



UNIVERSITÉ CATHOLIQUE DE LOUVAIN

Ecole Polytechnique de Louvain

Unité de Physico-Chimie et de Physique des Matériaux

Quantum transport in graphene based nanostructures

Dissertation présentée en vue de l'obtention du grade de

Docteur en Sciences de l'Ingénieur

par

Simon Mutien-Marie Dubois

Membres du jury:

Prof. Christian Bailly, président

Prof. Xavier Gonze

Prof. Stefano Sanvito

Dr. Sorin Melinte

Dr. Valerio Olevano

Dr. Luc Henrard

Prof. Jean-Christophe Charlier, promoteur

Prof. Gian-Marco Rignanese, promoteur

Novembre 2009

To Anne.
To Félix, his brothers and sisters.

Contents

Acknowledgements	i
Abstract	iii
List of Figures	v
List of Tables	ix
1 Preface	1
2 Concepts and theory	5
2.1 Introduction	5
2.2 The ground-state electronic density	8
2.2.1 The many-body problem	8
2.2.2 A functional of the electronic density	11
2.2.3 The self-consistent solution scheme	12
2.2.4 The exchange-correlation potential	12
2.2.5 Approximated XC functionals	13
2.2.6 Matrix representation	15
2.2.7 Beyond the mean-field approximation	16
2.3 the <i>Siesta</i> method	18
2.3.1 The numerical atomic orbitals	18
2.3.2 The electronic Hamiltonian	20
2.4 The electric current	22
2.4.1 The semi-classical approach	22
2.4.2 Phase-coherent quantum transport: <i>The Landauer-Büttiker formalism</i>	24
2.4.3 Phase-coherent quantum transport : <i>The Green's Function Formalism</i>	31
2.5 The <i>Smeagol</i> method	38
2.5.1 Calculation of the contact self-energies	38
2.5.2 The out-of-equilibrium density matrix	40

2.5.3	The self-consistent procedure	42
2.6	Achievements and limitations	44
2.6.1	Experimental characterization	44
2.6.2	Thermal fluctuations	45
2.6.3	Renormalization of the electronic levels	45
2.6.4	Inelastic scattering	46
2.7	Our approach	47
3	Quantum confinement in GNRs	49
3.1	Introduction	49
3.2	Electronic properties of graphene	51
3.2.1	Tight-binding model of graphene	52
3.2.2	Connection with the 2D massless Dirac equation	56
3.2.3	Electronic transport near the Dirac point	59
3.3	Electronic properties of graphene nanoribbons	60
3.3.1	Bands folding approximation	62
3.3.2	Electronic structure of the armchair ribbons	64
3.3.3	Electronic structure of the zigzag ribbons	68
3.3.4	Summary	73
3.4	Structure and stability of graphene edges	75
3.4.1	Edge formation energies	76
3.4.2	Gibbs free energies	83
3.4.3	Interpretation in terms of the Clar sextet theory	87
3.5	Conclusions	91
4	Topological Defects in GNRs	93
4.1	Vacancies and adatoms as primary defects	98
4.1.1	Primary defects in graphene	99
4.1.2	Primary defects in GNRs	102
4.2	Migration of defects	111
4.2.1	Relative stability of <i>bulk</i> and <i>edge</i> defects	111
4.2.2	Energy barriers	113
4.2.3	Defects at the edges	113
4.2.4	Clusters of defects	116
4.3	Hydrogenation and chemical reactivity	119
4.4	Further reconstructions of the edges	123
5	Quantum transport in GNRs	129
5.1	Introduction	129
5.2	Modeling setup	132
5.3	Quantum transport in pristine GNRs	134
5.4	Quasi-localized states and back-scattering	136

5.5	Defect positions and scattering	140
5.6	Conductance patterns of various topological defects	144
5.6.1	Quantum conductance of semi-conducting zGNRs .	144
5.6.2	Quantum conductance of metallic zGNRs	147
5.6.3	Quantum conductance of aGNRs	151
5.6.4	In conclusion	154
5.7	Conductance scaling at the mesoscopic scale	154
5.8	Conclusions	161
6	Conclusion	165

Acknowledgements

The time I have spent as a PhD research student in the group of Physico-Chemistry and Physics of Materials (PCPM) has been full of happy memories. The generosity and friendly nature of the people with whom I have had the pleasure of working have made the past five years seem to fly by.

I would like to thank my supervisors Jean-Christophe Charlier and Gian-Marco Rignanese who gave me an unending support and the liberty to find my own path. They have contributed to many aspects of my personal and scientific development and I definitely count their friendship among the indelible benefits of this PhD.

Over the years, I have shared my office with several outstanding personalities. I am thankful to Matthieu, Francois, Cristi, Pierre-Matthieu, Hakim, Paul, Xavier, Myrtha, Tonatiuh, Aurelien and Francois for providing me such an entertaining and stimulating environment. I am particularly indebted to Cristi who has accompanied my first steps in the area of quantum transport and to Aurelien and Francois who gave me very kind encouragements over the last ten months. Thanks are also due to Zeila, and Marcos, who have brought a lot of life and energy in the "Graphene Team". Many thanks go to everyone else in the group for making it such an interesting and nice place to work.

I am grateful to the CISM team for keeping the computers on the straight and narrow. Their support has been constant for the last five years. I am particularly indebted to Jean-Michel who should be given a medal for his friendly nature and willingness to help. I also would like to thank Bernard for his patience and for making me understand many computer's subtleties. Finally, I thank Jean-Paul, Fabrice and Alain who have all provided much needed help and advice at one time or another.

I am highly grateful to Sadia, Brigitte and Viviane, who provided a

spotless and very kind administrative support. They made my every day life significantly more enjoyable over these years.

Further thanks are due to a number of people who have made aspects of PCPM life particularly pleasurable: Jean-Michel, Sadia, Stephane, Anne, Arnaud, Sami, Claude, Karim, Nicolas, Luc, Sylvain, Fabiana, Matteo, Martin, David, Sebastien ("Le Grand"), Sebastien ("Le Petit"), as well as many others.

I must make a special mention of my family. My parents, brothers and sisters inspired me from a young age and continue to do so today. Finally, I owe much to my wife and our children, to whom this dissertation is dedicated. Anne, without your support and your love, I would not be writing this.

Abstract

Till recently, graphene was nothing but a theoretical concept. Nevertheless, a couple of years ago, researchers managed to actually prepare graphene samples. Owing to its unusual electronic properties and great promises for applications in nanoelectronics, this two-dimensional material has stirred a huge excitement in the scientific community. However, graphene is a zero-gap semiconductor preventing its use in most of field controlled applications such as field-effect transistors (FETs). Many efforts are therefore devoted to the patterning and characterization of graphene quantum dots and nanoribbons in which energy gaps may open due to the electronic confinement imposed by the edges. In this dissertation, the electronic and transport properties of graphene and graphene nanoribbons are explored by means of *ab initio* techniques. Special attention is devoted to the impact of topological imperfections, such as point-defects and edge reconstructions. In particular, we provide theoretical clues about the most stable defect topologies and we unveil the mechanisms that rule their electronic structure, chemical reactivity and scattering properties. Our forecasts are expected to be observed experimentally.

List of Figures

2.1	Schematic representation of a two-terminal transport setup connected to an external battery.	6
2.2	Schematic representation of the two-terminal transport setup.	27
2.3	Integration contour for the calculation of the density matrix.	41
2.4	Self-consistent cycle for the computation of the out-of-equilibrium density matrix and electric current.	43
3.1	Illustration of the carbon valence orbitals.	52
3.2	Graphene honeycomb lattice and its Brillouin zone.	53
3.3	Graphene π and π^* electronic bands.	56
3.4	Band structure of graphene DFT vs. MBPT+DFT.	57
3.5	Honeycomb lattice of graphene with both the zigzag and the armchair directions.	61
3.6	Naming convention for the N -zGNRs and N -aGNRs.	62
3.7	Principles of the band folding approximation.	63
3.8	Energy band structure of graphene projected on the zigzag and armchair directions.	63
3.9	Brillouin zone of graphene superimposed by a representation of the lines of allowed k -points in the simple <i>band-folding</i> topological approximation.	64
3.10	Energy band structures of armchair nanoribbons for various widths.	65
3.11	Deviation of the 17-aGNRs geometry with respect to the graphene plane.	67
3.12	Low energy electronic states of aGNRs	68
3.13	Energy band structures of zigzag nanoribbons for various widths.	70
3.14	Analytic form of the zigzag edge state in semi-infinite graphene planes.	71

3.15	Deviation of the 8-zGNR with respect to the graphene plane.	72
3.16	Spin polarized band structures of zigzag nanoribbons (8-zGNR).	73
3.17	Low energy electronic states of zGNRs	74
3.18	Schematic representation and electronic band structure of various possible edge passivations for the zigzag graphene ribbons : hydrogenation of the edges.	77
3.19	Schematic representation and electronic band structure of various possible edge passivations for the armchair graphene ribbons : hydrogenation of the edges.	78
3.20	Schematic representation and electronic band structure of various possible edge passivations for the zigzag graphene ribbons : reconstruction of the edges.	80
3.21	Schematic representation and electronic band structure of various possible edge passivations for the armchair graphene ribbons : reconstruction of the edges.	81
3.22	Formation energies of the edges (G_{H_2}) as a function of the chemical potential μ_{H_2}	85
3.23	Formation energies of the edges (G_{H_2}) as a function of the chemical potential μ_{H_2} : further comparison of the zigzag and armchair ribbons.	86
3.24	Representation of the benzenoid aromatic ring within the standard Clar's sextet scheme.	88
3.25	Clar's representations of z_1 -, z_{21} -, and a_{11} - GNRs of various widths.	90
3.26	Energy gaps oscillations in GNRs of increasing widths. . .	91
4.1	Experimental evidence for the presence of atomic defects in the graphene layer. Meta-stable defects found in HR-TEM image sequences.	94
4.2	Experimental evidence for the presence of atomic defects in the graphene layer. In situ observation of a topological defect induced by irradiation in a graphene layer.	95
4.3	Illustration of the spin density distribution ($\rho_\alpha - \rho_\beta$) induced by vacancies and adatoms in the graphene plane. .	99
4.4	Electronic energy band structures of pristine and defective graphene (i.e. in the presence of either a vacancy or an adatom)	101
4.5	Representation of the electrostatic potential (i.e. sum of the hartree potential and the local pseudo-potential) of graphene in the presence of a vacancy.	102

4.6	Electronic band structures of 17-aGNR and 8-zGNR. . . .	103
4.7	Schematic atomic representations of the nonequivalent orientations of a <i>bulk</i> vacancy in GNRs.	104
4.8	Magnetic configurations of a <i>bulk</i> vacancy in zGNRs. . . .	105
4.9	Impact of a <i>bulk</i> vacancy on the energy band structure of zGNRs.	107
4.10	Schematic atomic representations of the nonequivalent adsorption sites for <i>bulk</i> adatom in GNRs.	108
4.11	Magnetic configurations of <i>bulk</i> adatoms in zGNRs.	109
4.12	Impact of <i>bulk</i> adatoms on the electronic energy band structure of aGNRs.	110
4.13	Relative energies of defective zigzag and armchair GNR as a function of the defect position across the ribbon width.	112
4.14	Atomic representations of the ground-state geometries of vacancies and adatoms recombined at the graphene edges.	114
4.15	Impact of <i>edge</i> vacancies on the electronic energy band structure of zGNRs.	115
4.16	Impact of <i>edge</i> adatoms on the electronic energy band structure of aGNRs.	117
4.17	Atomic representations of the ground-state geometries of <i>bulk</i> di-vacancies and carbon dimers in graphene ribbons.	118
4.18	Atomic representations of the ground-state geometries of <i>bulk</i> and <i>edge</i> hydrogenated vacancies in GNRs.	120
4.19	Atomic representations of the ground-state geometries of <i>bulk</i> and <i>edge</i> hydrogenated adatoms in GNRs.	122
4.20	Atomic representations of the <i>Penta</i> , <i>Hepta</i> , <i>Dip</i> , D_{656} , D_{757} and D_{575} <i>edge</i> topologies.	124
5.1	Schematic representation of a GNR-Field Effect Transistor.	131
5.2	Schematic representation of the setup used to compute the intrinsic transport properties of graphene ribbons in the presence of an isolated defect.	132
5.3	Atomic structures, electronic band structures and quantum conductances (electronic transmission) of various graphene nanoribbons.	134
5.4	Effect of a <i>bulk</i> vacancy on the conductance of a 8-zGNR : conductance, density of states, representation of the transmission eigenchannels at $E = -0.65$ eV.	137
5.5	Effect of a <i>bulk</i> vacancy on the conductance of a 8-zGNR. Representation of the transmission eigenchannels at $E = -0.45$ eV.	138

5.6	Effect of a <i>edge</i> vacancy on the conductance of a 8-zGNR : conductance, density of states, representation of the trans- mission eigenchannels at $E = -0.45$ eV.	141
5.7	Effect of an adatom on the conductance of a 17-aGNR : conductance as a function of the defect position.	143
5.8	Effect of <i>bulk</i> defects on the conductance of a semi-conducting 8-zGNR.	146
5.9	Effect of <i>edge</i> defects on the conductance of a semi-conducting 8-zGNR.	148
5.10	Effect of <i>bulk</i> defects on the conductance of a metallic 8-zGNR (i.e. within the $\uparrow\uparrow$ spin configuration)	149
5.11	Effect of <i>edge</i> defects on the conductance of a metallic 8-zGNR (i.e. within the $\uparrow\uparrow$ spin configuration).	150
5.12	Effect of <i>bulk</i> defects on the conductance of a semi-conducting 17-aGNR.	151
5.13	Effect of <i>edge</i> defects on the conductance of a semi-conducting 17-aGNR.	153
5.14	Schematic representation of the pentagon, heptagon, D_{757} , and <i>Dip</i> defects considered in our mesoscopic calculations.	155
5.15	Impact of the pentagon, heptagon, D_{757} , <i>Dip</i> defects on the transport properties of aGNRs : effect of the hydro- genation.	156
5.16	Conductance of a single defect obtained by the simple topological TB Hamiltonian (solid line) and by the ad- justed TB Hamiltonian (red line) for the pentagon (a), heptagon (b) and <i>Dip</i> (c) defects. Ball-and-stick models of the defects are illustrated in the right panel.	158
5.17	Schematic representation of the pristine, pentagon de- fected and heptagon defected edge topologies with the associated adjusted tight-binding parameters	159
5.18	Conductance scaling of mesoscopic defective 35-aGNRs.	160
5.19	Localization length for a 35-aGNR with a 6×10^{-2} nm $^{-1}$ density of <i>Dip</i> defects.	162

List of Tables

3.1	Edge formation energies of various reconstructed zigzag ribbons.	82
3.2	Edge formation energies of various reconstructed armchair ribbons.	83
4.1	Relative stability of the meta-stable configurations of vacancies in armchair and zigzag GNRs.	106
4.2	Relative stability of the meta-stable configurations of adatoms in armchair and zigzag GNRs.	109
4.3	Formation energies of topological defects in GNRs.	126

Chapter 1

Preface

Graphene is the name given to the two-dimensional sheet of sp^2 bonded carbon atoms packed into an honeycomb structure. Till recently, graphene was nothing but a theoretical material, but researchers managed to actually isolate a graphene sample, a couple of years ago, allowing the measurement of its electrical properties [1, 2, 3]. The unusual features reported stirred a huge excitement in the scientific community and graphene rapidly became the center of an intense research activity. Owing to its geometry and the two dimensional confinement of its electrons, graphene has revealed many new physical phenomena and shown great promises for applications in nanoelectronics. [4]. Indeed, the ease to tune the type and concentration of charge carriers, as well as the extremely high carriers mobilities and coherence lengths experimentally reported make graphene attractive for high frequency integrated circuits. Furthermore, its high stability, extreme flexibility and large thermal conductivity are highly desirable for application in devices that operate in extreme conditions (high temperature, high pressure, irradiation). However, graphene is a zero-gap semiconductor preventing the achievement of high I_{on}/I_{off} current ratio in field controlled applications, such as field-effect transistors (FET). Many efforts are therefore devoted to the patterning and characterization of graphene quantum dots and nanoribbons.

Graphene nanoribbons

In contrast with graphene which is a semi-metal, quasi 1D graphene ribbons are semi-conducting owing to the electronic confinement imposed by the edges. Recently, significant progresses have been achieved in the synthesis of narrow graphene nanoribbons allowing the realization of carbon based field-effect devices [5, 6]. Though large I_{on}/I_{off} current

ratio ($> 10^5$) have been reported, the performances of such devices have to be significantly improved for the GNRs to be considered as reliable complements to the silicon-based technology. At the same time, chemical doping and introduction of dedicated defects in graphene based materials are being actively explored as a potential source of innovation to tailor the electronic properties of these nanostructures.

The properties of these novel class of hybrid carbon-based nanomaterials remain to be fully characterized. With this respect, numerical studies that explicitly account for the actual topology of the GNRs channel will surely help and facilitate the improvement of the devices characteristics. The work presented hereafter participates to this effort and aims to improve the understanding of the physical mechanism ruling the electronic and transport properties of defective graphene nanoribbons.

Quantum modelling

Understanding and modeling the electronic transport in nanoscopic devices is not at all an obvious task and certainly requires the use of dedicated tools. At short length scales, the quantum mechanical wave nature of the electrons plays a crucial role and the semi-classical models are not valid anymore. Besides, in most operating conditions, the potential bias that is imposed potentially brings the electronic population away from its equilibrium configuration. Addressing the transport problem at the atomic scale therefore requires a quantum theory of out-of-equilibrium systems.

Due to the nature of interactions between the particles, the equations of quantum mechanic cannot be solved analytically, with the notable exception of some highly prototypical systems. Therefore, to solve the quantum mechanical equations, we must turn to numerical simulations. Within the large set of quantum modelling methods that have been developed over the last few decades, the first-principles, or *ab initio* techniques refer to the methods that do not need any *a priori* assumption regarding the properties of the system under investigation. Most of the results presented throughout this dissertation have been computed within such an *ab initio* framework.

Outline of dissertation

In Chapter 2, we outline some concepts of quantum mechanics that are relevant to the solution of the transport problem. In many situations,

the out-of-equilibrium conditions associated with the transport problem only bring small corrections to the ground-state (GS) electronic density. A good practice is thus to rely on the GS electronic density as the guess density for the transport calculations. Therefore, the framework of Density Functional Theory (DFT) that provides a firm theoretical background for the calculation of the GS electronic density is reviewed in the beginning of Chapter 2. In the perspective of transport calculations, the implementation of the DFT equations in terms of a localized basis set presents some convenience. Some technical considerations regarding such an implementation are then outlined and the *Siesta* computational scheme is introduced [7]. Finally, the description of the electric current within the Non-Equilibrium Green's function formalism (NEGF) is described. Though the NEGF allows to account for the electronic correlation, it is worth mentioning that we focus on the description of the coherent propagation of carriers. To conclude, we present an overview of the actual procedure implemented within the *Smeagol* package for the calculation of the electric current [8] and we discuss the implicit approximations used throughout our dissertation.

In Chapter 3, the electronic structures of graphene and graphene nanoribbons are investigated by means of *tight-binding* and *ab initio* techniques. A particular attention is devoted to the mechanisms that rule the opening of energy gaps in the band structure of GNRs. While the energy gaps mainly originate from the quantum confinement imposed by the boundaries, additional effects such as the relaxation and reconstruction of the edges are reported to have a crucial role in determining the electronic properties of low energy electrons. Besides, the edge free energies associated with different reconstructed edge patterns are computed allowing us to draw some important conclusions regarding the relative stability of the different edge patterns. Finally, we show that the Clar's sextet theory may be successfully applied to GNRs in order to rationalized, to some extent, the close connection between the GNRs topology and its electronic, magnetic and stability characteristics. Some sections of this chapter have been published as part of a review paper [9]. Besides, the discussion regarding the reconstruction of GNRs at the edges is part of a forthcoming publication that should complete the previous studies presented in Refs. [10, 11, 12].

As supported by several experimental observations [13, 14, 15, 16], defects are unavoidable in carbon nanostructures and are likely to play an important role regarding the electronic, magnetic and transport properties of nanoribbons. In Chapter 4, the impact of point-defects on the

electronic states of GNRs is investigated. In particular, we focus on the electronic structures, formation energies and reconstruction mechanisms of the vacancies and carbon adatoms. Not only these defects are present at thermal equilibrium, they are also of technological interest since their concentration can be tuned by irradiation of the GNR samples. Owing to the high mobility of point defects on the graphene plane, our results suggest that the main pinning mechanism for vacancies and adatoms is the recombination with the edge. Finally, the computed formation energies outline the poor robustness of the zigzag shapes edges regarding the introduction of defects.

The study of quantum charge transport phenomena in actual defective GNRs is of particular interest for the engineering of novel functional devices that would complement the Silicon based CMOS technology. In Chapter 5, the conductance patterns of various *bulk* and *edge* defects are computed. The transport properties are predicted to strongly depend on the position, geometry and chemical reactivity of the defects. The impact of a single defect appears to range from a vanishing backscattering effect to the full suppression of conduction by the holes or electrons. Besides our results highlight the crucial role played by the electronic states localized along the zigzag edges in preserving the ballistic conductance of zigzag shaped GNRs. This account for a strong difference between the conductance patterns of zigzag and armchair ribbons. Finally, we report a tight-binding investigation of the electronic transport properties of mesoscopic armchair shaped GNRs. The consideration of long ribbons (up to $5\mu\text{m}$) allows us to rationalize the conductance gaps observed experimentally. In addition, we propose the full hydrogenation of the edge as a new route to tune the robustness of the electronic conductance against edge roughness. The discussion regarding the role played by the edge states should be introduced in a forthcoming publication. The investigation regarding the conductance scaling in long armchair GNRs has been recently accepted for publication.

Chapter 2

Electronic transport : concepts and theory

2.1 Introduction

At short length-scales, where the devices behavior is characterized by coherent tunneling, the semi-classical transport models are not valid anymore and the quantum mechanical wave nature of the electrons has to be considered. However, owing to the flow of carriers through the device, the transport problem can not be solved using the methods commonly encountered in quantum chemistry, where molecules are considered as closed systems, or in condensed matter physics, where advantage is taken from the periodicity of solids. Instead, a quantum theory that account for the inflows and outflow of carriers is needed.

Besides, in most operating conditions, the external bias that is imposed in order to maintain the carriers flow brings the active region away from its equilibrium configurations and impedes the use of a single Fermi distribution function to characterize its electronic population. Therefore, addressing the transport problem at short length-scales requires a quantum theory for open systems in an out-of-equilibrium configuration.

The transport setup

The physical system on which we focus throughout this work is depicted in Fig. 2.1. It is composed of a finite nanoscale cluster (e.g. a molecule or any set of atoms) functionalized to two bulk electrodes. The electrodes are assumed to be semi-infinite, periodic, defect-free (i.e. pristine crystals). The electronic states are thus largely delocalized inside the electrode and form continuous sets of allowed energy levels. The

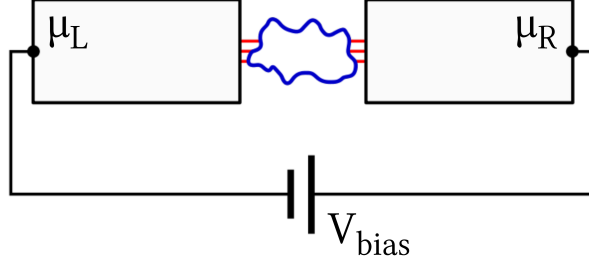


Figure 2.1: Schematic representation of a two-terminal transport setup connected to an external battery. The device, itself, is made from a finite nanoscale cluster functionalized to two bulk electrodes assumed to be at thermal equilibrium

electrodes are assumed to remain at the thermal equilibrium even if a given potential bias (V_{Bias}) is applied across the device. Under this latter assumption, the electronic distribution of the electrons deep inside the contact is ruled by the Fermi distribution function,

$$f(E) = \frac{1}{1 + \exp(\frac{E-\mu}{k_b T})}, \quad (2.1)$$

which depends on the temperature (T) and the electrochemical potential of the material (μ). On the other hand, the atomic cluster is assumed to be finite and sufficiently short in size in order to keep away all the polaronic effects that may appear when the length of the sample exceeds the electronic mean free path [17, 18]. Besides, we focus our dissertation onto those nanoscale systems where strong correlation effects are negligible. In particular, we will assume that the carrier equilibration occurs exclusively deep into the electrodes and that the transport of carriers through the device is mostly coherent.

The isolated cluster presents well confined electronic states with no electronic dispersion. The discrete energy levels are populated by an integer number of electrons. When the nanoscale cluster is contacted to the electrodes, some of the confined electronic orbitals couple with the electronic states belonging to the electrodes. As the cluster orbitals spread inside the electrodes, the electronic motion through the system brings the junction at the equilibrium. At the same time, a broadening of the discrete energy levels is induced by the coupling with the electrodes. At the equilibrium, the electronic distribution of the complete

system (leads + cluster) is ruled by a single Fermi electronic distribution function. In this situation no electron flows through the device.

In order to establish an electric current from one electrode (the source electrode) to the other (the drain electrode), the device has to be introduced in an external circuit containing a battery that may externally fix the electro-chemical potentials of the electrodes. The application of a bias brings the system out-of-equilibrium and an electric current may eventually flow through the device. The source electrode, whose energy levels have been raised up, keeps injecting electrons into the device in an attempt to bring it back in equilibrium. On the contrary, the drain electrode keeps pumping electrons from the device for the same reasons. In the general case, the electronic distribution function of the device and the electric currents are time-dependent. However, hereafter, we consider only the case of a steady-state current flow through the junction. One may reasonably assume this situation is reached when the battery maintains the source and drain electrodes at a different potential for sufficiently long time.

This pictorial presentation of the device setup highlights several aspects of the transport problem. First, the coupling between the electrodes and the nanoscale device is crucial in determining the chemical potential at equilibrium. Indeed, it fixes the redistribution of the charge within the junction and the alignment of the discrete energy levels with respect to the electrodes energy band structures. These aspects can be accurately described within a quantum theory of the equilibrium. Second, the electrostatic potential profile and the out-of-equilibrium electronic density depend directly on the applied voltage. The estimation of the I-V curve therefore involves to accurately account for the inflow and outflow of carriers that bring the molecular structure out-of-equilibrium.

Outline of chapter

In this introduction, the physical system of interest has been presented and the transport problem defined. The next sections aim to present the method used to formulate the quantum transport. A particular attention is devoted to the derivation of a computationally tractable scheme where the inflow and outflow of carriers is expressed in terms of Green's function.

Since the equilibrium situation is often a good starting point in order to address the general issue of atomic systems out-of-equilibrium. The main concepts of the Density Functional Theory (DFT) that allows to compute the ground-state electronic density of systems of electrons and nuclei, are introduced in Section 2.2. Some aspects specific to the im-

plementation of the DFT with localized basis sets, as done in the *Siesta* simulation code [7], are discussed in Section 2.3. In Section 2.4, the coherent transport of carriers from one electrode to the other is described both in terms of stationary scattering states and Green's functions. Finally, in Section 2.5, we present the self-consistent scheme recently implemented in the *Smeagol* package [8] in order to compute the out-of-equilibrium electronic density and the coherent electric current in nanoscale devices.

2.2 The ground-state electronic density

Over the years, the density functional theory (DFT) [19, 20] has proved to be a powerful framework for the description of many ground-state properties of both bulk and nanoscopic materials. This section introduces the way how DFT tackles the description of systems made of electrons and nuclei.

2.2.1 The many-body problem

In non-relativistic quantum mechanics, the theoretical treatment of the motion of particles relies on the Schrödinger equation. For one particle in a time-independent potential, it is commonly written in the form,

$$H\Psi = E\Psi , \quad (2.2)$$

with

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) , \quad (2.3)$$

where m is the particle mass and $V(\mathbf{r})$ the external potential. Together with appropriate boundary conditions, the Schrödinger equation forms a well-defined problem which, in the case of a single particle, is easily tractable and leads to well defined solutions. In the case of a system of electrons and nuclei, the Hamiltonian can be written as,

$$\begin{aligned} H = \sum_i -\frac{\hbar^2 \nabla_i^2}{2M_i} &+ \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j e^2}{|\mathbf{R}_i - \mathbf{R}_j|} - \sum_k \frac{\hbar^2 \nabla_k^2}{2m} \\ &+ \frac{1}{2} \sum_{k \neq l} \frac{e^2}{|\mathbf{r}_k - \mathbf{r}_l|} - \sum_{k,i} \frac{Z_i e^2}{|\mathbf{r}_k - \mathbf{R}_i|} , \end{aligned} \quad (2.4)$$

where $\mathbf{R}_{i/j}$, $\mathbf{r}_{k/l}$, $Z_{i/j}$, $M_{i/j}$ and m are the nuclei and electrons coordinates, the nuclear charges and masses, and the electron mass, respectively. In Eq. 2.4, three coupling terms (i.e. terms involving the coordinates of two particles) appear in addition to the kinetic energy operators. These correspond to the ion-ion, electron-electron and ion-electron

interactions. Though the problem is still well-defined, when the system contains a large number of interacting particles, the interaction terms make the Schrödinger equation too complex for an exact solution. Additional approximations have thus to be introduced in order to tackle the motion of electrons and nuclei in molecules and solids.

In a first attempt to simplify the general problem, two major approximations may be done.

- (i) The large masses of the nuclei, appearing in the nuclei kinetic energy operator, imply characteristic velocities much smaller than the ones of electrons. One may then argue that the electronic configuration will "instantaneously" reacts to the motion of the nuclei. On this basis, it is commonly assumed that the adaptation of the electronic density will not give rise to electronic transitions and will remain adiabatic. In this case, the first two terms of Eq. 2.4 may be treated independently of the others. It constitutes the so-called *Born-Oppenheimer* approximation [21].
- (ii) Among all the electrons of the system, only a small fraction effectively determines most of the material properties, these are the valence electrons. From this point of view, one can eliminate the explicit consideration of the core electrons by assuming them moving rigidly with the nuclei. The nuclei-electron interaction is then replaced by an artificial, weaker potential whose aim is to mimic the Coulomb attraction of the nuclei properly screened by the core electrons, and which acts on a set of pseudo-wave-function rather than the true valence wave-functions. This constitutes the *pseudo-potential* approximation [22, 23].

Upon these two approximations, the many-body Hamiltonian takes the form,

$$H = T^e + V^{e-e} + V^{ext} \quad (2.5)$$

with

$$T^e = \sum_{k'} -\frac{\hbar^2 \nabla_{k'}^2}{2m}, \quad V^{e-e} = \frac{1}{2} \sum_{k' \neq l'} \frac{e^2}{|\mathbf{r}_{k'} - \mathbf{r}_{l'}|}, \quad V^{ext} = \sum_i V_i^{pseudo}(\mathbf{r} - \mathbf{R}_i).$$

The k' and l' indexes are restricted to the valence electrons, and the nuclei positions are considered as external parameters. At this stage, we are left with an Hamiltonian still containing the coupling terms associated with the electron-electron interactions. This makes the problem still intractable. A desirable way to overcome this issue should be to find a

satisfactory expression for this interaction in terms of an effective one-particle potential,

$$V^{e-e} \simeq \sum_k V^{eff}(\mathbf{r}_k) . \quad (2.6)$$

In this case, assuming the separability of the many-body wave-functions, the problem reduces to a set of decoupled equations, each one being tractable,

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_n) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\dots\psi_n(\mathbf{r}_n) , \quad (2.7)$$

with

$$[T^e + V^{ext} + V^{eff}]\psi_i(\mathbf{r}_k) = \epsilon_i \psi_i(\mathbf{r}_k) . \quad (2.8)$$

The Hartree method is one of the simple recasting of the many-body problem in a set of single-particle equations is the Hartree method [24]. The idea behind the method is to consider each particle as moving independently in the mean field due to all the others. The resulting expression for the effective one-electron potential is

$$V^{eff}(\mathbf{r}_k) = \sum_{\substack{i \neq k \\ i \text{ occupied}}} e^2 \int d\mathbf{r}_i \frac{|\psi_i(\mathbf{r}_i)|^2}{|\mathbf{r}_k - \mathbf{r}_i|} \quad (2.9)$$

$$= e^2 \int d\mathbf{r} \frac{n(\mathbf{r})}{|\mathbf{r}_k - \mathbf{r}|} - e^2 \int d\mathbf{r} \frac{|\psi_k(\mathbf{r})|^2}{|\mathbf{r}_k - \mathbf{r}|} . \quad (2.10)$$

Equivalently, the effective potential may be viewed as originating from the interaction of the k^{th} -electron with the ground-state electronic density, reduced by the interaction of the k^{th} -electron with itself. The first term on the right of Eq. 2.10 is called the Hartree potential.

Despite its simplicity, this model interaction gives some insight about the properties of simple metals. However, to treat the large variety of materials we have to go beyond this approximation. One can show that by introducing the Pauli exclusion principle in the previous model and forcing the antisymmetry of the many-body wave-function, the quality of the model interaction is significantly increased, leading to the so called Hartree-Fock approximation [25, 26].

The density functional theory, which is described hereafter, is a method which provides another improved recasting of the many-body problem in an equivalent one-body description.

2.2.2 A functional of the electronic density

The density functional theory has been very popular for calculations in solid-state physics for a while. This is both due to many successful comparisons with experimental results and a reasonable computational time with respect to other methods. The theoretical footing of the density functional theory is made of two theorems.

- (i) The theorem of Hohenberg and Kohn [19] applies to systems of interacting electrons in an external potential. It states that, in such systems, the external potential is uniquely determined by the ground-state electronic density. In other words, the external potential, and by extension the Hamiltonian and the electronic energy, are functionals of the electronic density. Using the variational property of the electron energy operator, this result allows to reformulate the search of the ground-state electronic configuration of a many electrons system as a functional minimization over the electron density. Explicitly, for a system of N electrons, the energy functional that has to be minimized is,

$$E^{el}[n] = \langle \Psi^* | T^e | \Psi \rangle + \int d\mathbf{r} V^{ext}(\mathbf{r})n(\mathbf{r}) + \langle \Psi^* | V^{e-e} | \Psi \rangle \quad (2.11)$$

with the constraint,

$$\int d\mathbf{r} n(\mathbf{r}) = \int d\mathbf{r}_1, \dots, d\mathbf{r}_N \Psi^*(\mathbf{r}_1, \dots, \mathbf{r}_N) \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = N. \quad (2.12)$$

- (ii) The theorem of Kohn and Sham [20] provides a way to calculate the ground-state electronic density associated with a set of interacting electrons in an external potential (V^{ext}). It shows that the Hohenberg and Kohn energy functional is minimized both by the electronic density of the interacting electrons moving in the potential V^{ext} and by the electronic density of non-interacting electrons moving in an effective potential, called the Kohn-Sham potential V^{KS} . This effective potential is,

$$V^{KS}(\mathbf{r}) = V^{ext}(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} + V^{xc}[n]. \quad (2.13)$$

In this formulation, all the physics related to the electron-electron interaction is stored in what is called the exchange-correlation potential V^{xc} . One has to note that this potential is a functional of the electron density which is not known *a priori*.

In the following, the name *Density Functional Theory* will refer to the recasting of the many-body problem into a set of single particle KS equations that has to be solved self-consistently. With this respect, the *Density Functional Theory* results from the combined use of the Hohenberg and Kohn [19], and, Kohn and Sham [20] theorems.

2.2.3 The self-consistent solution scheme

Assuming that the exchange-correlation functional V^{xc} is known, the two theorems introduced in Section 2.2.2 allow to set up a self-consistent procedure in order to tackle the initial many-body problem. The solution of the system made of non-interacting electrons moving in the Kohn-Sham potential is easy to compute. It is a Slater determinant built upon the one electron wave-functions that are solutions of the one electron Schrödinger equation:

$$\left[\frac{\hbar^2 \nabla_k^2}{2m} + V^{KS}(\mathbf{r})\right]\psi_k(\mathbf{r}) = \epsilon_k \psi_k(\mathbf{r}) . \quad (2.14)$$

Due to the dependence of the exchange-correlation functional with respect to the "unknown" electronic density, Eq. 2.14 has to be solved self-consistently until the electron density, build as

$$n(\mathbf{r}) = \sum_{k \text{ occupied}} \psi_k^*(\mathbf{r})\psi_k(\mathbf{r}) , \quad (2.15)$$

is converged. The solution scheme involves the iterative improvement of the solution by the use, at each step, of the calculated KS states for the construction of the new potential. The Hohenberg and Kohn theorem states that this procedure, when convergence is reached, gives the exact ground state electronic density of the initial many-body problem.

2.2.4 The exchange-correlation potential

The main theoretical difficulty in the density functional theory is the treatment of the exchange-correlation (XC) energy since its exact form is unknown. However, coming back to the Hohenberg and Kohn theorem and Eq. 2.11, the physical content of the XC energy is readily identified. Let's rewrite the electronic energy functional as the sum of four contributions,

$$E^{el}[n] = \langle \Psi^* | T_0^e | \Psi \rangle + \int d\mathbf{r} V^{ext}(\mathbf{r})n(\mathbf{r}) + e^2 \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E^{xc}[n(\mathbf{r})] . \quad (2.16)$$

The four terms are : (i) a kinetic term, taken as the kinetic energy of the non-interacting electron gas of the same density, (ii) the contribution of the external potential which eventually contains the pseudo-potentials of all the ions, (iii) the Hartree energy which accounts for the interaction of each electron with the total electronic cloud, and (iv) a remaining piece which accounts for all the electron-electron interactions that are not included in the Hartree potential. This last piece ($E_{xc}[n(\mathbf{r})]$) is the XC energy functional, from which the XC potential is derived,

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})} . \quad (2.17)$$

By deriving an adiabatic connection between the Hamiltonian of the interacting electrons gas (Eq. 2.5) and the corresponding Kohn-Sham Hamiltonian (Eqs. 2.13 and 2.14), it can be shown that the $E_{xc}[n(\mathbf{r})]$ functional is an integral of the electronic density multiplied by an XC energy density [27], (ϵ^{xc}),

$$E^{xc}[n(\mathbf{r})] = \int d\mathbf{r}' n(\mathbf{r}') \epsilon^{xc}(\mathbf{r}', n(\mathbf{r})) . \quad (2.18)$$

While some mathematical properties of the XC energy density are known exactly, its exact formulation remains unknown and the actual implementation of the DFT have to rely on approximated functionals.

2.2.5 Approximated XC functionals

The simplest and most commonly used approximation of the exchange-correlation functional is the *local density approximation* (LDA). This latter assumes a simplified dependence of the ϵ^{xc} functional [27, 28, 29],

$$\epsilon_{lda}^{xc} = \epsilon^{xc}(\mathbf{r}', n(\mathbf{r}')) . \quad (2.19)$$

In this form, the XC functional does not depend anymore on the electronic density in the whole space but is purely local. Within the most common implementations, ϵ^{xc} is splitted in its exchange and correlation parts which are independently approximated. The exchange part ($\epsilon^x(\mathbf{r}', n(\mathbf{r}'))$) is obtained from the exchange energy of the homogeneous electron gas for which an exact analytical expression is known, while estimations of the correlation part are obtained from accurate Monte-Carlo simulations. The LDA functional provides an accurate description of the atomic structure, as well as the elastic and vibrational properties of most systems. However, the strong approximation, that is *locality*, implies an overestimation of the binding energies of molecules and solids, that can

reach ≈ 0.5 eV/atom.

The natural step beyond the *local density approximation* is to take into account the dependence of ϵ^{xc} with respect to the gradient and laplacian of the density. This is achieved in the *generalized gradient approximation* (GGA) [30, 31, 32] where the following form of the local exchange-correlation energy is assumed,

$$\epsilon_{gga}^{xc} = \epsilon^{xc}(\mathbf{r}', n(\mathbf{r}'), \nabla n(\mathbf{r}'), \nabla^2 n(\mathbf{r}')) . \quad (2.20)$$

The GGA functional brings large improvements with respect to the *local density approximation*. For instance, energy barriers, adsorption and binding energies are described in a more realistic way. However, semi-local GGA functionals still suffer some limitations. First, though common GGA functionals produce reliable results for all main types of chemical bonds, these fails to capture the essence of the long range van der Waals interaction. This latter comes from the correlated motion of electrons between distant atoms or molecules that appears owing to long range Coulomb interaction. Second, though sufficient for the structural and electronic investigation of most solids, the semi-local approximation is still too limited in order to generally insure the so-called *chemical accuracy*, that is binding energies with an accuracy better than 50 meV/atom [33, 34, 35]. Third, usual local and semi-local exchange-correlation functionals are rather versatile in predicting the magnetic behavior of solids. Indeed, the appearance of magnetic order results from a subtle competition between exchange and kinetic energy effects. Both LDA and GGA functionals are known to underestimate the Coulomb repulsion affecting the balance between electronic exchange and kinetic energy. The GGA functional has been used for all the DFT calculations presented in this work. The aforementioned drawbacks should not significantly affect the investigation of the structural, electronic and transport properties of graphene based nanostructures.

A number of fully non-local exchange-correlation functionals have also been developed. These include the *average density approximation* (ADA) and the *weighted density approximation* (WDA) that depend not only on the local electronic density ($n(\mathbf{r}')$) but also on the density in some region around each point $\mathbf{r}'$ [29]. Finally, one also has to mention the existence of orbital-dependent functionals where the dependence of ϵ^{xc} with respect to the electronic density is spited between the partial electronic densities associated with particular subset of electronic orbitals. In this class, one finds methods that involve LDA- or GGA-functionals coupled

with an additional term that depends on the KS-orbitals. The additional term may aim to correct the unphysical self-interaction of the initial functional, as in the *self-interaction correction* (SIC) scheme [36, 37], or to add some physical information about the electronic correlations in the form of an *Hubbard correction* (LDA+U) [38, 39]. These corrected schemes leads to a significantly improved description of the magnetic behavior of solids [40].

2.2.6 Matrix representation

Up to now, the computational aspects related to the solution of the KS equation (2.14) have not been tackled. The usual approach to solve the KS problem is to rely on a basis set of finite size for the expansion of the KS orbitals and to use the associated matrix representation of the operators in order to recast the KS equation into an eigenvalue problem. In combination with the self-consistent scheme introduced in Section 2.2.3, it forms a complete method for the calculation of the ground-state total-energy and ground state electronic density within the DFT. A more extended review of the modern DFT implementation schemes is provided elsewhere [41].

Various basis sets are commonly used to accurately compute the one particle states involved in the fully self-consistent DFT. Each of them present specific advantages and drawbacks.

- (i) On one hand, since they are the solutions of the KS equation in presence of a constant external potential, *plane-waves* (PW) appear to be the natural choice for the description of nearly free electrons. Moreover, plane waves form a complete, orthogonal, basis set that allows to naturally take into account the periodicity of crystals. The combination of PW with the pseudo-potential approximation provides therefore powerful methods for the description of periodic crystals. Finally, the completeness of the PW basis set is easily controlled by the progressive introduction of plane waves of higher kinetic energy. This is a major advantage, since it allows to determine the size of the basis set needed to assess the desired computational accuracy. However, plane-waves are not very efficient neither for the description of finite or inhomogeneous systems nor for the all-electron calculations. Indeed, plane-waves are poorly suited to expand localized states and a large number of waves are required to describe the rapidly oscillating wave-functions in the core region.

- (ii) The *real space* methods are alternative choices for the solution of the Poisson and Schrödinger equations. In contrast to plane-waves, real space methods are advantageous for finite, non-homogeneous, non-periodic systems. Moreover, the spatial nature of the methods allows to handle more easily non-local potential and to use adaptive grid to tackle the hard potentials and heterogeneities.
- (iii) On the other hand, linear combination of *atomic-like orbitals* sounds to be the natural way to describe the binding in molecules and crystals. Indeed, the set of atomic orbitals centered on the atoms of the material may be viewed as the minimal basis set for the electronic structure calculations. In addition to the limited number of orbitals needed to describe the electronic structure, one major advantage of the localized nature of the basis functions is the sparse form of the Hamiltonian matrix that simplifies greatly its diagonalization.

However, this approach suffers the lack of systematic method to insure the accuracy of the basis sets. Indeed, a given set of atomic like orbitals may be very efficient for the description of some atomic configurations and quite poor for others. Special attention has thus to be paid in order to insure the completeness and relative transferability of the basis sets.

2.2.7 Beyond the mean-field approximation

At this point, the many-body problem has been presented and the way to overcome it within the DFT has been described. The DFT provides a convenient recasting of the original many-body problem into a set of single-particle equations that have to be solved self-consistently. The unapproximated DFT allows to compute exactly the ground-state electronic density and total energy associated with the initial many-body problem. This is sufficient when one is interested in the structural properties of atomic systems and accounts for most of the successes of the theory. However, it has to be reminded that, in contrast to the electronic density, the KS eigenstates and energies are mean-field approximations of the exact solutions of the Schrödinger equation. Therefore, there is no firm theoretical justification for their identification with the actual electronic states and excitation spectra observed in experiments. Though the DFT has proved to produce quite accurate results in predicting the dispersion relations of valence and conduction bands in most of systems, the theory presents some pathologies in describing the system responses to external probes and excitations. One of these pathologies is known as the *band gap problem* and accounts for the failure of DFT when determin-

ing the energy band gap (E_{gap}) of semiconductors and insulators. This is an important drawback for the investigation of the transport properties of nanoscale systems where the electronic gap often plays a crucial role in determining the potential landscape felt by the propagating electrons.

Regarding the excited states, the physical informations related to the excitation spectra are contained within the one- and two-electrons Green's functions rather than the electronic density. The Many-Body Perturbation Theory (MBPT), that considers explicitly these Green's functions, is a method to improve the description of the excited electronic states within the DFT scheme. In this theory, the electronic correlation is not anymore described by the exchange-correlation potential but rather by a self-energy operator (Σ_{xc}) that is non-local, non-hermitian and energy dependent. The common implementations of this theory rely on the approximation of the self-energy operator as the product of the single-particle Green's function ($G(\mathbf{r}, \mathbf{r}', E)$) by the dynamically screened Coulomb interaction ($W(\mathbf{r}, \mathbf{r}', E)$) and are called GW approximations. Further description of the MBPT and its approximations can be found elsewhere [42, 43, 44].

Alternative methods to the Density Functional Theory, that do not suffer the drawbacks of the mean-field approximation, also exist for the solution of the many-body Schrödinger equation. For example, Quantum Monte Carlo (QMC) [45], as well as Configuration Interaction (CI) [46], and Coupled-Cluster (CC) [46, 47] methods explicitly account for the many-particle nature of the wave-functions. All these methods are much more accurate than the LDA and GGA implementations of the DFT but at the expense of larger computational demand.

In this work, the Density Functional Theory is used for the investigation of the energetics and structural properties of graphene-based nanostructures. These properties are known to be well described within the DFT. Therefore, the geometries and cohesive energies presented hereafter are directly meaningful. On the contrary, the computed energy gaps are largely underestimated owing to the well known *band gap problem*. Hopefully, most of the physical interpretations proposed in this work are independent of the E_{gap} value, and the *band gap problem* should not affect the conclusions drawn from the DFT computed band-structure. Further comparison of the band structures of graphene and graphene nanoribbons computed within the DFT and DFT+MBPT frameworks are provided in Chapter 3.

2.3 DFT in terms of Numerical atomic orbitals: the *Siesta* method

Many software packages provide implementations of the density functional theory. They differ in their robustness, accuracy and requirements in terms of computational time and memory. Moreover, some are most dedicated to the description of molecules and finite systems while others are specifically designed for crystals. The system of interest, as well as the required accuracy have thus to be taken into account within the choice of a specific implementation.

In the perspective of transport calculations, the use of a localized basis set, such as atomic-like orbitals, presents some convenience. Indeed, the localized nature of the basis functions involve a direct correspondence between well defined spatial regions and subsets of basis functions. This allows to split the infinite matrices (i.e. the operators) into blocks related to the electrodes and blocks related to the device. Moreover, since typical two probes transport setups often requires to account for several hundreds of atoms, a large computational gain is associated with the use of efficient localized basis sets. In conclusion, an implementation relying on such basis set (the *Siesta* method [7]) has been chosen for this study. In addition, the accuracy of our calculations has been assessed by comparison with results produced within a robust PW scheme (the *Abinit* package [48]).

The *Siesta* method is a fully self-consistent DFT method which uses linear combinations of numerical atomic orbitals (NAOs). It allows to treat the exchange-correlation part of the energy both within LDA and GGA, and can handle various type of norm-conserving pseudo-potentials. In this section, some specificities of the *Siesta* method are presented.

2.3.1 The numerical atomic orbitals

The *Siesta* method relies on strictly confined basis orbitals. Beyond a user defined radius, the orbitals are zero. Moreover, the basis are atomic like, which means that they are products of radial functions times spherical harmonics. A typical basis set is composed of orbitals (commonly between 5 and 20 orbitals per atom) centered on the atomic positions $\{\mathbf{R}_i, i = 1, \dots, N\}$, N being the number of atom entering the calculation. I.e.

$$\phi_{lm,k}^i(\mathbf{r}) = \phi_{l,k}^i(|\mathbf{r} - \mathbf{R}_i|)Y_{lm}(\hat{\mathbf{r}}), \quad (2.21)$$

where i labels the atoms, and, l, m refer to the angular and magnetic moment of the spherical harmonic. In addition, the suffix k is used to

distinguish the different radial functions associated with the same spherical harmonic ($Y_{lm}(\hat{\mathbf{r}})$). Following the nomenclature of quantum chemistry the use of several basis function with the same angular dependence generates what is called "multiple- ζ " basis set.

The minimal (single- ζ) basis set¹ is made of the valence eigenfunctions of the pseudo-atom introduced within a spherical potential well of radius r_c . In other words, the radial functions are taken as the numerical eigenfunctions of,

$$\left(-\frac{1}{2r} \frac{d^2}{dr^2} r + \frac{l(l+1)}{2r^2} + V_l(r) + V_l^{well}(r) \right) \phi_l(r) = (\epsilon_l + \Delta\epsilon_l^{well}) \phi_l(r) , \quad (2.22)$$

with $\phi_l^i(r) = 0$ for $r \geq r_c$. Here $V_l(r)$ is the l -component of the pseudo-potential. $V_l^{well}(r)$ and $\Delta\epsilon_l^{well}$ are the confining potential and the associated energy shift of the pseudo-atomic eigenvalue. On one hand, small cutoff radii (r_c) lead to well confined orbitals and fast calculations. On the other hand, these induce large displacement of the atomic energy levels (large $\Delta\epsilon_l$) and limit the quality of the model. Therefore, a compromise has to be found. A good practice consists in increasing all the (r_c) together up to the desired accuracy. This can be done by fixing an smaller and smaller upper limit to the allowed energy shift ($\Delta\epsilon$).

Starting with the minimal basis set, more complete set may be constructed by adding radial and angular flexibility. The *Siesta* scheme for adding radial degree of freedom [49] is based on the "split-valence" technique which is standard in quantum chemistry [50]. The idea is to complement the original orbital ($\phi_l^{\zeta^1}(r)$) by a second orbital ($\phi_l^{\zeta^2}(r)$), that account only for the slow-decaying tail of $\phi_l^{\zeta^1}(r)$. Practically, the initial orbital $\phi_l^{\zeta^1}(r)$ is complemented by an orbital $\phi_l^2(r)$, that obeys,

$$\phi_l^2(r) = \begin{cases} r^l(a_l - b_l r^2) & r < r_l^s \\ \phi_l^{\zeta^1}(r) & r \geq r_l^s \end{cases} . \quad (2.23)$$

The parameters a_l and b_l are fixed by applying continuity conditions on $\phi_l^{\zeta^2}(r)$. An additional variable r_l^s appears here, which allows to determine the relative norm of $\phi_l^{\zeta^1}(r)$ and $\phi_l^{\zeta^2}(r)$. This parameter r_l^s should be variationally optimized.

To account for the distortion of the atomic valence orbitals in the crystal, it is often necessary to include in the basis set more angular degrees of freedom than just the atomic valence orbitals. Two schemes

¹Other schemes exist for the generation of a minimal basis set to be used by *Siesta* but this one is the standard procedure implemented in the *Siesta* package

allow to realize this extension. The simplest one is to include the pseudo-atomic eigenfunctions of higher momentum into the basis set. However, for most pseudo-potentials, these states of higher momentum are unbound. Therefore, the orbitals obtained by Eq. 2.22 present large spatial extensions and their shape are mainly determined by the confinement potential. Consequently, one understands that this procedure often presents poor efficiency. The other method consists in including the *polarization* orbitals obtained from the valence atomic orbitals of highest angular momentum. The polarization is done by applying a small electric field using first-order perturbation theory. This latter procedure appears to be more efficient than the previous one. As a rule of thumb, it has been checked that a variationally optimized basis set of double- ζ plus polarization orbitals quality produces accurate results for most systems.

It is worth noting that this standard, robust scheme may be easily improved [51, 52]. A first possibility is to replace the infinite spherical potential well used to confine the pseudo-atomic orbital by a soft confinement potential. The variational optimization of the soft confinement potential directly leads to improvement in the pseudo-atomic orbital definition. However, such scheme has not been used in this work.

2.3.2 The electronic Hamiltonian

Once the basis set has been determined, the matrix representation of the KS equation has to be computed in order to allow the self-consistent solution scheme to be processed using matrices algebra.

Within the pseudo-potential approximation, the KS equation may be written as,

$$\hat{H}^e = \hat{T}^e + \sum_i \hat{V}_i^{pseudo}(\mathbf{r}) + \hat{V}^{Hart} + \hat{V}^{xc}(\mathbf{r}) , \quad (2.24)$$

where $\hat{V}_i^{pseudo}(\mathbf{r})$ is the pseudo-potential centered on the i^{th} atomic position, and $\hat{V}^{Hart}$ is the Hartree potential. In *Siesta*, the pseudo-potentials are read in their general semi-local form and transformed following the usual prescription of Kleinman and Bylander [53]. Explicitly, it means that the pseudo-potentials are first considered in the form,

$$\hat{V}^{pseudo}(\mathbf{r}) = |Y_{l,m}\rangle V_l(\mathbf{r}) \langle Y_{l,m}| , \quad (2.25)$$

where the $V_l(\mathbf{r})$ s are the local radial potentials accounting for the pseudo-potential approximation. Then, these are expressed as the sum of a fully local term and a non-local potential. The KB non-local formulation decomposes the pseudo-potential in terms of the pseudo-atomic eigenstates

(ϕ_{lmn}) of the semi-local potential. I.e.

$$\hat{V}^{pseudo}(\mathbf{r}) = V_{local}(\mathbf{r}) + \sum_{l,m} \sum_{n=1, N_{kb}} \frac{|\Delta V_l \phi_{lmn}\rangle \langle \phi_{lmn} \Delta V_l|}{\langle \phi_{lmn} | \Delta V_l | \phi_{lmn} \rangle}, \quad (2.26)$$

where $\Delta V_l = V_l(\mathbf{r}) - V_{local}(\mathbf{r})$, and $|\Delta V_l \phi_{lmn}\rangle$ are called the Kleinman-Bylander projectors. Since the pseudo-potentials have to reproduce exactly the ionic potential out of the core region, these projectors are atomic-like functions strictly localized within a sphere of radius r_{core} . Their similarity to the numerical atomic basis functions makes their matrix elements easy to treat as two-center integrals. The local part is then constructed as a positive charge distribution whose integral give the ion charge. Since this part is represented on a real-space grid, its arbitrary definition is used in order to insure its smoothness and limit the size of the grid use for its representation.

