disordered nanoribbons. All the computations were written in Python and executed on a computer equipped with an Intel Xeon (R) E-214G v5 CPU running at 3.50 GHz. We note that the generation of ML descriptors can be further optimised for extremely large structures, which means a further speed-beyond what is shown here is also possible. The different disordered nanoribbons here are unseen data for the neural network as they are not present in the data set. The size range for these different structures goes from 350 (diamond symbol and related panel) to almost 20000 atoms (square symbol).

Zigzag-edged nanoribbons’ magnetic profile predictions require a particular treatment as their longitudinal boundaries are terminated with Armchair-edges. As the goal of this section is preliminary to a broader in-depth spin-transport study (cf. chapter 5), the ZZ-edged nanoribbons are meant to be connected to semi-infinite leads to perform spin-transport related calculations. This requires the nanoribbons to be considered infinite in their longitudinal direction for the magnetic profile prediction to be correctly undertaken. Consequently, to distort the

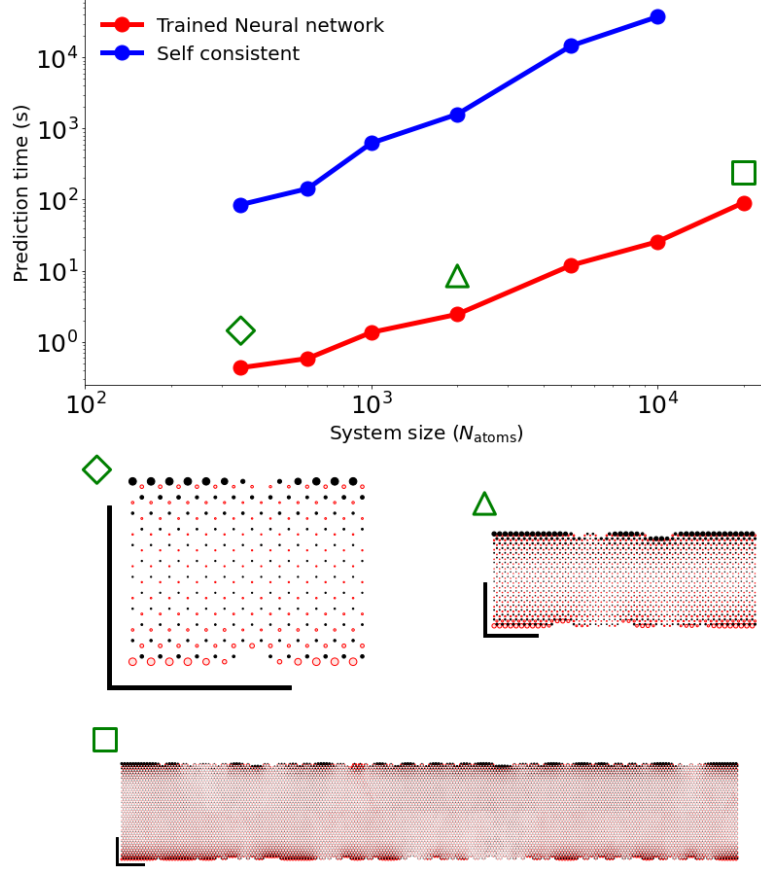


Figure 4.9: The difference of performance between the SC method and the trained neural network in predicting magnetic moment profile : For unseen edge-disordered ribbons of different sizes shown by their respective green symbols, comparisons between the prediction time of SC (blue lines) and NN (red lines) is shown in the top panel. The black lines on the bottom-left corner show a standard 1-nm long line in both longitudinal and transversal directions.

finiteness seen by the neural network and the self-consistent method, an informed number of pristine ZGNR unit-cells of similar width are added on both parts of the ribbons before performing the prediction. Once the prediction has been performed, these added sections are removed. This is discussed in more detail in chapter 5. Where our NN method is robust dealing with big system sizes, the SC method reaches quickly its boundary as the inversion of Hamiltonian matrix is constrained by the memory and processing capacities. In fact, the biggest system of roughly 20000 atoms (square symbol panel) is out of reach for the conventional SC method and can only be predicted by NN. As a matter of fact, the smallest ribbon has been predicted in 85 seconds and 0.43 seconds by SC and NN respectively. The second largest system consisting of a disordered ribbon of roughly 10000 atoms has been predicted in 91 seconds by NN and around 10 hours and 25 minutes for the conventional SC method. Thus at the expense of a slight loss in accuracy, we have access to the magnetic profile of systems that are near-to-unattainable with conventional methods.

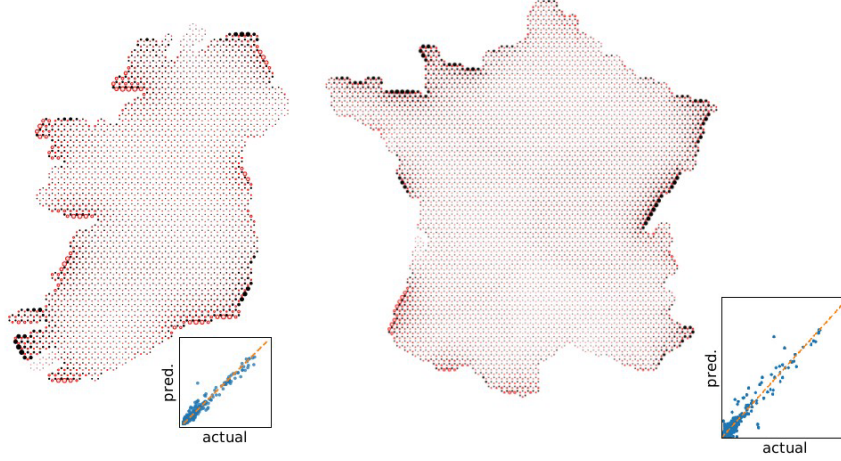


Figure 4.10: Predicted moments for unconventional geometries (Ireland’s coastline and France’s physical border) with features such as rugged peninsulas, which are not present in the training set. The insets compare the actual and predicted moments in each system. Adapted from [126].

It is evident that the ML technique enables fast and precise estimations of system-wide characteristics pertinent to both theoretical and experimental studies. The model generalizes to nanoflakes comparable to those on which it was trained successfully, but since they do not cover all potential edge profile types, it is worthwhile to look at how it performs in contexts other than the test set. This is significant for both geometries in Fig. 4.10, which is based on the Irish and French shoreline and physical border respectively. These have a variety of edges, angles, and local disorders that do not appear from the more straightforward etching techniques. Once more, ML predictions and conventional SC calculations match, and they particularly capture complex behavior.

## 4.6 Conclusion

In a half-filled bipartite lattice, neural networks provide a quick and accurate estimate of the Hubbard model’s mean-field solution. Since prediction cost scales linearly with system size, previously intractable systems can now be calculated quickly. The study of graphene edge magnetism has immediate applications since it allows for the exact and efficient calculation of a variety of graphene nanostructures’ electronic, magnetic, and transport properties. Given the model’s high versatility towards both geometries and quantities that were not present during the training process, it can be used to tackle a variety of problems.

Our method can also be used as a base for more thorough research or challenging problems. In SC calculations, ML profiles can be employed as almost-converged and informed starting points reducing the steps required to a desired mean-field accuracy. The simple geometric data in our descriptors may potentially be sup-

plemented to produce more accurate ML estimates. For instance, the DOS is closely related to magnetic moment formation [190], therefore adding a non-SC evaluation of this quantity could enhance model performance. Here, there will be a trade-off between the extra time necessary to generate the descriptor and the required accuracy. These strategies were not needed to achieve high accuracy in this work, but could help in more complicated cases. Examples include lattices away from half-filling, gated materials or with non-uniform background potentials, or of different materials, where exact solutions are difficult to calculate and display less intuitive trends.

In conclusion, the use of a machine learning approach to simulate large and disordered systems in graphene nanostructures can greatly accelerate the identification of suitable geometries for spintronic applications. This method is able to quickly and reliably estimate magnetic moment profiles using only geometric input, reproducing significant electronic and magnetic properties with excellent agreement with mean-field Hubbard calculations. This opens the possibility to conduct in-depth studies of spin transport in disordered graphene ribbons, where the impact of disorder is still not fully understood.

The work in this chapter was developed in collaboration with Seán McCann and Dr. Stephen Power. My contribution was the development and testing of different descriptors, development of SC routines, geometries and edge-disorder generation. I have also brought my contribution by an active benchmarking of the results from our predictions by ML with respect to the conventional SC method. Given the development and the promising results of the project in the prediction of magnetic profile, I also led the application of the method to extended ribbon geometries, which enabled the study of spin-transport discussed in papers [126] and [239], and in detail in the following chapter. The spin-transport section in this paper [126] is my principal contribution.

## Spin-polarized transport in edge-disordered graphene nanoribbons

### 5.1 Introduction

Graphene nanoribbons featuring zigzag edges (ZGNRs) have a lot of potential applications in spintronics since they can host spin-polarized transport channels near their edges [65, 66, 169]. Experimental achievements, such as on-surface synthesis alongside STS, provide unprecedented fine-tuned techniques for synthesizing and characterising such nanostructures [33, 34, 107, 220]. Yet even if somewhat mitigated, disorder is present in the synthesis of nanoribbons and in particular on the edges due to their propensity to be highly reactive [218]. It can manifest as vacancies on the edge of ribbons [31, 32, 217], known as rough disorder, or in the form of variations in the width or edge structure of the ribbon known as smooth disorder [34, 62, 222, 223, 240]. Bottom-up ribbons, which can be very precise when grown on metal substrates, will need to be transferred to other substrates for device applications. This transfer process can be detrimental as it often introduces disorder. Disorder, such as impurities or defects in a ZGNR, can significantly impact spin transport [210, 211]. One major effect is that disorder can cause scattering of electrons, which can lead to spin relaxation. This is the process by which the spin orientation of an electron becomes randomized, effectively reducing the amount of spin-polarized electrons that can be transported through the material. Disorder can also cause the formation of localized states within the bandgap of a ZGNR, which can trap electrons and hinder their movement through the material [188, 194]. Taking advantage of the detrimental power disorder has on spin-transport and it has also been suggested that engineering the edge structure is also a viable route to control spin-polarised currents in ZGNRs. For instance, Wimmer et al. [90] proposed to intentionally induce roughness on one edge to create a spin-current injector based on ZGNR.

Defect-engineering by edge chemical functionalisation is also another way to control spin-related transport in these structures [194, 209, 210].

For non-magnetic ribbons, edge roughness has been thoroughly investigated [109, 170, 171] and typically requires configurational averaging over a large numbers of configurations (in order to remove configuration-specific peaks and reveal the overall trends). In the context of spin-transport, theoretical investigations of disordered experimental-scale systems are computationally prohibitive as conventional techniques restrict the study to small or periodic systems. With our novel machine learning approach [126] (cf. chapter 4), accurate estimation of magnetic moments in arbitrarily large and disordered graphene nanoribbons is now achievable at a very moderate computational cost. Extending the scope of conventional techniques to realistic systems, investigations of the electronic, magnetic and transport properties of these promising materials are reachable. By identifying the types of disorder commonly present in fabricated ribbons, we conduct a detailed and systematic analysis of spin-transport in edge-disordered GNRs. Grasping the interplay between disorder profiles and local magnetism, we find that spin-polarised edge currents establish at low energy. Furthermore, the robustness of these spin-polarised edge channels is highly dependent on the roughness of the edges in ZGNRs. ZGNRs with sufficiently asymmetrical shaped edges are host to a finite net spin conductance.

By first giving an overview in section 5.2, of the edge disorder profiles in ZGNRs encountered in experiments, we start by presenting how to create the so-called “rough” and “smooth” edge disorders.

Based on the previous chapter, section 5.3 discusses the potential of our trained neural network model to accurately predict magnetic profile of edge disordered ribbons regardless of the disorder profile. This, in turn, shows to be a very powerful and efficient tool to perform spin-transport calculations in large and disorder ribbons, near-to-impossible task with conventional methods. This cost-effective combination of machine learning techniques with optimised transport software (TBtrans) [158] serve to the generation of various data sets.

Section 5.4 provides a detailed study on how spin-transport is impacted by edge disorder. Considering first spin-transport in pristine ZGNR, various edge disorder profiles are studied for ribbons of varying lengths and allow general trends to be observed. The robustness of spin-currents in such materials are highly dependent on the disorder profile a ribbon has. Finally, we envision in section 5.4.4, by an in-depth study, how to create an asymmetry in realistic devices, by investigating the combination of different disorder types on the edges of such systems. Robustness, spin-switching and various polarisations effects are reported, potentially leading to control spin-polarised currents for spintronics applications.

## 5.2 Disorder profiles

Even before graphene was successfully isolated [13] and triggered the booming interest for this material and its derivatives ever after, engineering a tunable bandgap by inducing edge confinement of the electrons was already predicted by seminal theoretical works [66, 169]. Required if graphene was ever to be used as a suitable candidate for the next generation transistor, questions about its experimental feasibility immediately raised as the first experiments on graphene nanoribbons [72] presented quite unexpected results. Indeed, there was a large discrepancy between experimentally measured bandgaps and those predicted by the theory. After several further investigations [113, 230, 241], it has been suggested that this difference resulted from the challenge of obtaining clean edges experimentally [242, 243].

ZZ-edged ribbons can host magnetic properties due to their low-energy states present at the edges. When electronic interactions are taken into account, spin-splitting is predicted to happen, leading to spin-polarized edge states because of the large density of electronic states at low energies. From all the finite-size structures that could be obtained from graphene, ZGNRs are the most interesting as when electron-electron interactions are considered, the magnetic ordering is ferromagnetic along one edge and antiferromagnetic across the ribbon, as each of the two edges is associated with a different sublattice [67, 88]. The formation of finite magnetic moments near the edges changes the band structure of ZGNRs at low energy. Despite this local spin-polarised current flow, the net spin current in pristine ZGNRs is negligible due to the cancellation of the oppositely-polarised contributions from each edge [67, 191]. Several theoretical ways to induce spin functionalities in ZGNRs among which transverse electric fields [67], gate voltage [89, 91], chemical functionalization [208–210] have been proposed. However the method that is in accordance with difficulties to precisely control the edge structure is through edge defect-engineering [90, 211]. A various amount of spintronic devices based upon these functionalities such as spin-filters [67, 92–94], spin-polarised beam splitter [95, 96], spin qubits [97, 98] and logic gates [99, 100] have been proposed.

GNRs can be experimentally fabricated by lithographic etching methods [61, 72, 219]. Although these promising advances in manufacturing techniques, some degree of disorder is inevitable in experiments [33, 105, 223, 224]. In the context of non-magnetic ribbons, top-down approaches which consist in creating edges by etching graphene with oxygen plasma, electron beam or by chemicals do not stem well-defined edges but result in a rough-edge pattern [212–215]. The edge roughness is here resulting from carbon atoms being torn out from the nanostructure during the etching process. Impressive achievements with the bottom-up approach resulted in a high degree of tunability to fabricate diverse GNRs with

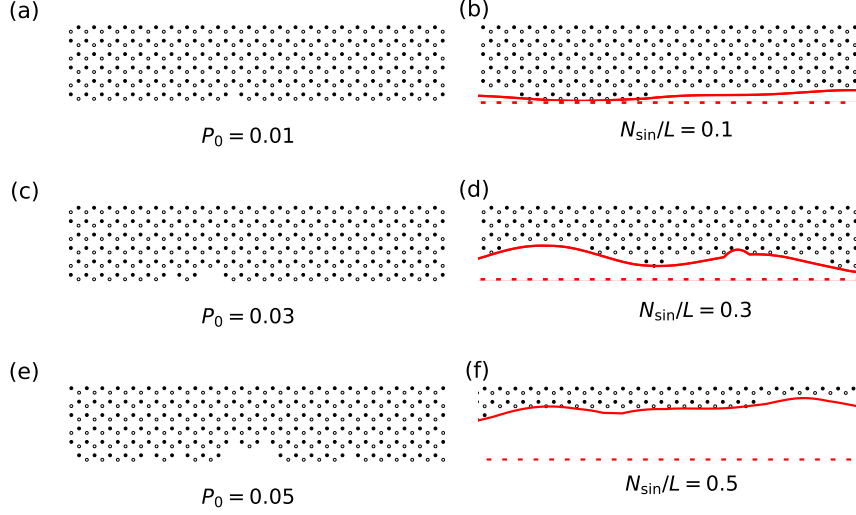


Figure 5.1: Different etching profiles where portions of the bottom edge are shown with increased values of disorder towards bottom panels. Left panels: rough disordered profiles. The values of Right Panels: smooth disordered profiles. The solid red lines shows the superposition of sine functions that results in the etching profile. The dashed red lines is showing where the initial bottom edge is after etching.

desired widths, edge shapes and topologies [107, 220, 221, 244]. STM and STS revealed the experimental presence of localised edge states by probing the local electronic structure of ZGNRs edges [34, 104, 105]. Driven by recent advancements in chemical synthesis methods, state-of-the-art epitaxial [62, 240] and bottom-up fabrication techniques also yield on-surface narrow AGNRs [33] and ZGNRs [34] with atomically precise edges. Even though strong local rough disorder are largely absent, these ribbons grown on substrates still include longer-ranged disorders, like smooth width fluctuations or irregular junctions. The fabricated ZGNRs have a smoother edge profile where random distributions of nanoconstriction as well as chiral edges are observed across the ribbons [74, 105, 223–226].

