









UNIVERSITÉ CATHOLIQUE DE LOUVAIN

École Polytechnique de Louvain

Institut de la Matière Condensée et des Nanosciences

## **Electronic and transport properties of boron nitride and graphene-based nanostructures**

Dissertation présentée en vue de l'obtention du grade de  
docteur en sciences de l'ingénieur

par

**Xavier Declerck**

### **Membres du jury :**

**Pr Jean-Christophe Charlier**, promoteur

**Pr Pierre Defrance**, président

**Pr Xavier Gonze**

**Pr Luc Henrard**

**Pr Gian-Marco Rignanese**

**Pr Humberto Terrones**

**Février 2013**



# Abstract

Graphene has been at the center of a tremendous research effort since its clear identification in 2004 by Andre Geim and Konstantin Novoselov. As a proof of the outstanding interest in graphene, Geim and Novoselov were awarded with the Nobel Prize in Physics in 2010, six years only after their seminal work. This interest is driven by the innovative character of graphene and its extraordinary combination of properties, unmatched by any other material known so far. Graphene is a two-dimensional one-atom thick layer of carbon. In-plane, it possesses one of the largest bond-strength (stronger than diamond), while keeping a high out-of-plane flexibility. Along with its mechanical properties, graphene exhibits exceptional chemical and optical properties. However, the most fascinating properties are undoubtedly its electronic properties. Electrons in graphene behave like massless particles, leading to new behaviors in condensed matter physics. In addition, graphene is a zero band gap semiconductor, meaning the conduction and valence band meet at exactly one single point. Finally, graphene exhibits very high electron mobilities, which are of particular interest for future electronic devices. As in conventional electronics, different ways to tailor the properties of graphene are currently under investigation (i.e. by altering locally its

## ABSTRACT

---

atomic structure or by incorporating foreign atoms in the carbon network) in order to create new specific devices for a large set of various applications.

The discovery of graphene initiated the research in other two-dimensional materials, among which the single sheet of boron nitride (BN). The latter shares with graphene analogous geometry but its electronic properties are drastically different. Indeed, a single layer of BN is an insulating material. More recently, interest has grown in combining graphene together with BN, using either boron nitride as a passive material (substrate, encapsulation), or as an active system to create a new range of properties, differing from the ones of the pristine components.

The present thesis investigates the properties of graphene and boron nitride nanostructures within the framework of density functional theory. Firstly, point defects as well as lines of defects are introduced in graphene. Their influence on the transport properties of graphene are estimated and transport fingerprints are predicted for each specific defect. Secondly, the doping of graphene by incorporation of boron and nitrogen atoms is examined. More specifically, scanning tunneling microscopy images are simulated in order to identify specific defects in experiments. Then, the electronic transport properties of BN-graphene composites are investigated and amazing spin filtering properties are evidenced. Finally, the electronic properties of graphene misorientedly stacked on a BN substrate are presented, evidencing, as observed experimentally, little alteration of the electronic properties of suspended graphene. These calculations suggest the BN single layer to be the ideal substrate for future graphene-based electronics.

# Acknowledgements

*First, I would like to thank Jean-Christophe Charlier, my thesis supervisor for the freedom he gave me for my research, as well as for his inspiring discussions. I am grateful to Xavier Gonze and Gian-Marco Rignanese for their help during these last four years. Moreover, I thank them, along with Pierre Defrance, Luc Henrard, and Humberto Terrones, for their comments and remarks on the present manuscript.*

*I am greatly indebted to the people with whom I have collaborated during this thesis. I would like to thank Simon Dubois for his availability, especially when I started my thesis. I wish to acknowledge the help provided by Aurlien Lherbier and Andrés Botello-Méndez. I greatly appreciated their deep insight and constructive discussions. Working with all of them has been a real pleasure. I would like to thank Jean-Michel Beuken and Alain Jacques for providing technical support, as well as Sadia Benyoub, Luc Coquillart and Annette Kreuwels for helping me through the more administrative tasks. Their help made my everyday life at the lab easier and saved me a lot of time. In addition, I would also like to thank all the members of the lab, past and present, for making it such a nice place not only to work but also to live, especially : Simon, Aurélien, Andrés, David, Nicolas, François, Martin, Geoffroy,*

## ABSTRACT

---

*Anna, Samuel, Yannick, Nicky, Guillermo, Matteo, Zeila, Fabiana, and Marcos.*

*I would like to thank my parents for their support and for making it possible for me to accomplish this PhD thesis. I am grateful to my family, especially my brothers. I would also like to thank my family in-law for their encouraging words, as well as my friends.*

*Finally, I would like to express my deepest recognition to Charlotte, which has supported me through these last years. She enlightened my life, particularly in the tougher times.*

# Contents

|                                                                |              |
|----------------------------------------------------------------|--------------|
| <b>Abstract</b>                                                | <b>iii</b>   |
| <i>Acknowledgements</i>                                        | <b>v</b>     |
| <b>Contents</b>                                                | <b>vii</b>   |
| <b>List of Figures</b>                                         | <b>xi</b>    |
| <b>List of Tables</b>                                          | <b>xxvii</b> |
| <b>Introduction</b>                                            | <b>1</b>     |
| <b>1 Graphene and BN's properties</b>                          | <b>9</b>     |
| 1.1 Electronic properties of graphene . . . . .                | 9            |
| 1.2 Electronic properties of a single layer of boron nitride . | 17           |
| <b>2 Methods</b>                                               | <b>21</b>    |
| 2.1 Density functional theory . . . . .                        | 22           |
| 2.2 Kubo-Greenwood formalism . . . . .                         | 37           |
| 2.3 Phase-coherent transport formalism . . . . .               | 40           |
| 2.4 Tersoff-Hamann formalism . . . . .                         | 48           |
|                                                                | <b>vii</b>   |

## CONTENTS

---

|          |                                                         |            |
|----------|---------------------------------------------------------|------------|
| <b>3</b> | <b>Topological defects in graphene</b>                  | <b>51</b>  |
| 3.1      | One-dimensional defects . . . . .                       | 55         |
| 3.2      | Zero-dimensional defects . . . . .                      | 62         |
| 3.3      | Conclusion . . . . .                                    | 84         |
| <b>4</b> | <b>Boron and nitrogen doping of graphene</b>            | <b>87</b>  |
| 4.1      | Nitrogen doping . . . . .                               | 89         |
| 4.2      | Boron doping . . . . .                                  | 99         |
| 4.3      | Conclusion . . . . .                                    | 116        |
| <b>5</b> | <b>G-BN nanoribbons and composites</b>                  | <b>117</b> |
| 5.1      | Graphene nanoribbons . . . . .                          | 118        |
| 5.2      | Boron nitride nanoribbons . . . . .                     | 123        |
| 5.3      | Graphene - boron nitride interface . . . . .            | 132        |
| 5.4      | Conclusion . . . . .                                    | 141        |
| <b>6</b> | <b>Graphene and boron nitride multilayers</b>           | <b>143</b> |
| 6.1      | Graphene/boron nitride moiré patterns . . . . .         | 144        |
| 6.2      | Graphite and h-BN with van der Waals interactions . .   | 149        |
| 6.3      | Properties of graphene-boron nitride bilayers . . . . . | 155        |
| 6.4      | Conclusion . . . . .                                    | 163        |
|          | <b>Conclusion</b>                                       | <b>165</b> |
|          | <b>List of publications</b>                             | <b>169</b> |
|          | <b>Bibliography</b>                                     | <b>171</b> |
| <b>A</b> | <b>Boron and nitrogen doping of graphene</b>            | <b>187</b> |







# List of Figures

|     |                                                                                                                                                                                                          |    |
|-----|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 0.1 | Two-dimensional graphene sheet. . . . .                                                                                                                                                                  | 2  |
| 1.1 | Graphene's lattice, showing the unit cell (grey) and the lattice vectors (green), the cell parameter and the interatomic distance, as well as the two hexagonal sublattices (red and blue dots). . . . . | 10 |
| 1.2 | Brillouin zone of graphene presenting the reciprocal lattice vectors (in red) and the high-symmetry $k$ points $\Gamma$ , M, K and $K'$ . . . . .                                                        | 12 |
| 1.3 | Brillouin zone of graphene showing the conduction band and the valence band meeting at the high-symmetry K and $K'$ points, as calculated with a tight-binding model. . . . .                            | 15 |
| 1.4 | Two-dimensional plane of boron nitride. Red stands for nitrogen, blue for boron. . . . .                                                                                                                 | 18 |
| 1.5 | Band structure for a single sheet of boron nitride. . . . .                                                                                                                                              | 19 |
| 2.1 | General evolution of $D(t)$ during a Kubo-Greenwood calculation. Its evolution defines different transport regimes. . .                                                                                  | 39 |

## LIST OF FIGURES

---

|     |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |    |
|-----|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 2.2 | Different points of view of a transport measurement. From an experimental one (a), a device is connected by two leads. For a transport calculation as in Transiesta (b), a central region connects two semi-infinite leads which are themselves composed of principal layers (PLs). . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | 46 |
| 3.1 | Common topological defects in graphene : (a) depicts the single vacancy ; (b) the STW defect (the red arrow indicates which bond is rotated to obtain the STW defect) ; (c) and (d) two types of divacancies, namely the 585 and the $t5t7$ . The red arrow in (c) depicts which bond has to be rotated to obtain the $t5t7$ divacancy starting from the 585 divacancy. .                                                                                                                                                                                                                                                                                                                                                                                                                                    | 52 |
| 3.2 | Formation of different extended lines of defects in graphene through the reconstruction of divacancies. Lines of defects are formed after the removal of carbon dimers (in red), either (a) perpendicular or (b) with a $30^\circ$ deviation from the zigzag direction. These extended arrays of defects are called (a) $l-d5d7$ (double-5 double-7 structure) and (b) $l-585$ (pentagon-octagon-pentagon structure), respectively. Further displacement of one graphene side by $1/2a$ (black arrow in b) is required to relax the $l-585$ grain boundary as observed in [63]. An extended array of defects composed of a series of a three pentagons and three heptagons ( $l-t5t7$ ) is also topologically possible when the divacancy reconstruction occurs along with a STW transformation (c). . . . . | 54 |
| 3.3 | <i>Ab initio</i> STM images at ( <i>left</i> ) constant current and ( <i>right</i> ) constant height for the $l-d5d7$ (a) and $l-585$ (b) extended lines of defect. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | 58 |

---

|     |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |    |
|-----|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 3.4 | <i>Ab initio</i> STM images at ( <i>left</i> ) constant current and ( <i>right</i> ) constant height for the 1- <i>t5t7</i> extended line of defect (a). Experimental STM image of the same 1- <i>t5t7</i> defect, extracted from [63] (b). . . . .                                                                                                                                                                                                                                                     | 58 |
| 3.5 | $\uparrow\downarrow$ and $\uparrow\uparrow$ electronic band structures for the 1- <i>d5d7</i> (a), 1-585 (b), and 1- <i>t5t7</i> (c). Red and black colors are used for the two spin components. . . . .                                                                                                                                                                                                                                                                                                | 60 |
| 3.6 | Spin-resolved conductance for the 1- <i>d5d7</i> (a), 1-585 (b), and 1- <i>t5t7</i> (c). Only the $\uparrow\uparrow$ spin polarization case is represented. Red and black colors are used for the two spin components. . . . .                                                                                                                                                                                                                                                                          | 61 |
| 3.7 | Converged unit cells used for the DFT simulations of zero-dimensional defects for : (a) the STW defect , (b) the 585 divacancy, and (c) the <i>t5t7</i> divacancy. . . . .                                                                                                                                                                                                                                                                                                                              | 63 |
| 3.8 | Electronic band structures computed using the SIESTA package along the high-symmetry lines in the Brillouin zone (a) for 7x7 unit cells containing, (b) one <i>t5t7</i> divacancy, (d) one STW defect, and (f) one 585 divacancy. The Fermi energy is set to zero and the Dirac energy is indicated with a horizontal blue dashed line. (c) and (e) show the new positions of the Dirac points. New K and K' Dirac cones are shifted to the positions of the blue and green dots, respectively. . . . . | 64 |

## LIST OF FIGURES

---

- 3.9 Electronic band structures of the three defects in a  $7 \times 7$  unit cell : (a) STW, (b) 585, and (c)  $t5t7$ . The path in reciprocal space is shorter than in Fig. 3.8. It is only composed of the three-segment path :  $\Gamma$ -M-K- $\Gamma$ . The band structures of the charged defects are shown for validation of the rigid band model. Charges ranging from -3 to +3 electrons per unit cell are simulated. The dashed lines are a shift of the neutral band structure. . . . . 67
- 3.10 *Left.* Comparison between the DFT band structure for graphene obtained with SIESTA (red) and the TB band structure obtained with TB parameters extracted from the SIESTA Hamiltonian. Both 1<sup>st</sup> (blue) and 3<sup>rd</sup> (black) nearest-neighbor models are presented. The path chosen is the usual one : K- $\Gamma$ -M-K. *Right.* The density of states is presented as one more comparison of the three models. The Fermi level is set to zero. . . . . 68
- 3.11 *Left.* Comparison of the band structures for (a) a STW, (b) a 585, and (c) a  $t5t7$  defect in a  $7 \times 7$  supercell. Red continuous lines show the DFT results, while the black dotted lines correspond to the TB results using up to 3<sup>rd</sup> NN. *Right.* Corresponding DOS. Green lines show the pristine-graphene's DOS calculated with the same TB model. Fermi level is set to zero while the Dirac energy position is marked by blue dashed lines. . . . . 70
- 3.12 Example of a small sample of defected graphene, including mixed defects and orientations. . . . . 71

---

|      |                                                                                                                                                                                                                                                                                                                   |    |
|------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 3.13 | TB DOS for a $7 \times 7$ unit cell (dashed lines) compared to the one for a large sheet (plain bold lines) for : (a) a STW defect, (b) a 585 defect, and (c) a $t5t7$ defect. The defect concentration is close to 1% of atomic concentration. The Dirac point is set to zero in order to align both DOSs. . . . | 72 |
| 3.14 | DOS for 1% mixtures of (a) STW/585 , (b) STW/ $t5t7$ , and (c) 585/ $t5t7$ (plain lines). As a comparison, the DOS for a 0.5% concentration of STW, 585, or $t5t7$ is also shown (dashed lines). Fermi level is indicated by the vertical arrow.                                                                  | 73 |
| 3.15 | Elastic mean free path for defected graphene having 1% of STW (plain line), 585 (red dashed line), or $t5t7$ (blue dot-dashed lines) defects. . . . .                                                                                                                                                             | 74 |
| 3.16 | Mean free paths in graphene planes with mixed (a) STW/585, (b) STW/ $t5t7$ , and (c) 585/ $t5t7$ defects. Concentrations are ranging from 0.1% to 1.0%. . . . .                                                                                                                                                   | 75 |
| 3.17 | Mobilities for the mixed-defect cases as a function of energy (left column) and carrier density (right column). (a) and (d) shows the mobility for the STW/585 case, (b) and (e) for the STW/ $t5t7$ case, and (c) and (f) for the 585/ $t5t7$ one. Defect concentrations range from 0.1% to 1.0%. . . .          | 77 |
| 3.18 | Semiclassical conductivity as a function of carrier density for graphene with only : STW defects ( <i>left</i> ), 585 defects ( <i>center</i> ) and $t5t7$ defects ( <i>right</i> ). . . . .                                                                                                                      | 78 |

## LIST OF FIGURES

---

|      |                                                                                                                                                                                                                                                                                                                                                                             |    |
|------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 3.19 | Semiclassical conductivities as a function of charge carrier energy (left panels) and as a function of charge carrier density (right panels) of graphene planes with, (a)(d) STW/585 defects, (b)(e) STW/ <i>t</i> 5 <i>t</i> 7 defects, and (c)(f) 585/ <i>t</i> 5 <i>t</i> 7 defects, for different defect concentrations ranging from $n_d = 0.1\%$ to $1.0\%$ . . . . . | 79 |
| 3.20 | Normalized time-dependent diffusion coefficient at three energies for a 1% concentration of STW in a graphene plane (a). Three-dimensional plot of the diffusion coefficient as a function of time and energy for a 1% concentration of STW in a graphene plane (b). . . . .                                                                                                | 81 |
| 3.21 | <i>Left.</i> Normalized time-dependent diffusion coefficient for four energies, for the three mixed-defects planes. <i>Right.</i> Three-dimensional plot of the diffusion coefficient as a function of time and energy for, (a)(d) the STW/585 defects, (b)(e) the STW/ <i>t</i> 5 <i>t</i> 7 defects, and (c)(f) the 585/ <i>t</i> 5 <i>t</i> 7 defects. . . . .           | 83 |
| 3.22 | Localization lengths for defected graphene planes containing : (a) STW/585 defects, (b) STW/ <i>t</i> 5 <i>t</i> 7 defects, and (c) 585/ <i>t</i> 5 <i>t</i> 7. Various defect concentrations are presented. . . .                                                                                                                                                          | 84 |
| 4.1  | STM images of more complex nitrogen-based defects (beyond single or double substitution) observed in [90] (a), [91] (b), and [92] (c). . . . .                                                                                                                                                                                                                              | 90 |
| 4.2  | Unit cells for the graphitic nitrogen substitution (a), and for the pyridinic substitution (b). Nitrogen and carbon atoms are represented in blue and black, respectively. . . . .                                                                                                                                                                                          | 91 |



---

|      |                                                                                                                                                                                                          |     |
|------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 4.3  | Unit cells for an up triangle (a), and for an up and down triangle (b). Nitrogen and carbon atoms are represented in blue and black, respectively. . . . .                                               | 92  |
| 4.4  | Unit cells for two close triangles : (a) an up and a down triangle, and (b) two up triangles. Nitrogen and carbon atoms are represented in blue and black, respectively. . . . .                         | 93  |
| 4.5  | Unit cells for two merged triangles : (a) configuration n°1, and (b) configuration n°2. Nitrogen and carbon atoms are represented in blue and black, respectively. . . . .                               | 95  |
| 4.6  | Unit cells for three triangles : (a) without the central carbon atom, and (b) with the central carbon atom. Nitrogen and carbon atoms are represented in blue and black, respectively.                   | 95  |
| 4.7  | Unit cells for two C <sub>3</sub> N <sub>4</sub> configurations with 16 nitrogen atoms (a), and 24 nitrogen atoms (b). Nitrogen and carbon atoms are represented in blue and black, respectively. . . .  | 96  |
| 4.8  | Simulated STM images for one triangle nitrogen island in graphene for a -200 (a) and 200 mV (b) tip voltage. Nitrogen and carbon atoms are represented in blue and black, respectively. . . . .          | 97  |
| 4.9  | Simulated STM images for a three-triangles nitrogen island in graphene for a -700 (a) and 700 mV (b) tip voltage. Nitrogen and carbon atoms are represented in blue and black, respectively. . . . .     | 98  |
| 4.10 | 7x7 unit cells with a homogeneous distribution of four boron atoms (a), or a BC <sub>3</sub> -like distribution (b). Boron atoms are depicted in red in the hexagonal carbon network (in black). . . . . | 100 |

## LIST OF FIGURES

---

|      |                                                                                                                                                                                                                                                                                                                                                               |     |
|------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 4.11 | Experimental constant height STM image of boron-doped graphene grown on copper. a,b, and c illustrate a specific type of boron-doped defect frequently observed experimentally. The voltage of the tip is set at 700 mV. The scale is identical to Fig. 4.12. From M. Pan, ORNL. . . . .                                                                      | 101 |
| 4.12 | Experimental constant current STM image of boron-doped graphene grown on copper. The voltage of the tip is set at 700 mV. The green circles highlight the “chevron” defect which is represented in Fig. 4.13. From M. Pan, ORNL. . .                                                                                                                          | 102 |
| 4.13 | Experimental STM image of the chevron defect (a). White lines highlighting the directions of the defect. Images at different bias (1 V, 500 mV, and -500 mV) show the evolution of the pattern (b). From M. Pan, ORNL. . . . .                                                                                                                                | 104 |
| 4.14 | Simulated STM images for one boron atom substituted in graphene for an energy window from -250 meV to 250 meV.                                                                                                                                                                                                                                                | 105 |
| 4.15 | Simulated STM images for three boron atoms in the croissant configuration at -300 mV (a) (from M. Pan, ORNL.) and 300 mV (b) tip bias. . . . .                                                                                                                                                                                                                | 106 |
| 4.16 | <i>Left.</i> Experimental image for the chevron defect. From M. Pan, ORNL. <i>Right.</i> Simulated STM images for three boron atoms in the croissant configuration for an energy window going from -200 meV to -100 meV. The green circle highlight the chevron defect. The blue rectangles highlight the pattern reproduced by the simulated images. . . . . | 106 |
| 4.17 | Simulated STM images for five boron atoms in a $BC_3$ configuration at -300 mV (a) and 100 mV (b) tip bias. The white lines highlight the secondary shell of peaks. . . . .                                                                                                                                                                                   | 108 |

---

|      |                                                                                                                                                                                                                                       |     |
|------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 4.18 | Simulated STM images for three boron atoms and a single vacancy in the croissant configuration at -300 mV (a) and 300 mV (b) tip bias. . . . .                                                                                        | 108 |
| 4.19 | Simulated STM images for one boron atom on the pentagon-site of a single vacancy at -300 mV (a) and 300 mV (b) tip bias. . . . .                                                                                                      | 111 |
| 4.20 | Simulated STM images for one boron atom on the nonagon-site of a single vacancy at -300 mV (a) and 300 mV (b) tip bias. . . . .                                                                                                       | 111 |
| 4.21 | Simulated STM images for one boron atom and a $t5t7$ divacancy at -200 mV (a) and 300 mV (b) tip bias. The boron atom is at the center of the divacancy. . . . .                                                                      | 112 |
| 4.22 | Simulated STM images for one boron atom and a $t5t7$ divacancy at -200 mV (a) and 200 mV (b) tip bias. The boron atom is at the first nearest neighbor to the center of the divacancy. . . . .                                        | 113 |
| 4.23 | Simulated STM images for one boron atom and a $t5t7$ divacancy at -200 mV (a) and 300 mV (b) tip bias. The boron atom is at the second nearest neighbor to the center of the divacancy. . . . .                                       | 114 |
| 4.24 | Simulated STM images for one boron atom and a $t5t7$ divacancy at -200 mV (a) and 300 mV (b) tip bias. The boron atom is at the third nearest neighbor to the center of the divacancy. . . . .                                        | 114 |
| 4.25 | Simulated STS curves for a tip centered on the boron atoms of the croissant defect (labeled by $B_1$ , $B_2$ , and $B_3$ ). In addition, the pDOS on the boron atoms (in red) is plotted along with the total DOS (in black). . . . . | 115 |

## LIST OF FIGURES

---

|     |                                                                                                                                                                                                                                                                                                                                       |     |
|-----|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 5.1 | Experimental evidence of GNRs. (a) is extracted from [101], (b) and (c) from [102]. The synthesis method is different, leading therefore to different geometries. . . . .                                                                                                                                                             | 118 |
| 5.2 | Preferred directions for the edges of GNRs: zigzag (red) and armchair (green). . . . .                                                                                                                                                                                                                                                | 119 |
| 5.3 | Atomic structures and electronic band structures of two aGNRs : (a) a 16-aGNR, and (b) a 17-aGNR. . . . .                                                                                                                                                                                                                             | 120 |
| 5.4 | Atomic structures and electronic band structures for a 8-zGNR : (a) with non-magnetic spin ordering, (b) and (c) with antiparallel spin alignment ( $\uparrow\downarrow$ ) and parallel spin alignment between edges ( $\uparrow\uparrow$ ), respectively. In (c), red and black colors are used for both spin polarizations. . . . . | 121 |
| 5.5 | Experimental evidences of zz57 reconstruction along with zigzag edges. Images extracted from Koskinen, <i>et al</i> [110].                                                                                                                                                                                                            | 122 |
| 5.6 | Atomic structure (a), electronic band structure (b) and quantum conductance (c) of an 8-zGNR with a reconstructed edge containing pentagons and heptagons (zz57). .                                                                                                                                                                   | 123 |
| 5.7 | HRTEM experimental images at different magnification of a complex BN structure (so-called nano-urchins). Some BN layers protrude from this structure, exposing their bare edges. Images extracted from [111]. . . . .                                                                                                                 | 124 |

---

|      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |     |
|------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 5.8  | Optimized atomic structures of two infinite BNNRs with (a) zigzag and (b) armchair non-passivated edges. The 10-zBNNR is $\sim 2$ nm wide and its unit cell contains 20 atoms (40 atoms in the present double unit cell) (a). The 20-aBNNR is $\sim 2.3$ nm wide and its unit cell contains 40 atoms (b). Blue and grey circles denote nitrogen and boron atoms, respectively. The direction of the periodicity is perpendicular to the represented unit cells. . . . . | 125 |
| 5.9  | Band structures of a 10-zBNNR (a) and a 20-aBNNR (b), displaying metallic and semiconducting behaviors, respectively. The Fermi energy is positioned at 0 eV. Both edge (ES) and dangling bond (DB) states are indicated by arrows.                                                                                                                                                                                                                                     | 127 |
| 5.10 | Edge (a) and dangling bond (b) states on the nitrogen edge of a 10-zBNNR. Analogous states are also present on the corresponding boron edge (not shown here). . . . .                                                                                                                                                                                                                                                                                                   | 128 |
| 5.11 | Spin polarization density for (a) the $N_{\uparrow\uparrow} - B_{\uparrow\uparrow}$ , (b) the $N_{\uparrow\uparrow} - B_{\downarrow\downarrow}$ , and (c) the $N_{\uparrow\uparrow} - B_{\uparrow\downarrow}$ spin polarization cases. The nitrogen edge is on the left, the boron one on the right. Red and green colors correspond to a positive and negative charge density of $0.005 e^-/\text{Bohr}$ . . . . .                                                     | 129 |
| 5.12 | Spin-dependent band structure for (a) the $N_{\uparrow\uparrow} - B_{\downarrow\downarrow}$ , (b) the $N_{\uparrow\uparrow} - B_{\uparrow\uparrow}$ , and (c) the $N_{\uparrow\uparrow} - B_{\uparrow\downarrow}$ spin polarization cases. The localized states (edge states and dangling bonds) are indicated by arrows on the first band structure. Green and red stands for the two spin orientations. . . . .                                                       | 130 |
| 5.13 | Conductance at equilibrium for (a) the $N_{\uparrow\uparrow} - B_{\uparrow\uparrow}$ , (b) the $N_{\uparrow\uparrow} - B_{\downarrow\downarrow}$ , and (c) the $N_{\uparrow\uparrow} - B_{\uparrow\downarrow}$ spin polarization cases. Green and red stands for the two spin orientations. . . . .                                                                                                                                                                     | 131 |

## LIST OF FIGURES

---

- 5.14 (a) Ball and stick representation of the supercell used for the full structural optimization of the zBNNR-zGNR interface. The 4<sup>th</sup> zBNNR and zGNR unit cells (highlighted in the picture) have been used respectively as references for the construction of the zBNNR and zGNR lead geometries. (b) Ball and stick representation of the transport setup. . . . 133
- 5.15 Electronic transmission functions for the two transport configurations : zBNNR( $\uparrow\uparrow$ )-zGNR( $\uparrow\uparrow$ ) (top panel) and zBNNR( $\uparrow\uparrow$ )-zGNR( $\downarrow\downarrow$ ) (bottom panel). Green and red curves correspond respectively to the majority and minority spin components. . . . . 135
- 5.16 Band structures of the bare BN (*left*) and graphene (*center*) nanoribbons within the  $\uparrow\uparrow$  magnetic configuration. The green and red curves correspond respectively to the majority and minority spin components. The electronic bands contributing to the electronic transmission at the Fermi level are highlighted. *Right*. Spatial representation at  $\Gamma$  of the wave functions corresponding to the electronic bands highlighted in the left pannel. The color scale is obtained from the value of the eigenstate within the plane corresponding to the maximum density of  $\pi - \pi^*$  electrons. Blue and red isocurves correspond respectively to positive and negative values of the wave function. . . . . 137