With these developments, the electronic Hamiltonian may be expressed as,

$$\hat{H}^e = \hat{T}^e + \sum_i \hat{V}_i^{local}(\mathbf{r}) + \sum_i \hat{V}_i^{KB} + \hat{V}^{Hart} + \hat{V}^{xc}(\mathbf{r}), \quad (2.27)$$

where $\sum_i \hat{V}_i^{local}$ accounts for the local components of the pseudo-potentials in their KB form, and $\sum_i \hat{V}_i^{KB}$ is the non-local part due to the KB projectors. To take full benefit from the localized nature of the basis functions, an additional transformation may be performed in order to eliminate the long range interactions associated with the $\hat{V}_i^{local}$ and allow the expression of $\hat{H}^e$ in a sparse matrix form. To reach this goal, the local potentials $\hat{V}_i^{local}$ are screened by the atomic potentials ($\hat{V}_i^{atom}$) associated with the atomic density ρ_i^{atom} . This latter is easily obtained by the appropriate population of the pseudo-atomic orbitals (the basis functions). Since, by definition, these pseudo-atomic orbitals are confined within an spherical volume, the screened neutral-atom potential $\hat{V}_i^{NA}$,

$$\hat{V}_i^{NA} = \hat{V}_i^{local} + \hat{V}_i^{atom} \quad (2.28)$$

is also limited to this volume. Finally, in order to recover the original electronic Hamiltonian, the potentials ($\hat{V}_i^{atom}$) are subtracted from the Hartree term. Defining $\Delta\rho$ as the difference between the self-consistent electronic density and the atomic densities,

$$\Delta\rho = \rho^{scf} - \sum_i \rho_i^{atom}, \quad (2.29)$$

and ΔV^{Hart} as the electrostatic potential generated by $\Delta\rho$, the electronic Hamiltonian may then be expressed as,

$$\hat{H}^e = \hat{T}^e + \sum_i \hat{V}_i^{KB} + \sum_i \hat{V}_i^{NA}(\mathbf{r}) + \hat{\Delta}V^{Hart} + \hat{V}^{xc}(\mathbf{r}) . \quad (2.30)$$

This last expression is the one used in the *Siesta* package to compute the KS single-particle eigenstates. Owing to the expansion of the KS eigenstates in terms of atomic basis functions, the KS equation has the matrix form,

$$\underline{\underline{H}}.\underline{\underline{c}}_m = \epsilon_m.\underline{\underline{S}}.\underline{\underline{c}}_m , \quad (2.31)$$

with

$$\psi_m(\mathbf{r}) = \sum_{\mu=1, N_{basis}} \phi_{m\mu}(\mathbf{r})c_{\mu,m} , \quad (2.32)$$

which is nothing else than a generalized eigenvalue equation, solvable either by direct diagonalization or by iteration techniques.

In brief, we have described how the original Kohn-Sham equation is implemented within the *Siesta* package in order to take benefit from the localized nature of NAOs. This scheme has been widely used throughout this work, and has proved to be efficient for the geometry optimization and electronic density calculation of systems composed of up to seven hundred atoms.

2.4 The electric current

The purpose of this section is to survey the theory that underlies the coherent quantum transport in nanoscale devices. We have chosen to introduce the concepts progressively and to limit our description to the theoretical aspects that are directly related to the simulations performed in this work. As such, it may yet be mentioned that this section as well as the subsequent chapters of this manuscript will focus on the description of the coherent transport only. All the non-coherent effects (e.g. the electron-electron, and electron-phonon interactions) are kept for future investigation.

2.4.1 The semi-classical approach

The understanding of charge transport at the mesoscopic level has both taken benefit from the evolution of the semiconductor industry and driven major progresses in microelectronic device. As a consequence, the fundamental developments have been closely related to the technological

needs. In semiconductor, carriers can be reasonably described as semi-classical particles within the effective mass or the $\mathbf{k}\cdot\mathbf{p}$ approximations and semi-classical transport models have been used for long to give a first understanding of the observed transport properties. In this section, we briefly present the Boltzmann transport equation which is the theoretical grounding of most of semi-classical methods.

With great intuition, the Boltzmann kinetic theory and previous Liouville's work introduce a connection between the regime of dynamics and the one of thermodynamics in order to describe the properties of atomic gasses. Early in the years 1870, Boltzmann introduced the concept of single-particle probability distribution function (usually denoted as $f(\mathbf{r}, \mathbf{p}, t)$) and proposed the well known Boltzmann transport equation (BTE) to rule its time evolution,

$$\begin{aligned} \frac{df(\mathbf{r}, \mathbf{p}, t)}{dt} &= \frac{\partial f}{\partial t} + \nabla_{\mathbf{r}} f \cdot \frac{d\mathbf{r}}{dt} + \nabla_{\mathbf{p}} f \cdot \frac{d\mathbf{p}}{dt} \\ &= \frac{\partial f}{\partial t} + \nabla_{\mathbf{r}} f \cdot \frac{\mathbf{p}}{m} + \nabla_{\mathbf{p}} f \cdot \nabla_{\mathbf{r}} V(\mathbf{r}, t) \\ &= \left. \frac{\partial f}{\partial t} \right|_{coll}, \end{aligned} \quad (2.33)$$

where the quantity $\left. \frac{\partial f}{\partial t} \right|_{coll}$ describes the effect of all the collisions in the electron gas and accounts for the scattering processes. Note that this equation derives directly from the Liouville's theorem which rules the particles flux conservation in phase space. Within the $\mathbf{k}\cdot\mathbf{p}$ approximation and under the assumption of an electrostatic potential, Eq. 2.33 simplifies to,

$$\frac{\partial f}{\partial t} + \frac{1}{\hbar} \nabla_{\mathbf{r}} f \cdot \nabla_{\mathbf{k}} E(\mathbf{k}) + \frac{q}{\hbar} \nabla_{\mathbf{k}} f \cdot \mathbf{E}(\mathbf{r}, t) = \left. \frac{\partial f}{\partial t} \right|_{coll}. \quad (2.34)$$

Moreover, it can be shown that in the absence of external fields and upon proper definition of the collision term, the BTE equation involves the evolution of $f(\mathbf{r}, \mathbf{p}, t)$ towards to the Fermi-Dirac distribution function. As it is, to solve the integro-differential BTE is a highly difficult numerical task. In practice, the common usage is to approach the BTE solutions using limited expansion of the equation with respect to small change of the momentum. These expansions lead to various useful equations including the popular drift-diffusion equation which has generated many successes in the understanding of semiconductor devices.

However, the Boltzmann distribution function is a classical object (the $\hat{r}$ and $\hat{p}$ observables do not commute in quantum mechanic) and the application of BTE fails at the extremely short length-scales and very high frequencies where the wave nature of electrons gives rise to the uncertainty principles. E.g. quantum effects such as the quantization of

electronic charge or the phase coherent propagation of electrons, which give rise respectively to the Coulomb blockade effect and the quantization of the conductance, are not accessible within the Boltzmann kinetic theory.

2.4.2 Phase-coherent quantum transport: *The Landauer-Büttiker formalism*

The modeling of transport at extremely short length scales faces the limitations of the Boltzmann transport equation and a quantum mechanical description of the electrons is thus needed. The formally simplest approach to this problem is the well-known theory pioneered by Landauer [54, 55] and Büttiker [56, 57]. They proposed an elegant way to address the phase coherent quantum transport. In this approach, the current is viewed as "*a consequence of the injection of carriers at the contacts and their probability to reach the other end*" [54].

The quantum of conductance :

We start by considering the simple and highly prototypical device made of a unique ballistic channel of length L (e.g. a region with constant or periodic potential and no scattering) attached to two large contacts assumed to be at thermal equilibrium and characterized by the Fermi distribution functions f_l and f_r . In this case, since the channel is purely ballistic, the probability of transmission is equal to one for all the electrons injected in the center part². The Hamiltonian of the system may be written as,

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{r}) \right] \Psi(\mathbf{r}) = E \Psi(\mathbf{r}) , \quad (2.35)$$

where $U(\mathbf{r})$ is the potential which realizes the electronic confinement in the x and y directions and is constant along the z -axis. The free propagating nature of electrons along the z -axis allows to write the wavefunctions as,

$$\Psi(\mathbf{r}) = \Psi_{nk}(\mathbf{r}) = e^{ikz} \cdot \chi_n(x, y) \quad \text{with} \quad E = E_n(k) = \frac{\hbar^2 k^2}{2m} + \epsilon_n \quad (2.36)$$

where ϵ_n is the quantized energy associated to the eigenmodes $\chi_n(x, y)$ of the confining potential. Finally, the group velocity of an electron in a

²Experimentally, this prototypical situation can be approached by the realization of a very tight constriction in a 2D electron gas

specific mode is given by,

$$v_n^\pm(E) = \pm \frac{1}{\hbar} \left| \frac{dE_n(k)}{dk} \right|_{E_n(k)=E}, \quad (2.37)$$

where the $\pm$ suffix is added in order to distinguish the right and left propagating modes, whose group velocities fulfill $v_n^+(E) = -v_n^-(E)$.

We assume further that the contacts are perfect absorbers, which means that any electrons coming from the ballistic region can enter the contact with a negligible probability of reflection³. The two contacts inject flux of electrons in the device; some are reflected at the interface between the contact and the ballistic region, the others are transmitted and go on, without scattering, through the ballistic region to the other contact. Since there is no back-scattering inside the channel and the contacts are reflection-less, the right/left propagating modes of the ballistic region may be thought as being populated only by propagating states incident from the left/right contacts. These latter are characterized by the f_l/f_r distribution functions.

Since an electronic density ($n_{km} = \frac{1}{L}$) is associated to each state in the ballistic region, the current $I^\pm = env^\pm$ incident from the left/right contacts may be expressed as

$$\begin{aligned} I^\pm &= 2e \sum_{k,m} n_{km} \cdot v_{km}^\pm \cdot f^{l/r}(E_m(k)) \\ &= \pm \frac{2e}{L\hbar} \sum_{k,m} \left| \frac{dE_m(k)}{dk} \right| \cdot f^{l/r}(E_m(k)) \\ &= \pm \frac{2e}{h} \sum_m \int_{-\infty}^{\infty} dk \left| \frac{dE_m(k)}{dk} \right| \cdot f^{l/r}(E_m(k)) \\ &= \pm \frac{2e}{h} \sum_m \int_{-\infty}^{\infty} dE f^{l/r}(E) \\ &= \pm \frac{2e}{h} \int_{-\infty}^{\infty} dE M(E) f^{l/r}(E). \end{aligned} \quad (2.38)$$

where the factor 2 accounts for the spin degeneracy and the function $M(E)$ corresponds to the counting of the $\chi_n(x, y)$ eigenmodes available at the incident energy E .

At the equilibrium, the two contacts present the same distribution functions and the I^+ and I^- currents cancel each other. On the contrary,

³While apparently very crude, both experience and numerical simulations show that this approximation is in agreement with the reality as long as the energy of the escaping electron is not too close to the bottom of the energy band of the contact

if the two contacts are maintained at two different electro-chemical potentials (μ_l and μ_r), a net electric current is expected to appear through the ballistic channel. It is given by the difference between I^+ and I^- . At $T = 0\text{K}$, the Fermi-Dirac distribution function is a step function, and the current expression becomes,

$$I = \frac{2e}{h} \left[\int_{-\infty}^{\mu_l} M(E) dE - \int_{-\infty}^{\mu_r} M(E) dE \right] = \frac{2e}{h} \int_{\mu_r}^{\mu_l} M(E) dE . \quad (2.39)$$

In the case of one single $\chi_n(x, y)$ in the energy range defined by the Fermi distribution functions $[\mu_r, \mu_l]$, the current expression can be further reduced to,

$$I = \frac{2e^2}{h} \cdot \frac{(\mu_l - \mu_r)}{e} = \frac{2e^2}{h} \cdot V_{bias} , \quad (2.40)$$

where V_{bias} is the voltage drop between the left and right electrodes. This development highlight the existence of a conductance $G_0 = (\frac{2e^2}{h}) = 12.9 [k\Omega]$, known as the quantum of conductance, associated with every ballistic channel connected to reflection-less contacts. This quantum of conductance has been measured early in the 1960^s [58]. The experiment has used quantum point contacts to create a constriction much shorter than the electron mean free path between two wide metallic contacts. Note that the appellation quantum of conductance does not mean that all the measured conductances have to be integer multiples of G_0 . Indeed, this is no more the case in the presence of scattering centers or at finite temperature.

A general approach of the scattering :

The simple approach presented in the last section can be generalized in order to tackle the coherent electronic transport in nanodevices. The system we would like to describe is represented in Fig. 2.41, where it has been conveniently divided into three parts: (i) the left and (ii) right leads that are assumed to be made of perfect, defect-free crystalline materials, and (iii) a central region that can be any kind of set of atoms. This region, which potentially corresponds to the active part of the device, could thus be a single atom, a molecule, a section of carbon nanotubes or even a bulk slab. Besides, the central part and the leads may either have the same cross-section dimensionality (e.g. a two-dimensional slab of magnetic material between two non-magnetic semi-infinite leads) or not (e.g. a single molecule stretched between two massive gold electrodes). However, we will assume hereafter that an account of the system dimensionalities can be achieved by recasting the problem into an equivalent

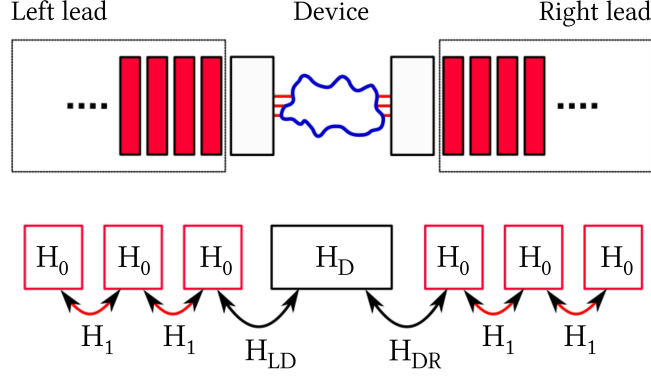


Figure 2.2: Schematic representation of the two-terminal transport setup. [Top panel] The device is contacted to two semi-infinite bulk electrodes assumed to be at thermal equilibrium. [Bottom panel] Block-decomposition of the Hamiltonian into sub-matrices associated with the central region and the principal layers of the semi-infinite leads. H_D contains all the interactions inside the central region. H_{LD} and H_{DR} describe the coupling between the central region and the leads. H_0 accounts for all the interactions inside the principal layers (PLs) of the leads. H_1 describes the coupling between nearest-neighbors PLs.

one which presents a translational symmetry along the directions perpendicular to the transport axis. In this way, the Bloch theorem holds along the transverse plane and the original transport problem can be conveniently divided into a set of independent problems associated each with one transverse k -point.

In order to facilitate the following discussions, it is convenient to describe the system by means of *principal layers*. A principal layer (PL) is the smallest set of atoms that represents a unit cell of the semi-infinite crystal forming the leads and which interacts only with the nearest-neighbors PLs. Therefore, owing to the decomposition onto a set of localized basis functions, the Hamiltonian of the system under consider-

ation can be written as,

$$\mathcal{H} = \hat{\phi}_k^\dagger \begin{pmatrix} \dots & \dots & \dots & \dots & & & \\ H_{-1} & H_0 & H_1 & 0 & \dots & & \\ 0 & H_{-1} & H_0 & H_{LD} & 0 & \dots & \\ \dots & 0 & H_{DL} & H_D & H_{DR} & 0 & \dots \\ & \dots & 0 & H_{RD} & H_0 & H_1 & 0 \\ & & \dots & 0 & H_{-1} & H_0 & H_1 \\ & & & \dots & \dots & \dots & \dots \end{pmatrix} \hat{\phi}_k. \quad (2.41)$$

Here, H_0 is the $[n \times n]$ matrix that describes all the interactions within the principal layers. Similarly (H_D) is the $[m \times m]$ matrix describing the interactions within the central region. Here, n and m are the total number of basis set localized within a principal layer and the central region, respectively. Finally, the interactions between nearest-neighboring PLs are contained in the $[n \times n]$ H_1 matrix, and the interactions between the central part and the left (right) lead is described in the $[n \times m]$ ($[m \times n]$) H_{LD} (H_{DR}) matrix. Besides, if the system preserves the time-reversal symmetry, $H_{-1} = H_1^\dagger$, $H_{DL} = H_{LD}^\dagger$ and $H_{DR} = H_{RD}^\dagger$. It is worth mentioning that in the case of non-orthogonal localized orbitals, the overlap matrix (S) adopts the same form as the Hamiltonian (H).

Open boundary conditions and scattering states :

With this notation in terms of PLs, the time-independent Schrödinger equation of the isolated contact $[H|\psi\rangle = E S|\psi\rangle]$ will assume the form,

$$K_{-1} C_{\alpha-1} + K_0 C_\alpha + K_1 C_{\alpha+1} = 0, \quad (2.42)$$

where C_m is a vector of length n , and α label the successive PLs. Here, we have introduced the K matrices defined as,

$$\begin{aligned} K_0 &= H_0 - ES_0 \\ K_1 &= H_1 - ES_1 \\ K_{-1} &= H_{-1} - ES_{-1}. \end{aligned} \quad (2.43)$$

Note that, for some application, it is also common to write the Eq. 2.42 in the so-called transfer-matrix form [59, 60, 61, 62, 63],

$$\begin{pmatrix} -(K_1)^{-1} \cdot K_0 & -(K_1)^{-1} \cdot K_{-1} \\ 1 & 0 \end{pmatrix} \cdot \begin{pmatrix} C_\alpha \\ C_{\alpha+1} \end{pmatrix} = \mathcal{T} \cdot \begin{pmatrix} C_\alpha \\ C_{\alpha+1} \end{pmatrix} = \begin{pmatrix} C_{\alpha-1} \\ C_\alpha \end{pmatrix}, \quad (2.44)$$

where T is called the transfer-matrix.

Since deep inside the contacts, the leads are periodic along the transport direction, the electronic scattering states of the system have to obey the asymptotic behavior of propagating Bloch states. The Schrödinger Eq. 2.42 inside the contact can therefore be re-expressed into the following eigenvalue problem:

$$\begin{pmatrix} -(K_1)^{-1} \cdot K_0 & -(K_1)^{-1} \cdot K_{-1} \\ 1 & 0 \end{pmatrix} \cdot \begin{pmatrix} C_\alpha \\ C_{\alpha+1} \end{pmatrix} = e^{ikd} \begin{pmatrix} C_\alpha \\ C_{\alpha+1} \end{pmatrix}, \quad (2.45)$$

where d is the length of the PLs along the direction of transport. Solving this equation for both leads, yields two sets of $2n$ complex waves-vectors ($k_j^{L/R} : j = 1, \dots, 2m$) and their associated bulk complex state-vectors ($\phi_{k_j}^{L/R}$). These propagating (and decaying) Bloch states are the basis functions on which the transport problem is developed. By convenience, we order the wave-vectors such that the first m states are incoming to the scattering region, and the other m outgoing from the scattering region. Finally, the open boundary conditions of our original transport problem can be described in terms of the bulk states $\phi_j^{L/R}$ by imposing the proper asymptotic form on the stationary scattering states of H :

$$\Psi_{k_j}^L(\mathbf{r}) = \begin{cases} \phi_{k_j}^L + \sum_{i=m+1}^{2m} r_{ij} \phi_{k_i}^L & r_z \in L \\ \sum_{i=m+1}^{2m} t_{ij} \phi_{k_i}^R & r_z \in R \end{cases} \quad (2.46)$$

where the transmission (t_{ij}) and reflection (r_{ij}) amplitudes have been introduced. Here, $\Psi_{k_j}^L$ are the scattering states that are incident from the left contact. These are characterized by k_j in an asymptotic sense, i.e. these originate from the bulk states ϕ_{k_j} . A similar expression is easily derived for the scattering states $\Psi_{k_j}^R$ that are incident from the right contact. The transmission and reflection amplitudes found here, are the usual quantities of the scattering theory and can be computed, for example, by use of the transfer matrix techniques [59, 60, 61, 62].

Computing the current :

In the presence of coherent processes only, a good strategy for the calculation of the expectation value of every operators is to rely on the equilibrium distribution functions $f^{l/r}$ to populate the $\Psi^{L/R}$ stationary scattering states. Following this prescription for the population of the electronic states, the out-of-equilibrium density operator of the system

is constructed as,

$$\hat{\rho} = \sum_{j=1}^m \left[|\Psi_{k_j}^L\rangle \langle \Psi_{k_j}^L| \cdot f^L(E) + |\Psi_{k_j}^R\rangle \langle \Psi_{k_j}^R| \cdot f^R(E) \right], \quad (2.47)$$

where the $f^{L/R}$ (which are the Fermi electronic distribution of the left and right leads) have been used to fix the electronic population of the $\Psi^{L/R}$ scattering states. The expectation value of the current density operators in the absence of a magnetic field $\hat{\mathbf{J}}(\mathbf{r})$,

$$\hat{\mathbf{J}}(\mathbf{r})\Psi(\mathbf{r}) = \frac{e\hbar}{2im} [\Psi^*(\mathbf{r})\nabla_{\mathbf{r}}\Psi(\mathbf{r}) - \Psi(\mathbf{r})\nabla_{\mathbf{r}}\Psi^*(\mathbf{r})], \quad (2.48)$$

may then be calculated as,

$$\mathbf{J}(\mathbf{r}) = Tr [\hat{\rho} \cdot \hat{\mathbf{J}}]. \quad (2.49)$$

Using the Landauer-Büttiker expression of the non-equilibrium density operator, the current density can be expressed as,

$$\mathbf{J}(\mathbf{r}) = \frac{e\hbar}{2im} \left[\sum_j W_{k_j}^L(\mathbf{r}) \cdot f^L + \sum_j W_{k_j}^R(\mathbf{r}) \cdot f^R \right], \quad (2.50)$$

with

$$W_{k_j}^{L/R}(\mathbf{r}) = \left(\Psi_{k_j}^{L/R}(\mathbf{r}) \right)^* \nabla_{\mathbf{r}} \Psi(\mathbf{r})_{k_j}^{L/R} - \Psi(\mathbf{r})_{k_j}^{L/R} \left(\nabla_{\mathbf{r}} \Psi_{k_j}^{L/R}(\mathbf{r}) \right)^*. \quad (2.51)$$

All the ingredients are now gathered to compute the total current through the device. It is given by the integration of the current density over the cross section of the device at a given position along the z -axis,

$$I(z) = \int_{S_{\perp,z}} dS_{\perp,z} \mathbf{J}(\mathbf{r}). \quad (2.52)$$

Since the current has to be conserved in the transport direction, the integration value can be performed at every cross section ($S_{\perp,z}$) along the z -axis. Of course, the easiest choice is to perform the integration in the leads where the asymptotic behavior of the scattering states is known. After some algebra, and using the orthogonality relations of the Bloch states in the leads, one can obtain the well-known Landauer-Büttiker formula for the total current through the device in terms of the transmission amplitudes,

$$I = \frac{2e}{h} \int dE T(E) [f^L(E) - f^R(E)] \quad (2.53)$$

where the transmission function of the system $T(E)$ has been defined as,

$$T(E) = \sum_{i=1}^m \sum_{j=m+1}^{2m} |t_{i,j}(E)|^2 \frac{|(v_j^R(E))|}{|(v_i^L(E))|} . \quad (2.54)$$

Here, v_i and v_j are the group velocity of the incident ($\phi_{k_i}^L$) and transmitted ($\phi_{k_j}^R$) bulk states, respectively. The transmission function defined in Eq. 2.54 is a convenient quantity to tackle the transport problem. Indeed, in the Landauer-Büttiker approach the steady-state electric current of a given system is completely determined by the knowledge of its transmission function since the electronic distribution in the leads are assumed to be the Fermi equilibrium distribution.

Note, that, up to now, the scattering potential for a given bias between the contacts has been assumed to be known, though no way has been provided to compute it. This is however, not a limitation of the Landauer-Büttiker theory. Indeed, prescriptions have been assumed for the calculation of the non-equilibrium electronic density in terms of the scattering states which are themselves of easy access. So that, the DFT self-consistent solution scheme could be applied in order to allow the calculation of the scattering potential.

2.4.3 Phase-coherent quantum transport : *The Green's Function Formalism*

Another approach to solve the quantum transport problem is the Green's function formalism [64, 65, 66, 67]. It is worth mentioning that the use of Green's functions, though convenient, is not needed to tackle the problem of the coherent electronic transport in nanoscale device. Indeed, the Green's function (GF) technique leads to the same expression as the Landauer-Büttiker formalism for the net coherent current (Eq. 2.53). But the real power of the Green's functions appears when incoherent processes such as the electron-electron, or the electron-phonon couplings are taken into account. However, we do not address these subjects in this work, so that we limit ourselves to the description of the equilibrium GF formalism.

The Green's function :

Hereafter, we will consider again the particular transport setup depicted in Fig. 2.2. Two semi-infinite, defect-free, electrodes are coupled to a central region, where all the scattering processes take place. We are

thus dealing with an infinite hermitian problem whose solutions are not accessible by application of the Bloch theorem owing to the central region that breaks the symmetry. However, the problem can be solved by computing the retarded Green's function of the single-particle Schrödinger equation. Roughly speaking, this function gives the response at any point of the system due to a particular excitation at any other. The retarded Green's function of the full system ($\mathcal{G}^R(E)$) is defined as follows,

$$[(E + i\delta) - \mathcal{H}] \mathcal{G}^r(E) = \mathcal{I} \quad (2.55)$$

where $\mathcal{I}$ is an infinite-dimensional identity matrix, $(E + i\delta)$ is the energy complemented with an infinitesimal imaginary part in order to insure the causality. $\mathcal{H}$ and $\mathcal{S}$ are the infinite dimensional matrix Hamiltonian and overlap matrix.

Another useful expression of the retarded GF is in terms of the complete, orthonormal, set of eigenfunctions $\{|\Psi_n(E)\rangle\}$ of the defining operator,

$$\mathcal{H}|\Psi_n(E)\rangle = E|\Psi_n(E)\rangle, \quad (2.56)$$

$$\mathcal{G}^r(E) = [(E + i\delta) - \mathcal{H}]^{-1} = \int dE' \sum_n \frac{|\Psi_n(E')\rangle \langle \Psi_n(E')|}{E - E' + i\delta}. \quad (2.57)$$

In addition to the retarded Green's function ($\mathcal{G}^r$), it is convenient for many situations to introduce the system spectral function ($\mathcal{A}$), defined as

$$\mathcal{A}(E) = i \left(\mathcal{G}(E) - \mathcal{G}^\dagger(E) \right) = 2\pi \sum_n |\Psi_n(E)\rangle \langle \Psi_n(E)|. \quad (2.58)$$

As shown from the last equality, the spectral function is a meaningful quantity. Its trace represent the density of states and within a spatial representation, its diagonal elements correspond to the local density of states (LDOS).

Finally, it is interesting to mention some properties of the GF associated with the perturbation theory, since it allows to set up a direct link between the retarded GF and the scattering theory. First, we note that the retarded GF gives the response of the system to a constant perturbation (f) of the Schrödinger equation. As an example, the solution of the equation,

$$(\mathcal{H} - (E + \delta i)) |\psi(E)\rangle = |f\rangle \quad (2.59)$$

is given by

$$|\psi(E)\rangle = -\mathcal{G}^r(E) |f\rangle. \quad (2.60)$$

where $\mathcal{G}^r = [\mathcal{H} - (E + \delta i)]^{-1}$. This also applies for a perturbation of the potential (V). Assuming, that the solutions of the unperturbed Schrödinger equation are known, ($\mathcal{H}^0 |\Psi_n^0\rangle = E_n |\Psi_n^0\rangle$), the solutions of the perturbed Schrödinger equation,

$$(\mathcal{H}^0 + V - (E + \delta i)) |\psi(\mathbf{r})\rangle = 0 , \quad (2.61)$$

are given by,

$$|\psi(E)\rangle = |\psi^0(E)\rangle + G^0(E) V |\psi(E)\rangle ; \quad (2.62)$$

or equivalently,

$$|\psi(E)\rangle = |\psi^0(E)\rangle + G(E) V |\psi^0(E)\rangle ; \quad (2.63)$$

where the $G^0(E)$ and $G(E)$ functions are the retarded GFs of the unperturbed and perturbed system, respectively. It is instructive, to apply these relations, called the Lippmann-Schinger equations, to the scattering problem. Indeed, this allows to straightforwardly connect the bulk propagating states of the isolated leads ($|\phi_{k_j}^L\rangle$), to the stationary scattering states of the complete system ($|\Psi_{k_j}^L\rangle$). Assuming that the perturbation of the system (V) corresponds to the coupling between the leads and the central region (i.e $V = H_{LD} + H_{DL} + H_{DR} + H_{RD}$, using the notation introduced in Eq. 2.41), the Lippmann-Schwinger Eq. 2.63 gives

$$|\Psi_{k_j}^L\rangle = |\phi_{k_j}^L\rangle + G(E_{k_j}) V |\phi_{k_j}^L\rangle . \quad (2.64)$$

Open boundary conditions and leads self-energies :

We now apply the Green's function formalism to the transport problem illustrated in Fig. 2.2. Similarly to what has been done in Section 2.4.2, we rely on a description in terms of localized basis set, and we assume a virtual partition of the left and right leads in PLs. Finally, we are interested in the retarded Green's function of the system. Though the matrix that has to be inverted is infinite-dimensional, the Green's function formalism allows to account naturally for the open boundary conditions that rule the asymptotic behavior of the transport problem. In what follows, we will see that the Green's function of the central part can be easily calculated separately, without calculating the whole Green's function. From the definition of the retarded Green's function,

we obtain,

$$\begin{pmatrix} \epsilon^+ \mathcal{S}_L - \mathcal{H}_L & \epsilon^+ \mathcal{S}_{LD} - \mathcal{H}_{LD} & 0 \\ \epsilon^+ \mathcal{S}_{DL} - \mathcal{H}_{DL} & \epsilon^+ S_D - H_D & \epsilon^+ \mathcal{S}_{DR} - \mathcal{H}_{DR} \\ 0 & \epsilon^+ \mathcal{S}_{RD} - \mathcal{H}_{RD} & \epsilon^+ \mathcal{S}_R - \mathcal{H}_R \end{pmatrix} \quad (2.65)$$

$$\cdot \begin{pmatrix} \mathcal{G}_L & \mathcal{G}_{LD} & \mathcal{G}_{LR} \\ \mathcal{G}_{DL} & G_D & \mathcal{G}_{DR} \\ \mathcal{G}_{RL} & \mathcal{G}_{RD} & \mathcal{G}_R \end{pmatrix} = \mathcal{I} \quad (2.66)$$

with,

$$\epsilon^+ = (E + \delta i) \quad (2.67)$$

where the Hamiltonian, overlap and Green's matrices have been divided into sub-matrices corresponding to the left/right leads and the central region. The $\mathcal{H}_{L/R}$ sub-matrices account for all the interactions inside the left and right leads. These blocks are thus infinite-dimensional $[\infty * \infty]$, as well as $\mathcal{S}_{L/R}$ and $\mathcal{G}_{L/R}$. On the contrary, the sub-matrices in which we are interested (i.e. S_D , H_D and G_D) have the dimension $[m * m]$, where m is the number of degrees of freedom (i.e orbitals) in the central region. Finally, the sub-matrices $\mathcal{H}_{LD}$, and $\mathcal{H}_{DR}$, that represent the interactions between the leads and the central region, have the dimension $[\infty * m]$ and $[m * \infty]$, respectively. However, these sub-matrices ($\mathcal{H}_{LD}$ and $\mathcal{H}_{DR}$) are actually zero with the exception of the bottom/top n lines that represent the coupling between the last PL and the central region (i.e. the H_{LD} and H_{DR} matrices introduced in Eq. 2.41). Here, n is the number of degrees of freedom (i.e orbitals) in the PL.

Selecting the three block-equations that involve G_D , the following system of equations is readily derived,

$$(\epsilon^+ \mathcal{S}_L - \mathcal{H}_L) \cdot \mathcal{G}_{LD} + (\mathcal{S}_{LD} - \mathcal{H}_{LD}) \cdot G_D = 0 \quad (2.68)$$

$$(\mathcal{S}_{DL} - \mathcal{H}_{DL}) \cdot \mathcal{G}_{LD} + (\epsilon^+ S_D - H_D) \cdot G_D + (\mathcal{S}_{DR} - \mathcal{H}_{DR}) \cdot \mathcal{G}_{RD} = 0 \quad (2.69)$$

$$(\mathcal{S}_{RD} - \mathcal{H}_{RD}) \cdot G_D + (\mathcal{S}_R - \mathcal{H}_R) \cdot \mathcal{G}_{RD} = 0 \quad (2.70)$$

Substituting the Eqs. 2.68 and 2.69 into Eq. 2.70, we obtain an explicit expression for the sub-matrix G_D which is the part we are actually interested in. The matrix (G_D) has the form,

$$G_D^r(E) = \left[\epsilon^+ S_D - H_D^{eff}(E) \right]^{-1} \quad (2.71)$$

with,

$$H_D^{eff}(E) = [H_D - \Sigma_L^r(E) - \Sigma_R^r(E)] \quad (2.72)$$

where the concept of the retarded self-energies associated with the left and right leads has been introduced,

$$\begin{aligned} \Sigma_L^r(E) &= [\epsilon^+ \mathcal{S}_{DL} - \mathcal{H}_{DL}] \cdot \mathcal{G}_L^{0r} \cdot [\epsilon^+ \mathcal{S}_{LD} - \mathcal{H}_{LD}] \\ \Sigma_R^r(E) &= [\epsilon^+ \mathcal{S}_{DR} - \mathcal{H}_{DR}] \cdot \mathcal{G}_R^{0r} \cdot [\epsilon^+ \mathcal{S}_{RD} - \mathcal{H}_{RD}] . \end{aligned} \quad (2.73)$$

Here, $\mathcal{G}_L^{0r}$ and $\mathcal{G}_R^{0r}$ are the retarded Green's function associated with the isolated leads,

$$\mathcal{G}_{L/R}^{0r} = [\epsilon^+ \mathcal{S}_{L/R} - \mathcal{H}_{L/R}]^{-1} . \quad (2.74)$$

Though it might seem that we have not gained much since this last equation still contains infinite matrices, this is not exact. Indeed, the self-energy can be computed easily by exploiting the fact that the interaction between the central region and the leads only involves a finite number of atoms close to the interface. Besides, owing to the sparsity of $\{\mathcal{H}_{DL}, \mathcal{S}_{LD}, \mathcal{H}_{DR}, \mathcal{S}_{RD}\}$, only the n lines of $\mathcal{G}_{L/R}^{0r}$ that correspond to the surface PL are actually needed in Eq. 2.73. This sub-matrix, that we call $G_{L/R}^{0r}$ has the finite dimension $[n * n]$ and can be computed either semi-analytically or by recursion methods. This point is further detailed in Section 2.5.1.

To conclude, we have seen that the Green's function expressed in Eq. 2.71 is defined within the central region only while the effect of the contact have been mapped into complex self-energies. We note that the imaginary part of the self-energies accounts from the finite lifetime of the electronic states inside the central region. Indeed, due to the interactions with the contact, eigenstates can leak out from the central region.

Spectral function and density matrix :

In order to set-up a complete formalism, an explicit expression for the out-of-equilibrium density matrix in the central region is needed. In the absence of inelastic processes, such an expression can be derived in several ways. A possible route is to properly translate the expression proposed in Section 2.4.2, in terms of the retarded Green's function. This can be done owing to the connection drawn by the Lippmann-Schwinger equations. Another appealing way, is to rely on the general expression derived within the Non-Equilibrium Green's Function (NEGF) formalism [65]. Interestingly, both approaches produce exactly the same result. Here, we deduce the form of the out-of-equilibrium density matrix from the physical meaning of the spectral function [68].

The spectral function is by definition closely related to the density-of-states (see Eq. 2.58). Using the projector operator P_D , that projects onto the central region, we define the spectral function of the central region as $A_D = P_D \mathcal{A} P_D$. At equilibrium ($\mu_L = \mu_R = \mu_D$) the complete system is characterized by a single Fermi-Dirac distribution function and the electronic density can be expressed as,

$$\rho = \frac{1}{2\pi} \int dE A_D f(E - \mu_D) . \quad (2.75)$$

This expression is not anymore valid when a bias is applied between the electrodes ($\mu_L - \mu_R \neq 0$). However, in case of coherent propagation of carriers, one can use equilibrium distribution functions in order to treat the out-of-equilibrium situation. As presented previously in Section 2.4.2, each scattering eigenstates can be considered in equilibrium with one of the two reservoir characterized by μ_L and μ_R . Here below, we show that A_D can be decomposed in two components A_L and A_R , that are associated with the scattering states incoming from the left and right leads, respectively. Upon the assumption of coherent transport only, an expression for the out-of-equilibrium density matrix can thus be derived.

The spectral function of the device can be decomposed in two parts A_L and A_R ,

$$\begin{aligned} A_D &= i(G_D - G_D^\dagger) = i G_D (G_D^{\dagger-1} - G_D^{-1}) G_D^\dagger \\ &= G_D \Gamma_L G_D^\dagger + G_D \Gamma_R G_D^\dagger \\ &= A_L + A_R . \end{aligned} \quad (2.76)$$

Here, the broadening $\Gamma_{L/R} = i \left[\Sigma_{L/R}^r - \Sigma_{L/R}^{r\dagger} \right]$ have been introduced. These account for the non-hermicity of the self-energy operators. At this point, it is worth mentioning that we have neglected the infinitesimal imaginary part introduced in Eq. 2.55, in order to insure the causality of the retarded Green's function. As a consequence, the second equality in Eq. 2.76 is not true when there are electronic states strictly localized in the device region that do not couple with the electrodes. In such case, $\Gamma_L = \Gamma_R = 0$, and the information about the localized states is neither contained in A_L , nor in A_R .

Using the Lippmann-Schwinger equation (2.63), one can show that the two parts of the device spectral function are built up from states originating from the left and right electrodes respectively. Indeed, the

part A_L can be expressed as,

$$\begin{aligned}
A_L &= 2\pi \sum_j P_D |\Psi_j^L\rangle \langle \Psi_j^L| P_D \\
&= 2\pi \sum_j P_D (|\phi_j^L\rangle + G V_L |\phi_j^L\rangle) \left(\langle \phi_j^L| + \langle \phi_j^L| V_L^\dagger G^\dagger \right) P_D \\
&= G_D \Gamma_L G_D^\dagger.
\end{aligned} \tag{2.77}$$

Since the same applies for the part A_R , we have shown that, in the absence of inelastic processes, the out-of-equilibrium density matrix of the central region can be expressed as,

$$\rho = \frac{1}{2\pi} \int dE [A_L f(E - \mu_L) - A_R f(E - \mu_R)] , \tag{2.78}$$

where the scattering states incoming from the left (right) are populated according to the equilibrium Fermi distribution of the left (right) electrode.

In summary, we have shown that an expression for the out-of-equilibrium density matrix can be derived from the decomposition of the spectral function into its component originating from the left and right electrode. However, this derivation do not account for the presence of localized states in the scattering region. Since these states do not couple with the left or right lead, it is unclear how to populate these localized states whose eigenenergy (ϵ_{loc}) lies between the left and right Fermi levels (i.e. $\epsilon_{loc} \in [\mu_L, \mu_R]$). Though such situation is seldom encountered in practice, the treatment of low-energy localized states is an important issue that limits the generality of the method presented above. Intuitively, one minds that the occupancy of these states should be determined by the non-coherent scattering processes that insure a small coupling between the localized states and the leads. Such processes are not modelled within the coherent approach derived here, the treatment of localized states would therefore require additional information on their filling.

Computing the current :

At this point, a complete scheme has been built in terms of the Green's functions and the electric current I through the device can be computed. Indeed, once the density operator is defined, it is possible to evaluate the current operator. After some manipulations, one can derive the following expression for the electric current through the junction [69],

$$I = \frac{e}{h} \int dE \text{Tr} \left[\Gamma_L G_D^{r\dagger} \Gamma_R G_D^r \right] [f(E - \mu_L) - f(E - \mu_R)] . \tag{2.79}$$

Since the quantity $[\Gamma_L G_D^{r\dagger} \Gamma_R G_D^r]$ may be interpreted as a transmission matrix [54], the expression (2.79) is fully equivalent to the Landauer formula.

2.5 Computing the Green's functions: The *Smeagol* method

The Green's function formalism outlined here above has been recently implemented in several computational codes. Throughout this work, the transport calculations have been performed with the *Smeagol* [8] package based on the density functional theory code *Siesta* [7]. In this section, we briefly describe some aspects of this particular implementation.

2.5.1 Calculation of the contact self-energies

In Section 2.4.3, we have shown that the computation of the Green's function for the central region relies on the proper evaluation of the self-energies associates with the left and right electrodes. Since, these latter have to be computed for each transverse k -vectors, and at several energies, a stable and efficient computational algorithm is crucial for the code performance.

The main computational cost in calculating the contact self-energies is related to the evaluation of the retarded Green's function of the isolated leads. Within the *Smeagol* package, these are constructed following a semi-analytical [8, 63, 70] scheme that is briefly presented here after. Globally, the scheme is composed of three steps. First, the Bloch states of the infinite system are derived. Second, these are used in order to build the retarded Green's function corresponding to the infinite leads. Then, appropriate boundary conditions are applied in order for the Green's function to vanish at the free surface of the semi-infinite leads.

(a) Owing to the division of the leads in PLs, the Hamiltonian and the overlap matrices are arranged in the trigonal form described in Eq. 2.41. In this formulation, H_0 and S_0 account for all the interactions and overlap integrals inside one PLs. H_1 and S_1 are the off-diagonal blocks that correspond to the interactions and overlap integrals between the nearest-neighbors PLs. In order to simplify the notation, we also introduce the matrices $K_\alpha = H_\alpha - ES_\alpha$ with $(\alpha = 0, 1, -1)$. In the case of an infinite periodic lead, the Bloch theorem applies along the transport direction (z -axis) and the bulk electronic states can be mapped into Bloch states,

$$\Psi_z = e^{ikz} \phi_k, \quad (2.80)$$

where $z = n * d$ is an integer multiple of the PL length (d) and k is the wave-vector along the z -axis. A method for the calculation of the set ϕ_k has been proposed in Section 2.4.2. In brief, the Schrödinger equation can be re-expressed in the form,

$$\left[K_{-1} e^{-ikd} + K_0 + K_1 e^{ikd} \right] \phi_k = 0. \quad (2.81)$$

Besides, this equation can be conveniently mapped into an eigenvalue calculation with the aid of the transfer-matrix (see Ref. [63]),

$$\mathcal{T} = \begin{pmatrix} -(K_1)^{-1} \cdot K_0 & -(K_1)^{-1} K_{-1} \\ I & 0 \end{pmatrix}. \quad (2.82)$$

The eigenvalues of $\mathcal{T}$ are the $2n$ roots $e^{ik_l d}$ that defines the complex wave-vectors of the Bloch states at energy E . The upper part (i.e. the n first elements) of the $2n$ eigenvectors are the expansion components of the Bloch electronic functions over the localized basis functions. In order to simplify the following discussion, we assume that the eigenvectors are ordered such that the electronic states with indices ranging from 1 to n corresponds to Bloch waves propagating/decaying in the right direction. On the contrary, the indices ranging from $n+1$ to $2n$ are associated with Bloch waves propagating/decaying in the left direction. Finally, it is worth mentioning that the solution of the eigenvalue problem (Eq. 2.82) assumes that K_1 is invertible. Moreover, the stability of the algorithm requires that K_1 is not ill defined. Therefore, a regularization procedure of K_1 is highly desirable. Though this point is crucial for the accuracy and stability of the code (see Refs. [8, 63, 70]), we will not enter these details here and assume that the K_1 matrix has been properly modified in order to be neither singular nor ill-conditioned.

(b) In order to construct the retarded Green's function of the infinite leads, one notes that the Green's function ($G_{zz'}$) is a simple wave-function for all $z \leq z'$. Since it also has to be retarded, and continuous at $z = z'$, one may assume the following form,

$$G_{zz'} = \begin{cases} \sum_{l=1}^n \phi_{k_l} e^{ik_l(z-z')} \alpha_{k_l}, & z \geq z' \\ \sum_{l=n+1}^{2n} \phi_{k_l} e^{ik_l(z-z')} \alpha_{k_l}, & z \leq z' \end{cases} \quad (2.83)$$

where the α_{k_l} coefficients have to be determined. Folding these expressions into the Schrödinger Eq. 2.81, one can show that,

$$\alpha_{k_l} = \tilde{\phi}_{k_l}^\dagger V^{-1}, \quad (2.84)$$

with,

$$V = (H_1^\dagger - ES_1^\dagger) \left[\sum_{l=1}^n \phi_{k_l} e^{ik_l(z-z')} \tilde{\phi}_{k_l}^\dagger - \sum_{l=n+1}^{2n} \phi_{k_l} e^{ik_l(z-z')} \tilde{\phi}_{k_l}^\dagger \right], \quad (2.85)$$

where the set of $\tilde{\phi}_{k_l}^\dagger$ is made from the duals of ϕ_{k_l} (i.e. $\tilde{\phi}_{k_l}^\dagger \phi_{k_m} = \delta_{lm}$).

(c) Finally, the Green's function of the semi-infinite leads, can be obtained from the Green's function of the infinite leads by subtracting from $G_{zz'}$ a linear combination of eigenvectors that insure the annihilation of the Green's function at the free surface. Consider, for example, the left lead which extends from $z = -\infty$ to $z = z_0 - 1$. The subtraction of the term,

$$\Delta_z(z' - z_0) = \sum_{l=1}^n \sum_{h=n+1}^{2n} \left(\phi_{k_h} e^{ik_l(z-z_0)} \tilde{\phi}_{k_l}^\dagger \right) \cdot \left(\phi_{k_l} e^{ik_l(z_0-z')} \tilde{\phi}_{k_l}^\dagger \right) V^{-1} \quad (2.86)$$

from $G_{zz'}$ gives a new retarded Green's function which vanishes at the principal layer $z = z_0$, taken as the surface. In this way, the retarded Green's function of the semi-infinite leads have been computed and all the ingredients are gathered for the calculation of the self-energies. We finally note that, the derivation of the self-energies proposed here above, assumes that the entire leads are undisturbed by the central region. This means that the interfaces at which the surface Greens functions are computed, have to be sufficiently far away from the scattering region in order for the scattering potential to be zero into the leads. Upon this assumption, the leads self-energies have to be computed only once and remain valid throughout the self-consistent determination of the scattering potential.

2.5.2 The out-of-equilibrium density matrix

Before to summarize the self-consistent procedure used for the calculation of the out-of-equilibrium scattering potential, we briefly come back to the out-of-equilibrium density matrix,

$$\rho = \frac{1}{2\pi} \int_{-\infty}^{\infty} dE [f_L(E - \mu_L) A_L(E) + f_R(E - \mu_R) A_R(E)] \quad (2.87)$$

where $f(E)$ is the equilibrium Fermi electronic distribution, and $\mu_{L/R}$ are the chemical potentials inside the left and right leads, respectively. It is worth noting that the integration in Eq. 2.87 is not a trivial computational task since the integral is unbound and the spectral functions $A_{L/R}$

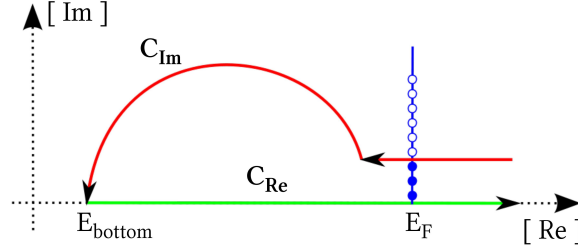


Figure 2.3: The closed contour ($C_{Im} + C_{Re}$) used to compute the equilibrium component of the electronic density matrix. Filled blue dots account for the poles of the Fermi distribution function enclosed in the complex integration part.

are not analytical. However, the computational cost of the integration can be significantly reduced by rewriting the integral (2.87) as the sum of two contributions, ρ_{equ} and ρ_{Δ} ,

$$\begin{aligned}
 \rho &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dE [f(E - \mu_L)A_L(E) + f(E - \mu_R)A_R(E)] \\
 &\quad + [f(E - \mu_L)A_R(E) - f(E - \mu_R)A_L(E)] \\
 &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dE A_D f_L(E - \mu_L) \\
 &\quad + \frac{1}{2\pi} \int_{-\infty}^{\infty} dE A_R(E) (f(E - \mu_R) - f(E - \mu_L)) \\
 &= \rho_{equ} + \rho_{\Delta} .
 \end{aligned} \tag{2.88}$$

The first term (ρ_{equ}) accounts for the "equilibrium" component of the electronic density. Indeed, it correspond to what should be obtained if both leads have the same chemical potential ($\mu_L = \mu_R$). All poles of the device spectral function (A_D) are lying on the real axis and the function is analytical elsewhere. Therefore, though unbound, the integration of A_D can be performed in the complex plane using contour integral techniques. The contour used in *Smeagol* is depicted in Fig. 2.3, where E_{bottom} is chosen below the deepest valence electronic state. For finite temperatures, the contour encloses some poles of the Fermi distribution function located at $\{z_{\alpha} = i(2\alpha + 1)\pi k_B T, \text{ with } \alpha = 1, \dots, n_{\alpha}\}$. The

residue theorem thus applies. Finally, the integral is computed as,

$$\begin{aligned} & \frac{1}{2\pi} \int_{-\infty}^{\infty} dE A_D(E) f_L(E - \mu_L) = \\ & - \int_{C_{up}} dz A_D(z) f_L(z - \mu_L) - 2\pi k_B T \sum_{\alpha=1}^{n_\alpha} A_D(z_\alpha) . \end{aligned} \quad (2.89)$$

The second term in Eq. 2.88 accounts for the corrections induced by the out-of-equilibrium conditions. The spectral functions $A_{L/R}$ are not analytical and the integration cannot be obtained using complex contours techniques. However, the integration is bounded by the two Fermi distribution functions and can be evaluated on a fine energy. Here, we remind that the formula (2.89) do not account for the contribution to the density of the electronic states that are localized within the scattering device and do not couple with the leads. In the presence of such states, Eq. 2.89 is not valid anymore and additional informations have to be supplied.

2.5.3 The self-consistent procedure

Finally, we describe the self-consistent procedure implemented in the *Smeagol* package aiming at the calculation of the out-of-equilibrium electronic density and electric current.

The main feature of the Green's functions DFT-based schemes is to extend the scope of the standard DFT codes based on localized basis sets, by calculating the out-of-equilibrium density matrix. As such, it is worth mentioning that, though the out-of-equilibrium electronic density does not minimize the density functional, these schemes rely on the Kohn-Sham Hamiltonian as the single particle Hamiltonian. Therefore, the self-consistency is very similar to the one encountered in standard DFT codes. The self-consistent procedure can be summarized in the diagram depicted in Fig. 2.4.

In many situations, the non-equilibrium condition only brings small corrections to the ground-state electronic density, it is therefore a good practice to use a DFT computed ground-state electronic density as the guess input density for the non-equilibrium calculations. This latter then proceeds in two steps. First, the electronic structure corresponding to the infinite leads is computed, in order for the contact self-energies to be build over the proper range of energies (i.e. the full bandwidth of the material). This step has to be done only once since the leads are assumed to remain in their equilibrium states. Second, the out-of-equilibrium density matrix is computed in a self-consistent way. The self-consistent

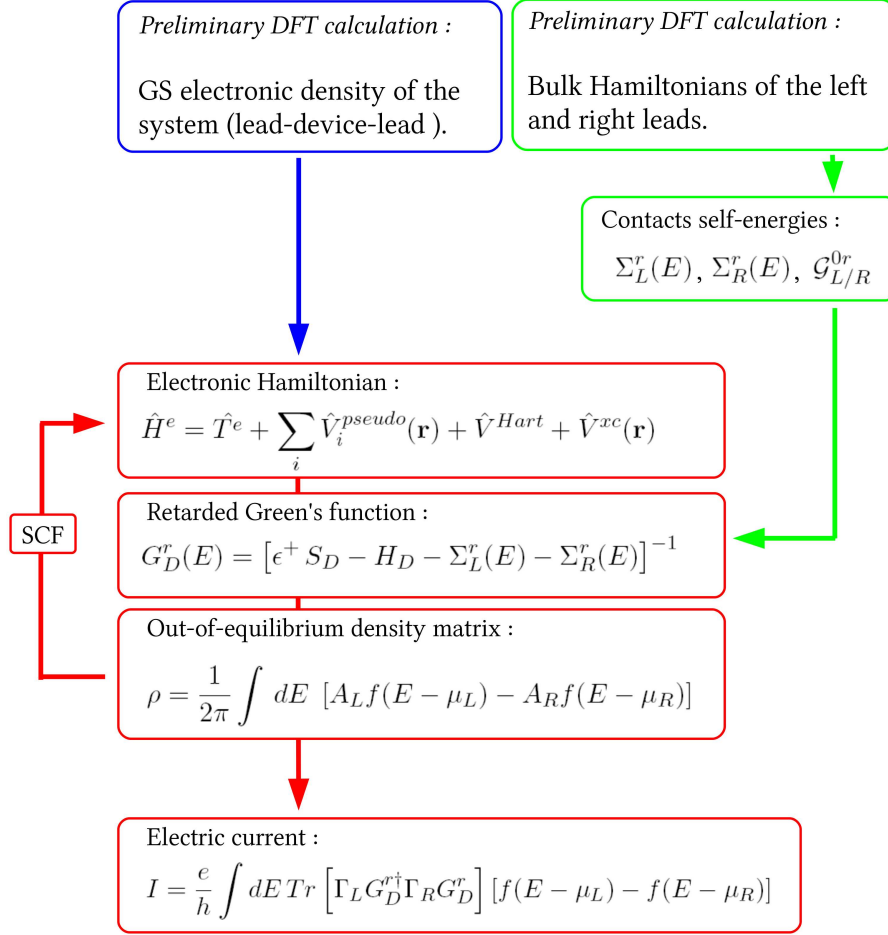


Figure 2.4: Diagram of the self-consistent cycle for the computation of the out-of-equilibrium density matrix and electric current. Blue frames correspond to the preliminary DFT calculation aiming at producing a good initial guess for the out-of-equilibrium electronic density. Green frames describe to the preliminary calculation of the leads self-energies. Red frames correspond to the main step of the actual self-consistent cycle.

cycle is accomplished by getting the Hartree (electrostatic) potential as a solution of the Poisson's equation with appropriate boundary conditions. Though the Poisson's equation can be solved in the real space, it is common to use fast-Fourier transform algorithms that are computationally efficient. This latter method is used in *Smeagol*. Actually, the electrostatic potential is calculated for a virtual periodic system obtained

by repeating the effective Hamiltonian $H_D^{eff}(E)$ along the transport direction. Besides, a saw-like term, whose drop is identical to the bias applied, is added to the Hartree potential in order to recover the correct voltage drop across the device. Finally, when convergence is reached, the electric current is computed as a by product of the retarded Green's function.

2.6 Solving the transport problem : achievements and limitations

Over the last decade, most of *ab initio* calculations of conductance in nanoscale junctions have rely on the use of the Landauer approach on top of the Density Functional Theory [71, 72, 73, 74]. Though this single-particle framework has proven to be reliable for the description of point contacts and some molecular junctions [75, 76, 77, 78], in the vast majority of situations, the predicted conductance exceeds experimentally measured values by several order of magnitudes [79, 80, 81]. On the one hand, this discrepancy raises questions about the theory and its underlying approximations. On the other hand, it is important to remind that predicting the conductance of nanoscale devices may be highly sensitive to the atomic arrangement of the actual device. Since the contact structure between leads and active region is experimentally difficult to control and characterize, the comparison between theoretical predictions and experimental measurements is plagued by uncertainty about the system geometry.

2.6.1 Experimental characterization

Several recent studies have attempted to reduce the gap between the theory and experiments. Obviously, the development of methods able to achieve a detailed microscopic characterization of the nanoscale devices is needed. Few years ago, Inelastic Electron Tunneling Spectroscopy (IETS) has appeared as the first experimental tool for the characterization of nanoscale and molecular junctions [82, 83, 84]. IETS is based on the analysis of the inelastic scattering of carriers by localized vibrational modes. Indeed, such inelastic processes come with identifiable fingerprints in the second derivative of the current with respect to the bias voltage. Though IETS gives crucial insights into the chemical composition and bonding characteristic of the junction, the experimental setup requires liquid helium temperatures and exceptional stability of the junction, limiting the range of IETS applicability. Another method that is

currently being investigated in order to characterize nanoscale junctions is Surface-Enhanced Raman Scattering (SERS) [85, 86].