To model the two main observed disorder profiles in ZGNRs, we adopt two different strategies to create specific type of disorder. As we want to create a sufficiently vast configurational space, these disorder creating processes are stochastic such that the randomly generated configurations are ideally unique. As seen on the left panels of the Fig. 5.1, rough edge profiles are created by removing randomly atoms from both edges following a uniform probability distribution. The depth and roughness of the disorder at the edges are parametrized by the number of etching sweeps,  $N_{\text{sweep}}$ , fixed at 10 for the rest of this chapter and the initial probability of etching per site  $P_0$ . The  $i$ -th sweep ( $i = 0, 1, \dots, 10$ ) probability of etching is mapped through the relation  $P_i = P_0 \left(1 - \frac{i}{10}\right)^2$ . As etching atoms in one sweep increases the number of atoms that could potentially be swept on the next iteration, we purposefully decrease the probability of etching following the aforementioned function. At the end of the different sweeps, dangling carbon

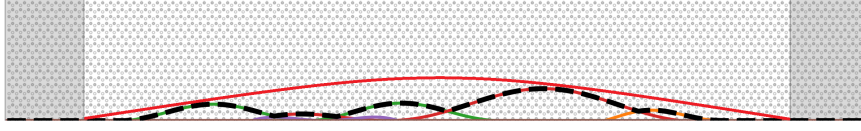


Figure 5.2: Smooth disorder profile creation : Here is shown how smooth disorder is applied to a pristine ribbon. The superposition of numerous sine functions with random start and end positions, periods and phases are first drawn. Then the atoms lying underneath the dashed-line are removed from the system resulting in a smooth-disordered edge. The red solid line represents the envelope function, ensuring the disorder to be confined in the central device region.

atoms with only a single neighboring atom are also removed from the system and we assume carbon atoms at the edges to be passivated by hydrogen such that the  $\pi$ -bands remain unaffected. For a device region with length  $L$  measured as the number of GNR unit cells in the central device region, smooth edge disorder profiles, corresponding to the right panels of Fig. 5.1, are built by removing atoms around both edges from the superposition of  $N_{\text{sin}}$  sine functions with randomized start and end points, amplitudes, periods and phases. The length normalisation of the number of sine functions,  $N_{\text{sin}}/L$ , guarantees to have a length-independent parameter, as is for the rough disorder parameter  $P_0$ . This allows us in turn comparative standpoints between ribbons of different lengths with different types of disorder. A more qualitative picture of how the atoms are removed given a certain number of random sine functions is shown in Fig. 5.2. The normalisation by the length of  $N_{\text{sin}}/L$  ensures the same level of smoothness for ribbons with different lengths and allows direct comparison. To avoid discontinuity of the etching caused by the random nature of the superposition, an envelope function (cf. Fig. 5.2) ensures a smooth transition towards the pristine edges of the semi-infinite leads.

### 5.3 Magnetic profile prediction: Benchmarking and scaling-up

In chapter 4, we have provided a detailed overview of our trained neural network model that could accurately predict the magnetic profile of graphene-based nanostructures such as nanoflakes and nanoribbons [126]. This neural network predicts the magnetic profile of arbitrarily large and disordered nanostructures and has shown its generalisation capacity for unseen structures (cf. Fig. 4.10) with a high degree of accuracy and at a very moderate computational cost. In the context of spin-transport, having access to magnetic profiles of disordered ZGNRs allows us to transform the non-magnetic spin-degenerate Hamiltonian into a spin-polarised one.

Fig. 5.3 summarises the workflow to perform spin-transport for a random con-

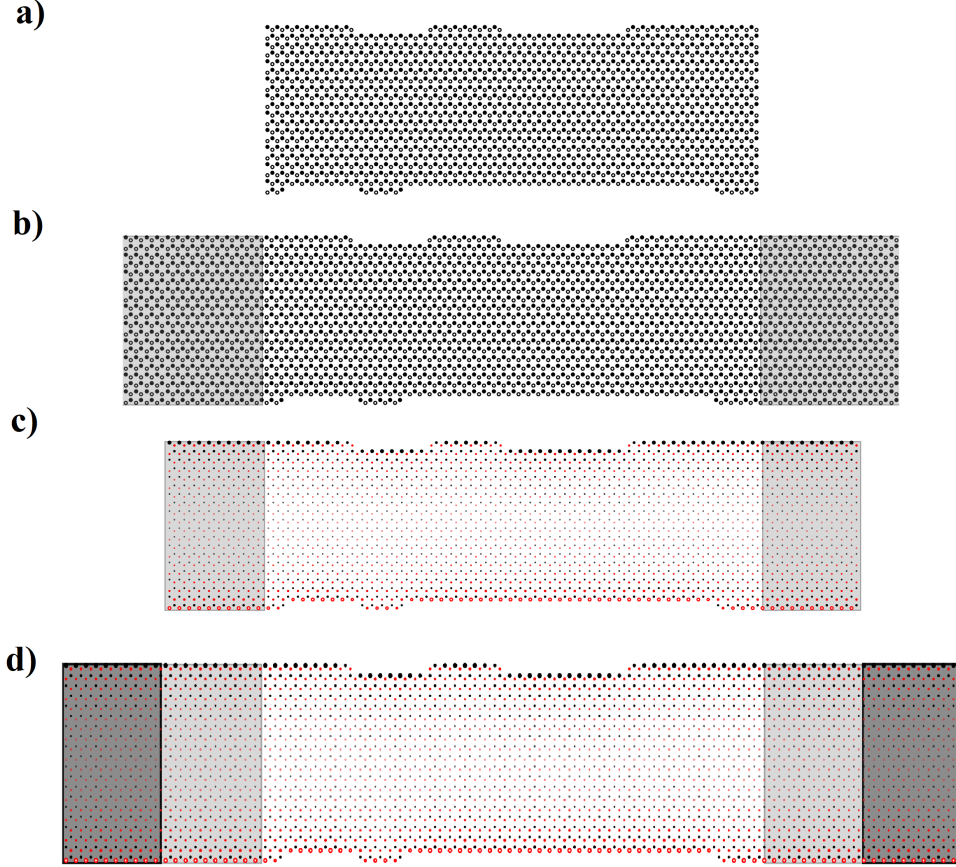


Figure 5.3: (a)- The central device region of a smooth-disordered ribbon. (b)- Extra unit-cells, shown by the grey-shaded rectangles, are added to both sides of the central device region to trick our neural network for correct magnetic profile prediction. (c)- After having partially removed the grey-shaded unit-cells in (b), it is necessary to keep spin-polarised buffer regions on the spin-polarised central device region. These regions ensure a smooth transition towards the pristine spin-polarised leads (dark grey-shaded rectangles) to perform spin-transport calculations shown in (d).

figuration. To find the magnetic profile of a device as shown in Fig. 5.3(a), we should remember that the device is located as a central device region between two leads and the entire system should be infinite in the longitudinal direction. The device in Fig. 5.3(a) presents AGNR sections and we have seen in the previous chapter that armchair portions hold no edge-states hence they have no magnetic moments at half-filling. As our model is distance-dependent (cf. Chapter 4), the presence of a nearby armchair edge completely disrupts the local magnetisation along the vertical ends of the ribbon. This is a problem as the attached leads are supposed to be spin-polarised. To mitigate this problem, we add two regions of an informed number of unit-cells to both ends of the ribbon before performing the prediction with our NN model as shown by the adjacent grey-shaded rectangles in Fig. 5.3(b). This added regions are here to “trick” the neural network and shift the armchair edge portions further away from the actual device. Once the prediction has been carried out, these added regions are partially removed as

seen in Fig. 5.3(c).

As disorder disrupts the local magnetisation, we need to be careful to the discontinuity that could appear between the central device region and the (SC-calculated) spin-polarised pristine leads. To ensure a smooth transition between the magnetic profiles of the device region and the leads, we keep an informed number of the previously added pristine unit-cells that we call buffer regions shown in Fig. 5.3(c). The condition is that the leftmost and rightmost unit-cells in these buffer regions should have the same magnetic profile as the leads' neighbouring unit-cells up to a tolerance threshold. Once this condition is met, we attach the spin-polarised leads (cf. Fig. 5.3(d)) with Dyson equation and perform spin-transport with TBtrans [158]. For each ribbon, we get three different Hamiltonians :

- The unpolarised Hamiltonian  $\mathcal{H}^0$ :

$$\mathcal{H}^0 = \sum_{i,j,\sigma} \gamma_{ij} \hat{c}_{j\sigma}^\dagger \hat{c}_{i\sigma}, \quad (5.1)$$

where we purposefully set the onsite potential to  $\varepsilon_i = 0$  for all site  $i$  across the entire device (cf. Eq. 2.1).

- The spin-polarised Hamiltonians  $\mathcal{H}^\sigma$ :

$$\mathcal{H}^\sigma = \mathcal{H}^0 - \sigma \frac{U}{2} \sum_i m_i \hat{c}_i^\dagger \hat{c}_i. \quad (5.2)$$

with spin  $\sigma = \{\uparrow / \downarrow\}$ , the Hubbard parameter  $U = 1.33|t|$  in good agreement with DFT-extracted results [88], and  $m_i$  the local magnetic moment at site  $i$  obtained with our NN model.

Once the Hamiltonians are calculated, TBtrans performs the spin-transport related calculations by preliminarily attaching the corresponding spin-polarised leads' self-energies and using the Caroli formula (cf. Eq. 2.59). It should be noted that we are only using ML to predict magnetic profiles and not directly estimating transmission as in the first chapter 3.

To see how accurate the spin-transport properties are, we benchmark our spin-transport results with self-consistently obtained magnetic profiles. The benchmarking results are displayed in Fig. 5.4 for two different ribbons presenting two different disorder profiles. Fig. 5.4(a) is a rough-edged ribbons where the magnetic profile is obtained with our NN model following the workflow in Fig. 5.3. The inset in Fig. 5.4(b) shows how the predicted (NN) and actual (SC) magnetic moments compares and we see a near-to-perfect agreement between the predicted and actual moment profiles. Fig. 5.4(b) shows the conductance as a function of energy (in units of  $|t|$ ) for the ML- (solid lines) and SC-obtained (dots) magnetic profiles which are matching almost perfectly either for spin up

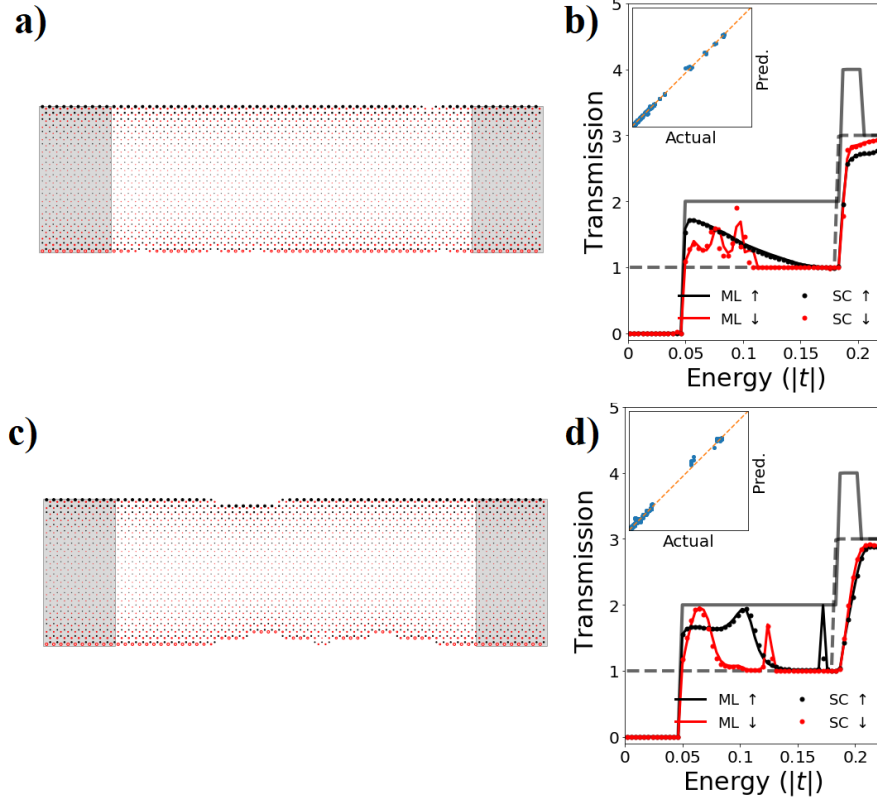


Figure 5.4: Benchmarking of the ML estimated moments and against the conventional SC method for a 24-ZGNR wide ribbon. (a) and (c) - Rough and smooth magnetic profiles estimated with the trained neural network. The grey areas represent the buffer regions added on each side of the device region. (b) and (d) - Transmission vs. energy for the configurations in the panels (a) and (c) respectively. The pristine transmission for the magnetic and non-magnetic cases are respectively shown by the solid and dashed grey lines. The spin-polarised transmissions resulting from the estimated magnetic profiles with ML are represented by the black and red lines. The SC estimated moments are allowing to find the spin-polarised transmissions shown by the red and black dots.

or down. Fig. 5.4(c)-(d) depict similar qualitative and quantitative behaviours for a smooth-disorder profile ribbon.

Given the high accuracy with which our ML model predicts magnetic profiles, we see that transmissions for spin-polarised and disordered nanoribbons is now computationally affordable. With roughly 5200 atoms for each ribbons presented in Fig. 5.4, still within the reach of SC calculations, it is easy to benchmark and assess the accuracy of our workflow combining ML with conventional yet optimised transport methods. However, the real power of these combined methods lies in the possibility to scale up the prediction to realistic-sized devices counting a huge amount of atoms. Fig. 5.5(a) shows once again the benchmarking of a ribbon presenting smooth-disorder as its edges. This ribbon is 17 nm long and 8.3 nm wide and present randomly etched macroscale portions of atoms resulting in randomly distributed nanoconstrictions. Here the system size starts to be conse-

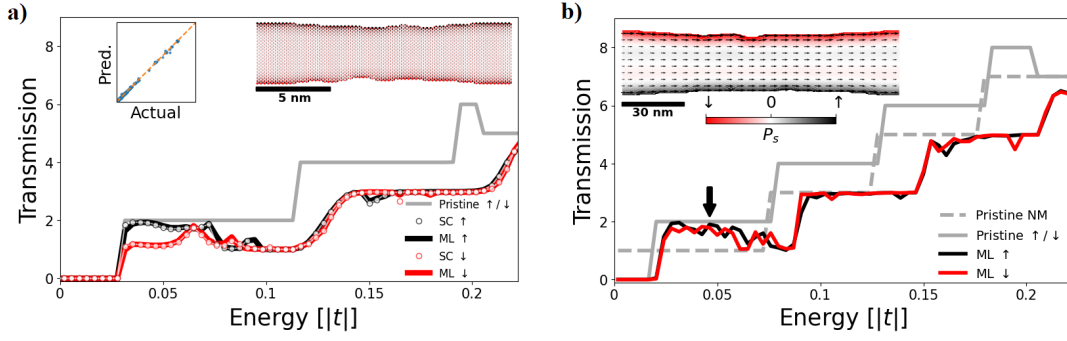


Figure 5.5: **(a)**- Spin-dependent transmission in an edge-disordered ZGNR, calculated using SC (dots) and ML (lines) moment profiles. The insets show the accuracy of the ML moments and the moment profile along the ribbon. **(b)**- Transmissions through a larger system. The inset maps the current flow and spin polarisation at the marked energy. Spin-polarised channels are visible along the smooth edges.

quent and become more and more untractable for conventional SC method as the number of atoms in this ribbon is around 9000. The accuracy and the mapping of the magnetic profile are shown in the top insets respectively. Whereas it took roughly 6 and half hours for this ribbon's magnetic profile to be calculated with SC-method, our ML-based prediction was realised in less than a minute. Still, we see how reliable and highly efficient our ML-based prediction is by comparing SC- and ML-obtained spin-up or spin-down conductances. The 2 spin-polarised transmissions are matching perfectly except at one or two particular energy bins. With high confidence in our method and having a prediction method that is less sensitive to scaling effects, we can investigate spin-transport related properties for systems that would be unbearable with conventional SC-methods. Fig. 5.5(b) shows the spin-up and down transmissions calculated for a ribbon that is roughly 122 nm long and 32 nm wide with around 30000 atoms in total. Once we have the magnetic profile, we can also calculate other properties such as the spin-currents at different energies for this large and disordered ribbon with ease which would not be possible with conventional SC method. The inset here shows the spin-polarisation of the edge currents at the energy shown by the black arrow. This ribbon is completely out-of-reach for SC-method due to matrix inversion related computational bottlenecks. In addition to the huge amount of iterations this system would take to converge to a suitable mean-field accuracy if the memory issues were to be solved, this typical system size prevents the generation of a vast amount of randomly generated configurations, necessary to conduct an in-depth disorder study. Our ML-based method provides a quick and accurate way to predict and feed the magnetic features into an optimised transport code to quickly calculate spin-transport for this type of realistic, arbitrarily large and disordered nanostructures. This framework allows us to investigate the local behaviour of spin-currents and back-scattering phenomena that can happen with regard to

the different disorder profiles. The next section gives a detailed study on how spin-currents are robust or not against edge disorder.