---

|      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                |     |
|------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 5.17 | Spatial representation of the left and right incoming transmission eigenchannels for the two transport configurations : zBNNR( $\uparrow\uparrow$ )-zGNR( $\uparrow\uparrow$ ) (a) and zBNNR( $\uparrow\uparrow$ )-zGNR( $\downarrow\downarrow$ ) (bottom panel). The color scale is obtained from the real part of the transmission eigenstate in the plane (parallel to the ribbon) corresponding to the maximum density of $\pi - \pi^*$ electrons. . . . . | 138 |
| 5.18 | Electronic density of states of zBNNR-zGNR junction projected on various subsets of atoms. The symbols $C_{1,2,\dots}$ and $BN_{1,2,\dots}$ designate respectively the zGNR and zBNNR unit cells counted from the zBNNR-zGNR interface. $C_{\text{Lead}}$ and $BN_{\text{Lead}}$ refer respectively to the carbon and BN atoms within the leads. The green and red curves correspond respectively to the majority and minority spin components. .              | 139 |
| 5.19 | Representation of the $\alpha$ and $\beta$ localized states (indicated in Fig. 5.18) corresponding to the sharp peaks observed in the DOS projected on different cells of the central region. . . .                                                                                                                                                                                                                                                            | 140 |
| 6.1  | Example of a moiré pattern between graphene (black plane) and BN (blue-red plane). . . . .                                                                                                                                                                                                                                                                                                                                                                     | 147 |
| 6.2  | (2,4) vector in graphene for the formation of a moiré pattern with BN (a) and (3,3) vector in BN for the formation of a moiré pattern with graphene (b). . . . .                                                                                                                                                                                                                                                                                               | 148 |
| 6.3  | (2,4)-(3,3) moiré pattern created by a (2,4) vector in graphene superimposed on a (3,3) vector in BN. The angle $\theta$ is the rotation angle between the moiré lattice and the graphene lattice. One unit cell is highlighted in red. . . .                                                                                                                                                                                                                  | 149 |

## LIST OF FIGURES

---

|      |                                                                                                                                                                                                                                                         |     |
|------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 6.4  | Hexagonal Brillouin zone depicting the high-symmetry $k$ points used for the band structure of Figs.6.5 and 6.6 . . .                                                                                                                                   | 151 |
| 6.5  | Electronic band structure for h-BN, calculated with LDA (black) and vdW-DF2 (red). The green circles highlight the HOMO and LUMO. . . . .                                                                                                               | 153 |
| 6.6  | Electronic band structure for graphite, calculated with LDA (black) and vdW-DF2 (red). . . . .                                                                                                                                                          | 154 |
| 6.7  | Unit cells for graphene-boron nitride bilayers defining a (2,4)-(3,3) (a) and an (8,4)-(7,5) (b) moiré pattern. Carbon, boron and nitrogen are depicted with black, red, and blue sticks, respectively. . . . .                                         | 155 |
| 6.8  | Top view of a 3x3 cell corresponding to an (8,4)-(7,5) moiré pattern. . . . .                                                                                                                                                                           | 156 |
| 6.9  | Electronic band structure for the (8,4)-(7,5) supercell graphene monolayer as calculated with LDA (black) and vdW-DF2 (red). . . . .                                                                                                                    | 157 |
| 6.10 | LDA electronic band structure for the (8,4)-(7,5) monolayer graphene (black) and the graphene-boron nitride bilayer (red). 159                                                                                                                          |     |
| 6.11 | vdW-DF2 electronic band structure for the (8,4)-(7,5) monolayer graphene (black) and the graphene-boron nitride bilayer (red). . . . .                                                                                                                  | 160 |
| 6.12 | Experimental dI/dV curve for different moiré patterns (a). The arrows mark the signatures of the superlattice Dirac cones. The energy corresponding to the dips is a function of the moiré pattern wavelength (b). Images extracted from [125]. . . . . | 161 |



---

|      |                                                                                                                                                                       |     |
|------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 6.13 | Electronic band structure for the (8,4)-(7,5) graphene-boron nitride bilayer without any constraints (red) and with a 0.5 Å perpendicular compression (blue). . . . . | 162 |
| A.1  | Simulated STM images for four boron atoms in a BC <sub>3</sub> configuration at -100 mV (a) and 100 mV (b) tip bias. . . . .                                          | 188 |
| A.2  | Simulated STM images for two boron atom combined with a <i>q5q7</i> divacancy at -100 mV (a) and 100 mV (b) tip bias. .                                               | 189 |
| A.3  | Simulated STM images for two boron atom combined with a 585 divacancy at -100 mV (a) and 100 mV (b) tip bias. .                                                       | 189 |
| A.4  | Simulated STM images for one boron atom combined with a STW defect at -100 mV (a) and 100 mV (b) tip bias. . . .                                                      | 190 |



## List of Tables

|     |                                                                                                                                                                                                                                                                    |     |
|-----|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 3.1 | Formation energies per atom ( $E_c$ ) and per unit of length ( $E'_c$ ) for the different lines of defects embedded in graphene (as illustrated in Fig. 3.2). . . . .                                                                                              | 57  |
| 3.2 | Energy differences between the $\uparrow\downarrow$ and $\uparrow\uparrow$ polarization cases for a h-15-zGNR including a linear defect. . . . .                                                                                                                   | 60  |
| 4.1 | Formation energy per nitrogen atom $E_c$ for the four configurations of Figs. 4.4 and 4.5. . . . .                                                                                                                                                                 | 94  |
| 4.2 | Formation energy per nitrogen atom $E_c$ for $C_3N_4$ based configurations with 16 and 24 nitrogen atoms. . . . .                                                                                                                                                  | 96  |
| 4.3 | Energy difference between arrangements of boron atoms distributed homogeneously and grouped in $BC_3$ islands. The data for different number of atoms and different unit cells (between parentheses) are presented. . . . .                                        | 100 |
| 4.4 | Energy difference between $E_\alpha$ and $E_{Sep.}$ , where $\alpha$ corresponds to the location of the boron atom. The most stable structure is the one where the boron atom is the 1 <sup>st</sup> nearest neighbor to the center atom of the divacancy. . . . . | 112 |

## LIST OF TABLES

---

|     |                                                                                                                                                                                                                                                        |     |
|-----|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 6.1 | Comparison between the experimental interlayer spacing for graphite and h-BN, and the one obtained by using LDA and vdW-DF2. . . . .                                                                                                                   | 150 |
| 6.2 | Comparison between the experimental cell parameter for graphite and h-BN, and the one obtained by using LDA and vdW-DF2. . . . .                                                                                                                       | 150 |
| 6.3 | Comparison between the experimental cohesive energy of graphite [135], and the one obtained by using LDA and vdW-DF2. . . . .                                                                                                                          | 154 |
| B.1 | Comparison between the length of an $(n,m)$ vector for graphene ( $ \mathbf{A} $ ) and for boron nitride ( $ \mathbf{B} $ ), with 1.80% lattice mismatch. The colors highlight the pairs of vectors used to define the studied moiré patterns. . . . . | 192 |

# Introduction

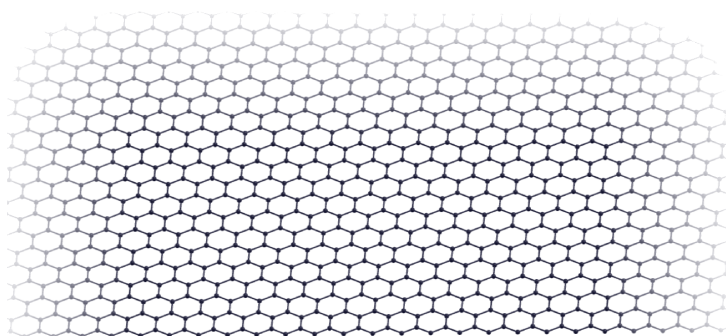
Graphene is a two-dimensional material made of carbon. The atoms are organized in a flat two-dimensional honeycomb lattice (see Fig. 0.1). When stacked, many of such sheets form graphite, a three-dimensional material that has multiple uses, the most everyday-life one being as pencil leads.

The immense interest in graphene originates from the publication in 2004 by Geim and Novoselov [1]. As a proof of the continuously growing interest in graphene and its expected potential, the 2010 Nobel Prize in Physics was awarded to them *”for groundbreaking experiments regarding the two-dimensional material graphene”*. Geim and Novoselov presented isolation of a single sheet of graphene and its manipulation to make it freestanding. Their method was easy and gave access to graphene to a lot of experimentalists. They obtained graphene by a micromechanical cleavage technique called exfoliation (also called the “scotch-tape” method). The idea is to put a small piece of graphite on a tape and to fold it many times in order to produce single sheet flakes. They also performed transport characterization on the first two-dimensional material. It is important to note that graphene was evidenced earlier in a recently rediscovered publication by Boehm and co-

## INTRODUCTION

---

workers [2] dating from 1962. In fact, in a recent paper [3] Boehm himself claims the first work on exfoliated graphite was actually performed by Schafhaeutl in 1840 [4]...



---

Fig. 0.1 - Two-dimensional graphene sheet.

---

Since 2004 many synthesis methods have been developed. Mechanical exfoliation has already been discussed. The top layer of a graphite crystal is submitted to a traction and the weak interlayer bonding makes it possible to separate entire layers. Chemical exfoliation also aims at breaking the bonds between layers. Some of these methods rely on a first oxidation of graphite [5]. Subsequent separation of different sheets is made easier by the presence of oxygen. It requires a reduction at some point of the process in order to recover graphene. Another approach uses carbon nanotubes (CNTs) as a starting point and cuts them open in order to get graphene nanoribbons [6, 7]. This latter approach benefits from the know-how acquired for CNTs and allows for a better control on the dimensions of the graphene flakes. This technique, however, is slower and less suited to mass production compared to the graphite oxide route.

---

A totally different approach uses silicon carbide (SiC). The idea is that when a chunk of SiC is brought at temperatures around  $1000^{\circ}\text{C}$ , silicon atoms will leave the bulk of the material, leaving graphene multilayers on the surface [8]. The number of layers can be controlled and single layers can be produced [9]. Although complicated, this method produces very high quality graphene.

Another much developed technique is the chemical vapor deposition method (CVD). The main drawback of this technique is that it requires a substrate for the deposition. One of the most used substrates is copper [10]. In order to produce devices out of this graphene sheet, a transfer step might be needed, which is one of the most complicated parts of this technique. However, innovative methods exist to produce large-scale graphene sheets [11].

Graphene possesses a unique combination of properties. It has an electron mobility of  $100000\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  for encapsulated graphene [12] (similar to suspended graphene). The electron mobility is a measure of the speed at which electrons can be put into motion. Another electrical property is the ability of graphene to sustain high current densities (several orders of magnitude higher than conventional materials used as interconnects) [13]. From the mechanical point of view, graphene is easily bendable out of plane but extremely strong in plane. Indeed, its Young's modulus is of 1 TPa and its intrinsic strength is as high as 130 GPa, making it almost as strong as diamond [14]. The Young's modulus is directly related to the strength of the carbon-carbon bond. As a comparison, the Young's modulus for steel is around one order of magnitude lower. Its thermal conductivity, which is related to the strength of the bonds and to the weight of the carbon atom, is very high ( $3000\text{ Wm}^{-1}\text{K}^{-1}$ ) and only beaten by diamond [15]. A very pecu-

liar property of graphene is its optical absorption. It was found to be exactly equal to  $\pi\alpha$  ( $\sim 2.3\%$ ), where  $\alpha = e^2/\hbar c$  is the fine structure constant [16]. Moreover, experimentalist succeeded to functionalize graphene in many ways : with hydrogen [17] (also called graphane), with fluorine [18] (also called fluorographene), and other elements as well as organic molecules. Finally, the impermeability to gases is one more property which might lead to applications of graphene.

A recent article by Novoselov and other leading scientists from different graphene-related fields proposes a roadmap for graphene [19]. The authors detail the current status of graphene applications as well as the possible future applications. They stress the fact that different types of applications need different qualities of graphene samples. The less perfect graphene sheets are already used in applications such as in paints for example. Usually, one thinks of graphene as a way to improve current technologies. Graphene is studied because it might replace a given material in some given device. Depending on the type of application, graphene is more or less close to maturity. Other applications, however, will combine all of graphene's properties in totally novel devices. This will require more intensive research but graphene will only realize its true technological potential in these new applications. Fields in which graphene is expected to improve the device properties are mainly electronics, energy production, composite materials, photonics, and bioapplications.

One of the biggest driving forces to research on graphene is the nearing of the theoretical downsizing limit of silicon electronics. However, in order to compete with it, graphene has to be able to be included in some devices (such as transistors for example). The main improvements required to bring graphene to large-scale applications are : a better control



---

of its electronic properties (electronic density, sheet resistance, band gap) ; and better ways to handle graphene, meaning not only a better way to move graphene from one place to another but also the improvement of the integration of graphene in a device which is composed of a substrate, connections,...

Different approaches are investigated to modify graphene's properties. One way is by modifying its dimensionality. This route includes the study of nanotubes and nanoribbons which are one-dimensional materials. Let us also mention fullerenes, which can be thought of as a ball made of graphene, and which has zero dimensionality. Quantum confinement modifies the properties and might open a band gap or induce spin polarization effects. Graphene nanoribbons will be introduced briefly in Chap. 5. A modification of the topology of graphene is yet another route to tune graphene's properties. The Stone-Thrower-Wales, the single vacancy, divacancies, and grain boundaries are common defects encountered in graphene samples. They are detailed, and their effects on the electronic properties, as well as on the transport properties are investigated in Chap. 3 (*"Topological defects in graphene : from structure to electronic and transport properties"*). Another common way to change graphene's properties is doping. Doping consists in introducing atoms in a bulk material, which differ from the host atoms. It is a very common technique used for three-dimensional materials, especially in electronics. The effect is usually quite simple. It increases the density of charge carriers (holes, electrons, or both). In two dimensions, however, doping has a more subtle effect. Boron is a common dopant. While it increases the number of holes in the common-used silicon, the configuration of boron in graphene is not clear yet : Do the boron atoms tend to stand alone? Do they form islands? What is

the size of these islands? Is there a tendency for the boron atoms to stabilize topological defects? The answer to these questions is needed to conceive applications from boron-doped graphene. Indeed, whereas doping has a straightforward effect in three dimensions, in two dimensions it is dependent on the local configuration. Chap. 4 (“*Boron and nitrogen doping of graphene*”) studies the scanning tunneling microscopy (STM) images of boron-doped graphene. STM is a useful experimental technique to study graphene but analysis of the images is all but straightforward. To help with this analysis, different simulated STM images are produced for different defect candidates. These are chosen to respect the symmetry of the experimentally observed defects. Combination with topological defects is also considered. A discussion tries to weigh the advantages and problems with the different candidates. The effect of nitrogen doping of graphene is also presented, focusing more on the energetics of bigger islands of nitrogen atoms in graphene. Simulated STM images are presented, but unfortunately, no comparison with experiments is possible.

The research on graphene has driven attention to other layered materials [20], either as an alternative to graphene or as another way to modify graphene’s properties by mixing it with other materials sharing the same structure or at least the same dimensionality. One of these is boron nitride (BN). BN and graphene share a lot from the structural point of view. The diamond analogous made of BN is called cubic BN (c-BN). It has a hardness similar to diamond’s. It is even harder at high temperature. Graphite-like BN exists as well. It is called hexagonal BN (h-BN or  $\alpha$ -BN). It is made of one-atom thick BN sheets. The stacking is different to the one in graphite. While it is of AB type in the latter, h-BN is of AA’ type. In other words, in graphite, each atom of one

---

layer lies either on top of a hexagon or on top of another atom from the underlying layer. In h-BN however, each boron (nitrogen) atom of a layer has nitrogen (boron) atoms as nearest neighbors in the next layers. Boron nitride has many applications. Cubic boron nitride is used mainly in cutting tools, while hexagonal boron nitride is used in high-temperature applications (such as furnaces), or as lubricant. Finally, it is worth mentioning the existence of BN nanotubes and nanoribbons, stressing even further the analogy between BN and carbon. The single BN sheet (sometimes called boronitrene) is one single layer composing the h-BN crystal, analogous to graphene. The closeness of these two materials makes it easier to manipulate BN. Indeed, it benefits from all the expertise acquired for graphite and graphene [21, 22]. From the electronic point of view, the picture changes starkly. Indeed, BN is always an insulator (5.8 eV band gap for h-BN [23]). BN can be mixed with graphene by stacking sheets of different kinds (graphene and BN) [24, 25] or mixed inside one single sheet creating islands of different kinds [26, 27]. The latter case is studied in Chap. 5 (“*Graphene-boron nitride nanoribbons and composites*”), while the former is the subject of Chap. 6 (“*Graphene and boron nitride multilayers*”). Multilayers are studied in order to quantify the influence of boron nitride on the properties of graphene. The effect of the inclusion of the van der Waals forces is investigated, due to their influence in layered materials. Graphene-boron nitride composites are studied as well. Transport properties are shown for a ribbon composed of a graphene nanoribbon joined to a boron nitride nanoribbon. The interface between the two materials is looked at into more details. The next section goes through the development which leads to graphene’s basic electronic properties.



# Chapter 1

## Graphene and boron nitride's properties

This chapter will present the basic electronic properties of graphene and BN using a simple tight-binding model.

### 1.1 Electronic properties of graphene

Graphene has multiple extraordinary properties, many of them linked to its simple geometry. In fact, graphene's geometry is so simple that by doing only a few approximations one can derive its electronic energy dispersion analytically [28]. This was first done by Wallace in 1947 [29], at a time when graphene only existed as a theoretical concept. Fig. 1.1 shows the main features of the graphene lattice. It is a honeycomb structure which is actually made of two hexagonal sublattices, shown as red and blue dots in Fig. 1.1. The interatomic distance between carbon atoms  $d_{CC}$  is 1.42 Å (for comparison its value is 1.54 Å

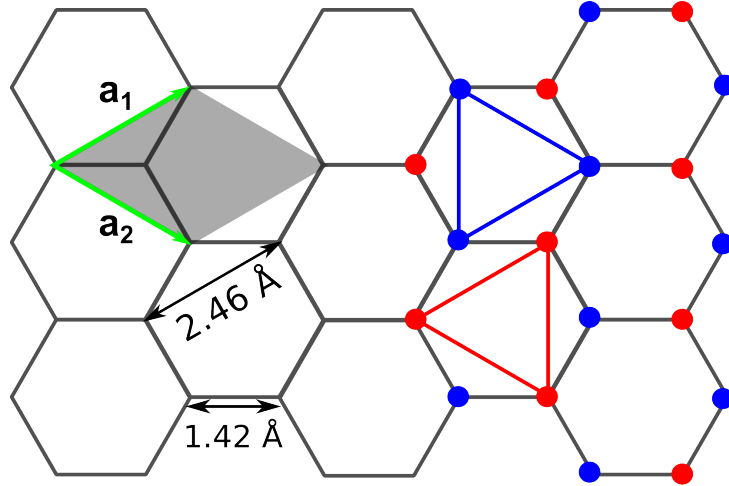
## 1. GRAPHENE AND BN'S PROPERTIES

---

in diamond). The unit cell contains two atoms, one on each sublattice (called either A/B or I/II). The cell vectors  $\mathbf{a}_1$  and  $\mathbf{a}_2$  have a magnitude of 2.46 Å. Their expressions are :

$$\mathbf{a}_1 = d_{CC} \left( \frac{3}{2}, \frac{\sqrt{3}}{2} \right) \quad (1.1)$$

$$\mathbf{a}_2 = d_{CC} \left( \frac{3}{2}, -\frac{\sqrt{3}}{2} \right). \quad (1.2)$$



---

Fig. 1.1 - Graphene's lattice, showing the unit cell (grey) and the lattice vectors (green), the cell parameter and the interatomic distance, as well as the two hexagonal sublattices (red and blue dots).

---

Each carbon atom is linked to three neighbors. From the initial four valence electrons, three of them are hybridized as  $sp^2$ . These are the ones that form the  $\sigma$  bonds between the atoms. The remaining occupies the

$2p_z$  orbital which is perpendicular to the graphene sheet. The overlap of the  $2p_z$  orbitals forms  $\pi$  bonds. They are the closest in energy to the Fermi level and govern the electronic properties. Graphene was therefore studied extensively with the so-called  $\pi - \pi^*$  model, where only one  $p_z$  orbital per atom is included in the basis set. The wave function in the tight-binding (TB) approximation is a combination of the atomic wave functions  $\phi_A$  and  $\phi_B$  where  $\phi_{A,B} = \phi(\mathbf{r} - \mathbf{R}_{A,B})$  and  $\phi(\mathbf{r})$  is a  $p_z$  orbital centered at the origin. The total wave function on the A and B lattices are :

$$\Phi_A = \sum_A e^{i\mathbf{k} \cdot \mathbf{R}_A} \phi(\mathbf{r} - \mathbf{R}_A) \quad (1.3)$$

$$\Phi_B = \sum_B e^{i\mathbf{k} \cdot \mathbf{R}_B} \phi(\mathbf{r} - \mathbf{R}_B), \quad (1.4)$$

where  $\mathbf{R}_{A,B}$  is the position vector of an A or B atom respectively, and  $k$  is a vector from the reciprocal lattice. The total wave function for the system is :

$$\Psi = \Phi_A + \lambda \Phi_B. \quad (1.5)$$

The reciprocal lattice is also hexagonal. Fig. 1.2 illustrates the Brillouin zone of graphene, the unit cell of the reciprocal lattice. The basis vectors are :

$$\mathbf{b}_1 = \frac{1}{d_{CC}} \left( \frac{2\pi}{3}, \frac{2\pi}{\sqrt{3}} \right) \quad (1.6)$$

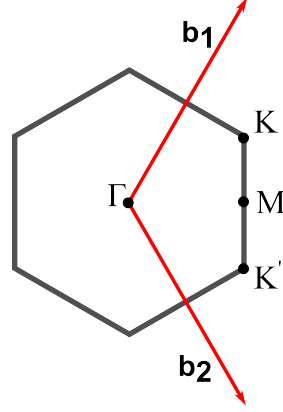
$$\mathbf{b}_2 = \frac{1}{d_{CC}} \left( \frac{2\pi}{3}, -\frac{2\pi}{\sqrt{3}} \right). \quad (1.7)$$

Substituting eq. 1.5 in the Schrödinger equation  $H\Psi = E\Psi$ , we end up with the following system to solve :

$$\begin{cases} H_{AA} + \lambda H_{AB} = ES \\ H_{BA} + \lambda H_{BB} = \lambda ES, \end{cases} \quad (1.8)$$

## 1. GRAPHENE AND BN'S PROPERTIES

---




---

Fig. 1.2 - Brillouin zone of graphene presenting the reciprocal lattice vectors (in red) and the high-symmetry  $k$  points  $\Gamma$ , M, K and  $K'$ .

---

where  $H_{AA} = \langle \Phi_A | H | \Phi_A \rangle$ ,  $H_{BB} = \langle \Phi_B | H | \Phi_B \rangle$ ,  $H_{AB} = \langle \Phi_A | H | \Phi_B \rangle = H_{BA}^*$ , and  $S = \langle \Phi_A | \Phi_A \rangle = \langle \Phi_B | \Phi_B \rangle$ . This last quantity  $S$  is equal to the number of unit cells in the crystal since we consider non-overlapping basis functions.

The system of equations 1.8 possesses an analytical solution :

$$E = \frac{1}{2S} \left[ H_{AA} + H_{BB} \pm \sqrt{(H_{AA} - H_{BB})^2 + 4|H_{AB}|^2} \right]. \quad (1.9)$$

By using the symmetry of the problem  $H_{AA}$  is equal to  $H_{BB}$  and the previous equation simplifies as :

$$E = \frac{1}{N} [H_{AA} \pm |H_{AB}|], \quad (1.10)$$

the plus sign defines the conduction band while the minus one corresponds to the valence band.  $N$  is the number of unit cells in the crystal. The values of the two terms  $H_{AA}$  and  $H_{AB}$  are found by explicitly writing



their expressions :

$$H_{AA} = \int \Phi_A^* H \Phi_A d\mathbf{x}, \text{ and} \quad (1.11)$$

$$H_{AB} = \int \Phi_A^* H \Phi_B d\mathbf{x}, \quad (1.12)$$

which, after replacing  $\Phi_A$  and  $\Phi_B$  with their expressions gives (eq. 1.3 and 1.4) :

$$H_{AA} = N [\varepsilon - t' T(\mathbf{k})] \quad (1.13)$$

$$H_{AB} = N t \sqrt{3 + T(\mathbf{k})} \quad (1.14)$$

$$\text{where } T(\mathbf{k}) = 2 \cos(\sqrt{3} k_y d_{CC}) + 4 \cos\left(\frac{\sqrt{3}}{2} k_y d_{CC}\right) \cos\left(\frac{3}{2} k_x d_{CC}\right). \quad (1.15)$$

In the last set of equations, different quantities have been introduced.  $\varepsilon$  is called the on-site energy and corresponds to the energy level of an isolated atom,  $t$  and  $t'$  are the hopping terms between nearest and next-nearest neighbors, respectively (other symbols for the nearest and next-nearest hopping terms are  $\gamma_0$  and  $\gamma_1$ , respectively). Their expressions are :

$$\varepsilon = \int \phi^*(\mathbf{r}) H \phi(\mathbf{r}) d\mathbf{x}, \quad (1.16)$$

$$t = \int \phi^*(\mathbf{r} - \boldsymbol{\delta}) (V_{\text{at}} - V_{\text{latt}}) \phi(\mathbf{r}) d\mathbf{x}, \quad (1.17)$$

$$t' = - \int \phi^*(\mathbf{r} - \boldsymbol{\delta}') (V_{\text{at}} - V_{\text{latt}}) \phi(\mathbf{r}) d\mathbf{x}, \quad (1.18)$$

where  $\boldsymbol{\delta}$  and  $\boldsymbol{\delta}'$  are some vectors connecting two neighboring atomic sites and two next-neighboring atomic sites respectively. Moreover,  $V_{\text{at}} - V_{\text{latt}}$  is the difference between the atomic potential and the potential of the full lattice. Combining eqs. 1.10, 1.13, 1.14, and 1.15, one

## 1. GRAPHENE AND BN'S PROPERTIES

---

finds the expression for the dispersion relation in graphene :

$$E(\mathbf{k})_{\pm} = \varepsilon \pm t\sqrt{3 + T(\mathbf{k})} - t'T(\mathbf{k}). \quad (1.19)$$

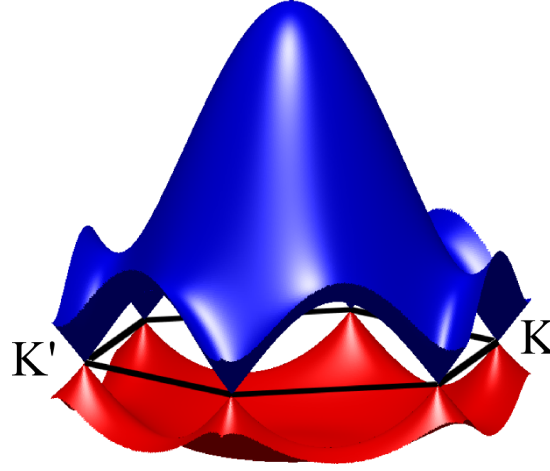
In this equation  $\varepsilon$  is actually the Fermi level  $\varepsilon_F$ . When we focus on the difference between the energy for the conduction band and the energy for the valence band, we notice that this difference has a very simple expression :

$$\Delta E = 2t\sqrt{3 + T(\mathbf{k})}. \quad (1.20)$$

For some values of  $\mathbf{k}$ , this difference becomes zero and the gap between the conduction and valence bands closes, merging into one single point. This particularity happens at the  $\mathbf{K}$  and  $\mathbf{K}'$  points of the Brillouin zone. Fig. 1.3 is a plot of the dispersion relation of eq. 1.19. The hexagonal Brillouin zone is superimposed as a guide to locate the  $\mathbf{K}$  and  $\mathbf{K}'$  points. The features that will govern graphene's electronic properties are around the  $\mathbf{K}$  and  $\mathbf{K}'$  points. Let us define the vector  $\mathbf{q}$  as  $\mathbf{k} = \mathbf{K} + \mathbf{q}$ . Around the  $\mathbf{K}$  point, the dispersion relation can be expanded to the first order as :

$$E(\mathbf{q})_{\pm} = \varepsilon_F \pm \frac{3td_{CC}}{2}|\mathbf{q}| + O(\mathbf{q}^2). \quad (1.21)$$

The dispersion is linear around the  $\mathbf{K}$  point. The factor multiplying  $\mathbf{q}$  defines the Fermi velocity  $v_F = 3td_{CC}/2$ , which is on the order of  $1.10^6 \text{ ms}^{-1}$ . This last equation defines a cone in a small window around the Fermi level. Electrons in graphene are called Dirac fermions because they obey the Dirac equation of quantum electrodynamics for massless particles, with the speed of light replaced by the Fermi velocity, which is the velocity of the electrons having an energy  $\varepsilon_F$ . The adjective *massless* to characterize the electrons in graphene translates the fact that the electrons indeed show very little resistance to movements.




---

Fig. 1.3 - Brillouin zone of graphene showing the conduction band and the valence band meeting at the high-symmetry K and K' points, as calculated with a tight-binding model.