2.6.2 Thermal fluctuations

On the theoretical side, recent developments aim to account for the thermal fluctuations of conductance [87, 81] and to overcome the limitation of the commonly used single-particle approximation [88, 89, 90, 91, 92, 81, 93, 94, 95]. Recently, several studies have emphasized the large fluctuation of conductance resulting from small modification of the atomic configurations [96, 97, 98, 99, 100, 81]. As an example, it has been reported that the conduction of molecular junctions with thiol-Au interfaces vary over orders of magnitude depending on the interface geometry [97, 98, 99, 100]. Besides, advanced computational schemes that couple the charge transport calculation with a molecular dynamic simulation have allowed to catch the essence of the conductance fluctuation [87, 81]. Though these studies accurately account for the dispersion reported in experimental conductance measurements, they fail in predicting the measured average conductance. Theoretically computed values of the conductance are typically a few times larger than those observed in experiments.

2.6.3 Renormalization of the electronic levels

Recently, the discrepancy between computed and measured values has been partly attributed to the use of approximated exchange-correlation (xc) functionals [88] and to correlation effects that are beyond the single-particle approximation [88, 90, 91, 92, 81, 93]. A reliable description of the electronic transport in nanoscale junctions, first of all, requires a reliable description of the energetic landscape across the junction. When a nanostructure is contacted with metal electrodes several physical phenomena involving many-electron processes contribute in determining the energetic landscape. Some of them are correctly described at the mean-field Kohn-Sham level, others are not. First, the self-consistent interaction between the device and the electrodes leads to a redistribution of the electronic density that may be highly sensitive to the XC functional. Second, the coupling between the electronic states localized within the device and the propagating Bloch states strongly depends on the energetic spectrum of the device. Besides, the broadening of the device energy levels and their alignment with respect to the electrode band structures play a crucial role in determining the low bias conductance of the junction. With this respect, the use of LDA KS-

eigenenergies, that are plagued by the well-known *energy-gap problem* may be an important source of errors in the conductance calculation. Finally, the proper description of the electrostatic effects at the junction interface is beyond the single-particle scheme. Indeed, the correlation energy associated with the polarization of the metallic contacts upon removal or addition of electrons in the device strongly affects the position of the affinity and ionization levels of the junction.

The aforementioned studies have attempted to assess the impact of such phenomena on the electronic transport in molecular and nanoscale junctions. Globally, in the case of molecules weakly coupled to metallic electrodes, the many-body effects have been shown to account for a renormalization of the junction energy levels at the metal-molecule interface leading to significant improvements of the predicted conductance. As an example, an appropriate shift of the ionization and affinity levels has allowed to compute conductance of aromatic molecules weakly coupled to metallic substrates in good agreement with experiments. In contrast, in the absence of well-defined metal-molecule interface, the renormalization of the energy levels does not strongly modify the qualitative picture provided by the mean-field approximation. In fully metallic junctions (e.g. metallic atomic wires), the changes in energy are small and mainly account for small modification of the carriers velocities. In semi-conducting junctions (e.g. semi-conducting carbon nanotubes), the renormalization of the energy levels globally acts as a rigid energy-shift of the unoccupied electronic states.

2.6.4 Inelastic scattering

Finally, a few recent studies have investigated the impact of non-coherent scattering and dissipative effects on the transport properties of nanoscale junctions [95, 94, 90, 88]. Since these are inelastic in essence, electron-phonon and electron-electron interactions results in the spread of the spectral weight and the redistribution of the conductance channels to different energies. This may play a important role in electronic transport by opening new diffusive conduction channels and preventing the propagation of coherent electrons. Practically, most of these results have been obtained within the Non-Equilibrium Green's Function (NEGF) formalism properly combined with (i) the Hedin's GW approximation (GWA) to account for the electronic correlation and (ii) the self-consistent Born approximation (SCBA) to include the electron-phonon interaction. It is worth mentioning that such approaches come with a huge computational demand that strongly restrict the size of the

systems studied. Therefore, such a detailed description of the electronic transport has been derived only for small prototypical nanojunctions.

2.7 Our approach

Several pioneering studies have underlined the important role of many-body processes in determining the conductance patterns of nanojunctions. However, it is highly computationally demanding to account for such complex phenomena within *ab initio* calculations, implicitly imposing a stringent limit on the size of the systems considered. Therefore, the current exploration of the electronic transport in nanoscale junctions mainly relies on two complementary approaches. On one hand, a large theoretical effort is dedicated to the improvement of the physical models of electronic transport at the atomic scale. Among other things, this includes the analysis of the inelastic effects and the derivation of a true out-of-equilibrium computational scheme. On the other hand, much work has still to be done in order to understand, at least qualitatively, the impact of the junction structure and shape on the transport properties of the device. For example, the elastic scattering by point-defects and impurities is expected to be the dominant scattering mechanism in many systems for which the approximation of coherent transport is therefore qualitatively convenient. This work clearly participates to this latter approach. All the transport calculations presented in the next chapters rely on the mean-field KS approach and the approximation of coherent transport only. We forecast that this scheme provides a qualitatively meaningful picture of the intrinsic transport properties of carbon based nanostructures such as graphene nanoribbons. Obviously, the conductance patterns computed from the Kohn-Sham eigenenergies are plagued by the well-known *energy-gap problem*. However, in the absence of metal-semi-conducting interface, this should not significantly affect the physical interpretation of the transport results. Besides, the carriers mobilities experimentally measured on graphene flakes are reported to be globally temperature independent, suggesting the mobility in graphene to be mainly limited by impurity scattering in nowadays samples [101, 1, 102, 2]. Finally, theoretical prediction highlights the edge roughness scattering as the dominant scattering mechanism in graphene nanoribbons, even at room temperature [103].

Chapter 3

Quantum confinement in graphene nanoribbons

3.1 Introduction

Carbon is the fourth most abundant chemical element by mass in the universe and is known to man since antiquity. Due to its ease to form various stable covalent bonds with small atoms, including carbon itself, it forms a huge number of different structures among which most of the organic compounds. Consequently, carbon nanomaterials reveal a rich polymorphism of various allotropes exhibiting each possible dimensionality : fullerene molecule (0D), nanotubes and graphene ribbons (1D), graphite platelets (2D) and nano-diamond (3D) are selected examples. Because of this extraordinary versatility of nanomaterials, carbon nanostructures exhibiting different physical and chemical properties are playing an important role in nanoscience and nanotechnology.

The fundamental building block of the carbon nanostructures (except for sp^3 -bonded diamond) is the graphene sheet. Graphene is the name given to the perfect infinite two-dimensional sheet of sp^2 -bonded carbon atoms packed into an honeycomb structure. For long time, this prototypical two-dimensional solid has been used to describe properties of many carbon-based materials, including graphite (where a large number of graphene sheets are stacked), nanotubes (where graphene sheets are rolled up into nanometer-sized cylinders), large fullerenes (where graphene sheets contain at least 12 pentagons displaying a spherical shape), and ribbons (where graphene is cut into strips).

Till recently, graphene was nothing but a theoretical concept since planar graphene was presumed to be unstable with respect to the formation of curved structures such as fullerenes and nanotubes. However,

a couple of years ago, researchers managed to actually prepare graphene by mechanical exfoliation (repeated peeling or micro-mechanical cleavage) of bulk graphite (highly oriented pyrolytic graphite, HOPG) [1, 2] or by epitaxial growth through thermal decomposition of SiC [3]. The discovery of such simple methods to prepare single atomic layer of carbon on top of a substrate suitable for the measurement of its electrical properties has generated a renewed interest in what was considered to be a prototypical, yet theoretical, two dimensional system. Graphene displays indeed, unusual electronic properties arising from confinement of electrons in two dimensions and peculiar geometrical symmetries.

Old theoretical studies of graphene [104, 105] reveal that the specific linear electronic band dispersion near the Brillouin zone corners (Dirac point) gives rise to electrons and holes that propagate as if they were massless fermions, with a velocity of the order of one hundredth of the speed of light. Charge excitations close to the Fermi level can thus be formally described as massless relativistic particles obeying a Dirac equation, whereas a new degree of freedom reflecting inherent symmetries (sub-lattice degeneracy) appears in the electronic states: the pseudospin. Because of the resulting pseudospin symmetry, electronic states turn out to be particularly insensitive to external sources of long-range elastic disorder, and as a result, charge mobilities in graphene layers as large as $10^5 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ have been reported close to the Dirac point [1]. In addition, in suspended graphene, the minimum conductivity at the Dirac point approaches a universal (geometry independent) value of $4e^2/\pi h$ at low temperature [106]. Low temperature electron mobility approaching $2 \times 10^5 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ were measured for carrier density below $5 \times 10^9 \text{ cm}^{-2}$. Such values cannot be reached in conventional semiconductors. In addition, graphene has been shown to exhibit anomalous quantum transport properties such as integer quantum Hall effect [102, 101], but also one of the most exotic and counter-intuitive consequences of quantum electrodynamics : the unimpeded penetration of relativistic particles through high and wide potential barriers, known as the Klein paradox [107]. These discoveries have stirred a lot of interest in the scientific community as well as in international media. The excitement behind this discovery has two main driving forces: basic science and technological implications [108]. Because of its high electronic mobility, structural flexibility, and capability of being chemically and/or structurally p- or n-doped-graphene is considered as a potential breakthrough in carbon-based nano-electronics.

The first section of this chapter reviews the electronic structure of graphene. The band structure of graphene is derived analytically and the close relation between the low energy electrons and the massless

Dirac fermions is highlighted. This section is mainly inspired by the Refs [4, 109]. The second section aims to show how the properties of graphene are conserved or modified in quasi-1D structures, known as graphene nano-ribbons (GNRs). In particular, the mechanisms that rule the opening of energy gaps are detailed and the similarities between GNRs and carbon nanotubes (CNT) are highlighted. This section takes much from the Refs [110, 111, 112, 113]. Finally, third section focuses on the structure and stability of the GNR edges. Since the topology of the edges determines the low energy electronic structure of GNRs, the relative stability of the different edge reconstruction is of crucial importance to achieve the experimental control necessary for technological applications. The results presented in this last section complete the former study of T. Wassmann et al. [10] and are part of a forthcoming publication.

3.2 Electronic properties of graphene

Graphene is the ideal bi-dimensional (2D) allotropic form of carbon in which the atoms are periodically arranged in an infinite hexagonal network (Fig. 3.1(a)). Such an atomic structure is characterized by two types of bonds and exhibits the so-called planar sp^2 hybridization of the C atoms. Indeed, among the four valence orbitals of the carbon atom (the $2s$, $2p_x$, $2p_y$ and $2p_z$ orbitals, where z refers to the direction perpendicular to the sheet), the (s, p_x, p_y) orbitals combine to form the in-plane σ (bonding or occupied) and σ^* (anti-bonding or unoccupied) orbitals. Such orbitals are even with respect to the planar symmetry. The σ bonds are strong covalent bonds responsible for most of the binding energy and for the elastic properties of the graphene sheet (Fig. 3.1(a)). The remaining p_z orbital, pointing out of the graphene sheet (Fig. 3.1(a)), presents an odd parity with respect to the honeycomb plane and cannot couple with the σ states. The lateral interaction with neighboring p_z orbitals creates the delocalized π (bonding) and π^* (anti-bonding) orbitals [104]. Graphite is comprised of coherently stacked layers of graphene. Two (three) layers are needed to define the unit cell in Bernal [AB] (rhombohedral [ABC]) graphite since the successive sheets are translated from each other by a C-C distance ($a_{CC}=1.42$ Å). The three-dimensional structure of graphite is therefore held together by weak interlayer van der Waals forces including some electronic delocalization [114]. The π bonds, perpendicular to the graphene sheet, are responsible for this weak interaction between carbon layers in graphite.

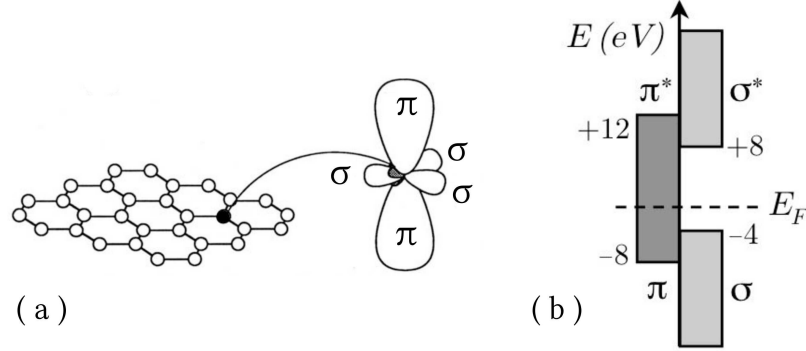


Figure 3.1: Illustration of the carbon valence orbitals (a): the three σ orbitals within the graphene plane and the π orbital perpendicular to the plane. The σ bonds in the carbon hexagonal network strongly connect the carbon atoms and are responsible for the binding energy and the elastic properties of the graphene sheet. The π bonds are perpendicular to the surface of the sheet. The corresponding bonding and the anti-bonding σ bands are separated by a large energy gap of $\sim 12\text{eV}$ (b), while the bonding and anti-bonding π states lie in the vicinity of the Fermi level (E_F). Consequently, the σ bonds are frequently neglected for the prediction of the electronic properties of graphene around the Fermi energy.

3.2.1 Tight-binding model of graphene

The electronic structure of graphene can be described using a rather simple tight-binding Hamiltonian, leading to analytical solutions for its eigenvalues and related eigenstates [109]. Since the bonding and anti-bonding σ bands are well separated in energy (by more than 12 eV at Γ), they are frequently neglected in semi-empirical calculations as they are too far away from the Fermi level to play a role (Fig. 3.1(b)). Only the remaining two π bands are thus needed to describe the low energy electronic properties of graphene [104] and graphite [105]. Indeed, the bonding (π) and anti-bonding (π^*) orbitals do form wide electronic valence and conduction bands (Fig. 3.1(b)) which cross the Fermi level at high-symmetry points in the Brillouin zone of graphene, as discussed in the following.

The graphene plane is an hexagonal lattice with two atoms (A and B) in the primitive cell defined by the lattice vectors ($\mathbf{a}_1, \mathbf{a}_2$),

$$\mathbf{a}_1 = \frac{a}{2}(3, \sqrt{3}), \quad \mathbf{a}_2 = \frac{a}{2}(3, -\sqrt{3}) \quad (3.1)$$

where a is the C-C inter-atomic distance ($\sim 1.42 \text{ \AA}$). Consequently, the graphene lattice is made from two inter-penetrated triangular sub-lattice

containing only one type of atoms (A or B). Graphene presents thus a bipartite topology where the direct neighbors of atoms of the sub-lattice A are atoms of the sub-lattice B. One defines $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$ as the vectors that connect each atom of the sub-lattice A to its nearest neighbors,

$$\mathbf{e}_1 = (a, 0), \quad \mathbf{e}_2 = \frac{a}{2}(-1, \sqrt{3}), \quad \mathbf{e}_3 = \frac{a}{2}(-1, -\sqrt{3}). \quad (3.2)$$

The reciprocal lattice vectors $(\vec{b}_1, \vec{b}_2)$ are derived from the direct lattice vectors by use of the relation $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij}$,

$$\mathbf{b}_1 = \frac{2\pi}{3a}(1, \sqrt{3}), \quad \mathbf{b}_2 = \frac{2\pi}{3a}(1, -\sqrt{3}). \quad (3.3)$$

Consequently, the first Brillouin zone is hexagonal. As detailed in Fig. 3.2(b), the three main points of high symmetry are labelled Γ , K and M .

When carbon atoms are placed onto the graphene hexagonal lattice (Fig. 3.2(a)), the electronic wave-functions from different atoms overlap. However, such an overlap between the p_z orbitals and the s or the p_x and p_y electrons is strictly zero by symmetry. Consequently, the p_z electrons, which form the π bonds in graphene, can be treated independently from the other valence electrons. Within this π -band approximation, the atoms are uniquely defined by one orbital per atom site [104].

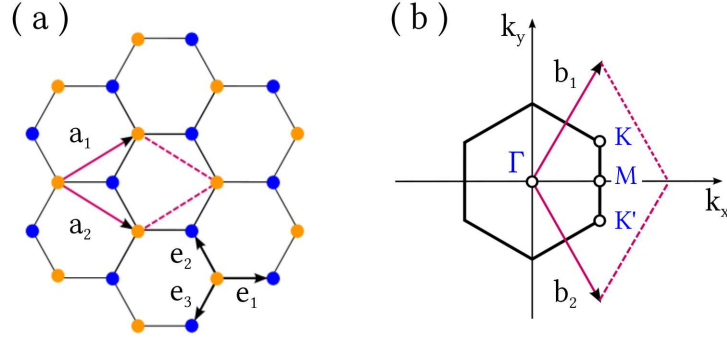


Figure 3.2: Graphene honeycomb lattice and its Brillouin zone. (a) Bipartite lattice structure of graphene characterized by the unit vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ and the nearest neighbor vectors $\mathbf{e}_{1,2,3}$. (b) Corresponding first Brillouin zone with its high symmetry points Γ , M , K and K' . Orange and blue circles represent carbon atoms belonging to different sub-lattice in the graphene structure.

To derive the electronic spectrum of graphene, the corresponding Schrödinger equation has to be solved. Within the so-called orthogonal tight-binding (TB) scheme, where the overlap integrals between

neighboring p_z orbitals are neglected, it amounts to diagonalizing the Hamiltonian,

$$\hat{H} = \sum_{\mathbf{R}} \left(\epsilon_a \hat{a}_{\mathbf{R}}^\dagger \hat{a}_{\mathbf{R}} + \epsilon_b \hat{b}_{\mathbf{R}+\mathbf{e}_1}^\dagger \hat{b}_{\mathbf{R}+\mathbf{e}_1} \right) + \sum_{\mathbf{R}} \sum_{i=1,3} -t \left(\hat{b}_{\mathbf{R}+\mathbf{e}_i}^\dagger \hat{a}_{\mathbf{R}} + \hat{a}_{\mathbf{R}}^\dagger \hat{b}_{\mathbf{R}+\mathbf{e}_i} \right), \quad (3.4)$$

where t is the nearest neighbor hopping energy, ϵ_a/b are the on-site energies, and $\{\hat{a}_{\mathbf{R}}^\dagger/\hat{b}_{\mathbf{R}}^\dagger\}$ and $\{\hat{a}_{\mathbf{R}}/\hat{b}_{\mathbf{R}}\}$ are the creation and annihilation operators for electrons on site $\mathbf{R}$ of sub-lattices A and B . Here, the atomic interactions have been restricted to first-nearest-neighbors only. Since all carbon atoms are equivalent in graphene, one can set $\epsilon_a = \epsilon_b = 0$ without loosing information. Owing to the lattice periodicity, the creation/annihilation operators may be written as Bloch sums,

$$\hat{a}_{\mathbf{R}} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k} \in BZ} e^{i\mathbf{k} \cdot \mathbf{R}} \hat{a}_{\mathbf{k}} \quad \text{and} \quad \hat{b}_{\mathbf{R}+\mathbf{e}_1} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k} \in BZ} e^{i\mathbf{k} \cdot (\mathbf{R}+\mathbf{e}_1)} \hat{b}_{\mathbf{k}}, \quad (3.5)$$

where N is the number of primitive cells in the solid. Inserting these expressions into Eq. 3.4 with $\epsilon_a = \epsilon_b = 0$, one gets

$$\hat{H} = \sum_{\mathbf{k} \in BZ} \left(h_{\mathbf{k}} \hat{b}_{\mathbf{k}}^\dagger \hat{a}_{\mathbf{k}} + h_{\mathbf{k}}^* \hat{a}_{\mathbf{k}}^\dagger \hat{b}_{\mathbf{k}} \right) \quad (3.6)$$

$$= \sum_{\mathbf{k} \in BZ} (\hat{a}_{\mathbf{k}}^\dagger \hat{b}_{\mathbf{k}}^\dagger) \cdot \begin{pmatrix} 0 & h_{\mathbf{k}}^* \\ h_{\mathbf{k}} & 0 \end{pmatrix} \cdot \begin{pmatrix} \hat{a}_{\mathbf{k}} \\ \hat{b}_{\mathbf{k}} \end{pmatrix}, \quad (3.7)$$

with

$$h_{\mathbf{k}} = -t \sum_{i=1,3} e^{-i\mathbf{k} \cdot \mathbf{e}_i} = |h_{\mathbf{k}}| e^{i\theta_{\mathbf{k}}}. \quad (3.8)$$

For each crystal momentum that belongs to the first hexagonal Brillouin zone, the set of allowed electronic energies and states is thus obtained by a 2x2 matrix diagonalization. This diagonalization can be obtained by means of a rotation in the sub-lattice space,

$$\begin{pmatrix} \hat{c}_{\mathbf{k},c}^\dagger \\ \hat{c}_{\mathbf{k},v}^\dagger \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} +e^{-i\frac{\theta_{\mathbf{k}}}{2}} & +e^{i\frac{\theta_{\mathbf{k}}}{2}} \\ +e^{-i\frac{\theta_{\mathbf{k}}}{2}} & -e^{i\frac{\theta_{\mathbf{k}}}{2}} \end{pmatrix} \cdot \begin{pmatrix} \hat{a}_{\mathbf{k}}^\dagger \\ \hat{b}_{\mathbf{k}}^\dagger \end{pmatrix}. \quad (3.9)$$

The newly defined $\hat{c}_{\mathbf{k},v}$ and $\hat{c}_{\mathbf{k},c}$ operators operate therefore in the sub-lattice space. The electronic spectrum is finally given by,

$$\hat{H} = \sum_{\mathbf{k} \in BZ_1} (\hat{c}_{\mathbf{k},c}^\dagger \hat{c}_{\mathbf{k},v}^\dagger) \cdot \begin{pmatrix} \epsilon_{\mathbf{k},c} & 0 \\ 0 & \epsilon_{\mathbf{k},v} \end{pmatrix} \cdot \begin{pmatrix} \hat{c}_{\mathbf{k},c} \\ \hat{c}_{\mathbf{k},v} \end{pmatrix}, \quad (3.10)$$

with

$$\begin{aligned}\epsilon_{\mathbf{k},c/v} &= \pm |\hbar \mathbf{k}| \\ &= \pm t \sqrt{1 + 4 \cos\left(\frac{\sqrt{3}}{2} a k_y\right) \cos\left(\frac{3}{2} a k_x\right) + 4 \cos^2\left(\frac{\sqrt{3}}{2} a k_y\right)}.\end{aligned}\quad (3.11)$$

With one p_z electron per atom in the π - π^* model¹, the negative energy branch in Eq. 3.11 is fully occupied, while the positive branch is empty. These occupied and unoccupied bands cross at the K or K' points which are connected by time reversal symmetry. It is easy to verify that $\epsilon(\mathbf{k}=\mathbf{K}) = \epsilon(\mathbf{k}=\mathbf{K}') = 0$. The Fermi level E_F (or charge neutrality point) is therefore the zero-energy reference in Fig. 3.3 and the Fermi surface is defined by the set of K and K' points. Since occupied and unoccupied bands do cross, the graphene sheet displays a metallic (zero gap) character. However, as the Fermi surface is of zero dimension (since it is reduced to a discrete and finite set of points), the term semi-metal with no overlap or zero-gap semiconductor is usually used.

In addition, the π -band electronic dispersion for graphene near the corners of the 2D hexagonal Brillouin zone is found to be linear. As illustrated in Fig. 3.3, the low-energy electronic structure of graphene can thus be approximated by "cones" located at the corners of the Brillouin zone. Within these cones, the electronic properties of graphene are appropriately described by an effective massless Dirac fermion model with linear dispersion and electron-hole symmetry. The two nonequivalent Brillouin zone corners (K and K') where the apex of the cones touch at the Fermi energy are referred as the Dirac points.

Finally, expanding Eq. 3.11 around the charge neutrality points (K and K') explicitly yields the linear energy-momentum relation obeyed by the low energy electrons,

$$\epsilon_{\mathbf{k},c/v} = \pm v_F |\boldsymbol{\kappa}| + \mathcal{O}^2, \quad (3.12)$$

where $\boldsymbol{\kappa} = \mathbf{k} - \mathbf{K}$ and $v_F = \frac{3ta}{2}$ is the electronic group velocity.

This simple orthogonal tight-binding model [104] yields valence (π) and conduction (π^*) bands which are symmetric with respect to E_F . This is due to the crude approximations used herewith. In fact, the electron-hole symmetry is broken if additional physical informations are included within the model. This can be achieved by the introduction of non-zero overlap integrals between the p_z orbitals of nearest neighbor

¹the three other electrons (s, p_x, p_y) fill the low-lying σ bands

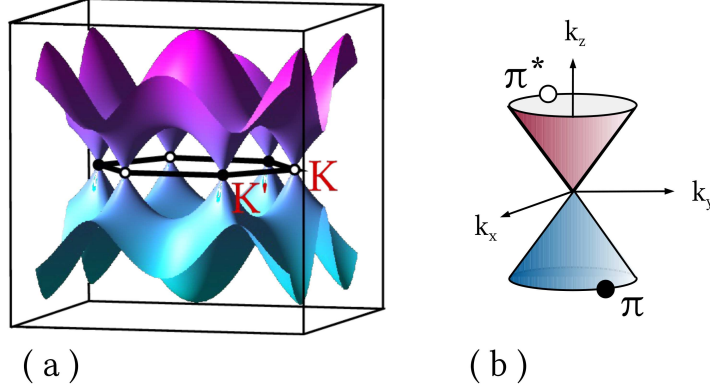


Figure 3.3: (a) Graphene π and π^* electronic bands. Within the nearest neighbors tight-binding approach, the π and π^* bands are symmetric with respect to the valence and conduction bands. (b) Linear dispersion relation close to the K (white dots) and K' (black dots) points of the first 2D Brillouin zone.

sites. A more complete TB parameterization, that includes the hopping terms up to the second-nearest neighbors would lead to analogous results [115], as well as more accurate first-principles calculations [109]. By sake of comparison, and in order to assess the accuracy of the model, the accurate band structure of graphene reported by P. E. Trevisanutto in Ref. [116] is depicted in Fig. 3.4. In good agreement with the TB predictions, the π and π^* bands computed by means of DFT are quasi-linear (linear very close to K or K' and near the Fermi energy), in contrast with the quadratic dependence of the energy on the momentum obeyed by electrons at band edges in conventional semiconductors. Besides, though the inclusion of many-body GW self-energy accounts for a renormalization of the Fermi velocity with an 17% increase, the GW correction does not open an energy gap in the graphene band structure.

3.2.2 Connection with the 2D massless Dirac equation

Graphene is highly specific for its linear energy-momentum relation and peculiar electronic properties that are specific to a 2D gas of particles described by the relativistic Dirac equation rather than the non-relativistic Schrödinger equation. In graphene, charge carriers mimic relativistic particles with zero mass and an effective *speed of light*.

The formal analogy between the non-relativistic Schrödinger equa-

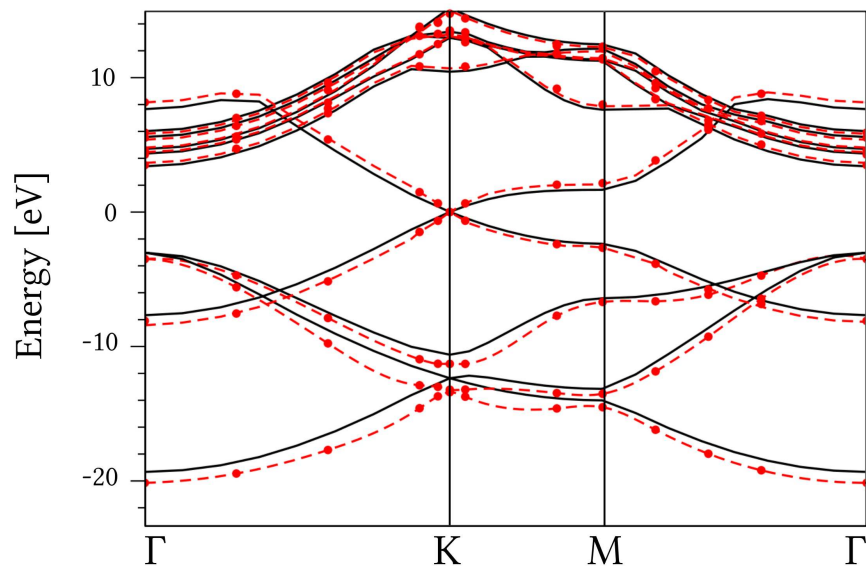


Figure 3.4: Representation of the energy-momentum relation in graphene along the Γ -K-M- Γ path of the Brillouin zone. Solid thick lines: band structure computed by means of DFT KS eigenenergies. Circles and dashed lines: band structure accounting for the many-body GW self-energy corrections. Picture adapted from Ref. [116]

tion that rules the low energy electronic properties of graphene and the relativistic Dirac equation is readily seen after a linear expansion of the full TB Hamiltonian around the K and K' Dirac points. Relying on the operators $\hat{a}_{\mathbf{K}/\mathbf{K}'}, \hat{b}_{\mathbf{K}/\mathbf{K}'}, \hat{a}_{\mathbf{K}/\mathbf{K}'}$ and $\hat{b}_{\mathbf{K}/\mathbf{K}'}$ to describe the low energy electronic states, the expansion of the Hamiltonian up to the linear order in $\boldsymbol{\kappa}$ yields,²

$$\begin{aligned}\tilde{h}(\mathbf{K} + \boldsymbol{\kappa}) &= -t \left(1 + e^{-i(\mathbf{K}+\boldsymbol{\kappa}) \cdot (\mathbf{e}_2 - \mathbf{e}_1)} + e^{-i(\mathbf{K}+\boldsymbol{\kappa}) \cdot (\mathbf{e}_3 - \mathbf{e}_1)} \right) \\ &\approx -\frac{3at}{2} (i\kappa_x + \kappa_y)\end{aligned}\quad (3.13)$$

$$\tilde{h}(\mathbf{K}' + \boldsymbol{\kappa}) \approx -\frac{3at}{2} (i\kappa_x - \kappa_y) , \quad (3.14)$$

and,

$$\begin{aligned}\tilde{H} &= -v_F \left[\tilde{\phi}_{\mathbf{K}}^\dagger \begin{pmatrix} 0 & (-i\kappa_x + \kappa_y) \\ (i\kappa_x + \kappa_y) & 0 \end{pmatrix} \tilde{\phi}_{\mathbf{K}} \right. \\ &\quad \left. + \tilde{\phi}_{\mathbf{K}'}^\dagger \begin{pmatrix} 0 & (-i\kappa_x - \kappa_y) \\ (i\kappa_x - \kappa_y) & 0 \end{pmatrix} \tilde{\phi}_{\mathbf{K}'} \right] ,\end{aligned}\quad (3.15)$$

where $\tilde{\phi}_{\mathbf{K}}^\dagger = (\tilde{a}_{\mathbf{K}}^\dagger \ \tilde{b}_{\mathbf{K}}^\dagger)$. By use of the Pauli matrices (σ_x, σ_y) , Eq. 3.15 finally reduces to the expression,

$$\begin{aligned}\tilde{H} &= -v_F \left[\tilde{\phi}_{\mathbf{K}}^\dagger (\sigma_x \kappa_x + \sigma_y \kappa_y) \tilde{\phi}_{\mathbf{K}} + \tilde{\phi}_{\mathbf{K}'}^\dagger (\sigma_x \kappa_x - \sigma_y \kappa_y) \tilde{\phi}_{\mathbf{K}'} \right] \\ &= -v_F \left[\tilde{\phi}_{\mathbf{K}}^\dagger \boldsymbol{\sigma} \cdot \boldsymbol{\kappa} \tilde{\phi}_{\mathbf{K}} + \tilde{\phi}_{\mathbf{K}'}^\dagger \boldsymbol{\sigma}^* \cdot \boldsymbol{\kappa} \tilde{\phi}_{\mathbf{K}'} \right] ,\end{aligned}\quad (3.16)$$

with $\boldsymbol{\sigma} = (\sigma_x, \sigma_y)$ and $\boldsymbol{\sigma}^\dagger = (\sigma_x, -\sigma_y)$. From this expression it appears that the low energy electronic states ($\Psi^{K/K'}(\boldsymbol{\kappa})$) are ruled by two copies of the 2D massless Dirac equation, one holding for the crystal momentum around K and the other for the crystal momentum around K' ,

$$-v_F (\boldsymbol{\sigma} \cdot \boldsymbol{\kappa}) \Psi(\boldsymbol{\kappa}) = E \Psi(\boldsymbol{\kappa}) . \quad (3.17)$$

²Though it is not explicitly mentioned in most articles in the literature, a unitary transformation $\hat{\mathcal{U}}$ is often introduced here in order to limit the appearance of phase factors within the linear expansion of $H_{\mathbf{k}}$;

$$\hat{\mathcal{U}} = \begin{pmatrix} 1 & 0 \\ 0 & e^{-i\mathbf{k} \cdot \mathbf{e}_1} \end{pmatrix} ,$$

which operates in the sub-lattice space such that,

$$\tilde{H}_{\mathbf{k}} = \begin{pmatrix} 0 & \tilde{h}_{\mathbf{k}}^* \\ \tilde{h}_{\mathbf{k}} & 0 \end{pmatrix} = \hat{\mathcal{U}} \cdot \hat{H}_{\mathbf{k}} \cdot \hat{\mathcal{U}}^\dagger \quad \text{and} \quad \begin{pmatrix} \tilde{a}_{\mathbf{k}} \\ \tilde{b}_{\mathbf{k}} \end{pmatrix} = \hat{\mathcal{U}} \cdot \begin{pmatrix} \hat{a}_{\mathbf{k}} \\ \hat{b}_{\mathbf{k}} \end{pmatrix} .$$

The low energy wave-functions are easily deduced from the Hamiltonian 3.15 and take the forms,

$$\Psi_{\pm}^K(\boldsymbol{\kappa}) = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-i\frac{\theta_{\boldsymbol{\kappa}}}{2}} \\ \pm e^{i\frac{\theta_{\boldsymbol{\kappa}}}{2}} \end{pmatrix}, \quad (3.18)$$

and

$$\Psi_{\pm}^{K'}(\boldsymbol{\kappa}) = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{i\frac{\theta_{\boldsymbol{\kappa}}}{2}} \\ \pm e^{-i\frac{\theta_{\boldsymbol{\kappa}}}{2}} \end{pmatrix}, \quad (3.19)$$

where the $\pm$ sign refers to the positive and negative eigenenergies, that is the π^* (conduction) and π (valence) bands. Note that if the phase (θ) appearing in the Hamiltonian is rotated by 2π , the eigenfunctions change sign. The phase shift of π under the rotation of the Hamiltonian is characteristic of spinors. Moreover, since the Hamiltonian commutes with the helicity operators $\hat{\chi} = \frac{1}{2}\boldsymbol{\sigma} \cdot \frac{\boldsymbol{\kappa}}{|\boldsymbol{\kappa}|}$, it is common in the graphene literature to regard the two components wave-functions ($\Psi^{K/K'}(\boldsymbol{\kappa})$) as one two-component (pseudo)spinor,

$$\hat{\chi}\Psi_{\pm}^K(\boldsymbol{\kappa}) = \pm \frac{1}{2}\Psi_{\pm}^K(\boldsymbol{\kappa}). \quad (3.20)$$

This implies that the electrons (holes) in the valence (conduction) band, have a positive (negative) helicity. Or equivalently, that the pseudo-spin of electrons (holes) points in the direction of (opposite to) the wave-vector. Several unusual transport properties of graphene derive from the linear dispersion and the chiral nature of the quasi-particles as introduced theoretically in Eqs. 3.17-3.20.

3.2.3 Electronic transport near the Dirac point

Since its electrons move ballistically over submicron distances even at high carriers concentrations and in the presence of chemical doping, graphene is frequently presented as a potential candidate for future electronics. In particular, the high mobility of low energy charge carriers in graphene should be an advantage for the realization of ultra-high frequency transistors and high speed interconnects. Most of the transport measurements reported in the literature have been performed on single-layer graphene field effect transistors (FETs) as a function of gate voltage [101]. Graphene FETs are fabricated with standard lithography and etching techniques using mechanically cleaved graphene flakes [2]. A degenerated doped silicon substrate commonly serves as the gate. While graphene samples are typically p-doped by adsorbates in ambient conditions, graphene itself appears to be a pronounced ambipolar

material in which charge carriers can be continuously tuned up to 10^{13} cm^{-2} electrons and holes densities. Resistivity measurements performed on a single-layer graphene FET reveal that the conduction is symmetric about the Dirac point. In the high-density regime, the mobility is roughly carrier-density and temperature-independent. Reported mobility values range from 2,000 to 20,000 cm^2/Vs , with the high end representing a long mean free path of $\sim 0.3 \text{ } \mu\text{m}$, comparable to that of single-wall carbon nanotubes (as described in the following sections). Its weak temperature dependence indicates impurity or defect scattering as the dominant mobility-limiting mechanism and provides room for future improvement. Possible sources of scattering include adsorbates and defects in the graphene lattice and ionized impurities in the SiO_2 substrate. In addition, transport measurements also reveal a remarkable property of 2D carriers in graphene. Although the carrier density approaches zero at the Dirac point, the 2D resistivity ρ_{xx} or conductivity σ_{xx} remains finite. Such behavior, dubbed "minimum" conductivity, has been observed in many devices with ρ_{xx} ranging from 2 to 7 $\text{k}\Omega$ [102, 101]. Slightly larger values of ρ_{xx} from 6 to 9 $\text{k}\Omega$ are also reported for bi-layer graphene [107]. In addition to its conductivity that never falls below a minimum value of e^2/h , graphene has also revealed other unusual transport phenomena characteristic of two-dimensional Dirac fermions, such as an anomalous integer quantum Hall effect, a cyclotron mass m of massless carriers with an energy E in graphene that is described by $E = mc^*{}^2$, and Shubnikov-de Haas oscillations in graphene which exhibit a phase shift of π due to Berry's phase [102, 101]. However, the accurate description of these unusual transport phenomena is beyond the scope of the present manuscript and can be found elsewhere [4].

3.3 Electronic properties of graphene nanoribbons

Its high electron mobility and long coherence length have made graphene the subject of intense studies for nanoscale electronic applications, even for the implementation of room-temperature ballistic (dissipation-free) electronics. However, a major issue in the development of graphene-based field-effect transistors is the inability to electrostatically confine electrons in graphene, because a single layer of graphite remains metallic even at the charge neutrality point. In order to overcome this problem, a way to open a gap in the electronic structure of graphene needs to be found. A straightforward solution is to pattern the graphene sheet into narrow ribbons. Thanks to recent progresses in the synthesis of sin-

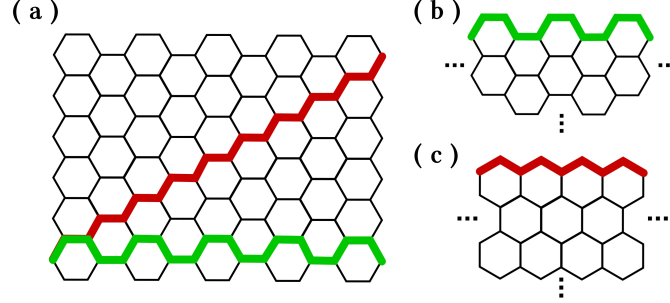


Figure 3.5: Honeycomb lattice of graphene (a) with both the zigzag (red) and the armchair (green) directions. Graphene nanoribbons cut in the ideal sheet along these two highly symmetric directions are called aGNRs (b) and zGNRs (c), respectively.

gle graphite layers on conventional device setups, graphene nanoribbons (GNRs) with varying widths have been synthesized and characterized experimentally [117, 5, 118].

Graphene nanoribbons (GNRs) are elongated stripes of graphene with a finite width that can be obtained by cutting the graphene plane along a given direction. Another appealing point of view, consists in considering GNRs as unfolded infinite CNTs. Due to the honeycomb structure of graphene, there are two basic shapes for graphene edges, namely the zigzag and armchair ones (see Fig. 3.5). Depending on the cutting direction, or equivalently on the axis direction of the tubes, the edges of the GNRs may then present an armchair shape (chiral angle $\phi = 0$), a zigzag shape ($\phi = \pi/6$) or a complex shape made of a mixture of armchair and zigzag shaped fragments ($0 < \phi < \pi/6$).

The atomic structure of nanoribbons with armchair and zigzag edges is further illustrated in Fig. 3.6 along with their unit cells. Following previous convention [111, 112, 119, 120, 121, 122, 123, 124, 125, 126, 110, 127], GNRs with armchair (zigzag) edges on both sides are characterized by the number of dimer lines (zigzag lines) across the ribbon width. In the following, N -aGNR and N -zGNR will refer to such prototypical armchair and zigzag GNRs, N being respectively the number of dimer and zigzag lines. Besides, if not otherwise stated, the carbon atoms at the edges are assumed to be mono-hydrogenated. Of course, these ideally shaped edges do not correspond to the experimental observations [128, 129, 130] where GNRs currently have a high degree of roughness at the edges. Some aspect of this edge disorder will be presented later on.

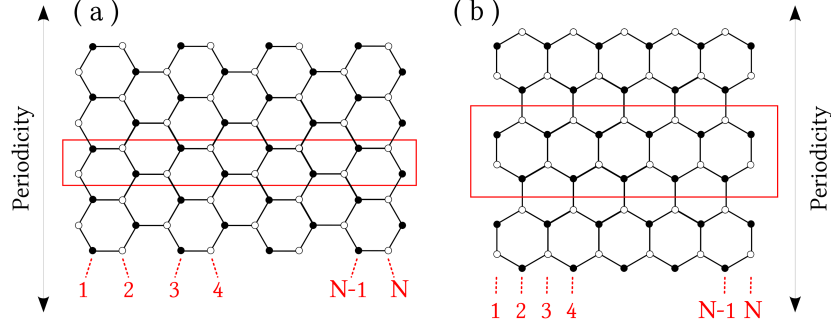


Figure 3.6: Carbon N -zGNR (a) and N -aGNR (b) composed of N armchair and zigzag lines, respectively. Black and white dots identify carbon atoms belonging to the two different graphene sub-lattices (A and B). The red rectangle represents the 1D unit-cell of the corresponding GNR. Atoms labeling follows the counting of zigzag chains (a) or dimer lines (b), from 1, 2, 3, 4, ... to $N-1$, N .

3.3.1 Bands folding approximation

Since GNRs are just geometrically terminated single graphite layers, their electronic structures have been predicted for long time by imposing appropriate boundary conditions on the Schrödinger's equation within the simple single-band tight-binding approximation [111, 112, 123, 124, 125, 126].

Starting from the band structure of the 2D graphene plane, a rough idea of the band structure of graphene ribbons can be easily obtained by applying the *band folding* principles. As illustrated in Fig. 3.7, this consists in projecting the bands of bulk graphene onto the one dimensional Brillouin zone of the graphene ribbon. As shown in Fig. 3.8, the projected band structures do preserve the linear dispersion relation observed in graphene around the Dirac points (K and K'). The apex of the Dirac cones which are responsible of the system metallicity are folded on $k = 0$ and $k = \pm \frac{2\pi}{3}$ in the case of aGNRs and zGNRs respectively.

In nanoribbons, the presence of the edges involves the confinement of the electrons in the direction perpendicular to ribbon axis. Owing to the quantum mechanical constriction of electronic wave-functions, the allowed wave-vectors are discretized along the confining direction. As a consequence, the graphene electronic spectrum is broken into sub-bands and a gap can possibly open. As detailed in Fig. 3.9, the allowed wave vectors of GNRs form lines in the reciprocal space. Neglecting the edge

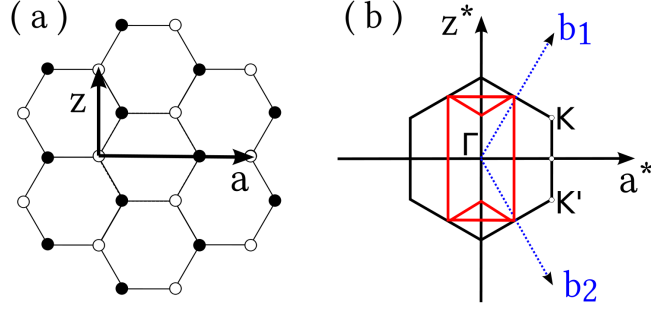


Figure 3.7: Band folding approximation. (a) Honeycomb network of graphene with the two directions of the electronic confinement (a and z black arrows) for the zigzag and armchair ribbons, respectively. (b) The first hexagonal Brillouin zone of graphene is folded into the first rectangular Brillouin zone (red), defined by the a^* and z^* directions. This rectangular Brillouin zone corresponds in the reciprocal space to the unit cell constructed using the a and z vectors in real space as illustrated in (a).

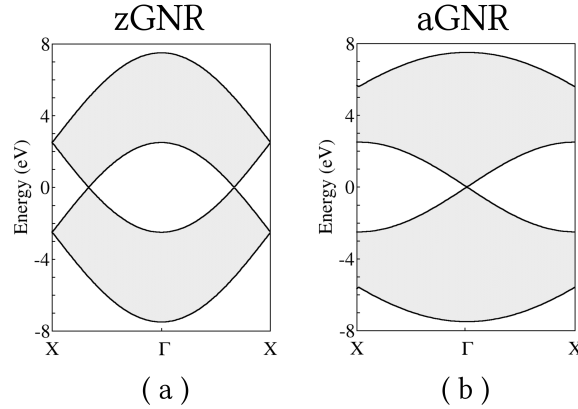


Figure 3.8: Energy band structure of graphene projected on the zigzag (a) and armchair (b) axis. The linear dispersion relations are conserved and localized at $k = 0$ for aGNRs and at $k = \frac{2\pi}{3}$ for zGNRs.

relaxation effects, one can thus approximate the electronic band structure of a specific GNRs by the superposition of the graphene energy bands along these lines. This highlights the dependence of the ribbon electronic structure with respect to both its orientation and its width. Depending on the effective or avoided crossing of the sub-bands with the Dirac points

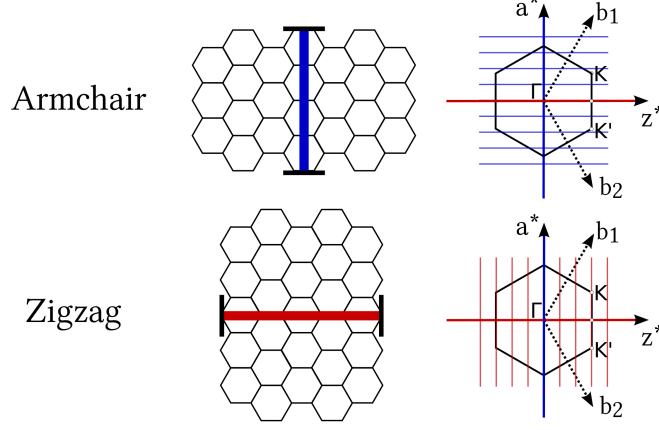


Figure 3.9: (left) Direction of electronic confinement in the GNRS, (right) Brillouin zone of graphene superimposed by a representation of the lines of allowed k -points in the simple *band-folding* topological approximation. The cases of armchair and zigzag ribbons are illustrated in the top and bottom panels respectively.

(K and K'), a specific GNR may be either metallic or semiconductor. Consequently, GNRS can be conveniently compared to carbon nanotubes : a metallic character is found for all the zigzag GNRS while a band gap oscillating as a function of the ribbon width is predicted in the case of armchair GNRS.

3.3.2 Electronic structure of the armchair ribbons

As detailed previously, the quantum constriction of electronic wavefunctions within the ribbon has a strong impact on the low energy electronic structures of GNRS. However, other effects, such as the relaxation of the edges (hydrogenated or not), may also play an important role around the Fermi level. In this section, the electronic structure of armchair ribbons is derived emphasizing the separate contributions of electronic confinement and edge related effects.

Within the simplest TB approximation the Hamiltonian of a GNR with hydrogenated edges is readily formulated as

$$\mathcal{H} = \sum_i \epsilon_i \hat{c}_i^\dagger \hat{c}_i + \sum_{\langle i,j \rangle} \gamma_{ij} \hat{c}_i^\dagger \hat{c}_j \quad (3.21)$$

where ϵ_i is the on-site energy of the i^{th} carbon atom, $\langle i,j \rangle$ denotes all

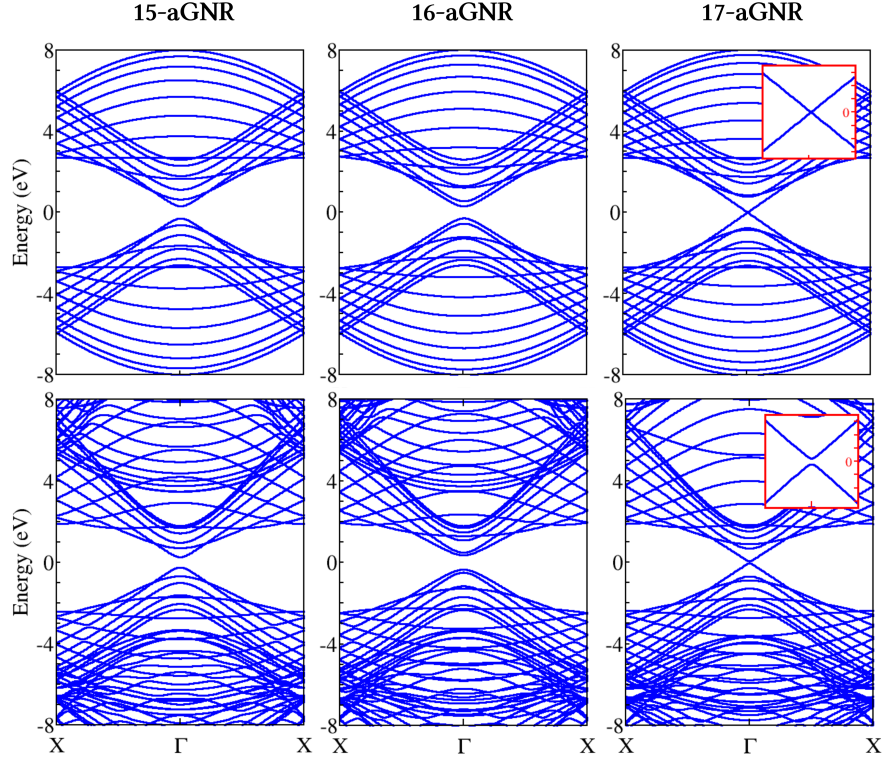


Figure 3.10: Energy band structures of armchair nanoribbons for various width ($N=15,16,17$). *Top*, band structures computed within the TB model with constant hopping energy between nearest neighbors. *Bottom*, band structures computed within the DFT framework.

pairs of nearest neighbors π -orbitals, γ_{ij} corresponds to the hopping energy between the i^{th} and j^{th} π -orbitals, and $\hat{c}_i$ is the electron creation operator associated with the i^{th} carbon site.

Owing to the periodicity along the ribbon axis, the $\hat{c}_i$ and $\hat{c}_i^\dagger$ operators may be expressed as Bloch sums,

$$\hat{c}_i = \frac{1}{\sqrt{N}} \sum_k e^{ikR_i} \hat{c}_k(i) \quad (3.22)$$

where R_i is the position of the i^{th} carbon site, and $\hat{c}_k(i)$ is one of the $\{\hat{c}_k^{1A}, \hat{c}_k^{1B}, \hat{c}_k^{2A}, \hat{c}_k^{2B}, \dots, \hat{c}_k^{NB}\}$ operators, named by reference to the unit cell sites $\{1_A, 1_B, \dots, N_A, N_B\}$ illustrated in Fig. 3.6.

Folding Eq. (3.22) into the Eq. (3.21), the Hamiltonian of armchair GNRs is easily expressed in terms of the basis set $\{\hat{c}_k^{1A}, \hat{c}_k^{1B}, \hat{c}_k^{2A}, \hat{c}_k^{2B},$

..., $\hat{c}_k^{NB}\}$,

$$\mathcal{H} = \sum_{k \in BZ} \mathcal{H}_k, \quad (3.23)$$

with,

$$\mathcal{H}_k = \hat{\phi}_k^\dagger \begin{pmatrix} \epsilon_1 & \gamma_1^\parallel \cdot e^{ik\frac{a}{2}} & 0 & \gamma_{12}^\perp & 0 & \dots \\ \gamma_1^\parallel \cdot e^{-ik\frac{a}{2}} & \epsilon_1 & \gamma_{12}^\perp & 0 & 0 & \dots \\ 0 & \gamma_{12}^\perp & \epsilon_2 & \gamma_2^\parallel \cdot e^{ik\frac{a}{2}} & 0 & \dots \\ \gamma_{12}^\perp & 0 & \gamma_2^\parallel \cdot e^{-ik\frac{a}{2}} & \epsilon_2 & \gamma_{23}^\perp & \dots \\ 0 & 0 & 0 & \gamma_{23}^\perp & \epsilon_3 & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \end{pmatrix} \hat{\phi}_k \quad (3.24)$$

and,

$$\hat{\phi}_k = [\hat{c}_k^{1A}, \hat{c}_k^{1B}, \hat{c}_k^{2A}, \hat{c}_k^{2B}, \dots, \hat{c}_k^{NA}, \hat{c}_k^{NB}]^T. \quad (3.25)$$

The energy band structures of armchair ribbons are then calculated by diagonalizing the Hamiltonian (3.24). The result is illustrated in Fig. 3.10 for three different ribbon widths. Note that the topological approximation ($\epsilon_i = 0$ and $\gamma_i^\parallel = \gamma_{ij}^\perp = \gamma = 2.7$ eV) has been used for the calculation, which is equivalent to assume that the bulk graphene geometry is conserved in the ribbon, even at the mono-hydrogenated edges. In agreement with the prediction of the band-folding approximation, a direct gap appears at $k = 0$ and the energy dispersion around Γ is reminiscent of the Dirac cones.

The calculated band structures confirm the crucial role of the ribbon width upon the energy gap. While two third of the armchair ribbons exhibit a semi-conducting behavior, the remaining third keeps the graphene semi-metallic behavior. At $k = 0$, the eigenvalues of the tight-binding Hamiltonian can be extracted analytically, leading to an energy gap (Δ_N) which is width dependent :

$$\Delta_N = \begin{cases} \Delta_{3\ell} & = |\gamma_0| \left(4\cos\frac{\pi\ell}{3\ell+1} - 2 \right) \\ \Delta_{3\ell+1} & = |\gamma_0| \left(2 - 4\cos\frac{\pi(\ell+1)}{3\ell+2} \right) \\ \Delta_{3\ell+2} & = 0 \end{cases} \quad (3.26)$$

with $\Delta_{3\ell} > \Delta_{3\ell+1} > \Delta_{3\ell+2} = 0$. Here N and ℓ are integers and N refers to the ribbon width.

As a consequence, the present tight-binding approach predicts that N -aGNRs are metallic for every $N = 3\ell + 2$ (where ℓ is a positive integer), and semi-conducting in the other cases. However, such simple TB

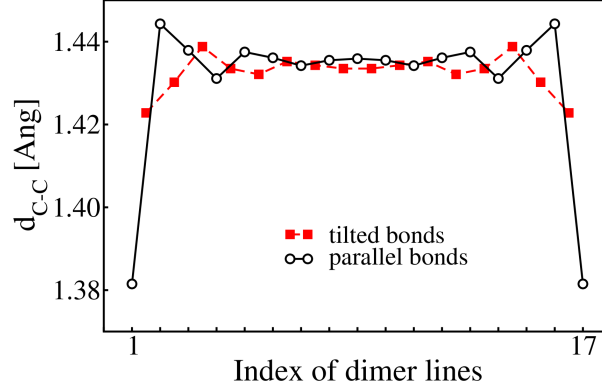


Figure 3.11: Evolution of the carbon-carbon bond length (d_{C-C}) across the 17-aGNR ribbon width as computed by an *ab initio* geometry optimization. In red, length of the carbon-carbon tilted with respect to the ribbon axis. In black, length of the carbon-carbon parallel to the ribbon axis

model with one orbital per site and constant site energies and hopping integrals between nearest neighbors does not account for the relaxation of the hydrogen passivated carbon atoms at the edge which is observed in most of large aromatic molecules. Indeed, the carbon atoms at the edges of the ribbon are passivated by hydrogen atoms (by some foreign atoms or molecules in general) so that one may expect the on-site energies at the edges to be different from those in the middle of the GNR. The bonding distances between carbon atoms at the edges are expected to change accordingly (see Fig. 3.11) leading to a shortening of the inter-atomic distance and an increase of the hopping integral between π -orbitals. The introduction of these modified on-site and hopping energies at the edges within the above TB model leads to the opening of small extra-gaps at $k = 0$ even for the $3\ell + 2$ -GNRs. The relaxation of the edge implies thus the semi-conducting behavior of all the aGNRs [110, 127]. These results compare well with *ab initio* calculations. For a ribbon of ~ 2 nm with a metallic behavior predicted by the topological tight-binding model, the *ab initio* estimated band gap is off ~ 0.05 eV (see Fig. 3.10). Furthermore the band structures computed either by means of adjusted TB or *ab initio* techniques are in excellent agreement with the experimental observation regarding the quantization energy (i.e. the energy spacing between the one dimensional sub-bands) and the energy splitting between the bands originating from the $\mathbf{K}$ and $\mathbf{K}'$ high symmetry points [131]. Finally, it has to be noted that the *ab initio* energy gap are further increased when the electron-electron correlations are taken into

account by means of GW corrections [132]. However, considering this effect, the energy gaps still decrease as the widths of the aGNR increase, reaching the zero-gap value of graphene for the infinite width.