## 5.4 Spin-transport in disordered ZGNRs

### 5.4.1 Pristine ZGNRs

Before we can consider the impact of disorder on transport, it is worth looking in detail at the transport properties of pristine magnetic ZGNRs.

Edge-induced confinement gives rise to subbands in the band structure of graphene as discussed in chapter 3. The left inset of Fig. 5.6(a) shows that quantisation occurs for higher energy (grey) bands in non-magnetic ZGNRs, but the lowest energy (bold, black) subband displays unique features. The zero-energy flat band, which is localised at the ribbon edges, connects the two valleys and has no correspondence in the band structure of bulk graphene. At the  $K$  point, this band merges with a dispersive band (also shown in bold) which has a sublattice-dependent node at each edge and so principally carries current through the central region of the ribbon, as shown by the current map in Fig. 5.6(b). This band structure gives rise to a transmission sequence  $T(E) = 2n + 1$  for each spin channel in a non-magnetic ribbon, as shown by the dashed black curve in Fig. 5.6(a). Here  $n$  indicates the number of valley-degenerate higher-order modes available at a particular energy.

Electron-electron interactions lead to a spin-splitting of the localised edge states and the formation of local magnetic moments. These moments are largest along the edges of the ZGNR, and decay towards its centre as can be qualitatively observed in Fig. 5.4(a) and (c). The exposed sites along a zigzag edge all reside on the same sublattice, and their associated moments align ferromagnetically. However, the opposite edges of a ZGNR expose sites from opposite sublattices and consequently are antiferromagnetically polarised. The strength of this coupling, and the resulting band gap  $E_G$  at the Dirac points, depends on the width of the ribbon. Aside from a gap opening, the band structure of a magnetic ribbon shows other qualitative changes from the non-magnetic case (see insets of Fig. 5.6(a)). The higher-order subbands are largely unchanged, as is the dispersive segment of the lowest energy mode which continues to carry currents of both spin orientations through the central region of the ribbon. However, the previously flat portions of the band now also gain dispersion and provide an additional transport channel for each spin in the energy range  $\frac{E_G}{2} < |E| \lesssim 0.6|t|$ . These new transport channels lie along the edges of the ribbon, so that the total current flow at low energies, as mapped in Fig. 5.6(c), is a combination of bulk and edge contributions.

Although the band structures for up- and down- spin electrons are identical, the

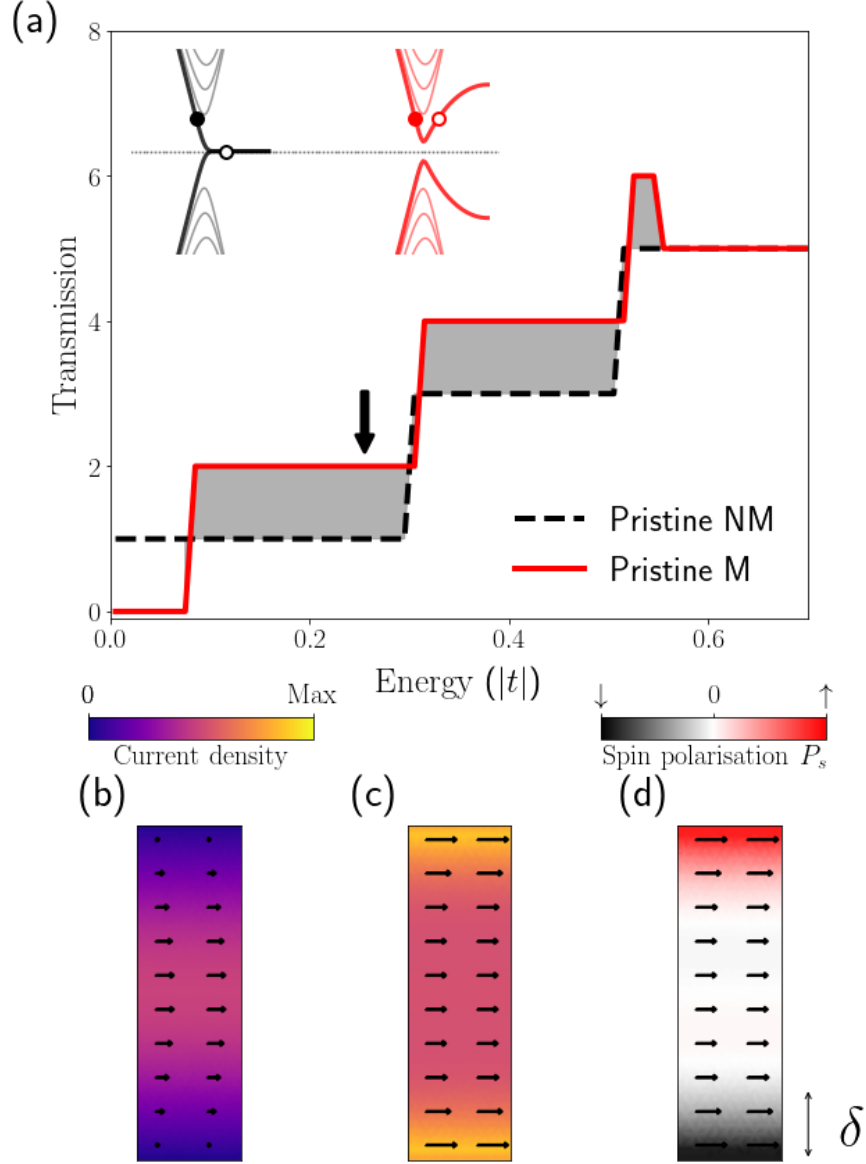


Figure 5.6: (a) - Transmission vs. energy in unit of  $|t|$  for a 40-ZGNR pristine ribbon. The grey shaded area respectively between the pristine NM (dashed) and M (solid red) curves is where transmissions are carrying spin information. The inset shows the band structures in the vicinity of the Fermi energy for a non-magnetic ribbon (black) and a magnetic ribbon (red). (b) and (c) - The current densities for a portion of the pristine ribbon for the NM and M cases respectively. The arrow fields show the net current flow through the ribbon. (d) - For the M pristine ribbon is shown the spin polarisation  $P_s$  across a transversal section.  $\delta$  represents the bandwidth onto which the quantity  $\langle \bar{S} \rangle$  is integrated in Fig. 5.9(b).

new dispersive states for each spin are located on opposite sides of the ribbon. This means that the new transport channels near the ribbon edges are strongly spin-polarised. This is shown clearly by the colour shading in Fig. 5.6(d). The current flowing near the ribbon edges, in the edge-localised modes, takes strong and opposite polarisations on either side of the ribbon. The centre of the ribbon also carries current, but this is almost completely unpolarised, as the bulk modes for both spin orientations are nearly degenerate.

The band structure changes and spin-polarised transport channels are also reflected in the transmission spectrum, shown by the red curve in Fig. 5.6(a). A small band gap occurs for low energies, giving  $T = 0$ , but then  $T_M = T_{NM} + 1$  for each spin over the energy range where the edge channels occur. Beyond this, the transmission reverts back to the  $T(E) = 2n + 1$  plateau sequence. An enhancement of the transmission above this sequence at low energies is a key signature of the presence of spin-polarised edge currents in a ZGNR and is here represented by the grey-shaded area in Fig. 5.6(a)

#### 5.4.2 Rough disorder

The transmission spectra of a wide range of 40-ZGNRs with rough edge disorder were calculated using ML generated moments, and Fig. 5.7 presents an overview of the key results. The configurations are characterised by the length of the disordered region,  $20 \leq L \leq 150$ , in terms of ZGNR unit cells, corresponding to  $4.5 \leq L \leq 37.5$  nm, and by the etching probability  $0.005 \leq P_0 \leq 0.05$ , where larger values of  $P_0$  correspond to rougher-edged ribbons. For each set of parameters  $\{L, P_0\}$ , 200 different configurations are generated and used to perform configurational averaging in order to remove configuration specific peaks from the transmission spectra in Fig. 5.7. This corresponds to the generation of 28000 ribbons with different disorder profiles and lengths. As the same levels of disorder are applied to both edges, the transmission results for both spin channels are the same after configurational averaging, and so we limit the results and discussion here to the spin-up case.

The coloured curves in Fig. 5.7(a) show the evolution of the transmission spectrum for an intermediate disorder strength ( $P_0 = 0.03$ ) as the length of the disordered region is varied. The solid and dashed black lines in this plot show the corresponding transmissions for pristine magnetic and non-magnetic ZGNRs respectively. We note that for  $L \gtrsim 100$  (red-shaded curves) the transmissions lie near or slightly below the pristine NM result over the first plateau. This suggests that the spin-dependent edge-channels are almost completely quenched by this level of edge disorder. At higher energies, the survival of spin-polarised transmission curves above the NM pristine threshold is non-existent even for shorter devices. However, within the first plateau the transmission is greater than the

non-magnetic ribbon for disorder lengths  $L \lesssim 100$ . A similar trend is noted if we consider ZGNRs with a constant disorder length  $L = 110$  and varies the strength of the edge disorder as shown in Fig. 5.7(b). As  $P_0$  increases, the edge-channel signature quickly vanishes in higher-order plateaus, but a more robust signal is seen in the first plateau until  $P \sim 0.3$ . The averaged transmissions in

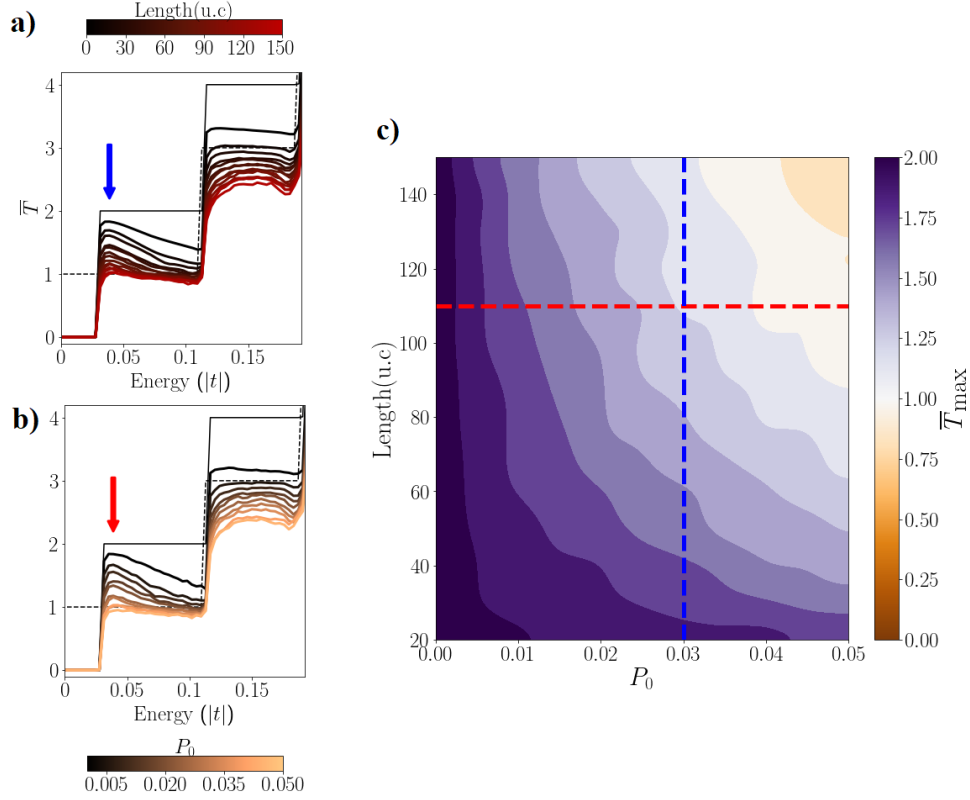


Figure 5.7: (a)- Averaged transmissions vs. energy increasing the length of the 40-ZGNR device and keeping the roughness  $P_0 = 0.03$  constant. It consists in following the blue dashed line in the bottom panel. (b)- Averaged transmissions vs. energy increasing the roughness of the device and keeping the length  $L = 110$  unit-cells constant or following the red line in the bottom panel. For top panels, the solid and dashed black lines represent the pristine transmission for the magnetic and non-magnetic case respectively. The red and blue arrows show where the transmission is picked for the contour plot and respectively represent the straight lines to follow in the bottom panel. (c)- Contour plot of the maximal averaged transmission for each data set  $\{L, P_0\}$  taken at  $E = 0.038|t|$ .

Fig. 5.7(a)-(b) peak early in the first plateau at  $E = 0.038|t|$ , marked by blue and red arrows in the panels. We take the value of the averaged transmission here,  $\bar{T}_{\max} = \bar{T}(E = 0.038|t|)$ , as a figure-of-merit for the robustness of the spin channel for a given set of disorder parameters  $\{L, P_0\}$ . Fig. 5.7(c) shows a contour plot of  $\bar{T}_{\max}$  as both the length and strength of the disorder are varied. Dark purple regions indicate near-perfect transmission, with white indicating a complete suppression of the edge-channel transmission bump. Orange regions correspond to  $T < 1$ , indicating that the bulk transport channel in the centre of the ribbon is also being diminished. The peaks of the curves shown by arrows in Fig. 5.7(a)-

(b), which are taken at constant  $P_0$  and  $L$  respectively, lie along the blue and red dashed lines superimposed on the contour plot. We note that the spin-dependent bump is quickly quenched as either the  $L$  or  $P_0$  are increased, suggesting that even in the first plateau, spin-dependent edge channels are quite sensitive to the presence of rough edge disorder.

To confirm that the transmission features discussed above correspond to a suppression of spin-polarised edge currents, in Fig. 5.8 we map the local current and spin polarisation of two different disordered nanoribbons. Fig. 5.8(a)-(b) show instances of  $P_0 = 0.02$  and  $0.04$ , respectively, in a  $L = 110$  ZGNR. From Fig. 5.7(b), we see that disorders of these strengths correspond, respectively, to partial and complete suppression of the peak associated with spin transport in the first plateau.

This is borne out by the spin-polarised current maps, where the spin-polarised edge channels are still visible for the weaker disorder observable in Fig. 5.8(a). This is shown more clearly by the zoomed sections in Fig. 5.8(d)-(e), which can be compared to the situation in a pristine ribbon (Fig. 5.8(c)). Fig. 5.8(d)-(e) are taken at the same energy, and with the same normalisation of current and spin-polarisation, so directly show the change in both spin current and polarisation between the three cases. The current flow and spin polarization for  $P_0 = 0.02$  strongly resemble the pristine case, but with somewhat diminished spin-polarised edge states. Very weak remnants of the spin-up channel at the top edge of the ribbon are visible for the  $P_0 = 0.04$  case, whereas the spin-down channel at the bottom edge is completely quenched. A more quantitative insight of the survival of spin currents is depicted in Fig. 5.8(f). It shows how the magnitude of the spatially averaged (lengthwise) spin polarisation ( $\bar{J}_S = \bar{J}_\uparrow - \bar{J}_\downarrow$ ) varies across the width of the ribbons in Fig. 5.8(a)-(b). A small running average has also been applied in the transverse direction to remove short-ranged oscillations and sublattice effects. The dashed black curves correspond to a pristine ZGNR, with the spin-polarised edge states giving rise to sharp peaks near the edges (cf. Fig. 5.8(c)). The flatness of the averaged spin currents in the central regions of the ribbon also shows that current in the bulk is almost completely unpolarised. However, a weak remnant oscillation of the spin polarisation can be seen across the bulk of the ribbon. These are due to asymmetries between the spin-up and spin-down variants of the bulk mode, and have much weaker spin polarisation than the edge channels. We see that  $\bar{J}_S$  is nearly equal to zero over the entire transversal direction for the ribbon in Fig. 5.8(b) shown by the strongly disordered case (magenta curve) in Fig. 5.8(f). This suggests that the spatial polarisation of the spin currents near the edges is completely lost for this particular disorder value. The bottom edge value for  $\bar{J}_S$  for the weakly disordered case (green curve) seems concordant with the spatial mapping of the spin polarisation across the