---

The first-order development of the dispersion relation mentioned above gives rise to a symmetrical behavior for electrons and holes. Going to higher order expansions breaks this symmetry and adds a term depending on the direction of the  $\mathbf{k}$  vector. The latter is the so-called trigonal warping.

Around Fermi level, the equation for electrons in graphene can be recast in a Dirac-like equation :

$$-i v_F \boldsymbol{\sigma} \cdot \nabla \psi(\mathbf{r}) = E \psi(\mathbf{r}), \quad (1.22)$$

with  $\boldsymbol{\sigma} = (\sigma_x, \sigma_y)$ ,  $\sigma_x$  and  $\sigma_y$  being the two first Pauli matrices. Actually one such equation is solved for each of the two cones, at K and K', and for each spin (therefore leading to four equations). The solution to one of these equations can be shown to be a two-component spinor.

## 1. GRAPHENE AND BN'S PROPERTIES

---

Each component of the latter defines the pseudospin. It is different from the real spin. It refers instead to the sublattice in real space. We have an index for each of the quantities introduced here :

- a spin index which is the classical spin index as used in general quantum mechanics
- a valley index which identifies which Dirac cone we consider (+1 for K and  $-1$  for K')
- a sublattice or pseudospin index which links spatially to the sublattice (A or B)
- a band index which identifies the band, valence or conduction one (+1 for conduction band and  $-1$  for valence band).

It has to be noted that a lot of these indexes lose their purpose and meaning as soon as we consider electrons further away from the Fermi level, where the Dirac equations cease to apply. Electrons in graphene are also chiral. Chirality or helicity is defined as :

$$\chi = \frac{1}{2} \boldsymbol{\sigma} \cdot \frac{\mathbf{p}}{|\mathbf{p}|}. \quad (1.23)$$

It projects the momentum operator (the direction of motion) along the pseudospin direction. It has two eigenvalues denoted by  $+1$  or  $-1$ . It can be shown to be linked to the valley and band index. It has a positive value for the conduction band at K and the valence band at K', and a negative value for the valence band at K and the conduction band at K'. This property has a powerful consequence : if there is no intervalley scattering and perfect symmetry between sublattices, electrons in the conduction band, close to the K point (having therefore a positive

chirality) having different pseudospin index will travel in opposite directions. This gives rise to the Klein paradox [30], for which an electron that meet a potential barrier at normal incidence will tunnel through it with a one hundred percent probability. This is in stark contrast with what happens for massive electrons for which the transmission probability is always smaller than one.

## 1.2 Electronic properties of a single layer of boron nitride

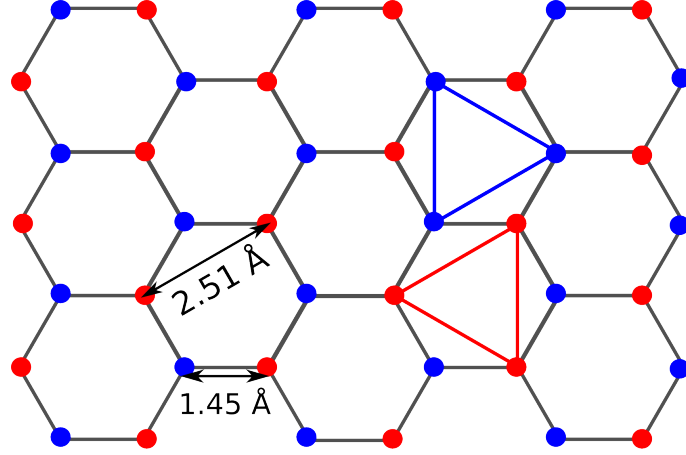
From a structural point of view, boron nitride (BN) and graphene are very similar. Boron and nitrogen are neighbors of carbon in the periodic table of elements, having respectively five and seven as atomic number. Fig. 1.4 shows the geometry of the BN lattice. The boron-nitrogen bond distance is slightly bigger than the carbon-carbon one in graphene, reaching 1.45 Å. The two hexagonal sublattices are obvious in BN, boron atoms standing on one sublattice, nitrogen on the other. Following the same approach as for graphene, one can study BN's electronic properties with a simple model. Considering a  $2p_z$  orbital basis and neglecting every interaction further away than next-neighbor ones, the solution to the problem is identical to graphene until eq. 1.9. The simplification made for graphene that  $H_{AA}$  and  $H_{BB}$  are identical is no longer valid for BN. Therefore, the expression for the energy becomes :

$$E = \frac{1}{N} \left[ E_m \pm \frac{1}{2} \sqrt{E_G^2 + 4|H_{AB}|^2} \right], \quad (1.24)$$

with  $E_m = (H_{AA} + H_{BB})/2$  and  $E_G = |H_{AA} - H_{BB}|$  is the band gap. In order for the conduction and valence bands to meet at one point, one

## 1. GRAPHENE AND BN'S PROPERTIES

---

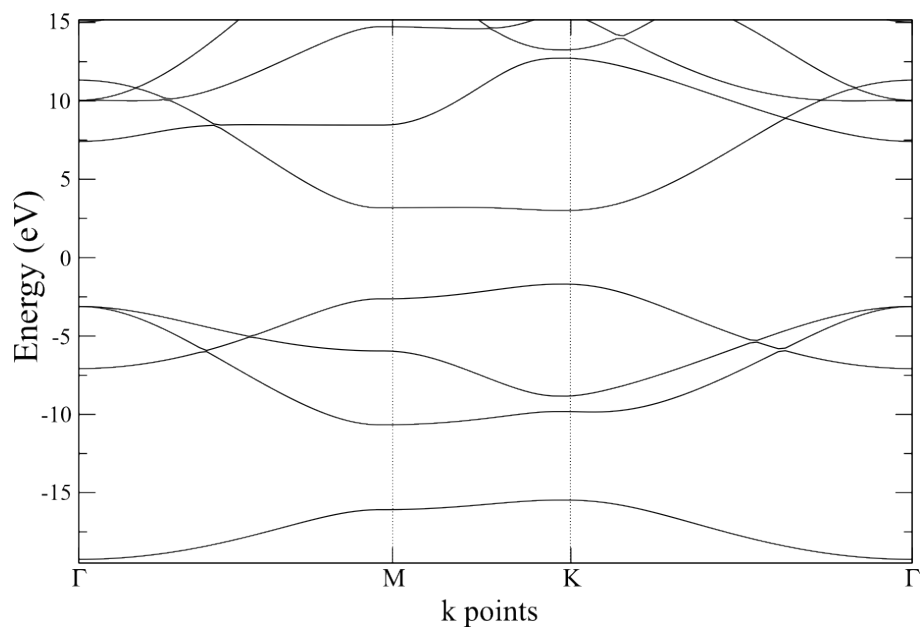


---

Fig. 1.4 - Two-dimensional plane of boron nitride. Red stands for nitrogen, blue for boron.

---

have to cancel the expression under the square root, which is impossible since  $|H_{AB}|^2$  stays positive or equal to zero. Therefore, the simple fact that two different species composes BN instead of one (as in graphene) leads to the opening of a band gap. This band gap is around 6 eV [31]. As a consequence, one way to open a gap in graphene is to break the lattice symmetry, making A and B sublattices unequivalent. The electronic band structure for a single sheet of boron nitride is represented in Fig. 1.5. The details of the calculation are presented in another chapter (p.126). The calculated band gap is of 4.7 eV (this underestimation is due to the approximations used for the calculation), in agreement with [31].



---

Fig. 1.5 - Band structure for a single sheet of boron nitride.

---





## Chapter 2

### Methods

In this chapter, the different formalisms used to investigate the electronic and transport properties of graphene- and BN-based nano-systems will be introduced and described in close connection with their implementation in various simulation codes. The first part will focus on density functional theory (DFT) and its implementation in the SIESTA [33] code. The majority of the results presented in this manuscript are obtained within the framework of DFT, using SIESTA [33] most of the time, but sometimes also ABINIT [34,35]. Afterwards, this chapter will present the Kubo-Greenwood formalism (KG) for the study of transport in graphene using the dynamic evolution of a wave packet that spreads into the nanostructure. The Landauer-Büttiker formalism will be introduced as well. It allows the calculation of the conductance of a sample between two contacts, similar to the experimental setup. The end of the chapter will introduce the Tersoff-Hamann theory for simulating scanning tunneling microscopy (STM) images, one of the most frequently used experimental tools for investigation of the structure of graphene at

## 2. METHODS

---

the atomic level.

### 2.1 Density functional theory

Before going through the main ideas of density functional theory, a commonly-used approximation will first be introduced : the Born-Oppenheimer approximation.

#### **Born-Oppenheimer approximation**

The nuclei being much heavier than the electrons, one can consider the electrons to react instantaneously to any movement of the nuclei. This simple idea is the so-called Born-Oppenheimer approximation [36]. Although simple, this approximation has powerful consequences on the resolution of the many-body Schrödinger equation :

$$H\Psi = E\Psi, \quad (2.1)$$

where  $H$ ,  $E$ , and  $\Psi$  are the Hamiltonian, the total energy and the many-body wave function respectively. This Hamiltonian can be written for a collection of electrons and nuclei as :

$$H = T_e + T_n + V_{e-e} + V_{n-n} + V_{e-n}, \quad (2.2)$$

where  $T_{e,n}$  corresponds to the kinetic energy operator for electrons and nuclei respectively, and where  $V_{e-e}$ ,  $V_{n-n}$ , and  $V_{e-n}$  corresponds to the interaction term between electrons, between nuclei, and between elec-

trons and nuclei respectively. Their expressions are :

$$T_e = \sum_{l=1}^{N_e} \frac{-\hbar^2}{2m} \nabla_{\mathbf{r}_l}^2, \quad (2.3)$$

$$T_n = \sum_{\lambda=1}^{N_n} \frac{-\hbar^2}{2M_\lambda} \nabla_{\mathbf{R}_\lambda}^2, \quad (2.4)$$

$$V_{e-e} = \sum_{1 \leq l \leq m \leq N_e} \frac{e^2}{|\mathbf{r}_l - \mathbf{r}_m|}, \quad (2.5)$$

$$V_{n-n} = \sum_{1 \leq \lambda \leq \mu \leq N_n} \frac{e^2 Z_\lambda Z_\mu}{|\mathbf{R}_\lambda - \mathbf{R}_\mu|}, \text{ and} \quad (2.6)$$

$$V_{e-n} = - \sum_{l, \lambda=1}^{N_e, N_n} \frac{e^2 Z_\lambda}{|\mathbf{r}_l - \mathbf{R}_\lambda|}, \quad (2.7)$$

with  $Z_\lambda$  the charge of nucleus  $\lambda$  (as a multiple of the electronic charge  $e$ ),  $m$  and  $M_\lambda$  the mass of an electron and of nucleus  $\lambda$  respectively. The Born-Oppenheimer approximation splits this Hamiltonian in two terms : the first one being the kinetic energy operator for the nuclei, the second one including the other terms.

$$H = T_n(\nabla_{\mathbf{R}}) + H_0(\mathbf{r}, \nabla_{\mathbf{r}}, \mathbf{R}) \quad (2.8)$$

$$H_0(\mathbf{r}, \nabla_{\mathbf{r}}, \mathbf{R}) = T_e + V_{e-e} + V_{n-n} + V_{e-n} \quad (2.9)$$

The nuclei coordinates  $\mathbf{R}$  can be treated as parameters in the Hamiltonian  $H_0$ . Furthermore, the eigenfunctions of this Hamiltonian are also eigenfunctions of the Hamiltonian without the interaction term between nuclei  $V_{n-n}$  (which depends only on  $\mathbf{R}$ ). The problem of solving the initial Schrödinger equation (2.1) becomes slightly easier : one has to solve the Schrödinger equation for  $N_e$  electrons in a potential created by a fixed set of positions for the nuclei. Once this is done, the nu-

## 2. METHODS

---

clei positions can be changed and the electronic problem can be solved again.

### **Hohenberg, Kohn, and Sham**

Density functional theory is an *ab initio* theory based on quantum mechanics and electromagnetism. Its goal consists in finding the solution to the Schrödinger equation for an ensemble of electrons and nuclei by resolving a system of one-body Schrödinger equations. The *ab initio* (also called “first principles”) character lies in the fact that the only input needed is the initial geometry. These methods differ therefore from other empirical or semi-empirical theories. The many-body Schrödinger equation (eq. 2.1) is impossible to solve for any real system, except very simple ones like the hydrogen or helium atom. The two main issues are the heavy many-body wave function, and the complexity of the Hamiltonian which usually includes many-body interaction terms. To tackle these problems Hohenberg, Kohn, and Sham came up with DFT. Two main ideas are at the heart of the theory :

- Hohenberg and Kohn [37] demonstrated that the total energy can be written as a unique functional of the electronic density (hence the name of the theory), and
- Kohn and Sham [38] showed how the interacting problem could be recast in an equivalent non-interacting problem, involving a set of self-consistent equations.

## From an interacting to a non-interacting problem

To solve the Schrödinger equation for the total system requires (after using the Born-Oppenheimer approximation) to solve the following electronic Hamiltonian :

$$H_e = \sum_{l=1}^{N_e} \left( -\frac{\hbar^2}{2m} \nabla_{\mathbf{r}_l}^2 - \sum_{\lambda=1}^{N_n} \frac{e^2 Z_\lambda}{|\mathbf{r}_l - \mathbf{R}_\lambda|} \right) + \sum_{1 \leq l \leq m \leq N_e} \frac{e^2}{|\mathbf{r}_l - \mathbf{r}_m|}. \quad (2.10)$$

Hohenberg and Kohn [37] have shown that two Hamiltonians of the form :

$$H_v = T_e + V_{e-e} + \sum_{l=1}^{N_e} v(\mathbf{r}_l), \quad (2.11)$$

differing only by the external potential  $v(\mathbf{r}_l)$  which is a local potential, correspond to different electronic densities  $n(\mathbf{r})$ . The knowledge of the electronic density leads to the knowledge of the external potential. The energy corresponding to the previous Hamiltonian can be expressed as the functional :

$$E_v[n] = \int v(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + F[n], \text{ with} \quad (2.12)$$

$$F[n] = \langle \phi | T_e + V_{e-e} | \phi \rangle, \quad (2.13)$$

with two conditions on the wave function  $\phi$ .

1. First the wave functions have to generate the right density that in turn integrates to the right number of total electrons in the system :

$$\int \phi^*(\mathbf{r}_1, \dots, \mathbf{r}_{N_e}) \phi(\mathbf{r}_1, \dots, \mathbf{r}_{N_e}) d\mathbf{r}_1 \dots d\mathbf{r}_{N_e} = \int n(\mathbf{r}) d\mathbf{r} = N_e.$$

2. Second, this set of wave functions has to be the one that minimizes :

$$\langle \psi | T_e + V_{e-e} | \psi \rangle.$$

## 2. METHODS

---

Hohenberg and Kohn have also proved this functional  $F[n]$  to be minimum for the exact electronic density. If one finds a way to compute  $F[n]$  for a set of wave functions, this latest result gives a convenient manner to know if we are getting closer to the ground state wave functions. Although  $F[n]$  has a defined expression, its value is difficult to compute. One more step is needed in order to make any use from it. The answer to this problem is given by Kohn and Sham [38]. The idea is to avoid the difficulty of dealing with  $F[n]$  and to subtract some contributions from it for which the analytical expressions are known.

$$F[n] - T_{e,0}[n] - \int \frac{e^2}{2} \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r} = E_{xc}[n] \quad (2.14)$$

This last equation introduces three new terms :  $T_{e,0}[n]$  follows the same definition as  $F[n]$  but with the interaction term  $V_{e-e}$  set equal to zero (thus corresponding to the kinetic energy for non-interacting electrons) ;  $\int \frac{e^2}{2} \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}$  is the Hartree energy ; and  $E_{xc}$  is the so-called exchange-correlation energy. The expression of  $F[n]$  contains two terms for which we know an analytical expression :  $T_{e,0}$  and the Hartree energy. The unknown part of  $F[n]$  reduces therefore to  $E_{xc}$ . The trick introduced by Kohn and Sham [38] is to notice that the minimization problem of interacting electrons in an external potential  $v(\mathbf{r})$  requires the same conditions as the problem of non-interacting electrons in an external potential  $v_{KS}(\mathbf{r})$ . The Kohn-Sham potential  $v_{KS}(\mathbf{r})$  has the following expression :

$$v_{KS}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{en(\mathbf{r})}{|\mathbf{r} - \mathbf{r}_1|} d\mathbf{r}_1 + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}, \quad (2.15)$$

with the second term being called the Hartree potential  $v_H(\mathbf{r})$  and the last one the exchange-correlation potential  $v_{xc}(\mathbf{r})$ . If an expression for  $E_{xc}[n]$  is available, the solution to the initial interacting problem can be

found by solving a non-interacting system in a self-consistent manner. Indeed, the solution is known for the Schrödinger equation for non-interacting electrons in a potential  $v_{\text{KS}}(\mathbf{r})$  :

$$\left[ \frac{-\hbar^2}{2m} \nabla^2 + v_{\text{KS}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i. \quad (2.16)$$

In this equation  $\phi_i$  are one-electron wave functions, called Kohn-Sham orbitals. The many-electron solution is obtained by building a Slater determinant based on these Kohn-Sham orbitals. Once this solution is known, one can calculate the electronic density by using :

$$n(\mathbf{r}) = \sum_{i=1}^{N_e} \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}). \quad (2.17)$$

With the newly calculated electron density, we can update the value of  $v_{\text{KS}}(\mathbf{r})$  using eq. 2.15. The last three equations form the self-consistent cycle one has to solve to find the solution of our initial problem. Ideally, it should be possible to reach a point where the values for all the quantities will not change between successive cycles. In practice, a tolerance on some quantity is imposed below which we consider the convergence to be reached.

## Approximation for the exchange-correlation energy

The exchange-correlation energy has the form :

$$E_{\text{xc}}[n] = \int n(\mathbf{r}) \varepsilon_{\text{xc}}(\mathbf{r}, [n]) d\mathbf{r}, \quad (2.18)$$

where  $\varepsilon_{\text{xc}}(\mathbf{r}, n)$  is the local exchange-correlation energy per particle. The first approximation to  $\varepsilon_{\text{xc}}(\mathbf{r}, n)$  that comes to mind is the local density approximation (LDA). The expression for  $\varepsilon_{\text{xc}}(\mathbf{r}, n)$  is :

$$\varepsilon_{\text{xc}}^{\text{LDA}}(\mathbf{r}, [n]) = \varepsilon_{\text{xc}}^{\text{homogenous}}[n(\mathbf{r})], \quad (2.19)$$

## 2. METHODS

---

where  $\epsilon_{xc}^{\text{homogenous}}[n(\mathbf{r})]$  is the exchange-correlation energy per particle for a homogenous electron gas having the same electronic density as the original system. It depends therefore only on the local coordinates, hence the name of the approximation. When using LDA in calculations, the exchange and correlation part are usually splitted. The exchange part is known analytically and the correlation part is obtained by different parametrizations based on accurate calculations (Monte-Carlo simulations). When not specified, the LDA functional used throughout this thesis is the Ceperley-Alder flavor [39]. A way to improve the approximation would be to include gradients of the electronic density. This gives rise to the generalized gradient approximation (GGA) :

$$E_{xc}^{\text{GGA}}[n] = \int n(\mathbf{r}) \epsilon_{xc}^{\text{GGA}}(\mathbf{r}, [n(\mathbf{r})], \nabla n(\mathbf{r})) d\mathbf{r}. \quad (2.20)$$

As for LDA, GGA is parametrized in different ways. More complex approximations exist. For example, if one wants to include van der Waals interactions, the exchange-correlation energy is written as :

$$E_{xc}^{\text{VDW-DF}}[n] = E_x^{\text{GGA}}[n] + E_c^{\text{l}}[n] + E_c^{\text{nl}}[n]. \quad (2.21)$$

The superscripts l, and nl stand for *local* and *non-local* respectively. It has to be noted that only the correlation part has to be modified in order to include van der Waals interactions. These contribute to an additional non-local part in the correlation energy functional. Usually LDA and GGA are formulated in such a way that some errors compensate in the exchange and correlation part of the exchange-correlation energy. In the case of van der Waals functionals, since only the exchange is GGA, the functional chosen for this part is as close as possible to exact exchange. The calculations performed in this thesis use the vdW-DF2



functional [40]. In this case, PW86 [41] is chosen for exchange because it minimizes the bonding effect of the exchange part compared to other common functionals such as PW91 [42] or revPBE [43] which is used in an other vdW functional proposed by Dion, *et al.* [44] (vdW-DF). However, some bonding persists at longer distances, resulting in slightly larger bond lengths. The general expression for the non-local part of the correlation energy ( $E_c^{\text{nl}}[n]$ ) is written as :

$$E_c^{\text{nl}}[n] = \int d\mathbf{r} \int d\mathbf{r}' n(\mathbf{r}) \phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}'). \quad (2.22)$$

In this last equation,  $\phi(\mathbf{r}, \mathbf{r}')$  is a function of  $|\mathbf{r} - \mathbf{r}'|$  and of the electronic density at  $\mathbf{r}$  and  $\mathbf{r}'$ . More details on the calculation of  $E_c^{\text{nl}}[n]$  can be found in [40] and [44].

## Pseudopotentials

So far, we are able to solve the problem of many electrons around fixed nuclei by using the Kohn-Sham equations and by specifying an expression for the exchange-correlation functional. To simplify the problem even further, one usually uses the pseudopotential approximation. Instead of including all the electrons in the problem, we consider that only some electrons will actually be far enough from their nucleus to interact with other electrons and with ions. The other electrons are considered to be close to the nucleus, too close to have any influence on the properties of the system composed of many atoms. They define the core region. The pseudopotential approach uses this idea and replaces the potential of the nucleus and of the core region by a pseudopotential which mimics the behavior of the potential on the valence electrons. In this case, the valence electrons are the electrons which are included

## 2. METHODS

---

in the calculation and which are not part of the core region. They are the ones that are explicitly taken into account. The other electrons which are included in the pseudopotential (the ones from the core region) are called core electrons. Pseudopotentials are largely used and many ways to implement them are available. To generate a new pseudopotential, one usually computes the properties for the isolated atom and compares them with all-electron calculations. Therefore, a choice has to be made regarding the exchange-correlation functional we want to use. A given pseudopotential is used only in calculations with a given exchange-correlation functional : the one that was used for its generation. Different flavors of pseudopotential exist. The most common, and the one used throughout this work is the norm-conserving one. The idea behind it is that in order for the real wave function and pseudo-wave-function to be equal outside the core region, the integral of the squared wave functions (real and pseudo) inside the core region must be equal. This is equal to saying that the charge inside the core region must be identical with the pseudopotential and with the true atomic potential. The most common scheme to determine the pseudopotential is given by Troullier and Martins [45]. Their method involves the optimization of a polynomial of order six in  $r^2$  in the determination of the wave function. Seven constants are determined by fulfilling seven conditions. The first one is the norm conservation of the wave function. The continuity of the pseudo-wave-function and up to its fourth derivative are five more conditions. The last condition to satisfy is the zero curvature of the screened pseudopotential at the origin.

## Simulation of solids

In order to deal with periodic solids, which are by definition three-dimensional and infinite, one has to find a way to deal with the infinite number of electrons and ions. The way to achieve this is by exploiting the periodic character of the problem. The potential corresponding to a periodic solid fulfills the following relation :  $v(\mathbf{r} + \mathbf{R}_i) = v(\mathbf{r})$  where  $\mathbf{R}_i$  is a linear combination of the vectors  $\mathbf{R}_1$ ,  $\mathbf{R}_2$ , and  $\mathbf{R}_3$  which are the primitive vectors of the the periodic lattice :  $\mathbf{R}_i = n_1\mathbf{R}_1 + n_2\mathbf{R}_2 + n_3\mathbf{R}_3$ . Parallel to the real-space lattice, we also have the reciprocal lattice. It has primitive vectors  $\mathbf{G}_{\{1,2,3\}}$  defined as :

$$\exp(i\mathbf{R}_{\{1,2,3\}} \cdot \mathbf{G}_{\{1,2,3\}}) = 1. \quad (2.23)$$

Bloch's theorem expresses the wave function in a periodic potential as the product of a phase and a periodic function :

$$\psi_{\mathbf{k}}(\mathbf{r}) = N \exp(i\mathbf{k} \cdot \mathbf{r}) u_{\mathbf{k}}(\mathbf{r}). \quad (2.24)$$

$N$  is a normalization constant and the periodic function  $u_{\mathbf{k}}(\mathbf{r})$  satisfies the same relation as the potential  $u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}_i) = u_{\mathbf{k}}(\mathbf{r})$ . When solving the Kohn-Sham equations, the eigenfunctions that we really calculate are these periodic functions  $u_{\mathbf{k}}(\mathbf{r})$ . At the end, solving the Kohn-Sham equations in a three-dimensional periodic solid gives us access to the wave functions up to a phase factor. However, one can find the expression of  $\psi_{\mathbf{k}}(\mathbf{r})$  by the knowledge of the wave vector  $\mathbf{k}$  and using eq. 2.24. To end this section, it is important to stress the consequences of having a code that simulates infinite periodic systems. When studying ideal materials with no defects, everything works well. When dealing with defects however, one has to take great care to take sufficiently large

## 2. METHODS

---

cells to avoid interaction between defect images in neighboring cells. Depending on the defects and on the properties we are interested in, this might lead to substantially bigger cells.

### **Smearing**

The electrons in a metal obey the Fermi-Dirac distribution. At zero temperature, the transition between occupied and empty states is infinitely steep. Integrals including the Fermi-Dirac function exhibit therefore bad convergence properties. What one does in general to avoid this problem is to include a non-zero temperature for the electrons, thus smoothening out the Fermi-Dirac function. It has to be noted that this is only a numerical trick. In no ways does it correspond to a simulation of the system at a non-zero temperature. To achieve this, one needs to include phonons in the problem, which would increase considerably the complexity and time required for the calculations.

### **An implementation of DFT : the SIESTA method**

Many implementations of DFT exist. They differ by their accuracy, speed, completeness, memory usage, parallelization, price,... As will be developed hereafter, an important element of the implementation is the basis set : the functions we decide to represent the electronic wave functions with. It has a dramatic influence on the speed, the accuracy and the memory requirements to run the code. Some codes have more advanced features, depending on the community developing it and on the ones using it. One has to measure the pros and cons of each code when choosing one. A last important fact that must be considered is the

price. Indeed, some codes are available for free while others require to buy a licence. The majority of the results obtained in this work has been obtained using the SIESTA [33] code which will be introduced briefly in the following section.

### The basis set

At the heart of each code lies the basis set used to represent the electronic wave functions. This might be the choice that constrains the most the development of the code. SIESTA uses linear combinations of atomic orbitals. They are defined to be zero beyond a certain radius, being therefore strictly localized. Inside this radius a basis function has the following form :

$$\phi_{\lambda lmn}(\mathbf{r}) = \phi_{\lambda ln}(r_\lambda) Y_{lm}(\hat{\mathbf{r}}_\lambda), \quad (2.25)$$

where  $\lambda$  refers to an atom,  $\mathbf{r}_\lambda = \mathbf{r} - \mathbf{R}_\lambda$ ,  $r_\lambda = |\mathbf{r}_\lambda|$ ,  $\hat{\mathbf{r}}_\lambda = \mathbf{r}_\lambda / r_\lambda$ ,  $l$  and  $m$  label the angular momentum of the electronic wave function,  $\phi_{\lambda ln}(r_\lambda)$  is a radial function, and  $Y_{lm}(\hat{\mathbf{r}}_\lambda)$  is a spherical harmonic. The remaining index  $n$  shows that some wave functions can have the same angular part, but differ in their radial part. Basis sets that include more than one radial function per angular momentum are called “multiple- $\zeta$ ”.