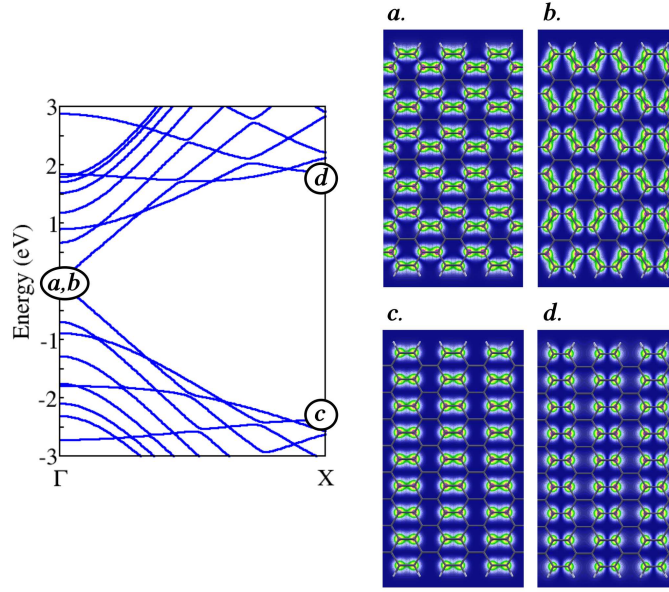


Figure 3.12: Energy band structure of 17-aGNR (left panel). Representations of the low energy electronic states (right panel). (a-d) Representations of the density of states associated with Bloch wave-functions either computed at the Γ or at the X high symmetry points as mentioned by letters in the left panel.

Finally, for sake of comparison with the case of zigzag shaped GNRs which is detailed hereafter, the local density of states associated with some low energy electronic states are plotted in Fig. 3.12. In spite of the edge relaxation, the low energy density of states (both occupied and unoccupied) is spread across the complete ribbon width and no edge states are reported. This is in striking contrast with the situation in zGNRs

3.3.3 Electronic structure of the zigzag ribbons

In this section, the same approach as presented herein for the aGNRs is applied to the zigzag shaped ribbon. The tight-binding derivation of the low energy band structure is presented and compared with DFT calculations.

As detailed before, by taking into account the periodicity of the ribbon, the tight-binding Hamiltonian is readily expressed as a Bloch sum ($\mathcal{H} = \sum_{k \in BZ} \mathcal{H}_k$). In the case of zGNRs, the ribbon topology leads to the following expression for $\mathcal{H}_k$,

$$\mathcal{H}_k = \gamma_0 \hat{\phi}_k^\dagger \begin{pmatrix} \epsilon_1 & 2 \cos(\frac{ka}{2}) & 0 & 0 & 0 & \dots \\ 2 \cos(\frac{ka}{2}) & \epsilon_2 & 1 & 0 & 0 & \dots \\ 0 & 1 & \epsilon_3 & 2 \cos(\frac{ka}{2}) & 0 & \dots \\ 0 & 0 & 2 \cos(\frac{ka}{2}) & \epsilon_4 & 1 & \dots \\ 0 & 0 & 0 & 1 & \epsilon_5 & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \end{pmatrix} \hat{\phi}_k \quad (3.27)$$

where $\hat{\phi}_k = [\hat{c}_k^{1A}, \hat{c}_k^{1B}, \hat{c}_k^{2A}, \hat{c}_k^{2B}, \dots, \hat{c}_k^{NA}, \hat{c}_k^{NB}]^T$.

In a first approximation, the topological approximation ($\epsilon_i = \epsilon = 0$ and $\gamma_{ij} = \gamma = 2.7\text{eV}$) is used. The energy band structures of zigzag ribbons are then obtained by diagonalizing the Hamiltonian of Eq. (3.27) on a regular grid of k -point along the 1D Brillouin zone. In agreement with the prediction of the band-folding approximation, a dispersion relation reminiscent of the Dirac cones appears around $k = \pm 2\pi/3$ (see Fig. 3.13(a)). However, an unpredicted feature appears independently of the ribbon width: the highest valence and lowest conduction bands form two partially flat bands at the Fermi level that extend on one third of the BZ ($2\pi/3 \leq |k| \leq \pi$) inducing a sharp peak in the density of states at E_F . Owing to the presence of these peculiar flat bands, the zigzag GNRs are thus predicted to remain metallic independently of the ribbon widths. This is confirmed by the energy band structures computed within the spin-degenerated DFT framework (see Fig. 3.13(b)). Besides, the energy gaps between the occupied and unoccupied *bulk* states (all states with the exception of those associated with the partially flat bands) present a monotonic decrease when increasing the ribbon width.

The origin of the quasi-flat bands is easy to understand analytically, as first demonstrated by Fujita and co-workers [113]. Considering a semi-infinite graphene plane with a zigzag-shaped edge, the translational symmetry of the semi-infinite graphene sheet along the edge allows to apply the Bloch theorem in the edge direction. One can thus associate the relative weights $\{c_i = (\dots, e^{ik(n-1)}, e^{ikn}, e^{ik(n+1)}, \dots)\}$ with the Bloch wave-function on the successive edge sites. Here, n indexes the edge sites as depicted in Fig. 3.14. For the electronic wave-function to be exact at $E = 0$, the topological tight-binding approximation (i.e. constant on-site energies and hopping integrals) imposes that for all atomic site β : $\sum_{\alpha} H_{\alpha\beta} c_{\alpha} = 0$, where the sum runs only over the nearest neigh-

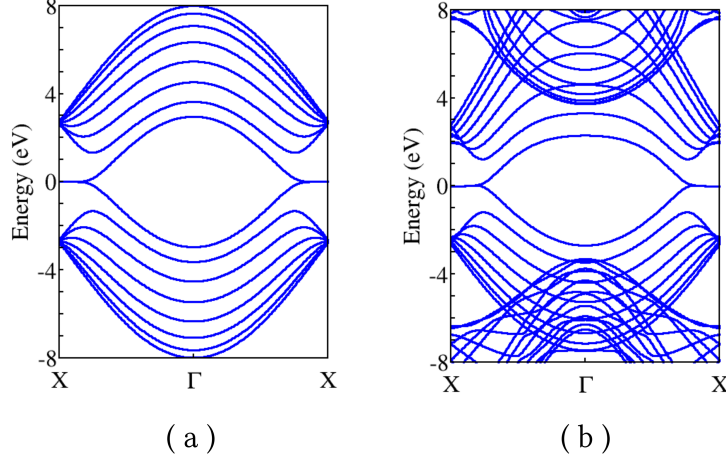


Figure 3.13: Energy band structure of zigzag nanoribbons (8-zGNR). Note that, contrarily to the case of armchair ribbons, the band structure does not change periodically with the ribbon width. (a) band structure computed within the TB model with constant hopping energy between nearest neighbors. (b) band structure computed within the DFT framework.

bor atomic sites. Applied to all atomic sites, this condition gives access to the components of the ($\epsilon = 0$) wave-function inside the semi-infinite plane. E.g. when applied to the atomic sites indicated by a cross in Fig. 3.14, the condition $\sum_{\alpha} H_{\alpha\beta} \cdot c_{\alpha} = 0$ produces the following system of equations,

$$\begin{cases} 0 = e^{ik(n+1)} + e^{ikn} + x \\ 0 = e^{ik(n)} + e^{ik(n-1)} + y \\ 0 = x + y + z \end{cases} \quad (3.28)$$

From which the wave function components x, y, z are found to be $x = D_k e^{ik(n+1/2)}$, $y = D_k e^{ik(n-1/2)}$ and $z = D_k^2 e^{ikn}$ with $D_k = -2\cos(k/2)$. Finally, the charge density appears to be proportional to $D_k^{2(m-1)}$ on the atomic sites belonging to the m^{th} zigzag chain counted from the edges. Since the charge density should not diverge within the semi-infinite graphene sheet, the condition $|D_k| \leq 1$ applies. This criterion defines the region of the Brillouin zone ($2\pi/3 \leq |k| \leq \pi$) where the flat band appears. The edge states thus penetrate progressively the semi-infinite graphene sheet for wave-vectors going from π to $2\pi/3$.

These analytical results are in good agreement with the low-energy electronic density distribution obtained with *ab initio* calculations (see

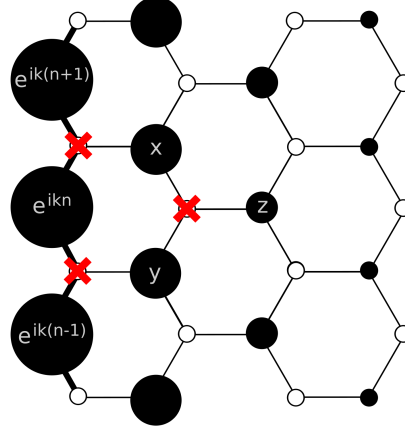


Figure 3.14: Analytic form of the edge state in semi-infinite graphene planes. The bold line represents the zigzag edge. The black circles represent the charge density on the atomic site belonging to the edge sub-lattice. The red cross denotes the sites where $E = 0$ conditions are applied.

Fig. 3.17). Note that, in contrast with the case of armchair GNRs, the modification of the carbon-carbon bonding distance at the edges (see Fig. 3.15) does not lead to significant changes in the low energy electronic structures. Indeed, the partially flat bands at the Fermi energy originate from topological reasons and are insensitive to the exact value of the hopping energy across the ribbon width. The *ab initio* computed eigenstates around the Fermi level reveal that these electronic states are mainly located at the zigzag edges of the GNR, and penetrates progressively into the ribbon for wave-vectors going from $k = \pi$ to $k = 2\pi/3$. In the ribbon, however, some dispersion appears before $k = 2\pi/3$ since the edge states coming from the opposite edges meet within the ribbon, overlap and form bonding and anti-bonding states. Previous theoretical works which have investigated the appearance of edge states for GNRs with general edge shapes (i.e. made of a succession of armchair and zigzag fragments), predict that sequences of four zigzag sites at the edge are sufficient to give rise to edge states [111]. Experimentally, STM and STS measurements [133] seems to corroborate the presence of edge states along homogeneous zigzag edges and around zigzag-like defects in armchair edge.

Another important feature related to zGNRs consists of the presence of magnetic order (spin degree of freedom) along the zigzag shaped edges. As mentioned above, the zigzag topology induces narrow-band

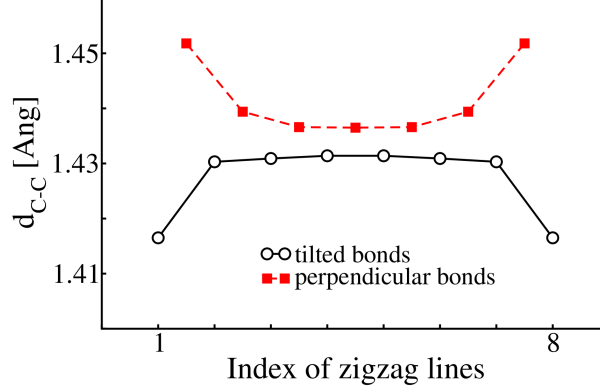


Figure 3.15: Evolution of the carbon-carbon bond length (d_{C-C}) across the 8-zGNR ribbon width as computed by an *ab initio* geometry optimization. In red, length of the carbon-carbon perpendicular to the ribbon axis. In black, length of the carbon-carbon tilted with respect to the ribbon axis

edge states at the Fermi energy allowing possible magnetic order along the edges [112, 121, 122, 110, 127]. Because the edge states lead to a sharp peak in the density of states at the Fermi level, zGNRs exhibit a Curie-like temperature dependence of the Pauli paramagnetic susceptibility [112]. Consequently, a crossover is predicted from high-temperature diamagnetic to low-temperature paramagnetic behavior in the magnetic susceptibility in zGNRs [112].

Upon inclusion of the spin degrees of freedom in the *ab initio* calculation, the zGNRs are predicted to have a magnetic insulating ground state with ferromagnetic order along the edges and anti-parallel spin orientation between the edges (Fig. 3.16). The difference in total energy per edge atom between non-spin-polarized and spin-polarized edge states is of the order of a few tens of meV [110]. For example, the electronic ground state of the ideal 8-zGNR reveals anti-parallel ($\uparrow\downarrow$) spin orientations between the edges (Fig. 3.16(a)) leading to a semi-conducting band structure (0.5 eV band gap) with full spin degeneracy. On the other hand, the magnetic configuration with parallel ($\uparrow\uparrow$) spin orientations between the edges (Fig. 3.16(b)) is found to be meta-stable (11 meV/edge-atom higher in energy). This configuration displays a metallic behavior, as the $\pi_{\uparrow}^*$ and $\pi_{\downarrow}$ bands are crossing at the Fermi energy, and presents a total magnetic moment of $0.51 \mu_B$ per edge atom.

Consequently, when the spin degree of freedom are taken into account, the presence of energy gaps for electrons in zGNRs can be ex-

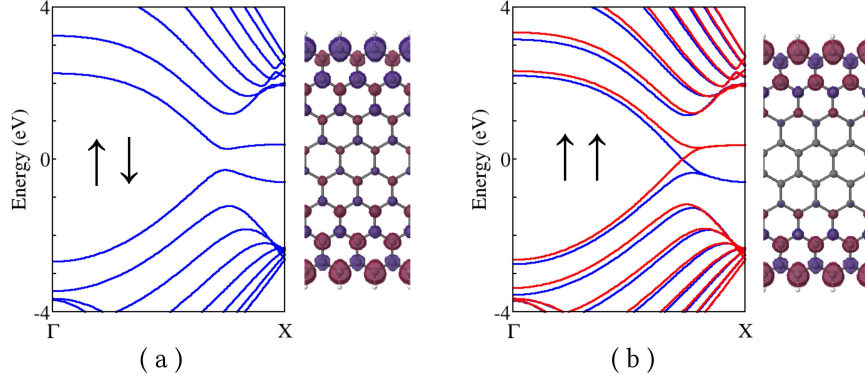


Figure 3.16: Spin polarized electronic structure of zigzag nanoribbons (8-zGNR). (a) $\uparrow\downarrow$ configuration (ground-state): upon the inclusion of the spin degree of freedom, the ribbon presents ferromagnetic order along its axis and anti-parallel coupling between the edges. (b) $\uparrow\uparrow$ configuration (11 meV/edge-atom higher in energy): the ribbon present ferromagnetic order along its axis and parallel coupling between the edges. On the left, energy band structure computed within the spin-DFT framework. On the right, Spin polarized electronic densities ($\rho_{\uparrow} - \rho_{\downarrow}$) iso-surfaces

plained in terms of the staggered sub-lattice potentials resulting from the magnetic ordering [134]. Such a situation is realized because the spin-polarized *edge*-states on opposite edges occupy different sub-lattices. Since the strength of the staggered potentials in the middle of the ribbon decreases as the ribbon width increases, the band gaps of zigzag GNRs are inversely proportional to the zGNRs width. Finally, it is worth noting that the band structure of zGNRs is slightly modified by the GW correction associated with the electron-electron correlation. Indeed, as detailed in Ref. [132], the self-energy corrections enlarge the energy gaps of all zGNRs and slightly increase the dispersion of the bands associated with the edge states.

3.3.4 Summary

In summary, as for 2-D graphene, such a simple topological tight-binding model is found to describe low energy properties with a degree of approximation high enough for many applications and is widely employed for studying transport properties in GNRs [111, 135, 136, 137, 138, 139]. However, *ab initio* calculations [110] reveal that GNRs with hydrogen passivated armchair or zigzag shaped edges both have nonzero band gaps

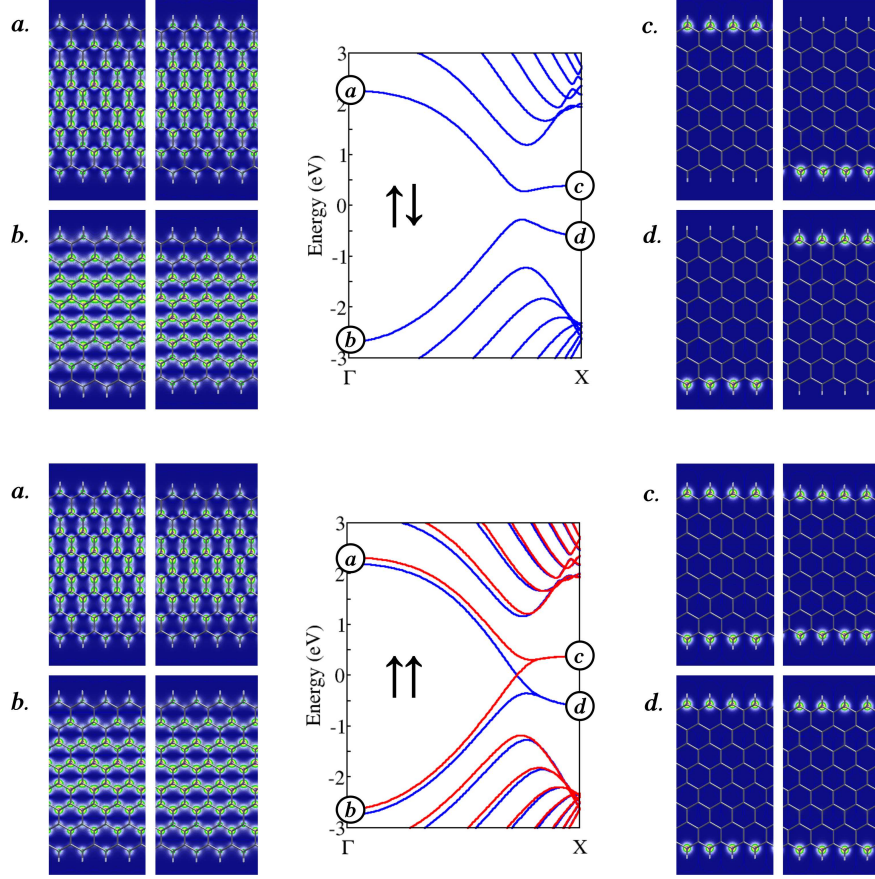


Figure 3.17: Low energy electronic states of zGNRs. Energy band structure of 8-zGNR (central panels) surrounded by representations of the low energy electronic states. (a-d) Representations of the density of states associated with Bloch wave-functions either computed at the Γ or at the X high symmetry points as mentioned by letters in the central panel. Top panel, the 8-zGNR in its ground state ($\uparrow\downarrow$) magnetic configuration. Bottom panel, the 8-zGNR in ($\uparrow\downarrow$) magnetic configuration.

independently of their width. In armchair ribbons, this is due to the noticeable modification of the bonding characteristics between atoms at the edges [120, 123]. In zigzag ribbons, the gap opening originates in the sub-lattice potential induced by the magnetic order.

3.4 Structure and stability of graphene edges

As illustrated in the previous sections, the atomic structure of the edges is responsible to a large extent for the electronic properties of graphene nanoribbons. This applies for many nanoscale materials where the surfaces and edges fix the symmetry inside the "bulk" and determine the corresponding low energy electronic structure. In GNRs, the edges also turn out to rule the appearance of flat π bands at the Fermi level and ferromagnetic ordering of π electrons along the ribbon axis. Aiming at future applications of graphene in electronic and/or spintronic devices, the precise control of the edges is thus crucial.

On one hand, a large portion of the theoretical studies of graphene is devoted to the physics of the edges (see e.g. Ref. [10, 11, 110, 111, 122, 127, 140, 141, 142, 143]). However, very few works consider the possibility for the edge to relax towards other geometries than the standard mono-hydrogenated zigzag and armchair patterns [10, 11]. On the other hand, experimental studies of the edge are even more rare due to the difficulty to resolve atomically the graphene at the edges. For example, in most of experimental studies which characterize the graphene boundaries using Scanning Tunneling Microscopy (STM) or Atomic Force Microscopy (AFM), graphene is not atomically resolved at the edges, and the crystallographic orientation of the edges is determined with respect to the atomic scale contrast observed within the bulk of the samples [128, 144, 145, 146]. Recently, alternative characterization routes based on Transmission Electron Aberration-corrected Microscope (TEAM) have been proposed [130, 147]. But, though impressive pictures have been produced, the detailed atomic geometries of graphene edges still remains a matter of interpretation. In addition, while TEAM microscopes provide access to the structure and dynamic of the atomic network, the electron beam (typically ~ 80 keV) acts as an energy bath so that it is difficult to estimate in what extent the observed structures correspond to stable geometries in ambient conditions.

The lack of edge characterization continues to prevent a deep understanding of many experimental results. For example, despite theoretical calculations that predict nearly flat bands around the Fermi level for the zigzag edges, the experimental measurements reveal a semi-conducting behavior for all tested GNRs. Besides, the measured transport properties of actual ribbons seem to be independent of their crystallographic orientation [6, 117, 148, 149]. Many reasons related to the samples preparation (e.g. presence of adsorbates, substrate effects,...) or to the appearance of mobility gaps induced by edge disorder have been proposed to explain this disagreement between theory and experiments [139, 150, 151].

However, being able to determine the actual edge structure at given experimental conditions would surely help in solving this issue.

In this section, the relative stability of zigzag and armchair edges is investigated by means of *ab initio* calculations. We report spin polarized DFT calculations of the formation energy and electronic structure of various hydrogen-terminated edge patterns. The ribbons studied are periodic and present the same atomic structure on both edges. The *ab initio* calculation of the total energies relies on the generalized gradient approximation (GGA) to describe the exchange-correlation part of the Hamiltonian and a numerical atomic orbital (NAO) basis set of DZP quality has been used to expand the wave-functions in conjunction with Trouiller-Martin norm-conserving pseudo-potentials³.

3.4.1 Edge formation energies

Many edge patterns have been considered, these are illustrated in Figs. 3.18-3.21. The pristine zigzag and armchair patterns with various hydrogen coverage of the carbon atoms on the edges have been included in the study. Hereafter, these structures are labelled as $z_{n_1 n_2 \dots n_x}$ and $a_{m_1 m_2 \dots m_x}$ respectively, where n_i and m_i refer to the number of hydrogen atoms covalently bonded to the i^{th} edge side, and x is the number of adjacent edge-sites within the unit-cell of length a (see Figs. 3.18 and 3.19). As an example, z_{211} refers to a GNR with zigzag shaped edges whose unit cell is build from a sequence of three elementary zigzag units. The carbon atoms on the edges of the first zigzag unit are doubly hydrogenated, the other ones are saturated by one hydrogen per carbon site.

In addition to these zigzag and armchair patterns, other reconstructions of the edges have been considered. The $z(57)_{ij}$ structure depicted in Fig. 3.20(b) is a reconstruction of the zigzag edge where two adjacent hexagons of the edge transform in a pentagon and an heptagon. This edge pattern would correspond to a cut through a line of Stone-Wales

³In order to get accurate energies, the double- ζ plus polarization basis set has been complemented by the 3s numerical atomic orbital for carbon atoms. Furthermore, since NAOs basis sets suffer a lack of systematic variational convergence, it is important to carefully check the validity of the basis set. In particular, while minimal basis sets are sometimes appropriate for semi-quantitative calculations of electronic properties around the Fermi level, a high degree of accuracy and a well converged basis set are required to tackle the relative stability of edges structures with different stoichiometries. In order to test the accuracy and completeness of the basis set used throughout this study, the computed relative edge formation energies have been compared with values obtained within the PAW computational scheme. As detailed hereafter, the agreement between the NAOs and PAW results allows us to be confident with respect to the completeness of the NAOs basis set.

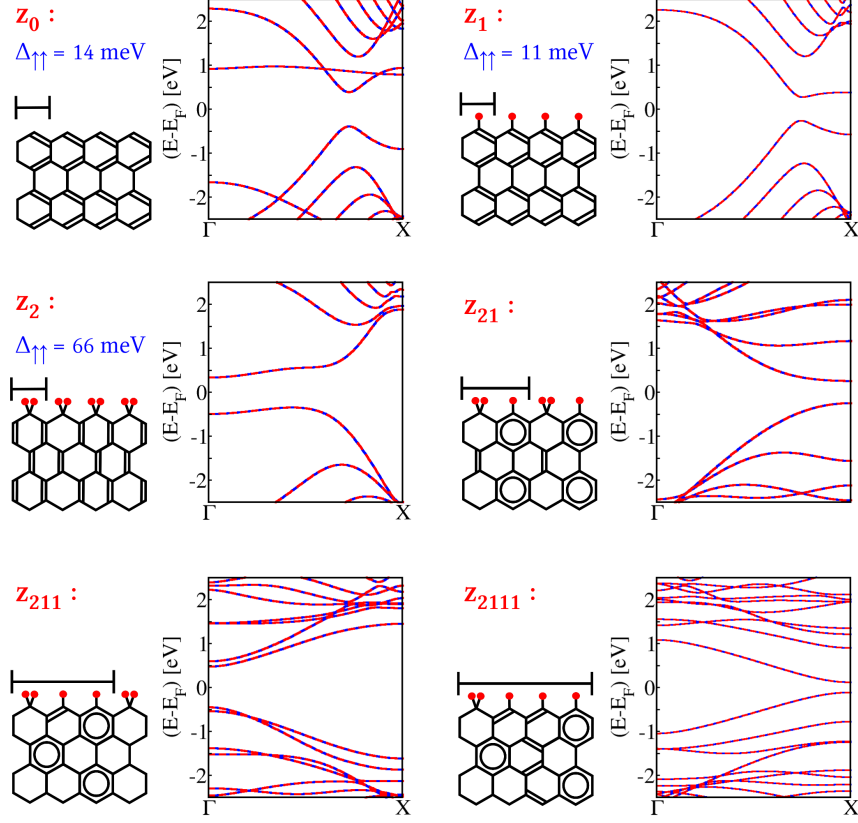


Figure 3.18: Schematic representation and electronic band structure of various possible edge reconstructions for the zigzag graphene ribbons. The atomic structures depicted are periodic along the ribbon edge. The length of the unit cell is represented by a line segment. The carbon network is represented within the Clar's sextet notation (black lines), the hydrogen atoms are the filled red circles. The electronic band structure are represented along the one dimensional unit cell between the Γ and X special points. The α and β collinear spin orientations correspond to the solid blue and dotted red lines. All the band structures present full spin degeneracy. In case of relevance, the energy differences $\Delta_{\uparrow\uparrow} = E_{\uparrow\uparrow} - E_{\uparrow\downarrow}$ are mentioned. Note that the band structures represented are all associated with the $\uparrow\downarrow$ magnetic configuration.

defects [152] and should allow to connect the graphene plane with a Haackelite structure [153]. It has recently been proposed as a possible spontaneous reconstruction of the z_{00} edge [11]. The $z(600)_{ijkl}$ structure

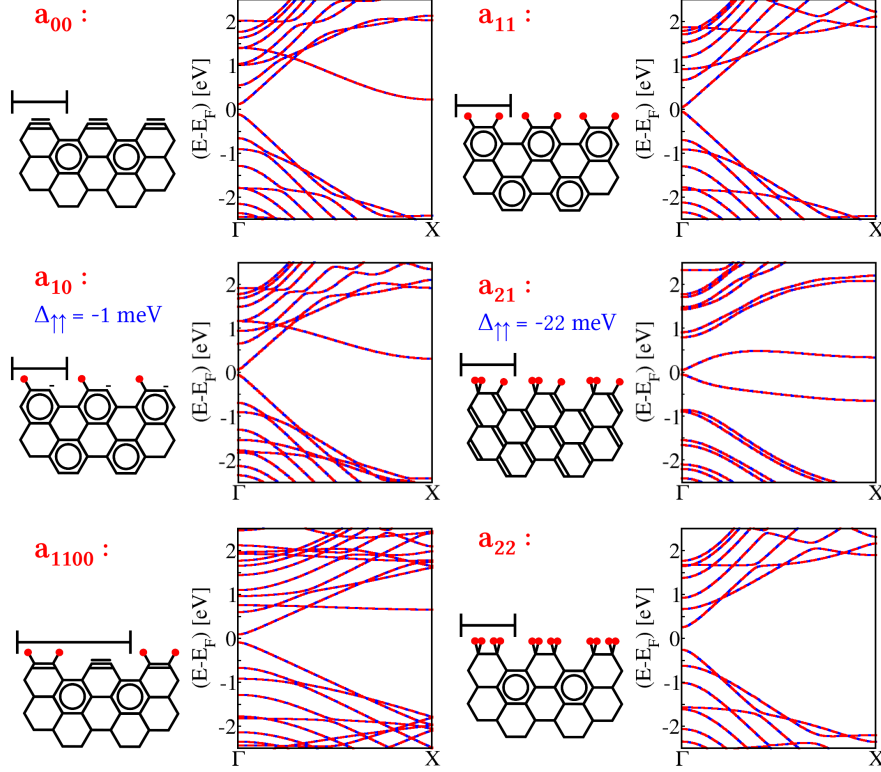


Figure 3.19: Schematic representation and electronic band structure of various possible edge reconstructions for the armchair graphene ribbons. The atomic structures depicted are periodic along the ribbon edge. The length of the unit cell is represented by a line segment. The carbon network is represented within the Clar's sextet notation (black lines), the hydrogen atoms are the filled red circles. The electronic band structure are represented along the one dimensional unit cell between the Γ and X special points. The α and β collinear spin orientations correspond to the solid blue and dotted red lines. All the band structures present full spin degeneracy. In case of relevance, the energy differences $\Delta_{\uparrow\uparrow} = E_{\uparrow\uparrow} - E_{\uparrow\downarrow}$ are mentioned. Note that the band structures represented are all associated with the $\uparrow\downarrow$ magnetic configuration.

(see Fig. 3.20(a)) has also been reported recently [10]. Its geometry corresponds to a zigzag edge from which two third of the carbon atoms on the edges have been removed giving rise to a saw blade pattern. The $z(TDP)_{ij\dots}^a$ structure (see Fig. 3.20(c)) is a new reconstruction that we propose here. It may be obtained from the periodic adsorption of ad-

atoms along the zigzag edges and involves an sp^3 hybridization of several carbon atoms at the edge. Geometrically, this hypothetical structure consists in the periodic repeat of triangular di-pyramids (TDP) of carbon atoms along the zigzag edge. Within the $z(TDP)_{ij...}^a$ notation, the a superscript refers to the number of hydrogen atoms bonded to the apex of the pyramids and the $ij...$ subscripts describe the hydrogenation level of the carbon sites at the GNR edge.

The $a(677)_{ij}$ edge pattern (see Fig. 3.21(b)) has been proposed recently as a probable structure competing with the standard armchair edge [11]. This pattern is similar in nature with the $a(57)_{ij}$ (see Fig. 3.21(c)) since they both corresponds to a reconstruction of the edge by a Stone-Wales-like mechanism (i.e. the 90° rotation of carbon-carbon σ -bond) [152]. Note that the $a(57)$ structure is highly interesting since its specific topology would allow to connect armchair and zigzag ribbons side by side. Finally, the $a(56)_i$ structure (see Fig. 3.21(c)) is slightly different since its formation requires the diffusion of carbon atoms in order to obtain the alternation of hexagons and pentagons along the edge.

We now turn to the stability analysis. At zero temperature and for isolated systems, it is quite common to rely on the edge formation energies (ξ_{H_2}),

$$\xi_{H_2} = \frac{1}{2a} \left(E_{GNR} - N_C E_{Bulk} - N_H \frac{E_{H_2}}{2} \right) \quad (3.29)$$

in order to compare the relative stability of systems with different number of carbon and hydrogen atoms inside. Here, a corresponds to the length of the GNR unit cell. E_{GNR} , E_{Bulk} and E_{H_2} are respectively the total energies of the GNR unit cell, the energy associated with one carbon atom in the pristine graphene plane and the total energy of the isolated H_2 molecule. N_C and N_H are the numbers of carbon and hydrogen atoms in the GNR unit cell. The *ab initio* computed values of ξ_{H_2} associated with the various reconstructions of the zigzag and armchair edges are reported in tables 3.1 and 3.2 for ribbons of ~ 2 nm width (i.e. 8-zGNRs and 17-aGNRs).

By comparing the edge formation energies ξ_{H_2} , the relative stability of the isolated systems can be determined. The computed energies reveal that, in such conditions, the most stable edge is the $z(600)_{2222}$ pattern. This is in striking contrast with the recent proposals for the most stable GNRs edges [11, 10]. These results confirm, however, that neither the standard zigzag nor the standard armchair edges present the lowest edge formation energy. The $z(600)_{2222}$ configuration is followed directly by the a_{22} pattern (~ 10 meV above in energy), and then by the a_{11} , z_{21} , z_{211} , and z_{2111} configurations (more than 100 meV above in energy).

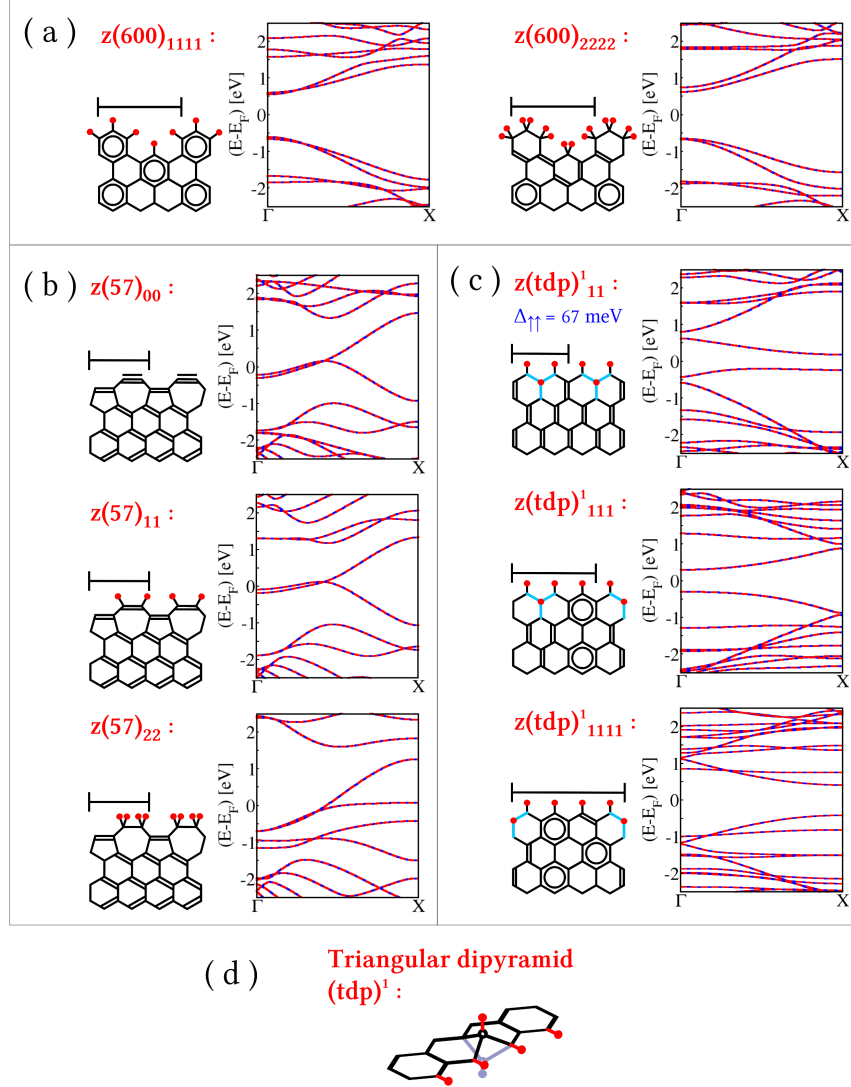


Figure 3.20: Schematic representation and electronic band structure of various possible edge reconstructions for the zigzag graphene ribbons. The atomic structures depicted are periodic along the ribbon edge. The length of the unit cell is represented by a line segment. The carbon network is represented within the Clar's sextet notation (black lines), the hydrogen atoms are the filled red circles. The electronic band structure are represented along the one dimensional unit cell between the Γ and X special points. The α and β collinear spin orientations correspond to the solid blue and dotted red lines. All the band structures present full spin degeneracy. Examples of $z(600)_{ijkl}$ (a), $z(57)_{ij}$ (b) and $z(tdp)_{ij...}^a$ (c) reconstructions of the zigzag edges. The C-C involved in the triangular di-pyramid arrangement are colored in light blue (d) Structural details of the triangular di-pyramid arrangement. In case of relevance, the energy differences $\Delta_{\uparrow\uparrow} = E_{\uparrow\uparrow} - E_{\uparrow\downarrow}$ are mentioned. Note that the band structures represented are all associated with the $\uparrow\downarrow$ magnetic configuration.

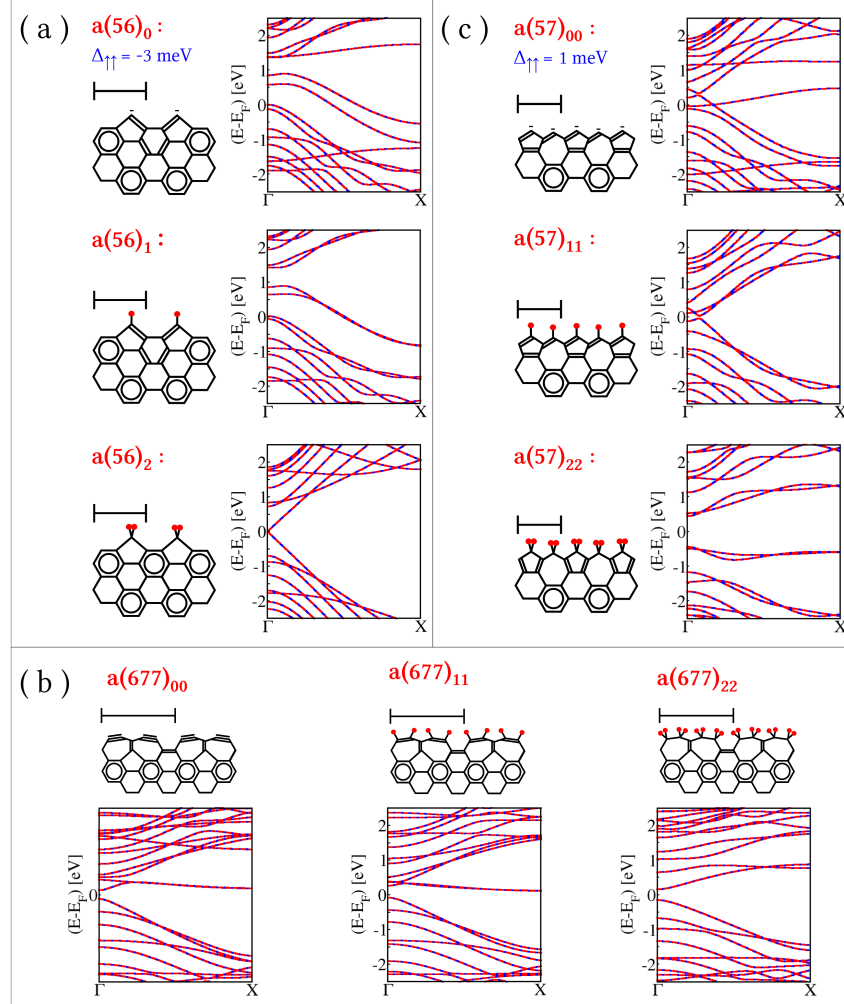


Figure 3.21: Schematic representation and electronic band structure of various possible edge reconstructions for the armchair graphene ribbons. The atomic structures depicted are periodic along the ribbon edge. The length of the unit cell is represented by a line segment. The carbon network is represented within the Clar's sextet notation (black lines), the hydrogen atoms are the filled red circles. The electronic band structure are represented along the one dimensional unit cell between the Γ and X special points. The α and β collinear spin orientations correspond to the solid blue and dotted red lines. All the band structures present full spin degeneracy. Examples of $a(56)_i$ (a), $a(677)_{ij}$ (b) and $a(57)_{ij}$ (c) reconstructions of the armchair edge. In case of relevance, the energy differences $\Delta_{\uparrow\downarrow} = E_{\uparrow\downarrow} - E_{\downarrow\uparrow}$ are mentioned. Note that the band structures represented are all associated with the $\uparrow\downarrow$ magnetic configuration.

These are the standard armchair and zigzag shapes with various hydrogen coverages of the carbon atoms on the edge. In the next section, the concepts of aromaticity will bring some additional clarifications on the close connections between the ribbon topology, its relative stability and its electronic/magnetic properties.

	ρ_H ($\text{\AA}^{-1}$)	ξ_{H_2} (eV/ $\text{\AA}$)	
		NAOs	PAWs
z_0	0.000	1.175	1.167
z_1	0.403	0.078	0.078
z_2	0.798	0.170	0.192
z_{21}	0.601	0.003	0.017
z_{211}	0.536	-0.005	
z_{2111}	0.503	0.012	
$z(57)_{00}$	0.000	1.047	1.147
$z(57)_{11}$	0.410	0.342	
$z(57)_{21}$	0.611	0.344	
$z(57)_{22}$	0.816	0.243	
$z(600)_{0000}$	0.000	1.340	
$z(600)_{1111}$	0.535	0.032	
$z(600)_{1221}$	0.803	0.023	
$z(600)_{2112}$	0.802	0.014	
$z(600)_{2222}$	1.070	-0.130	
$z(TDP)_{00}^0$	0.000	2.357	
$z(TDP)_{11}^0$	0.402	1.273	1.099
$z(TDP)_{22}^0$	0.795	2.033	
$z(TDP)_{00}^1$	0.403	1.796	
$z(TDP)_{11}^1$	0.806	0.772	
$z(TDP)_{22}^1$	1.193	1.915	
$z(TDP)_{111}^1$	0.672	0.441	
$z(TDP)_{1111}^1$	0.605	0.309	
$z(TDP)_{11111}^1$	0.565	0.247	

Table 3.1: Edge formation energy and hydrogen density ($\rho_H = \frac{N_H}{2a}$) for the various reconstructions of zigzag ribbons. Comparison between the values calculated within the NAOs and PAWs computational schemes.

	ρ_H ($\text{\AA}^{-1}$)	ξ_{H_2} (eV/ $\text{\AA}$)	
		NAOs	PAWs
a_{00}	0.000	1.059	0.999
a_{10}	0.232	0.644	
a_{11}	0.464	0.022	0.026
a_{21}	0.695	0.177	
a_{22}	0.928	-0.119	-0.083
a_{1100}	0.232	0.519	
$a(56)_0$	0.000	1.394	
$a(56)_1$	0.237	0.715	
$a(56)_2$	0.476	0.405	0.386
$a(677)_{00}$	0.000	1.170	
$a(677)_{11}$	0.476	0.440	
$a(677)_{22}$	0.948	0.240	
$a(57)_{00}$	0.000	1.954	
$a(57)_{11}$	0.447	0.661	
$a(57)_{21}$	0.668	0.832	
$a(57)_{22}$	0.889	0.741	

Table 3.2: Edge formation energy and hydrogen density ($\rho_H = \frac{N_H}{2a}$) for the various reconstructions of armchair ribbons. Comparison between the values calculated within the NAOs and PAWs computational schemes.

3.4.2 Gibbs free energies

Though the edge formation energies ξ_{H_2} bring some insights on the relative stability of GNRs, ξ_{H_2} does not account for the gas phase environment presents in most of experimental and application situations. At given conditions of pressure (P) and temperature (T), the relative stability of different condensed systems in a multicomponent gas phase environment is ruled out by their surface/edge free energies. A detailed methodology for the DFT calculation of surface free energy is given in Ref. [154]. In the two dimensional cases considered here, in presence of molecular H_2 gas at partial pressure P_{H_2} , one can define the GNRs edge free energy as,

$$G_{H_2}(T, P) = \frac{1}{2a} \left(G_{GNR}(T, P) - N_C G_{Bulk}(T, P) - \frac{N_H}{2} \mu_{H_2}(T, P_{H_2}) \right) \quad (3.30)$$

where G_{GNR} is the Gibbs free energy per unit cell of the GNRs, G_{Bulk} is the Gibbs free energy per atom of the bulk graphene plane, N_C and N_H

are the numbers of carbon and hydrogen atoms within the GNR unit cell, and μ_{H_2} is the chemical potential of molecular H_2 gas [$\mu_{H_2}(T, P_{H_2}) = G_{H_2}(T, P_{H_2})$].

As presented hereafter, the G_{H_2} formula can be reformulated in such a way to refer only to energies easily tractable within the DFT scheme and data tabulated in standard thermodynamic tables. The chemical potential of an ideal gas can be written as,

$$\mu_X(T, P_X) = \mu_X(T, P_X^\circ) + k_B T \ln\left(\frac{P_X}{P^\circ}\right). \quad (3.31)$$

This allows us to calculate μ_{H_2} at any pressure knowing the value of $\mu_{H_2}(T, P^\circ)$. Furthermore, since μ is nothing but a Gibbs's free energy, the chemical potential of molecular H_2 gas can be expressed as,

$$\begin{aligned} \mu_{H_2}(T, P_{H_2}) &= \mu_{H_2}(0, P_{H_2}^\circ) + [\mu_{H_2}(T, P_{H_2}^\circ) - \mu_{H_2}(0, P_{H_2}^\circ)] \\ &\quad + k_B T \ln\left(\frac{P_{H_2}}{P^\circ}\right), \\ &= \mu_{H_2}(0, P_{H_2}^\circ) + [H_{H_2}^\circ(T) - H_{H_2}^\circ(0) - TS_{H_2}^\circ(T)] \\ &\quad + k_B T \ln\left(\frac{P_{H_2}}{P^\circ}\right), \end{aligned} \quad (3.32)$$

where H° , S° are the enthalpy and entropy at the pressure of reference usually taken as $P^\circ = 1$ bar. The values of H° and S° are tabulated for most chemical components in thermodynamical tables (e.g. in Ref. [155]). The value of $\mu_{H_2}(0, P_{H_2}^\circ)$, which is the enthalpy of the H_2 molecule at $T = 0$ K, commonly serves as the energy reference in thermodynamic. One can conveniently define the chemical potential on the DFT energy scale as,

$$\begin{aligned} \mu_{H_2}^{dft}(T, P_{H_2}) &= E_{H_2}^{dft}(T = 0) + [H_{H_2}^\circ(T) - H_{H_2}^\circ(0) - TS_{H_2}^\circ(T)] \\ &\quad + k_B T \ln\left(\frac{P_{H_2}}{P^\circ}\right) \end{aligned} \quad (3.33)$$

$$= E_{H_2}^{dft}(T = 0) + \mu_{H_2}^{rel}(T, P_{H_2}). \quad (3.34)$$

Finally, the GNRS edge free energy can be rewritten as,

$$\begin{aligned} G_{H_2}^{dft}(T, P) &= \frac{1}{2a} \left(G_{GNR}^{dft}(T, P) - N_C G_{Bulk}^{dft}(T, P) - \frac{N_H}{2} \mu_{H_2}^{dft}(T, P_{H_2}) \right), \\ &\simeq \frac{1}{2a} \left(G_{GNR}^{dft}(0, P) - N_C G_{Bulk}^{dft}(0, P) - \frac{N_H}{2} \mu_{H_2}^{dft}(T, P_{H_2}) \right), \\ &\simeq \frac{1}{2a} \left(E_{GNR}^{dft}(0, P) - N_C E_{Bulk}^{dft}(0, P) - \frac{N_H}{2} \mu_{H_2}^{dft}(T, P_{H_2}) \right), \\ &\simeq \xi_{H_2} - \left(\frac{N_H}{2L} \right) \frac{\mu_{H_2}^{rel}}{2}, \end{aligned} \quad (3.35)$$

where the second equality is true under the assumption that the temperature dependence of G_{GNR} and G_{Bulk} is negligible with respect to that of the gas phase. Note that molecular dynamics calculations can provide corrections in order to go beyond the athermal limit. However, we will restrict our calculations to this "athermal" approximation. Traditionally, in phase diagrams, $G_{H_2}T, P$ is plotted as a function of μ^{rel} . Using the relation (3.35), we have computed the phase diagrams associated with the reconstruction of the zigzag and armchair graphene boundaries. These are plotted in Fig. 3.22. For comparison, we note that at ambient conditions ($P = 1$ bar and $T = 300$ K), the partial pressure P_{H_2} is about 5.10^{-7} bar which leads to a value of $\mu_{H_2}^{rel}(300K) \sim -0.69$ eV.

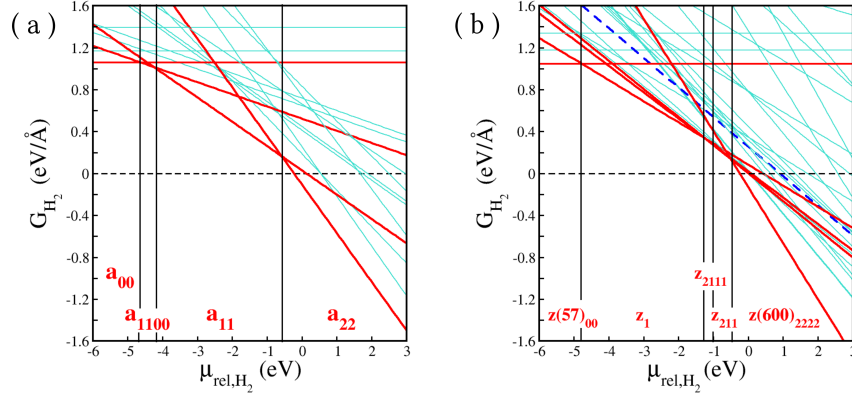


Figure 3.22: Formation energies (G_{H_2}) as a function of the chemical potential μ_{H_2} for all the edge configurations investigated in the present work. The left and right panels detail the case of reconstructed armchair and zigzag edges, respectively. The red lines correspond to edge configurations which appear to be the most stable for some values of the chemical potential. The vertical black lines indicate the limits of the stability regions. The other edge configurations are represented with by turquoise lines. The dotted blue line corresponds to the $z(TDP)_{1111}^1$ edge configuration.

The curves of G_{H_2} as a function μ_{H_2} associated with the different reconstructions of the edges are plotted in Fig. 3.22. The armchair and zigzag ribbons are further compared in Fig. 3.23. At a given chemical potential μ_{H_2} , the most stable ribbon configuration is the one with the lowest edge free energy. In addition, to the total energies, the electronic band structures of the various GNRs have also been computed, and are depicted in Figs. 3.18-3.21.

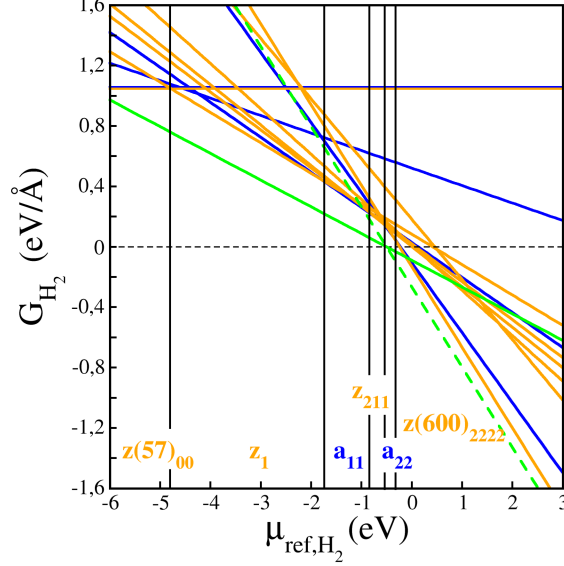


Figure 3.23: Formation energies ($G_{H_2}^{dft}$) as a function of the chemical potential μ_{H_2} for all the edge configurations investigated in the present work. The blue and orange lines correspond respectively to armchair and zigzag configurations. The vertical black lines indicate the limits of the stability regions.

Various conclusions can be drawn from the data presented here above (Figs. 3.18-3.23). First, one notes that, depending on their edge profile, zigzag and armchair GNRS may exhibit either a semi-conducting or metallic behavior. Furthermore, the topology of the edge rules the presence of partially filled electronic states at the edges and the appearance of magnetic ordering along the ribbon axis. Second, our analysis in terms of the edge free energy strongly contrasts with the widely spread idea that armchair shaped edges are globally more stable. Indeed, our results evidence the strong dependence of the most stable edge structure on the experimental conditions. At 300K, for standard and high hydrogen partial pressure ($P_{H_2} > 5.10^{-10}$ bar), three edge configurations are particularly relevant, namely the z_{211} , a_{22} and $z(600)_{1111}$ patterns. Third, the most commonly studied a_{11} and z_1 edge structures appear to be stable only at low and very low hydrogen concentrations ($P_{H_2} < 5.10^{-10}$ bar). Furthermore, this observation extends to all the edge topologies that involve partially filled states along the edges, evidencing the poor robustness of such states upon the GNRS functionalization. Finally, at high hydrogen concentrations, G_{H_2} becomes negative suggesting that graphene is

not anymore the most stable carbon configuration. Indeed, in such extreme conditions, the high pressure of hydrogen allows the stabilization of various hydrogenated allotropes. By sake of comparison, the energy associated with the complete hydrogenation of the graphene plane (i.e. the formation energy of graphane) is reported in Fig. 3.23 (green lines). Note that, in the case of graphane, the formation energy is a surface property expressed in $[eV/\text{\AA}^2]$.

3.4.3 Interpretation in terms of the Clar sextet theory

The concept of aromaticity has long been used in the chemical literature. Many experimental and theoretical studies using different approaches and methods have contributed to build a unified description of both the local and global characteristics of aromaticity. One of the outstanding contributions in this field was made by Clar in the 1970s. He proposed an interpretation of the electronic structure of polycyclic aromatic hydrocarbons (PAHs) based on the formal arrangement of delocalized π -electrons in aromatic sextets [156, 157]. Here, an aromatic sextet (sometimes called benzenoid aromatic ring) is defined as the benzene-like arrangement of six delocalized π -electrons on a ring. In terms of resonance theory, it can be viewed as the resonance between two hexagonal rings with alternating single and double bonds (see Fig. 3.24). Clar's theory describes the π -electronic system of hydrocarbons on the basis of the resonance structure that maximizes the number of aromatic sextets drawn for the system. (i.e. according to Clar, the most stable isomers of a given hydrocarbon are those with the highest numbers of aromatic sextets). Notably, this satisfactorily describes the observed stability of large PAHs and provides reliable indications on their magnetic behavior [158, 159, 160]. While, Clar's concepts originate from an intuitive interpretation of experimental facts, there have been many works grounding their theoretical justification [161, 162]. Within the Huckel framework for example, it is reported that the preferred resonance structures of PAHs are those that maximize the number of isolated aromatic sextets.