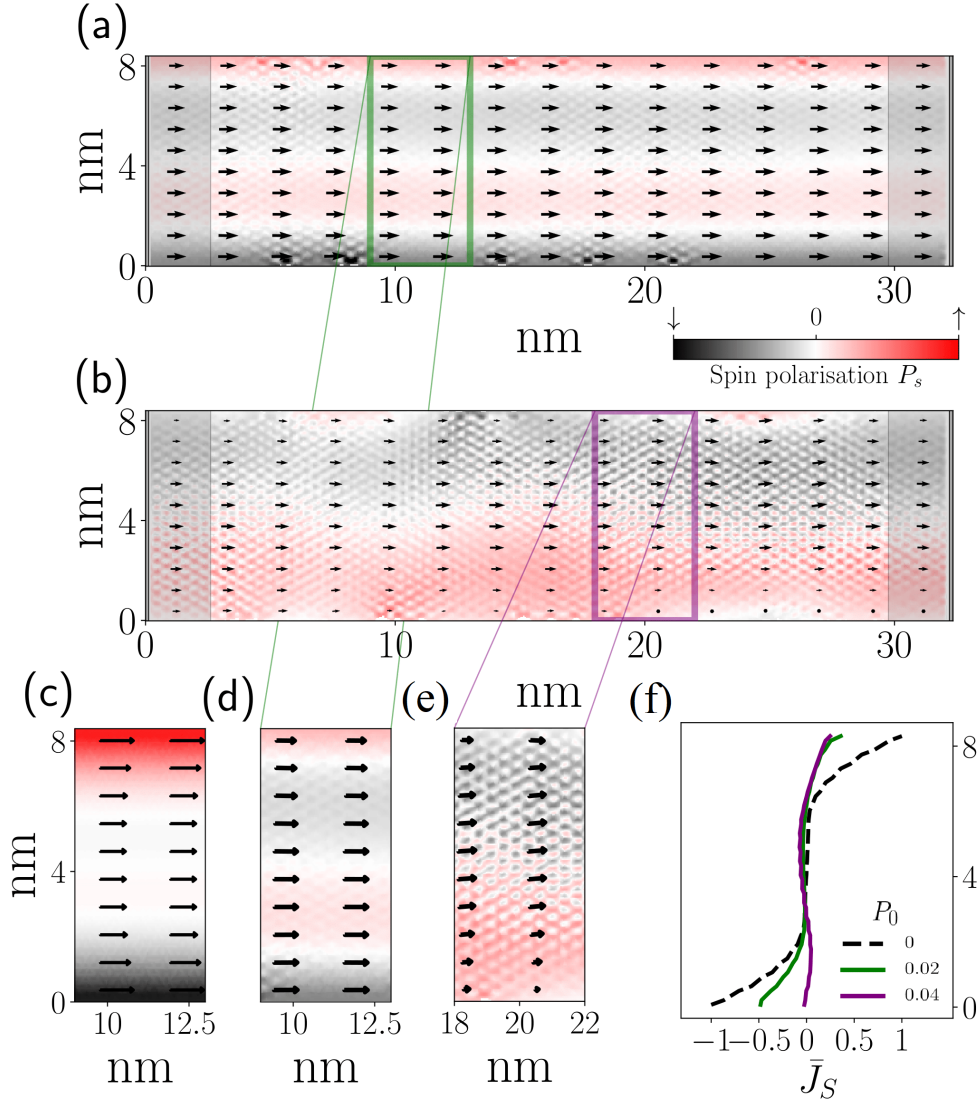


Figure 5.8: **(a)** and **(b)** - Two rough profiles configurations of  $L = 110$  unit-cells with edge roughness characterised with  $P_0 = 0.02$  and  $0.04$  respectively. The spin polarisation  $P_s$ , as a background color, shows the local distribution of spin-polarised states across the ribbon whereas the arrow field shows the local net spin-current flow. **(c)**, **(d)** and **(e)** - Sections of the magnetic pristine, and two zoomed sections from panels **(a)** and **(b)** respectively for comparative purposes. **(f)** - The spatially averaged spin-polarisation  $\bar{J}_S$  across the width of the ribbon. This quantity is normalised with respect to the pristine spin-polarisation and allows a quantitative comparison between different configurations. The dashed black line is the pristine case distribution showing a  $\pm 1$  polarisation value at both edges. The green and magenta curves represent  $\bar{J}_S$  for panels **(a)** and **(b)** respectively.

ribbon in Fig. 5.8(a). Even if both the edges are disordered with  $P_0 = 0.02$  in this ribbon, we see how the randomness of the rough disorder profile can result in survival or quenching of the spin currents along the edges. Indeed, even though the bottom edge has a value of  $\bar{J}_S \approx 50\%$  of the pristine case, the top edge has no sign of spin-polarisation confirming the necessity in averaging the configuration-to-configuration specific features.

These local maps give a qualitative picture of the breakdown of spin-polarised edge currents. However, local current flow can vary considerably between different ribbons with same levels of disorder, and even between different regions of the same ribbon. To quantitatively investigate the breakdown of spin-polarised edge transport, we examine the spatial dependence of spin-polarised currents, averaged over all instances of the same disorder and along the entire disordered length of each instance. To characterise the decay of edge currents further, we define the edge spin current strength

$$\langle \bar{S} \rangle = \frac{1}{S_0} \int_0^\delta dy (\bar{J}_\uparrow(y) - \bar{J}_\downarrow(y)) . \quad (5.3)$$

The integral here gives the total spin current through a narrow strip of width  $\delta = 1$  nm at the edge of the ribbon, as shown in Fig. 5.6(d). This is both spatially and configurationally averaged, to remove local or configuration-specific features, and then renormalised relative to the value in a pristine ribbon  $S_0$ . In Fig. 5.9, we plot both the configurationally-averaged total maximal transmission  $\bar{T}_{\text{Max}} = \bar{T}_{\text{Max}}^\uparrow + \bar{T}_{\text{Max}}^\downarrow$  in (a), and the edge current strength  $\langle \bar{S} \rangle$  in (b), as a function of length for the range of considered  $P_0$  values. This allows us to compare the suppression of the edge spin current to that of the total current. The decay of the spin current at the edges is much faster than the decay of the total current. This can be explained by the resilience of the bulk current, which is largely spin-degenerate, to edge disorders. The forward and backward-propagating edge modes for a given spin are confined to a narrow region on the same edge and spin-polarised current at the edge can be backscattered more easily. This is particularly true for rough edges. A peculiar situation may occur for highly disordered rough-edged magnetic ribbons. The lowest energy mode in non-magnetic ribbons is extremely robust against edge disorder. Both the forward and reverse-propagating modes reside in the bulk of the ribbon, and have very little weight at the ribbon edges, as shown in Fig. 5.6(b). Therefore the probability of edge vacancies scattering electrons between these modes is very low. This results in an almost perfect transmission across the first plateau, with very weak dependence of the transmission on the length and strength of edge disorder. This does not extend to higher-order bulk modes, which have a more even distribution across the ribbon width, and are more easily scattered by edge disorder. The bulk modes in magnetic ribbons have a similar distribution across the ribbon width, but with

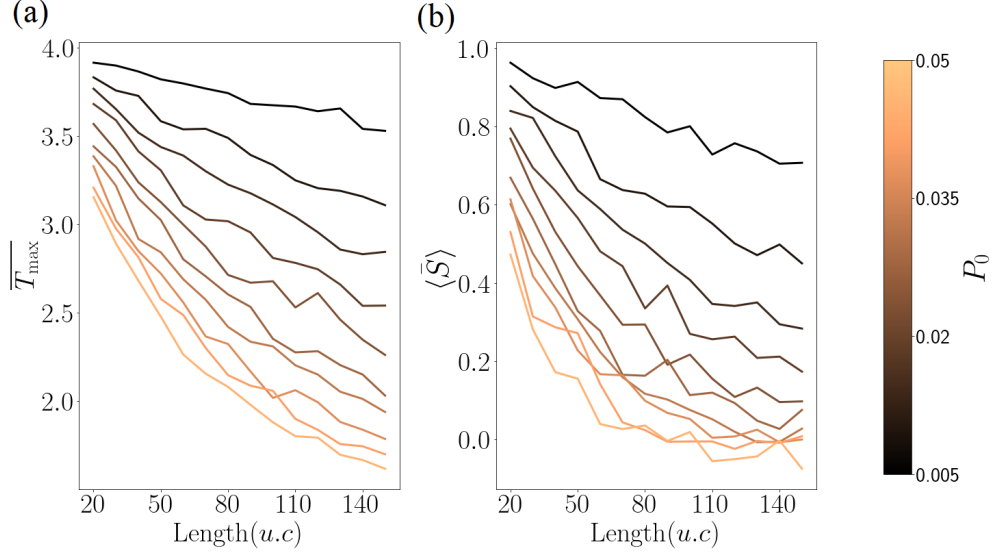


Figure 5.9: (a)- Total averaged current  $\bar{T}_{\text{Max}} = \bar{T}_{\text{Max}}^{\uparrow} + \bar{T}_{\text{Max}}^{\downarrow}$  taken at  $E = 0.038|t|$  vs length of the 40-ZGNR. (b)- Edge spin current strength vs. length of the ribbon (cf. Eq. 5.3).

a slight spin-dependent asymmetry, as observed earlier in Fig. 5.6(c). These are considerably more robust than the edge channels, where the edge channel is completely suppressed in the presence of disorder, leaving only current in the bulk. By looking at the panel Fig. 5.9(a), we observe that the total current flowing for strong edge disorder is lower in a magnetic than a non-magnetic ribbon which typically is equal to  $\bar{T}_{\text{Max}} = 2$ . This is somewhat surprising, as we may expect the transmission in both to be identical once disorder has fully quenched the edge channels in the magnetic ribbon. However, the additional edge channels in a magnetic ribbon also provide additional backscattering possibilities for bulk electrons. Edge disorder couples edge and bulk modes, and allows forward-propagating bulk electrons to be backscattered into backward-propagating channels at the edges. This means that the introduction of spin-polarised edge channels, which increase the total transmission in a pristine system, actually has a detrimental impact in the presence of edge disorder. Although the spin channel is eventually quenched at all energies by rough edge disorder, it is significantly more robust within the first plateau. This effect is more pronounced for smooth disorder, and will be discussed in detail in the next section.

#### 5.4.3 Smooth disorder

Even though epitaxially-grown ribbons on substrates like SiC are less subject to disorder, they still present smooth disorder edges [62, 240]. Therefore, being able to characterise the impact of this type of disorder profile, still common even in the most novel experimental synthesis techniques is crucial.

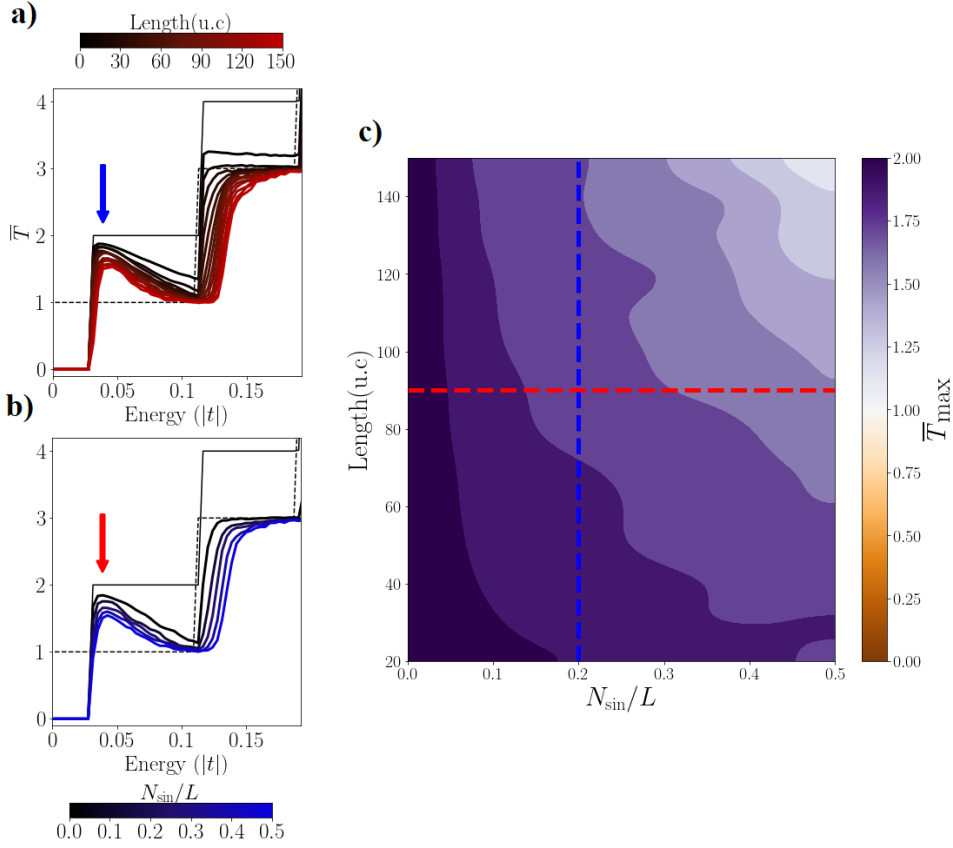


Figure 5.10: (a)- Averaged transmissions vs. energy increasing the length of the 40-ZGNR device and keeping the parameter  $N_{\text{sin}}/L = 0.2$  constant or following the blue dashed line in the bottom panel. (b)- Averaged transmissions vs. energy increasing the roughness of the device and keeping the length  $L = 110$  unit-cells constant or following the red line in the bottom panel. For top panels, the solid and dashed black lines represent the pristine transmission for the magnetic and non-magnetic case respectively. The red and blue arrows show where the transmission is picked for the contour plot and respectively represent the straight lines to follow in the bottom panel. (c)- Contour plot of the maximal averaged transmission for each data set  $\{L, N_{\text{sin}}/L\}$  taken at  $E = 0.038|t|$ .

Fig. 5.10 shows the overall picture on how smooth disorder impacts the averaged transmission spectrum. Large numbers (14000) of configurations have been generated to ensure the removal of configuration-specific features. Each configuration is characterized by the length,  $L$  of its device region in unit-cell and the quantity  $N_{\text{sin}}/L$ , the number of sine function per length in the range  $0 \leq N_{\text{sin}}/L \leq 0.5$ . The spin-dependent transmission spectra of 200 configurations, given the prior predicted magnetic moment profiles obtained with ML, are averaged for each set  $\{L, N_{\text{sin}}/L\}$ . By applying the same level of disorder on top and bottom edges, the averaged spin-up and spin-down transmission show similar trends. Hence the discussion of results for spin-up transmission are sufficient to comprehend how the smooth disorder influences the spin-transport properties.

Fig. 5.10(a) reflects how the averaged spin-up transmission spectra evolves when

keeping the parameter  $N_{\text{sin}}/L = 0.2$  constant and by increasing the ribbon length  $L$ . One immediate difference with the rough-profile equivalent panel in Fig. 5.7(a) is the behaviour of the averaged transmission curves in the vicinity of the peak at  $E = 0.038|t|$ . The depletion of the transmission spectra at this particular energy is significantly less pronounced and suggest a robustness of the spin-polarised transmissions even as the length is increased. The maximum transmission  $\bar{T}_{\text{max}}$  of the longest ribbon  $L = 150$  at this particular energy is 1.52. This figure-of-merit demonstrates that spin-currents are robust when compared to  $\bar{T}_{\text{max}}^{\text{NM}} = 1$  for the non-magnetic pristine ribbon and rough disordered ribbons. The behaviour for energies away from the peak within the first plateau displays similar trends as for the rough case. Fig. 5.10(b) displays for a  $L = 90$  fixed ribbon length how the averaged spin-polarised transmission evolves when the disorder strength is varied. Around the peak in transmission, we can see the maximum only slightly affected by varying the disorder strength. When compared to the rough case, we see how robust the spin-polarised currents are in the smooth case even as disorder is increased. When higher energy plateaus are considered for both panels (a) and (b) in Fig. 5.10, we see that the averaged spin-transmissions are almost completely quenched except for either very small and low-disordered ribbons. The contour plot in Fig. 5.10(c) maps how the figure-of-merit for robustness of the spin-transmission,  $\bar{T}_{\text{max}}$ , unfolds when disorder and length are varied. As seen on the top-right white color region, a concomitant high value for  $N_{\text{sin}}/L$  and  $L$  are necessary to observe the spin-signal's suppression for the smooth disorder profile. Even though the roughness parametrised by  $N_{\text{sin}}/L$  and the length are increased, we observe that the contour mapping  $\bar{T}_{\text{max}}$  portray a global enhanced robustness when compared to Fig. 5.7(c).