The first- $\zeta$  radial orbital for one species is obtained by solving the Schrödinger equation in a spherical box for electrons experiencing a pseudopotential corresponding to this species  $v_l(r)$  (dropping the index  $n$ ) :

$$\left( -\frac{1}{2r} \frac{d^2}{dr^2} r + \frac{l(l+1)}{2r^2} + v_{\lambda l}(r) \right) \phi_{\lambda l}(r) = (\epsilon_{\lambda l} + \delta\epsilon_l) \phi_{\lambda l}(r). \quad (2.26)$$

The term  $\delta\epsilon_l$  is the energy gain due to confinement to a spherical box of radius  $r_l^c$  ( $\phi_l(r) = 0$  for  $r \geq r_l^c$ ). By tuning this parameter we actually

## 2. METHODS

---

change the extension of the basis orbitals. In order to get a well-build basis set,  $\delta\epsilon$  is usually the same for the whole basis set generation. Once the first  $\zeta$  has been found this way, the second  $\zeta$  is calculated to fulfill the following equation :

$$\phi_{\lambda l}^{2\zeta}(r) = \begin{cases} r^l(a_l - b_l r^2) & \text{if } r < r_l^s \\ \phi_{\lambda l}^{1\zeta} & \text{if } r \geq r_l^s \end{cases} \quad (2.27)$$

where  $a_l$  and  $b_l$  are fitted to match both the value and the slope at radius  $r_l^s$ . These second  $\zeta$  orbitals have the same tail as the first  $\zeta$  orbitals beyond radius  $r_l^s$  and are smoother before. The radius  $r_l^s$  is determined by fixing the ratio of the norm of the second  $\zeta$  orbital before and beyond this radius (default value is set to 15%). In order to increase the completeness of the basis set, it is common to include polarization orbitals :

$$\phi_{\lambda, l+1, m}(\mathbf{r}) = N\phi_{\lambda, l+1}(r)Y_{l+1, m}(\hat{\mathbf{r}}), \quad (2.28)$$

where  $l$  is the maximum angular momentum. Moreover,  $\phi_{\lambda, l+1}(r)$  obeys the equation :

$$\left( -\frac{1}{2r} \frac{d^2}{dr^2} r + \frac{(l+1)(l+2)}{2r^2} + v_{\lambda l}(r) - E_l \right) \phi_{\lambda, l+1}(r) = -r\phi_{\lambda l}(r), \quad (2.29)$$

where  $N$  is a normalization constant. The previous scheme is a way to define a basis set based on a few parameters. The main part of this work uses DZP basis sets, that is a double- $\zeta$  basis set plus a polarization orbital. However, when dealing with van der Waals functionals, the basis set was specified explicitly in the input after going through a concomitant optimization process for both the basis set and the van der Waals pseudopotential. This optimization was done with a simplex algorithm method included to the SIESTA package.

The basis set used in SIESTA being only combinations of atomic orbitals does not form a complete basis set. Therefore, there is no way to increase systematically the precision of a calculation. However, the use of a multiple  $\zeta$  basis set increases the completeness of the basis set and consequently the precision of the calculation and its duration. A consequence of the incompleteness is the need to check the results obtained using SIESTA with a plane-wave code (as ABINIT [34, 35] for example), for which the precision of the calculation can be increased in a systematic way. When possible, calculations are checked using the ABINIT code in order to validate the basis set of the SIESTA simulation. Usually, this verification is done on the simplest system. The basis set is assumed to work well for more complex systems studied afterwards exclusively with SIESTA.

### The electronic Hamiltonian

The one-electron Kohn-Sham Hamiltonian from eq. 2.16 is generally rewritten, using pseudopotentials, as :

$$H = T_e + \sum_{\lambda} v_{\lambda}^{\text{local}}(\mathbf{r}) + \sum_{\lambda} v_{\lambda}^{\text{KB}} + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}). \quad (2.30)$$

In this formulation, the pseudopotential has been split in two parts : one local  $v_{\lambda}^{\text{local}}(\mathbf{r})$ , and one non-local  $v_{\lambda}^{\text{KB}}$ . The pseudopotential is semilocal meaning that different radial potentials are calculated for different angular momenta. The idea from Kleinman and Bylander (KB) [46, 47] is to express this semilocal part as a local and a non-local part :

$$v_{\lambda}(\mathbf{r}) = v_{\lambda}^{\text{local}}(\mathbf{r}) + v_{\lambda}^{\text{KB}}, \text{ with} \quad (2.31)$$

$$v_{\lambda}^{\text{KB}} = \sum_{l=0}^{l_{\text{KBmax}}} \sum_{m=-l}^l \sum_{n=1}^{N_l^{\text{KB}}} \frac{|\phi_{lmn}^0 \delta v_{\lambda l}\rangle \langle \delta v_{\lambda l} \phi_{lmn}^0|}{\langle \phi_{lmn}^0 | \delta v_{\lambda l} | \phi_{lmn}^0 \rangle}. \quad (2.32)$$

## 2. METHODS

---

Here,  $\delta v_{\lambda l}$  is defined as  $\delta v_{\lambda l}(\mathbf{r}) = v_{\lambda l}(\mathbf{r}) - v_{\lambda}^{\text{local}}(\mathbf{r})$ , and  $\phi_{lmn}^0$  are the wave functions of the atom having the pseudopotential as nucleus potential. There is some arbitrariness in the choice of  $v_{\lambda}^{\text{local}}$ . It is chosen in order to ease calculations and convergence properties.

One final modification to the last Hamiltonian will bring us to the Hamiltonian that is effectively used in SIESTA. To remove the long range interaction of  $v_{\lambda}^{\text{local}}(\mathbf{r})$  we define  $v_{\lambda}^{\text{NA}}$  the screened neutral-atom potential as  $v_{\lambda}^{\text{NA}}(\mathbf{r}) = v_{\lambda}^{\text{local}}(\mathbf{r}) + v_{\lambda}^{\text{atom}}(\mathbf{r})$ . The potential  $v_{\lambda}^{\text{atom}}$  is created by a density  $\rho_{\lambda}^{\text{atom}}$  which is the density obtained by populating the basis functions of the atom with its corresponding valence orbitals. Finally, by defining  $\delta v_{\text{H}}(\mathbf{r})$  as the electrostatic potential generated by  $\delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \sum_{\lambda} \rho_{\lambda}(\mathbf{r})$ , the Hamiltonian looks like :

$$H = T_{\text{e}} + \sum_{\lambda} v_{\lambda}^{\text{KB}} + \sum_{\lambda} v_{\lambda}^{\text{NA}}(\mathbf{r}) + \delta v_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}). \quad (2.33)$$

The two first terms of this Hamiltonian are computed in reciprocal space, the other terms are calculated on a three-dimensional real-space grid.

This ends the part on density functional theory and how it is implemented in SIESTA. The main idea have been presented, trying to stress the advantages, disadvantages and limits of this approach. To get more into the details refer to the references given in this section.

The DFT framework gives access to ground state properties only. Therefore, one relies on other formalisms to investigate the electronic transport properties. The two next sections concern particularly the Kubo-Greenwood, Landauer-Büttiker, and Green's functions formalisms. These theories have different points of view regarding electronic transport and allow the calculation of different properties. The Kubo-Greenwood will be detailed first.



## 2.2 Kubo-Greenwood formalism

The Kubo-Greenwood formalism is a theory to investigate quantum transport in nanostructures that gives access to both semiclassical and quantum properties, including scattering and interferences [48–50]. It is based on linear response theory, for independent electrons. The main idea is that the analysis of the dynamics of a wave packet, at a given energy  $E$ , gives access to many transport properties. The quantity that is used to monitor the different transport regimes is the time-evolution of the diffusivity  $D(E, t)$ . It is defined as a very simple function of the quadratic spreading ( $\Delta R^2$ ) of the wave packet as :

$$D(E, t) = \frac{\Delta R^2(E, t)}{t} \quad (2.34)$$

$$\Delta R^2 = \Delta X^2 + \Delta Y^2. \quad (2.35)$$

Focus is on two-dimensional systems since this formalism will only be applied to graphene. The quadratic spreading for  $X$  is found with the following equation :

$$\Delta X^2(E, t) = \frac{Tr [\delta(E - \hat{H}) |\hat{X}(t) - \hat{X}(0)|^2]}{Tr [\delta(E - \hat{H})]}, \quad (2.36)$$

The trace  $Tr$  is calculated over the  $p_z$  orbitals basis set<sup>1</sup>. The position operators are expressed in Heisenberg representation :  $\hat{X}(t) = \hat{U}^\dagger(t) \hat{X}(0) \hat{U}(t)$ , where  $\hat{U}(t)$  is the time-evolution operator :

$$\hat{U}(t) = \prod_{n=0}^{N-1} \exp\left(\frac{i\hat{H}\Delta t}{\hbar}\right), \quad (2.37)$$

<sup>1</sup> A  $p_z$  orbital basis set is usually enough to describe graphene's electronic properties, as shown in the previous chapter.

## 2. METHODS

---

with  $\Delta t$  the time step used for the calculation. Moreover,  $\rho(E) : Tr[\delta(E - \hat{H})]/S$  is the total density of states (DOS) per unit surface  $S$ .

The evolution of  $D(E, t)$  determines different transport regimes as seen on Fig. 2.1. The first steps of the calculation correspond to the ballistic regime. Then, after some time, a maximum is reached, and defines the beginning of the diffusive regime. From this point on two cases can arise :

1. There are no quantum interferences and the diffusivity approaches its asymptotic semiclassical limit (i.e. the steady state).
2. There are quantum interferences and localization effects appear, leading to a decrease of the diffusivity.

Depending on the regime we are in, different properties can be calculated. In the ballistic regime for example the velocity of the wave packet  $v(E)$  can be derived from the evolution of  $D(E, t)$  since the diffusivity is proportional to  $v^2(E)t$ . The mean free path  $l_e(E)$  on the other hand is obtained once in the diffusive regime, that is, when the diffusivity has reached its maximum value :  $D_{\max}(E) = 2v(E)l_e(E)$ . The general expression for the conductivity is :

$$\sigma(E_F, T_F) = - \int_{-\infty}^{\infty} \frac{\partial f(E', T_F)}{\partial E'} \sigma^{0K}(E') dE', \quad (2.38)$$

where  $f(E, T_F)$  is the Fermi-Dirac function for a given temperature  $T_F$ ,  $E_F$  is the tunable Fermi level, and  $\sigma^{0K}(E)$  obeys the following equation :

$$\sigma^{0K}(E_F) = \frac{1}{4} e^2 \rho(E_F) \lim_{t \rightarrow +\infty} \frac{\partial}{\partial t} \Delta R^2(E_F, t). \quad (2.39)$$

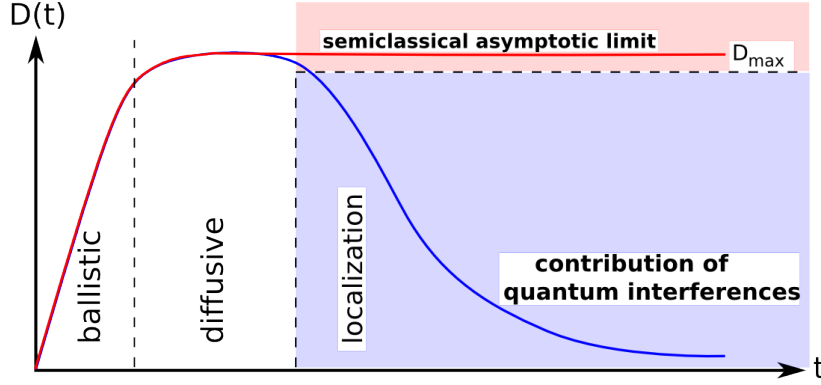


Fig. 2.1 - General evolution of  $D(t)$  during a Kubo-Greenwood calculation. Its evolution defines different transport regimes.

In the semiclassical regime for an infinitely long time, the quadratic spreading depends linearly on time. Therefore, the derivative in eq. 2.39 can be replaced by a division by  $t$ . Recalling that  $D(E, t) = \Delta R^2/t$ , the equation can be rewritten as :

$$\sigma_{\text{sc}}^{0\text{K}}(E) = \frac{1}{4}e^2\rho(E) \lim_{t \rightarrow +\infty} D(E, t), \text{ and} \quad (2.40)$$

$$\sigma_{\text{sc}}^{0\text{K}}(E) = \frac{1}{4}e^2\rho(E)D_{\text{max}}(E). \quad (2.41)$$

In this last equation, the modulated Fermi level  $E_F$  has been replaced by  $E$  in order to avoid confusion with the equilibrium Fermi level. Knowing  $\sigma_{\text{sc}}$  allows to find the mobility, which is of utter importance concerning charge transport. It can be found through :

$$\mu(E, T) = \frac{\sigma_{\text{sc}}(E, T)}{en(E, T)}, \quad (2.42)$$

## 2. METHODS

---

with  $n(E, T)$  the charge carrier density, obtained with the integration of the DOS from the Fermi level to the energy  $E$ . To characterize the localization effects, one relies on the parameter  $\xi(E)$ , the localization length :

$$\xi(E) = \sqrt{2}l_e(E)\exp\left(\frac{\pi h\sigma_{sc}^{OK}(E)}{2e^2}\right) \quad (2.43)$$

The main interest of the Kubo-Greenwood formalism as implemented here is the size of the systems that can be calculated. It is implemented in an order-N real-space approach (details of it can be found in [51]). The order-N scaling allows to study much bigger systems than in the  $N^3$ -scaling DFT used in this thesis. Both the simulated system size and quantities are available to experiment. Therefore, a direct comparison between experiment and theory is possible. In order to include the effect of the contacts, another formalism is needed. The next section introduces the phase-coherent transport formalism, with two different approaches.

### 2.3 Phase-coherent transport formalism

The transport formalism developed in this section focuses on electronic transport that conserves the phase of the electrons. In addition, the contacts are explicitly taken into account. The two theories presented below share the same point of view on the electronic transport. The Landauer-Büttiker formalism explained hereafter focuses on a ballistic conductor. This formalism can be generalized to take scattering effects into account. However the Green's functions formalism includes scattering effects in the conductor as well, but it provides in addition a convenient way to calculate the current flowing through the conductor.

## Landauer-Büttiker formalism

In the Landauer-Büttiker (LB) formalism [52] the current is considered as the result of the injection of electrons at one end and depends on the probability of reaching the other end. The LB formalism is focused on the electronic transport measure as done in an experiment, taking therefore the contacts into account. Moreover, the system of interest is supposed to only experience ballistic quantum transport. The system is viewed as having a number of channels available for transport. The quantification in channels is a consequence of the confinement of the lateral dimensions of the ballistic conductor :

$$E(n, k) = \varepsilon_n + \frac{\hbar^2 k^2}{2m} \quad (2.44)$$

In this equation,  $n$  refers to the channel (or mode). The energy  $\varepsilon_n$  is the contribution to the energy due to the lateral confinement of the wave functions in the conductor. The electrons behave like free electrons along the conductor length direction  $z$ . The wave vector  $k$  is therefore  $k = 2\pi/z$ . As a consequence, no state belonging to the channel  $n$  is available for an energy  $E$  below  $\varepsilon_n$ . The total number of modes available at a given energy is written as :

$$M(E) = \sum_n \theta(E - \varepsilon_n), \quad (2.45)$$

with  $\theta(E)$  the Heaviside function. The current can be calculated by assuming reflectionless contacts<sup>2</sup>. As a consequence, electrons with a positive wave vector  $k$  can only originate from the left lead and electrons with a negative  $k$  can only come from the right lead. The expression for

---

<sup>2</sup>Incoming electrons on the contact area are entirely transmitted.

## 2. METHODS

---

the current is found by using the relation :  $I = env$ , with  $v$  and  $n$  the velocity and density of the charge carriers, respectively. The velocity  $v(n, k)$  of a particle from channel  $n$  is linked to its energy  $E(n, k)$  as :

$$v(n, k) = \frac{1}{\hbar} \frac{\partial E(n, k)}{\partial k}. \quad (2.46)$$

One last ingredient is needed to calculate the current : the density  $n$  of charge carriers. The number of electrons associated with one mode and one  $k$  point is one. Since the length along  $z$  of the ballistic conductor is known and equal to  $L$  the density of charge carriers for one mode and at a certain  $k$  point is :  $n_{n,k} = 1/L$ .

The current has as expression :

$$I^\pm = e \frac{1}{L} \sum_k v^\pm(k) f^\pm(E(k)) = \pm \frac{e}{L} \sum_k \frac{1}{\hbar} \left| \frac{\partial E(k)}{\partial k} \right| f^\pm(E(k)), \quad (2.47)$$

for one single mode. The  $+$  and  $-$  signs stand for left-originating and right-originating states, respectively. The distribution function  $f(E)$  describes the population of the states as a function of the energy. For the rest of this section, it will be taken to be the Fermi-Dirac distribution function<sup>3</sup>. Using the expression for the density of states at one dimension as a function of  $k$  and as a function of  $E$  :

$$D(k)dk = \frac{2L}{2\pi} dk = \frac{2L}{2\pi} \frac{\partial E}{\partial k} dk = \frac{2L}{2\pi} dE = D(E)dE. \quad (2.49)$$

---

<sup>3</sup>As a reminder, the Fermi-Dirac distribution defines the probability of occupation of a given state of energy  $E$  for an electron gas of chemical potential  $\mu$  :

$$f(E) = \frac{1}{e^{(E-\mu)/(k_B T)} - 1} \quad (2.48)$$

The sum in the expression of the current can be changed to an integral :

$$I^\pm = \pm \frac{2e}{h} \int_{\varepsilon}^{\infty} f^\pm(E) dE, \quad (2.50)$$

where  $\varepsilon$  is the energy for a zero wave-vector particle :  $\varepsilon_n$  in eq. 2.44 for the single channel considered here. For  $M(E)$  channels (eq. 2.45), the expression for the current becomes :

$$I^\pm = \pm \frac{2e}{h} \int_{-\infty}^{\infty} f^\pm(E) M(E) dE. \quad (2.51)$$

At zero temperature, the Fermi-Dirac reduces to the Heaviside function. Assuming a constant number of modes on the energy range  $\mu_l$  and  $\mu_r$  (the chemical potential of the left and right lead, respectively), the total current  $I = I^+ + I^-$  is expressed as :

$$I = \frac{2e^2}{h} M \frac{\mu_l - \mu_r}{e} = \frac{2e^2}{h} M \Delta V. \quad (2.52)$$

From this last equation, one derives the expression for the conductance :

$$G = \frac{2e^2}{h} M. \quad (2.53)$$

For only one mode, it simplifies and  $G = 2e^2/h \equiv G_0$ , the quantum of conductance. Since the ballistic conductor lets the electrons flow freely, the resistance  $G_0^{-1} = 12.9 \text{ k}\Omega$  is only originating from the presence of contacts. The picture changes when including scattering effects in the conductor, as will be shown below.

## 2. METHODS

---

### Green's functions in the quantum transport formalism

This section will expose the ingredients involved in the transport calculation as implemented in Transiesta [53]. The complete development can be found in [52, 54–57]. In Transiesta, the transport properties are calculated using the Green's functions. Different kinds of Green's functions exist but only the retarded is used in the following discussion. It is defined as :

$$\mathcal{G}^r(E) = (E + \delta i - H)^{-1}, \quad (2.54)$$

and is the solution to the equation

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

The  $\delta i$  is an infinitesimally small imaginary part, added to ensure the causality. The retarded Green's function can indeed be viewed as the consequent response at any point to an excitation at a particular point in space. The last equation is close to the Schrödinger equation and differ only by the non-zero right-hand side identity matrix  $I$ . The Green's function has an interesting property. The solution to the perturbed Schrödinger equation :

$$H^0 + V - (E + \delta i) |\psi\rangle = 0 \quad (2.56)$$

can be found based on the solution to the unperturbed case

$$H^0 - (E + \delta i) |\psi^0\rangle = 0, \quad (2.57)$$

as well as on the Green's functions based on  $|\psi\rangle$  and  $|\psi^0\rangle$  :

$$\mathcal{G}^r(E) = (E + \delta i - H^0 - V)^{-1} \quad (2.58)$$

$$\mathcal{G}^{r0}(E) = (E + \delta i - H^0)^{-1} \quad (2.59)$$

$$\mathcal{G}^r(E)^{-1} = \mathcal{G}^{r0}(E)^{-1} - V. \quad (2.60)$$



The Lippmann-Schwinger equations give a way to calculate  $|\psi\rangle$  as :

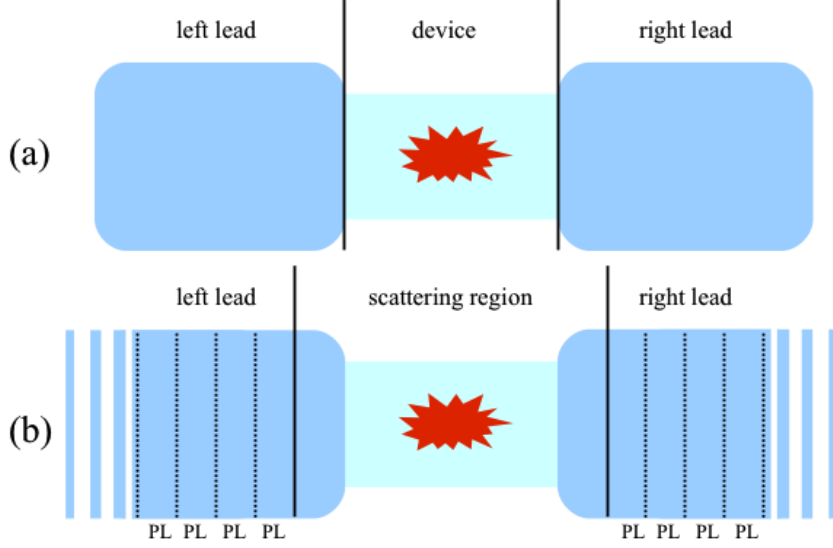
$$|\psi(E)\rangle = |\psi^0(E)\rangle + \mathcal{G}^r(E)V|\psi^0(E)\rangle. \quad (2.61)$$

When doing a transport measurement, one usually thinks of two leads connected by a device for which one wants to measure the properties (Fig. 2.2(a)). However, in order to solve the problem in Transiesta, the picture has to be changed (Fig. 2.2(b)). Instead, one has a scattering region in the center, composed of the initial device plus some part of the leads. The leads on the other hand are now approximated to be semi-infinite crystalline materials and are composed of an infinite repetition of principal layers (PLs) which form the elementary repetition unit of the leads. The PL are defined in such a way that they only interact with their direct neighbors. In order to have a seamless junction between the leads and the scattering region, the latter has to include enough atoms to recover the properties of the leads at its boundaries. This description of the problem leads to the following Hamiltonian :

$$H = \begin{pmatrix} \ddots & \ddots & \ddots & \ddots & \ddots & \dots \\ \dots & 0 & H_I^\dagger & H_{PL} & H_I & 0 & \dots \\ & \dots & 0 & H_I^\dagger & H_{PL} & H_{LS} & 0 & \dots \\ & & \dots & 0 & H_{SL} & H_S & H_{SR} & 0 & \dots \\ & & & \dots & 0 & H_{RS} & H_{PL} & H_I & 0 & \dots \\ & & & & \dots & 0 & H_I^\dagger & H_{PL} & H_I & 0 & \dots \\ & & & & & \dots & \ddots & \ddots & \ddots & \ddots & \ddots \end{pmatrix}.$$

## 2. METHODS

---




---

Fig. 2.2 - Different points of view of a transport measurement. From an experimental one (a), a device is connected by two leads. For a transport calculation as in Transiesta (b), a central region connects two semi-infinite leads which are themselves composed of principal layers (PLs).

---

The overlap matrix  $S$  shares the same structure as the Hamiltonian. This Hamiltonian contains numerous submatrices.  $H_S$ ,  $H_{SR}$ , and  $H_{LS}$  contain the interaction inside the scattering region, between the scattering region and the right lead, and between the left lead and the scattering region, respectively.  $H_{PL}$  and  $H_I$  contain the interaction inside a principal layer, and the interaction between principal layers, respectively. The Lippmann-Schwinger relation (eq. 2.61) can be used in the case of the transport problem as formulated above. Let  $|\phi_{k_j}\rangle$  be the state vectors for the semi-infinite leads corresponding to a complex  $k_j$  vector. Let  $\mathcal{G}^r(E_{k_j})$  be the retarded Green's function associated with the state

$|\psi_{k_j}\rangle$ , the states corresponding to the system composed of the semi-infinite leads and the scattering region. The Lippmann-Schwinger relations in this case writes :

$$|\psi_{k_j}\rangle = \mathcal{G}^r(E_{k_j})V|\phi_{k_j}\rangle + |\phi_{k_j}\rangle, \quad (2.62)$$

with  $V$  the potential that couples the leads and the central region ( $V = H_{LS} + H_{SL} + H_{SR} + H_{RS}$ ).

The calculation of  $\mathcal{G}^r(E_{k_j})$  involves the Hamiltonian of the full system which is therefore of infinite dimension. However, the Green's function of interest is  $\mathcal{G}_S^r(E)$ , the Green's function for the scattering region. It can be expressed as :

$$\mathcal{G}_S^r(E) = \left( \varepsilon^+ S_S - H_S^{\text{eff}}(E) \right)^{-1}, \quad (2.63)$$

with  $S_S$  the overlap matrix for the scattering region,  $\varepsilon^+ = (E + \delta i)$ , and  $H_S^{\text{eff}}$  defined as :

$$H_S^{\text{eff}}(E) = H_S - \Sigma_L^r(E) - \Sigma_R^r(E), \quad (2.64)$$

where  $\Sigma_L^r(E)$  and  $\Sigma_R^r(E)$  are the (retarded) self-energies and are defined as :

$$\Sigma_L^r(E) = (\varepsilon^+ S_{SL} - H_{SL}) \mathcal{G}_L^{r0} (\varepsilon^+ S_{LS} - H_{LS}) \quad (2.65)$$

$$\Sigma_R^r(E) = (\varepsilon^+ S_{SR} - H_{SR}) \mathcal{G}_R^{r0} (\varepsilon^+ S_{RS} - H_{RS}). \quad (2.66)$$

The self-energies reflect the coupling between the scattering region and the leads. They originate from the truncation of the problem to the scattering region. In these last equations  $\mathcal{G}_{R/L}^{r0} = (\varepsilon^+ S_{R/L} - H_{R/L})^{-1}$  are the Green's function for the isolated leads. The Green's function is no longer needed for the whole system. The calculation of the Green's

## 2. METHODS

---

function for the scattering region is based on an effective Hamiltonian which includes the effect of the coupling through the self-energies. The latter depends on the Green's function of the isolated leads and is of infinite dimension. However, in the calculation of the self-energies, only the part of the principal layers neighbors of the scattering region are needed. Therefore, the problem becomes of finite dimension.

Finally, the current can be calculated using the following equation :

$$I = \frac{e}{h} \int Tr \left[ \Gamma_L \mathcal{G}_S^{r\dagger} \Gamma_R \mathcal{G}_S^r \right] [f(E - \mu_L) - f(E - \mu_R)] dE, \quad (2.67)$$

with  $\Gamma_{R/L} = i \left( \Sigma_{R/L}^r - \Sigma_{R/L}^{r\dagger} \right)$  the broadening. Every element in this equation is known and can be calculated. This equation is similar to eq. 2.51 but takes into account the effect of scattering in the central region. This scheme is the one implemented in Transiesta.

The formalism developed above is also valid for electrons tunneling from one electrode to another. This could be useful to calculate the current flowing from a sample to the tip of a scanning tunneling microscope. However, much simpler approximations allow to simulate STM images, relying only on ground state informations. This theory was developed by Tersoff and Hamann and will be the object of next section.

### 2.4 Tersoff-Hamann formalism

A method of choice in the study of graphene is the scanning tunneling microscope (STM). This technique probes the tunneling current flowing to a tip brought closely enough to the surface of the sample. The voltage of the tip can be varied to modify the current. Tersoff and Hamann [58] have developed a theory that provides expressions for the tunneling cur-

rent, depending on the sample properties, and tip geometry and properties. Bardeen's formalism, a theory of electron tunneling gives the following expression for the tunneling current :

$$I = \frac{2\pi e}{\hbar} \sum_{\mu, \nu} f(E_\mu) [1 - f(E_\nu)] |M_{\mu\nu}|^2 \delta(E_\mu - E_\nu), \quad (2.68)$$

with  $f(E)$  the Fermi-Dirac distribution,  $V$  the applied voltage (positive voltage corresponds to a higher potential at the tip than at the sample),  $\delta(E)$  is the Dirac delta function, and  $M_{\mu\nu}$  is the tunneling matrix between states of the probe ( $\psi_\mu$ ) and states of the surface ( $\psi_\nu$ ). At low voltage and low temperature the expression for the current is :

$$I = \frac{2\pi e^2 V}{\hbar} \sum_{\mu, \nu} |M_{\mu\nu}|^2 \delta(E_\nu - E_F) \delta(E_\mu - E_F), \quad (2.69)$$

where  $E_F$  is the Fermi level with zero voltage applied. This expression can be simplified further on by considering the tip to be ideal. An ideal tip possesses states at any energy. Each electron of the sample will find a corresponding state in the tip and will be able to tunnel into it. The expression for the tunneling therefore depends only on the wave functions of the sample :

$$I \propto \sum_{\nu} |\psi_\nu(\mathbf{r}_{\text{Tip}})|^2 \delta(E_\nu - E_F). \quad (2.70)$$

The current depends on the square amplitudes of the wave functions of the sample at the tip position  $\mathbf{r}_{\text{Tip}}$ . In other words, the tunneling current is directly related to the local density of states (LDOS) at Fermi level. In order to reproduce images between the Fermi level and a given voltage, one simply sums the LDOS between these two energies. Because SIESTA uses localized basis sets, the LDOS is the addition of

## 2. METHODS

---

all the occupied states between the energy window of interest. This operation is straightforward within the SIESTA code. Considering the crude approximations that are made, the representation of isocontours of the LDOS presents a surprisingly good agreement with experimental STM images. STM works in two different modes : constant current and constant height. The latter scans the sample with the tip at a fixed height, leading to a map of the sample with different tunneling currents, while the former uses a feedback loop to modify the height of the tip in order to keep the current constant. Since the tunneling current is exponentially depending on the top-to-sample distance changing the scale of the color scheme used for the isocontours of the LDOS, one can either simulate constant current or constant height images. A linear-scale color scheme gives constant current images and a log-scale color scheme gives constant height images.