Similarly to large PAHs, various properties of carbon nanosystems can be understood to a large extent by the analysis of the π -electronic structure. Recently, the Clar's rules have been shown to provide a satisfactory description of the electronic and chemical properties of carbon nanotubes [163, 164]. Such simple concepts of organic chemistry have also been used to rationalize the stability and electronic properties of GNRs [12, 10]. Here, we extend the previous studies and we describe both the edge stability and the electronic properties of reconstructed

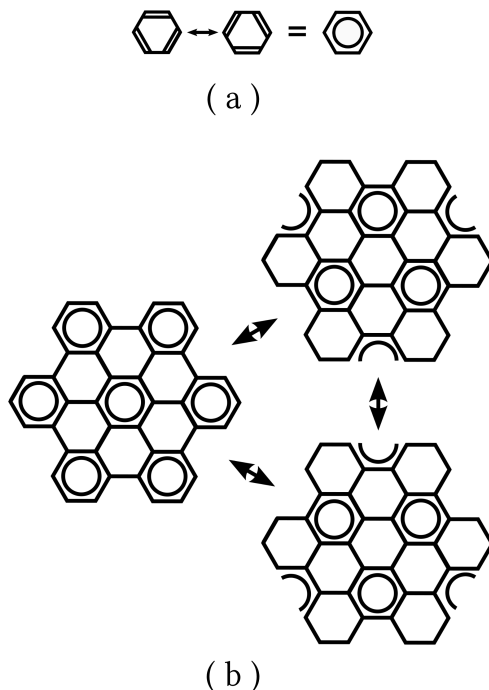


Figure 3.24: (a) Representation of the benzenoid aromatic ring within the standard Clar's sextet scheme. (b) Three equivalent representations of the bulk graphene as the ideal case of aromaticity. All the π electrons belong to a benzenoid ring and the sextet density $\rho_{sx} = \frac{1}{3}$.

armchair and zigzag GNRS in terms of Clar sextet theory.

Within Clar's theory, graphene is the ideal 2D case of delocalized π -electrons. Indeed, graphene can be viewed as the resonance between three structures where all π -electrons belong to an aromatic sextet (represented by circles in Fig. 3.24). In each resonance structure, one third of the hexagonal rings is benzenoid and no double bonds have to be drawn. Here, we use the sextet density $\rho_{sx} = (\# \text{ sextets} / \# \text{ hexagons})$ to characterize the benzenoid (aromatic) character of GNRS. An example of full benzenoid structure is given by the graphene plane where ($\rho_{sx} = \frac{1}{3}$). In Figs. 3.18 to 3.21, the edge profiles are drawn in a representation that maximizes the number of aromatic sextets. The Clar's representations of the standard armchair (a_{22}) and zigzag (z_1) edge profiles appear to be completely different, illustrating the two extreme cases of fully benzenoid ($\rho_{sx}(a_{22}) = \frac{1}{3}$) and non-benzenoid ($\rho_{sx}(z_1) = 0$) systems.

According to Clar's rule, the z_1 edge profile is thus expected to be less stable than other edge shapes compatible with a fully benzenoid GNR. From this point of view, the z_1 edge shape is not a favorable boundary profile for the hexagonal network of π -electrons and may be seen as a good candidate for reconstruction. As reported in Fig. 3.18, periodic hydrogenation of the zigzag edge modifies the aromatic character of the zGNRs. The z_{21} , z_{211} and z_{2111} edge profiles restore a partial aromaticity within the ribbon ($\rho_{sx}(z_{21}) = \frac{1}{4}$, $\rho_{sx}(z_{211}) = \frac{1}{3}$, $\rho_{sx}(z_{2111}) = \frac{1}{4}$). According to Clar's rule, the z_{211} profile is then expected to be the most stable zigzag edge profile.

In contrast with the z_1 edge profile, the a_{11} and a_{22} profiles are compatible with the bonding pattern of the infinite graphene plane. Consequently, one may expect the a_{11} and a_{22} edge to be stable and relatively inert. This is globally true for all the edge structures that preserve the *armchair* boundary of the $\pi - \pi^*$ electronic network (i.e. a_{22} , a_{11} , a_{1100} , a_{00}). Note that while the $a(56)$ edge is compatible with the fully benzenoid character of the GNR, the large edge strains introduced by the pentagonal terminations makes this edge profile less stable. These predictions are in good agreement with the *ab initio* computed edge-formation energies presented in Table 3.1.

In addition, as pointed out by T. Wassmann and co-workers [10], we note that all the "aromatic" edge structures (those with a sextet density $\rho_{sx} = \frac{1}{3}$) do not produce edge states and consequently do not give rise to magnetic order along the edges. This situation can be understood in terms of the Clar's concepts as well. When the sextet density in the vicinity of the edge is smaller than the one of bulk graphene, the low energy electronic structure of the ribbon results from a competition between the bulk, where the aromaticity prevails, and the edge, where all carbon atoms tends to form four saturated bonds. It is precisely such a competition, which, by forcing some edge atoms to be over- or under-saturated gives rise to these electronic defects, i.e. the edge states.

Finally, Clar's structures also allow us to rationalized the dependence of the electronic properties of GNRs with respect to their width. It is well known that the electronic properties of standard a_{11} -GNRs, such as their energy gap, fluctuate periodically with the ribbon width. On one hand, the monotonic decrease of the energy gap for increasing widths is the direct manifestation of the electronic confinement in the direction perpendicular to the ribbon axis. On the other hand, the periodic pattern superimposed to this monotonic decrease is due a periodic variation of the electronic structure at the ribbon termination as highlighted by the Clar's representation. Here, we show that this periodic behavior happens for all the benzenoid or partially benzenoid GNRs.

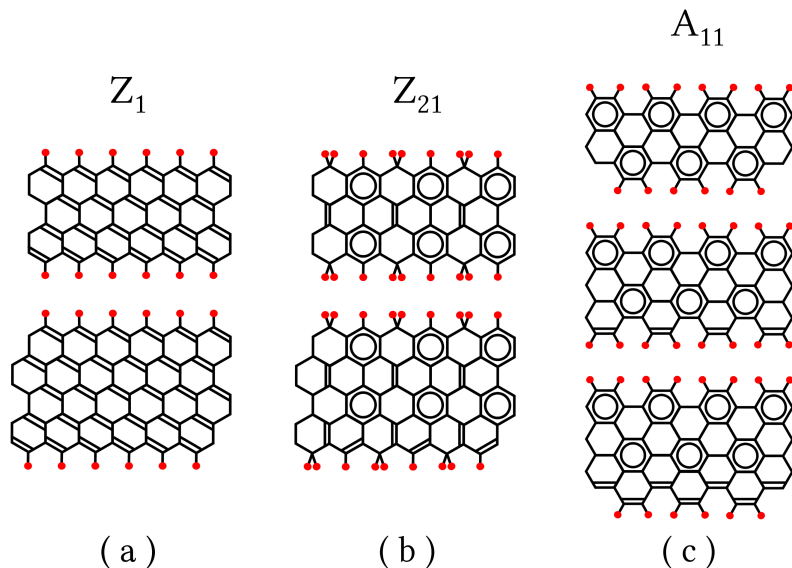


Figure 3.25: Clar's representations of $[z_1]$ -, $[z_{21}]$ -, and $[a_{11}]$ - GNRs of various widths. (a) $[z_1]$ -GNRs of widths ($N = 4$ and $N = 5$). (b) $[z_{21}]$ -GNRs of widths ($N = 4$ and $N = 5$). (c) $[a_{11}]$ -GNRs of widths ($N = 6$, $N = 7$ and $N = 8$).

The Clar's representation of GNRs with z_1 , z_{21} and a_{11} edge profiles are depicted for different ribbon widths in Fig. 3.25. We note that the representation of the (partially) benzenoid GNRs (i.e. z_{21} and a_{11}) depends on the ribbon width. Varying the width of these GNRs thus implies a modification of the aromaticity along the ribbon edges. On the contrary, the representation of the non-benzenoid GNRs (e.g. z_1) is independent of their width. The ribbons keep a non-benzenoid character for all widths. As shown in Fig. 3.26, the variations of the edge aromaticity have an important impact on the electronic properties of the ribbons. The energy gap of the $[a_{11}]$ -GNRs and $[z_{21}]$ -GNRs exhibits an oscillating behavior with respect to changes of the ribbon width. The larger gaps are observed for the fully benzenoid structures.

These results demonstrate that, simple bonding theories, such as the Clar's sextet theory, can be easily extended in order to bring some clarification on the stability and electronic properties of the graphene edges. Though they cannot be used to make quantitative predictions, these concepts of aromaticity would probably help in the search for the most stable edge patterns in various chemical environments.

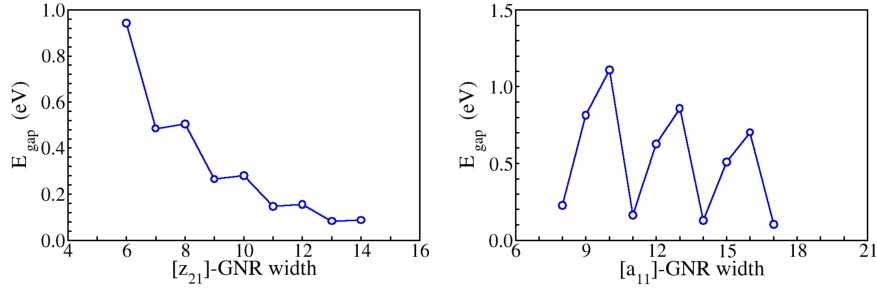


Figure 3.26: Energy gaps of GNRs of increasing width. The abscissa refers to the number of zigzag/dimer lines of carbon atoms across the GNR width. The cases of $[z_{21}]$ -GNRs and $[a_{11}]$ -GNRs are plotted on the left and right panels respectively.

3.5 Conclusions

In summary, the electronic properties of graphene and graphene nanoribbons (GNRs) have been reviewed. A particular attention has been devoted to the mechanisms that rule the formation of sub-bands and the opening of energy gaps in GNRs. Though the quantum confinement of the electronic wave-functions is the main origin of the appearance of energy gaps that decrease with the width of the ribbon, additional effects originating in the topology and the reconstruction of the GNR edges have been reported.

Regarding the electronic structure of the mono-hydrogenated armchair and zigzag ribbons (a_{11} and z_1), our results agree well with the previous study of Son et al. [110]. The relaxation of the edge is shown to play a crucial role in determining the low energy electronic structure of the a_{11} patterned ribbon by forcing the opening of energy gaps that oscillates with the ribbon width. Owing to the presence of magnetically ordered states along the zigzag shaped edges, two magnetic configurations are reported for the z_1 ribbons corresponding to the parallel ($\uparrow\uparrow$) and anti-parallel ($\uparrow\downarrow$) coupling of the magnetic moments between the edges. The anti-parallel ($\uparrow\downarrow$) configuration is reported to be the ground state and present a semiconducting character. In contrast, the parallel configuration, that is higher in energy by a few meV, is reported to be metallic.

Furthermore, the electronic and energetic properties of various *reconstructed* edge patterns have been unveiled by means of spin-polarized DFT calculations. Though the interest of the scientific community has

been focused on the properties of the standard (a_{11} and z_1) edge patterns, the computed edge free energies reveal that these latter are stable at very low hydrogen concentrations, suggesting that, in most experimental conditions, the standard edges do reconstruct. Though the most stable edge structures are likely to be dependent on the actual chemical environment, our study highlights the z_{211} , a_{22} and $z(600)_{2222}$ edge patterns as the most probable candidates for the edge reconstruction. One notes that none of these patterns do present magnetic order along the edges.

Finally, we have shown that the electronic and stability properties of hydrogen-terminated graphene ribbons can be, to some extent, rationalized by applying the Clar's rules of aromaticity.

Chapter 4

Topological defects in Graphene Nanoribbons

Introduction

Disorder is ubiquitous in graphene. Graphene is a two-dimensional system which limits intrinsically the order of the carbon atoms. In agreement with the Hohenberg-Mermin-Wagner theorem [165], thermal fluctuations are expected to destroy the long range positional order in two dimensional systems. True hexagonal order is thus strictly possible only at zero temperature in free standing graphene. Therefore, disorder is always expected in actual samples, and topological defects have been observed by many research groups [13, 14, 15, 147]. As an example, Fig. 4.1, reports High-Resolution Transmission Electronic Microscopy (HR-TEM) images that evidence the presence of meta-stable defects in the graphene layer.

Interestingly, the introduction of topological defects in the honeycomb network also offers the opportunity to tailor the electronic properties of graphene can in many different ways. The sources of disorder in graphene are many and vary from the effects of the substrate, the impact of dopant or impurities on the substrate, to the introduction of adsorbed molecules, substitutional doping or irradiation induced defects in the graphene plane. An experimental evidence of topological defects induced by irradiation is reported in Fig. 4.2. HR-TEM images reveal the creation of pentagon-heptagon pair in the graphitic network after irradiation of the samples. Previous theoretical studies have tackled the deposition of metal atoms [166, 167], the adsorption of molecules [168, 169, 170], the substitutional incorporation of boron and/or nitrogen dopants in the structure [171, 172]. In this chapter, we will focus on the defects

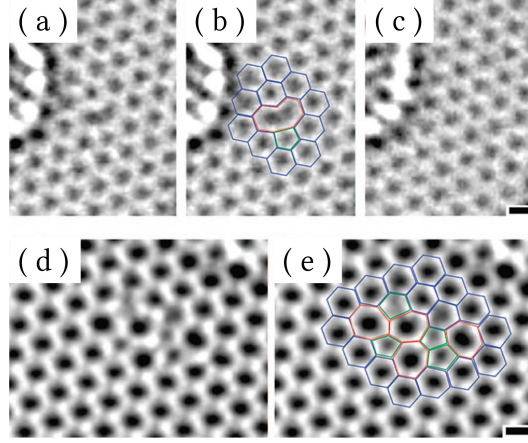


Figure 4.1: Experimental evidence for the presence of atomic defects in the graphene layer. Meta-stable defects found in HR-TEM image sequences. (a-c) Reconstructed vacancy: (a) original image and (b) with atomic configuration; a pentagon is indicated in green. (c) The unperturbed lattice is recovered 4s later. (d and e) Defect image and configuration consisting of four pentagons (green) and heptagons (red). Scale bars are 2 Å. *Pictures from Ref. [147]*

induced by irradiation of the graphene nanoribbons. This is further motivated by the recent observation of ferro-magnetism in irradiated graphite [173, 174, 175].

Irradiation induced defects

Various kinds of topological defects are reported at room temperature in sp^2 carbon allotropes. These are extended defects such as graphene edges and cracks, or point-defects such as vacancies, adatoms and odd-membered carbon rings (heptagons and pentagons). As illustrated in various theoretical [176, 177, 178, 179, 180] and experimental studies [14, 147], combinations of defects, such as pairs or small clusters of defects, are also frequently encountered. One intuitively minds that if a carbon atom is displaced from its original position in the sp^2 network, the resulting system will contain not only a vacancy but also an adatom. This combination of a vacancy and an adatom is commonly named a Frenkel pair [180]. In a similar way, if pentagons and heptagons are introduced in the planar sp^2 lattice (either by addition/removal of atoms or by rotation of carbon-carbon bonds), the relaxed carbon network will tend to reduce the defect induced distortion by counterbalancing the effects of pentagons by nearby heptagons giving rise to small clusters of

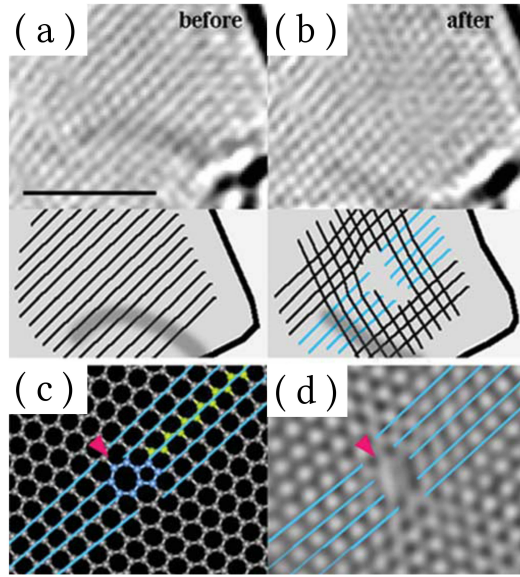


Figure 4.2: Experimental evidence for the presence of atomic defects in the graphene layer. In situ observation of a topological defect induced by irradiation in a graphene layer. (a and b), HR-TEM images of a single graphene layer with a topological defect induced by electron irradiation (before (a) and after (b)). An edge dislocation is unambiguously visible at the middle of the network where one zig-zag chain is missing through it. The missing zig-zag chain is shown schematically in the bottom part of each panel. (c) An atomistic model of the pentagon-heptagon pair in the graphitic network. (d) A simulated HR-TEM image shows a good comparison with the HR-TEM image shown in (b). Scale bar is 2 nm long. *Images from A. Hashimoto et al. [13]*

odd membered rings.

Among the large variety of topological defects, we will focus here on vacancies and adatoms. Not only these are present at thermal equilibrium, they are also of particular relevance for technological applications of GNRs since they can be induced by proton irradiation of the graphene samples, which offers the opportunity to tune their number and concentration. Upon collision of light ions, e.g. H or He, with graphitic structures, the main damage is the creation of Frenkel pairs [181, 182]. Moreover, for an ion energy of a few MeV, the number of defects created is much larger than the number of implanted ions. As an example, parameterized energetic ion stopping calculations [176, 183] indicate that one 2.25 MeV H-ion gives rise to 15 pairs of vacancies and interstitials in highly oriented pyrolytic graphite. However, vacancies and adatoms, as well as H ions are highly mobile in graphene [176, 177, 178, 179] and their vast majority is expected to recombine or form clusters which are predicted to be more stable. As a consequence, the most abundant defects expected in irradiated graphene samples are meta-stable vacancies and adatoms, H-vacancies and H-adatom complexes, as well as voids (di-/tri-vacancies) and small carbon clusters [176].

Defect induced magnetism

New light nonmetallic magnet with a Curie point above the room temperature have long generated a high scientific and technological interest. The recent experimental observation of room temperature ferromagnetism in irradiated graphite has thus stimulated a large research effort aiming to understand the magnetic properties of carbon based systems [173, 174, 175]. Up to recently, the graphitic samples were thought to be traditional diamagnetic materials. The debate around the origin of magnetism in these systems was initiated in 2000 with the observation of magnetization hysteresis loops in highly oriented pyrolytic graphite samples [184]. Today, while the origin of magnetism in graphene-like systems is still actively investigated [16, 185], it is commonly accepted that topological defects such as under-coordinated atoms and zigzag edges are at the heart of the mechanism. On one hand, point defects such as vacancies and carbon adatoms are reported to come with local magnetic moments. The ferro-/anti-ferro-magnetic order which arises from their interaction is then called *atomic* magnetism. On the other hand, atoms at the edges of graphitic fragments either passivated or not may give rise to electronic states with large degeneracies at the Fermi energy. Upon magnetic instability, a ferro-/anti-ferro-magnetic order may develop as it is the case along the edge (z_1) of the zigzag graphene nanoribbons.

This is called *superatomic* magnetism. While seemingly different, both processes share the same simple physical origin. The topological defects come with localized electronic orbitals and generate finite densities of states at the Fermi energy. As such, the defective graphene structures are prone to flat band magnetic instability.

A considerable number of works have recently addressed the defect-mediated magnetism in graphene with the help of both the tight-binding and mean field Hubbard approximations [143, 186, 187, 188]. The result of these works is a set of simple rules which links the spatial arrangement of the defects to the emerging magnetic order. In compliance with second Lieb's theorem [189] about half-filled bipartite lattice, the total spin (S_{tot}) of a given defective structure depends on its sub-lattice imbalance (i.e. $S_{tot} = |N_A - N_B|$, where $N_{A/B}$ refers to the number of sites within the sub-lattices). A well balanced bipartite lattice (such as 2D-graphene or graphene ribbons) should therefore present a vanishing total magnetic moment in its ground-state configuration, which is indeed the case. However, while Lieb's theorem provides meaningful predictions for the total spin, it does not preclude the appearance of spin density distributions in the systems with total spin $S_{tot} = 0$. For such systems, the Hubbard model solutions are globally characterized by the anti-parallel coupling of the magnetic moments on the two atomic sub-lattices. As a consequence, magnetism is predicted to locally develop in the nanometer-size regions characterized by the dominance of topological defects in one of the sub-lattices. In such a situation, it is predicted that semi-conducting ribbons behave like diluted magnetic semiconductor and present giant Zeeman splitting under the application of an external magnetic field such that $g\mu_B H \geq k_B T$ [188].

While the literature on the subject is abundant, most of previous studies rely on the topological nature of defects and does not account for the possible defect reconstructions. In particular, the hopping integrals are generally not modified in order to take into account the modification in the carbon-carbon bond lengths. In the following sections, the electronic and magnetic structures of graphene nanoribbons in the presence of topological defects are investigated within the framework of spin-polarized density functional theory. In order to improve the accuracy of the theoretical predictions, careful atomic structural relaxations are performed and the mechanism of defect-induced magnetism are unveiled.

In this chapter, the structural, electronic and magnetic properties of GNRs in the presence of topological defects are investigated. In section 4.1, the structure and stability of vacancies and adatoms in GNRs are detailed and compared with the graphene case. In agreement with

previous *ab initio* calculations, these defects are reported to come with a magnetic moment, inducing locally a spin polarized charge density. In addition, our results highlight the strong impact of such point defects on the magnetic properties of zigzag GNRs. In section 4.2, the recombination of primary defects with the GNR edges and the formation of small defect clusters is investigated. Owing the high mobility of primary defects, the *ab initio* computed defect formation energies suggest that point-defects are like to contribute to the roughness of the edges. In section 4.3, the chemical reactivity of the defects is assessed. The large stabilization of defects upon hydrogenation highlights the active role played by defects in the chemical functionalization of graphene ribbons. Finally, the relative stability of both *bulk* and *edge* defects is discussed in section 4.4. The formation energies of the primary defects are further compared with those of various edge reconstructions actually observed in low voltage aberration-corrected transmission electron microscopy (TEAM) experiments. Finally, the computed formation energies of defects at the armchair and zigzag edges suggest that the armchair edges are more robust than the zigzag edge with respect to the introduction of topological defects.

The results presented in this chapter, in particular the discussion regarding the relative stability of topological defects in GNRs, will be parts of a forthcoming publication.

4.1 Vacancies and adatoms as primary defects

As discussed in the introduction, the most probable primary defects in realistic irradiated graphene samples are vacancies and adatoms. Here, we focus on their structural, electronic and magnetic properties. The calculations presented hereafter have been performed within the spin-polarized DFT as implemented in the *Siesta* package [190].

A common issue in modelling isolated defects in bulk systems is the definition of appropriate boundary conditions. Either the defect is introduced in a finite simulation box without periodic boundary conditions or a periodic model is used, where defects are periodically repeated. In the non-periodic approach, the system size has to be taken large enough in order for the spurious surface effects to not modify the electronic density around the defect. In the periodic approach, the size of the unit cell has to be large enough for the translated defects to not interact between each others. Here, the later approach, called super-cell technique, has been adopted.

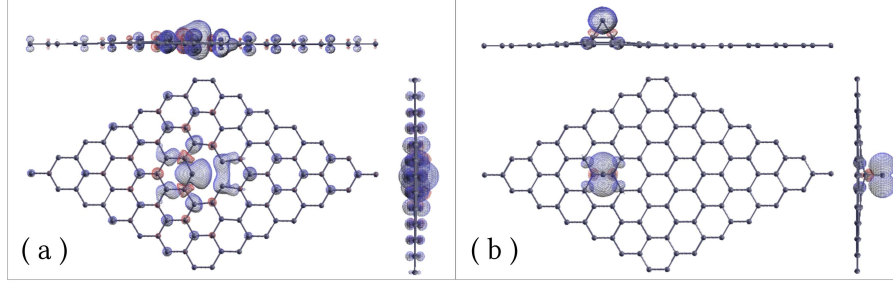


Figure 4.3: Illustration of the spin density distribution ($\rho_\alpha - \rho_\beta$) induced by vacancies (a) and adatoms (b) in the graphene plane. Blue and Red surfaces correspond to an excess of spin α and spin β electrons, respectively.

In what follows, vacancies and adatoms are introduced within zigzag and armchair GNRs and their behavior is compared to the one reported previously for the defective graphene sheet. The lateral dimensions of the computational cells (i.e. those not involved in the system periodicity, $(\mathbf{a}_x, \mathbf{a}_y)$ for GNRs and $(\mathbf{a}_x)$ for graphene) have been fixed in order to insure 25 Å of vacuum between parallel ribbons and planes. The numerical atomic orbital basis set described in section 3.4.1 has been used in conjunction with norm-conserving pseudo-potentials. The electronic states are populated using a Fermi-Dirac distribution with an electronic temperature of 250K. The integration over the 1D Brillouin zone is replaced by a summation over a regular grid corresponding to 40 k -points for the GNRs unit cells (40x40 k -points for the graphene unit cell). The geometries are fully relaxed, until forces on the atoms and the unit cell are below 0.01 eV/Å and 0.05 eV/Å, respectively. The small spin-orbit coupling of carbon atoms is neglected and independent collinear spin orientations, labeled α and β , are considered.

4.1.1 Primary defects in graphene

Though they have been widely discussed in the literature, we calculate the structural and magnetic properties of vacancies and adatoms again for sake of comparison.

(a) *Vacancy* - A vacancy is created by moving a carbon site from the atomic network. Upon relaxation, the defective 7x7 graphene supercell undergoes a Jahn-Teller distortion. Two of the unsaturated carbon atoms come closer and form a weak covalent bond ($d_{C_1-C_2} = 1.93$ Å

compared to the 1.42 Å of the ideal graphene), inducing a pentagon like rearrangement. The third unsaturated carbon atom moves out of the plane of about 0.24 Å [176, 179]. Consequently, the initial D_{3h} symmetry of the hexagonal network is lost in favor to the C_s symmetry [191]. The resulting ground-state electronic structure is magnetic, with a magnetic moment of 1.4 μ_B . The spin density distribution is illustrated in Fig. 4.3(a).

(b) *Adatom* - A carbon adatom is created by adding an extra carbon atom on the graphene plane. After relaxation, the additional atom, initially located 1Å above an asymmetric position on the graphene plane, adsorbs in a bridge-like position (i.e. on top of a C-C bond that links two atoms of the graphene sheet). The ground-state electronic structure present a spin density distribution with a magnetic moment of 0.54 μ_B . The spin density distribution (see Fig. 4.3(b)) reveals the large contribution of the p -orbitals of the adatom to the magnetic moment.

In order to characterize the energetics of defects, the vacancy and adatom formation energies have been computed. Taking the pristine graphene as the energy reference, the defect formation energies are given by:

$$\xi = (E^{tot} - N_C \cdot E_{graph}^C) , \quad (4.1)$$

where E^{tot} is the total energy of the defective graphene super-cell, E_{graph}^C is the energy per carbon atom of the pristine graphene plane, and N_C is the number of carbon atoms in the defective super-cell. The calculated energies are of 7.7 and 6.7 eV for the vacancy and adatom in graphene, respectively¹.

The presence of vacancies and adatoms also leads to strong changes in the local structure of low energy carriers. The band structures plotted in Fig. 4.4 highlight the appearance of nearly flat bands (low electronic group velocity) around the Fermi level [191]. Those bands originate from the presence of quasi-localized states ($\psi_d(\mathbf{r})$) around the defects. As shown in Figs. 4.4(d,e), defects may give rise to different types of electronic states. Some are directly associated with the dangling bonds. These are strictly localized and present very small coupling with the π - π^* bands of graphene (states labelled d1, d4, e1, e2, e5 and e6). Others

¹Another way, commonly used to characterize the energy of vacancies and adatoms in graphene is to refer to the energy of the isolated carbon atom in its triplet state. By moving one atom of the sp^2 network far away from the graphene plane (i.e. until the total energy converges), one computes a vacancy formation energy of 15.7 eV. Similarly, by moving an isolated carbon atom up to its adsorption on the graphene plane, the computed adsorption energy is -1.2 eV.

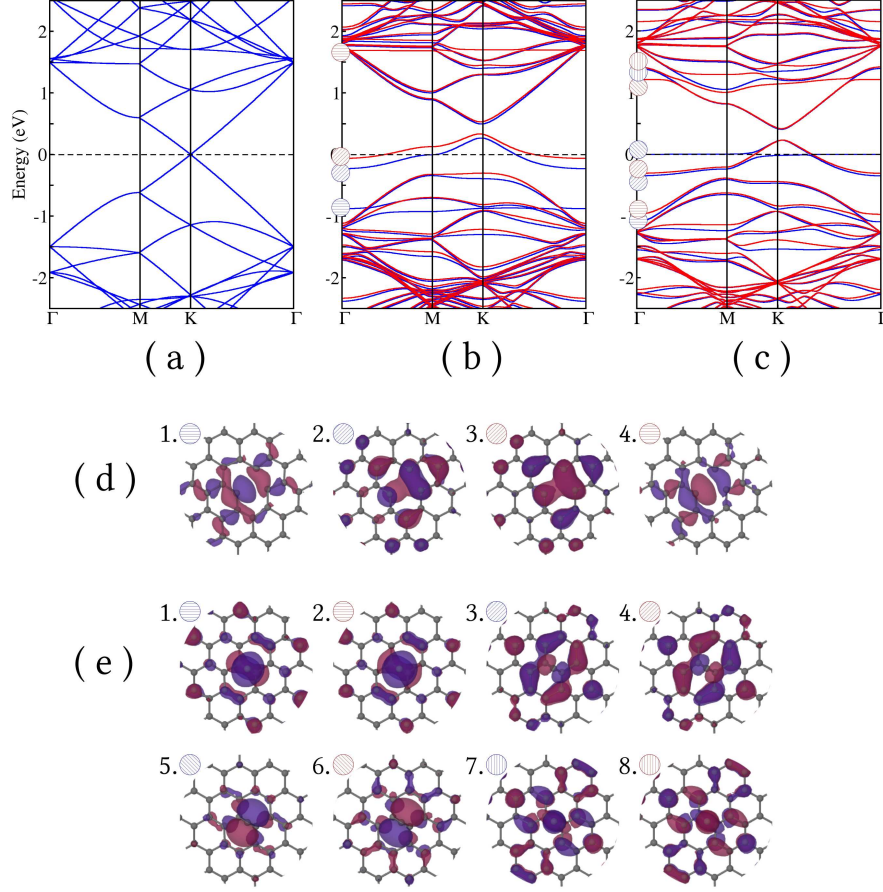


Figure 4.4: [Top panel] Electronic energy band structure of pristine (a) and defective graphene including a vacancy (b) and an adatom (c). A 7×7 graphene super-cells (either pristine or with one defect) have been used for the *ab initio* calculations. [Bottom panel] Representation of the low energy electronic states induced by these defects. Blue and red surfaces are associated with positive and negative values of the electronic wave-function. Quasi-localized electronic states induced by a vacancy (d) and an adatom (e).

do not present the dangling bonds symmetry and extend over several nanometers owing to the contribution of the p_z orbitals of the graphene network [186, 192, 193, 194]. These states are said quasi-localized.

Finally, we note that both defects come with a fractional magnetic moment. This may be explained by the self-doping (i.e. charge transfer

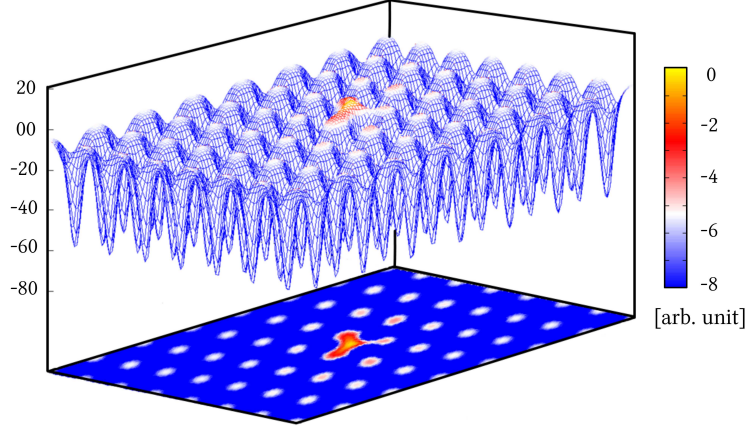


Figure 4.5: Representation of the electrostatic potential (i.e. sum of the hartree potential and the local pseudo-potential) of graphene in the presence of a vacancy. One notes the increase of the potential in the vicinity of the defect, depicting the charge transfer from the bulk graphene to the quasi-localized defect states.

from the bulk graphene to the quasi-localized $\psi_d(\mathbf{r})$ states) which arises from assymetric distribution of defect-induced states around the Fermi level [192]. As illustrated in Fig. 4.5 for the case of a vacancy, in the presence of adatoms and vacancies, the self-doping effect is characterized by an increase of the potential in the nanoscale region surrounding the defects.

All these results are in good agreement with previous studies performed both with localized basis set and within plane-waves and PAW schemes [191, 176, 186]. This supports the use of our double- ζ plus polarization basis set for the investigation of topological defects in graphene nanostructures.

4.1.2 Primary defects in GNRs

We now focus on the defective graphene nanoribbons. Vacancies and carbon-adatoms are introduced within hydrogen passivated 8-zGNR and 17-aGNR whose width are ~ 18 Å. One-dimensional super-cells are considered, leading to a distance of ~ 20 Å between nearest-neighboring defects and a defect concentration of $\sim 0.6\%$.

The computed band structures of pristine 8-zGNR and 17-aGNR is reported in Fig. 4.6. The ground state configuration of 8-zGNR reveals

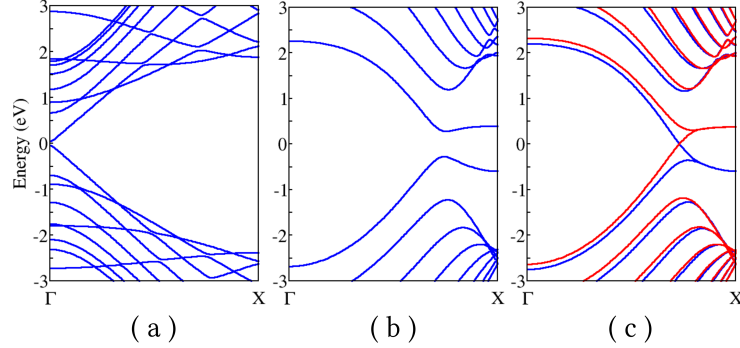


Figure 4.6: Electronic band structures of 17-aGNR and 8-zGNR. (a) Semi-conducting band structure ($E_{gap}(\Gamma) = 0.1$ eV) of 17-aGNR. (b) Semi-conducting band structure ($E_{gap}(\Gamma) = 0.5$ eV) of 8-zGNR in its ground-state configuration ($\uparrow\downarrow$ spin orientations between the edges). (c) Metallic band structure of 8-zGNR in its meta-stable $\uparrow\uparrow$ configuration.

an anti-parallel ($\uparrow\downarrow$) spin orientations between the edges leading to a semi-conducting band structure (0.5 eV band gap) with full spin degeneracy. In addition, 8-zGNRs may also present a parallel ($\uparrow\uparrow$) spin orientations between the edges. This configuration is found to be meta-stable (11 meV/edge-atom higher in energy). The 8-zGNR then displays a metallic behavior, as the π_α^* and π_β bands are crossing at the Fermi energy, and presents a total magnetic moment of $0.51 \mu_B$ per edge atom. Finally, the ground state electronic structure of the pristine 17-aGNR does not present any edge states. The associated electronic band structure presents a complete spin- α /spin- β degeneracy and an energy band gap of 0.1 eV. These results are in good agreement with the previous study of Son et al. [127].

(a) *Vacancy* - Upon the introduction of a vacancy in the GNRs supercells (see Figs. 4.7 and 4.8), the systems undergo a similar reconstruction as in graphene. A Jahn-Teller distortion of the honeycomb structure is observed and the ground-state electronic density appears to be locally spin-polarized. In GNRs, however, several defects configurations are found to be meta-stable. Indeed, the C_s symmetry of the reconstructed vacancy leads to nonequivalent orientations ("*parallel*", "*perpendicular*" and "*tilted*") of the vacancy mirror plane with respect to the ribbon axis. Figure 4.7 illustrates the nonequivalent vacancy orientations in both zigzag and armchair GNRs.

In addition, the interaction between the magnetic moment localized

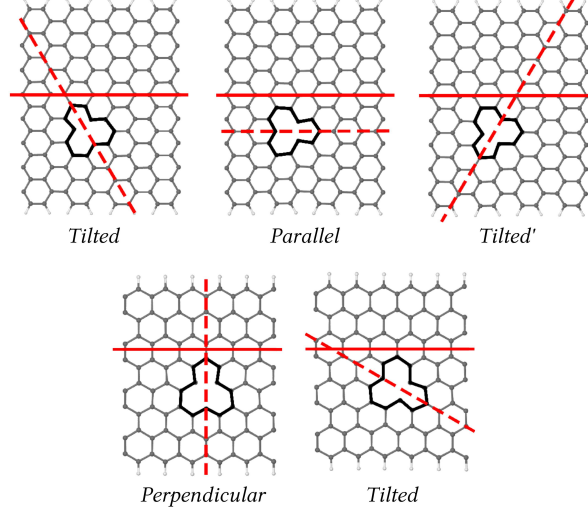


Figure 4.7: Schematic atomic representations of the nonequivalent vacancy orientations in GNRs. (top panel) *Tilted*, *parallel*, and *tilted'* nonequivalent reconstructions of vacancy in armchair-GNRs. (bottom panel) *Perpendicular*, and *tilted* nonequivalent reconstructions of vacancy in zigzag-GNRs.

on the defect and the spin ordered edge states of zGNRs gives rise to various possible magnetic configurations. We find that four magnetic configurations correspond to a local minimum of the energy and are therefore meta-stable in the eyes of the *ab initio* computed total energies. In the following, these are labeled X_Y , where X refers to the parallel ($\uparrow\uparrow$) or anti-parallel ($\uparrow\downarrow$) spin orientations between the ribbon edges while Y refers to the parallel (P) or anti-parallel (AP) spin orientation between the defect and the nearest edge. As an example, Fig. 4.8 details the four meta-stable configurations of a zigzag shaped GNR resulting from the introduction of a titled vacancy.

The spin density distribution induced by the vacancy is found to affect the energetic of the inter-edge magnetic couplings. Indeed, the enhanced exchange energy gain of the anti-parallel ($\uparrow\downarrow$) configuration originates from the constructive interference between the magnetic tails of the electronic states localized at the edges and is therefore sensitive to the presence of any destructive spin density distribution across the ribbon [122]. On the one hand, by breaking the bipartite character of the carbon network, the vacancy locally destroys the staggered sub-lattice potentials associated with the anti-parallel ($\uparrow\downarrow$) magnetic ordering. On

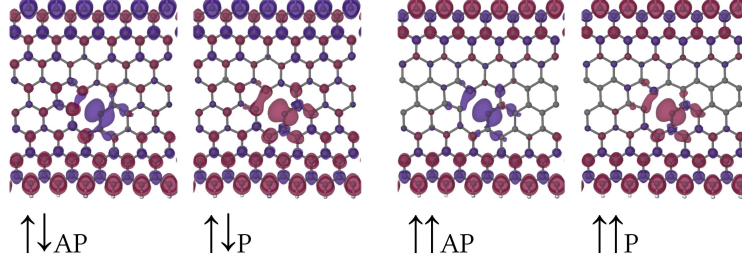


Figure 4.8: Magnetic configurations of a vacancy in a zigzag ribbon (8-zGNR). Spin polarized electronic densities ($\rho_\alpha - \rho_\beta$) iso-surfaces for the four meta-stable magnetic configurations associated with a tilted vacancy. Blue and red iso-surfaces correspond to an excess of spin- α and spin- β respectively.

the other hand, the vacancy induces a spin density distribution which conflicts with the ground-state magnetic order of the pristine ribbon. Both mechanisms impede the extra stabilization of the anti-parallel ($\uparrow\downarrow$) configuration and favor the parallel ($\uparrow\uparrow$) coupling between the edges which does not give rise to significant spin density distribution away from the ribbon edges.

The *ab initio* computed formation energies associated with the different geometry and magnetic configurations are reported in Table 4.1. In order to isolate the energetic of defects, the formation energies (ξ^{defect}) are computed as,

$$\begin{aligned}\xi^{defect} &= \left[(E^{tot} - E^{GNR}) - \Delta N_C \cdot E_{graph}^C \left(-\Delta N_H \cdot \frac{E_{H_2}}{2} \right) \right] \\ &= \xi^{tot} - \xi^{GNR}.\end{aligned}\quad (4.2)$$

That is the difference between the formation energies associated with the defective and pristine graphene ribbon. Here, E^{tot} and E^{GNR} are the total energies of the defective and pristine GNR super-cells. ΔN_C and ΔN_H account for the different number of carbon and hydrogen atoms within the defective and pristine GNR super-cells. Finally, E_{graph}^C and E_{H_2} are the energies associated with a carbon atom in the pristine graphene plane and with the H_2 molecule, respectively.

The computed formation energies are very close to the one obtained previously for the graphene plane. Nevertheless, the comparison of the values detailed in Table 4.1 gives some insights into the behavior of vacancies. First, the data reveals that the tilted (parallel) orientation is the more stable within zigzag (armchair) GNRs. These orientations are

aGNR		zGNR			
Para.	7.601	Perp.	$(\uparrow\downarrow)_{AP}$	7.760	$(\uparrow\uparrow)_{AP}$ 7.675
Tilted	7.696		$(\uparrow\downarrow)_P$	7.732	$(\uparrow\uparrow)_P$ 7.690
Tilted'	7.705	Tilted	$(\uparrow\downarrow)_{AP}$	7.716	$(\uparrow\uparrow)_{AP}$ 7.658
			$(\uparrow\downarrow)_P$	7.678	$(\uparrow\uparrow)_P$ 7.586

Table 4.1: Relative stability of the meta-stable configurations of vacancies in armchair and zigzag GNRS: *Ab initio* computed formation energies (ξ). Values are reported in eV.

associated with the formation of a stronger carbon-carbon bond during the reconstruction process. It can intuitively be understood that, for geometrical reasons, ribbons adapt more easily to the strains in the direction perpendicular to the axis. As a result, zigzag (armchair) ribbons present a small shrinking of their width ($\sim 1.0\%$) around tilted (parallel) vacancies. Conversely, a small stretching ($\sim 0.7\%$) appears in the case of the perpendicular and diagonal orientations. The energy gains ($\Delta_\theta E$) associated with the preferred orientation are of 89 meV and 95 meV within the zigzag and armchair GNRS, respectively. Second, while the energy difference $\Delta_{\uparrow\uparrow}E$ between the parallel ($\uparrow\uparrow$) and anti-parallel ($\uparrow\downarrow$) spin configurations is of 88 meV in pristine 8-zGNR, this value is strongly reduced in the presence of a vacancy. Our calculations give $\Delta_{\uparrow\uparrow}E = -2$ meV in the presence of a vacancy. Interestingly, this means that in the presence of *bulk* defects, the parallel ($\uparrow\uparrow$) spin orientation between the edges may become the ground-state configuration. While this result strictly holds for the case of periodic arrays of vacancies, it may probably be extended to randomly disordered configurations. Indeed, the value of $\Delta_{\uparrow\uparrow}E$ is roughly independent of the spin orientation on the vacancy. The effect should therefore remain the same whatever the magnetic coupling between the set of defects.

Finally, we report that the presence of vacancies in the graphene ribbons has a crucial impact on the electronic structure. The introduction of a vacancy in the GNRS super-cell induces quasi-flat bands around the Fermi energy and induces a rigid energy shift of the π - π^* electronic bands. By looking at the low energy electronic states, contributions from the π - π^* defect states can be identified within the $[-0.5, 0.5]$ eV energy window around the Fermi level. The electronic states associated with the sp^2 -like dangling bonds appears at lower and higher energies (see Fig. 4.9 for an example). As a consequence, analogous charge transfer as in the graphene plane is reported.

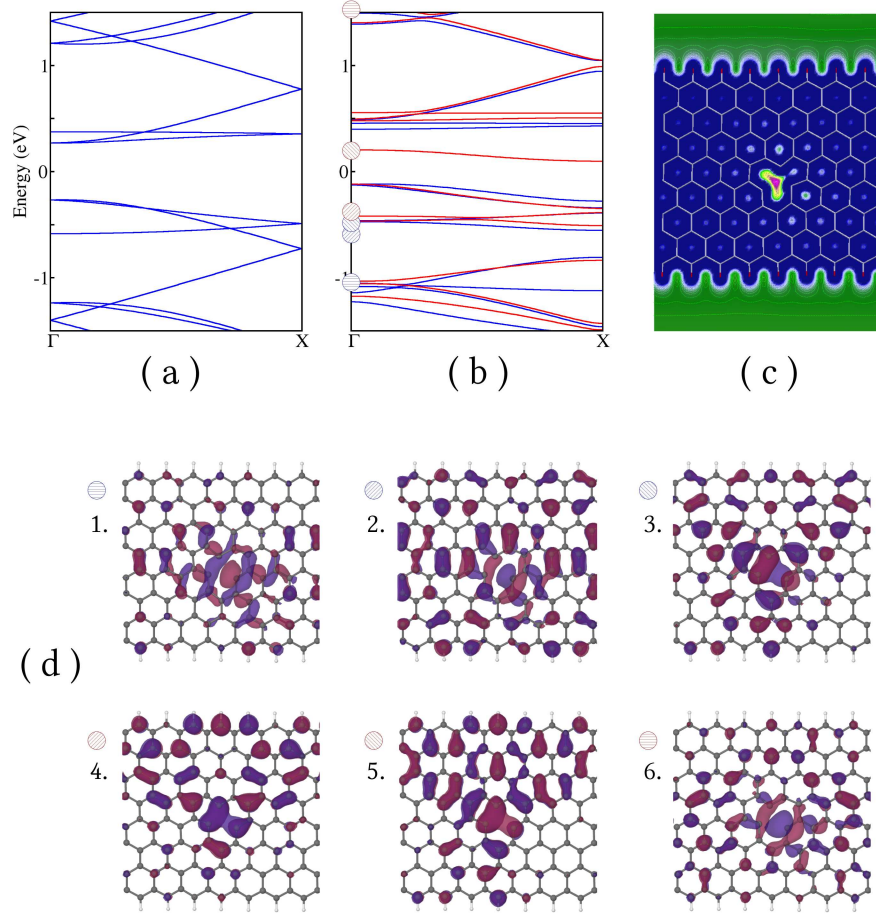


Figure 4.9: [Top panel] Electronic energy band structures of 8-zGNR, pristine (a) and in the presence of vacancies (b). $8 \times 1 \times 1$ GNR super-cells (either pristine or with one defect) have been used for the *ab initio* calculations. (c) Representation of the electrostatic potential of the defective super-cell (i.e. sum of the hartree potential and the local pseudo-potential) integrated along the axis perpendicular to the zGNR plane. It is worth noting the increase of the potential in the close vicinity of the defect, illustrating the charge transfer from the bulk graphene to the quasi-localized defect states. [Bottom panel] Representation of the low energy electronic states induced by the vacancy. Blue and red surfaces are associated with positive and negative values of the electronic wave-function.

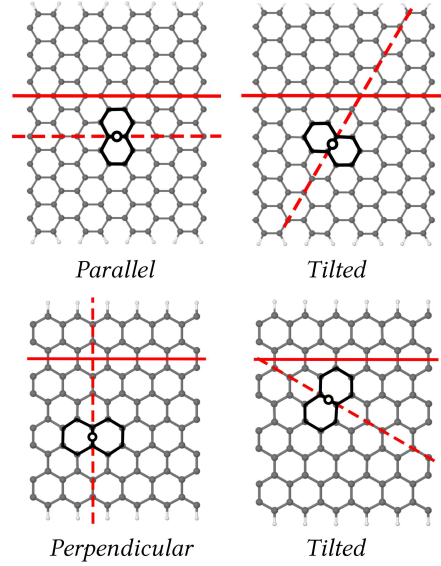


Figure 4.10: Schematic atomic representations of the nonequivalent adsorption sites for carbon adatom in GNRs. (top panel) *parallel*, and *tilted* nonequivalent carbon-carbon bonds in armchair-GNRs. (bottom panel) *perpendicular*, and *tilted* nonequivalent carbon-carbon bonds in zigzag-GNRs.

(b) *Adatom* - Upon relaxation, the additional carbon (initially located $1\text{\AA}$ over an asymmetric position on the graphene plane) stabilizes in a bridge-like position. As expected due to the presence of unsaturated dangling bonds, the adatom induces a polarization of the neighboring electronic density. This behavior is similar to the one reported in section 4.1.1 for the graphene plane. The situation is however slightly more complicated in graphene ribbons since inequivalent adsorption sites are present. As detailed in Fig. 4.10, the carbon-carbon bond hosting the adatom may be either *parallel*, *perpendicular* or *tilted* with respect to the ribbon axis. Besides, since adatoms induce local magnetic moments, their interaction with the magnetically ordered edges-states gives rise to various meta-stable configurations in zigzag GNRs. As detailed in Fig. 4.11, these are labeled using the aforementioned X_Y syntax.

The computed adsorption energies relative to various configurations of adatom in zigzag and armchair ribbons are reported in Table 4.2. A careful comparison of the adsorption energies first reveals a better stabilization of the adatom when located upon strong carbon-carbon bond.

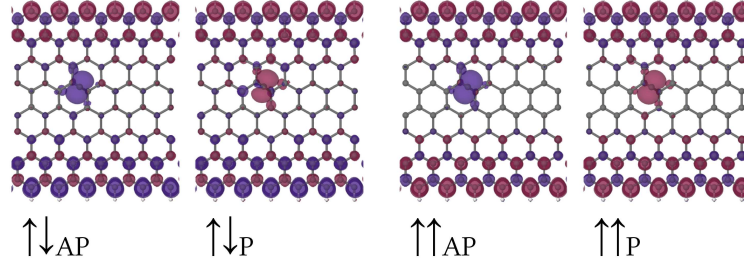


Figure 4.11: Magnetic configurations of adatoms in zigzag ribbon. Spin polarized electronic densities ($\rho_\alpha - \rho_\beta$) iso-surfaces for the four meta-stable magnetic configurations associated with a tilted adatom in 8-zGNR. Blue and red iso-surfaces correspond to an excess of spin α and spin β respectively.

aGNR		zGNR			
Para.*	6.727	Perp.	$(\uparrow\downarrow)_{AP}$	6.855	$(\uparrow\uparrow)_{AP}$ 6.770
Tilted**	6.683		$(\uparrow\downarrow)_P$	6.877	$(\uparrow\uparrow)_P$ 6.753
		Tilted	$(\uparrow\downarrow)_{AP}$	6.726	$(\uparrow\uparrow)_{AP}$ 6.612
			$(\uparrow\downarrow)_P$	6.706	$(\uparrow\uparrow)_P$ 6.614
*weak C-C bond, **strong C-C bond.					

Table 4.2: Relative stability of the meta-stable configurations of adatoms in armchair and zigzag GNRs: *Ab initio* computed formation energies (ξ). Values are reported in eV.

In zGNRs, the tilted carbon-carbon bonds, which are smaller than the perpendicular ones, are associated with smaller adsorption energies. Similarly, smaller adsorption energies are always reported for smaller bonds in aGNRs. Second, in the same way as vacancies do, carbon adatoms modify the energetics of the inter-edge magnetic coupling in zGNRs. The local magnetic moment interferes with the ground-state spin density distribution (i.e. the $\uparrow\downarrow$ coupling between the edges) and contributes to further stabilize the $\uparrow\uparrow$ magnetic configuration. As a result, the energy difference $\Delta_{\uparrow\uparrow}E = (E_{\uparrow\uparrow} - E_{\uparrow\downarrow})$ is strongly reduced in the presence of an adatom. In the presence of an adatom at the center of the ribbon, the parallel spin orientation between the edges becomes the ground-state configuration as $\Delta_{\uparrow\uparrow}E = -9$ meV.

Consequently, the carbon adatom is found to have a large impact on the low energy electronic structure of the graphene ribbons. Additional

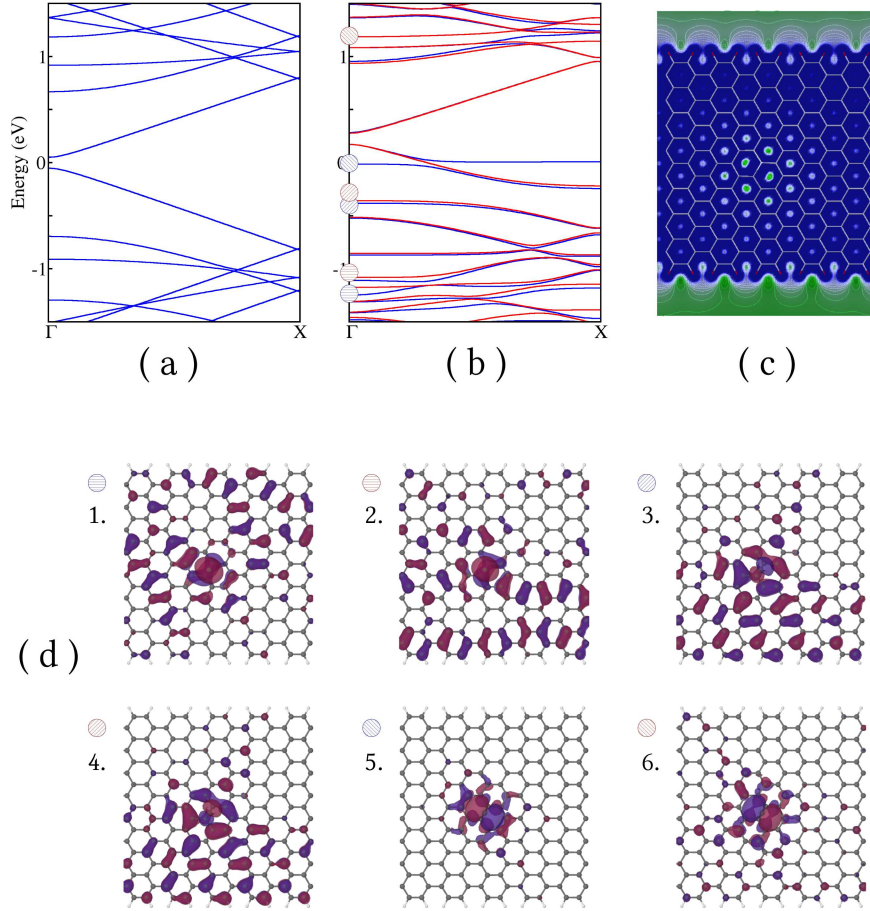


Figure 4.12: [Top panel] Electronic energy band structure of 17-aGNR (a) pristine, (b) in the presence of adatoms. $5 \times 1 \times 1$ GNR super-cells (either pristine or with one defect) have been used for the *ab initio* calculations. (c) Representation of the electrostatic potential of the defective super-cell (i.e. sum of the hartree potential and the local pseudo-potential) integrated along the axis perpendicular to the aGNR plane. It is worth noting the increase of the potential in the close vicinity of the defect, illustrating the charge transfer from the bulk graphene to the quasi-localized defect states. [Bottom panel] Representation of the low energy electronic states induced by the vacancy. Blue and red surfaces are associated with positive and negative values of the electronic wave-function.

electronic energy bands induced by the quasi-localized defect states are reported around the Fermi level. While the electronic contributions coming from the sp^2 -like dangling bond are located around 1 eV below the Fermi energy, the unpaired π -orbital of the adatom as well as others quasi-localized states give rise to flat energy bands in the $[-0.5, 0.5]$ eV energy window. As described previously, these electronic states involve a small charge transfer from the ribbon to the defect induced electronic states. As an example, the case of adatoms adsorbed on a 17-aGNR is detailed in Fig. 4.12.

4.2 Migration of defects

In graphene ribbons, the local atomic environment range from the D_{3h} hexagonal symmetry around the GNR axis to the C_s symmetry at the edges. The structural and electronic properties of vacancies and adatoms are thus expected to vary with the defect position across the ribbon width.

4.2.1 Relative stability of *bulk* and *edge* defects

Hereafter, we compare the structural and electronic properties of vacancies and adatoms for different positions (see Fig. 4.13 for the labelling of the defect positions). The aim of this section consists in finding some trends about the stability of point-defects in GNRs.

Figure 4.13 presents the computed relative energy of defects as a function of their positions. The zigzag and armchair ground-state configurations are reported as circles and squares respectively, while the error bars account for the meta-stable configurations higher in energy. Away from the GNR edges, topological defects behave like in the graphene sheet and the formation energy slightly decrease when moving from the ribbon axis towards the ribbon edges. At the same time, an increase of the energy dispersion associated with the meta-stable configurations is reported. Indeed, the energy gain associated with the preferred vacancy orientation in the zigzag ribbon ranges from $\Delta_\theta E(p_8) = 55$ meV in the ribbon center up to $\Delta_\theta E(p_3) = 355$ meV closer to the edge. Similar values are found in armchair ribbon (i.e. $\Delta_\theta E(p_8) = 95$ meV and $\Delta_\theta E(p_4) = 390$ meV).