The robustness of spin currents when smooth disorder is applied can also be observed more qualitatively in Fig. 5.11. Here the ribbon picked from our data set corresponds to a  $L = 110$  unit-cells long nanoribbon with  $N_{\text{sin}}/L = 0.2$  as a level of disorder on both edges. Fig. 5.11(a)-(b) show the current maps of this particular configuration at  $E = 0.038|t|$  (cf. the peak in transmission) and  $E = 0.11|t|$ , at the onset of the second plateau respectively. For these values of  $(L, N_{\text{sin}}/L)$ , the spin transmissions of Fig. 5.10(a) shows a high spin-polarisation value around the peak and a complete suppression at higher energy. Local current maps in panels (a) and (b) of Fig. 5.11 respectively depict comparable qualitative behaviours as their spin-polarised transmissions counterparts in Fig. 5.10(a). Indeed, Fig. 5.11(a) shows strong and continuous polarised currents at both edges, responsible of the high transmission value at this particular energy despite large portions of atoms being removed. Panels Fig. 5.11(c)-(d) underpin the closeness of the pristine and disordered transmission spectra as these two sections are qualitatively similar. This is also clear from Fig. 5.11(f) that the spatially-averaged current map of this ribbon at this particular energy is nearly perfectly

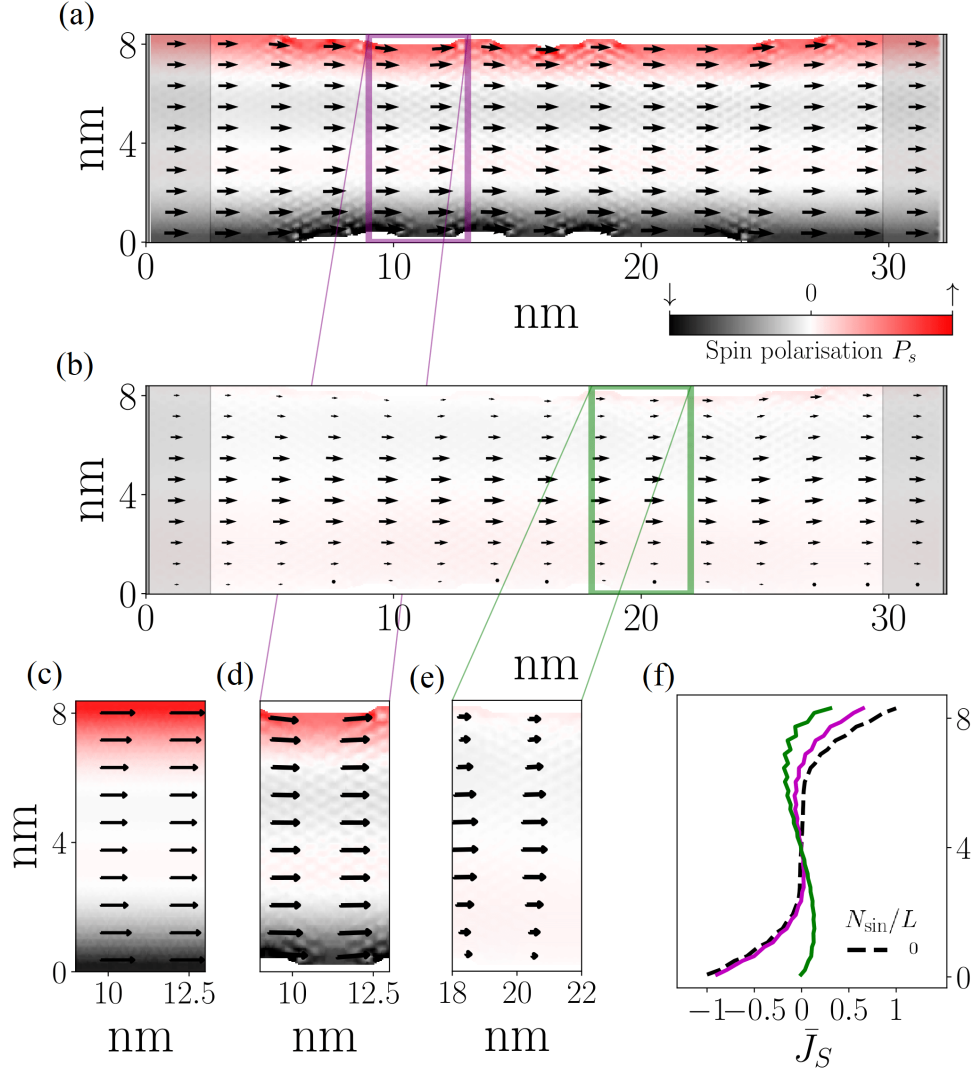


Figure 5.11: **(a)** and **(b)** - One smooth configuration of  $L = 110$  40-ZGNR characterised with  $N_{\text{sin}}/L = 0.2$  picked at  $E = 0.038|t|$  and  $E = 0.11|t|$  respectively. **(c)**, **(d)** and **(e)** - Sections of the magnetic pristine, and two zoomed sections from panels **(a)** and **(b)** respectively for comparative purposes of the spin-polarisation  $P_s$  and net spin flow (arrow field). **(f)** - The spatially averaged spin-polarisation  $\bar{J}_S$  across the width of the ribbon for the pristine (dashed dark) and the configuration in panels **(a)** (magenta) and **(b)** (green).

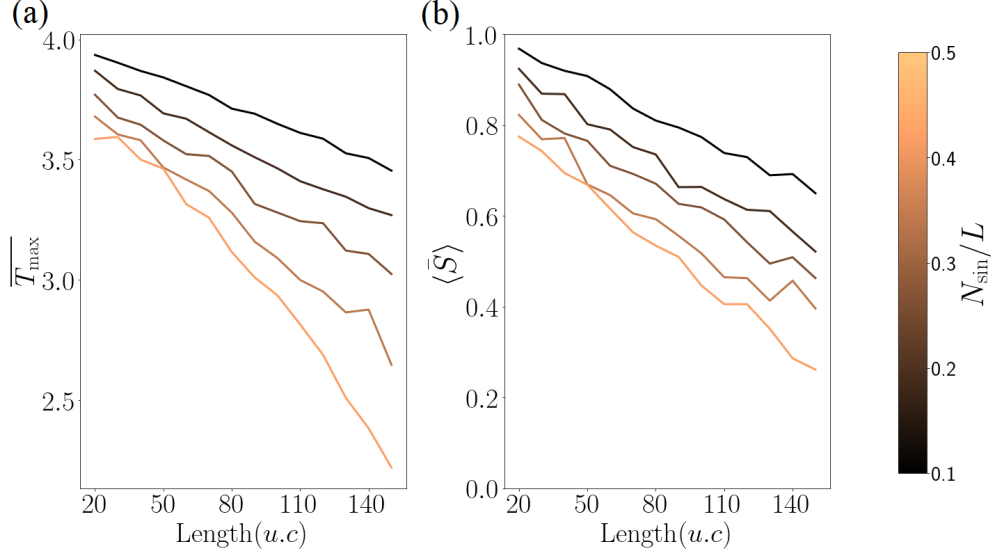


Figure 5.12: **(a)**- Total averaged current  $\bar{T}_{\text{Max}} = \bar{T}_{\text{Max}}^{\uparrow} + \bar{T}_{\text{Max}}^{\downarrow}$  taken at  $E = 0.038|t|$  vs length of the 40-ZGNR. **(b)**- Edge spin current strength vs. length of the ribbon (cf. Eq. 5.3). For both panels, the curves have a higher value of  $N_{\text{sin}}/L$  as the curves gets brighter.

matching the transversal spin-polarisation of the pristine ribbon. At the higher energy depicted in panels 5.11**(b)** and **(e)**, we see a complete suppression of spin-polarised currents in the current map. However, non-polarised bulk currents are qualitatively observable and show a maximum in the centre of the ribbon which is why the transmission in the second plateau matches almost the NM pristine transmission in Fig. 5.10**(a)**.

The quantitative investigation of spin-polarised edge current in smooth disorder, when all instances of the same disorder and lengths at the energy peak are averaged over, is shown in Fig. 5.12. The panel (b) displays the edge current strength for different levels of disorder. Unlike rough edge disorder, smooth profiles hold better the edge current in the vicinity of the edges despite increasing disorder and length. Where  $\langle \bar{S} \rangle$  falls down to zero as length and disorder are increased for the rough profiles, it still holds around 35% for similar lengths and enhanced values of disorder in the smooth case. Following the same trend, the total averaged current  $\bar{T}_{\text{max}}$  in Fig. 5.12**(a)** is not as impacted as its rough-edged counterparts when compared to Fig. 5.9**(a)**. This suggests that spin-polarised transmissions are still detectable on average as the total transmission sits above  $\bar{T}_{\text{max}}^{\text{NM}} = 2$  for the non-magnetic pristine ribbon.

To understand the survival of the spin transport channel in both rough or smooth cases, it is worth investigating the backscattering possibilities that could quench the spin current. Fig. 5.13**(a)** represents the pristine magnetic ZGNR band structure where filled and hollow circles of different colours with arrows represent

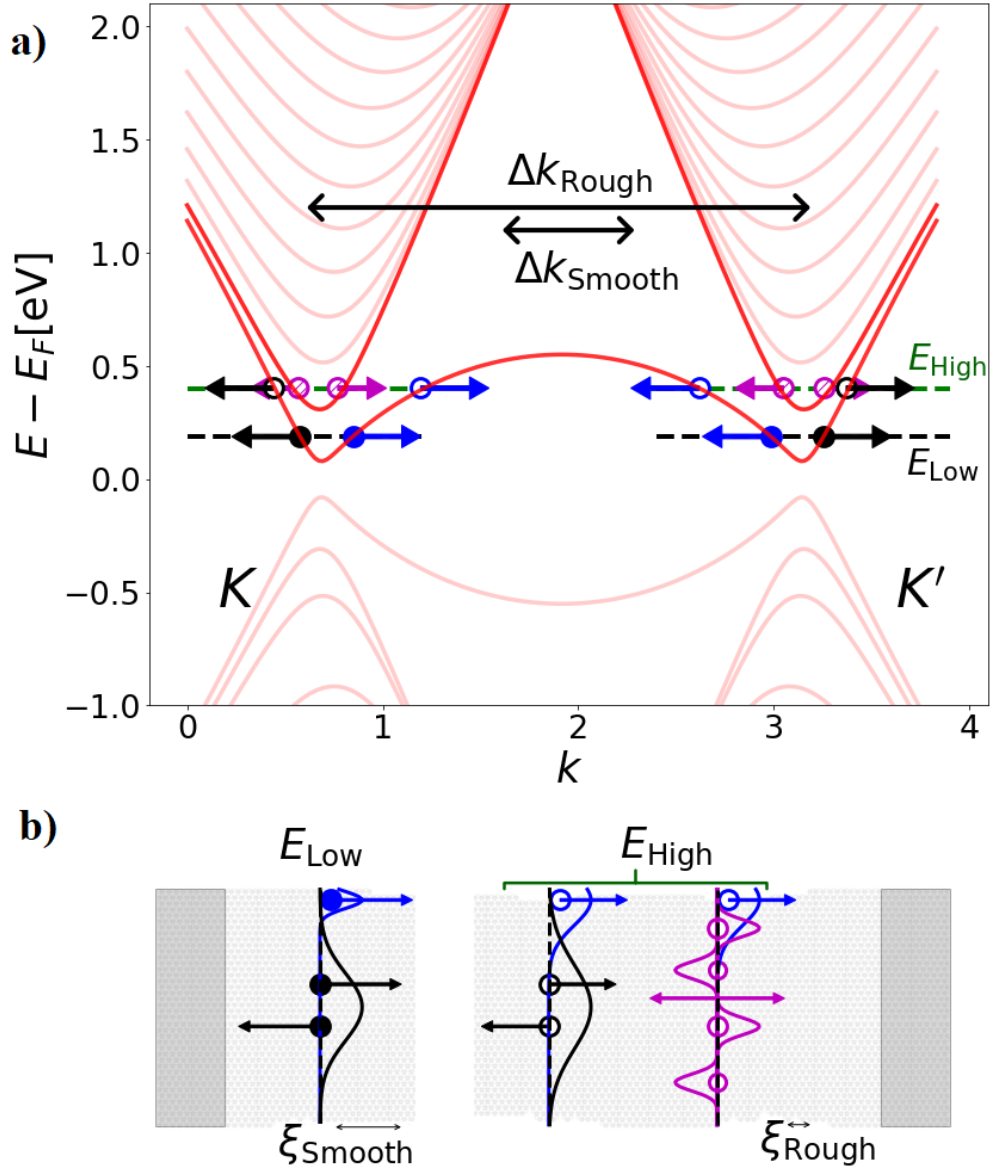


Figure 5.13: **(a)**- Band structure of a pristine magnetic nanoribbon where the  $K$  and  $K'$  valleys are shown. For simplicity, we focus only on two different energies  $E_{\text{Low}}$  and  $E_{\text{High}}$  above the Fermi energy as we focus on a singular spin. Bulk modes are represented by black and magenta hollow circles and their propagating directions are given by the associated arrows. Spin-polarised modes are shown by red and blue hollow circles and their corresponding arrows for their propagation. **(b)**- Schematics of a disordered nanoribbon and the spatial broadenings of the different modes at different energies on the panel **(a)**.  $\xi_{\text{Rough}}$  and  $\xi_{\text{Smooth}}$  are the characteristic lengths of their respective disorder profiles.

propagating modes in different directions at different energies. In both panels of Fig. 5.13(a)-(b), the black-coloured circles feature the bulk modes and the blue-coloured circles show the edge spin-polarised propagating modes. The purple-coloured modes are spin-polarised bulk modes that appears only at higher energy. Fig. 5.13(b) illustrates schematically a disordered ribbon and shows how for a single spin, the corresponding spin-polarised edge and bulk states are spatially distributed for different energy regimes. The curves associated with each propagating mode is a schematical representation of the overlap between bulk and edge modes at different energies.

The low energy channel for a given spin is largely located on sites near one of the ribbon's edges. Unlike system subject to spin Hall effect, right- and left-propagating modes, shown by blue right and left-oriented arrows in both panels of Fig. 5.13 for a given spin are located on the same edge. The back-scattering is possible along an edge without a spin flip, as can be seen on the Fig. 5.13(b). However, such back-scattering requires a large change in momentum, as the left- and right-going modes are associated with widely-separated states in reciprocal space, as the two modes are located near opposite valleys (cf. Fig. 5.13(a)). Such scattering requires short-ranged disorder ( $\xi_{\text{Rough}}$  in Fig. 5.13(b)) as this corresponds to a large momentum change ( $\Delta k_{\text{Rough}}$  in Fig. 5.13(a)) when moving to  $k$ -space. At low energies, it explains why rough disordered profiles are more prone to backscattering, finally resulting in suppression of the spin bump in the first plateau as length and roughness are increased. Nanoconstrictions created by smooth-edge disorder have a bigger characteristic length ( $\xi_{\text{Smooth}}$  in Fig. 5.13(b)). The corresponding equivalent change in momentum in  $k$ -space,  $\Delta k_{\text{Smooth}}$  in Fig. 5.13(a), is not large enough at low energies to cause intervalley scattering, resulting in a lower backscattering probability compared to the rough case.

While the spin transport channel survives at low energies in disordered systems, it vanishes quickly as the energy is increased. There are two contributing factors which explain this effect. Firstly, the counter-propagating edge modes move closer in reciprocal space as energy increases, so that scattering between the two is more likely by longer-ranged disorders (cf. Fig. 5.13(a)). These modes also become less dispersive, and more prone to localization effects, at higher energies. Secondly, higher-order valley-degenerate modes (magenta hollow circles and arrows in Fig. 5.13(a)-(b)) have more weight near the edges so that back-scattering from the spin-polarised channels into these modes is more likely. We note that a spin-dependent signal in the two disordered systems considered here only occurs within the first conductance plateau, and is not present at any energy after the onset of higher order modes.

#### 5.4.4 Asymmetry and net spin-polarisation

To observe a net spin-current in spin-polarised nanoribbons, it is necessary to create an asymmetry between the oppositely polarised currents at either edge [90]. Realistic ribbon devices synthesized experimentally are still subject to either rough [61, 72, 222] or smooth disorder [33, 34] depending on the fabrication techniques. A mix of these disorder profiles is more likely but the lack of edge characterization still prevents a deep understanding of many experimental results. The purposeful disordering of one edge with rough disorder could be conceived as a route to achieving this asymmetry. Understanding the effect of such variation on spin transport properties is an important step if they are ever to be used in spintronics applications. For instance, designing a spin-filter ZGNR device could be achieved just by purposefully making one edge rougher than the other even though the edges already present smooth disorder [90]. However, as we demonstrate here, the spintronic effect achieved also strongly depends on any disorder present before the deliberate introduction of rough disorder to one of the edges.

As this section focuses on the relationship between edge asymmetry and the net-spin polarisation of the ribbon, all the structures on top of which disorder will be added consist initially in a fixed  $L = 90$  ZGNR unit-cell long and 40-ZGNR wide and fixed ribbon length corresponding respectively to a  $8.3 \times 22.5$  nm ribbon.