In the next chapter, SIESTA is used in combination with the Kubo-Greenwood formalism to study the effect of structural defects and their impact on the mesoscopic transport properties. In Chap. 4, the formalism developed in the present section is used to provide STM images for numerous boron-based defects. A comparison with experimental images is given. Moreover, a study of the energetics of nitrogen clusters is presented. In Chap. 5, SIESTA and Transiesta are utilized to study the combination of boron nitride and graphene in the same sheet. The transport and spin-filtering properties of graphene-boron nitride composites are studied. In Chap. 6, SIESTA is used with the vdW-DF2 van der Waals functional to investigate the effect of the presence of incommensurate stacked boron nitride on graphene.

## Chapter 3

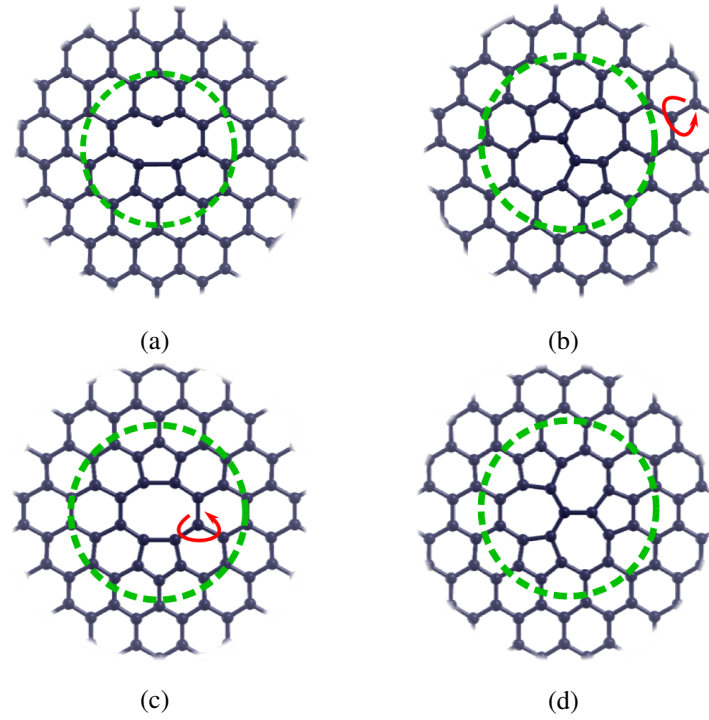
# Topological defects in graphene : from structure to electronic and transport properties

One way to tailor graphene's electronic properties is to modify its local geometry. One usually considers defects that conserve the planar character of graphene, either because we want it to be kept for applications or because they usually are the most stable ones. The basic elementary defects are zero-dimensional. The most obvious to think of is the single vacancy. It is simply a missing carbon atom in the honeycomb lattice. These defects are quite mobile (migration energy  $\sim 1.3$  eV [59]). When two single vacancies come together they form a divacancy. This process lowers the total energy and therefore reduces significantly the mobility of the divacancy compared to a single vacancy. Another common defect in graphene is the Stone-Thrower-Wales (STW) defect. It is obtained by rotating one bond by  $90^\circ$ . The resulting structure is composed of two

### 3. TOPOLOGICAL DEFECTS IN GRAPHENE

---

pentagons and two heptagons. The divacancy reconstruction appears in two different forms. The first one is made of two pentagons and one octagon. It is the result of the relaxation of the lattice in which two neighboring carbon atoms are removed. This form is usually referred to as a 585 divacancy. The second form is obtained by applying a STW transformation to the 585 divacancy. The bond involved in the rotation



---

Fig. 3.1 - Common topological defects in graphene : (a) depicts the single vacancy ; (b) the STW defect (the red arrow indicates which bond is rotated to obtain the STW defect) ; (c) and (d) two types of divacancies, namely the 585 and the  $t5t7$ . The red arrow in (c) depicts which bond has to be rotated to obtain the  $t5t7$  divacancy starting from the 585 divacancy.

---



---

is the bond from the octagon the furthest away from the pentagons. The resulting divacancy is reconstructed in three pentagons and three heptagons, therefore referred to as a  $t5t7$  divacancy. These defects are illustrated in Fig. 3.1. All of them are evidenced experimentally. They are obtained (in carbon nanotubes) by  $\text{Ar}^+$  irradiation [60, 61]. Moreover, transport characterization of defected graphene has already been performed and shows minimum conductivity [62]. As mentioned before, the influence of structural modifications in graphene is larger compared to three-dimensional materials. The aim of the present chapter is to analyze the precise influence of different topological defects on the electronic transport properties of graphene. Looking at larger-size defects, one-dimensional (1D) structural deformations can also be observed in graphene. Some of these lines join different flakes of graphene with different orientations and are therefore called grain boundaries. Others are defects inside one flake with the same geometry on both sides of the defect. Fig. 3.2 shows three of these one-dimensional defects. The first defect is a line for which each unit cell contains two pentagons and two heptagons. It is therefore called a  $l-d5d7$  (the prefix “l-” is used to differentiate the linear defects from the point defects). The formation path is depicted on Fig. 3.2(a). It involves first a divacancy and is followed by a STW transformation. The second defect starts with divacancies. After reconstruction, a shear deformation leading to a displacement of half a cell vector ( $1.23 \text{ \AA}$ ) results in the  $l-585$  defect (following the same convention, it is composed of two pentagons and one octagon). The last one is obtained by starting with a STW transformation and following with a divacancy. The resulting geometry is made of three pentagons and three heptagons per unit cell. It is called a  $l-t5t7$ . Formally, only the second defect is a grain boundary since the left and right side of

### 3. TOPOLOGICAL DEFECTS IN GRAPHENE

---

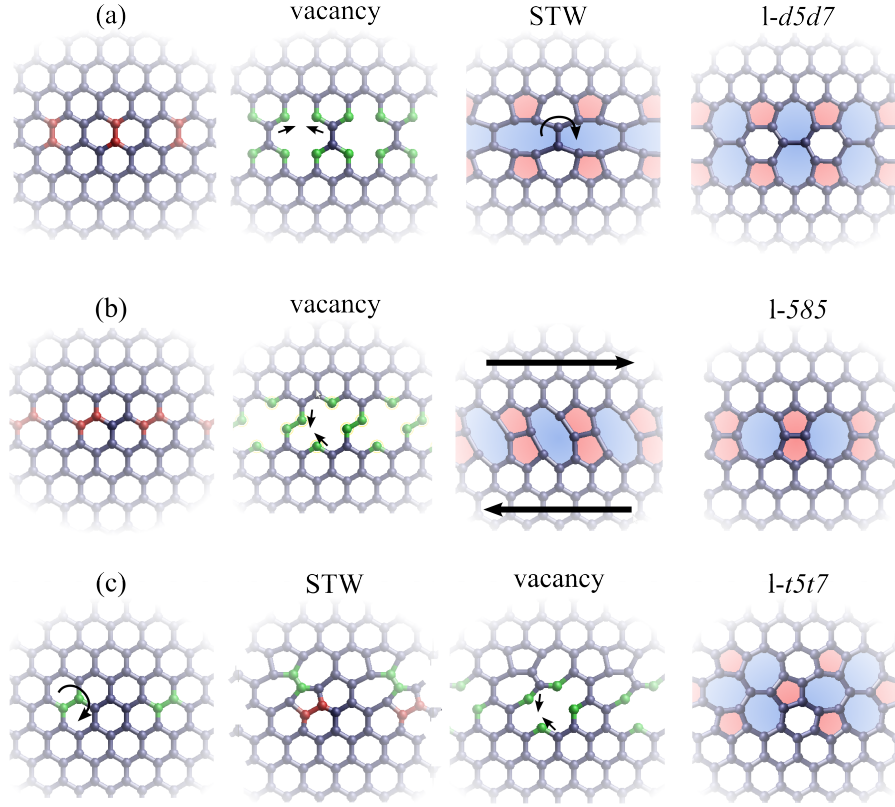


Fig. 3.2 - Formation of different extended lines of defects in graphene through the reconstruction of divacancies. Lines of defects are formed after the removal of carbon dimers (in red), either (a) perpendicular or (b) with a  $30^\circ$  deviation from the zigzag direction. These extended arrays of defects are called (a) 1-*d5d7* (double-5 double-7 structure) and (b) 1-585 (pentagon-octagon-pentagon structure), respectively. Further displacement of one graphene side by  $1/2a$  (black arrow in b) is required to relax the 1-585 grain boundary as observed in [63]. An extended array of defects composed of a series of a three pentagons and three heptagons (1-*t5t7*) is also topologically possible when the divacancy reconstruction occurs along with a STW transformation (c).

---

the defect are shifted. The formation of this defect is actually different from the path depicted here. Carbon atoms can stand on two different sites on a nickel substrate. As demonstrated experimentally [63], two graphene flakes grown on two different sites will merge and reconstruct in the 1-585 grain boundary in order to accommodate the mismatch between the two flakes. The following section will study the electronic properties of the three different linear defects. Scanning tunneling microscopy images are simulated in order to confirm the experimental results of [63], as well as to predict the images corresponding to the three lines of defects in order to allow future comparison with experimental images. The two next sections will investigate the properties of one-dimensional [64] and point defects [65, 66].

### 3.1 One-dimensional defects

The results presented in this section were published in [64]. The three previously introduced linear defects are studied using SIESTA. Their formation energies are compared, STM images are predicted, and their electronic properties are analyzed. A DZP basis set is used to expand the wave functions. Both LSDA and GGA are used for the exchange-correlation functional, along with norm-conserving pseudopotentials. The linear defects are studied in a two-dimensional graphene plane. The supercell is big enough to ensure a distance of approximately 22 Å between neighboring lines of defects. Moreover, 20 Å vacuum is introduced between neighboring graphene planes to avoid interaction between them. The defects are also studied in 33 Å wide hydrogenated zigzag graphene nanoribbons (h-15-zGNR). The defects are more or

less 11 Å away from the edges. The geometry is relaxed to reach forces on each atom lower than 0.005 eV/Å and stresses lower than 0.005 GPa.

#### Formation energies

The formation energy is defined in two different ways. The first definition, which is the most common one, is :

$$E_c(\alpha) = \frac{E_T(\alpha) - N_\alpha E_{\text{gr}}}{\eta_\alpha} \quad (3.1)$$

Here,  $\alpha$  refers to one of the three defects considered.  $E_T$  is the total energy of the system, while  $E_{\text{gr}}$  corresponds to the energy for one carbon atom in perfect graphene.  $N_\alpha$  and  $\eta_\alpha$  are respectively the total number of atoms and the number of atoms involved in the defect.  $E_c$  therefore gives an idea of the energy required to create the defect out of ideal graphene. However, this definition is not the best choice to compare the linear defects since they have different numbers of atoms  $\eta_\alpha$  intervening in their reconstruction. In other words, the unit cell of each defect lacks two carbon atoms but the length of the cells are different. Therefore, the ratio  $N_\alpha/\eta_\alpha$  is different for the three cases. Consequently one usually uses the linear formation energy instead :

$$E'_c(\alpha) = \frac{E_T(\alpha) - N_\alpha E_{\text{gr}}}{d_\alpha} \quad (3.2)$$

with  $d_\alpha$  the length of the unit cell along the defect direction. Since none of either LDA or GGA calculations accurately predict the length of the cell parameters (LDA and GGA under- and overestimates, respectively), both were used. The following table summarizes the formation energies  $E_c$  and  $E'_c$  calculated with both LDA and GGA. The

| $\alpha$       | $E_c^{\text{LDA}}(\text{eV/at})$ | $E_c^{\text{LDA}}(\text{eV/\AA})$ | $E_c^{\text{GGA}}(\text{eV/at})$ | $E_c^{\text{GGA}}(\text{eV/\AA})$ |
|----------------|----------------------------------|-----------------------------------|----------------------------------|-----------------------------------|
| 1- <i>d5d7</i> | 0.264                            | 0.760                             | 0.415                            | 0.145                             |
| 1-585          | 0.258                            | 0.527                             | 0.270                            | 0.133                             |
| 1- <i>t5t7</i> | 0.171                            | 0.512                             | 0.691                            | 0.231                             |

Table 3.1 - Formation energies per atom ( $E_c$ ) and per unit of length ( $E'_c$ ) for the different lines of defects embedded in graphene (as illustrated in Fig. 3.2).

1-585 defect requires to have a mismatch between two graphene flakes. Although it is found to be more stable than the two others for GGA, the growth conditions will either allow its formation (preventing the 1-*d5d7* and 1-*t5t7* from appearing) or block it. The 1-*t5t7* is found to be the most stable when using LDA, a similar result was obtained previously with plane waves and GGA [67]. For a top down approach, the competition between 1-*t5t7* and 1-*d5d7* would very likely be driven by kinetics. Finally, since some point defects lead to out-of-plane deformation [68] it has been checked that the planar configuration of linear defects is indeed maintained.

## STM images

Scanning tunneling microscopy (STM) is a very powerful tool to identify defects in graphene [69]. STM probes the local density of charge and is strongly dependent on the doping of the sample. Moreover, small structural differences can lead to both slight changes and more important ones making therefore the accurate analysis of STM observation very tricky sometimes. Simulated images can be of highest interest in these cases (see p.48 for the Tersoff-Hamann theory for STM images).

### 3. TOPOLOGICAL DEFECTS IN GRAPHENE

---

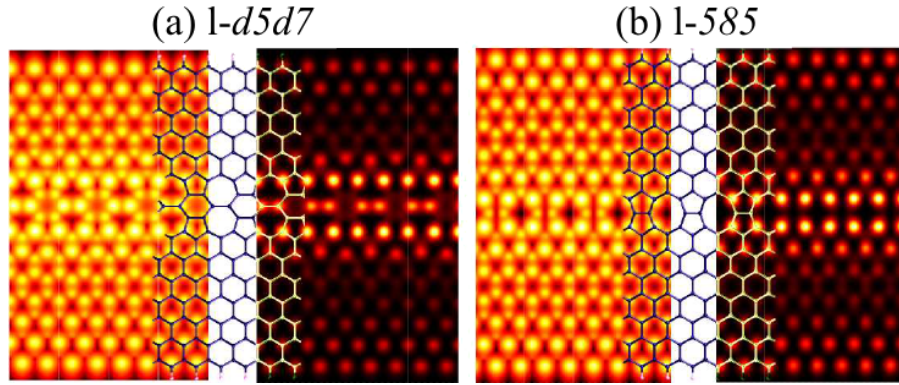


Fig. 3.3 - *Ab initio* STM images at (*left*) constant current and (*right*) constant height for the 1- $d5d7$  (a) and 1-585 (b) extended lines of defect.

---

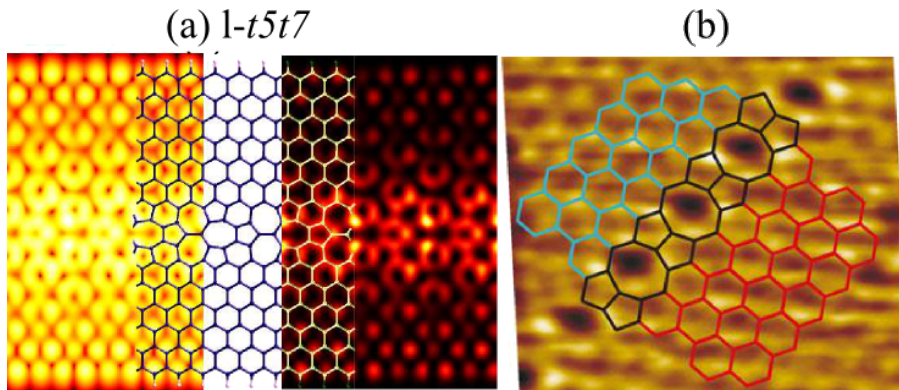


Fig. 3.4 - *Ab initio* STM images at (*left*) constant current and (*right*) constant height for the 1- $t5t7$  extended line of defect (a). Experimental STM image of the same 1- $t5t7$  defect, extracted from [63] (b).

---

Simulation clearly links a known geometry to STM fingerprints and allows specifying the window of energy which we are interested in as well as the doping concentration of the system. Comparison of these images with experimental STM observations makes the identification of the defects possible. The window used to simulate the STM images is between 0.2 and 0.3 eV relative to the Fermi level in order to reproduce an n-type doping substrate. Constant current and constant height images are shown for *l-d5d7*, *l-585*, and *l-t5t7* defects on Figs. 3.3 and 3.4. It has to be noted that the simulated image for the *l-585* defect shows good agreement with the defect in [63] (see Fig. 3.4 (b)), therefore confirming their results.

### **Electronic and quantum conductance properties**

In order to investigate the electronic properties of these defects, they are inserted into zigzag graphene nanoribbons (h-15-zGNR). Perfect h-zGNRs exhibit spin polarization localized at their edges. This polarization is ferromagnetic on each edge, but antiferromagnetic between edges ( $\uparrow\downarrow$ ) [70]. It is at the origin of the band gap opening for small zGNRs. Moreover, another spin polarization exists, consisting of ferromagnetic ordering both on the edges and between the edges ( $\uparrow\uparrow$ ). The energy difference between the two polarization states is found to be 2.9 meV, the  $\uparrow\downarrow$  being the most stable one. However, this difference is below the energy resolution of DFT. After including the lines of defects, the energy difference between the polarization cases will change since the interaction between opposite edges will be more or less screened. These differences are summed up in Tab. 3.2. For two cases (*l-d5d7* and *l-585*), the difference between the polarization states decreases. For

### 3. TOPOLOGICAL DEFECTS IN GRAPHENE

|                                                       | 1- <i>d5d7</i> | 1-585 | 1- <i>t5t7</i> |
|-------------------------------------------------------|----------------|-------|----------------|
| $E_{\uparrow\downarrow} - E_{\uparrow\uparrow}$ (meV) | -0.72          | -1.93 | 5.94           |

Table 3.2 - Energy differences between the  $\uparrow\downarrow$  and  $\uparrow\uparrow$  polarization cases for a h-15-zGNR including a linear defect.

the 1-*t5t7* however, the energy difference changes sign, meaning the  $\uparrow\uparrow$  case becomes more stable than the  $\uparrow\downarrow$ <sup>1</sup>. The electronic band structures are shown on Fig. 3.5. For the antiparallel spin configuration  $\uparrow\downarrow$ , the spin-up and spin-down band structures are identical. Although very small, the  $\uparrow\downarrow$  presents a gap for both the 1-*d5d7* and the 1-585 cases. In contrast, the  $\uparrow\uparrow$  is metallic for these cases. The 1-*t5t7* case, however, is metallic independently of the spin configuration. This case would

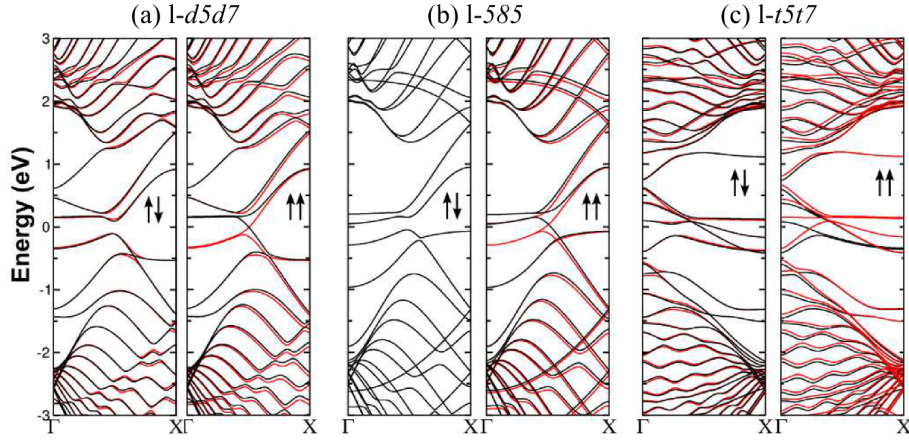
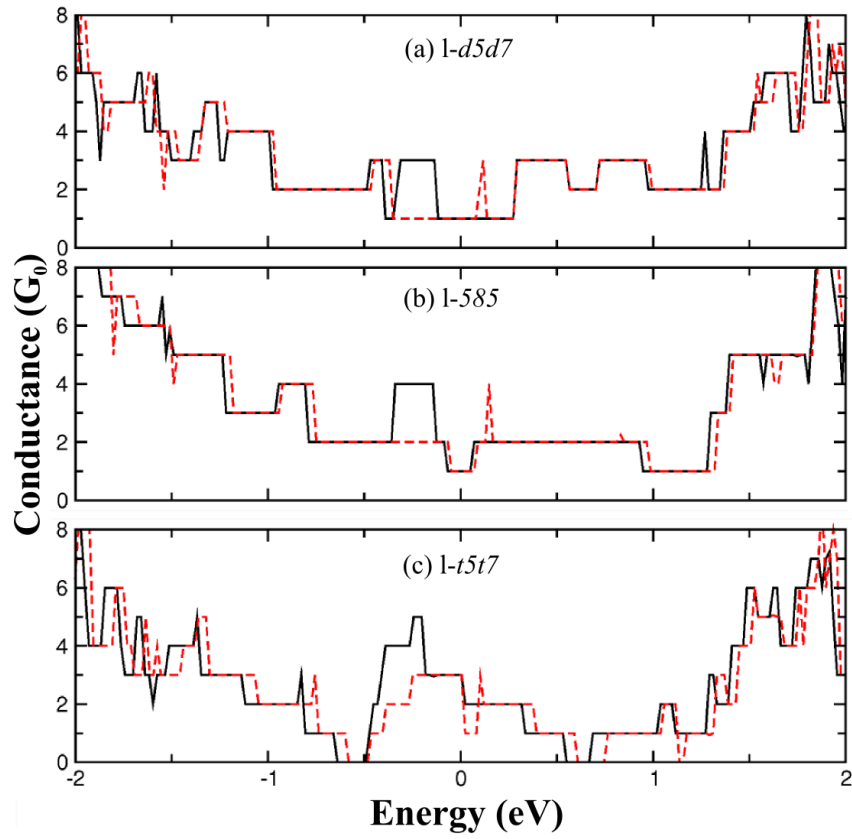


Fig. 3.5 -  $\uparrow\downarrow$  and  $\uparrow\uparrow$  electronic band structures for the 1-*d5d7* (a), 1-585 (b), and 1-*t5t7* (c). Red and black colors are used for the two spin components.

<sup>1</sup>Still, this difference remains below the DFT energy resolution.



therefore be of great interest for applications because it remains metallic whatever its spin polarization is. Using Landauer formalism and surface Green's functions matching method (p.44), one obtain the conductance for the three nanoribbons (Fig. 3.6). It has to be noted that




---

Fig. 3.6 - Spin-resolved conductance for the 1-*d5d7* (a), 1-585 (b), and 1-*t5t7* (c). Only the  $\uparrow\uparrow$  spin polarization case is represented. Red and black colors are used for the two spin components.

---

additional conduction channels have been introduced at the Fermi level in the  $1-t5t7$  case. This result is in agreement with the picture of a localized one-dimensional metallic wire embedded in the graphene ribbon, as seen on the STM images. Achieving this could therefore be of great interest for application in nanoelectronics. This could be done by electron beam irradiation or scanning tunneling lithography for example. These techniques would introduce vacancies which would recombine in divacancies and would lose their mobility, enabling for some tailoring of line of defects.

## 3.2 Zero-dimensional defects

The three point defects presented at the beginning of this chapter (Fig. 3.1), once embedded in a graphene sheet, are studied within a multi-scale approach. A first round of DFT calculations is used to get the relaxed local geometry, band structure and density of states ; and one goes on with a second round of  $O(n)$  Kubo-Greenwood calculations to study the mesoscopic transport properties and density of states using a tight-binding (TB) model. This TB model is fitted on the DFT band structure and afterwards used in the Kubo-Greenwood calculation. SIESTA is used for the DFT part. GGA is chosen along with Troullier-Martins pseudopotentials. A double- $\zeta$  plus polarization orbital basis set is used to represent the electronic wave functions. Due to the periodic approach of SIESTA, a convergence study is done on the size of the unit cell (from  $3 \times 3$  to  $7 \times 7$ ). Fig. 3.7 shows the three relaxed  $7 \times 7$  unit cells used. This size is found to be enough for the potential associated with the defect to get close to zero at the edges of the unit cell. The distortion of the neighborhood of the defects is more or less important. The

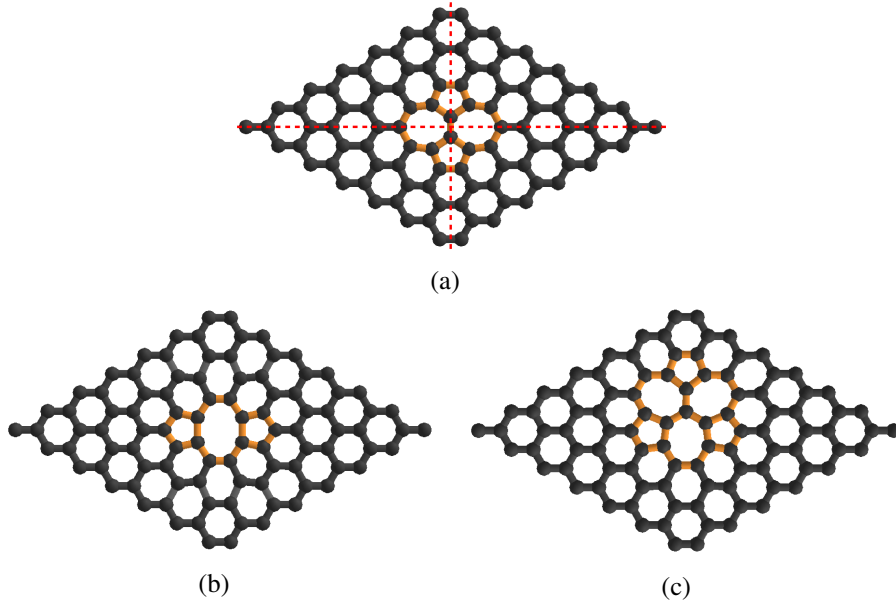


Fig. 3.7 - Converged unit cells used for the DFT simulations of zero-dimensional defects for : (a) the STW defect , (b) the 585 divacancy, and (c) the  $t5t7$  divacancy.

STW defect induce only very light distortions, the  $t5t7$  slightly more important ones, and the 585 significantly bigger ones.

### First principles results - electronic properties

Fig. 3.8(a) shows the path used to plot the electronic band structures. Because of the anisotropic character of the distortion induced by the defects, the unit cell loses its hexagonal symmetry. Therefore, a more complete path is constructed to keep track of the different modifications at different high-symmetry points.