In the direct proximity of the ribbon boundary, vacancies and adatoms definitely loose their *bulk*-like behavior and recombine with the edges. As shown in Fig. 4.13, defects then undergo an improved stabilization and smaller defect formation energies are predicted.

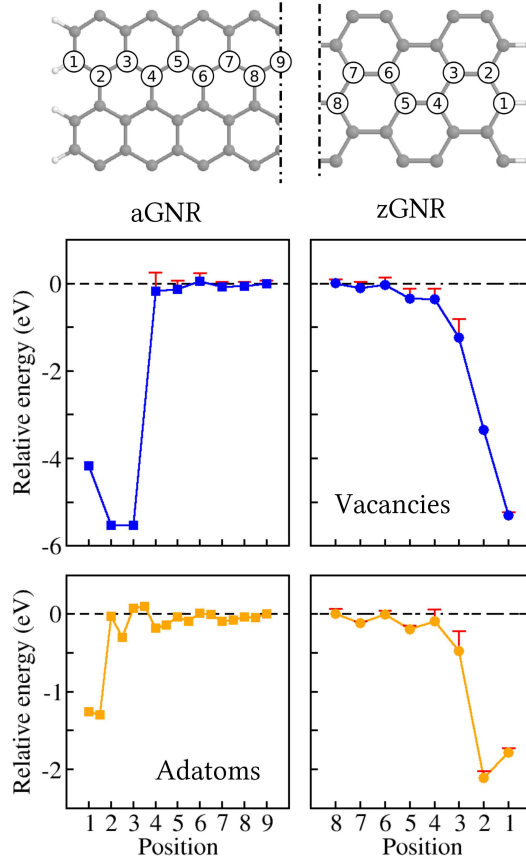


Figure 4.13: [Top panel] Labels of the different carbon sites across the width of a 17-aGNR (on the left), (on the right) and a 8-zGNR (on the right). [Bottom panel] Relative energies of defective zigzag and armchair GNR as a function of the defect position across the ribbon width. 8x1x1 (5x1x1) super-cells of 8-zGNR (17-aGNR) have been used for the *ab initio* calculations.

4.2.2 Energy barriers

The variation of the defect formation energy across the GNRs suggests a probable migration of *bulk*-like defects towards the ribbon edges. The actual migration of vacancies and adatoms depends on the energy barriers (E_{barrier}) encountered along the migration path. Two methods are commonly used to estimate these barriers. The Nudged Elastic Band method (NEB) [195] and the activation-relaxation technique (ART) [196] both allow to compute saddle points and minimum energy paths between suggested equilibrium configurations. We did not perform such calculations here since many previous studies have reported calculations of these E_{barrier} for both the adatom and vacancy in graphene.

The theoretically computed energy barriers for the migration of adatoms on the graphene plane is $E_{\text{barrier}}^{\text{th}} = 0.47$ eV [177, 178]. Such a low energy barrier means that adatoms are highly mobile on the sp^2 carbon plane and will most probably be pinned by other defects. Such a low value also explains the difficulty to experimentally observe adatoms on the graphene plane. Concerning the migration of vacancies, the theoretical prediction is about $E_{\text{barrier}}^{\text{th}} = 1.4$ eV [176, 179, 197, 198, 199], which is very different from the value of $E_{\text{barrier}}^{\text{exp}} = 3.1$ eV [182] deduced from experimental results. However, it is commonly thought that experimental results are, in fact, associated with the diffusion of di-vacancies rather than mono-vacancies. While this has to be further investigated, it should explain the disagreement between theoretical predictions and actual measurements. One can thus reasonably assume that primary defects are mobile on the graphene plane at room temperature.

If defects are mobile, then they are likely to diffuse until pinned in a more stable configuration or annihilated by recombination with another defect (e.g. an adatom that meets a vacancy). In graphene ribbons, pinning/recombination at the graphene boundary would therefore be an important process in determining the most probable electronic structure of defective ribbons. Besides, one cannot exclude the formation of small clusters of defects within the ribbon *bulk*, such as holes made from a few vacancies or small carbon clusters on the GNRs surface.

In what follows, the structural and electronic properties of vacancies and adatoms recombined with the graphene edges is detailed and the formation of small clusters of defect is discussed.

4.2.3 Defects at the edges

In graphene ribbons, the structure of the edges is known to have a major impact on the electronic properties, as previously illustrated in

Chapter 3. As a consequence, the control of the edge structure would be a highly desirable achievement for the development of new carbon-based electronic components. In this section, the actual contribution of the primary defects (i.e. vacancies and adatoms) to the edges disorder is investigated. In particular, the structural and electronic properties of the defects recombined at the edges are detailed. We show that the recombination of vacancies and adatoms with the graphene boundaries involves the appearance of sp^3 -like reconstruction of the edges and the introduction of odd-membered carbon rings into the honeycomb network. As a consequence, the electronic properties of vacancies and adatoms essentially differ from those in the bulk as the defect merges with the edge.

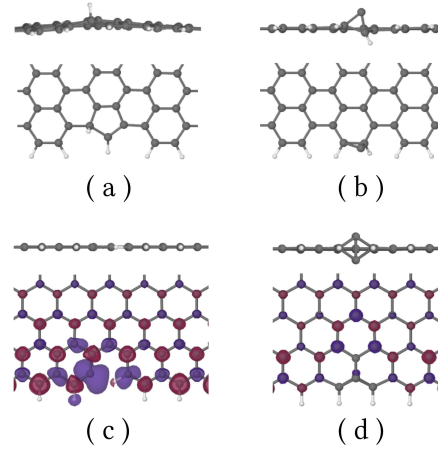


Figure 4.14: Atomic representations of the ground-state geometries of vacancies and adatoms recombined at the graphene edges. (a) Vacancy at the armchair edge, (b) adatom at the armchair edge, (c) vacancy at the zigzag edge, (d) adatom at the zigzag edge. The transparent surfaces correspond to spin polarized electronic densities ($\rho_\alpha - \rho_\beta$) iso-surfaces. Blue and red colors are associated with an excess of spin- α and spin- β , respectively.

(a) *Vacancy* - In the proximity of the ribbon edges, the carbon network does not present the local D_{3h} symmetry anymore. Consequently, the reconstruction of the atomic network upon the removal of a carbon atom is different from that reported in bulk graphene.

In order to find the most stable vacancy configuration, different starting geometries have been considered (by removing different carbon atoms and breaking the remaining symmetries). After relaxation of the de-

fective super-cells, the most-stable geometries are those represented in Figs. 4.14(a,c). While the vacancy in zGNR still presents a dangling bond and comes with a spin polarized density distribution, the reconstruction of the armchair edge implies the saturation of all the carbon atoms. Consequently, no spin polarization is reported. In this case, the reconstruction involves the formation of a pentagon of carbon atoms as shown in Fig. 4.14(a). The computed vacancy formation energies are 0.855 and 2.239 eV for the armchair and zigzag edges respectively. These values represent a significant reduction with respect to those of the *bulk* vacancies.

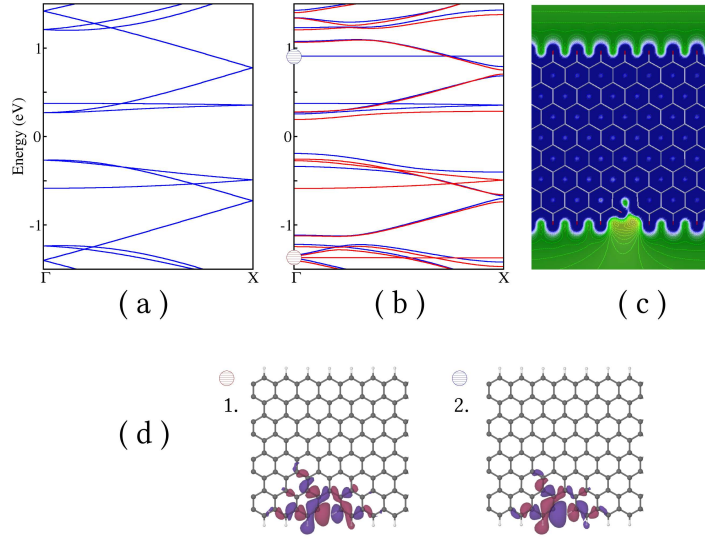


Figure 4.15: [Top panel] Electronic energy band structures of 8-zGNR (a) pristine and (b) in the presence of an *edge* vacancy. $8 \times 1 \times 1$ GNR super-cells (either pristine or with one defect) have been used for the *ab initio* calculations. (c) Representations of the electrostatic potential of the defective super-cell (i.e. sum of the hartree potential and the local pseudo-potential) integrated along the axis perpendicular to the zGNR plane. [Bottom panel] Representation of the low energy electronic states induced by the vacancy. Blue and red surfaces are associated with positive and negative values of the electronic wave-function.

Besides the structural contrast with their bulk counterpart, vacancies at the edges affect differently the low energy electronic structure of the GNRs. This statement is detailed in Fig. 4.15 for the zigzag edge. Within the $[-0.5, 0.5]$ eV energy window, the GNR electronic states are

globally unperturbed by the vacancy at the edge. The only significant contribution from the defect electronic states to the low energy electronic structure appears at ± 1 eV. It will be shown later that this difference between *bulk* and *edge* vacancies is crucial when determining their electronic scattering profiles.

(b) *Adatom* - The same happens for the carbon adatom recombined with the GNR edge. The proximity of the edge allows the carbon to move away from the bridge-like configuration and to recombine in an sp^3 -like configuration. In zGNR, the reconstructed adatom stabilizes on top of a carbon atom at the edge (see Fig. 4.14(d)) and forms what we have called previously a *triangular di-pyramid* (TDP) with two unsaturated sp^3 orbitals at the apexes. Though the two sp^3 orbitals are not involved in strong σ bonds, they interact together in a bonding/anti-bonding way leading to a non magnetic defect configuration. The geometry of the adatom recombined at the armchair edge is close to the bridge configuration (see Fig. 4.14(b)). However, upon relaxation, the adatom undergoes a slight displacement along the ribbon axis. As a consequence, the bridge symmetry is broken and the adatom loses its sp^2 hybridization in favor of an sp^2/sp^3 mixed configuration. At equilibrium, the sp^2 - and π -like adatoms' dangling bonds are not orthogonal anymore and the electronic density around the defect is not spin-polarized. The computed adatom formation energies are of 5.591 and 4.869 eV for the armchair and zigzag edges, respectively. Again, these values represent significant reductions with respect to the *bulk* adatom formation energies. In a way similar to the one reported for the *edge* vacancy, the impact of the adatom on the electronic band structure is strongly reduced when recombined with the armchair or zigzag edges. The situation in armchair ribbons is detailed in Fig. 4.16.

In conclusion, we have shown that the pinning of vacancies and adatoms by the edges leads to the formation of sp^3 like tetrahedra and odd membered carbon rings. Besides the perturbation induced by the defects on the π - π^* electronic structure of the ribbon is globally reduced upon the edge reconstruction.

4.2.4 Clusters of defects

As mentioned previously, low energy barriers are reported for the migration of primary defects on the sp^2 carbon plane and these defects are expected to diffuse at room temperature until they are pinned by other defects. This can be either by interaction with an extended defect (e.g. GNR edges) or by combination with other point-defects (e.g. vacancies and adatoms). The predominant mechanism will probably depend

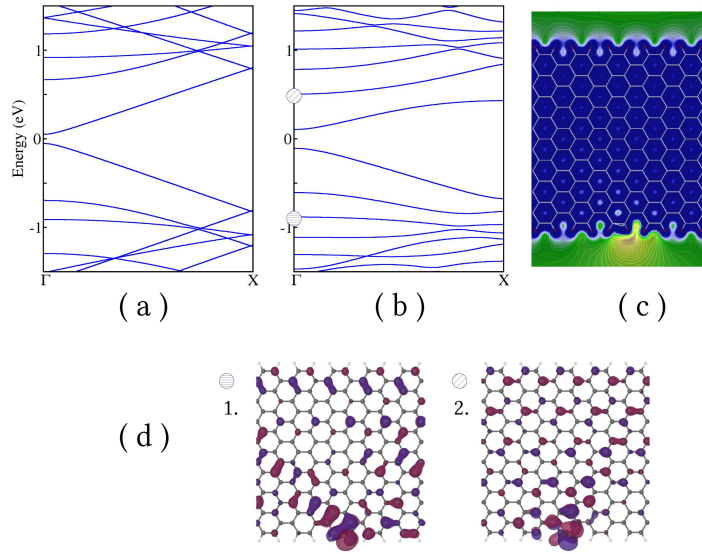


Figure 4.16: [Top panel] Electronic energy band structure of 17-aGNR (a) pristine and (b) in the presence of an *edge* adatom. 5x1x1 GNR super-cells (either pristine or with one defect) have been used for the *ab initio* calculations. (c) Representation of the electrostatic potential of the defective super-cell (i.e. sum of the hartree potential and the local pseudo-potential) integrated along the axis perpendicular to the aGNR plane. One notes the increase of the potential in the close vicinity of the defect, what illustrates the charge transfer from the bulk graphene to the quasi-localized defect states. [Bottom panel] Representation of the low energy electronic states induced by the vacancy. Blue and red surfaces are associated with positive and negative values of the electronic wave-function.

on the ribbon width, the defect density as well as the relative stability of the recombined defects. In this section, we focus on the formation of the smallest clusters of defects (i.e. the di-vacancy and carbon dimer).

(a) *Di-vacancy* - A di-vacancy is formed when two vacancies come sufficiently closer to interact and finally coalesce [200]. Upon relaxation, the atomic structure presents two pentagonal carbon rings whose parallel carbon-carbon bonds are sufficiently strong (1.65 Å) to ensure the saturation of the vacancy dangling bonds (see Fig. 4.17(a)). Besides, upon coalescence, the vacancies lose their localized magnetic moments.

In graphene ribbons, di-vacancies present different geometries depending on the relative orientations (i.e. *parallel*, *tilted* and *perpendicular*) of the defect mirror plane with respect to the ribbon axis. For the same reasons as those reported for single vacancies, the tilted and parallel orientations are respectively the most stable within zigzag and armchair ribbons. The presence of the di-vacancy is found to have an impact on the energetics of the inter-edge magnetic coupling in zigzag ribbons. Similarly to what has been reported for the vacancy, the energy difference $\Delta E_{\uparrow\uparrow} = E_{\uparrow\uparrow} - E_{\uparrow\downarrow}$ is strongly reduced. In the case of di-vacancy at the center of 8-zGNR, the computed value is $\Delta E_{\uparrow\uparrow} = 24$ meV to be compared with $\Delta E_{\uparrow\uparrow} = 88$ meV in pristine zGNR. The computed formation energies of the di-vacancy in its ground-state configurations are 6.858 and 6.743 eV in armchair and zigzag ribbons respectively. This represents an energy gain of ~ 7 eV with respect to the situation of two isolated vacancies. It is thus likely that vacancies will form clusters within the graphene ribbons.

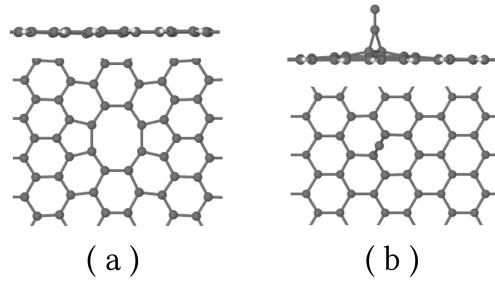


Figure 4.17: Atomic representations of the ground-state geometries of *bulk* di-vacancies (a) and carbon dimers (b) in graphene ribbons. Note that these geometries are independent of the ribbon orientation.

(b) *Carbon dimer* - The smallest carbon cluster is the carbon dimer. In order to find the ground state configuration, various initial geometries have been tested. After relaxation, the configuration with the smallest energy is the linear pile up depicted in Fig. 4.17(b). Though the system still presents dangling bonds, no local magnetization is found. This suggests that the dangling bonds associated with the upper carbon atom are not orthogonal and form bonding and anti-bonding electronic states. The formation energy associated with the carbon dimer is of 7.192 eV (7.515 eV) in zigzag (armchair) GNRs. While being larger than most of the formation energies reported up to now, this represents a large energy gain with respect to the case of two isolated adatoms and highlights the high probability of finding carbon clusters adsorbed on graphene ribbons.

4.3 Hydrogenation and chemical reactivity

Defects have a large influence on the chemistry of graphene. As we have shown in the previous section, the prototypical defects that are vacancies and adatoms come with unsaturated dangling bonds. Therefore, defects are likely to be highly reactive sites and, in ambient conditions, one may expect these dangling bonds to be saturated by gaseous molecules. For example, it has been reported that structural defects play a central role for the reaction of molecular oxygen with graphite [201, 202]. Here we use hydrogenation as an example of chemisorption on both the *bulk* and *edge* primary defects in order to assess their chemical reactivity.

(a) *Hydrogenated vacancy* - When an hydrogen atom encounters a bare *bulk* vacancy, the hydrogen bonds with the out-of-plane carbon atom. Upon relaxation, the new carbon-hydrogen bond form a tilted protrusion with respect to the ribbon plane (see Fig. 4.18(a)). This configuration is non-magnetic, contrasting with the unsaturated defect. The formation energy of the hydrogenated vacancy is lowered by ~ 2 eV with respect to the bare vacancy, emphasizing the high chemical reactivity of the vacancy site.

Similar energy gains are reported upon the hydrogenation of the *edge* vacancy. In zigzag ribbons, the absorption of an hydrogen atom on the *edge* vacancy allows to restore locally the saturation of all the carbon atoms (see Fig. 4.18(d)) and the defect formation energy decreases down to $\xi = 0.005$ eV. On the contrary, the removal of the hydrogen atom from the *edge* vacancy implies the formation of a pentagon of carbon atoms

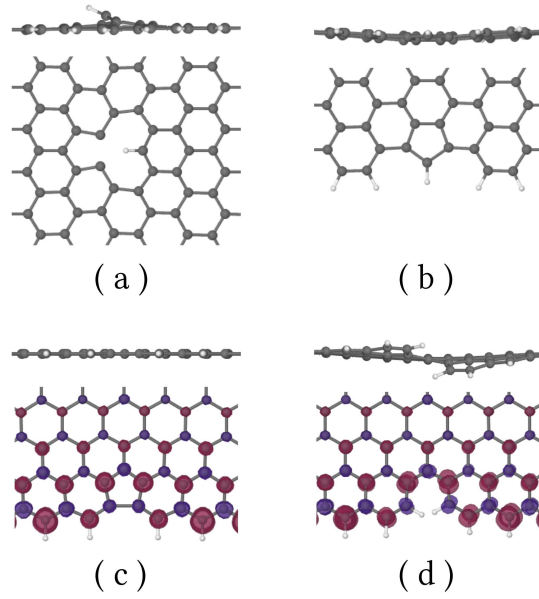


Figure 4.18: Atomic representations of the ground-state geometries of vacancies for various hydrogenation levels. (a) mono-hydrogenated *bulk* vacancy (b) dehydrogenated vacancy at the armchair edge, (c) dehydrogenated vacancy at the zigzag edge, (d) di-hydrogenated vacancy at the zigzag edge. The transparent surfaces correspond to spin polarized electronic densities ($\rho_\alpha - \rho_\beta$) iso-surfaces. Blue and red colors are associated with an excess of spin- α and spin- β respectively.

and leads to a higher formation energy (see Fig. 4.18(c)). Indeed, while suppressing the dangling bond, the new carbon-carbon bond (1.72 Å) is too weak to compensate the distortion induced along the ribbon axis. As a consequence, the computed formation energy is of 2.811 eV which is higher than the value reported for the bare edge vacancy. In armchair ribbons, the removal of the out-of-plane hydrogen atom from the *edge* vacancy also implies the formation of a mono-hydrogenated pentagon at the edge (see Fig. 4.18(b)). While the local saturation of all carbon atoms is preserved, this configuration is however associated with a higher formation energy ($\xi = 1.948$ eV). This is due to the appearance of quasi-localized electronic states around the Fermi energy that were not reported in the case of the bare vacancy.

(b) *Hydrogenated adatom* - Since carbon is tetravalent and presents a high affinity to bond with hydrogen, carbon adatoms are expected to be further stabilized upon both mono- and di-hydrogenation. The geometries of the mono- and di-hydrogenated *bulk* adatoms are described in Figs. 4.19(a,b). Upon structural optimization, a pile up geometry is found for the mono-hydrogenated adatom. The adatom keeps its bridge-like position and the upper hydrogen stabilizes on its top. Finally, the carbon adatom keeps an unpaired p_z orbital which is parallel to the graphene plane giving rise to the ground-state electronic spin-density distribution represented in Fig. 4.19(a). The adsorption of a second hydrogen completes the saturation of the adatom and the ground state electronic density is not spin-polarized anymore. The computed formation energies indicate an energy gain of ~ 2 and ~ 2.7 eV for the first, and second hydrogenation, respectively.

The ground-state geometries of the hydrogenated and di-hydrogenated carbon adatoms at the zigzag edge are reported in Figs. 4.19(e,f). Upon the adsorption of an hydrogen on the upper carbon atom, the symmetry of the di-pyramid with respect to the graphene plane is lost. The upper carbon atom adopts an sp^2 -like configuration and moves slightly in the direction of the ribbon edge. Finally, the p_z orbital of the adatom mixes with the π band of the ribbon and no significant spin polarization is observed on the defect. Again a stabilization of ~ 2 eV is found for the hydrogenation. While it does not modify significantly the defect geometry, the adsorption of a second hydrogen on the carbon adatom allows the complete saturation of the carbon network and a further stabilization of ~ 1 eV is reported. The ground-states geometries of the adatom at the armchair edge are represented in Figs. 4.19(c,d). Upon hydrogenation, the carbon adatom loses one of its dangling bonds and a more

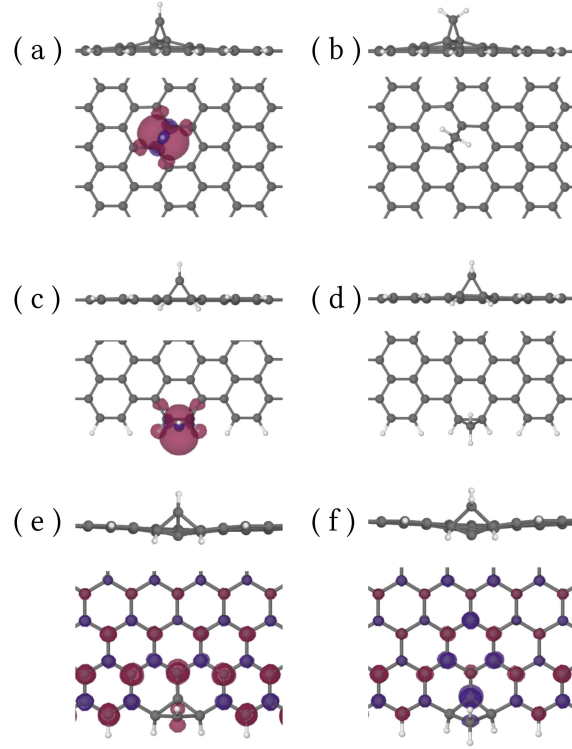


Figure 4.19: Atomic representations of the ground-state geometries of carbon adatoms for various hydrogenation levels. (a) mono-hydrogenated *bulk* adatom (b) di-hydrogenated *textit{bulk}* adatom, (c) mono-hydrogenated adatom at the armchair edge, (d) di-hydrogenated adatom at the armchair edge, (e) mono-hydrogenated adatom at the zigzag edge, (f) di-hydrogenated adatom at the zigzag edge. The transparent surfaces correspond to spin polarized electronic densities ($\rho_\alpha - \rho_\beta$) iso-surfaces. Blue and red colors are associated with an excess of spin- α and spin- β respectively.

symmetric configuration is found. A local magnetic moment due to the presence of a single unpaired p_z orbital appears on the defect. Upon dihydrogenation, the saturation of the carbon adatom is achieved and the local magnetic moment disappears. Energy gains of ~ 1.9 and ~ 1.6 eV are reported for the first, and second hydrogenation, respectively.

In conclusion, the adsorption of hydrogen atoms has been used as a test case in order to assess the chemical activity of topological defects in GNRs. It has been shown that the topological defects act as highly reactive centers and play a key role in the chemical functionalization of graphene ribbons. Besides, our calculations reveal that most of the considered defects lose their magnetic moment upon hydrogenation. This highlights the poor stability of defect induced magnetism upon chemisorption. In addition, the comparison of the defect formation energies reported above reveals that fully hydrogenated vacancies and adatoms at the edge are the most stable primary defect configurations in both armchair and zigzag graphene ribbons. Indeed, the computed formation energies of the hydrogenated *edge* defects are significantly lower than those reported for the hydrogenated *bulk* defects as well as those associated with the di-vacancy and carbon dimer. As a consequence one can expect the recombination at the edges to be the main mechanism for pinning mobile primary defect in narrow GNRs.

4.4 Further reconstructions of the edges

While the presence of defects along the edges is likely to be unavoidable, very few is known about the actual structures and electronic properties of defective edges. In particular, the experimental investigation of the graphene boundaries has lagged behind due to intrinsic difficulties in achieving atomic scale resolution of the actual edge profiles with the traditional scanning tunneling (STM) and atomic force (AFM) microscopies. As a consequence, the obvious questions "*What are the most probable defects at the edge ?*" and "*What are their impact on the electronic properties of GNRs?*" are still open.

Nevertheless, recent developments of the low voltage aberration-corrected transmission electron microscopy (TEAM) allowed to achieve significant improvements in the resolution and characterization of graphene fragments. In particular, two recent papers gave insights into the variety of reconstructions at the graphene boundaries [130, 147]. As a main result, these studies revealed the presence of both odd-membered ring and atomic roughness at the edges of actual GNRs. Motivated by these

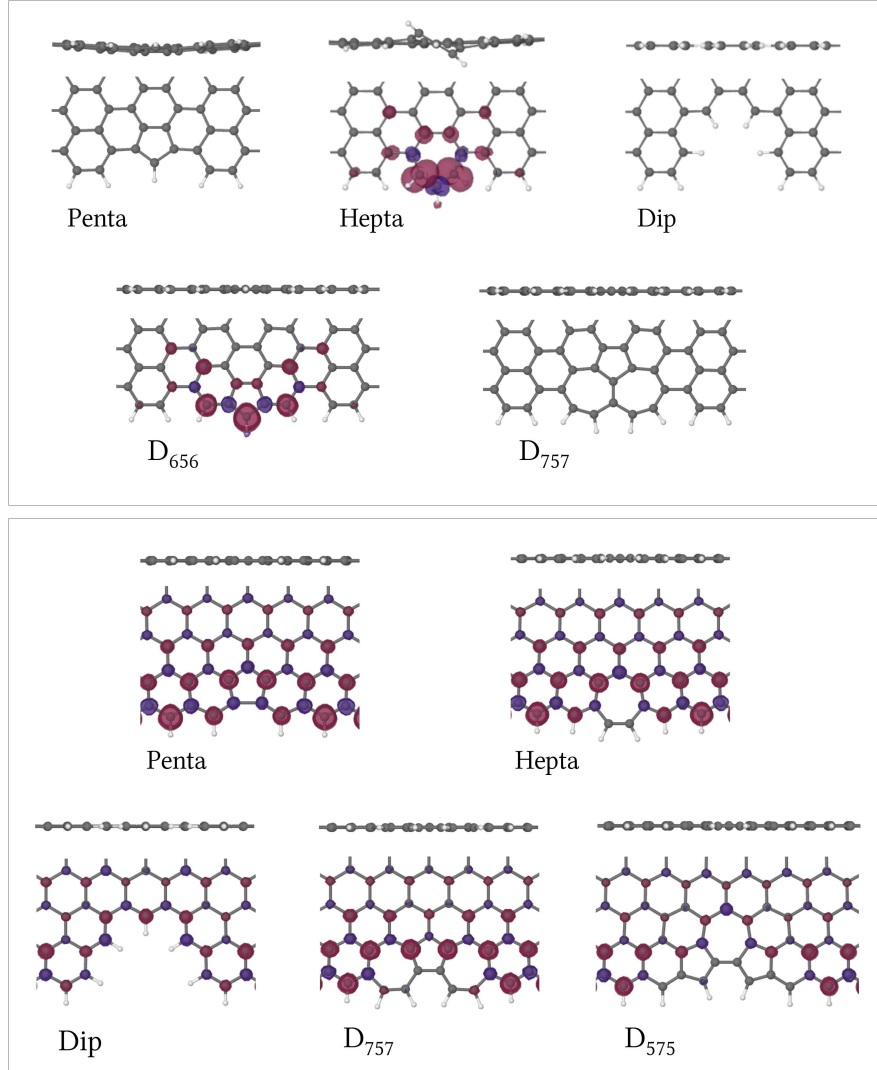


Figure 4.20: Atomic representations of the *Penta*, *Hepta*, *Dip*, D_{656} , D_{757} and D_{575} edge topologies. [Top panel] Defects along the armchair edge. [Bottom panel] Defects along the zigzag edge. The transparent surfaces correspond to spin polarized electronic densities ($\rho_\alpha - \rho_\beta$) iso-surfaces. Blue and red colors are associated with an excess of spin- α and spin- β respectively.

pictorial results and by other scanning tunneling (STM) [203, 204] and electronic transmission (TEM) [129, 205] microscopy studies, we report here the formation energies of various defects directly inspired by the experiments (see Fig. 4.20).

The defect topologies D_{757} and D_{575} are combinations of odd-membered rings of carbon atoms. In those structures, the distortions induced by pentagons and heptagons are expected to compensate partially leading to an increased stability. By sake of comparison, and in order to isolated their effects, point-defects consisting in single pentagon and heptagon of carbon atoms have also been considered (i.e. defects labelled *penta*, *hepta* and D_{656}). Finally, the defect topologies labelled *Dip* aim to account for the atomic roughness of the edges.

The computed formation energies are gathered in Table 4.3 and compared with the values reported in the previous sections. On the one hand, the energetic of *bulk* defects is very similar in both armchair and zigzag shaped ribbons. This is not surprising since the influence of the edge topology becomes insignificant as defects are introduced far away from the ribbon boundaries. On the other hand, the armchair edge seems to be more robust than the zigzag edge with respect to the introduction of topological defects. Indeed, the computed formation energy of an hydrogenated vacancy at the zigzag edge is of 0.005 eV only. Even more surprising is the negative energy associated with the formation of *Dip*-like defects. Such low formation energies are not found for the armchair edge. We note that these observations are coherent with the results presented in chapter 3 about the relative stability of the reconstructed zigzag and armchair ribbons. The introduction of defects along the armchair edges locally destroys the benzenoid structure of the edge. This process is not energetically favorable since it limits the aromatic stabilization of the *pi*-electrons. On the contrary, the zigzag edges are not at all benzenoid and such considerations do not apply.

Finally, the nature of the charge transfer (i.e. *acceptor*, *donor* or *neutral*) induced by the defects, as well as their magnetic characteristics are summarized in Table 4.3. Though the origin of the charge transfer between the carbon network and the point-defects (i.e. the *self-doping*) is further investigated in Chap. 5, one already notes that topological defects may act as acceptor and donor depending on their configuration. The most stable *bulk* and *edge* defects (i.e. those recombined or fully-hydrogenated) do not come with an electronic density that is locally spin-polarized. Our results therefore predict that the observation of defect-induced magnetism in graphene ribbons is limited to the case where a significant amount of primary defects are not recombined. With this respect, the presence of the ribbon edges, which facilitate the defect

recombination, should impede the observation of magnetism associated with point-defects.

17-aGNR [eV]				8-zGNR [eV]		
<i>Bulk</i> Vacancies and adatoms :						
adatom	6.683	μ_B	<i>accept.</i>	6.697	μ_B	<i>accept.</i>
adatom + H	4.774	μ_B	<i>neutral</i>	4.697	μ_B	<i>neutral</i>
adatom + H ₂	2.041	–	<i>neutral</i>	1.980	–	<i>neutral</i>
vacancy	7.601	μ_B	<i>accept.</i>	7.671	μ_B	<i>accept.</i>
vacancy + H	5.452	–	<i>accept.</i>	5.618	–	<i>accept.</i>
Small clusters :						
carbon dimer	7.515	–	–	7.192	no μ_B	–
di-vacancy	6.858	–	<i>donor</i>	6.743	no μ_B	<i>donor</i>
<i>Edge</i> Vacancies and adatoms :						
adatom	5.591	–	<i>accept.</i>	4.869	–	<i>neutral</i>
adatom + H	3.715	μ_B	<i>neutral</i>	2.597	–	<i>neutral</i>
adatom + H ₂	1.156	–	<i>neutral</i>	1.302	–	<i>donor</i>
vacancy	0.855	–	<i>neutral</i>	2.389	μ_B	<i>neutral</i>
vacancy + H				0.005	–	<i>neutral</i>
vacancy - H	1.948	–	<i>accept.</i>	2.811	–	<i>neutral</i>
<i>Experimental</i> defects :						
penta	1.948	–	<i>accept.</i>	2.811	–	
hepta	0.839	μ_B	<i>donor</i>	2.381	–	<i>accept.</i>
D ₇₅₇	1.598	–	<i>donor</i>	2.062	–	<i>accept.</i>
D ₅₇₅				3.379	–	<i>accept.</i>
D ₆₅₆	0.573	μ_B	<i>accept.</i>			
Dip	0.268	–	<i>neutral</i>	-0.712	–	<i>neutral</i>

Table 4.3: *Ab initio* computed formation energies associated with various topological defects in both 8-zGNR and 17-aGNR. The energy computation relies on 8x1x1 and 5x1x1 super-cells for the zigzag and armchair cases, respectively. The symbol μ_B (–) refers to the presence (absence) of a spin-polarized electronic density distribution induced by the defect. Finally, the charge transfer between the topological defects and the graphene ribbon is mentioned.

Conclusion

In this chapter, the structural, electronic, and magnetic properties of vacancies and adatoms in graphene nanoribbons have been unveiled. Our results highlight the large stabilization of defects upon both the re-

combination at the edges and the formation of defect clusters. On the one hand, the di-hydrogenated adatoms and the di-vacancy are reported as the most stable defect configurations within the graphene plane. On the other hand, the recombination of the point-defects at the armchair and zigzag ribbon edge leads to the formation of sp^3 like tetrahedra and odd membered carbon rings that are even more stable. Therefore, upon migration, vacancies and adatoms are likely to contribute to the reconstruction of the graphene boundaries. Besides, one observes that the perturbation induced by the defects on the low energy electronic structure is globally reduced upon the recombination at the edge. Similarly, though the isolated defects are reported to come with local magnetic moments and to induce a locally spin-polarized electronic density in the graphene network, no magnetic behavior is reported for the most probable configurations of the defective edges. Finally, the comparison of the armchair and zigzag edges highlights the robustness of the armchair edges with respect to the formation of topological defects. This seems to be the natural consequence of the absence of aromatic stabilization along the zigzag shaped boundaries.

Chapter 5

Quantum transport in graphene nanoribbons

5.1 Introduction

The recent progresses in the synthesis and characterization of single sheet of graphite has initiated a considerable experimental and theoretical research effort aiming to understand and control the transport properties of this outstanding material. As a truly 2D crystal where electrons and holes behave like massless Dirac fermions, graphene offers the opportunity to observe many new transport phenomena, such as electron mobilities up to 150 times greater than in silicon, anomalous quantum Hall effect at room temperature, quantum conductivity that never fall belows a minimum value, absence of weak localization, or unimpeded tunnelling of electrons through high and wide energy barriers [4].

In addition to being a direct window onto the physics of low-dimensional systems, graphene also shows promises as a future material for nanoelectronics. Graphene is easy to process, can be patterned with existing lithographic technologies and is therefore compatible with the industry-standard processes. It reveals extremely high stability, flexibility, and presents a thermal conductivity predicted to be twice as big as that of diamond. Within graphene, the type and concentration of charge carrier is easily tuned by a gate electrode. Applications in high frequency integrated circuits would take advantage of the graphene's extremely high carriers mobilities and low scattering. Finally, the ability to realize spin injection and the observation of very long spin relaxations lengths suggest potential uses in spintronic devices.

While graphene is a zero-gap semiconductor, significant progress has been achieved in the synthesis of narrow graphene nanoribbons allowing

the realization of carbon based field-effect devices. Lithographic patterning of graphene sheets has proven to be efficient for the fabrication of GNRs down to widths of ~ 20 nm [117, 206, 118]. While lithographic patterning is one of the simplest way to produces GNRs, the resulting carbon samples are characterized by an important roughness on the edge ~ 5 nm. Therefore, chemical methods have been developed that allows to produce ribbons with width below 10 nm that exhibit ultra-smooth edges [207, 208, 148, 209, 210]. The chemical route is based on expandable graphite (i.e. graphite intercalation compounds) that is exfoliated under the influence of heat and broken into ribbons by sonication. Unfortunately, this highly reliable method allows to produces only a very small quantity of nanoribbons. The use of chemical vapor deposition (CVD) has been reported for massive production (grams per day) of GNRs [211]. While the method is highly successful for producing long and highly crystalline metallic ribbons, another way has to be found for bulk production of semi-conducting GNRs. Very recently, two methods have been reported that bring some hope for a larger-scale production [206, 212]. These rely on unzipping multi-walled carbon nanotube (CNT) either by the chemical oxidation of the CNTs carbon-carbon bonds or by an Argon plasma etching method. The GNRs produced by plasma etching are highly appealing since they present smooth edges and a narrow width distribution (from 10 to 20 nm). Importantly, unzipping CNTs with well-defined structures opens the road towards a better control of the width and edge pattern of the actual ribbons. For the five past years, these experimental achievements greatly feed the interest for carbon based field-effect transistors.

Most commonly, GNRs-based field-effect transistors are built from graphene ribbons dispersed on a SiO_2/Si chip. The bottom Si layer is highly doped and act as a back gate, while the top SiO_2 layer serves as gate dielectric. The device source and drain are made of metallic contact most frequently in Palladium. A prototypical device setup is illustrated in Fig. 5.1. At room temperature, large on-off current ratios ($I_{on}/I_{off} > 10^5$) have been reported for narrow GNRs (width < 10 nm) even for low source-drain bias ($V_{SD} < 1$ V). In addition, electron mobilities ranging from a few hundred to $> 1000 \text{ cm}^2/\text{Vs}$ for GNRs wider than 20 nm have been measured [148, 6].

Though graphene ribbons combines many attracting features, the actual performances of GNRs-FET have to be significantly improved in order to compete with the silicon-based technology. In this respect, various fundamental questions still need to be addressed. For example, the intrinsic carrier mobility in narrow ribbons remain essentially unknown. Though it is very likely that defects, and edge roughness will appears

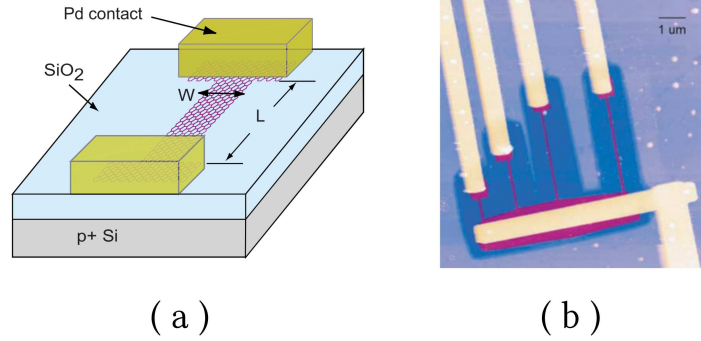


Figure 5.1: (a) Schematic representation of a GNR-Field Effect Transistor where the GNR channel is contacted by two metallic electrodes (source and drain) and the p-doped Silicon substrate acts as the back gate electrode. (b) AFM image of actual GNRs-FET devices with different channel lengths. Pictures from Ref. [148]

along the GNR channel inducing local changes in the actual electronic structure of the ribbon, very few is known about the impact on the carriers propagation. One commonly guess that the roughness of the edges causes an increased scattering-induced resistivity in the narrow ribbons, but there is no firm theoretical justification for such a mechanism. More intriguingly, though theory predicts a dependence of the energy gaps of narrow ribbons with respect to their crystallographic orientation, this behavior is not evidenced by transport measurements.

In view of these open issues, numerical studies that explicitly take into account the presence of imperfections will surely help in designing appropriate routes for GNRs-FET fabrication and facilitate the improvement of devices characteristics. In this chapter, we focus on the electronic transport properties of pristine and defective graphene ribbons. In particular, *ab initio* tools are used to investigate the impact of topological defects on the intrinsic conductance properties of prototypical armchair and zigzag shaped ribbons.

Though the results presented in Chapter 3 clearly indicate that the thermodynamical stability of the a_{11} and z_1 edge profiles is restricted to specific experimental conditions (i.e. low hydrogen content in the environment), the study presented here below highlights physical processes that are common to all GNRs. The scope of our results should therefore extend beyond the specific ribbon geometries considered in this chapter. In addition, as the z_1 topology gives rise to electronic states localized at

the edge while the a_{11} profile does not, our results should give insights into the electronic transport properties of both magnetically ordered and diamagnetic GNRS.

5.2 Modeling setup

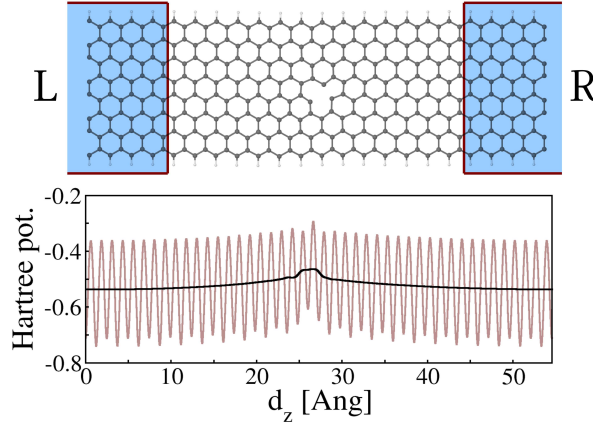


Figure 5.2: [Top panel] Schematic representation of the setup used to compute the intrinsic transport properties of graphene ribbons in the presence of an isolated defect. The central part that contains the defect is made of a super-cell large enough to insure the screening of the defect induced charge transfer. Left and right leads are semi-infinite pristine GNRS. [Bottom panel] Planar average of the Hartree potential as a function of the position along transport direction.

Coherent quantum transport in mesoscopic and low dimensional systems are commonly investigated either with the Kubo-Greenwood [213] or the Landauer-Büttiker formalisms [214]. Deriving from the fluctuation-dissipation theorem, the first approach allows to evaluate the intrinsic conduction regimes, and gives a direct access to the fundamental transport length scales, such as the elastic mean free path (l_e) and the localization length (η). When l_e becomes longer than the length of the conduction channel in between voltage probes, the carriers propagate ballistically and contact effects prevail. In such a situation the Landauer-Büttiker formalism becomes more appropriate, since it provides direct access to the energy resolved transmission properties and allows to readily derive the conductance profiles for open systems and arbitrary interface geometries. Besides, its formal extensions (Non Equilibrium Green's

Functions-NEGF and Keldysh formalism) further enable to investigate quantum transport in situations far from the equilibrium, of relevance for high-bias regimes or situations with dominating contribution of Coulomb interactions. Interestingly, to investigate coherent quantum transport in a ribbon of length L with reflection-less contacts (ideal contact) to external reservoirs, both transport formalisms are formally fully equivalent at zero bias. In the present work, the electronic transport properties of defective graphene nanoribbons are examined within the Landauer-Büttiker formalisms [214].

Though most of the theoretical efforts to solve the problem of conductance in defective systems has been made so far within simple tight-binding approximations (one onsite energy per carbon site and overlap integrals restricted to nearest-neighbors carbon atoms), we use fully self-consistent *ab initio* techniques to compute the scattering profiles of defects. If not otherwise stated, the *ab initio* conductances presented in the following have been obtained within the Green's functions framework as implemented in the *Smeagol* code [8]. The one-particle Hamiltonian obtained from DFT calculations are used as a starting point for the solution of the coherent quantum transport equation. The modelling setup for GNRs is illustrated in Fig. 5.2. The region of interest (i.e. the one where all the scattering processes take place) is connected to two semi-infinite leads. In order to simulate open boundary conditions, the self-energies associated with the leads are then included within the self-consistent calculation of the potential. Finally, the electronic transmission functions are evaluated by using the Fisher-Lee relation,

$$T(E) = \text{tr}\{\Gamma_L(E)G_D^{r\dagger}(E)\Gamma_R(E)G_D^r(E)\} \quad (5.1)$$

where $G_D^r = \{EI - H_D - \Sigma_L - \Sigma_R\}^{-1}$ is the one particle Green's function of the device, $\Sigma_{R/L}$ are the self-energies accounting for the coupling with the right (left) electrodes, and $\Gamma_{R/L} = \Sigma_{R/L} - \Sigma_{R/L}^\dagger$ are the broadening functions associated with right (left) electrodes.

Since we are interested in the intrinsic conductance of defective ribbons, perfect ribbon-based leads are considered. In such a way, there is no symmetry mismatch at the interface between the two leads and the scattering region. Due to the presence of a defect, the size of the central region has to be carefully converged in order to avoid discontinuity in the potential profile at the interface. Hereafter, scattering regions of ~ 35 Å long are considered.

Convergence studies have shown that such lengths allow to accurately screen the electrostatic potential of the topological defects. Within the scattering region, the atomic positions have been fully optimized within

the periodic boundary approximation until the forces on the atoms and the unit cell are below $0.01 \text{ eV/\AA}$ and $0.05 \text{ eV/\AA}$ respectively. Note that in order to insure a perfect match between the scattering region and the leads, the first and last GNRs cells of the scattering region have been moved as rigid blocks during the geometry optimization. The modelling of reflection-less contact is thus achieved and carriers can move in/out the central region without significant back-scattering.

5.3 Quantum transport in pristine GNRs

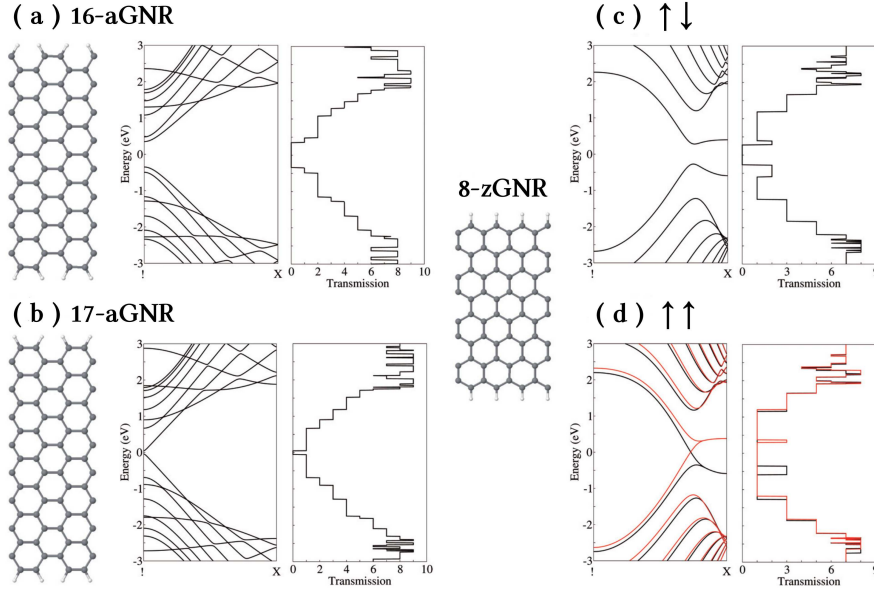


Figure 5.3: Atomic structures, electronic band structures and quantum conductances (electronic transmission) of various graphene nanoribbons. (a) 16-armchair GNR, (b) 17-armchair GNR, (c) and d) 8-zigzag GNR with anti-parallel ($\uparrow\downarrow$) and parallel ($\uparrow\uparrow$) spin orientations between the two magnetic edges. The spin-dependent transport has been evaluated for both magnetic configurations of the 8-zigzag GNR (c-d) but it is only noticeable for the parallel ($\uparrow\uparrow$) spin orientation. The majority (α -spin) and minority (β -spin) spin orientations are represented in black and red, respectively.

For a graphene ribbon of length L in between metallic contact reservoirs, the transport regime is ballistic if the measured conductance is L -independent, and only given by the energy-dependent number of available quantum channels $N(E)$ times the conductance quantum $G_0 =$

e^2/h , that is $G_{(\alpha/\beta)}(E) = e^2/h \times N_{(\alpha/\beta)}(E)$, where (α/β) account for the spin degrees of freedom. This occurs only in case of perfect (reflectionless) or ohmic contacts between the nanostructure and metallic voltage probes. In this regime, the expected energy-dependent conductance spectrum is easily deduced, from band structure calculations, by counting the number of channels at a given energy. As a consequence, quantum transport properties of GNRs are expected to strongly depend on whether their edges exhibit the armchair or the zigzag configurations.

As mentioned earlier (see Chapter 3), the gaps of the N -aGNRs depend on N , separating the ribbons in three different categories (all exhibiting direct band gaps at Γ). The band structures and the corresponding quantum conductances of two armchair GNRs are illustrated in Figs. 5.3(a-b). The 16-aGNR is a semiconductor with a gap of ~ 0.8 eV, thus inducing a quite large energy interval where no transmission is allowed (Fig. 5.3(a)). The opening of a small energy gap at the Fermi energy produced by the reconstruction of the armchair edges can be observed in the 17-aGNR. Around, this region of zero conductance the linear electronic energy bands provide one quanta ($= 2e^2/h$, the factor 2 account for the spin degeneracy) to the conductance and lead to a plateau of conductance around the charge neutrality point. A very small external electric field would thus induce an electronic transmission through one channel. Note that this single-channel window, which is globally the same as in zigzag-shaped ribbon, decreases rapidly for GNR of larger width. At higher energies, the conductance increases as more channels become available for the conduction.

Identically, nanoribbons with zigzag shaped edges exhibit direct band gaps which decrease with increasing width. However, in zGNRs, the quantum transport is dominated by edge states which are expected to be spin-polarized owing to their high degeneracy. The band structures and the spin-dependent quantum conductances of a 8-zGNR are illustrated in Figs. 5.3(c-d) for both the ferromagnetic ($\uparrow\uparrow$) and anti-ferromagnetic ($\uparrow\downarrow$) couplings between the edges. The antiferromagnetic ($\uparrow\downarrow$) spin configuration of the 8-zGNR conserves the semi-conducting behavior of the GNR family, and its electronic transmission function displays a gap of 0.3 eV around the Fermi energy (Fig. 5.3(c)). One note that the presence of the spin-polarized edge states do not lead to a spin polarized transmission due to the symmetry between the edges with opposite magnetization. In order to obtain net spin injection, the symmetry has to be broken [215]. This may be realized by the incorporation of defects (such as vacancies or adatoms) or by the presence of roughness at the edge.

The ferromagnetic ($\uparrow\uparrow$) spin configuration of 8-zGNR is metallic and shows a non-zero electronic transmission function at the Fermi energy

(Fig. 5.3(d)) The spin-dependent conductance calculation reveals that the transmission of the π electrons with α -spin orientation is favored for an energy region around -0.35 eV below the charge neutrality point. The π^* electrons with β -spin orientation are more easily transmitted around $+0.35$ eV above the Fermi energy. One note here that, the presence of the spin polarized channels suggests that doped ferromagnetic ($\uparrow\uparrow$) zGNRs may serve as spin injectors.

In conclusion, the intrinsic conductance of pristine GNRs is completely determined by the energy-dependent number of conduction channels. The transport properties should therefore present the same versatility as the electronic energy band structures. In particular, the ribbon width and the atomic configuration at the edges are predicted to have a strong impact on the low bias conductance of GNRs. At this point, it is important to notice that the *ab initio* values predicted for the conductance are the uppermost theoretical limits that would be experimentally measured. In practical situations, lower values are observed since the transmission at the interface between the voltage probes (metallic leads) and the ribbons is fundamentally limited by interface symmetry mismatch, inducing Bragg-type back-scattering. Additionally, local structural defects or imperfections at the edge, which usually cannot be avoided experimentally, introduce intrinsic back-scattering along the ribbon that reduces its transmission capability. The consequences of such back-scattering are investigated in the next sections.

5.4 Quasi-localized states and back-scattering

Nanoribbons intrinsically have defects in the bulk and at the edges that may come with quasi-localized states in the low energy region. As such, defects are expected to have a large impact on the electronic transport properties and to influence the merits of GNRs for their use in micro-electronic applications. In this section, we focus on the case of the *bulk* and *edge* mono-vacancy. Their conductance pattern are computed by means of *ab initio* techniques and the fundamental mechanisms in charge of the conductance reduction are highlighted.

In the presence of a single vacancy, previous TB calculations [216] predict the appearance of dips in the conductance of GNRs positioned symmetrically with respect to the Fermi energy. We show that the *ab initio* computed conductance patterns differs from the TB prediction. Large electron-hole asymmetries and finite spin conductance are evidenced for both the *bulk* and *edge* vacancies.

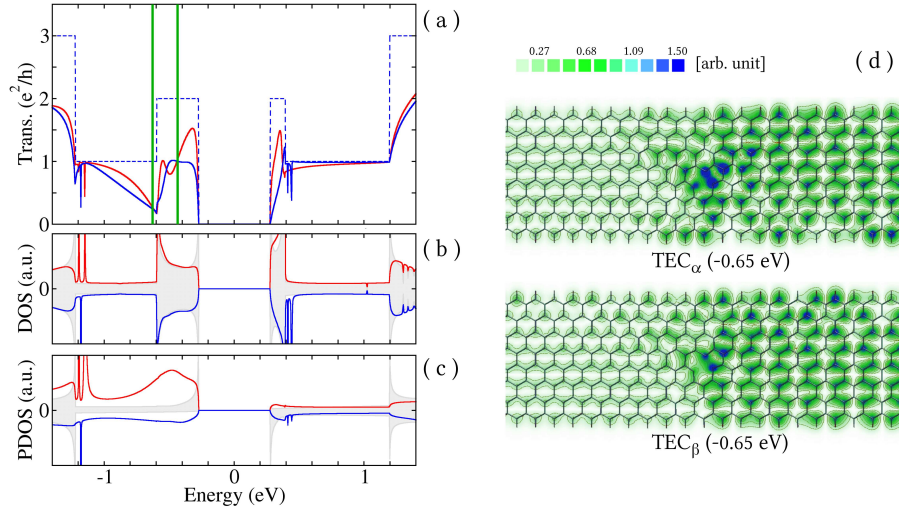


Figure 5.4: Effect of a *bulk* vacancy on the conductance of a 8-zGNR. (a) The conductance as a function of the incident energy. Blue and red plain lines correspond to the α - and β -spin electrons, respectively. Dotted lines represent the conductance of the pristine ribbon. (b) Density of states (DOS) of the pristine (grey area) and defective (plain lines) 8-zGNR. The DOS of the α - and β -spin electrons are represented with aids of negative and positive half-planes, respectively. (c) Density of states projected (PDOS) onto three carbon atoms of the pristine ribbon (grey area) and onto the three carbon atoms forming the vacancy (plain lines). The PDOS of the α - and β -spin electrons are represented negative and positive values, respectively. (d) Representation of the transmission eigenchannels for the α -spin (top) and β -spin (bottom) electrons coming from the right lead with an energy of $E = -0.65$ eV. The two-dimensional representation of the charge density associated with the transmission eigenchannels is obtained by its integration along the axis perpendicular to the ribbon plane.

Conductance pattern of the *bulk* vacancy

In the presence of a single vacancy, the *ab initio* computed conductance of carbon nanotubes shows four dips around the Fermi energy as reported by Choi and coworkers [217]. Three dips are very narrow. These are due to the resonant back-scattering of the incoming electrons by the broken σ bonds. The fourth one is broad and associated with a quasi-localized defect state that presents a π -like parity.