For all the different situations, 200 instances have been generated and their magnetic profiles estimated given our ML tool. The spin-transport quantities and spin-current mappings to observe the spatial distributions of each configuration have then been computed. Each edge is associated with a different spin current channel. In all the considered different cases, the bottom edge will have a superimposed rough disorder and will serve to introduce an asymmetry between the opposite edges. Three different scenarios are portrayed :

##### **Pristine top edge**

Here is considered the ideal case where rough disorder is deliberately added to one edge of a pristine ribbon. Fig. 5.14(a) shows the net-spin transmission,  $\bar{T}_\uparrow - \bar{T}_\downarrow$ , resulting from the added rough disorder on the bottom edge as a function of energy. Without any disorder, this quantity is negligible as the two contributions from each spin are cancelling each other. This panel shows, as expected, that the rougher the bottom edge, the more enhanced is the net-spin current. This is observable in Fig. 5.14(b) as the spin-up transmission,  $\bar{T}_\uparrow$  matches perfectly the pristine magnetic ribbon's transmission and the spin-down transmission associated with the solely disordered edge is decreasing towards that of a non-magnetic ribbon as roughness increases. Even with the opening of a new transmission

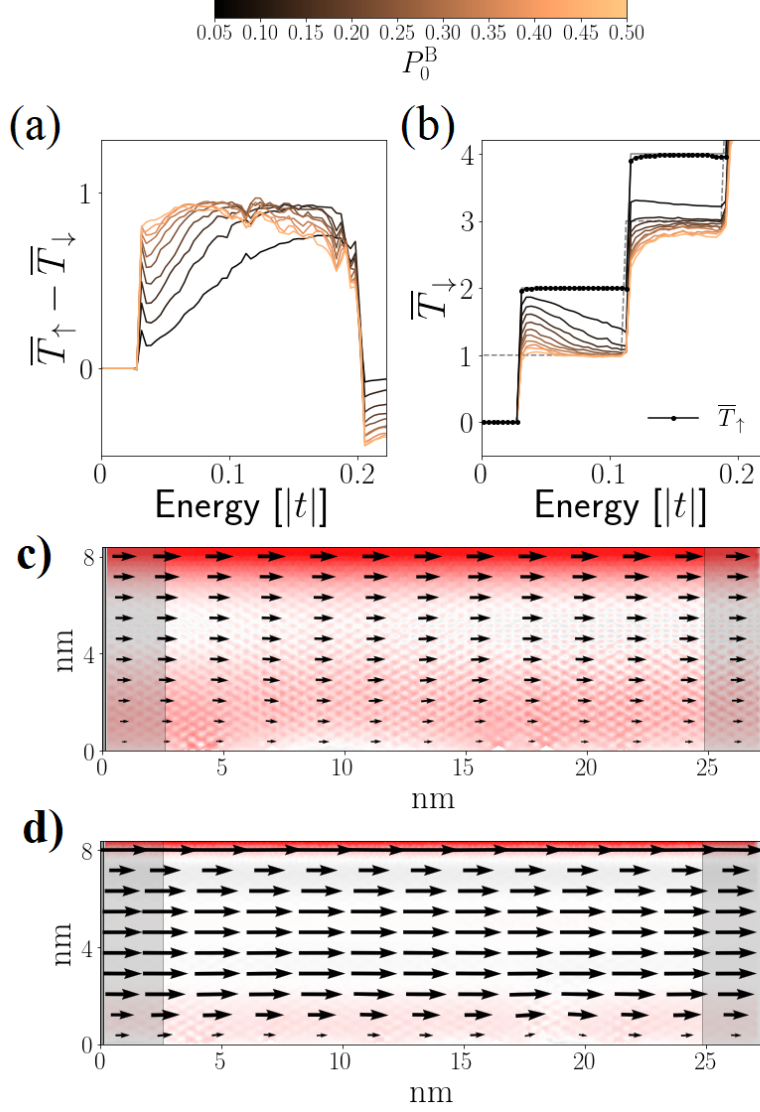


Figure 5.14: (a)- The averaged net spin-polarised transmission  $\bar{T}_\uparrow - \bar{T}_\downarrow$  vs. energy for the pristine kept 40-ZGNR top and roughly-disordered bottom edge. The colorbar shows the different levels of  $P_0^B$  applied to the bottom edge. (b)-  $\bar{T}_\downarrow$  vs. energy. The averaged spin-down transmission is depicted by different colour curves where the level of roughness is low for dark curves and dark for very rough bottom edge. The dotted black lines represents the  $\bar{T}_\uparrow$  associated with the top edge channel which matches the pristine magnetic conductance (grey solid) here. The grey dashed line represents the non-magnetic pristine transmission. (c)-(d) - Spin-current mappings of one particular configuration where the bottom edge is disordered with  $P_0^B = 0.04$ . The upper and lower panels shows the ribbon at  $E = 0.038|t|$  and  $E = 0.11|t|$  respectively. The arrows show the net current strength across the ribbon.

channel appearing at  $E \approx 0.11|t|$ , the spin-polarisation of the transmitted signal persists. These 2 low- and high-energy behaviours are qualitatively observed in Fig. 5.14(c)-(d) respectively. Here is shown a configuration where the top edge is pristine and the bottom edge presents a rough disorder parameterised by  $P_0 = 0.04$  at  $E = 0.038|t|$ , e.g the peak in transmission in the first plateau for Fig. 5.14(c) and  $E = 0.12|t|$  at the onset of the second plateau for Fig. 5.14(d).

For Fig. 5.14(c), we see the top edge carrying a strongly polarised spin-up current near its edge whereas the bottom edge carries little to no current due to the presence of strong rough disorder. The rest of the ribbon is also spin-polarised with the slight asymmetrically spin-polarised bulk-current that we can also observe in the centre portions of the ribbon. As we increase the incoming electron energy in Fig. 5.14(d), we lose the entire spin-polarisation across the ribbon except at the pristine top edge still carrying polarised spin-up current. This spin-channel results the net-spin transmission observed in Fig. 5.14(a) even for higher energy. Also we note the presence of strong-bulk currents, unaffected by bottom edge disorder and responsible for the transmission to be very close to the NM pristine transmission (solid step-like black line). Once more, this is a clear manifestation of how detrimental rough disorder is onto the survival of spin-current and how it could be used as a way to tune spin-polarisation in such devices. Obtaining pristine edged ribbons being still an open question, edge-disordered devices, as experimentally synthesised, have to be considered as prototypes for selective edge disordering process. Also we note that these results are completely in accordance with the work done by Wimmer et al. [90], where rough-disorder was thought as a way to inject spin-polarised currents in graphene-based devices.

### Rough disordered top edge

We next consider how deliberate edge disorder of one edge could be used to engineer a spin current in a more realistic ribbon, which already contains a rough disorder. The top edge is initially roughly disordered with  $P_0^T = 0.2$  and fixed. The lack of a better characterisation scheme being still a brake in investigating realistic ribbons, we assume here rough edge disorder being present initially on both edges. This situation seems to be rather common particularly in the context of graphene nanoribbons etched by lithographic methods [31, 245].

Fig. 5.15 summarises our findings. We intuitively expect the net-spin polarisation in transmission to be stronger as the difference between  $P_0^B$  and  $P_0^T = 0.2$  is increased. The averaged spin-up transmission associated with the fixed disordered top edge is shown by the black dotted line in Fig. 5.15(b). This value of  $P_0$  has been considered as it lies in the middle range of our rough disorder profile. Fig. 5.15(a) shows separately the averaged net-spin transmissions with different colours associated with different level of  $P_0^B$ . Firstly, when  $P_0^B = P_0^T = 0.2$ , the curves seem to be completely flat and holds no sign of net spin current as expected. As the asymmetry is increased or the two values for  $P_0^B$  and  $P_0^T$  are further apart, we observe that the resulting net spin transmission is higher particularly at the peak of transmission in Fig. 5.15(b) for  $E = 0.038|t|$ . When  $P_0^B \sim 0.05$  sits at its lowest value, we observe a negative net-spin current that is surviving over the total energy range considered here, even when a new channel of transmission opens.

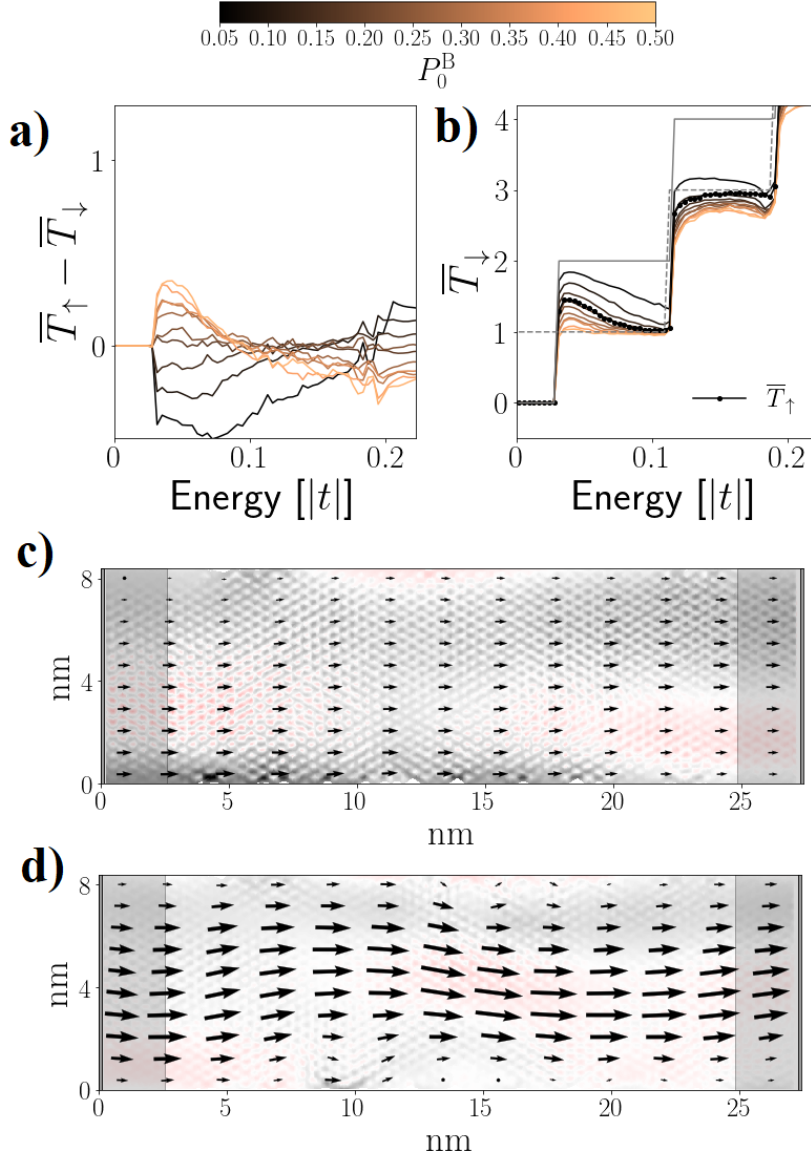


Figure 5.15: **(a)**- The averaged net spin-polarised transmission  $\bar{T}_{\uparrow} - \bar{T}_{\downarrow}$  vs. energy for the 40-ZGNR. The top edge is already presenting a rough disorder of parameter  $P_0^T = 0.02$  and the different curves show the conductance resulting for the varying disorder  $P_0^B$  applied to the bottom edge. **(b)**-  $\bar{T}_{\downarrow}$  vs. energy. The averaged spin-down transmission is depicted by different colour curves where the level of roughness is low for dark curves and dark for very rough bottom edge. The dotted black lines represents the  $\bar{T}_{\uparrow}$  associated with the top edge channel. The grey solid and dashed line represent the magnetic and non-magnetic pristine transmissions. **(c)**-**(d)** - Spin-current mappings of one particular configuration where the top and bottom edges are disordered with  $P_0^T = 0.02$  and  $P_0^B = 0.04$  respectively. The upper and lower panels shows the ribbon at  $E = 0.038|t|$  and  $E = 0.11|t|$  respectively. Net current strength across the ribbon is shown by the arrow field.

This is explained by the robustness of  $\bar{T}_{\downarrow}$  for this particular disorder level across the entire first plateau in Fig. 5.15(b). Whereas all the averaged transmissions for rougher edges are constantly decreasing to the NM pristine transmission value  $T = 1$  at the end of the first transmission plateau, the  $\bar{T}_{\downarrow}$  for  $P_0^B = 0.05$  still holds

at 1.4, resulting in this surviving negative net-spin transmission in Fig. 5.15(a). However, this is not the case when  $P_0^B \sim 0.5$  is at its highest. Indeed, the positive net spin transmission is lower as the energy gets closer to the onset of the second transmission channel and hardly gets higher than 0.3 in magnitude. All the spin-polarised transmissions associated with  $P_0^B > 0.2$  show a similar sign switching trend at the onset of the second plateau as can be observed in Fig. 5.15(a). This sign switching in net-spin transmission results from the relative position of  $\bar{T}_\uparrow$  with respect to the other  $\bar{T}_\downarrow$  transmissions in Fig. 5.15(b). However, we notice that almost all the averaged transmissions are lying beneath the NM pristine transmission  $T = 3$ , in the second plateau. This is strongly supporting against the presence of any source of spin-polarised transmissions. Therefore, this sign switching occurring for values of disorder higher than the fixed  $P_0^T = 0.2$  for the top edge results from a mathematical artefact as it is required that both  $T_\uparrow$  and  $T_\downarrow$  must be higher than the  $T_{NM}$  for observing a real net-spin signal signature at higher-energy modes. Fig. 5.15(c)-(d) show a configuration where  $(P_0^T, P_0^B) = (0.2, 0.4)$  at  $E = 0.038|t|$  and  $E = 0.12|t|$  respectively. Fig. 5.15(c) shows an overall very slight spin-polarisation for its current all across the ribbon. We also observe some local spin-up polarised red areas across the ribbon mainly on top edge and on the region just on top of the bottom edge where spin-polarised bulk states are expected. This is strongly advocating that there is little to no spin-information that is carried in this particular configuration and that rough-edge disorder induced asymmetry is difficult way to control spin-currents in such devices. Fig. 5.15(d) shows an even lesser spin-polarisation across as the energy is increased to the second transmission plateau. The bulk-modes are slightly affected by the edge disorder even though we see some current constriction from either side of the ribbon as we see on the current map shown by the arrow field. It indicates that as energy is increased the bulk states are increasingly sensitive to edge disorder as the bulk states are more prone to overlap with edge states.

### Smooth disordered top and bottom edges

In this situation, both top and bottom edges are initially smoothly disordered with  $N_{\text{sin}}/L = 0.2$  and corresponds to a scenario where ribbons are synthesised with epitaxial growth on substrates. Indeed, epitaxial growth techniques are well-established and count many successes in fabricating ZGNRs with sufficient control of the edge structure [62, 240]. Systematic characterisation of experimental findings is still missing to greatly support the global perspective in using GNRs as the next-generation spintronic devices but we expect smooth-disorder to still be present when synthesized. We are deliberately adding a rough disorder to a GNR with smooth-disordered edges. The corresponding transmission and polarisation panels show how to compare the different spin-polarised transmissions in top panels of Fig. 5.16. Here, the main message is clear : On average, smooth-disordered

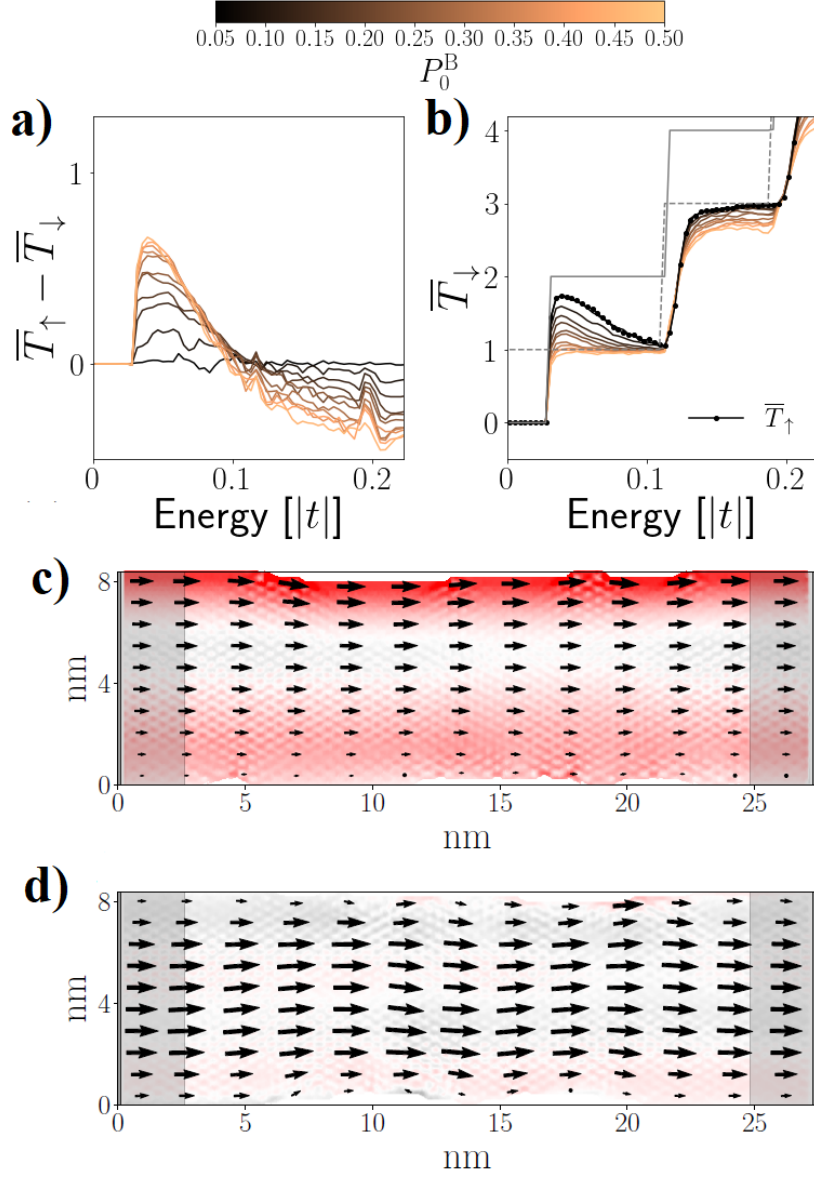


Figure 5.16: (a)- The averaged net spin-polarised transmission  $\bar{T}_{\uparrow} - \bar{T}_{\downarrow}$  vs. energy. The top edge is already presenting a smooth disorder of parameter  $N_{\text{sin}}/L = 0.2$  and the different curves show the conductance resulting for the varying rough disorder  $P_0^B$  applied to the bottom edge. (b)-  $\bar{T}_{\downarrow}$  vs. energy. (c)-(d) - Spin-current mappings of one particular configuration where the bottom edges is disordered with  $P_0^B = 0.04$ . The upper and lower panels shows the ribbon at  $E = 0.038|t|$  and  $E = 0.11|t|$  respectively. Net current strength across the ribbon is shown by the arrow field.