By changing the size of the unit cell, one changes the doping con-

### 3. TOPOLOGICAL DEFECTS IN GRAPHENE

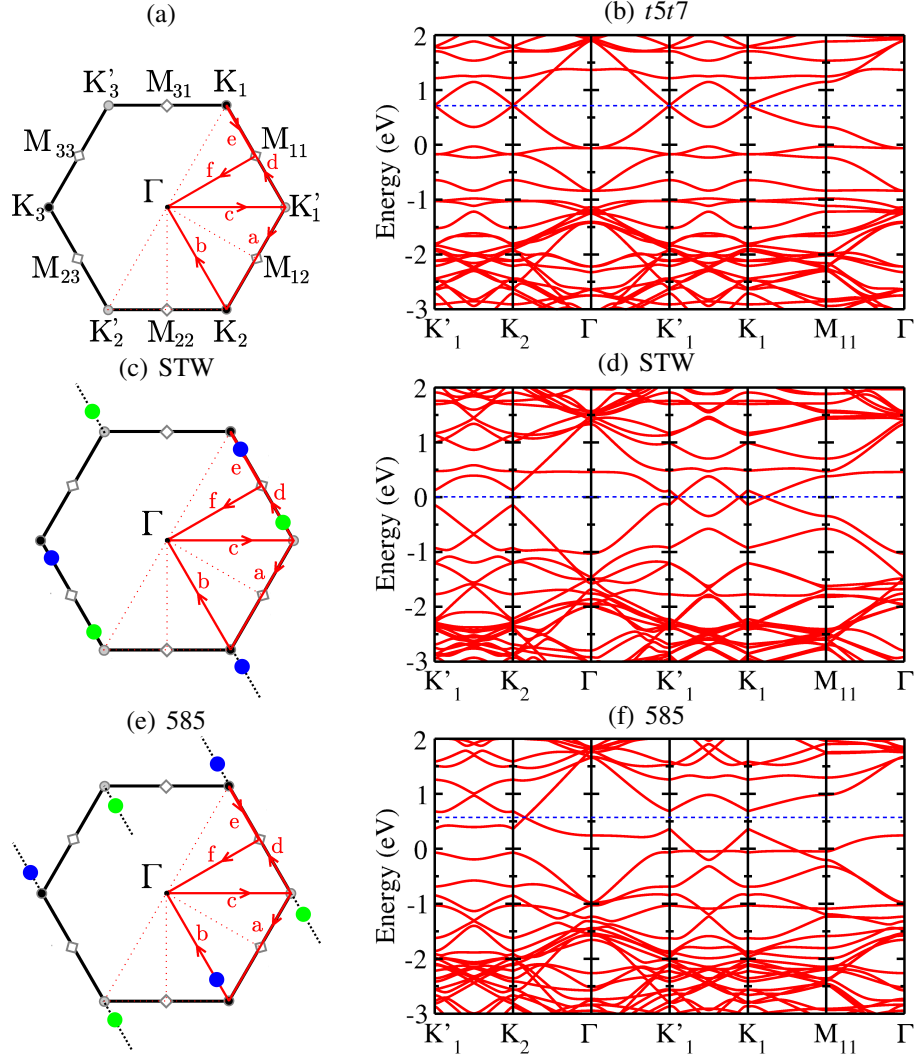


Fig. 3.8 - Electronic band structures computed using the SIESTA package along the high-symmetry lines in the Brillouin zone (a) for  $7 \times 7$  unit cells containing, (b) one  $t5t7$  divacancy, (d) one STW defect, and (f) one 585 divacancy. The Fermi energy is set to zero and the Dirac energy is indicated with a horizontal blue dashed line. (c) and (e) show the new positions of the Dirac points. New K and K' Dirac cones are shifted to the positions of the blue and green dots, respectively.

centration. One defect in a  $7 \times 7$  unit cell corresponds to a concentration  $n_d \simeq 3.9 \times 10^{13} \text{cm}^{-2}$  or  $n_d \simeq 1\%$ . The electronic band structures (Figs. 3.8(b), (d), and (f)) exhibit interesting features. For the STW defect (Fig. 3.8(d)) the Dirac and Fermi energies match which means the Stone-Thrower-Wales defect does not induce any doping. The  $t5t7$  divacancy (Fig. 3.8(b)) has its Dirac energy 0.7 eV higher than its Fermi level which corresponds to a p-type doping effect on graphene. The 585 defect (Fig. 3.8(f)) has a slightly lower p-type doping effect. Indeed, the difference between the Dirac and Fermi energy is of 0.6 eV. From the geometries in Fig. 3.7 it is easy to see that the STW and the 585 share the same  $D_{2h}$  symmetry, while the  $t5t7$  has a  $D_{3h}$  symmetry. The latter is the symmetry of the Dirac cones. Therefore, the conventional three-segments  $k$  point path contains the whole information regarding electron dispersion. The two other structures, on the other hand, break the Dirac cones symmetry. They are therefore shifted to other places in the Brillouin zone. Fig. 3.8(c) and 3.8(e) show the positions of the shifted Dirac cones. The cones are shifted along the  $K_1$ - $K'_1$  direction. Each cone is shifted in the opposite way for the two defects.

Some interesting features can be deduced from the band structures. The presence of flat bands is associated to localized states, usually on or close to the defects. These states usually appear in transport experiments as resonance peaks which might quench the conductance. For the  $t5t7$  divacancy, three such states are seen : around 1.35, 0, and  $-1$  eV from the Fermi level. Relative to the Dirac energy, these defects are located at 0.45,  $-0.7$ , and  $-1.7$  eV. It has to be recalled here that once embedded in mesoscopic-sized flakes and in proportions closer to experiment, i.e. much lower than 1%, the shift of the Fermi level will reduce to zero. The Fermi level of the mesoscopic graphene flake will

### 3. TOPOLOGICAL DEFECTS IN GRAPHENE

---

lie at the Dirac energy. Therefore, it makes more sense to locate the flat bands regarding the Dirac energy. The STW defect shows flat bands at energies 0.5 eV above, and 1.75 eV below the Dirac energy (which in this case matches the Fermi energy). Finally, the 585 divacancy shows some flat band regions around 0 and 0.25 eV, corresponding to energies below Dirac energy as much as 0.35 and 0.60 eV.

In the next section, mesoscopic transport properties will be studied at different charged levels. The tight-binding model used to this end will be fitted on the band structure of the neutral defects. Therefore, one has to check that the so-called rigid band model is valid for the three defects used. The rigid band model states that the band structure of a charged system is simply a shift of the equilibrium band structure. Fig. 3.9 shows the band structures of the neutral defects along with the charged band structures. Charges of -3, -2, -1, +1, +2, and +3 electrons per unit cell are used. The highest charge corresponds to a carrier density of  $n \simeq 1.2 \times 10^{14} \text{ cm}^{-2}$ . One notices that the charged band structures for  $\pm 3|e|$  show little divergence from the shifted neutral band structures (red dashed lines). Moreover, the important features for transport lie in an energy window of about -1 to +1 eV around the Fermi level. This region remains almost unchanged for the charged systems. To end this paragraph, let us stress the importance of the chosen path for the band structure representation. Indeed, by choosing the conventional  $\Gamma$ -M-K- $\Gamma$  path, one would conclude that some cases exhibit energy gaps. Therefore, it is important in these cases to use an extended path. Although useful information is gathered from the DFT calculations, getting to higher system sizes, closer to experiments, requires other methods. Next section will focus on the tight-binding Kubo-Greenwood approach.

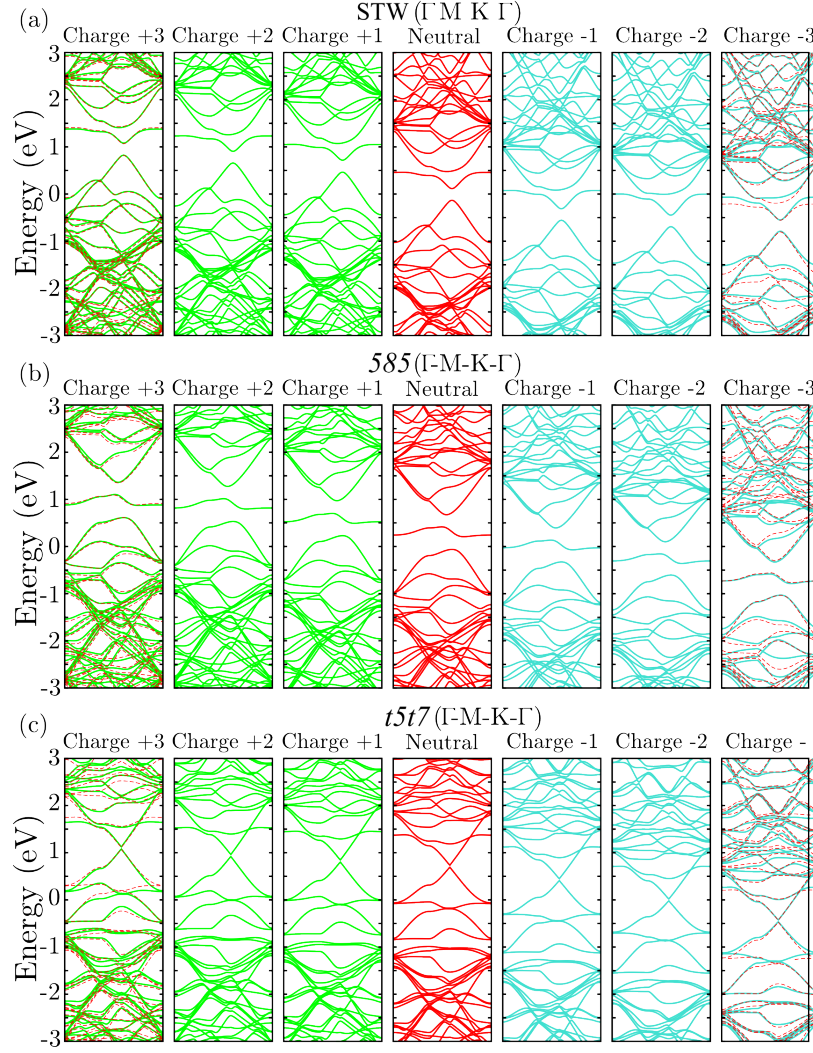


Fig. 3.9 - Electronic band structures of the three defects in a 7x7 unit cell : (a) STW, (b) 585, and (c)  $t5t7$ . The path in reciprocal space is shorter than in Fig. 3.8. It is only composed of the three-segment path :  $\Gamma$ -M-K- $\Gamma$ . The band structures of the charged defects are shown for validation of the rigid band model. Charges ranging from -3 to +3 electrons per unit cell are simulated. The dashed lines are a shift of the neutral band structure.

#### Tight-binding description

The first step in the calculation of the transport properties of a mesoscopic sample is to find a “suitable” set of TB parameters. The suitability of this set depends on what one wants to do with it. Since one has the DFT band structure, one way to obtain TB parameters is to minimize the difference between the TB and DFT band structures. This difference is calculated for a set of  $k$  points that has to be specified. Although very common, this is not what was done here. Since SIESTA uses local-

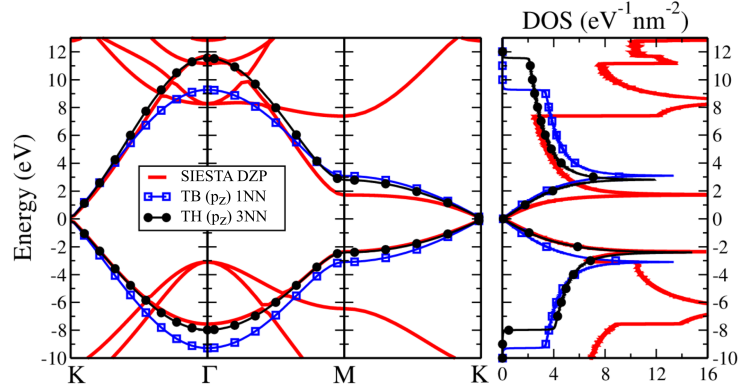


Fig. 3.10 - *Left*. Comparison between the DFT band structure for graphene obtained with SIESTA (red) and the TB band structure obtained with TB parameters extracted from the SIESTA Hamiltonian. Both 1<sup>st</sup> (blue) and 3<sup>rd</sup> (black) nearest-neighbor models are presented. The path chosen is the usual one : K-Γ-M-K. *Right*. The density of states is presented as one more comparison of the three models. The Fermi level is set to zero.

ized orbitals to express the Hamiltonian, a set of TB parameters can be extracted by performing a number of operations [71]. The initial basis set has to be reduced to orthogonal  $p_z$  orbitals. Indeed, as explained in



a previous chapter, a TB model using only these orbitals is enough to reproduce the characteristics of graphene which interest us<sup>2</sup>. It was also pointed out that either 1<sup>st</sup> or up to the 3<sup>rd</sup> nearest-neighbors (NN) can be included. Here, the latter option is used. As an example, Fig. 3.10 shows the agreement between the band structure obtained with a TB model using the extraction method and the one obtained with SIESTA. Both the 1<sup>st</sup> and 3<sup>rd</sup> NN models are presented in order to highlight the improvement of the latter with respect to the former. The 1<sup>st</sup> NN model is unable to reproduce the asymmetry between valence and conduction bands while the 3<sup>rd</sup> NN model is. Fig. 3.11 shows the band structures for the three point defects. The methodology is the same as the one used for pristine graphene. However, only the on-site energies are adjusted. The hopping terms are kept at the pristine graphene values. In addition, the geometry is also taken into account. The neighboring atoms are modified in order to correspond to the local defected geometry. The TB model fits rather well the DFT band structure. This is especially true for the valence bands. The conduction bands are slightly shifted upwards compared to the DFT bands. This is due to the inability of the  $\pi - \pi^*$  model to describe the K-M conduction branch. Therefore, when going to energies higher than the Dirac energy, the energy bands are shifted with respect to the DFT band structure. This shift is usually not a big issue since it is more or less constant, meaning one can still analyze the results. Sometimes however, the shift might be more important. This is the case of the flat band just above the Dirac energy for the  $t5t7$  defect. This band is shifted by hand by modifying the on-site energy in order to match the DFT band more closely. This is done specifically because of

---

<sup>2</sup>An exception is the K-M branch which requires the inclusion of  $d$  orbitals in order to match the DFT band structure.

### 3. TOPOLOGICAL DEFECTS IN GRAPHENE

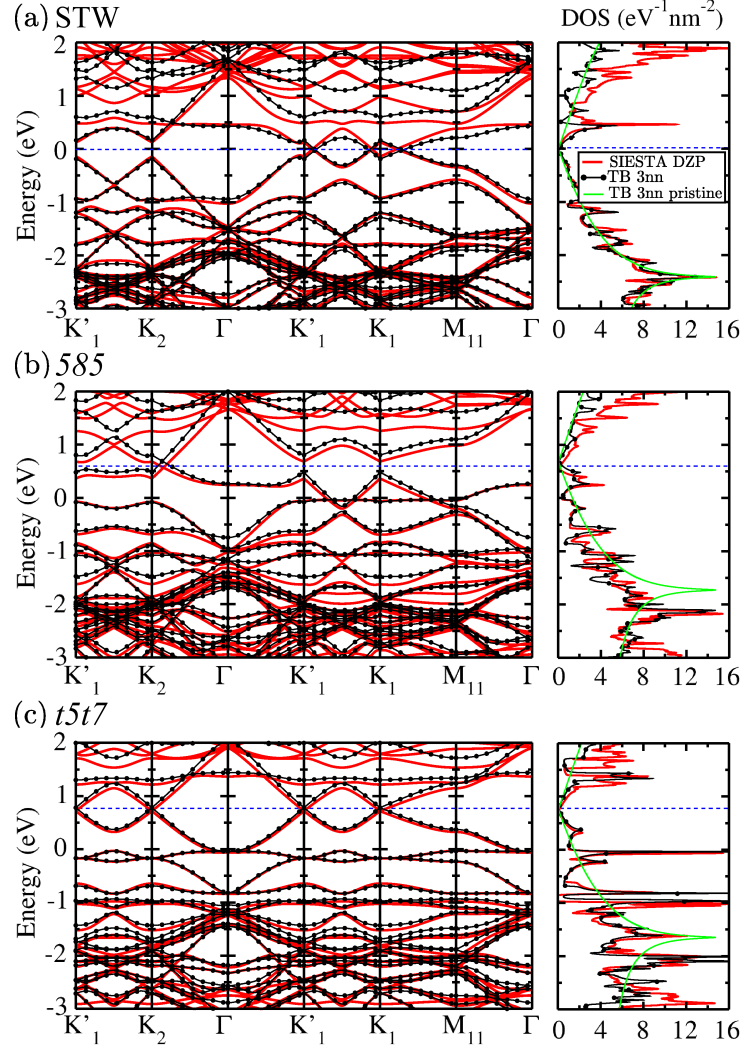
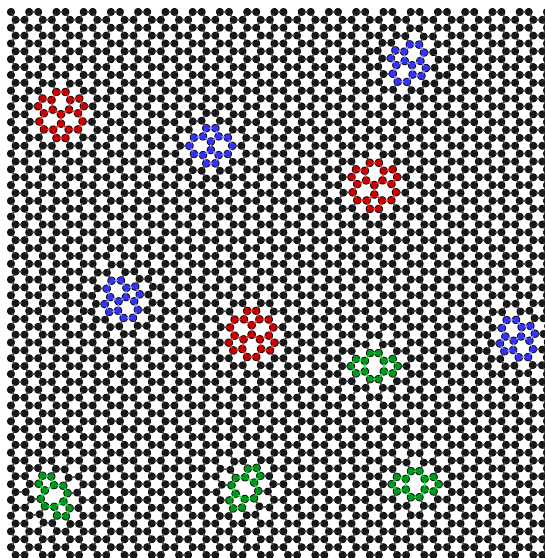


Fig. 3.11 - *Left*. Comparison of the band structures for (a) a STW, (b) a 585, and (c) a  $t5t7$  defect in a  $7 \times 7$  supercell. Red continuous lines show the DFT results, while the black dotted lines correspond to the TB results using up to 3<sup>rd</sup> NN. *Right*. Corresponding DOS. Green lines show the pristine-graphene's DOS calculated with the same TB model. Fermi level is set to zero while the Dirac energy position is marked by blue dashed lines.

the proximity of the Dirac cones, which will be of interest for the transport properties. A proper reproduction of the DFT results in this energy window is therefore required. To check the matching of the DFT and TB results, the DOS is also shown in Fig. 3.11. The pristine graphene DOS is also plotted, highlighting the resonance peaks close to the Dirac energy.

### Mesoscopic transport properties

Once the TB model has been parametrized, one can investigate defective graphene through the Kubo-Greenwood transport formalism (p.37). The systems involved in this study are mesoscopic and contain either



---

Fig. 3.12 - Example of a small sample of defected graphene, including mixed defects and orientations.

---

### 3. TOPOLOGICAL DEFECTS IN GRAPHENE

single or mixed-type defects at different concentrations (Fig. 3.12). Since the defects have different symmetries compared to graphene, different defect orientations are included in order to have a true randomized distribution. In order to get closer to experiment, only mixtures of defects have been studied. The size of the samples is of the order of  $2.8 \times 10^6$  atoms ( $250 \times 300$  nm). The density of states (DOS) for the three cases is plotted in Fig. 3.13. Compared to the periodic lattice

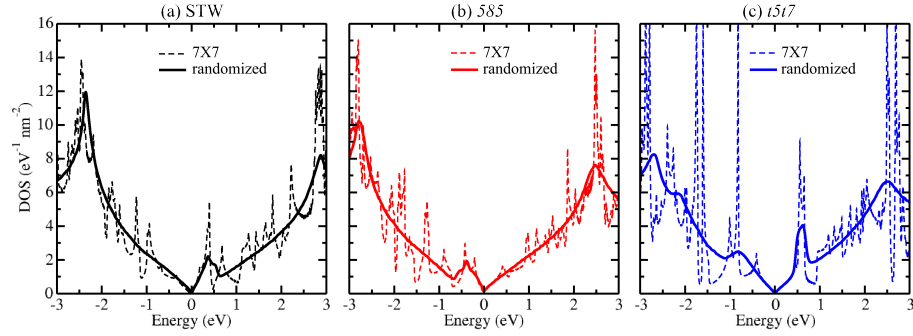


Fig. 3.13 - TB DOS for a  $7 \times 7$  unit cell (dashed lines) compared to the one for a large sheet (plain bold lines) for : (a) a STW defect, (b) a 585 defect, and (c) a  $t5t7$  defect. The defect concentration is close to 1% of atomic concentration.

The Dirac point is set to zero in order to align both DOSs.

of defects ( $7 \times 7$  unit cell) the random distribution of defects in a mesoscopic sample has a much smoother DOS. Indeed, one can notice that most of the peaks in the  $7 \times 7$  DOS are smoothed out in the DOS for a large sample. This can be explained by the lower density close to the Dirac point, which avoid the defect resonances to be smoothed out. Further away from the Dirac point, the density of states for graphene being more important, the peaks associated to the defects are smoothed out.

Fig. 3.14 shows the DOS of graphene containing a mixture of defects. A 1% concentration of mixed STW/585, STW/*t*5*t*7, and 585/*t*5*t*7 defects are incorporated into a big graphene sheet. These DOSs are compared to the ones for single-defect graphene with 0.5% of STW, 585, and *t*5*t*7. It is obvious from this figure that the mixed DOS is roughly the merge of the two corresponding single-defect DOSs. It is also interesting to note that the STW/585 case shows two symmetrical peaks around the

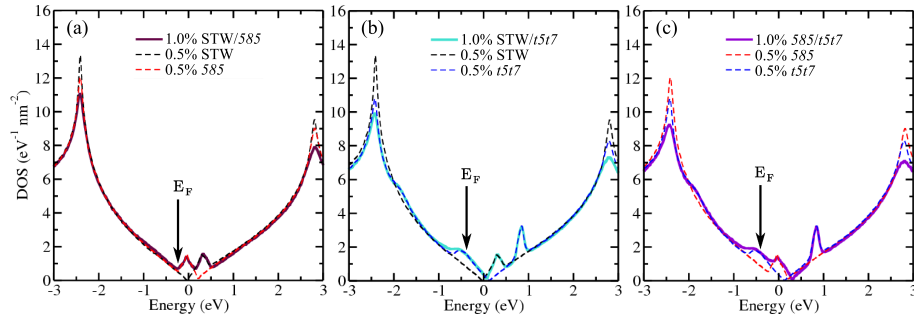


Fig. 3.14 - DOS for 1% mixtures of (a) STW/585 , (b) STW/*t*5*t*7, and (c) 585/*t*5*t*7 (plain lines). As a comparison, the DOS for a 0.5% concentration of STW, 585, or *t*5*t*7 is also shown (dashed lines). Fermi level is indicated by the vertical arrow.

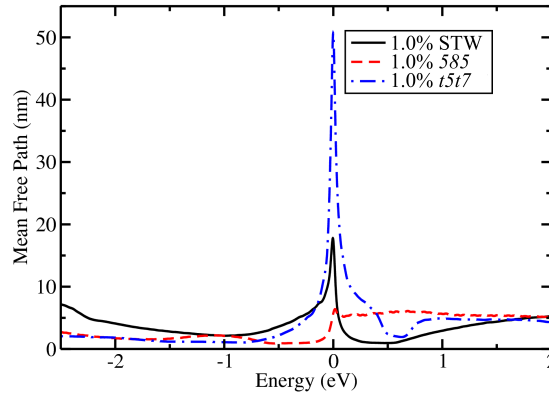
Dirac point. Moreover, because the peaks are close to the Dirac point, they overlap with it and therefore, the DOS increases at this point. One no longer have a minimum of DOS at the Dirac point. Although it will be detailed later, it is important to notice that this increase in DOS corresponds to localized states. It will not contribute to the electronic transport and will even quench it.

The mean free path for each type of defect is depicted in Fig. 3.15. A 1% concentration of defects is introduced in the sample. The peaks

### 3. TOPOLOGICAL DEFECTS IN GRAPHENE

---

at zero energy correspond to the Dirac point. The defects have a very different influence on the size of this peak. Indeed, while the mean free path for the  $t5t7$  reaches values up to 50 nm, the one for the STW is below 20 nm, and the one for the 585 is barely visible. This can be explained based on the DOS and band structure. The peaks associated with the  $t5t7$  defect are too far away from the Dirac point to affect its transport properties. The 585 and STW defects show



---

Fig. 3.15 - Elastic mean free path for defected graphene having 1% of STW (plain line), 585 (red dashed line), or  $t5t7$  (blue dot-dashed lines) defects.

---

peaks at approximately 0.4 eV around the Fermi level. However, the effect of the 585 peaks seems to be much more important. A look at the band structures (Fig. 3.8) provides an explanation. The peak in the DOS of the STW defect corresponds to a flat band at 0.5 eV above the Dirac point. The peak in the DOS of the 585 defect corresponds to two bands, one at 0.5 eV below Dirac point, and one at only 0.25 eV below the Dirac point. The peak in the DOS of the 585 defect is actually made of two peaks who overlap. The effect of the 585 peak closest to

the Dirac point has a much stronger impact on the mean free path. The signature of the Dirac point has actually vanished, meaning the Dirac-like behavior of electrons is lost. This last case exhibits an interesting behavior with a clear step in the mean free path at the Fermi level, with

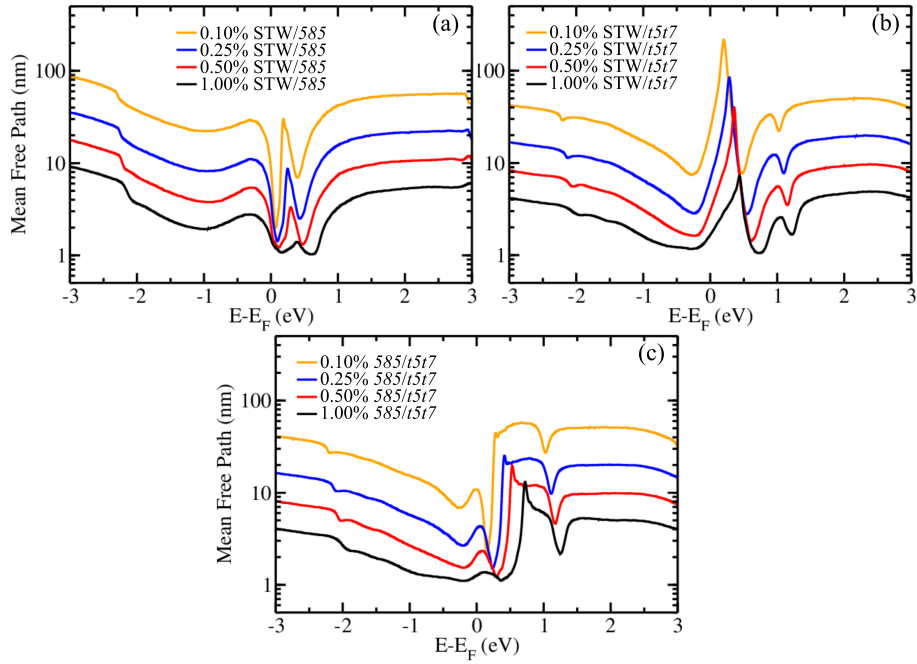


Fig. 3.16 - Mean free paths in graphene planes with mixed (a) STW/585, (b) STW/t5t7, and (c) 585/t5t7 defects. Concentrations are ranging from 0.1% to 1.0%.

almost constant values before and after the step. Fig. 3.16 shows the mean free path for the mixed systems. Note that the scale is not linear as in Fig. 3.15 but logarithmic. Each peak in the DOS gives rise to a dip in the mean free path. The only case that still shows a divergence

### 3. TOPOLOGICAL DEFECTS IN GRAPHENE

---

of the mean free path corresponding to the Dirac point is the STW/*t5t7*. When the 585 divacancy is included, no peak is present anymore. For the STW/585 mix, after each dip, the value of the mean free path gets almost back to its value before the dip. For the 585/*t5t7* mix, a steep step occurs above the Fermi level. This sudden and clear change of the mean free path offers interesting perspectives in terms of transport gaps [72]. For the smallest concentration, the maximum values are in the  $[60, 200]$  nm range, while the minimum lies below 10 nm. For the biggest concentration every value lies below 10 nm for the energy range considered here  $([-3, 3]$  eV). It has to be noted that the lowest concentration available for calculations are limited by two factors. First, the smaller defect concentrations will result in increasingly bigger mean free paths. When reaching the size of the sample ( $250 \times 300$  nm), the mean free path will not be defined anymore. Moreover, decreasing concentrations lead to a stronger ballistic transport. Therefore, the calculation will take more time to reach diffusive transport and will eventually prevent calculations to end in a suitable time.