As shown in Figs. 5.4(a-c), the situation is very similar in the case of GNRs with single vacancy, though more complex. The broken σ bonds give rise to very narrow dips at energies above (+0.22 eV) and below (-1.09 eV) the Fermi energy. These σ states are essentially orthogonal to the π - π^* orbitals and the coupling between these states and the conduction channel is very small. This explains the tiny energy dispersion of the associated dip in the electronic transmission function (see Fig. 5.4(a)). On the other hand, the broad decrease of the conductance that appears -0.3 eV below the Fermi energy is associated with a quasi-localized states that presents a *pi*-like parity with respect to the ribbon plane.

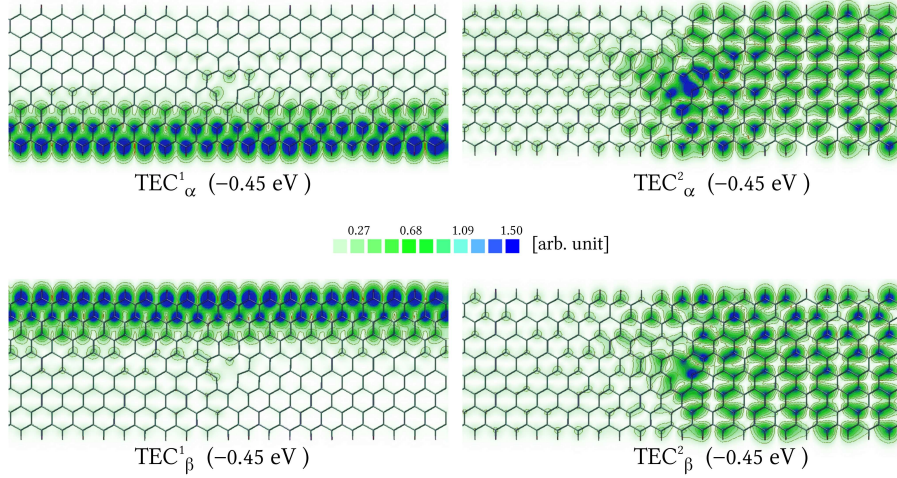


Figure 5.5: Effect of a *bulk* vacancy on the conductance of a 8-zGNR. Representation of the two transmission eigenchannels (TEC) for α -spin (top) and β -spin (bottom) electrons coming from the right lead with an energy of $E = -0.45$ eV. The two-dimensional representation of the charge density associated with the transmission eigenchannels is obtained by its integration along the axis perpendicular to the ribbon plane.

Decomposition in terms of eigenchannels

In order to gain insight into the mechanisms that limit the conductance at these energies, we have computed the transmission eigenchannels (TEC) for various energies within the single channel energy window (i.e. $[-1.1, 1.1]$ eV). Since we are dealing with an open system, periodic boundary conditions do not apply anymore and the relevant electronic states within the central region are those eigenstates that verify the scattering boundary conditions. Though the Green's function is the fundamental quantity in our calculation, the computation of the transmission eigenchannels allows to interpret the conductance patterns in terms of scattering states. Indeed, the transmission eigenchannels are nothing else but a convenient unitary transformation of the incoming scattering states at a given energy that provides a way to decompose the transmission into non-mixing channels (in the sense that the transmission of the sum of two eigenchannels is given by the sum of the individual transmissions). The eigenchannels incoming from the right lead with energies of -0.3 and -0.22 eV are plotted in Figs. 5.4(d) and 5.5.

At 0.3 eV below the Fermi level, the eigenchannels clearly indicate that carriers injected at this energy are back-scattered by the vacancy induced potential. At this energy the propagating electrons interact with a quasi-localized state that presents a π -like parity. At 0.22 eV below the Fermi energy, the decomposition of the transmission function in non-mixing channels highlights the crucial impact of the edge states. Indeed, as shown in Fig. 5.5, from the four eigenchannels (two for each spin orientation) available for the electronic conduction in pristine zGNRs, two are destroyed by the vacancy while the two others that closely remind the edge states of zGNRs are not affected and contribute for one quantum ($\frac{e^2}{h}$) to the conductance.

The present result can be understood in terms of the electronic band structure of the pristine ribbon. Directly below (above) the Fermi level, two eigenchannels are available for the electronic conduction. Both are made from the highest occupied (lowest unoccupied) π -band (π^* -band) but one arises from the states localized at the ribbon edges, while the other originates from the π - π bonds within the bulk of the ribbon. As a consequence, the electrons injected within the *bulk*-like bands are prone to be scattered by the *bulk* defects and to remain globally insensitive to the scattering potential at the edges. Similarly, the electrons originating from the *edge* states are insensitive to the perturbation of the potential within the ribbon *bulk* but are scattered by defects at the edges. In this sense, the separation of the highest occupied (lowest unoccupied) π -band (π^* -band) into components originating from the bulk and from the edge

of the ribbon strengthens the robustness of the low energy conductance with respect to the disorder.

Conductance pattern of the *edge* vacancy

Such analysis is further confirmed by the calculation of the conductance profile associated with the *edge* vacancy. As shown in Figs. 5.6(a-c), when vacancies are recombined with the zigzag boundary, their impact on the conductance of low energy carriers is consequently decreased. Localized electronic states associated with the broken σ -bond are reported away from the Fermi level (i.e. at ± 1.09 eV) and no quasi-localized electronic states with π -like parity perturbs the conductance pattern within the single channel energy window. The only significant effect is the suppression of the transmission associated with the eigenchannels localized at the defective zigzag edge, as shown in Fig. 5.6(d). As a consequence the conductance of low energy carriers is reduced to ($G = 3 \frac{e^2}{h}$). Finally, as a consequence of the ferromagnetic order along the zigzag edges, the conductance profile of the *edge* vacancy is spin polarized, meaning that zigzag nanoribbons with defective edges could be used for spin injection into graphene. However, while such systems theoretically appear as an appealing device for spin-injection, their experimental relevance is not at all obvious as it requires one of the zigzag edges to exhibit a long range perfect crystallinity.

5.5 Defect positions and scattering

With respect to their electronic and transport properties graphene ribbons are often compared with the carbon nanotubes. Indeed, graphene ribbons may be regarded as unrolled nanotubes and their electronic structures present many similarities. The behavior of low energy electrons is mainly determined by the confinement effects in both systems, giving rise to similar dependence of the electronic energy gaps with respect to the width/diameter and crystallographic orientation of GNRs and CNTs.

However, though nanotubes have many mirror planes parallel to the tube axis, implying equivalent atomic sites all around the tube circumference, the ribbons only present two mirroring planes. One contains the ribbon plane and fixes the parity of the π and σ bonds, the second is perpendicular, contains the ribbon axis, and reflects one ribbon edge on the other one. As a consequence, the atomic sites across the ribbon width are non-equivalent. In this section, the bonding/anti-bonding energies of the quasi-localized states are shown to be strongly affected by

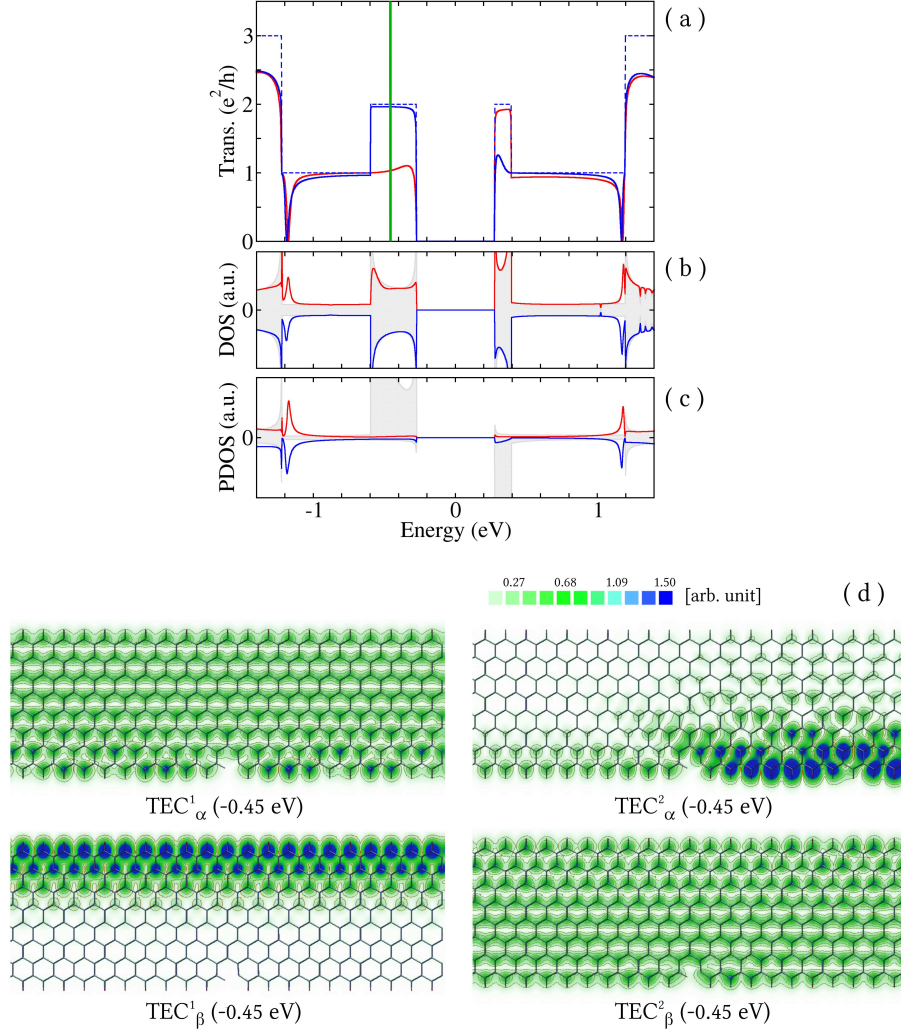


Figure 5.6: Effect of an *edge* vacancy on the conductance of a 8-zGNR. (a) The conductance as a function of the incident energy. Blue and red plain lines correspond to the α - and β -spin electrons, respectively. Dotted lines represent the conductance of the pristine ribbon. (b) Density of states (DOS) of the pristine (grey area) and defective (plain lines) 8-zGNR. The DOS of the α - and β -spin electrons are represented with negative and positive values, respectively. (c) Density of states projected (PDOS) onto three carbon atoms of the pristine ribbon (grey area) and onto the three carbon atoms forming vacancy (plain lines). The PDOS of the α - and β -spin electrons are represented with negative and positive values, respectively. (d) Representation of the transmission eigenchannels for α - and β -spin carriers coming from the right lead with an energy of $E = -0.45$ eV. The two-dimensional representation of the charge density associated with the transmission eigenchannels is obtained by its integration along the axis perpendicular to the ribbon plane.

the position of the topological defect. In addition, prevented scattering due to symmetry reasons is reported when the defect configuration preserves the "axial" mirror symmetry. Note that a similar behavior has been reported in doped GNRs [218]. These peculiar geometrical aspects of the electronic transport in defective graphene ribbons are illustrated hereafter for the case of carbon adatom adsorbed on 17-aGNRs.

The scattering profiles of adatoms at various positions within the aGNR are reported in Figs. 5.7(a-e). As described previously, the defect induces various dips in the transmission function due to the back-scattering of incident electrons by the corresponding quasi-localized states. The energies at which these dips occur are determined by the binding energies of the defect induced electronic states. As illustrated in Figs. 5.7(b-c) *bulk* adatoms introduce two quasi-localized electronic states within the single-channel energy window. The lower one (at -0.65 eV) is associated with the sp^2 dangling bond of the adatom and has a limited overlap with the π conduction channel leading to the well defined scattering energy. In contrast, the upper dip (at -0.5 eV) corresponds to a defect induced states with a π -like parity that interacts widely with the propagating electrons and leads to a broad decrease of the conductance. In addition, by comparing Figs. 5.7(b) and 5.7(c), one notices the dependence of the resonant energy of the π -like quasi-localized state with respect to the defect position. Even more surprising is the large variation of the coupling strength between the defect states and the conduction channel. As reported previously in Chapter 4, the recombination of the adatom with the armchair edge reduces the defect-induced perturbation of the GNRs conductance since the π -like quasi-localized electronic states disappear when the reconstruction of the defect occurs.

The fluctuation of the conductance pattern with respect to the defect position highlights the high sensitivity of the GNRs transport properties to the presence of a random distribution of defects across the ribbon width. Indeed, in the case of adatom within aGNRs, such a distribution would lead to a uniform decrease of the conductance of the low energy electrons. This theoretical prediction strongly contrasts with the case of CNTs, where each kind of defects leads to a series of well defined dip in the conduction channel.

Finally, we turn to the analysis of the conductance profile reported in Fig. 5.7(a) that corresponds to an adatom exactly at the center of the ribbon. Intriguingly, this defect configuration does not lead to any reduction of the electronic transmission probability. The defect-induced potential seems thus to have no influence on the propagation of incoming electrons. This can be explained by analyzing the symmetries of the conduction eigenchannel and the defect quasi-localized states. Since the

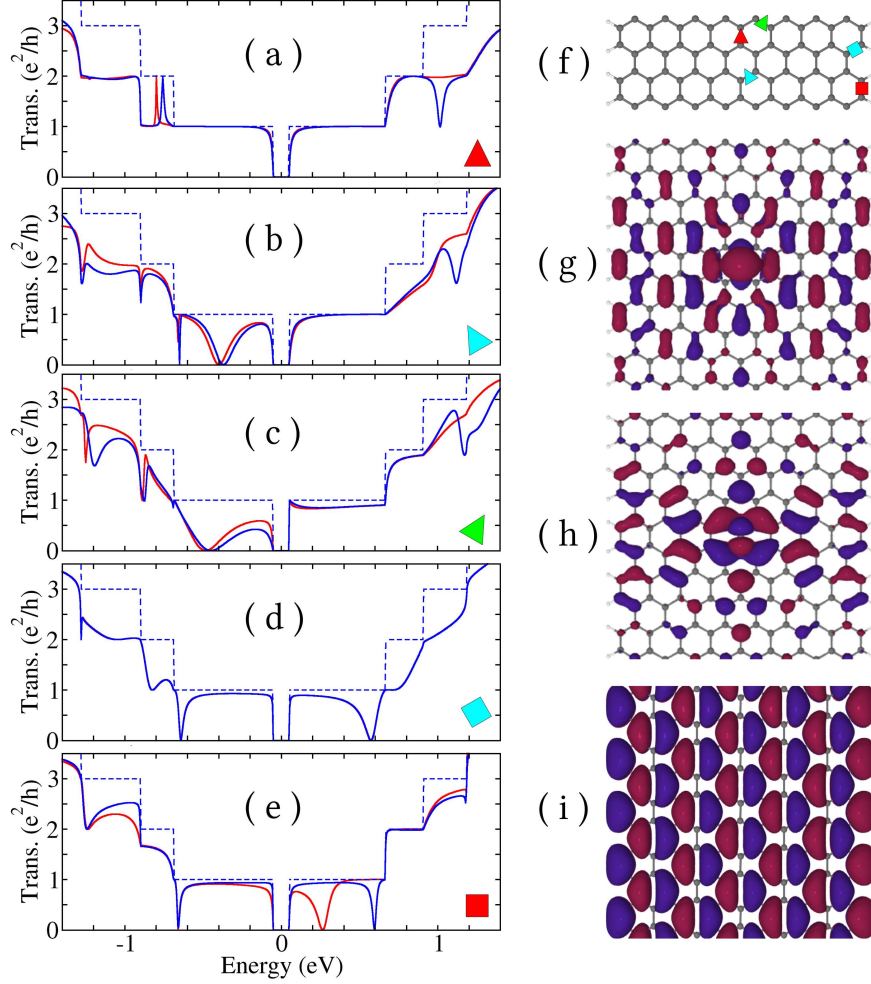


Figure 5.7: Effect of an adatom on the conductance of a 17-aGNR. (a-e) The conductance as a function of the incident energy for various positions of the defect. Blue and red plain lines correspond to the α - and β -spin electrons, respectively. Dotted lines represent the conductance of the pristine ribbon. (f) Representation of a portion of 17-aGNR illustrating the investigated defect configurations. (g-h) Representation of the two adatom-induced quasi-localized states reported within the single channel energy window. (i) Representation of the transmission eigenchannel associated with the low energy propagating electrons. Red and blue surfaces indicates positive and negative lobes of the electronic states.

"axial" mirror plane is preserved, both the eigenchannel and the quasi-localized states have to present a well defined parity with respect to these planes. As shown in Figs. 5.7(g-i), though the transmission eigenchannel presents an odd parity across the ribbon width. In contrast, the defect induced states whose energies are in the single channel window, present an even parity. As a consequence, the incoming electrons never overlap with the defect induced states and the transmission function is not perturbed.

In conclusion, owing to their geometry, the conductance patterns of defective graphene ribbons are shown to depend drastically on the defect position. This is related to the variation of the binding energies of defect-induced quasi-localized states. This phenomenon, which is not present in CNT, should increase the sensibility of the GNRs transport properties with respect to random distribution of defects. On the other hand, such a distribution of defects pinned within the GNR *bulk* could provide a way to engineer the energy band gaps in GNRs. In addition, the transport properties of defective GNRs are found to vary depending on the symmetries of the defective ribbon.

5.6 Conductance patterns of various topological defects

In the previous sections, the mechanisms ruling the impact of the topological defects on the transport properties of GNRs have been unveiled. We now review and compare the conductance patterns of the various defect topologies that may originate from the presence of (either bare or recombined) primary defects in graphene ribbons. The different defect geometries that have been described in the previous chapter are here considered with respect to their scattering properties.

The section is organized as follow: the case of defective zigzag ribbons in the ground-state anti-parallel ($\uparrow\downarrow$) spin configuration is first detailed. Then the parallel ($\uparrow\uparrow$) and anti-parallel ($\uparrow\downarrow$) spin orientations between the zigzag edges are compared. Finally, armchair ribbons are tackled.

5.6.1 Quantum conductance of semi-conducting zGNRs

In section 5.4, we have highlighted the role played by the electronic states localized at the edges in determining the conductance of the low energy carriers in zigzag ribbons. The crucial role of the edge states is confirmed here. The conductance of semi-conducting 8-zGNRs with various types of isolated *bulk* and *edge* defects have been computed. As

a main result, we report that, independently of the defect introduced in the system, the zGNRs always present at least one ballistic conduction channel in the vicinity of the charge neutrality point. This appears to be due to the "protecting" effect of the electronic states localized at the edges.

(a) *Bulk defects* - The conductance profiles of semi-conducting zGNRs in the presence of *bulk* primary defects are reported in Fig. 5.8(a). For all the zGNRs configurations, the presence of the isolated *bulk* defect introduce dips into the conductance at the energies where incident electrons and holes are back-scattered by quasi-localized states. Besides it appears that vacancies and adatoms differs with respect to their impact on the electronic transmission. This is especially striking when comparing the most stable defect configurations (i.e. the di-vacancy and the di-hydrogenated adatom). While the vacancies induce quasi-localized states that limit the electronic transmission through the *bulk* transmission eigenchannels in the directs proximity of the Fermi level, this is not the case in the presence of adatoms. In particular, the hydrogenated and di-hydrogenated adatoms presents electronic states far away from the Fermi energy and the low energy conduction channels remain undisturbed in the presence of these defects.

In order to further identify the origin of this difference, the density of states projected onto the adatom and the vacancy, have been computed. These are depicted in Fig. 5.8(b). The projection reveals that the low energy electronic states induced by the adatom come mainly from the top carbon atom (i.e. the one out-of-plane) while the basal carbon atoms do not contribute to the DOS at these energies. This unveils the poor coupling between the quasi-localized states and the propagating π -electrons. Moreover, these contributions to the DOS disappear upon hydrogenation of the defect. On the contrary, the quasi-localized states induced by the vacancy originate from the π -electrons of the ribbon. In addition, these defect-induced states remain stable with respect to the hydrogenation process. This explains the global difference between the scattering profiles of *bulk* adatoms and vacancies.

Finally, we note that the presence of quasi-localized states close to the charge neutrality point seems to induce a small transfer of charge between the ribbon and the defect. This process is called *self-doping*. Depending on the sign (positive or negative) of the charge transferred from the bulk to the localized states, defects are commonly labelled as *donor* or *acceptor*, respectively. In case of *bulk* vacancies and adatoms in semi-conducting zGNRs, the analysis of the electrostatic potential indicates an acceptor character for all the topological defects with the exception of the hydrogenated and di-hydrogenated adatoms that are

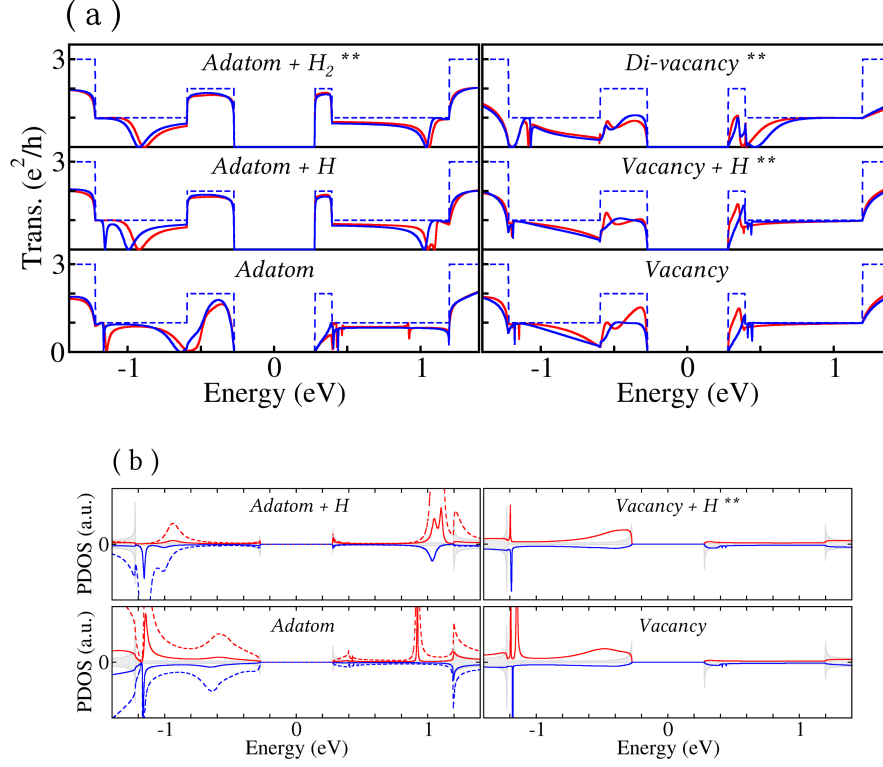


Figure 5.8: Effect of various *bulk* defects on the conductance of a semi-conducting 8-zGNR. (a) The conductance as a function of the incident energy for various defect configuration. Blue and red plain lines correspond to the α - and β -spin electrons, respectively. Dotted lines represent the conductance of the pristine ribbon. [Left panel] 8-zGNR in the presence of an isolated adatom, a mono-hydrogenated adatom and a di-hydrogenated adatom. [Right panel] 8-zGNR in the presence of an isolated vacancy, a hydrogenated vacancy and a di-vacancy. (b) Density of states (DOS) projected onto the *bulk* adatom and vacancy defects. Blue and red plain lines correspond to the contribution of the basal carbon atom (those lying within the GNR plane) to the α - and β -spin DOS, respectively. Blue and red dotted lines correspond to the contribution of the out-of-plane carbon adatom. Grey areas indicate the contribution of the basal carbon atom in the case of pristine 8-zGNR. Note that the most stable defect configurations are note with an asterisk (**) sign.

reported to be neutral.

(b) *Edge* defects - In the presence of a defect at the zigzag edge, the electronic conduction through the eigenchannels associated with states localized along the defective edge is prevented. The main characteristics of the conductance profiles of zigzag ribbons with *edge* defects are easily extracted from the conductance patterns depicted in Figs. 5.9(a,b). First, the eigenchannels localized along the defective edges are characterized by the complete back-scattering of the electrons and holes incoming with a low energy (i.e. $[-0.6 < E < 0.4]$ eV). On the contrary, the eigenchannels made from the electronic states localized along the pristine edge contribute for one quantum to the low energy electronic conductance. Second, in the absence of defect-induced quasi-localized states that extend within the ribbon, the *bulk* transmission eigenchannels also contribute to one quantum of conductance throughout the single channel energy window (i.e. $[-1.2 < E < 1.2]$ eV). However, if such extended defect-induced states are present, dips are found in the transmission owing to resonant back-scattering by the quasi-localized states. Third, regarding the most stable defect configurations, one notes that, the hydrogenated vacancy only has a significant impact on the *edge* eigenchannels while the di-hydrogenated adatom and the *Dip* defects also impinge the propagation of carriers through the *edge* eigenchannels.

Finally, the analysis of the electrostatic potential reveals that most of the *edge* defects do not come with a transfer of charge between the ribbon and the defect. However, due probably to topological reasons, the D_{757} , D_{575} and *Hepta* defects configurations are associated with a small acceptor character. More intriguingly, the di-hydrogenated adatom induces a small donor effect. As shown in Fig. 5.9(c), this is associated with the presence of partially filled states localized within the energy gap.

5.6.2 Quantum conductance of metallic zGNRs

The ground-state configuration of zigzag graphene ribbons shows an anti-parallel coupling ($\uparrow\downarrow$) between the edges and the opening of a gap due to the staggered sub-lattice potentials. However, we have shown previously that another configuration that presents parallel spin orientations between the edges is reported only ~ 11 meV/unit-cell higher in energy. Furthermore, the stability analysis reported in section 4.1 reveals that this latter configuration may eventually become the most stable one in the presence of defects. It is therefore appealing to investigate the electronic transport properties of the ($\uparrow\uparrow$) zigzag ribbons in the presence of

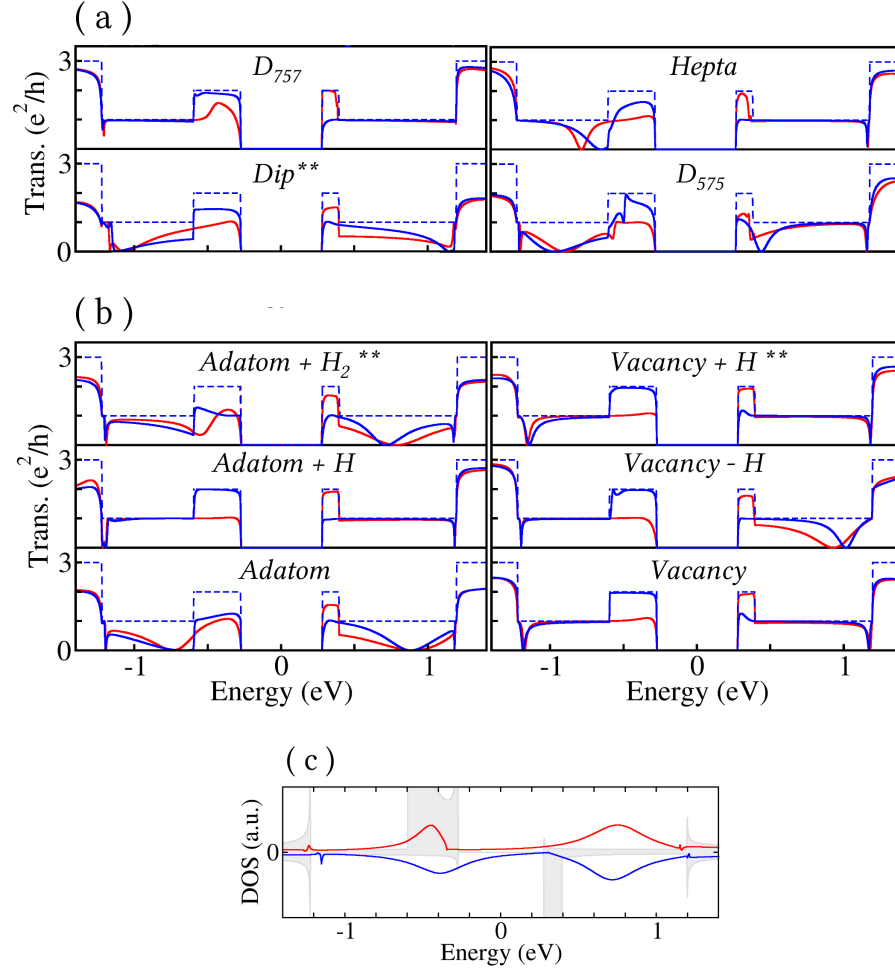


Figure 5.9: Effect of various *edge* defects on the conductance of a semi-conducting 8-zGNR. The conductance as a function of the incident energy for various defect configurations : (a) odd-membered rings at the edge, and (b) adatoms and vacancies at the edge. Blue and red plain lines correspond to the α - and β -spin electrons, respectively. Dotted lines represent the conductance of the pristine ribbon. (c) Density of states (DOS) projected onto the di-hydrogenated *edge* adatom. Blue and red plain lines correspond to the contribution of the basal carbon atom (those lying within the GNR plane) to the α - and β -spin DOS, respectively. Grey areas indicate the contribution of the basal carbon atoms in case of pristine 8-zGNR. Note that the most stable defect configurations are note with an asterisk (**) sign.

topological defects.

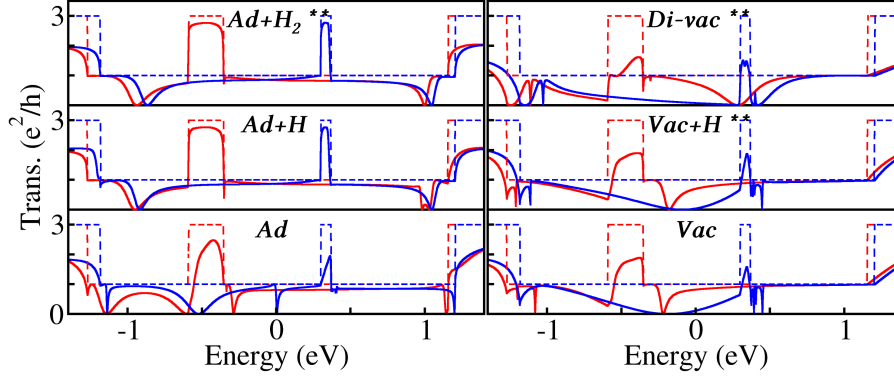


Figure 5.10: Effect of various *bulk* defects on the conductance of a metallic 8-zGNR (i.e. within the $\uparrow\uparrow$ spin configuration). The conductance as a function of the incident energy for various positions of the defect. Blue and red plain lines correspond to the α - and β -spin electrons, respectively. Dotted lines represent the conductance of the pristine ribbon. [Left panel] 8-zGNR in the presence of an isolated adatom, a mono-hydrogenated adatom and a di-hydrogenated adatom. [Right panel] 8-zGNR in the presence of an isolated vacancy, a hydrogenated vacancy and a di-vacancy. Note that the most stable defect configurations are note with an asterisk (**) sign.

In this section, we will show that in the presence of both *bulk* and *edge* defects, the two main characteristics of the zigzag ribbons within the $\uparrow\uparrow$ spin configuration (i.e. metallicity and spin-polarized transmission of the low energy carriers) are preserved. In addition, the impact of the electronic states localized at the edge is once more emphasized.

(a) *Bulk* defects - The computed conductance patterns of various *bulk* vacancies and adatoms are presented in Fig. 5.10. Similarly to the case of the $\uparrow\downarrow$ spin configuration, the adatoms have a lesser impact than the vacancies on the transmission function of low energy carriers. Though the quasi-localized states associated with the adatoms give rise to narrow dips in the transmission function, a quasi-uniform decrease of the conductance associated with the π electrons with β -spin orientation is found in the presence of a vacancy. As shown previously, vacancies induce quasi-localized states that strongly interact with the π electrons whose transmission is therefore affected. This effect impact the β -spin electrons incoming within a broad energy range $[-1.1, -0.4]$ eV. As a result, although the ribbon always keeps its metallic behavior independently of the scattering potential induced by the defect, the conductance is strongly

spin-polarized at the Fermi energy in the presence of vacancies. Finally, we note that similarly to the case of the $\uparrow\downarrow$ spin configuration, ballistic conduction channels are always reported at the energies -0.35 eV and $+0.35$ eV. These are the energies where the electronic states localized at the edges are reported.

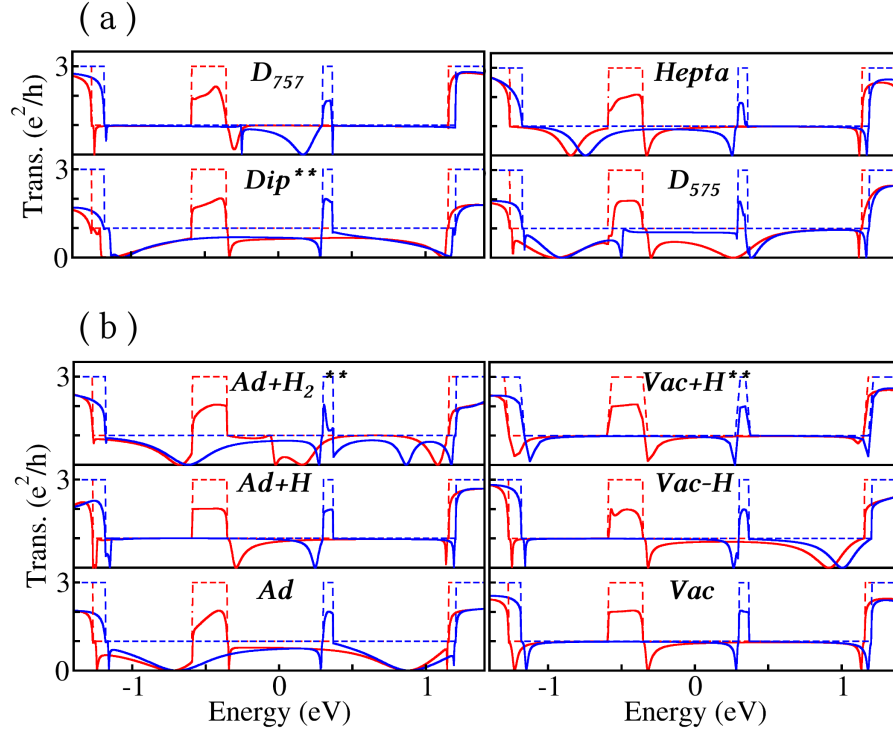


Figure 5.11: Effect of various *edge* defects on the conductance of a metallic 8-zGNR (i.e. within the $\uparrow\uparrow$ spin configuration). The conductance as a function of the incident energy for various positions of the defect: (a) odd-membered ring at the edges, and (b) adatoms and vacancies at the edge. Blue and red plain lines correspond to the α - and β -spin electrons, respectively. Dotted lines represent the conductance of the pristine ribbon. Note that the most stable defect configurations are note with an asterisk (**) sign.

(b) *Edge* defects - The situation within metallic zGNRs is very similar to the one reported within semi-conducting zGNRs. The presence of defects along the edge accounts for the suppression of one conduction channel associated with the edge state. Besides, depending on the defect-induced quasi-localized states, the propagation of carriers through the

bulk eigenchannels may or not be affected. Regarding the most stable defect configurations, the impact of the hydrogenated vacancy is mainly restricted to the *edge* conduction channel, while the *Dip* defect and, even more, the di-hydrogenated adatom do affect the propagation of carriers within the complete single-channel energy window.

5.6.3 Quantum conductance of aGNRs

Though the prediction of ferro-magnetism order along the zigzag-shaped edges has triggered a large interest in view of the possible applications in spintronic devices, it should be reminded that the most stable edge profiles at ambient conditions are predicted not to present partially filled electronic states localized at the edge. From our point-of-view, this situation is therefore the most relevant for practical applications of GNRs in future electronic devices.

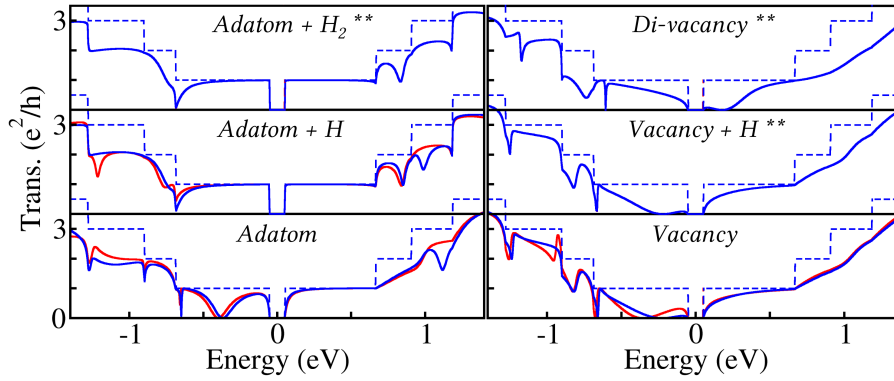


Figure 5.12: Effect of various *bulk* defects on the conductance of a semi-conducting 17-aGNR. The conductance as a function of the incident energy for various positions of the defect. Blue and red plain lines correspond to the α - and β -spin electrons, respectively. Dotted lines represent the conductance of the pristine ribbon. [Left panel] 8-aGNR in the presence of an isolated adatom, a mono-hydrogenated adatom and a di-hydrogenated adatom. [Right panel] 17-aGNR in the presence of an isolated vacancy, a hydrogenated vacancy and a di-vacancy. Note that the most stable defect configurations are noted with an asterisk (**) sign.

In this section, we show that the transmission properties of low energy carriers in aGNRs are highly sensible to the presence of *bulk* defects. This is due to the absence of the "protective" electronic states at the edges that insure the ballistic conduction in zGNRs. However, the impact of

edge defects on the conductance is significantly reduced with respect to their *bulk* counterpart.

(a) *Bulk* defects - The conductance profile of 17-aGNRs with a single *bulk* defect has been computed for various adatoms and vacancies configurations. The transmission function reported in Fig. 5.12 presents the typical characteristic of the vacancy and adatom defects. The π electrons are the most affected. The overlap between the quasi-localized states and the propagating π eigenchannels is relatively small in the presence of adatoms, leading to well defined dips into the transmission function. On the contrary, the vacancy-induced electronic states widely couple with the π eigenchannels decreasing the electronic transmission of π electrons over a wide energy range. The impact of *bulk* defects is therefore very similar to the one encountered in zGNRs.

The main differences between the transmission functions of defective zigzag and armchair ribbon directly reflect the absence of *edge* states along the armchair edges. Though the impact of defect-induced backscattering was limited in zGNRs owing to the splitting of the conduction between *bulk* and *edge* eigenchannels, this is no more the case in aGNRs where a single eigenchannel is available for the propagation of electrons incoming with an energy in the $[-0.7, 0.7]$ eV range. As a consequence, the defect induced reflection of incoming electrons causes the reduction of the total transmission function down to zero.

Finally, the analysis of the electrostatic potential indicates similar charge transfer between *bulk* and the honeycomb lattice as in the case of zGNRs. *Bulk* defects come with an acceptor character with the exception of the (di)hydrogenated adatom that remains neutral.

(b) *Edge* defects - The impact of various *edge* defect configurations on the electronic transmission function is detailed in Fig. 5.13. Upon the recombination with the edge most of the defect induced quasi-localized states are pushed away from the Fermi level, limiting the impact of defects on the low energy transmission function. This is particularly striking regarding the most-stable adatom and vacancy configurations (i.e. the bare vacancy and the di-hydrogenated adatom). This statement is however not valid in the presence of mono-hydrogenated pentagons and heptagons. As reported in Fig. 5.13, these edge patterns induce quasi-localized states in the vicinity of the Fermi energy.

Finally, the analysis of the *self-doping* effect reveals that most *edge* defects remain neutral. However, the bare adatom as well as the dehydrogenated vacancy and the D_{656} defect configuration are reported as charge acceptors while the heptagon defect presents a donor character.

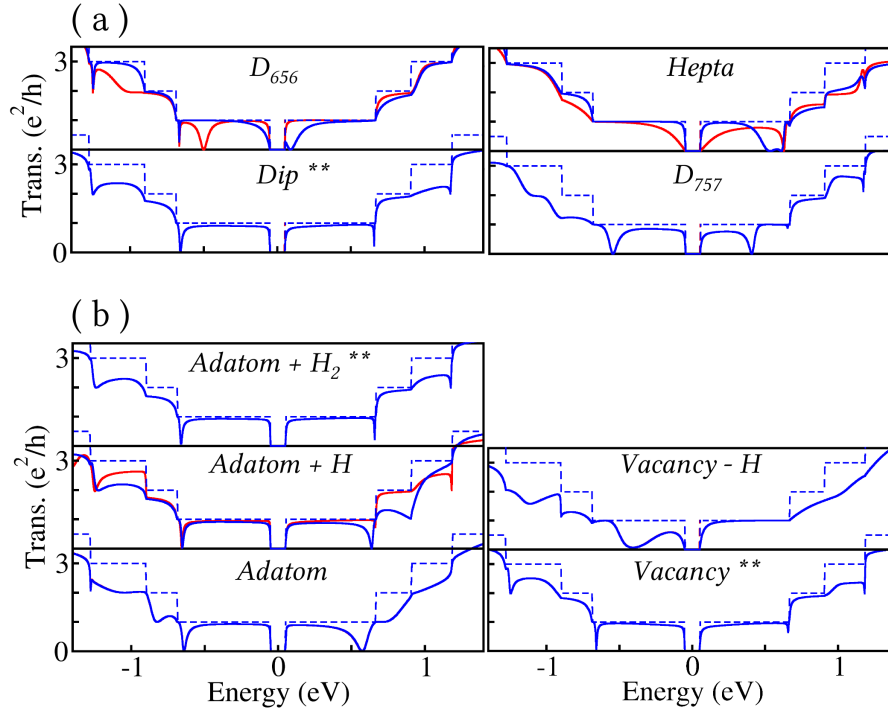


Figure 5.13: Effect of various *edge* defects on the conductance of a semi-conducting 17-aGNR. The conductance as a function of the incident energy for various positions of the defect : (a) odd-membered rings at the edge, and (b) adatoms and vacancies at the edge. Blue and red plain lines correspond to the α - and β -spin electrons, respectively. Dote represent the conductance of the pristine ribbon. Note that the most stable defect configurations are noted with an asterisk (**) sign.

5.6.4 In conclusion

Conductance profiles of both zigzag and armchair GNRs in the presence of various topological defects have been computed within an *ab initio* framework. Concerning the zigzag shaped ribbons, the electronic states localized along the edges have been shown to have a strong impact on the transmission of low energy electrons and holes. Indeed, *edge* states act as a protecting layer and preserve the ballistic propagation of low energy carriers in the presence of single defects. In this respect, our *ab initio* calculations strengthen previous tight-binding simulations of *D. Areskin* and co-workers that predict the occurrence of ballistic transport in long disorder zGNRs [219]. However, our results highlight the appearance of large defect-induced back-scattering within the single-channel energy window. This is in striking contrast with the above mentioned TB simulations that predict a $G \sim G_0$ conductance for these channels, even in the presence of edge disorder. Finally, our results suggest that the conductance of zGNRs in the ferromagnetic ($\uparrow\uparrow$) spin configuration preserve its metallic and spin polarized characteristics independently of the presence of *edge* and *bulk* defects. Such magnetically ordered GNRs should therefore provide a robust way to inject spin-polarized electrons in graphene. However, the experimental relevance of this system has still to be established.

Concerning the conductance profiles of defective armchair ribbons, our results highlight the crucial impact of *bulk* defects. This opens a route for the engineering of the conduction gap by the proper introduction of *bulk* defects in armchair shaped ribbons. On the contrary, the proper recombination of topological defects with the armchair edges has been shown to restore a high electronic transmission around the Fermi energy.

Finally, the analysis of variation of the electrostatic potential along the ribbons has revealed that topological defects may either remain *neutral* or induce *donor* and *acceptor* doping of the ribbons depending on their topologies.

5.7 Conductance scaling at the mesoscopic scale

In the previous sections, the mechanisms ruling the decrease of the conductance in defective GNRs have been unveiled. The transport signature due to a single defect at low energy turns out to range from a full suppression of either hole or electron conduction, to a vanishingly small correction of the conductance profile for other types of defect topology.

In this section, a different point-of-view is adopted. In order to further substantiate the effect of *edge* defects on the actual mesoscopic

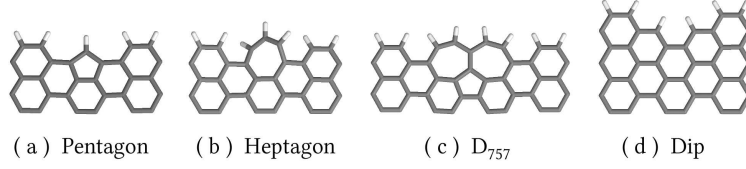


Figure 5.14: Schematic representation of the pentagon (a), heptagon (b), D_{757} (c), and *Dip* defects (d) considered in our mesoscopic calculations.

transport properties of armchair ribbons, a different approach, which relies on the ground-state equilibrium Hamiltonian, is used to tackle the transport properties of long ribbons with random distribution of defects at the edges. This non-self consistent computation of the electronic transmission function can be implemented either in a tight-binding or fully *ab initio* flavor [220, 221]. In the latter case, ground-state calculations are first performed to obtain the Hamiltonian and overlap matrices associated with short nanoribbon sections. Then, long disordered systems are built up by randomly assembling elementary parts containing a single or a few defects together with sections of pristine nanoribbons. Finally, standard decimation techniques are used for the calculation of Green functions and transmission probabilities [220].

The defects illustrated in Fig. 5.14 are considered in our mesoscopic calculations. For that purpose, defects have been introduced at the edge of a wide 34-aGNR whose width (~ 4 nm) is into the experimental range. One dimensional super-cells of ~ 30 Å, relaxed until the forces on the atoms and the unit cell are below 0.01 eV/Å and 0.05 eV/Å respectively, have been used as the building blocks of our mesoscopic study.

The conductance signatures of the isolated defects are shown in Fig. 5.15. It is worth noting that, in order to save computational time, the spin degrees of freedom do not have been taken into account for these calculations. However, this should not affect the validity of the results since neither the armchair a_{11} edges nor the considered defects do induce a spin-polarized electronic density distribution. A strong acceptor and donor character appears respectively for the pentagon and heptagon defects (see Figs. 5.15(a,b)), indicating an effective defect-driven doping. In contrast, the double heptagon and pentagon (d_{757}) exhibits only two narrow conductance suppression dips (Fig. 5.15(c)), symmetric with respect to the charge neutrality point. The conductance pattern related to the *Dip* defect is depicted in Fig. 5.15(d). Albeit some impact is reported in the higher energy sub-bands, the conduction remains very robust in

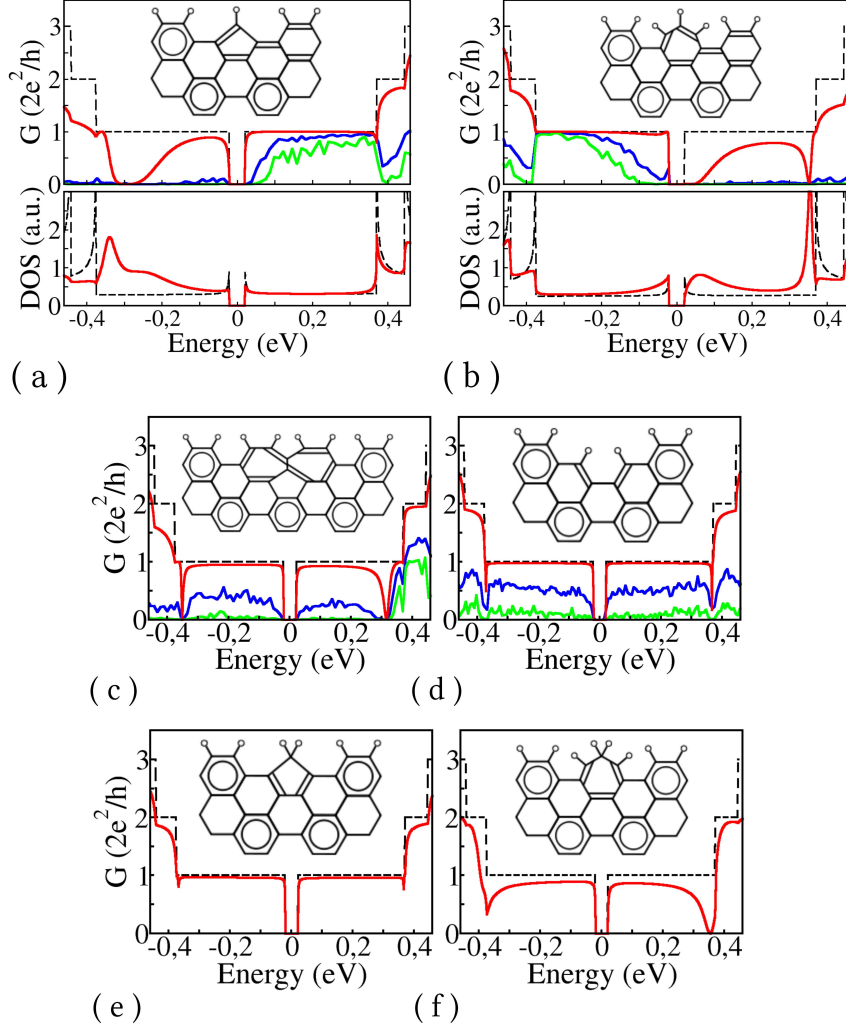


Figure 5.15: Effects of the pentagon (a), heptagon (b), D_{757} (c), and *Dip* (d) defects on the electronic and transport properties of a armchair GNR. (e-f) Impact of the di-hydrogenation on the properties of the pentagon (e) and heptagon(f) defects. Conductances (top) and densities of states (bottom) of 34-aGNR as a function of the incident energy: pristine ribbon (black dotted line), single topological defect (red line), average and minimal conductance for 50 nm long GNRs containing 30 defects (blue and green lines respectively), computed over 20 different defect configurations.

the first plateau. For all defective GNRs, total densities of states (DOS) are calculated, invariably revealing the presence of quasi-bound states at

the energies where the transmission function of the aGNR is affected by the presence of the defect.

The high chemical reactivity of the pentagon and heptagon defects is further explored by assuming a di-hydrogenation of the carbon atom sitting at the edge. The resulting conductance profiles for the new defects (see Figs. 5.15(e,f)) strongly differ from the mono-hydrogenated cases (see Figs. 5.15(a,b)). Indeed, in the presence of additional passivation, the conductance is fully restored for the pentagon defect whereas the signature for the heptagon defect becomes similar to that of the double heptagon and pentagon (d_{757}). In both cases, the initial strong reduction of electron or hole conductance is markedly suppressed. This clearly suggests a possibility to tune the transport properties from a metallic to a truly insulating state (or vice versa) upon varying the coverage of mono atomic hydrogen, as recently discussed experimentally for 2D graphene [222].

The Clar's sextet representation [156, 157] (Fig. 5.15(insets)) provides a pictorial scheme to understand the impact of edge defects [12] on the transport properties. Clar's theory describes the π -electronic system of hydrocarbons on the basis of the resonance structures that maximize the number of benzenoid sextets drawn for the system. With this respect, perfect aGNRs are considered as fully benzenoid systems since all π -orbital of the ribbon are involved in a benzenoid sextet. However, in the presence of defects non passivated odd-membered rings, the bonding at the edge of aGNRs can be seen as the superposition of two mirroring Kekulé structures that partially destroy the benzenoid character of the aGNRs (Figs. 5.15(a,b)). By increasing the localization of π electrons in carbon-carbon double bonds, such defects destroy the local aromaticity at the ribbon edge and are thus expected to have a large effect on the π - π^* conduction channels. On the contrary, the di-hydrogenation of the pentagon and heptagon defects restores the complete benzenoid character of the ribbon as illustrated by Clar's sextet representations (Figs. 5.15(e,f)).

To further substantiate the effect of these topological defects on the mesoscopic transport properties, one needs to explore the behavior of long disordered aGNRs with random distribution of edge defects. In Fig. 5.15, the conductance of 500 nm long disordered aGNRs containing 30 defects (blue lines and green area) are superimposed to the single defect results (red lines). Explicitly, the blue and green lines correspond respectively to the average and minimal conductance computed from a set of 20 different defects configurations. The light green areas account for the fluctuations between the configurations. The original conductance fingerprints of the considered defects are further exacerbated when

longitudinal disorder is introduced, resulting for D_1 (D_2) in an almost fully suppressed hole (electron) conduction for low defect density.

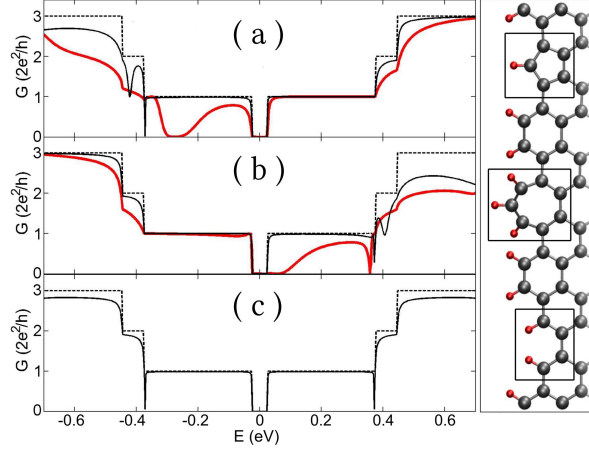


Figure 5.16: Conductance of a single defect obtained by the simple topological TB Hamiltonian (solid line) and by the adjusted TB Hamiltonian (red line) for the pentagon (a), heptagon (b) and *Dip* (c) defects. Ball-and-stick models of the defects are illustrated in the right panel.

Ab initio transport calculations are highly computationally demanding and the elaboration of an accurate TB model is therefore extremely useful for achieving a complete mesoscopic study. Though most of previous studies rely on a simple topological nearest-neighbor TB Hamiltonian to derive the conductance patterns of mesoscopic GNRS, when compared to *ab initio* results, this turns out to yield a wrong description of transport properties in the case of non-neutral defects. Figure 5.16 shows the conductance profiles of three different defects computed either within a topological TB model (black solid lines) or within an adjusted TB model (red solid lines). Though the agreement between *ab initio* and topological TB results is good for the *Dip* defect, strong discrepancies are found for pentagon and heptagon defects. In the latter cases, the topological model leads to a severe underestimation of the backscattering efficiency. In contrast, the adjustment of the TB parameters allows to reproduce the conductance evaluated by means of the full DFT Hamiltonian [223]. In this work, the renormalized onsite and hopping energies have been readily extracted from the self-consistent *ab initio* Hamiltonian. The adjusted TB parameters are detailed in Fig. 5.17. On one hand, the fine tuning of the on-site energies allows to deal with the defect-induced charge transfer. On the other hand, the variation of the hopping param-

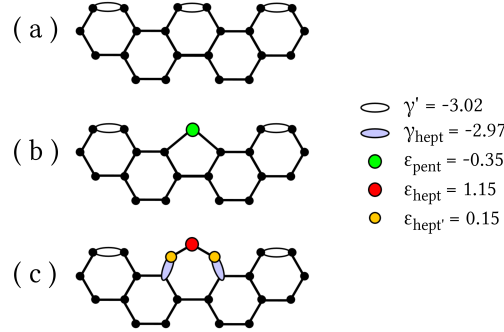


Figure 5.17: Schematic representation of three edge topologies and the associated adjusted tight-binding parameters: (a) pristine armchair edge, (b) pentagon defect and (c) heptagon defect. Black dots and lines represent unadjusted onsite energies ($\epsilon = 0$ eV) and hopping integrals ($\gamma = -2.7$ eV), respectively. All values are given in eV.

eters accounts for the local modifications of the inter-atomic distance. By reducing the computational costs, the TB technique enables the investigation of disordered ribbons with lengths up to several micrometers.

Within this adjusted TB model, the transport properties of disordered aGNRs are investigated by considering lengths varying up to $L=5 \mu\text{m}$ and random distribution of defects with a density of $6 \times 10^{-2} \text{ nm}^{-1}$. Figures 5.18(a-d) display the conductance of long disordered aGNRs (averaged over 100 different configurations), as a function of energy and ribbon length. Besides, the regions of the (L, E) -plane where the conductance is experimentally insignificant (i.e. $G(E) \leq 0.01G_0$) are delineated by white lines. This allows us to determine the length dependent conduction gaps.