ribbon still holds a spin-signal in the vicinity of  $E = 0.038|t|$ . The embedded rough disorder on the bottom edge is progressively killing the spin-signal as the roughness is increased. Once again, we observe a sign switching in the net-spin transmission at the onset of the second plateau in Fig. 5.16(a). What is truly characterised as a net-spin transmission in the first plateau is not in the second plateau. Indeed, the fixed top edge channel transmission and the more disordered bottom edge ones are both lying underneath the pristine NM transmission

( $T = 3$  for this energy range) in Fig. 5.16(b). As already discussed in the rough disorder section, turning on electron-electron interactions in ZGNRs creates an additional spin-polarised edge channel of transmission at low energy. This provides additional backscattering possibilities for bulk electrons. By coupling edge and bulk modes, rough disorder allows forward-propagating bulk electrons to be backscattered into backward-propagating channels at the edges therefore reducing the overall spin-polarised transmissions at higher-energy modes. Two current mappings in Fig. 5.16(g) and (h) show one configuration from this particular case where the roughness on the bottom edge is parameterised by  $P_0^B = 0.3$ . At  $E = 0.038|t|$  (cf. Fig. 5.16(g)) and  $E = 0.12|t|$  (cf. Fig. 5.16(h)), different trends are observed depending on the energy at which the spin-current mappings are taken at. At  $E = 0.038|t|$ , we see a strong spin-up polarisation of the top edge and the absence of spin-down polarisation on the bottom edge due to the additional rough disorder. Close to the top edge however, we see a bordering white region which is a clear sign of the presence of an asymmetrical spin-down polarised bulk channel that cancels out with the global polarisation of the ribbon. At  $E = 0.11|t|$  is only left the predominance of bulk-currents as expected. The loss of spin-up polarisation across the ribbon is expected as discussed in the smooth section 5.4.3. So the “so-called” inversion in polarisation is spin-polarised, but emerges also from bulk channel effects. Hence, the prospect of intentionally disordering one edge to control the spin-current in ZGNRs is feasible. Rough disorder, by its detrimental effect on the robustness of spin-polarised edge current, could be efficiently used as a way to create asymmetry, essential in observing net-spin signal in such nanostructures.

## 5.5 Conclusion

This study provided a detailed overview of the edge disorder profiles in ZGNRs encountered in experiments and presented preliminary methods to create either “rough”- or “smooth”-edged ribbons. The potential of a trained neural network model to accurately predict the magnetic profile of edge-disordered ribbons was also discussed. This is found to be a powerful and efficient tool for performing spin-transport calculations in large and disordered ribbons, which would otherwise be a near-impossible task with conventional methods. The results section further provided a detailed study on how spin-transport is impacted by edge disorder, and general trends were observed for ribbons of different disorder profiles with varying lengths and strengths. First, we have established that pristine magnetic ZGNRs have an additional transmission channel located on the edge due to consideration of electronic interactions. Our results showed that the robustness of spin-currents in ZGNRs is highly dependent on the disorder profile of the ribbon. We have found, in the low-energy regime, that even a moderate roughness

as defined in our work, suffices to disrupt the establishment of spin-currents along the edges. Longer-ranged disorder or from the smooth type are less detrimental and the robustness of spin-currents in such materials is preserved. Whereas these findings are correct at low-energy, the spin polarisation of edge currents is completely suppressed when energy is increased for both disorder types. In rough disorder profiles, the additional spin-polarised transmission channel offers more backscattering possibilities, reducing the overall transmission. Finally, the study envisioned how to create an asymmetry in realistic devices, potentially leading to control of spin-polarised currents for spintronics applications. Disorder asymmetry between the edges results in observing net-spin polarised currents in the studied devices. Yet purposeful disordering by superimposing rough disorder to control spin-currents seems viable only if the edge are sufficiently clean in the first place.

As we are considering nanostructures made of graphene at half-filling and because the AFM solution is energetically favourable, the role of the exchange interaction plays a crucial role in determining the behavior of electron spins for large systems [246]. Electrons can tunnel into this coupled spin system and when they do so, they can inelastically excite a spin reversal in any of the electrons in the system. The inelastic excitation mentioned leads to a transition between the singlet and triplet states of the coupled electron spins [205, 246]. The singlet state is characterized by opposite (antiparallel) spins, while the triplet state consists of parallel spins and this type of spin excitations could play a role in our findings. It will be great to explore potential extensions of our methods with consideration of inelastic scattering to explore more in-depth spin-polarised GNRs.

## Future work and conclusions

**6.1 Future work and perspectives**

Knowing how detrimental is edge disorder on the robustness of spin-currents (cf. chapter 5), many ways to protect spin-polarised currents in such nanostructures have been considered. By thoroughly looking at many rough-disordered edge structures, one can appreciate a general qualitative behaviour for the presence of localised magnetic moments in ZZ-edge portions : The presence of localised edge states, hence magnetic moments, starts whenever 3 atoms, at least, form a zigzag-shaped edge [89, 202]. Furthermore, at low energy, the observation of a strong spin-polarised transmission has mainly to do with some percolation phenomenon [247], where ZZ-edge portions are correlated to one another despite the presence of disorder disrupting its establishment. Not only this observation is true on any zigzag-edge ribbon but it is also true for subtractive geometries such as triangular antidots [88, 93, 132]. Spin filters have been proposed using triangular antidots owing to their low-energy localized magnetic states and a net sublattice imbalance [88, 94, 248].

One of our hypotheses is the possibility of combining the features from the states located on the edges of the triangles with those present on the edges of the ribbon. Indeed, the zigzag geometry whether it is on the edges of a ribbon or on the edges of an impurity of macroscopic size like a triangular antidot is subject to the presence of localized states of low energy on these edges. In the preliminary work presented here, we investigate the transport properties of ZGNRs with embedded ZZ-edged triangular antidots and see how we could efficiently use nanopatterning of antidots to control spin-polarised currents in such geometries.

Graphene antidot lattices (GALs) are graphene-based material that has been

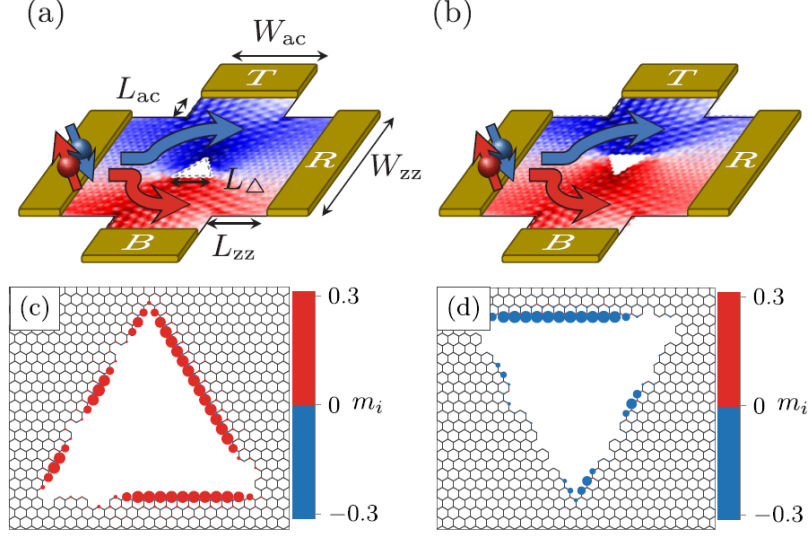


Figure 6.1: Adapted from [93]: (a) and (b)- Two differently oriented triangular antidots that splits incoming spin-degenerate into spin-polarised currents due to their orientations and the magnetic moments they carry. These 4-terminal schematics is a proposed device to realise spin-filter applications with triangular antidots. Adapted from [132]: (c) and (d)- Magnetic profile of triangular antidots presenting rough disorder on their edges. The remaining magnetic moments are spin-polarised according to the orientation of the triangular antidots. These orientations offers FM or AFM coupling possibilities with nearby strongly spin-polarised edges.

structured into a pattern of small, periodic holes known as antidots [98, 131, 249]. This structure can be achieved by lithographic methods [250–252] or chemical doping [253] among other techniques. The lattice structure affects the electronic properties of graphene, creating a bandgap [98], which enables the material to be used in electronic applications such as transistors [98] and photodetectors [251]. Additionally, GALs can exhibit unique mechanical [254], optical [253] and thermal properties [255]. Finite-size graphene nanoribbons with patterned antidots can also be obtained via e-beam lithography [256]. An alternative approach is to use a lithographic mask made of hexagonal boron nitride, which naturally etches into triangular holes with ZZ-edges [251, 257].

Triangular antidots are of particular interest because of their ZZ-edged vertices, that are potential host to magnetic properties when electronic interactions are taken into account [88, 195, 203, 205]. Fig. 6.1(c) and (d) shows how, the same way ZZ-edge portions in disordered ZGNRs have magnetic moments that are disrupted by AC edges, junctions and corners, disordered ZZ-edged triangular antidots host magnetic moments on their ZZ-portions. These two  $0^\circ$  and  $180^\circ$  oriented triangles are the only two orientations that can hold magnetic moments owing to the graphene sixfold symmetry. This, in turn, can split the spin-degeneracy of incoming unpolarised current into spin-polarised currents at either top or bot-

tom edge depending on the antidot orientation. Based on this well-known and studied behaviour [88, 93, 132], we propose in section 6.1.1 to use arrays of ferromagnetically (FM) coupled triangular antidots in the vicinity of spin-polarised edge channels to mitigate the effect of rough disorder. On the contrary in section 6.1.2, we propose a filter with anti-ferromagnetically (AFM) coupled arrays of triangle could be also thought as a way to manipulate net spin currents by blocking purposefully the edge current on one edge. Surprisingly, we find that this geometry can also be used to block the bulk component for current for that spin also, creating a highly efficient filter.

### 6.1.1 Alleviating detrimental edge disorder

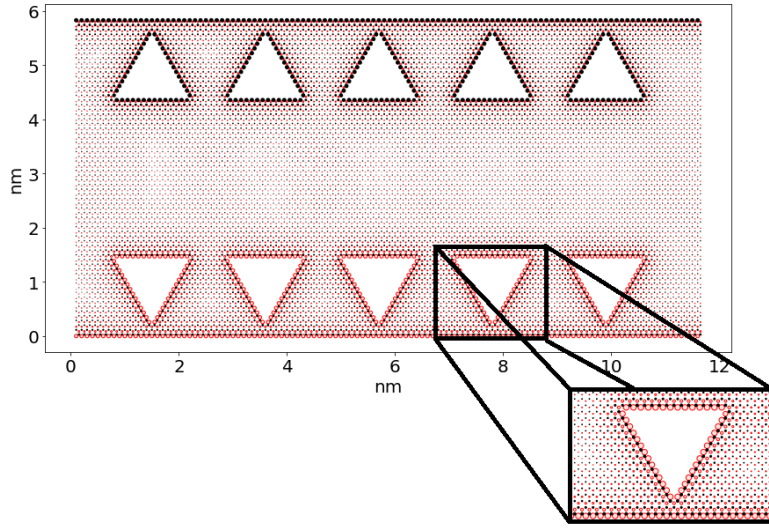


Figure 6.2: Magnetic profile (ML-obtained) of a nanopatterned ZGNR with triangular antidots : The ribbon is a 68-ZGNR unit-cell repeated 232 times in the longitudinal direction, corresponding to an approximate  $6 \times 12$  nm ribbon. The equilateral triangular antidots have 2 nm-long vertices. These antidots are host to localised states on their edges, as observed for the edges of this ribbon. The zoomed section shows the moments to be maximal for the triangle's and bottom edges and ferromagnetically coupled. For each edge associated with a specific spin-polarised localised moment region, this specific orientation of the triangular antidots extends and correlates the moments present at the edge and on the triangles.

Pristine magnetic ZGNR, extensively studied in section 5.4, are known to host anti-ferromagnetically (AFM) coupled spin-polarised currents on each of its edges [65, 66, 169]. The previous chapter concluded by stating that rough disorder has a detrimental effect on the robustness of such currents to be maintained in the edge's vicinity. Here we propose to create either ferromagnetic (FM) coupled between spin-polarised moments on the edge and the nearby array of triangular antidots to protect the establishment of such currents. Indeed, many possibilities can be realised with such potential configurations to alleviate the altered transport properties for ribbons subject to rough disorder.

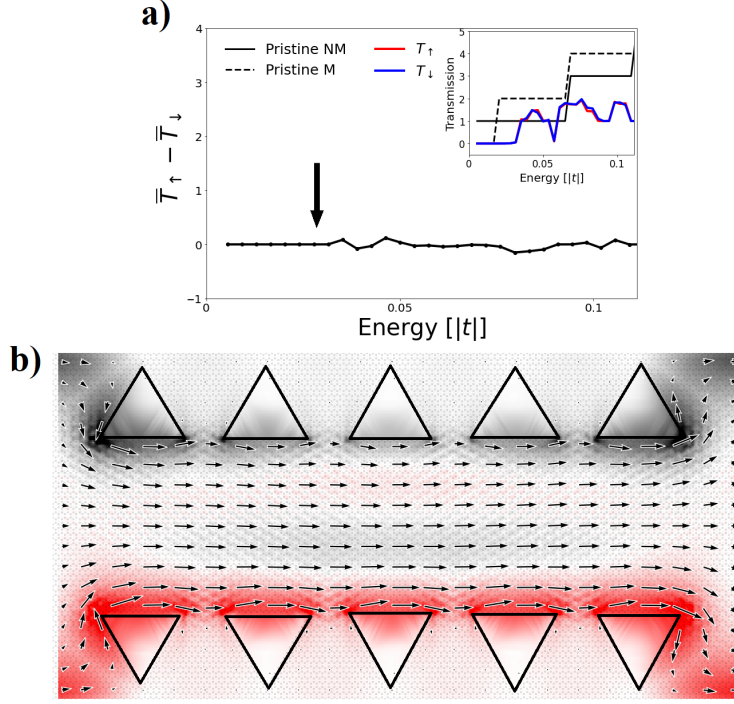


Figure 6.3: (a)- Net spin-polarised transmission,  $T_{\uparrow} - T_{\downarrow}$  vs. energy (in units of  $|t|$ ) for the ribbon shown in Fig. 6.2. The inset shows the detail of each spin-transmissions which are found to be almost perfectly matching for this energy range resulting in no net spin-signal. (b)- Current flow shown by the arrows and spin-currents mapping shown by the red and black areas in the density plot.

Fig. 6.2 shows a configuration where each array of triangular antidots is FM-coupled to its neighbouring ribbon edge. This ribbon of roughly 14000 atoms has its magnetic profile calculated with our NN-model, presented and extensively discussed in chapters 4 and 5, otherwise it would have taken a considerable amount of time with the conventional SC method. We see in the zoomed section of Fig. 6.2 the FM coupling between the moments of atoms lying both on the edges of the ribbon and triangle respectively due to sublattice. Fig. 6.3(a) shows the net spin-polarised transmission  $T_{\uparrow} - T_{\downarrow}$  as a function of energy for this particular ribbon. The net-spin polarised transmission is flat and equal to zero almost everywhere for this energy region. This is also well expressed by the inset showing the spin-polarised transmissions  $T_{\uparrow}$  (red line) and  $T_{\downarrow}$  (blue line) respectively which seem to match almost at all energy in this range. Fig. 6.3(b) display the current flow and polarisation shown respectively by the arrows and the background red (spin-down) and black (spin-up) current densities. Intriguingly enough, the presence of the FM-coupled arrays of triangular antidots deviates the normally spin-polarised edge currents toward the bulk of the material, where it is carried by the antidot edges instead of the ribbon edges. Some percolation effects seem to occur between the different horizontal ZZ portions of the triangles for each spin current. The triangular antidot arrays act like wave-guides for the different

spin-current channels that normally locate at the edges of such systems. This nanopatterned device encourages our first hypothesis by which this kind of system could potentially alleviate edge disorder as all the spin-polarised currents deviate inside the bulk and consequently be less sensitive to disorder present on the edges.