Next figure (Fig. 3.17) shows the mobility for the mixed cases. A divergence occurs because the electronic density appears at the denominator in the expression for the mobility. Therefore, the vanishing DOS close to the Dirac point leads to the peak seen in the mobilities. The shifting of the peaks in the mobility versus energy corresponds to the p-type doping induced by the divacancies. This shift increases with defect density. Therefore it is also bigger when mixing the two divacancy flavors than when only one is mixed with STW defects. The mobility as a function of the density carrier is also represented. The reason for this is that the carrier density directly relates to the back-gate voltage in an experimental setup, while the dependence on the energy is usually not



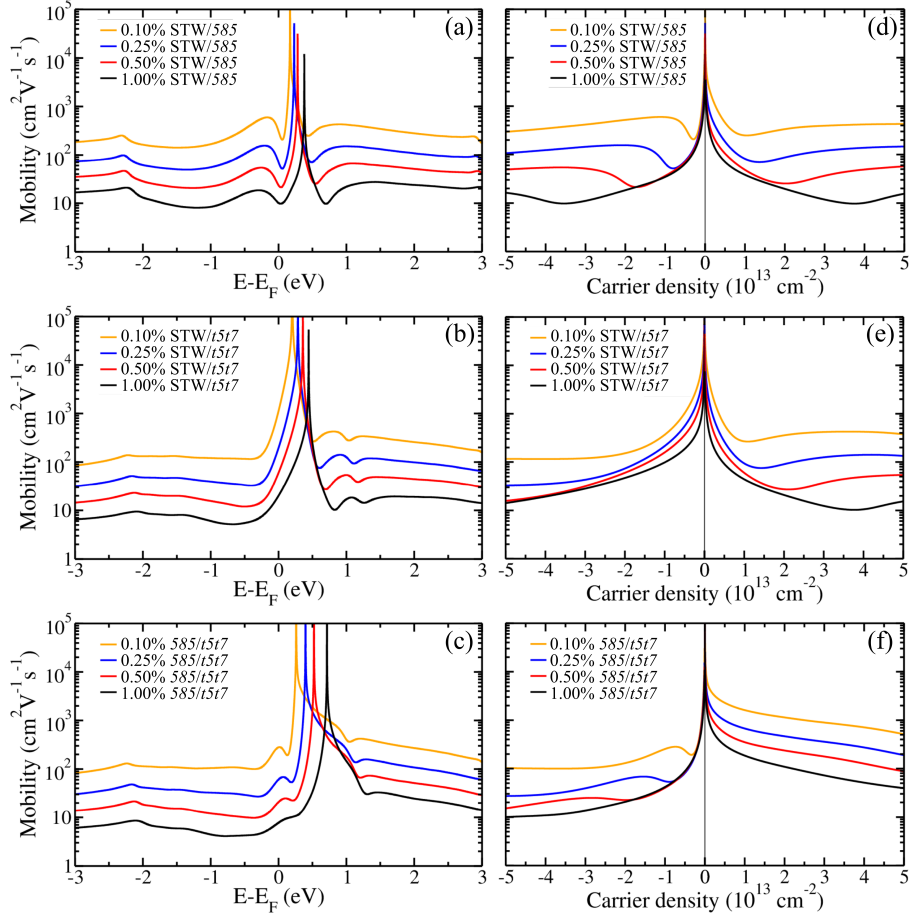


Fig. 3.17 - Mobilities for the mixed-defect cases as a function of energy (left column) and carrier density (right column). (a) and (d) shows the mobility for the STW/585 case, (b) and (e) for the STW/t5t7 case, and (c) and (f) for the 585/t5t7 one. Defect concentrations range from 0.1% to 1.0%.

available. The relation between the carrier density and the back-gate

### 3. TOPOLOGICAL DEFECTS IN GRAPHENE

parameters is the following :

$$ne = \Delta V_{\text{bg}} C_{\text{bg}}, \quad (3.3)$$

with  $V_{\text{bg}}$  and  $C_{\text{bg}}$  the back-gate voltage and capacitance, respectively. The effect of this transformation is a smoothing of the variations. Moreover, the peaks are obviously aligned at zero. Although less sharp, the drop in mobility is still huge, especially for the holes in the 585/ $t5t7$  defected graphene. This last case shows again asymmetry in its properties. The mobility is indeed roughly one order of magnitude higher for electrons than for holes. This difference seems to increase with decreasing defect concentrations. An optimum defect concentration should exist that maximizes this asymmetry.

Fig. 3.18 and 3.19 show the semiclassical conductivity for the single-defect and mixed-defects samples. For the single-defect graphene

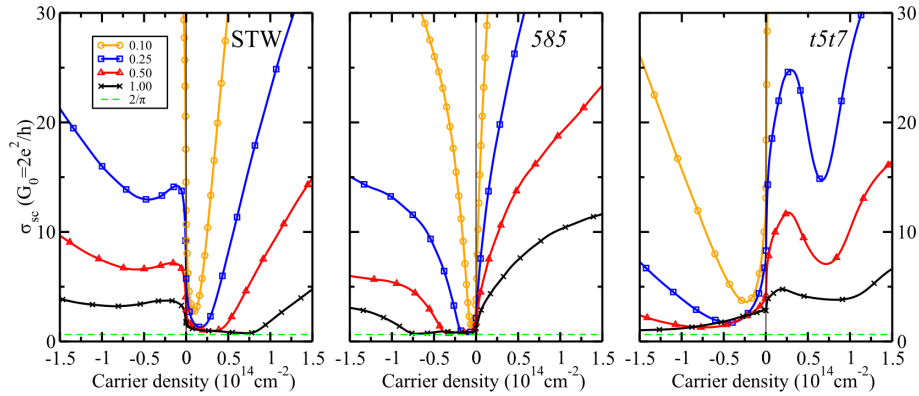


Fig. 3.18 - Semiclassical conductivity as a function of carrier density for graphene with only : STW defects (*left*), 585 defects (*center*) and  $t5t7$  defects (*right*).

planes, the conductivity is strongly dependent on the defect concentration  $n_d$ . The STW and 585 divacancy having mainly one resonance peak close to the Dirac point, their signature is relatively straightfor-

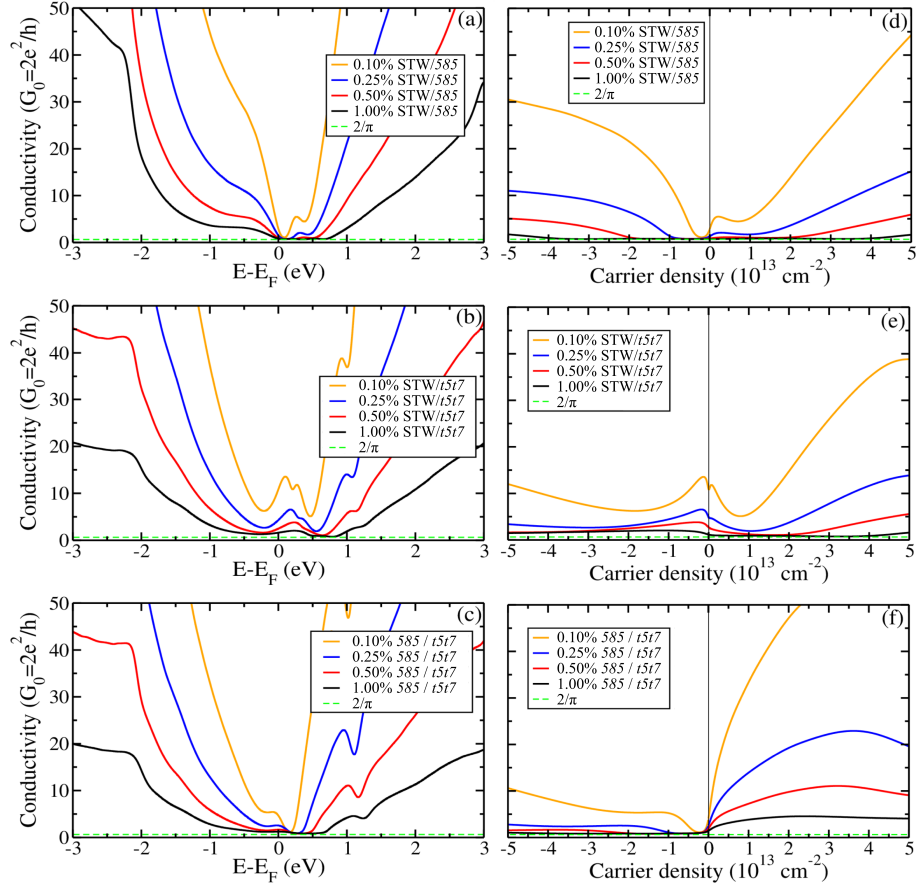


Fig. 3.19 - Semiclassical conductivities as a function of charge carrier energy (left panels) and as a function of charge carrier density (right panels) of graphene planes with, (a)(d) STW/585 defects, (b)(e) STW/ $t5t7$  defects, and (c)(f) 585/ $t5t7$  defects, for different defect concentrations ranging from  $n_d = 0.1\%$  to  $1.0\%$ .

### 3. TOPOLOGICAL DEFECTS IN GRAPHENE

---

ward. Indeed, when increasing the defect concentration, a dip develops at energies corresponding to the energy of the resonance states. This dip first becomes deeper until it reaches the value of the minimum conductivity in graphene  $\sigma_{sc}^{\min} = 2G_0/\pi = 4e^2/\pi h$ . Afterwards, the dip widens and a plateau appears. The  $t5t7$  case is more complicated since more than one resonance state is associated with this defect. However, one still sees decreases in the conductivity at energies corresponding to the resonance energies. The conductivity for the mixed-defects graphene planes shows a more subtle behavior. Dips appear at energies corresponding to resonance energies associated with the defect. The minimal conductivity appears therefore at energies that differ from the Dirac energy. In general, the minimum conductivity associated with the Dirac point is very sharp. The present calculations being done at 300 K, the dip at the Dirac energy is almost totally smoothed out. It is only slightly visible for the STW/ $t5t7$  (Fig. 3.19(b) at around 0.2 eV or (e) at zero carrier density). The minimum conductivity never goes below the conductivity limit  $4e^2/\pi h$ . As in the case of single-defect planes, plateaus develop around the resonance energies. Because of this quenching, the conductivity curves show different evolutions. The analysis is easier on the figures as a function of the carrier density. For example, a linear behavior is observed for electrons for the STW/585 and to a smaller extent for the STW/ $t5t7$  case. A quadratic evolution links conductivity and carrier density both for electrons and holes close to the Dirac point, and more importantly close to the resonance energies. A sublinear behavior is seen for holes in the STW/585 case and for electrons in the 585/ $t5t7$ . Finally, as explained previously, for increasing defect densities, constant values of conductivity appear on significant carrier density ranges (plateaus).

This ends the part on the semiclassical transport properties. The main conclusion is the effect of the resonance states on transport. One observes a quenching of the properties at the energies of the resonance peaks. Therefore, one could theoretically use the transport properties as a fingerprint of the defect.

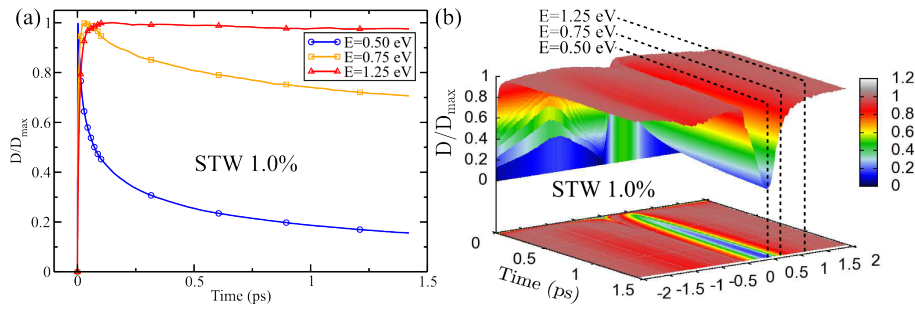


Fig. 3.20 - Normalized time-dependent diffusion coefficient at three energies for a 1% concentration of STW in a graphene plane (a). Three-dimensional plot of the diffusion coefficient as a function of time and energy for a 1% concentration of STW in a graphene plane (b).

The main quantum transport quantity that is studied here is the localization. Localization happens through quantum interferences that increase the backscattering probability. The requirement to reach this regime is to keep the phase of electrons, and therefore avoid the events that cause phase decoherence, such as electron-phonon scattering. Keeping the phase of electrons usually requires to work at low temperatures. This is not the case in graphene, for which electron-phonon scattering was found to be extremely low [73, 74]. It was also shown that conductivity decreases logarithmically with the sample size (for two-dimensional systems) when in the weak localization regime. A higher disorder in-

### 3. TOPOLOGICAL DEFECTS IN GRAPHENE

---

duces strong localization which leads to an exponential decay for the conductivity. The last case is so efficient that the electron transport becomes totally quenched. Graphene then becomes an insulator regarding its transport properties. Causes for this localization regime include hydrogen [17, 75–79], epoxy oxygen atoms [80–82], vacancies and other structural defects [65, 83–86], or noble metals [87].

One is able to identify the moment when the quantum interferences kick in and lead to a quenching of the transport properties by keeping track of the time evolution of the diffusivity. Fig. 3.20 shows the diffusivity evolution over time for the 1% concentration STW defected plane. Fig. 3.21 shows the diffusivity for the mixed-defect graphene planes. A three-dimensional plot shows the evolution of the diffusivity (normalized to  $D_{\max}$ ) as a function of time and energy. Two-dimensional plots focus on the time evolution of the diffusivity for some selected energies. The energies at which localization effects occur are clearly seen. The closer to the energy of the resonance state we are, the faster the decay of diffusivity is. Far away from any resonance energy, the diffusivity keeps its maximum value during the whole simulation time, meaning one does not exit the semiclassical diffusive regime.

Once in the localization regime, one can estimate the localization lengths  $\xi$ . Fig. 3.22 shows the localization lengths for the mixed-defect cases. For a 1% defect concentration, localization lengths as small as 10 – 20 nm are observed for the mixed-defect planes, as well as the single-defect cases (not shown). For these values, the conductivity reaches its minimum value. Eq. 2.43 therefore becomes :

$$\xi(E) = \sqrt{2}l_e(E)\exp(2). \quad (3.4)$$

Using the values of  $\xi$  one finds values of  $l_e$  around 1 nm. When go-

ing away from the resonance energies the localization length increases rapidly due to the exponential of the conductivity in eq. 2.43. This makes it very difficult to observe localization experimentally.

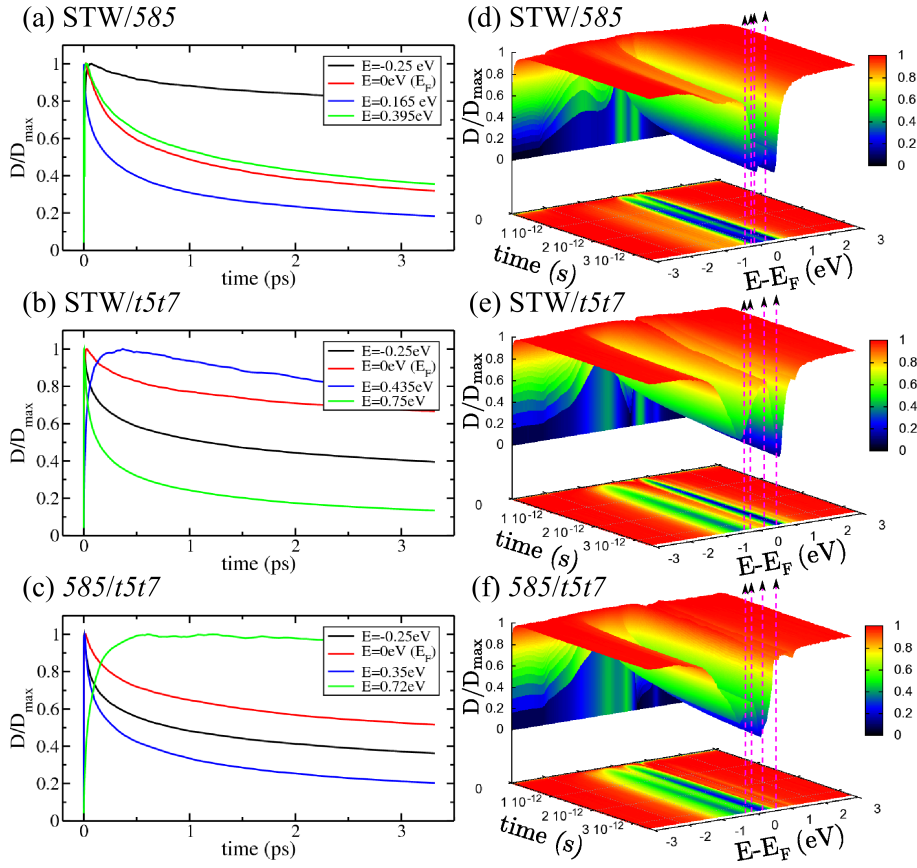


Fig. 3.21 - *Left*. Normalized time-dependent diffusion coefficient for four energies, for the three mixed-defects planes. *Right*. Three-dimensional plot of the diffusion coefficient as a function of time and energy for, (a)(d) the STW/585 defects, (b)(e) the STW/ $t5t7$  defects, and (c)(f) the 585/ $t5t7$  defects.

### 3. TOPOLOGICAL DEFECTS IN GRAPHENE

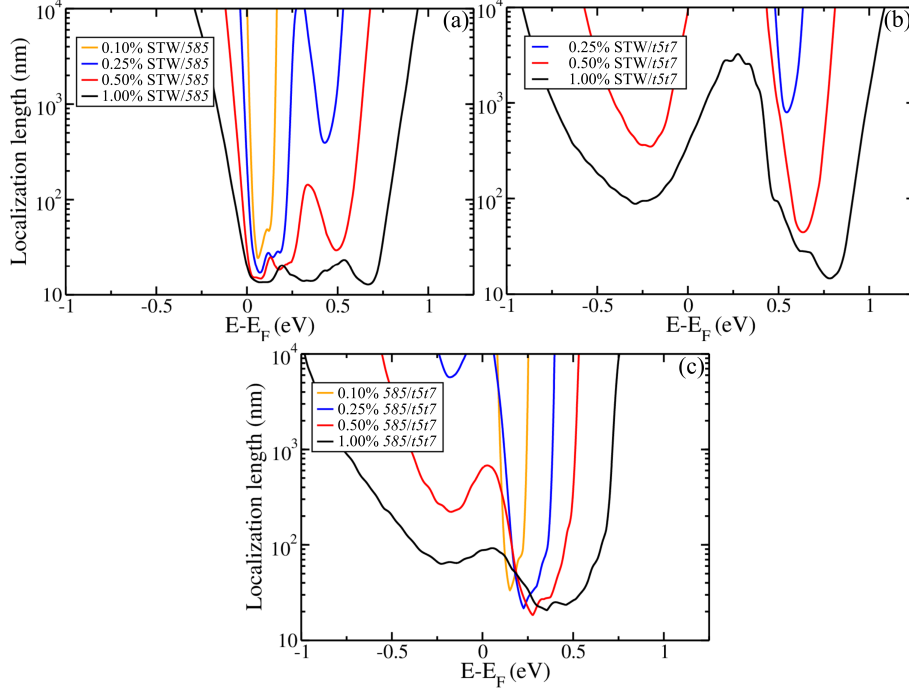


Fig. 3.22 - Localization lengths for defected graphene planes containing : (a) STW/585 defects, (b) STW/ $t5t7$  defects, and (c) 585/ $t5t7$ . Various defect concentrations are presented.

### 3.3 Conclusion

Geometrical modifications of the graphene lattice can induce a variety of different effects on the electronic and transport properties of pristine graphene. Focus is put on defects created by bond rotations and vacancies. Combining these two simple ingredients allows to tailor a whole set of defects. Three one-dimensional defects are presented. They arise through local damaging of graphene or to accomodate some mismatch



between graphene flakes of different alignment. Their stability is investigated based on their formation energy. STM images are presented and agree with experimental data. The transport properties are calculated by embedding these linear defects into graphene ribbons. The  $1-t5t7$  defect is shown to be more promising than the others as it introduces one more conduction channel available for electronic transport. It results therefore in a metallic wire embedded in graphene which could be of particular interest for applications. Point defects are also studied : STW, and  $585$  and  $t5t7$  divacancies. Each of these are associated to resonance energies. Their transport properties, both quantum and semiclassical are investigated in a mesoscopic graphene sample, and explained based mainly on their band structures and DOSs. The main effect of the defects is to induce a quenching of the transport properties at energies corresponding to the resonance peaks of the considered defect. As a result of this, fingerprints are shown for each defect, as well as for mixtures of two defects. These results can serve to experimentally identify topological defects based on their electronic transport properties.

The following chapter will focus on another way to tailor graphene's properties : the doping of graphene with boron or nitrogen. This time however, simulated STM images will be shown for boron doped graphene in parallel with experimental images. The purpose is to help the identification of the defects. The energetics of nitrogen islands will be investigated as well.



## Chapter 4

# Boron and nitrogen doping of graphene

In the search for new ways to tailor graphene's electronic properties, doping is frequently suggested as an interesting process. Indeed, doping corresponds to the incorporation of foreign atoms in graphene. The most obvious choices are carbon's neighbors in the periodic table of elements : boron and nitrogen. A major difference between three-dimensional and two-dimensional doping lies in the nature of the doping. In three dimensions, an atom might take the place of a host atom (substitutional doping), or stand between atoms (interstitial doping). In two dimensions however, doping happens mainly in substitution. The effect of boron and nitrogen consists respectively in adding holes and electrons. The atomic structure, however, is different for the two cases. Boron has a tendency to form  $\text{BC}_3$  islands, reproducing the arrangement of the  $\text{BC}_3$  compound [88]. Nitrogen doping is found to take more random positions, although it can form  $\text{C}_3\text{N}_4$ -like islands by combina-

#### 4. BORON AND NITROGEN DOPING OF GRAPHENE

---

tion with vacancies [89]. Some applications can benefit from one or the other type of doping. In order to produce graphene with a specific type of defect, different synthesis parameters are needed such as the precursor, the temperature, the substrate, etc. Moreover, a precise characterization is required to know exactly which kind of defect is favored for which synthesis parameters. The next section will focus on the energetics of nitrogen doped graphene. So far, experimental images are only available for low doping concentrations ( $\sim 1\%$  atomic concentration). The case which will be developed in this thesis requires higher concentrations and a direct comparison to experiment is therefore not yet possible. The tool of choice for graphene characterization is the scanning tunneling microscope (STM). As explained before, STM images are well reproduced by plotting local density of states. The last section of this chapter will show simulated images for boron-doped graphene, and a comparison with experimental images will be illustrated when possible.

For these calculations, a DZP basis set is used along with LDA. GGA is also tested in order to check the influence of the exchange-correlation functional on the STM images, but no difference is observed. For boron, structural optimization of the ions is performed in a cell with dimensions fixed to their relaxed value for perfect graphene. In addition, different cell sizes are used to see the evolution of the STM images. For nitrogen, full relaxation of the ions and cells are performed. Convergence is done on the  $k$  point grid and other relevant parameters (electronic temperature, density of the grid for the real-space operations, ...).

## 4.1 Nitrogen doping

Along with boron, nitrogen is one of the most studied species for graphene doping. From the experimental point of view, both low [90–93] and high concentrations [94] are obtained, high concentration meaning more than 5% atomic percentage. This section focuses on the energetics of defects with more than two nitrogen atoms that adopt the  $C_3N_4$  configuration [89]. The case of single substitution has already been investigated theoretically [95, 96] and experimentally [90, 91]. It was found that STM experimental and theoretical images match, proving the presence of single substitution in the synthesized samples. A characterization of the nitrogen defect distributions was done. A majority of these defects are single substitution. Others remain unexplained (Figs. 4.1(a) and (b)). The effect of single substitution is mainly to induce an n-doping to graphene. In addition, although the formation mechanism is still not clear, depending on the experimental setup the nitrogen atoms substitute either preferentially carbon atoms from the same sublattice [90] or randomly from the A or B sublattice [91]. The sublattice substitution asymmetry leads to different transport behavior for electrons and holes [96]. Other synthesis conditions favor double substitution [92]. Already with just two atoms, the STM images are not straightforward to interpret. Lv, *et al.* [92] presented a combined study of theoretical and experimental data. The simulated STM images corresponded to the experimental ones. In order to cross-check these results scanning tunneling spectroscopy (STS) images were produced, which again confirmed the geometry of the double substitution defect : the two nitrogen atoms lie on next-nearest neighbor positions, thus both on the same sublattice. Moreover, along with the global n-type doping

#### 4. BORON AND NITROGEN DOPING OF GRAPHENE

---

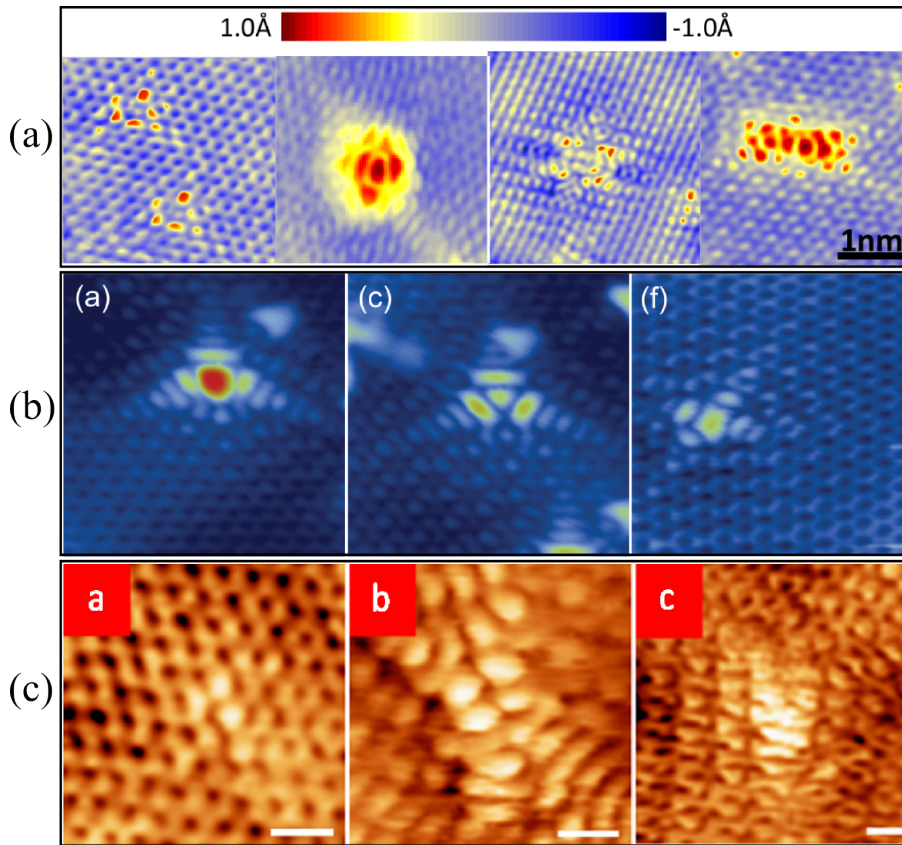


Fig. 4.1 - STM images of more complex nitrogen-based defects (beyond single or double substitution) observed in [90] (a), [91] (b), and [92] (c).

---

effect of the nitrogen substitution, the STS measures and calculations allowed to find signatures of the studied defect. It has to be noted that, here again, some bigger defects were evidenced without being able to identify the local atomic structure (Fig. 4.1(c)).

The goal of the present study is to evidence the general trends in the en-

energetics of nitrogen atoms combined to single vacancies. The properties of the nitrogen-doped graphene sheet might differ if nitrogen prefers to cluster or, on the contrary, if it adopts a homogeneous distribution. The starting point of this work consists in predicting the properties of the simplest cases in order to validate the present simulations. The unit cell used in all the calculations is a  $9 \times 9$  unit cell, containing as much as 162 atoms. Although performed for single substitution, a recent study showed this size to be enough to grasp the details of the nitrogen defect [97]. Fig. 4.2 shows the two simplest structures including one nitrogen atom : the graphitic case (a), and the pyridinic case (b) which involves a single vacancy.

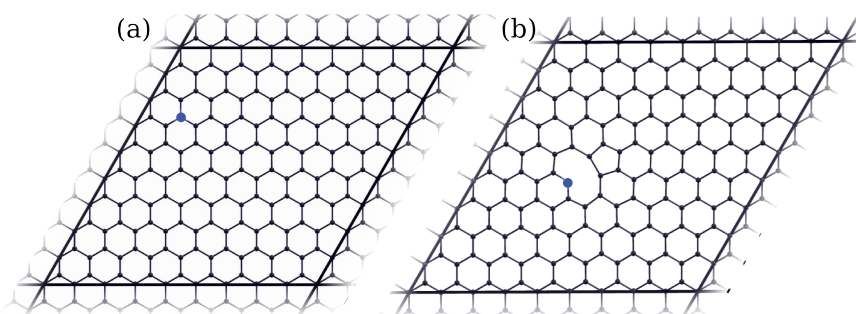


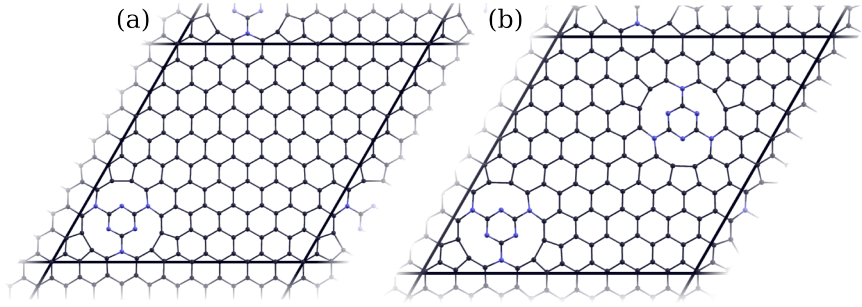
Fig. 4.2 - Unit cells for the graphitic nitrogen substitution (a), and for the pyridinic substitution (b). Nitrogen and carbon atoms are represented in blue and black, respectively.