In the presence of charged defects (i.e. pentagon and heptagon defects), the conductance scaling behavior of long disordered aGNRs presents a striking electron-hole asymmetry. Figures 5.18(a,b) clearly show that depending on the energy at which carriers are injected, the electronic transport ranges from ballistic to localized regimes. In pentagon defected aGNRs (Fig. 5.18(a)), the propagation of electrons in the first plateau remains quasi-ballistic up to a length $L > 5 \mu\text{m}$. As a consequence of the acceptor character of pentagon defects, the hole conduction, in the same energy window, is almost fully suppressed for length $L < 0.5 \mu\text{m}$. In contrast, in the presence of heptagon defects (Fig. 5.18(b)), holes in the first plateau remains conductive up to length

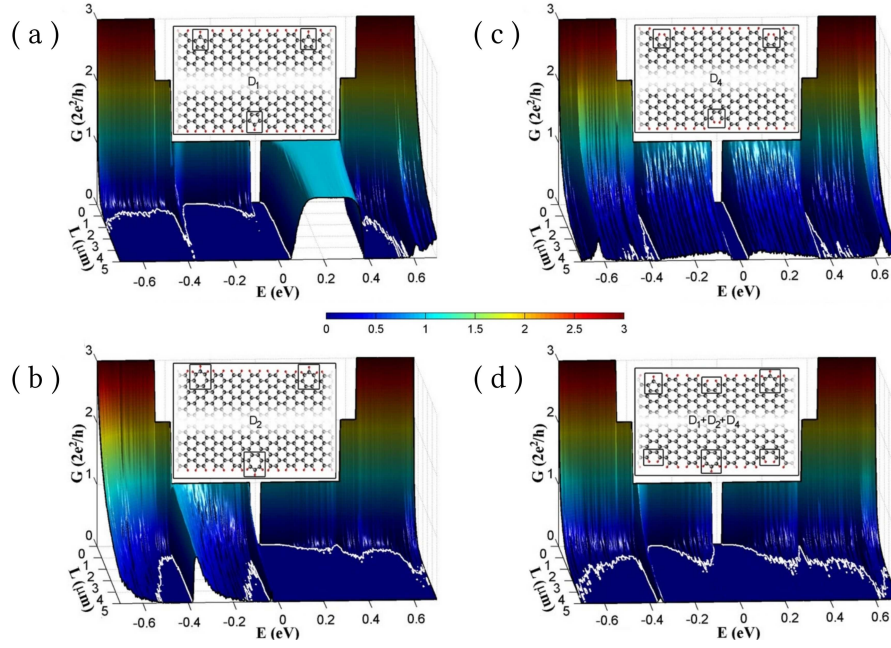


Figure 5.18: Conductance of a 35-aGNR with a $6 \times 10^{-2} \text{ nm}^{-1}$ density of (a) pentagon defects and, (b) heptagon defects, (c) *Dip* defects, and, (d) mix of pentagon, heptagon, and *Dip* defects. The conductance is given as a function of the carrier energy (E) and the length of the ribbon (L). $G(L, E)$ has been averaged over 100 different defect distributions. The white lines delineate the (L, E) regions for which the conductance value $G \leq 0.01G_0$ (criterion for the experimental conduction gap [117]).

$L > 5\mu\text{m}$, while the donor character of the heptagon defects involves the suppression of electron conduction in the same energy window. Obviously, such disordered edge defect profiles with a single defect type are rather unlikely, but it shows however that spectacular fluctuations of transport length scales occur in some specific situations.

The comparison with more realistic defect distributions is rather instructive. Figures 5.18(c,d) detail the conductance scaling in the presence of a random distribution of *Dip* defects, and a mix of three types of defects (pentagons, heptagons and *Dip* defects) for the same edge defect density. For both defect distributions, the conductance decay is rather homogeneous within the first electron and hole plateaus. However, while the marked electron-hole asymmetries associated with the pentagons and heptagons defects compensate each other, the presence of odd membered rings continues to crucially impact the electron and hole localization. This appears evident by looking at the white line in the (L, E) -plane. The presence of defects that are non compliant with the benzenoid character of aGNRs (i.e. pentagons and heptagons) thus appears to strongly impinge the ballistic propagation of carriers, even for the low defect concentration considered here. This is further emphasized by the estimated localization lengths that are reported in Fig. 5.19 as a function of the carrier energy. While the distribution of *Dip* defects gives rise to a localization length $\xi \sim 1\mu\text{m}$ for low energy carriers, the introduction of charged defects strongly reduces the average value in the $[-0.5, 0.5]$ eV energy window. Note that the fluctuations of ξ in correspondence of the van Hove singularities for *Dip* defects are due to the increased scattering induced by the high density-of-states at these points. In the case of the mixed disorder, these fluctuations are absent or considerably reduced owing to the strong smearing effect that disorder produces in the density-of-states.

5.8 Conclusions

In this chapter, The quantum transport properties of defective graphene nanoribbons have been investigated by means of state-of-the-art *ab initio* calculations. In agreement with previous calculations [127, 224], the main mechanism that limit the carriers propagation in the presence of local defects is the resonant back-scattering of the incoming carriers by the defect induced quasi-localized states. As a consequence, the presence of an isolated defect introduces dips in the transmission at the energies that are resonant with the defect induced quasi-localized states. The conductance patterns of various *bulk* and *edge* defect configurations have

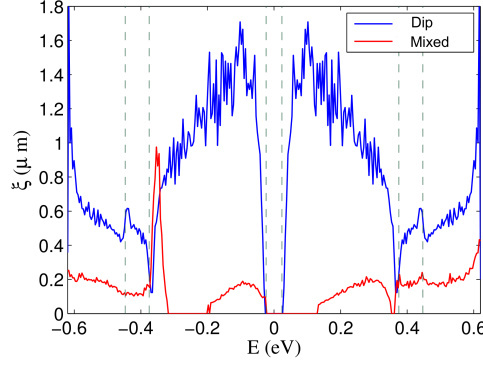


Figure 5.19: Localization length ξ for a 35-aGNR with a $6 \times 10^{-2} \text{ nm}^{-1}$ density of *Dip* defects (blue line) and a mix of {pentagon, heptagon, *Dip*} defects. The vertical dashed lines correspond to the position of the van Hove singularities. In some energy regions, ξ is very short (below 100 nm) and it cannot be extracted from the data. In this case, we set $\xi = 0$. As already arguable from Fig. 5.18, the localization length for the *Dip* defects is up to almost one order of magnitude longer than in the case of mixed defects.

been computed. The impact of single defect is reported to range from a vanishing contribution of backscattering to the complete suppression of a transmission channel, depending on the defect topology and the ribbon geometry.

Within zigzag shaped GNRS, the conduction of low energy carriers is splitted between *bulk* and *edge* transmission eigenchannels. Therefore, in the presence of a single *bulk* defect, the *edge* eigenchannels may still insure the ballistic conduction of low energy carriers. Similarly, the presence of a single point defects on one edge, do not impinge the ballistic propagation of carriers trough the other *edge* and *bulk* eigenchannels. In this latter configuration, the computed transmission function of the zGNRS is widely spin-polarized, whatever the nature of the defect. Though appealing for the realization of spin-injection devices, such characteristic requires a perfect cristallinity along the undefected edge, what is likely to be not the case in actual GNRS samples.

Within armchair shaped GNRS, a single channel is available for the propagation of low energy carriers (i.e. no edge state is reported along the armchair edge). As a consequence, aGNRS are reported to be highly sensitive to the presence of *bulk* defects that come with quasi-localized states within the π - π^* energy window. For example, the presence of a single *bulk* vacancy largely impinge the propagation of electrons within the $[-0.5, 0.0]$ eV energy range. When recombined at the edge the im-

pact of most isolated point defect is reduced as the recombination process limits the appearance of defect induced quasi-localized states. Nevertheless, topological defects such as pentagons and heptagons are predicted to destroy the electron and hole conduction channels, respectively. However, we have shown that hydrogenation of the armchair edge allows to improve the conductance robustness of aGNRs.

Besides, the mesoscopic conductance of large aGNRs has been investigated by means of an accurately parameterized tight-binding model. The conduction gaps driven by defect-induced localization effects, have been shown to not only depend on the defect density and ribbon length but also on the geometry and chemical reactivity of edge imperfections.

Finally, one note that the above analysis is drawn from physical processes that are general in essence. The scope of the results should therefore extend beyond the edge profiles considered in this study. In particular, we forecast similar fluctuations of the conductance to be reported for other GNRs whose ground-state π -electronic structure is aromatic according to Clar's rule [10].

Chapter 6

Conclusion

Owing to the important role that carbon allotropes are promised to play in nanoscience and nanotechnology, the synthesis and characterization of carbon nanostructures is a field of intense research activity. Obviously, the fine understanding of fundamental processes in low dimensional nanomaterials requires both advanced quantum simulations and dedicated experiments. The present dissertation reports on the electronic and transport properties of reconstructed and defective graphene nanoribbons by means of *ab initio* techniques. In particular, our study relies on the density functional theory to make accurate predictions regarding the total energies and electronic densities of the GNRs. These latter are then used to investigate the coherent propagation of carriers within the Green's function framework.

Summary

In this dissertation, various outcomes regarding the electronic and transport properties of graphene nanoribbons have been presented. These are expected to be explored experimentally. Our discussion about the relative stability of the reconstructed edges outlines the crucial impact of the chemical environment in determining the most stable edge configuration. In agreement with previous studies [10, 11], we find that the mono-hydrogenated zigzag and armchair edge patterns are likely to undergo reconstructions in ambient conditions. Besides, the computed free energies suggest the a_{22} , z_{211} and $z(600)_{2222}$ patterns as the most probable edge configurations. Since the topology of the edges determines the low energy electronic structure of GNRs, this latter original result should be of some technological importance. In particular, it provides a possible explanation for the absence of experimental evidence of magnetically ordered states along the zigzag shaped edges. Besides, extending the

arguments presented in Refs. [10, 12], we show that the close connection between the GNR topology and its low energy electronic properties can be rationalized in terms of the Clar's sextet theory.

Regarding the configurations of point-defects in GNRs, we report that adatoms and vacancies are likely to recombine with the graphene boundaries accounting for the introduction of odd-membered ring along the edges. Upon migration, vacancies and adatoms seem thus to contribute to the reconstruction of the graphene edges. Besides, while vacancies and adatoms are reported to introduce local magnetic moments in the graphene plane, no magnetic behavior is found when they are recombined at the edge. The recombination mechanism is thus likely to impede the observation of defect induced magnetism in narrow GNRs. Finally, the very small formation energies reported for defects recombined at the zigzag edge highlights the poor robustness of the mono-hydrogenated zGNRs with respect to the formation of edge roughness.

Regarding the transport properties of GNRs, in agreement with previous studies [217, 224], we report that resonant backscattering of the incident carriers by the defect induced quasi-localized states is the dominant mechanism accounting for the reduction of the conductance in the presence of defects. The impact of a single defect is found to range from insignificant backscattering to the complete suppression of conductance channels depending on the effective coupling between the defect's quasi-localized state and the conductance channels. Furthermore, our calculations reveal the large impact of the *edge* states with respect to the propagation of the low energy electrons. In the presence of *edge* states, additional spin-polarized conduction channels are reported around the Fermi level, facilitating the propagation of low energy carriers. Besides, owing to the magnetic behavior of these channels, spin polarized conductance patterns are reported in the presence of asymmetric defect configurations between the edges. Though it suggests that defective zGNRs could be used for spin injection into graphene, one notes that the experimental relevance of such GNR configuration is not at all obvious.

In contrast, in the absence of *edge* states, a single conduction channel is available for the propagation of low energy carriers in GNRs. In such configurations, the transport properties of GNRs are highly sensible to the presence of defects that interact with the $\pi - \pi^*$ electronic channels. As an example, the presence of a single *bulk* vacancy is reported to suppress the electron conduction within the $[-0.5, 0.0]$ eV energy window. Finally, we have investigated the conductance scaling of defective aGNRs

at the mesoscopic scale. Accurately parameterized tight-binding models have allowed us to study long aGNRs (up to $5\mu\text{m}$). The conduction gaps driven by defect-induced localization effects have been shown to strongly depend on the topology and chemical reactivity of the *edge* defects. As a consequence, our results outline the full hydrogenation of the edges as a way to increase the robustness of GNRs against roughness induced scattering.

Further work

As demonstrated within this dissertation, the understanding of the fundamental properties of nanostructures certainly requires the confrontation between quantum modelling predictions and experimental observations. Throughout this work, we tried to produce answers to topical questions regarding the electronic and transport properties of defective graphene nanoribbons by means of *ab initio* techniques: *What are the actual edge configuration of GNRs?*, *What are the most probable defects in GNRs?*, *Are the defects responsible for the conduction gap measured in GNRs?*, *Are the GNRs good candidates for application in spintronic devices?*, *What are the actual performance limits of GNRs in terms of carriers mobility and frequency dependent response?*,.... Obviously, our work did not definitely close these questions and this topic would deserve further investigations. Here below, we report a very brief list of research topics that are, to our opinion, of a particular interest.

Our study focussed on the intrinsic conductance patterns of GNRs at equilibrium. However, the transport properties of actual devices are likely to be strongly affected by the interfaces between the GNR based channel and the device terminals. Obviously, the interfaces between the GNR and the metallic leads are a source of additional back-scattering. Besides, the GNR based channel is unlikely to remain at equilibrium in operating conditions. The potential profile that will result from the bias between the metallic leads may potentially lead to significant modifications of the conductance patterns. Finally, the substrate is also in close interaction with the GNR channel. On the one hand, the transversal electric field applied to control the carriers population may modify the electronic structure of GNR's defects. On the other hand, the presence of defects and impurities on the substrate is thought to strongly affect the performance of actual devices. In particular, the trapping of charge carriers by defects in the substrate is proposed as the main origin for the poor signal to noise ratio reported in GNRs. With this respect, the inves-

tigation of the frequency dependent behavior of contacted GNRs would undoubtedly help to improve the performances of the actual GNRs based devices.

The investigation of the electronic and transport properties of carbon nanostructures is a huge, highly diversified and rapidly evolving area. Various systems closely related to the defective graphene nanoribbons would also deserve a particular attention. Recent experimental measurements have shown that the properties of graphene nanoribbons can be conveniently tuned by chemical doping. Though the covalent bonding of gas molecules along the edges has been proposed as a possible scheme, questions remains regarding the actual doping mechanism. The stability analysis presented in Section 3.4 could be successfully extended to assess the structure and stability of chemically doped GNRs. Similarly, the controlled hydrogenation and oxidation of graphene materials has been recently explored in order to monitor the metal/insulator transition in these materials. These achievements are a possible source of innovation regarding the realization of electronic applications and the study presented here above could be straightforwardly extended in order to unveil the transport properties of these materials.

Bibliography

- [1] Novoselov, K. S. *et al.* Electric field effect in atomically thin carbon films. *Science* **306**, 666–669 (2004).
- [2] Novoselov, K. S. *et al.* Two-dimensional atomic crystals. *Proceedings Of The National Academy Of Sciences Of The United States Of America* **102**, 10451–10453 (2005).
- [3] Berger, C. Electronic confinement and coherence in patterned epitaxial graphene. *Science* **312**, 1191–1196 (2006).
- [4] Castro Neto, A. H., Guinea, F., Peres, N. M. R., Novoselov, K. S. & Geim, A. K. The electronic properties of graphene. *Reviews Of Modern Physics* **81**, 109–162 (2009).
- [5] Li, X. L., Wang, X. R., Zhang, L., Lee, S. W. & Dai, H. J. Chemically derived, ultrasmooth graphene nanoribbon semiconductors. *Science* **319**, 1229–1232 (2008).
- [6] Wang, X. R. *et al.* Room-temperature all-semiconducting sub-10-nm graphene nanoribbon field-effect transistors. *Physical Review Letters* **100**, 206803 (2008).
- [7] Soler, J. M. *et al.* The siesta method for ab initio order-n materials simulation. *Journal Of Physics-Condensed Matter* **14**, 2745–2779 (2002).
- [8] Rocha, A. R. *et al.* Spin and molecular electronics in atomically generated orbital landscapes. *Physical Review B* **73**, 085414 (2006).
- [9] Dubois, S. M. M., Zanolli, Z., Declerck, X. & Charlier, J. C. Electronic properties and quantum transport in graphene-based nanostructures. *European Physical Journal B* **72**, 1–24 (2009).

-
- [10] Wassmann, T., Seitsonen, A. P., Saitta, A. M., Lazzeri, M. & Mauri, F. Structure, stability, edge states, and aromaticity of graphene ribbons. *Physical Review Letters* **101**, 096402 (2008).
 - [11] Koskinen, P., Malola, S. & Hakkinen, H. Self-passivating edge reconstructions of graphene. *Physical Review Letters* **101**, 115502 (2008).
 - [12] Baldoni, M., Sgamellotti, A. & Mercuri, F. Electronic properties and stability of graphene nanoribbons: An interpretation based on clar sextet theory. *Chemical Physics Letters* **464**, 202–207 (2008).
 - [13] Hashimoto, A., Suenaga, K., Gloter, A., Urita, K. & Iijima, S. Direct evidence for atomic defects in graphene layers. *Nature* **430**, 870–873 (2004).
 - [14] Suenaga, K. *et al.* Imaging active topological defects in carbon nanotubes. *Nature Nanotechnology* **2**, 358–360 (2007).
 - [15] Smith, B. W. & Luzzi, D. E. Electron irradiation effects in single wall carbon nanotubes. *Journal Of Applied Physics* **90**, 3509–3515 (2001).
 - [16] Meyer, J. C. *et al.* Direct imaging of lattice atoms and topological defects in graphene membranes. *Nano Letters* **8**, 3582–3586 (2008).
 - [17] Ness, H., Shevlin, S. A. & Fisher, A. J. Coherent electron-phonon coupling and polaronlike transport in molecular wires. *Physical Review B* **63**, 125422 (2001).
 - [18] Ness, H. & Fisher, A. J. Quantum inelastic conductance through molecular wires. *Physical Review Letters* **83**, 452–455 (1999).
 - [19] Hohenberg, P. & Kohn, W. Inhomogeneous electron gas. *Physical Review B* **136**, B864–& (1964).
 - [20] Kohn, W. & Sham, L. J. Self-consistent equations including exchange and correlation effects. *Physical Review* **140**, 1133–& (1965).
 - [21] Born, M. & Oppenheimer, R. Quantum theory of molecules. *Annalen Der Physik* **84**, 0457–0484 (1927).
 - [22] Phillips, J. C. Energy-band interpolation scheme based on a pseudopotential. *Physical Review Letters* **1**, 349–349 (1958).

-
- [23] Cohen, M. L. & Heine, V. The fitting of pseudopotentials to experimental data and their subsequent application. *Solid state physics: advances in research and applications/Solid state physics: advances in research and applications* 37–248 (1970).
- [24] Hartree, D. R. The wave mechanics of an atom with a non-coulomb central field part iii term values and intensities in series an optical spectra. *Proceedings Of The Cambridge Philosophical Society* **24**, 426–437 (1928).
- [25] Adams, W. H. Stability of hartree-fock states. *Physical Review* **127**, 1650–& (1962).
- [26] Slater, J. C. A simplification of the hartree-fock method. *Physical Review* **81**, 385–390 (1951).
- [27] Langreth, D. C. & Perdew, J. P. Exchange-correlation energy of a metallic surface - wave-vector analysis. *Physical Review B* **15**, 2884–2901 (1977).
- [28] Harris, J. & Jones, R. O. Surface-energy of a bounded electron-gas. *Journal Of Physics F-Metal Physics* **4**, 1170–1186 (1974).
- [29] Gunnarsson, O. & Lundqvist, B. I. Exchange and correlation in atoms, molecules, and solids by spin-density functional formalism. *Physical Review B* **13**, 4274–4298 (1976).
- [30] Langreth, D. C. & Mehl, M. J. Beyond the local-density approximation in calculations of ground-state electronic properties. *Physical Review B (Condensed Matter)/Physical Review B (Condensed Matter)* **vol.28, no.4**, 1809–34 (1983).
- [31] Becke, A. D. Density functional calculations of molecular-bond energies. *Journal Of Chemical Physics* **84**, 4524–4529 (1986).
- [32] Perdew, J. P. Density-functional approximation for the correlation-energy of the inhomogeneous electron-gas. *Physical Review B* **33**, 8822–8824 (1986).
- [33] Zupan, A., Burke, K., Emzerhof, M. & Perdew, J. P. Distributions and averages of electron density parameters: Explaining the effects of gradient corrections. *Journal Of Chemical Physics* **106**, 10184–10193 (1997).

-
- [34] Hammer, B., Hansen, L. B. & Norskov, J. K. Improved adsorption energetics within density-functional theory using revised perdew-burke-ernzerhof functionals. *Physical Review B* **59**, 7413–7421 (1999).
- [35] DalCorso, A., Pasquarello, A., Baldereschi, A. & Car, R. Generalized-gradient approximations to density-functional theory: A comparative study for atoms and solids. *Physical Review B* **53**, 1180–1185 (1996).
- [36] Perdew, J. P. & Zunger, A. Self-interaction correction to density-functional approximations for many-electron systems. *Physical Review B* **23**, 5048–5079 (1981).
- [37] Svane, A. & Gunnarsson, O. Localization in the self-interaction-corrected density-functional formalism. *Physical Review B* **37**, 9919–9922 (1988).
- [38] Anisimov, V. I., Aryasetiawan, F. & Lichtenstein, A. I. First-principles calculations of the electronic structure and spectra of strongly correlated systems: The lda+u method. *Journal Of Physics-Condensed Matter* **9**, 767–808 (1997).
- [39] Anisimov, V. I., Zaanen, J. & Andersen, O. K. Band theory and mott insulators - hubbard-u instead of stoner-i. *Physical Review B* **44**, 943–954 (1991).
- [40] Norman, M. R. Band theory and the insulating gap in coo. *Physical Review B* **40**, 10632–10634 (1989).
- [41] Martin, R. *Electronic structure: basic theory and practical methods* (Cambridge Univ Pr, 2004).
- [42] Fetter, A. & Walecka, J. *Quantum theory of many-particle systems* (Dover Pubns, 2003).
- [43] Mahan, G. *Many-particle physics* (Plenum Pub Corp, 2000).
- [44] Gross, E., Runge, E. & Heinonen, O. *Many-particle theory* (Hilger, 1991).
- [45] Binder, K. *Monte-Carlo Methods* (Vch Verlagsgesellschaft Mbh, 2005).
- [46] Cramer, C. *Essentials of computational chemistry: theories and models* (John Wiley & Sons Inc, 2004).

-
- [47] Crawford, T. D. & Schaefer, H. F. An introduction to coupled cluster theory for computational chemists. *Reviews In Computational Chemistry, Vol 14* **14**, 33–136 (2000).
- [48] Gonze, X. *et al.* First-principles computation of material properties: the abinit software project. *Computational Materials Science* **25**, 478–492 (2002).
- [49] Artacho, E., Sanchez-Portal, D., Ordejon, P., Garcia, A. & Soler, J. M. Linear-scaling ab-initio calculations for large and complex systems. *Physica Status Solidi B-Basic Research* **215**, 809–817 (1999).
- [50] Huzinaga, S. Gaussian basis sets for molecular calculations. *Gaussian basis sets for molecular calculations* vii+426 (1984).
- [51] Junquera, J., Paz, O., Sanchez-Portal, D. & Artacho, E. Numerical atomic orbitals for linear-scaling calculations. *Physical Review B* **64**, 235111 (2001).
- [52] Anglada, E., Soler, J. M., Junquera, J. & Artacho, E. Systematic generation of finite-range atomic basis sets for linear-scaling calculations. *Physical Review B* **66**, 205101 (2002).
- [53] Kleinman, L. & Bylander, D. M. Efficacious form for model pseudopotentials. *Physical Review Letters* **48**, 1425–1428 (1982).
- [54] Landauer, R. Spatial variation of currents and fields due to localized scatterers in metallic conduction. *Ibm Journal Of Research And Development* **1**, 223–231 (1957).
- [55] Landauer, R. Electrical resistance of disordered one-dimensional lattices. *Philosophical Magazine* **21**, 863–& (1970).
- [56] Buttiker, M. 4-terminal phase-coherent conductance. *Physical Review Letters* **57**, 1761–1764 (1986).
- [57] Buttiker, M. Coherent and sequential tunneling in series barriers. *Ibm Journal Of Research And Development* **32**, 63–75 (1988).
- [58] Sharvin, Y. V. & Bogatina, N. I. Investigation of focusing of electron beams in a metal by a longitudinal magnetic field. *Soviet Physics JETP-USSR* **29**, 419–& (1969).
- [59] Osbourn, G. C. & Smith, D. L. Transmission and reflection coefficients of carriers at an abrupt GaAs-GaAlAs (100) interface. *Physical Review B* **19**, 2124–2133 (1979).

-
- [60] Lee, D. H. & Joannopoulos, J. D. Simple scheme for surface-band calculations .2. the greens-function. *Physical Review B* **23**, 4997–5004 (1981).
 - [61] Schulman, J. N. & Chang, Y. C. Reduced hamiltonian method for solving the tight-binding model of interfaces. *Physical Review B* **27**, 2346–2354 (1983).
 - [62] Ting, D. Z. Y., Yu, E. T. & McGill, T. C. Multiband treatment of quantum transport in interband tunnel devices. *Physical Review B* **45**, 3583–3592 (1992).
 - [63] Sanvito, S., Lambert, C. J., Jefferson, J. H. & Bratkovsky, A. M. General green’s-function formalism for transport calculations with spd hamiltonians and giant magnetoresistance in co- and ni-based magnetic multilayers. *Physical Review B* **59**, 11936–11948 (1999).
 - [64] Datta, S. *Electronic Transport in Mesoscopic Systems* (Cambridge University Press, Cambridge, 1997).
 - [65] Haug, H. & Jauho, A. *Quantum kinetics in transport and optics of semiconductors* (Springer Verlag, 2007).
 - [66] Caroli, C., Saintjam.D, Combescio.R & Nozieres, P. Direct calculation of tunnelling current .4. electron-phonon interaction effects. *Journal Of Physics Part C Solid State Physics* **5**, 21–& (1972).
 - [67] Ferrer, J., Martinrodero, A. & Flores, F. Contact resistance in the scanning tunneling microscope at very small distances. *Physical Review B* **38**, 10113–10115 (1988).
 - [68] Paulsson, M. & Brandbyge, M. Transmission eigenchannels from nonequilibrium green’s functions. *Physical Review B* **76**, 115117 (2007).
 - [69] Meir, Y. & Wingreen, N. S. Landauer formula for the current through an interacting electron region. *Physical Review Letters* **68**, 2512–2515 (1992).
 - [70] Rungger, I. & Sanvito, S. Algorithm for the construction of self-energies for electronic transport calculations based on singularity elimination and singular value decomposition. *Physical Review B* **78**, 035407 (2008).
 - [71] Taylor, J., Guo, H. & Wang, J. Ab initio modeling of quantum transport properties of molecular electronic devices. *Physical Review B* **63**, 245407 (2001).

-
- [72] Xue, Y. Q., Datta, S. & Ratner, M. A. Charge transfer and "band lineup" in molecular electronic devices: A chemical and numerical interpretation. *Journal Of Chemical Physics* **115**, 4292–4299 (2001).
- [73] Brandbyge, M., Mozos, J. L., Ordejon, P., Taylor, J. & Stokbro, K. Density-functional method for nonequilibrium electron transport. *Physical Review B* **65**, 165401 (2002).
- [74] Thygesen, K. S., Bollinger, M. V. & Jacobsen, K. W. Conductance calculations with a wavelet basis set. *Physical Review B* **67**, 115404 (2003).
- [75] Nielsen, S. K. *et al.* Conductance of single-atom platinum contacts: Voltage dependence of the conductance histogram. *Physical Review B* **67**, 245411 (2003).
- [76] Djukic, D. *et al.* Stretching dependence of the vibration modes of a single-molecule pt-h-2-pt bridge. *Physical Review B* **71**, 161402 (2005).
- [77] Thygesen, K. S. & Jacobsen, K. W. Conduction mechanism in a molecular hydrogen contact. *Physical Review Letters* **94**, 036807 (2005).
- [78] Strange, M., Thygesen, K. S. & Jacobsen, K. W. Electron transport in a pt-co-pt nanocontact: Density functional theory calculations. *Physical Review B* **73**, 125424 (2006).
- [79] Stokbro, K., Taylor, J., Brandbyge, M., Mozos, J. L. & Ordejon, P. Theoretical study of the nonlinear conductance of di-thiol benzene coupled to au(111) surfaces via thiol and thiolate bonds. *Computational Materials Science* **27**, 151–160 (2003).
- [80] Heurich, J., Cuevas, J. C., Wenzel, W. & Schon, G. Electrical transport through single-molecule junctions: From molecular orbitals to conduction channels. *Physical Review Letters* **88**, 256803 (2002).
- [81] Quek, S. Y. *et al.* Amine-gold linked single-molecule circuits: Experiment and theory. *Nano Letters* **7**, 3477–3482 (2007).
- [82] Stipe, B. C., Rezaei, M. A. & Ho, W. Single-molecule vibrational spectroscopy and microscopy. *Science* **280**, 1732–1735 (1998).

-
- [83] Hahn, J. R., Lee, H. J. & Ho, W. Electronic resonance and symmetry in single-molecule inelastic electron tunneling. *Physical Review Letters* **85**, 1914–1917 (2000).
- [84] Wang, W. Y., Lee, T., Kretzschmar, I. & Reed, M. A. Inelastic electron tunneling spectroscopy of an alkanedithiol self-assembled monolayer. *Nano Letters* **4**, 643–646 (2004).
- [85] Ward, D. R. *et al.* Electromigrated nanoscale gaps for surface-enhanced raman spectroscopy. *Nano Letters* **7**, 1396–1400 (2007).
- [86] Dieringer, J. A., Lettan, R. B., Scheidt, K. A. & Van Duyne, R. P. A frequency domain existence proof of single-molecule surface-enhanced raman spectroscopy. *Journal Of The American Chemical Society* **129**, 16249–16256 (2007).
- [87] Andrews, D. Q., Van Duyne, R. P. & Ratner, M. A. Stochastic modulation in molecular electronic transport junctions: Molecular dynamics coupled with charge transport calculations. *Nano Letters* **8**, 1120–1126 (2008).
- [88] Thygesen, K. S. Impact of exchange-correlation effects on the iv characteristics of a molecular junction. *Physical Review Letters* **100**, 166804 (2008).
- [89] Thygesen, K. S. & Rubio, A. Conserving gw scheme for nonequilibrium quantum transport in molecular contacts. *Physical Review B* **77**, 115333 (2008).
- [90] Darancet, P., Ferretti, A., Mayou, D. & Olevano, V. Ab initio gw electron-electron interaction effects in quantum transport. *Physical Review B* **75**, 075102 (2007).
- [91] Mowbray, D. J., Jones, G. & Thygesen, K. S. Influence of functional groups on charge transport in molecular junctions. *Journal Of Chemical Physics* **128** (2008).
- [92] Neaton, J. B., Hybertsen, M. S. & Louie, S. G. Renormalization of molecular electronic levels at metal-molecule interfaces. *Physical Review Letters* **97**, 216405 (2006).
- [93] Quek, S. Y., Choi, H. J., Louie, S. G. & Neaton, J. B. Length dependence of conductance in aromatic single-molecule junctions. *Nano Letters* **9**, 3949–3953 (2009).

-
- [94] Kristensen, I. S., Paulsson, M., Thygesen, K. S. & Jacobsen, K. W. Inelastic scattering in metal-h-2-metal junctions. *Physical Review B* **79**, 235411 (2009).
- [95] Lee, W., Jean, N. & Sanvito, S. Exploring the limits of the self-consistent born approximation for inelastic electronic transport. *Physical Review B* **79**, 085120 (2009).
- [96] Hu, Y. B., Zhu, Y., Gao, H. J. & Guo, H. Conductance of an ensemble of molecular wires: A statistical analysis. *Physical Review Letters* **95** (2005).
- [97] Geng, W. T., Nara, J. & Ohno, T. Impacts of metal electrode and molecule orientation on the conductance of a single molecule. *Applied Physics Letters* **85**, 5992–5994 (2004).
- [98] Hu, W. P. *et al.* Electron transport in self-assembled polymer molecular junctions. *Physical Review Letters* **96**, 027801 (2006).
- [99] Basch, H., Cohen, R. & Ratner, M. A. Interface geometry and molecular junction conductance: Geometric fluctuation and stochastic switching. *Nano Letters* **5**, 1668–1675 (2005).
- [100] Solomon, G. C., Reimers, J. R. & Hush, N. S. Overcoming computational uncertainties to reveal chemical sensitivity in single molecule conduction calculations. *Journal Of Chemical Physics* **122**, 224502 (2005).
- [101] Zhang, Y. B., Tan, Y. W., Stormer, H. L. & Kim, P. Experimental observation of the quantum hall effect and berry’s phase in graphene. *Nature* **438**, 201–204 (2005).
- [102] Novoselov, K. S. *et al.* Two-dimensional gas of massless dirac fermions in graphene. *Nature* **438**, 197–200 (2005).
- [103] Fang, T., Konar, A., Xing, H. & Jena, D. Mobility in semiconducting graphene nanoribbons: Phonon, impurity, and edge roughness scattering. *Physical Review B* **78**, 205403 (2008).
- [104] Wallace, P. R. The band theory of graphite. *Physical Review* **71**, 622–634 (1947).
- [105] Charlier, J. . C., Michenaud, J. . P., Gonze, X. & Vigneron, J. . P. Tight-binding model for the electronic properties of simple hexagonal graphite. *Physical Review B (Condensed Matter)/Physical Review B (Condensed Matter)* **vol.44, no.24**, 13237–49 (1991).

-
- [106] Du, X., Skachko, I., Barker, A. & Andrei, E. Y. Approaching ballistic transport in suspended graphene. *Nature Nanotechnology* **3**, 491–495 (2008).
- [107] Novoselov, K. S. *et al.* Unconventional quantum hall effect and berry’s phase of 2π in bilayer graphene. *Nature Physics* **2**, 177–180 (2006).
- [108] Geim, A. K. & Novoselov, K. S. The rise of graphene. *Nature Mater.* **6**, 183–191 (2007).
- [109] Charlier, J. C., Blase, X. & Roche, S. Electronic and transport properties of nanotubes. *Reviews Of Modern Physics* **79**, 677–732 (2007).
- [110] Son, Y. W., Cohen, M. L. & Louie, S. G. Energy gaps in graphene nanoribbons. *Physical Review Letters* **97**, 216803 (2006).
- [111] Nakada, K., Fujita, M., Dresselhaus, G. & Dresselhaus, M. S. Edge state in graphene ribbons: Nanometer size effect and edge shape dependence. *Physical Review B* **54**, 17954–17961 (1996).
- [112] Wakabayashi, K., Fujita, M., Ajiki, H. & Sigrist, M. Electronic and magnetic properties of nanographite ribbons. *Physical Review B* **59**, 8271–8282 (1999).
- [113] Fujita, M., Wakabayashi, K., Nakada, K. & Kusakabe, K. Peculiar localized state at zigzag graphite edge. *Journal Of The Physical Society Of Japan* **65**, 1920–1923 (1996).
- [114] Charlier, J. C., Gonze, X. & Michenaud, J. P. Graphite interplanar bonding - electronic delocalization and van-der-waals interaction. *Europhysics Letters* **28**, 403–408 (1994).
- [115] Reich, S., Maultzsch, J., Thomsen, C. & Ordejon, P. Tight-binding description of graphene. *Physical Review B* **66**, 035412 (2002).
- [116] Trevisanutto, P. E., Giorgetti, C., Reining, L., Ladisa, M. & Olivano, V. Ab initio gw many-body effects in graphene. *Physical Review Letters* **101**, 226405 (2008).
- [117] Han, M. Y., Ozyilmaz, B., Zhang, Y. B. & Kim, P. Energy band-gap engineering of graphene nanoribbons. *Physical Review Letters* **98**, 206805 (2007).

-
- [118] Tapasztó, L., Dobrik, G., Lambin, P. & Biro, L. P. Tailoring the atomic structure of graphene nanoribbons by scanning tunnelling microscope lithography. *Nature Nanotechnology* **3**, 397–401 (2008).
- [119] Miyamoto, Y., Nakada, K. & Fujita, M. First-principles study of edge states of h-terminated graphitic ribbons. *Physical Review B* **59**, 9858–9861 (1999).
- [120] Kawai, T., Miyamoto, Y., Sugino, O. & Koga, Y. Graphitic ribbons without hydrogen-termination: Electronic structures and stabilities. *Physical Review B* **62**, R16349–R16352 (2000).
- [121] Okada, S. & Oshiyama, A. Magnetic ordering in hexagonally bonded sheets with first-row elements. *Physical Review Letters* **87**, 146803 (2001).
- [122] Lee, H., Son, Y. W., Park, N., Han, S. W. & Yu, J. J. Magnetic ordering at the edges of graphitic fragments: Magnetic tail interactions between the edge-localized states. *Physical Review B* **72**, 174431 (2005).
- [123] Ezawa, M. Peculiar width dependence of the electronic properties of carbon nanoribbons. *Physical Review B* **73**, 045432 (2006).
- [124] Brey, L. & Fertig, H. A. Electronic states of graphene nanoribbons studied with the dirac equation. *Physical Review B* **73**, 235411 (2006).
- [125] Sasaki, K., Murakami, S. & Saito, R. Stabilization mechanism of edge states in graphene. *Applied Physics Letters* **88**, 113110 (2006).
- [126] Abanin, D. A., Lee, P. A. & Levitov, L. S. Spin-filtered edge states and quantum hall effect in graphene. *Physical Review Letters* **96**, 176803 (2006).
- [127] Son, Y.-W., Cohen, M. L. & Louie, S. G. Half-metallic graphene nanoribbons. *Nature* **444**, 347–349 (2006).
- [128] Ritter, K. A. & Lyding, J. W. The influence of edge structure on the electronic properties of graphene quantum dots and nanoribbons. *Nature Materials* **8**, 235–242 (2009).
- [129] Liu, Z., Suenaga, K., Harris, P. J. F. & Iijima, S. Open and closed edges of graphene layers. *Physical Review Letters* **102**, 015501 (2009).

-
- [130] Girit, C. O. *et al.* Graphene at the edge: Stability and dynamics. *Science* **323**, 1705–1708 (2009).
- [131] Lin, Y. M. & Avouris, P. Strong suppression of electrical noise in bilayer graphene nanodevices. *Nano Lett.* **8**, 2119–2125 (2008).
- [132] Yang, L., Park, C. H., Son, Y. W., Cohen, M. L. & Louie, S. G. Quasiparticle energies and band gaps in graphene nanoribbons. *Physical Review Letters* **99**, 186801 (2007).
- [133] Kobayashi, Y., Fukui, K., Enoki, T., Kusakabe, K. & Kaburagi, Y. Observation of zigzag and armchair edges of graphite using scanning tunneling microscopy and spectroscopy. *Physical Review B* **71**, 193406 (2005).
- [134] Kane, C. L. & Mele, E. J. Quantum spin hall effect in graphene. *Physical Review Letters* **95**, 226801 (2005).
- [135] Wakabayashi, K. Electronic transport properties of nanographite ribbon junctions. *Physical Review B* **64**, 125428 (2001).
- [136] Peres, N. M. R., Neto, A. H. C. & Guinea, F. Conductance quantization in mesoscopic graphene. *Physical Review B* **73**, 195411 (2006).
- [137] Munoz-Rojas, F., Jacob, D., Fernandez-Rossier, J. & Palacios, J. J. Coherent transport in graphene nanoconstrictions. *Physical Review B* **74**, 195417 (2006).
- [138] Zheng, H. X., Wang, Z. F., Luo, T., Shi, Q. W. & Chen, J. Analytical study of electronic structure in armchair graphene nanoribbons. *Physical Review B* **75**, 165414 (2007).
- [139] Gunlycke, D., Areshkin, D. A. & White, C. T. Semiconducting graphene nanostrips with edge disorder. *Applied Physics Letters* **90**, 142104 (2007).
- [140] Barone, V., Hod, O. & Scuseria, G. E. Electronic structure and stability of semiconducting graphene nanoribbons. *Nano Letters* **6**, 2748–2754 (2006).
- [141] Yao, W., Yang, S. A. & Niu, Q. Edge states in graphene: From gapped flat-band to gapless chiral modes. *Physical Review Letters* **102**, 096801 (2009).

-
- [142] Shenoy, V. B., Reddy, C. D., Ramasubramaniam, A. & Zhang, Y. W. Edge-stress-induced warping of graphene sheets and nanoribbons. *Physical Review Letters* **101**, 245501 (2008).
- [143] Yazyev, O. V. Magnetism in disordered graphene and irradiated graphite. *Physical Review Letters* **101**, 037203 (2008).
- [144] Brar, V. W. *et al.* Scanning tunneling spectroscopy of inhomogeneous electronic structure in monolayer and bilayer graphene on sic. *Applied Physics Letters* **91**, 122102 (2007).
- [145] Rutter, G. M. *et al.* Scattering and interference in epitaxial graphene. *Science* **317**, 219–222 (2007).
- [146] Ishigami, M., Chen, J. H., Cullen, W. G., Fuhrer, M. S. & Williams, E. D. Atomic structure of graphene on sio₂. *Nano Letters* **7**, 1643–1648 (2007).
- [147] Meyer, J. C., Girit, C. O., Crommie, M. F. & Zettl, A. Imaging and dynamics of light atoms and molecules on graphene. *Nature* **454**, 319–322 (2008).
- [148] Li, D., Mueller, M. B., Gilje, S., Kaner, R. B. & Wallace, G. G. Processable aqueous dispersions of graphene nanosheets. *Nature Nanotechnol.* **3**, 101–105 (2008).
- [149] Chen, Z., Lin, Y.-M., Rooks, M. J. & Avouris, P. Graphene nanoribbon electronics. *Physica E* **40**, 228–232 (2007).
- [150] Sols, F., Guinea, F. & Neto, A. H. C. Coulomb blockade in graphene nanoribbons. *Physical Review Letters* **99**, 166803 (2007).
- [151] Querlioz, D. *et al.* Suppression of the orientation effects on bandgap in graphene nanoribbons in the presence of edge disorder. *Applied Physics Letters* **92**, 042108 (2008).
- [152] Stone, A. J. & Wales, D. J. Theoretical-studies of icosahedral c₆₀ and some related species. *Chemical Physics Letters* **128**, 501–503 (1986).
- [153] Terrones, H. *et al.* New metallic allotropes of planar and tubular carbon. *Physical Review Letters* **84**, 1716–1719 (2000).
- [154] Bailey, C. L., Wander, A., Mukhopadhyay, S., Searle, B. G. & Harrison, N. M. Ab initio surface thermodynamics in multi component environments. Tech. Rep., DL Technical Reports, DL-TR-2007-004 (2007).

- [155] Chase, M. W. *et al.* Janaf thermochemical tables - 3rd edition .2. *Journal Of Physical And Chemical Reference Data* **14**, 927–1856 (1985).
- [156] Clar, E. & Schoental, R. *Polycyclic hydrocarbons* (Academic Press, 1964).
- [157] Clar, E. *The aromatic sextet* (John Wiley & Sons, 1972).
- [158] Kastler, M., Schmidt, J., Pisula, W., Sebastiani, D. & Mullen, K. From armchair to zigzag peripheries in nanographenes. *Journal Of The American Chemical Society* **128**, 9526–9534 (2006).
- [159] Randic, M. Aromaticity of polycyclic conjugated hydrocarbons. *Chemical Reviews* **103**, 3449–3605 (2003).
- [160] Moran, D., Stahl, F., Bettinger, H. F., Schaefer, H. F. & Schleyer, P. V. Towards graphite: Magnetic properties of large polybenzenoid hydrocarbons. *Journal Of The American Chemical Society* **125**, 6746–6752 (2003).
- [161] Hosoya, H. & Yamaguchi, T. Sextet polynomial - new enumeration and proof technique for resonance theory applied to aromatic-hydrocarbons. *Tetrahedron Letters* 4659–4662 (1975).
- [162] Li, S. H. & Jiang, Y. S. Bond lengths, reactivities, and aromaticities of benzenoid hydrocarbons based on the valence-bond calculations. *Journal Of The American Chemical Society* **117**, 8401–8406 (1995).
- [163] Matsuo, Y., Tahara, K. & Nakamura, E. Theoretical studies on structures and aromaticity of finite-length armchair carbon nanotubes. *Organic Letters* **5**, 3181–3184 (2003).
- [164] Ormsby, J. L. & King, B. T. Clar valence bond representation of pi-bonding in carbon nanotubes. *Journal Of Organic Chemistry* **69**, 4287–4291 (2004).
- [165] Mermin, N. D. & Wagner, H. Absence of ferromagnetism or antiferromagnetism in one- or 2-dimensional isotropic heisenberg models. *Physical Review Letters* **17**, 1133–& (1966).
- [166] Calandra, M. & Mauri, F. Electronic structure of heavily doped graphene: The role of foreign atom states. *Physical Review B* **76**, 161406 (2007).

-
- [167] Uchoa, B., Lin, C. Y. & Neto, A. H. C. Tailoring graphene with metals on top. *Physical Review B* **77**, 035420 (2008).
- [168] Schedin, F. *et al.* Detection of individual gas molecules adsorbed on graphene. *Nature Materials* **6**, 652–655 (2007).
- [169] Leenaerts, O., Partoens, B. & Peeters, F. M. Adsorption of h₂o, nh₃, co, no₂, and no on graphene: A first-principles study. *Physical Review B* **77**, 125416 (2008).
- [170] Wehling, T. O. *et al.* Molecular doping of graphene. *Nano Letters* **8**, 173–177 (2008).
- [171] Martins, T. B., Miwa, R. H., da Silva, A. J. R. & Fazzio, A. Electronic and transport properties of boron-doped graphene nanoribbons. *Physical Review Letters* **98**, 196803 (2007).
- [172] Peres, N. M. R. *et al.* Electron waves in chemically substituted graphene. *Europhysics Letters* **80**, 67007 (6pp.) (2007).
- [173] Esquinazi, P. *et al.* Ferromagnetism in oriented graphite samples. *Physical Review B* **66**, 024429 (2002).
- [174] Esquinazi, P. *et al.* Induced magnetic ordering by proton irradiation in graphite. *Physical Review Letters* **91**, 227201 (2003).
- [175] Barzola-Quiquia, J. *et al.* Experimental evidence for two-dimensional magnetic order in proton bombarded graphite. *Physical Review B* **76**, 161403 (2007).
- [176] Lehtinen, P. O., Foster, A. S., Ma, Y. C., Krashenninnikov, A. V. & Nieminen, R. M. Irradiation-induced magnetism in graphite: A density functional study. *Physical Review Letters* **93**, 187202 (2004).
- [177] Lehtinen, P. O. *et al.* Magnetic properties and diffusion of adatoms on a graphene sheet. *Physical Review Letters* **91**, 017202 (2003).
- [178] Heggie, M., Eggen, B. R., Ewels, C. P., Leary, P. & Ali, S. Ldf calculations of point defects in graphites and fullerenes. *Recent Advances In The Chemistry And Physics Of Fullerenes And Related Materials, Vol 6* **98**, 60–67 (1998).
- [179] El-Barbary, A. A., Telling, R. H., Ewels, C. P., Heggie, M. I. & Briddon, P. R. Structure and energetics of the vacancy in graphite. *Physical Review B* **68**, 144107 (2003).

-
- [180] Telling, R. H., Ewels, C. P., El-Barbary, A. A. & Heggie, M. I. Wigner defects bridge the graphite gap. *Nature Materials* **2**, 333–337 (2003).
- [181] Banhart, F. Irradiation effects in carbon nanostructures. *Reports On Progress In Physics* **62**, 1181–1221 (1999).
- [182] Thrower, P. A. & Mayer, R. M. Point-defects and self-diffusion in graphite. *Physica Status Solidi A-Applied Research* **47**, 11–37 (1978).
- [183] Ziegler, J. F. Stopping of energetic light ions in elemental matter. *Journal Of Applied Physics* **85**, 1249–1272 (1999).
- [184] Kopelevich, Y., Esquinazi, P., Torres, J. H. S. & Moehlecke, S. Ferromagnetic- and superconducting-like behavior of graphite. *Journal Of Low Temperature Physics* **119**, 691–702 (2000).
- [185] Cervenka, J., Katsnelson, M. I. & Flipse, C. F. J. Room-temperature ferromagnetism in graphite driven by two-dimensional networks of point defects. *Nature Physics* **5**, 840–844 (2009).
- [186] Yazyev, O. V. & Helm, L. Defect-induced magnetism in graphene. *Physical Review B* **75**, 125408 (2007).
- [187] Kumazaki, H. & Hirashima, D. S. Nonmagnetic-defect-induced magnetism in graphene. *Journal Of The Physical Society Of Japan* **76**, 064713 (2007).
- [188] Palacios, J. J., Fernandez-Rossier, J. & Brey, L. Vacancy-induced magnetism in graphene and graphene ribbons. *Physical Review B* **77**, 195428 (2008).
- [189] Lieb, E. H. 2 theorems on the hubbard-model. *Physical Review Letters* **62**, 1201–1204 (1989).
- [190] Ordejon, P., Artacho, E. & Soler, J. M. Self-consistent order-n density-functional calculations for very large systems. *Physical Review B* **53**, 10441–10444 (1996).
- [191] Amara, H., Latil, S., Meunier, V., Lambin, P. & Charlier, J. C. Scanning tunneling microscopy fingerprints of point defects in graphene: A theoretical prediction. *Physical Review B* **76**, 115423 (2007).

-
- [192] Pereira, V. M., Guinea, F., Lopes dos Santos, J. M. B., Peres, N. M. R. & Castro Neto, A. H. Disorder induced localized states in graphene. *Phys. Rev. Lett.* **96**, 036801– (2006).
- [193] Mizes, H. A. & Foster, J. S. Long-range electronic perturbations caused by defects using scanning tunneling microscopy. *Science* **244**, 559–562 (1989).
- [194] Kelly, K. F. & Halas, N. J. Determination of alpha and beta site defects on graphite using c-60-adsorbed stm tips. *Surface Science* **416**, L1085–L1089 (1998).
- [195] Mills, G., Jonsson, H. & Schenter, G. K. Reversible work transition-state theory - application to dissociative adsorption of hydrogen. *Surface Science* **324**, 305–337 (1995).
- [196] Barkema, G. T. & Mousseau, N. The activation-relaxation technique: an efficient algorithm for sampling energy landscapes. *Computational Materials Science* **20**, 285–292 (2001).
- [197] Kaxiras, E. & Pandey, K. C. Energetics of defects and diffusion mechanisms in graphite. *Physical Review Letters* **61**, 2693–2696 (1988).
- [198] Xu, C. H., Fu, C. L. & Pedraza, D. F. Simulations of point-defect properties in graphite by a tight-binding-force model. *Physical Review B* **48**, 13273–13279 (1993).
- [199] Xu, C. H., Wang, C. Z., Chan, C. T. & Ho, K. M. Simulated-annealing studies of structural trends in carbon clusters. *Physical Review B* **47**, 9878–9880 (1993).
- [200] Krasheninnikov, A. V., Lehtinen, P. O., Foster, A. S. & Nieminen, R. M. Bending the rules: Contrasting vacancy energetics and migration in graphite and carbon nanotubes. *Chemical Physics Letters* **418**, 132–136 (2006).
- [201] Atamny, F., Kollmann, H., Bartl, H. & Schlogl, R. Microstructure of nanocrystalline carbon allotropes - application of stm to loose particles. *Ultramicroscopy* **48**, 281–289 (1993).
- [202] Henschke, B., Schubert, H., Blocker, J., Atamny, F. & Schlogl, R. Mechanistic aspects of the reaction between carbon and oxygen. *Thermochimica Acta* **234**, 53–83 (1994).

-
- [203] Niimi, Y. *et al.* Scanning tunneling microscopy and spectroscopy of the electronic local density of states of graphite surfaces near monoatomic step edges. *Physical Review B* **73**, 085421 (2006).
- [204] Kobayashi, Y., Fukui, K., Enoki, T. & Kusakabe, K. Edge state on hydrogen-terminated graphite edges investigated by scanning tunneling microscopy. *Physical Review B* **73**, 125415 (2006).
- [205] Jia, X. T. *et al.* Controlled formation of sharp zigzag and armchair edges in graphitic nanoribbons. *Science* **323**, 1701–1705 (2009).
- [206] Kosynkin, D. V. *et al.* Longitudinal unzipping of carbon nanotubes to form graphene nanoribbons. *Nature* **458**, 872–U5 (2009).
- [207] Schniepp, H. C. functionalized single graphene sheets derived from splitting graphite oxide. *J. Phys. Chem. B* **110**, 8535–8539 (2006).
- [208] Rollings, E. Synthesis and characterization of atomically thin graphite films on a silicon carbide substrate. *J. Phys. Chem. Solids* **67**, 2172–2177 (2006).
- [209] Ci, L. J. Controlled nanocutting of graphene. *Nano Res.* **1**, 116–122 (2008).
- [210] Datta, S. S., Strachan, D. R., Khamis, S. M. & Johnson, A. T. C. Crystallographic etching of few-layer graphene. *Nano Lett.* **8**, 1912–1915 (2008).
- [211] Campos-Delgado, J. Bulk production of a new form of sp² carbon: crystalline graphene nanoribbons. *Nano Lett.* **8**, 2773–2778 (2008).
- [212] Jiao, L. Y., Zhang, L., Wang, X. R., Diankov, G. & Dai, H. J. Narrow graphene nanoribbons from carbon nanotubes. *Nature* **458**, 877–880 (2009).
- [213] Kubo, R. Fluctuation-dissipation theorem. *Reports On Progress In Physics* **29**, 255–& (1966).
- [214] Buttiker, M., Imry, Y., Landauer, R. & Pinhas, S. Generalized many-channel conductance formula with application to small rings. *Physical Review B* **31**, 6207–6215 (1985).
- [215] Wimmer, M., Adagideli, I., Berber, S., Tomanek, D. & Richter, K. Spin currents in rough graphene nanoribbons: Universal fluctuations and spin injection. *Physical Review Letters* **100**, 177207 (2008).

-
- [216] Gorjizadeh, N., Farajian, A. A. & Kawazoe, Y. The effects of defects on the conductance of graphene nanoribbons. *Nanotechnology* **20**, 015201 (6pp) (2009).
- [217] Choi, H. J., Ihm, J., Louie, S. G. & Cohen, M. L. Defects, quasibound states, and quantum conductance in metallic carbon nanotubes. *Physical Review Letters* **84**, 2917–2920 (2000).
- [218] Biel, B., Blase, X., Triozon, F. & Roche, S. Anomalous doping effects on charge transport in graphene nanoribbons. *Physical Review Letters* **102**, 096803 (2009).
- [219] Areshkin, D. A., Gunlycke, D. & White, C. T. Ballistic transport in graphene nanostrips in the presence of disorder: Importance of edge effects. *Nano Letters* **7**, 204–210 (2007).
- [220] Triozon, F., Lambin, P. & Roche, S. Electronic transport properties of carbon nanotube based metal/semiconductor/metal intramolecular junctions. *Nanotechnology* **16**, 230–233 (2005).
- [221] Lopez-Bezanilla, A., Triozon, F., Latil, S., Blase, X. & Roche, S. Effect of the chemical functionalization on charge transport in carbon nanotubes at the mesoscopic scale. *Nano Letters* **9**, 940–944 (2009).
- [222] Bostwick, A. *et al.* Quasiparticle transformation during a metal-insulator transition in graphene. *Physical Review Letters* **103**, 056404 (2009).
- [223] Avriller, R., Roche, S., Triozon, F., Blase, X. & Latil, S. Low-dimensional quantum transport properties of chemically-disordered carbon nanotubes: From weak to strong localization regimes. *Modern Physics Letters B* **21**, 1955–1982 (2007).
- [224] Biel, B., Triozon, F., Blase, X. & Roche, S. Chemically induced mobility gaps in graphene nanoribbons: A route for upscaling device performances. *Nano Letters* **9**, 2725–2729 (2009).