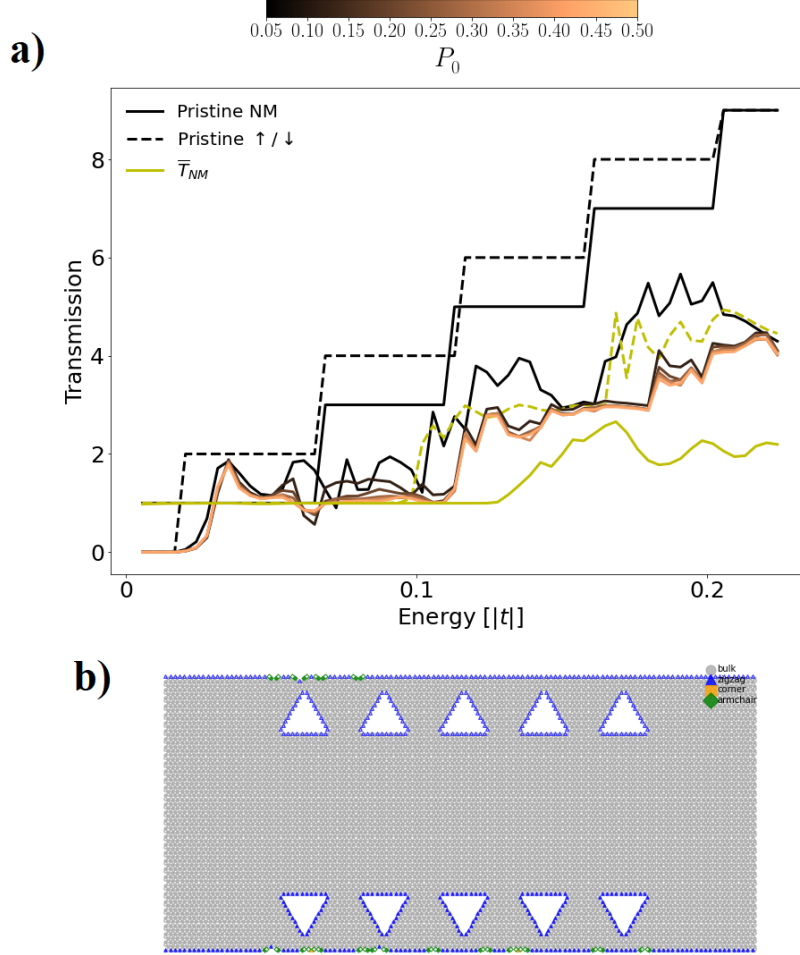


Figure 6.4: **(a)**- Transmission vs. energy for different rough-disordered ribbons with arrays of FM-coupled triangular antidots close to the edges. **(b)**- A configuration used to generate the transmissions in **(a)** with rough-edge disorder on both edges parametrised by  $P_0 = 0.05$ .

To answer this question, we have generated 50 configurations presenting each for different levels of rough disorder on the edge of the ribbon and presented in Fig.6.4. Here the rough disorder present on both edges of our ribbons is parametrised by  $0.01 \leq P_0 \leq 0.05$  and the etching process has already been introduced in chapter 5. The triangular antidots have vertices of size 1.4 nm and are completely pristine. One of the configuration, with  $P_0 = 0.05$ , so a very rough edge disorder ribbon is shown in Fig.6.4(b). Fig.6.4(a) show the averaged spin-up transmissions for the different configurations gathered by their different

levels of disorder. The spin-down averaged transmission follow the exact same behaviour from symmetrical arguments and therefore, they are intentionally omitted here. The dashed and solid black curves represent the pristine magnetic and non-magnetic transmission for the ribbons without the triangular antidot arrays. The solid black curve shows the transmission for the ribbon when the triangular arrays are present but when the edges are kept pristine and the yellow-coloured curve represent the averaged transmission of the un-polarised ribbons subject to edge disorder. In the first transmission channel, we see a peak very close to the pristine magnetic transmission value at  $E \sim 0.035|t|$  for all the different transmissions, seemingly very slightly affected by disorder. This particular robustness for various levels of disorder suggest the behaviour observed in Fig. 6.4(b) where the spin-edge currents are crossing the ribbon via the bulk instead of being located in the vicinity of their respective edges. Further analysis have to be conducted to see how resilient is this phenomenon and if it can be extended to a wider energy range within the first plateau.

Extending edge disorder to the edge of the triangular antidots themselves and adding realistic sources of other kinds of disorder must also be considered. Indeed, experimental synthesis of graphene-based antidot lattices suffers from spatial non-periodicity altering the promising electronic properties such systems could display [125]. Difficulties in orienting exactly the triangles with the preferred  $0^\circ$  and  $180^\circ$  angles could also arise and consequently, a more in-depth study should be conducted on how this proposal can be feasible and observed by experimental groups. Also, generative design such as genetic algorithms [258] and other optimisation methods within the ML realm could be used to find an optimal arrangement of the triangular antidots to protect efficiently the spin polarisation of the transmission in these devices.

### 6.1.2 Asymmetry for spin-polarised current manipulation

Here, we propose the opposite usage of the triangular antidots instead to block the spin-polarised transmission on one edge and investigate the effect of resulting asymmetry triggering spin-polarisation and manipulation in these devices. Antiferromagnetically coupling an edge, as seen in Fig. 6.5 to an array of triangular antidots could indeed impede a spin-polarised transmission channel from being established at one edge. Here the zoomed section in Fig. 6.5 shows the opposite spin-polarisation between the magnetic moments carried by the ribbon and triangles' edges. This AFM coupling results in a strongly net spin-polarised transmission in Fig. 6.5(a). Here we see a net-spin polarisation of 2, which means for this particular energy range, that the system act as a pure spin-filter. The details of the spin-polarised up and down transmission, shown in red and blue curves in the inset of Fig. 6.5(a) also shows a total quenching of the spin-down polarisation

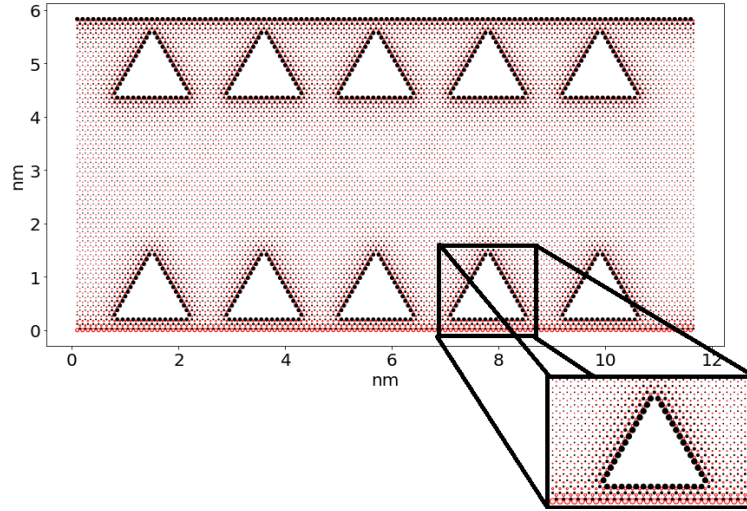


Figure 6.5: Magnetic profile (ML-obtained) of a nanopatterned ZGNR with triangular antidots : The top edge and the triangular antidots underneath are ferromagnetically coupled. We expect the edge channel to benefit from the presence of the triangles extending the presence of localised magnetic moments. However, the bottom edge and the triangular antidots above are antiferromagnetically coupled. We expect this configuration to be detrimental and to block the establishment of the spin-down polarised current channel, normally associated with the bottom edge.

over the entire first transmission plateau and a very high spin-up signal due to the FM-coupled array of triangles on top edge. Fig. 6.5(b) shows the local details of current flow and polarisation across the nanopatterned ribbon and we clearly see how strongly spin-polarised is the ribbon at this particular energy. The enhanced polarisation around the horizontal vertices of the top triangles suggests, as also seen in Fig. 6.3, that a percolation effect occurs from the ZZ-edge portions of the triangles on the crossing of spin-currents. Interestingly, for this geometry, not only is the edge channel for one spin completely blocked, but also the bulk channel and that for a large energy regime. It then suggests that this particular geometry is worth investigating as this device concretely shows half-metallic behaviour.

Again, this work is preliminary and requires a more in-depth study to see the real potential of these triangles to manipulate spin-transport in edge-disordered ribbons.

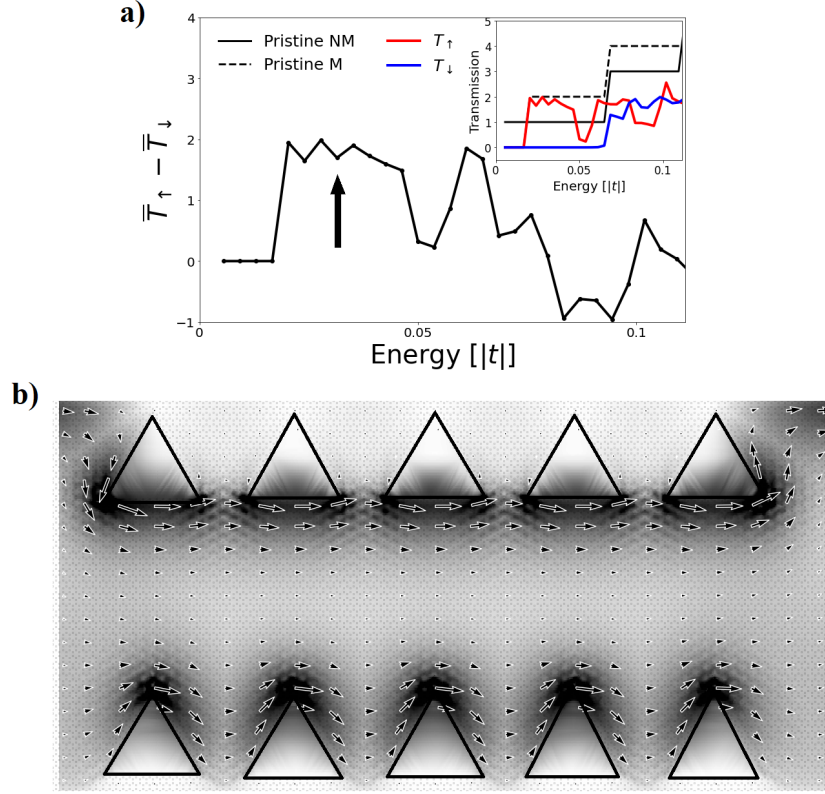


Figure 6.6: (a)- Net spin-polarised transmission,  $T_{\uparrow} - T_{\downarrow}$  vs. Energy (in units of  $|t|$ ) for the ribbon shown in Fig. 6.5. The inset shows the detail of each spin-transmissions. The spin-down transmission is completely quenched due to the presence of the AFM-coupled array of triangular antidots on the bottom edge. (b)- Current flow shown by the arrows and spin-currents mapping taken at the energy shown by the black arrow in (a). The black background color in the density plot suggest as in (a) that this ribbon is entirely and strongly spin-up polarised.

## 6.2 Summary and conclusion

This thesis has considered various topics relating to graphene-based structures, and in particular those subject to disorder whether bulk disorder in the form of impurities or edge disorder in the form of vacancies. The work in this thesis has combined theoretical and computational approaches to provide a deep understanding in how disorder, whether present during the synthesis of nanostructures or intentionally added, can be characterised and used to control and manipulate electronic, magnetic and transport properties in nanostructures. This is essential if graphene systems are ever to be used for spintronic applications. In this section, the principal methods and findings of the thesis will be summarised alongside suggestions for possible extensions.

Chapter 2 detailed the general theoretical and computational framework employed throughout this thesis. Green's function, the backbone quantity to cal-

culate many electronic properties and essential for quantum transport was introduced. GF allows to calculate the density of states of a physical system, an important quantity from which can be derived various physical properties. Integrating GFs to obtain physical quantities of interest via complex plane integration has also been considered. Magnetic properties in nanostructures were considered within the scope of the Hubbard model and the Hartree-Fock approximation. We have also outlined the steps of a self-consistent procedure to include magnetic moments within the formalism developed earlier. The quantum transport formalism was presented alongside many different algorithms and techniques, provided for efficient and accurate calculations. In the context of large and disordered systems, the Dyson equation and the RGF method have also been considered. Finally, global perspectives on machine learning techniques were described and provided insights on how this tool can be used to tackle optimisation problems in nanoelectronics.

Chapter 3 explored the use of machine learning to predict quantum transport in disordered graphene nanoribbons. Through a preliminary study of the effect of impurities, the chapter demonstrated that geometrical considerations can be used to accurately predict transport properties. Indeed, the study showed that the distance to an edge and to a lesser extent, the sublattice, play a major role in the relationship between quantum transport and structural properties in the presence of impurities. Improvements were also foreseen when other informations such as the inter-impurity distance were given only for narrow ribbons. As we consider longer and wider ribbons, the quantum confinement effect due to the narrowness of the edges is less pronounced leading to self-averaging effects. This results in less variety in the transmission, making it difficult for our ML models to learn useful details. An important ingredient for the success of the ML methods lies in the diversity and non-uniformity of the configurations in the training set. Machine learning techniques can capture the complexity of disordered nanostructures and can be used to complement conventional techniques in the context of quantum transport. The KRR and NN approaches were used to predict electronic transport in these structures and effectively captured the impact of structural defects on their properties. The results of this work served as a proof-of-concept and a cornerstone for the following chapters and to foresee ML as a tool that could be used in many context for nanoelectronics.

In chapter 4, we have shown the concrete use of ML methods to tackle the problem of magnetism in carbon-based structures. In carbon-based devices, when electronic interactions are considered, the magnetic moment at a site depends strongly on its location relative to nearby edges as well as their different structural nature and sublattice degree of freedom. This dependence was discussed with reference to the literature and simple models calculations alongside addressing the

experimental scope on how to observe such magnetic signatures in nanodevices. Estimation of magnetic moment profiles in nanostructures made of carbon are not difficult to acquire however these theoretical calculations using either DFT or the mean-field approach are constrained to small or periodic systems. By addressing these arising difficulties when one wants to predict profiles for larger and disordered systems, we have trained a neural network with the purpose of making magnetic profile prediction for various carbon-based structure geometries, less demanding in computational resources. Isolating the relevant crucial features and capturing them into a descriptor, we have then addressed our results showing excellent agreement with conventional methods. In addition to the accuracy, the computational cost and time resources are largely reduced allowing to use this tool intensively for other purposes such as studying spin-transport properties of disordered ribbons.

Chapter 5 has addressed spin-transport for edge-disordered ZGNRs. A particular attention was initially brought to review different fabrication techniques for GNRs. Indeed, edge disorder, being less observed due to novel and state-of-the-art techniques, is still present in either rough or smooth forms. Incentivized by the different profiles of disorder observed in nanoribbons, we have addressed two disorder profiles of our own and benchmarked the spin-transport properties obtained given our NN-model alongside conventional transport techniques. Our prediction of spin-transport shows great accuracy when compared to conventional methods and so we moved forward by generating a huge amount of different configurations to investigate thoroughly the relationship between disorder and spin-transport. We have found that rough edge disorder is detrimental on the establishment of spin-current around the edges due to the presence of short-ranged scatterers creating backscattering. On the other hand, smooth disorder has a lesser impact on the spin-transport properties being a type of long-ranged disorder where spin currents are more robust. This type of disorder has restricted backscattering possibilities compared to the rough disorder profile. From these findings, we considered the purposeful superposition of rough disorder to create asymmetry and consequently, to observe net spin-polarised transport quantities in these nanostructures. Considering different scenarios of ribbons that could be realistically synthesized, we have varied the disorder strength on one edge and considered if these nanoribbons could be used for spintronic applications.

Lastly, chapter 6 considered possible extensions to our work about how to protect or to block spin-currents purposefully by nanopatterning ZGNRs with arrays of triangular antidots. We have seen the spin-filtering possibility offered by an array of triangular antidots antiferromagnetically-coupled with its nearby edge completely impeding the spin-current.

In chapter 4, our NN-model holds great promise for tackling problems in many contexts, as shown by the detailed study done for the spin-transport in disordered GNRs in chapter 5. Yet, we think this model could be extended to evaluate magnetic properties and signatures away from half-filling. Indeed at the moment, we are able to quickly and accurately predict magnetic profile at half-filling but extending this tool to predict gated or doped nanostructures would be a great advantage. Speaking of doping, embedding magnetic impurities in the bulk or functionalisation at the edge of nanoribbons are other ways to tune the spin-transport properties of carbon-based materials. Encompassing our NN-tool to accurately predict the effect that such impurities could play would be beneficial for the entire community working on graphene spintronics.

The nanopatterning of GNRs with triangular antidots could potentially yield a very promising leap forward in the research for spintronic devices. Within the reach of experimental groups, a collaboration could be foreseen where theoretical and experimental efforts would maybe witness promising spin-filtering applications for this type of devices. This will consecrate the non-intuitive statement the effects of edge disorder could be alleviated with additional disorder!

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