In absolute value, the graphitic case is energetically more favorable. However, when comparing the case of a single vacancy and a nitrogen atom far away from it, and the case of a nitrogen atom on a single vacancy (the pyridinic case), the result is clear. The pyridinic case

#### 4. BORON AND NITROGEN DOPING OF GRAPHENE

---

lies 3.14 eV lower than when the vacancy and the nitrogen atom are separated. This result is in very good agreement with recent calculations [98, 99]. Other substitution sites of the single vacancy for the nitrogen atom are investigated (not shown) but the conclusion is that the pyridinic site is the most stable one, as confirmed by [99]. The next step is to study larger defects, including vacancies in order to reproduce the  $C_3N_4$  ratio. Fig. 4.3(a) shows the smallest defect studied which will be called a triangle and corresponds to the unit repetition to generate a  $C_3N_4$  sheet. The triangle of Fig. 4.3(a) is an up-triangle ( $\Delta$ ), as opposed to the down-triangle ( $\nabla$ ) in order to distinguish the two possible orientations.




---

Fig. 4.3 - Unit cells for an up triangle (a), and for an up and down triangle (b). Nitrogen and carbon atoms are represented in blue and black, respectively.

---

The formation energy per nitrogen atom  $E_c$  of these defects is calculated as :

$$E_c = \left[ E_d - n_C \frac{E_{\text{graph}}}{2} - n_N \frac{E_{N_2}}{2} \right] / n_N, \quad (4.1)$$

with  $E_d$  the total energy of the defected graphene sheet,  $n_C$  ( $n_N$ ) the



number of carbon (nitrogen) atoms in the unit cell, and  $E_{\text{graph}}$  ( $E_{\text{N}_2}$ ) the total energy for a two-atoms unit-cell graphene plane (nitrogen molecule). It is important to remark that the defects involve not only nitrogen atoms but also carbon atoms. The exact number of carbon atoms to be associated with the defect is not possible to determine without further calculations. The assumption in this formula is that each carbon atom has an energy associated to half the graphene energy, and that the number of atoms involved in the defect is  $n_{\text{N}}$ , the number of nitrogen atoms. The formation energy  $E_c$  for one up triangle or for one up and one down triangle (Fig. 4.3(b)) is respectively 1.83 eV and 1.86 eV. Therefore, the presence of two triangles (11 Å between centers) does not seem to influence the energetics of the system.

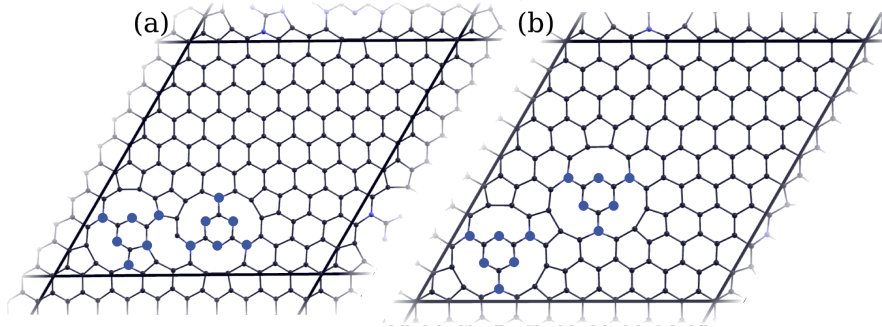


Fig. 4.4 - Unit cells for two close triangles : (a) an up and a down triangle, and (b) two up triangles. Nitrogen and carbon atoms are represented in blue and black, respectively.

The defects of Figs. 4.4 and 4.5 are studied in order to compare different cases which lead to the next case, the three merged triangles (Fig. 4.6). They depict two triangles, one up and one down which are joined to-

#### 4. BORON AND NITROGEN DOPING OF GRAPHENE

gether ( $\Delta\nabla$ -c, the “c” stands for “close”) (Fig. 4.4(a)) ; two up triangles joined together ( $\Delta\Delta$ -c) (Fig. 4.4(b)) ; and two configurations of two merged triangles ( $\Delta\Delta$ -m1 and  $\Delta\Delta$ -m2) (Fig. 4.5). The energetics of these four cases is summarized in the following table :

| defect     | $\Delta\nabla$ -c | $\Delta\Delta$ -c | $\Delta\Delta$ -m1 | $\Delta\Delta$ -m2 |
|------------|-------------------|-------------------|--------------------|--------------------|
| $E_c$ (eV) | 1.662             | 1.715             | 1.688              | 1.873              |

Table 4.1 - Formation energy per nitrogen atom  $E_c$  for the four configurations of Figs. 4.4 and 4.5.

All these values are similar. However, these configurations have different numbers of atoms, no account has been taken of the formation energy of the single vacancy. The conclusion is that from the point of view of the energetics, each of these configurations could happen. In addition, if a single vacancy is present somewhere in the graphene sheet, it is more favorable for this vacancy to cluster with the nitrogen defect.

The next configurations contain more nitrogen atoms than the previous cases : three triangles are joined together. Two variations of this defect are shown in Fig. 4.6. The only difference between them is the presence or absence of the central carbon atom in the defect. The formation energy for the case without central atom is 20.92 eV lower than for the case with a central carbon atom. This confirms the stability of the triple pyridine defect, found at the central part of the three triangles defect [98]. This huge energy difference might be explained by the fact that the triple pyridine defect is so stable that the addition of a central carbon atom results in a very weak bonding between this carbon atom and its three nitrogen neighbors.

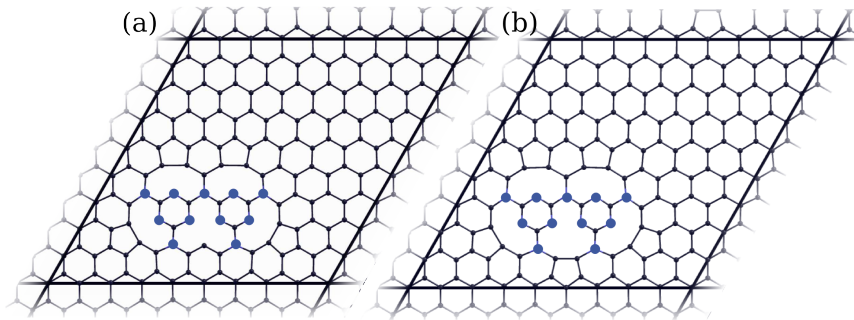


Fig. 4.5 - Unit cells for two merged triangles : (a) configuration n°1, and (b) configuration n°2. Nitrogen and carbon atoms are represented in blue and black, respectively.

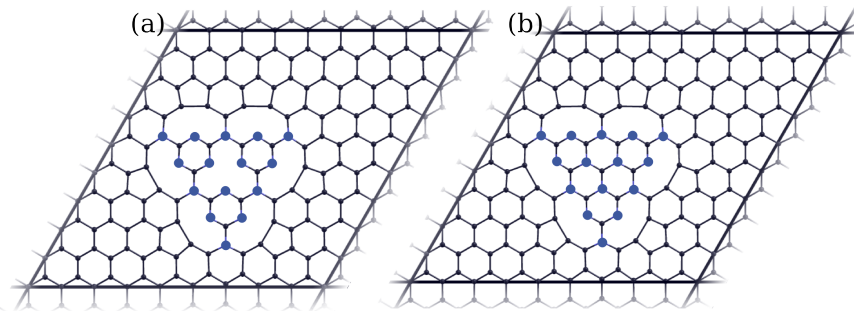


Fig. 4.6 - Unit cells for three triangles : (a) without the central carbon atom, and (b) with the central carbon atom. Nitrogen and carbon atoms are represented in blue and black, respectively.

The last structures are different from the other studied so far. Indeed, the previous defects have their boundary composed of vacancies. The next defects try to keep the vacancies at the inside of the defects, max-

#### 4. BORON AND NITROGEN DOPING OF GRAPHENE

imizing the number of triple pyridine defects (Fig. 4.7). The formation energy per nitrogen atom is summarized in Tab. 4.2. Although not large ( $\sim 40$  meV) the energy decreases for the defects with a higher number of nitrogen atoms. It is important to note that the number of vacancies is identical for these two configurations. This result shows that the ni-

| configuration | 16N-142C | 24N-134C |
|---------------|----------|----------|
| $E_c$ (eV)    | 0.128    | 0.089    |

Table 4.2 - Formation energy per nitrogen atom  $E_c$  for  $C_3N_4$  based configurations with 16 and 24 nitrogen atoms.

trogen island becomes more favorable for larger sizes. A final feature worth mentioning is the out of plane displacement of the most loose hexagon at the center of the the defect made of 24 nitrogen atoms.

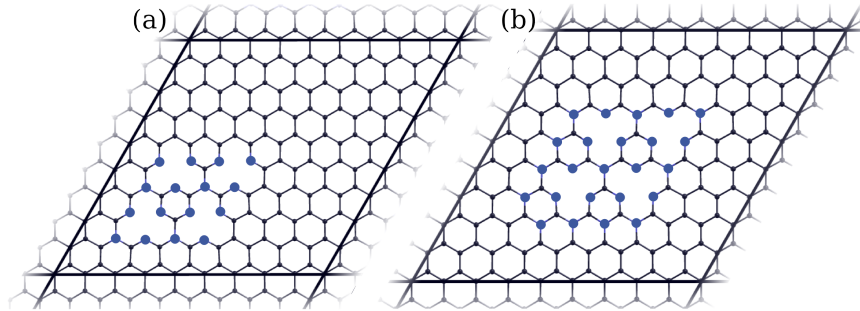


Fig. 4.7 - Unit cells for two  $C_3N_4$  configurations with 16 nitrogen atoms (a), and 24 nitrogen atoms (b). Nitrogen and carbon atoms are represented in blue and black, respectively.

This study indicates that islands of nitrogen are more favorable than isolated nitrogen defects when vacancies are involved. From an experimental point of view, the presence of vacancies is confirmed, as is the presence of divacancies. Since the kinetics involved in the formation of  $C_3N_4$  islands is not known, as well as the interaction with divacancies, the feasibility of  $C_3N_4$  islands in graphene is not necessarily possible. Experimental STM measures and images should help clearing this out. Unfortunately, only images for low nitrogen concentrations are found

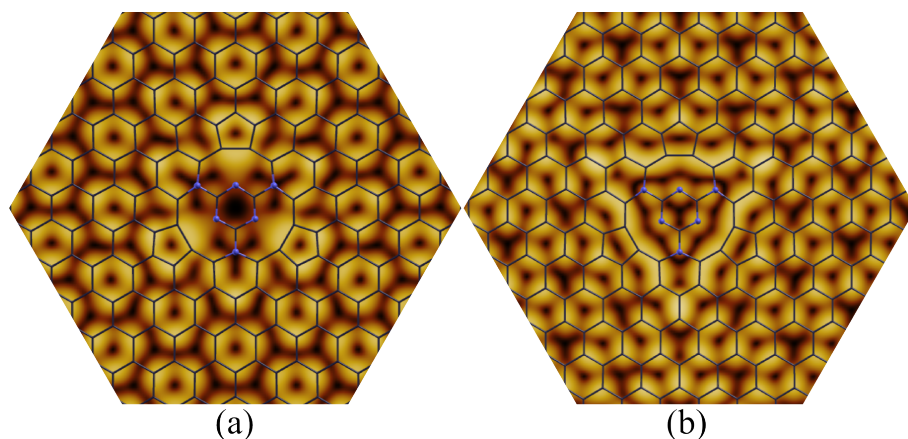
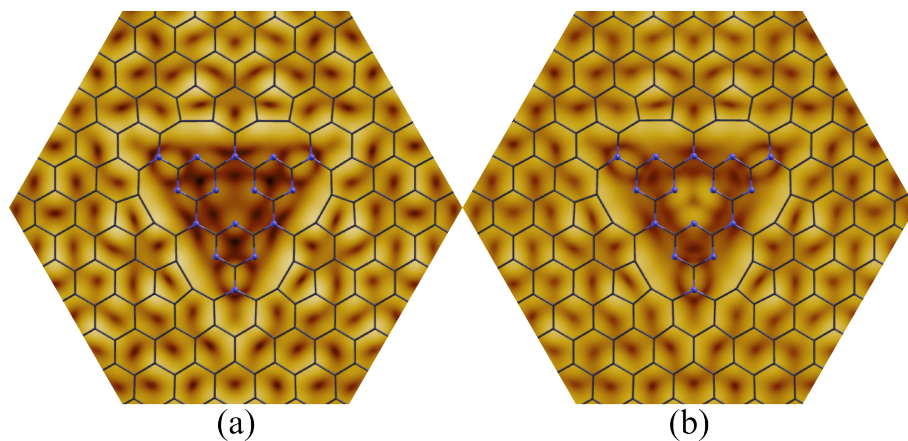


Fig. 4.8 - Simulated STM images for one triangle nitrogen island in graphene for a -200 (a) and 200 mV (b) tip voltage. Nitrogen and carbon atoms are represented in blue and black, respectively.

so far. Nevertheless, Figs. 4.8 and 4.9 present simulated STM images for positive and negative bias, corresponding to one triangle and three triangles, respectively. These images could serve as reference for future experiments. A common feature to the two cases is the outer triangular shape, delimiting the nitrogen islands. This characteristic seems to be

#### 4. BORON AND NITROGEN DOPING OF GRAPHENE

---



---

Fig. 4.9 - Simulated STM images for a three-triangles nitrogen island in graphene for a -700 (a) and 700 mV (b) tip voltage. Nitrogen and carbon atoms are represented in blue and black, respectively.

---

present over a wide range of energies, making it very likely to be seen in experimental images.

## 4.2 Boron doping

The assumption is that boron will prefer to form  $BC_3$  islands. It is based on evidence of a stable  $BC_3$  structure [88]. The very first step in the simulation is to check that it is indeed energetically favorable. Different configurations with different numbers of atoms and cell sizes are studied. Fig. 4.10 illustrates how four boron atoms can be distributed in a  $7 \times 7$  cell, either in a homogeneous way, or in a  $BC_3$ -like arrangement. It has to be noted that different configurations can fulfill the  $BC_3$  ratio. For the energetics study, only one configuration is taken into account. Tab. 4.3 compares the total energy difference ( $E_{stab}$ ) between the case of boron in a  $BC_3$  configuration and the case of a homogeneous distribution of boron :

$$E_{stab} = E_{homogeneous} - E_{BC_3} \quad (4.2)$$

The more compact  $BC_3$ -like islands are energetically favorable compared to the more homogeneous case. For a given cell size, the energy difference is more important for higher boron concentrations. Moreover, the value for nine boron atoms in a  $9 \times 9$  cell is twice as big as for ten atoms in a  $7 \times 7$ . The former corresponds to a ratio of  $\sim 5\%$  while the latter corresponds to  $\sim 10\%$ . Although not very clear yet, this huge difference confirms that the boron atoms do prefer to form  $BC_3$  islands, even over being more isolated as they are in the  $9 \times 9$  cell. It has to be noted that only this last case can be truly homogeneous (nine atoms in a  $9 \times 9$  unit cell is equivalent to one in a  $3 \times 3$ ). For the other cases, the atoms are arranged in the most homogeneous possible configuration : some are closer to others meaning there might be fluctuations in the en-

#### 4. BORON AND NITROGEN DOPING OF GRAPHENE

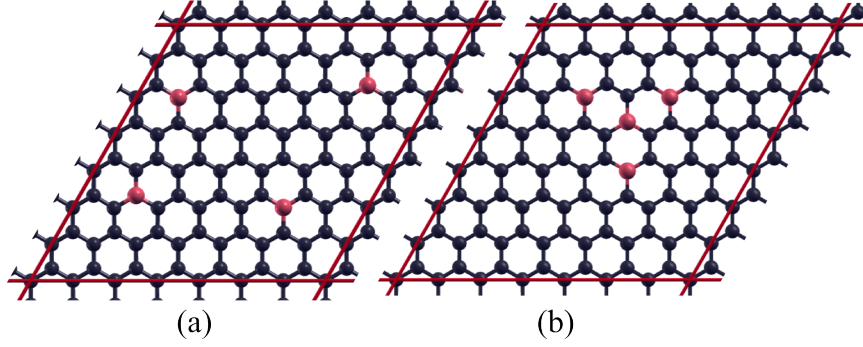


Fig. 4.10 - 7x7 unit cells with a homogeneous distribution of four boron atoms (a), or a BC<sub>3</sub>-like distribution (b). Boron atoms are depicted in red in the hexagonal carbon network (in black).

ergy differences. The calculations with GGA (results not shown) lead to the same conclusion since the energy differences ( $E_{\text{stab}}$ ) are very close although slightly more important than for LDA.

|                        | 3B(7x7) | 4B(7x7) | 10B(7x7) | 4B(9x9) | 9B(9x9) |
|------------------------|---------|---------|----------|---------|---------|
| $E_{\text{stab}}$ (eV) | 0.117   | 0.354   | 0.993    | 0.101   | 1.821   |

Table 4.3 - Energy difference between arrangements of boron atoms distributed homogeneously and grouped in BC<sub>3</sub> islands. The data for different number of atoms and different unit cells (between parentheses) are presented.

The main goal of the present study is to help analyzing and explaining STM images (see p.48 for the theory). The experimental images are provided by Minghu Pan from the Oak Ridge National Laboratory (ORNL). The sample is a boron-doped graphene sheet grown on a copper substrate. The exact boron concentration is not known, making the analysis more complicated. The next figures represent the different im-



ages provided. The two first (Figs. 4.11 and 4.12) are the largest images, obtained in constant-height mode and constant-current mode, respectively.

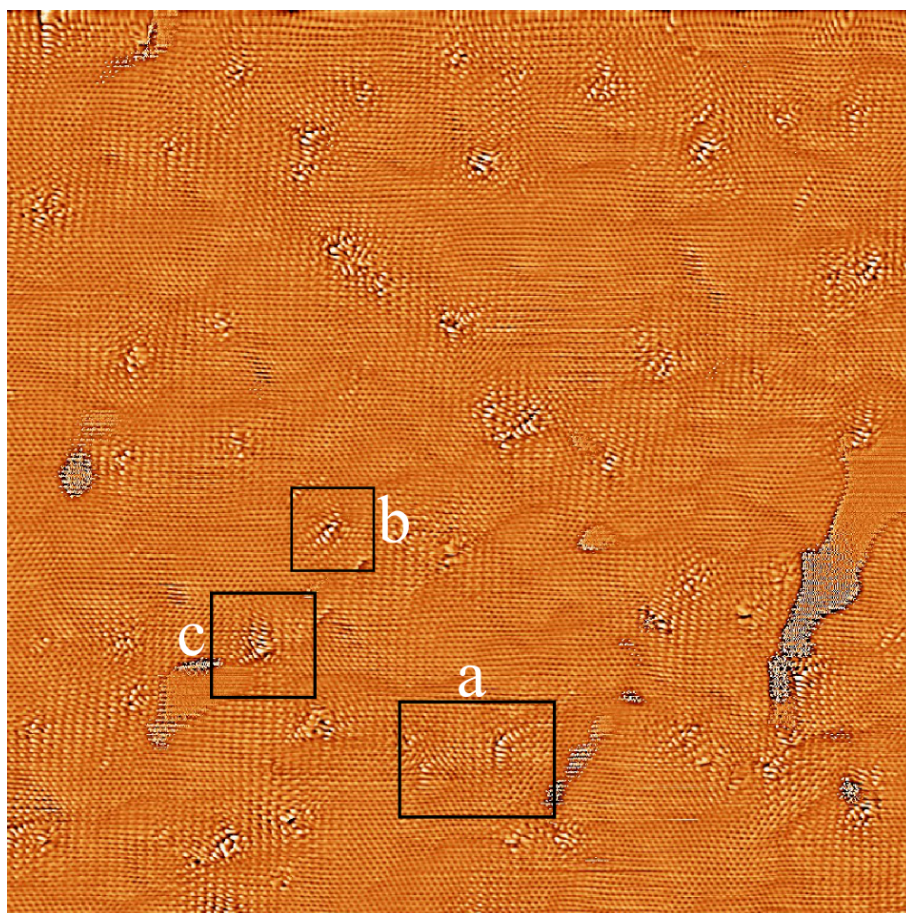
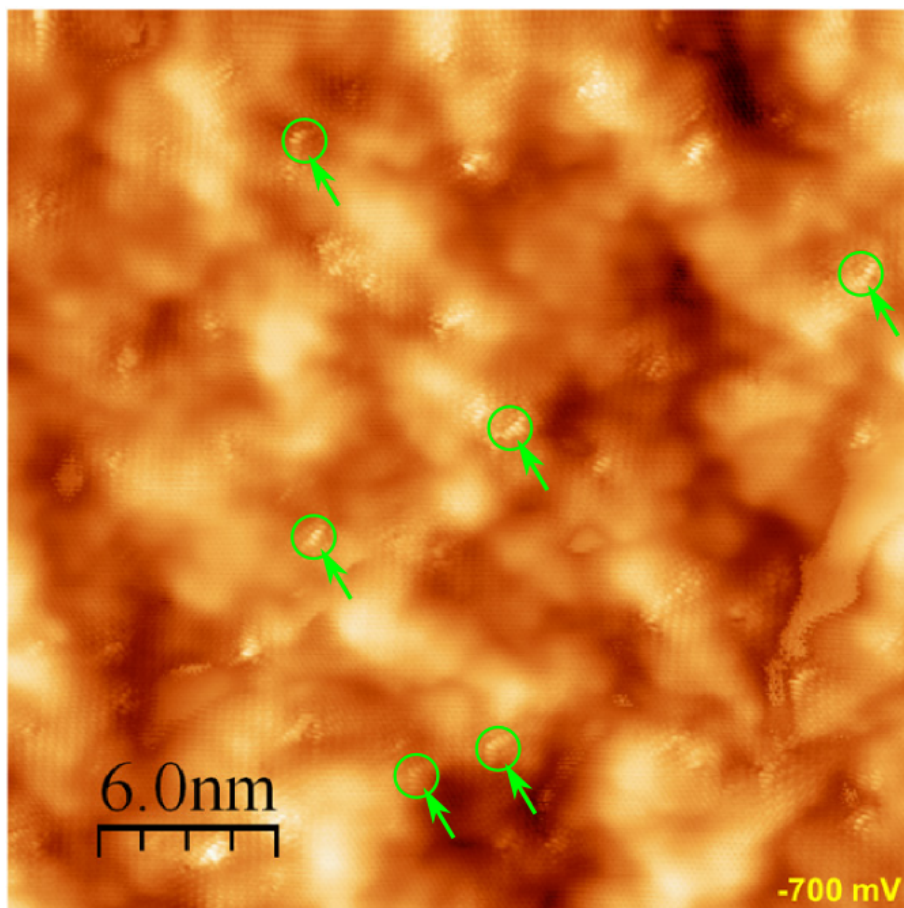


Fig. 4.11 - Experimental constant height STM image of boron-doped graphene grown on copper. a,b, and c illustrate a specific type of boron-doped defect frequently observed experimentally. The voltage of the tip is set at 700 mV. The scale is identical to Fig. 4.12. From M. Pan, ORNL.

#### 4. BORON AND NITROGEN DOPING OF GRAPHENE

---



---

Fig. 4.12 - Experimental constant current STM image of boron-doped graphene grown on copper. The voltage of the tip is set at 700 mV. The green circles highlight the “chevron” defect which is represented in Fig. 4.13. From M. Pan, ORNL.

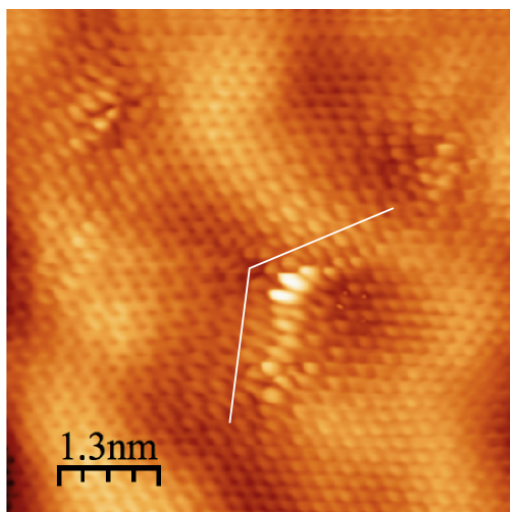
---

Figs. 4.13(a) and (b) display the images corresponding to the main defect investigated here. Focus is held on this particular defect because it is one of the simplest and one of the most abundant in the sample

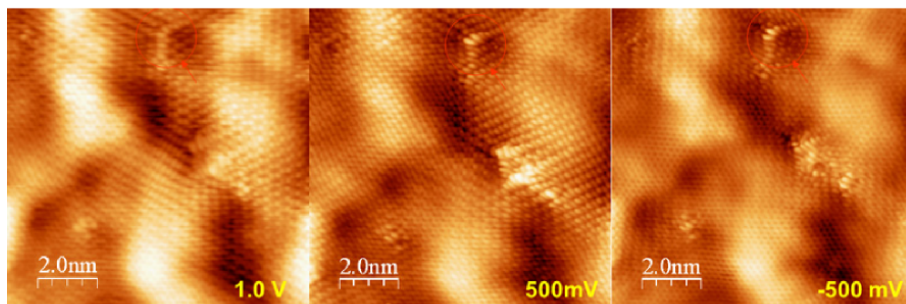
(Fig. 4.12). This defect has two or three bright spots in the middle and two lines of satellite peaks at  $120^\circ$ . It will be called the “chevron” defect because of its specific shape. The methodology to identify the atomic structure of the defect is first to start from the simplest case : one boron atom surrounded by perfect graphene (Fig. 4.14). Note that the result is similar to the one obtained in [95]. One can see some interesting features, as the presence of satellite peaks. However, the symmetry of the pattern is not correct. This defect has three branches of satellite peaks instead of only two for the chevron defect. To get closer to the defect, more boron atoms are added, always respecting the  $BC_3$  arrangement. In order to reproduce the correct symmetry, only structures exhibiting exactly one mirror plane and therefore no threefold symmetry are selected. Two boron atoms would not suit this criterium because the corresponding STM image would have two perpendicular mirror planes. Therefore, the next number of boron atoms which can be investigated is at least three. A problem arises when increasing the size of the defects. The calculations are performed in a fixed-size supercell. Larger defects mean smaller distances between defects and their image from neighboring cells, and therefore larger interaction effects. The size of the cell is increased for the larger defects when possible. Much larger unit cells ( $18 \times 18$ ,  $\sim 650$  atoms) are used for the most promising candidates for the chevron defect. Another issue linked to the size of the unit cells and to the experimental setup is the effect of doping on the Fermi level. Unfortunately the experimental position of the Fermi level is not known. It is a sum of doping arising from the addition of boron and of doping from the substrate. The former has a p-type doping effect while the latter has an n-type doping effect. To make things even worse, the corrugation of the surface (Fig. 4.12) gives rise to different doping

#### 4. BORON AND NITROGEN DOPING OF GRAPHENE

---



(a)



(b)

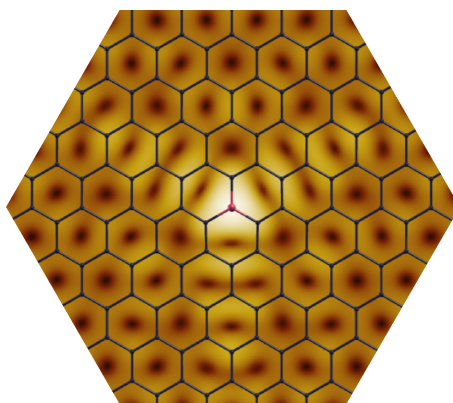
---

Fig. 4.13 - Experimental STM image of the chevron defect (a). White lines highlighting the directions of the defect. Images at different bias (1 V, 500 mV, and -500 mV) show the evolution of the pattern (b). From M. Pan, ORNL.

---



levels in different areas of the graphene sample. From a calculation point of view, changing the size of the unit cell without changing the number of incorporated boron atoms changes the doping concentration. Therefore, great care has to be taken when comparing defects inside different unit cells. Comparison with experiment is not straightforward since the Fermi levels are not aligned in the experiment and in the simulations. To cope with this issue STM images are produced for different energy windows which correspond to different tip voltages. The energy windows are sometimes shifted in order to reproduce different doping effects.




---

Fig. 4.14 - Simulated STM images for one boron atom substituted in graphene for an energy window from -250 meV to 250 meV.

---

The next figures present simulated images for the main defects investigated here. An image is given for a negative tip voltage (left images) and for a positive tip voltage (right images). Fig. 4.15 illustrates the case of the “croissant” defect. Three boron atoms are placed in the most compact arrangement that keeps the  $BC_3$  ratio. This defect is among the

#### 4. BORON AND NITROGEN DOPING OF GRAPHENE

---

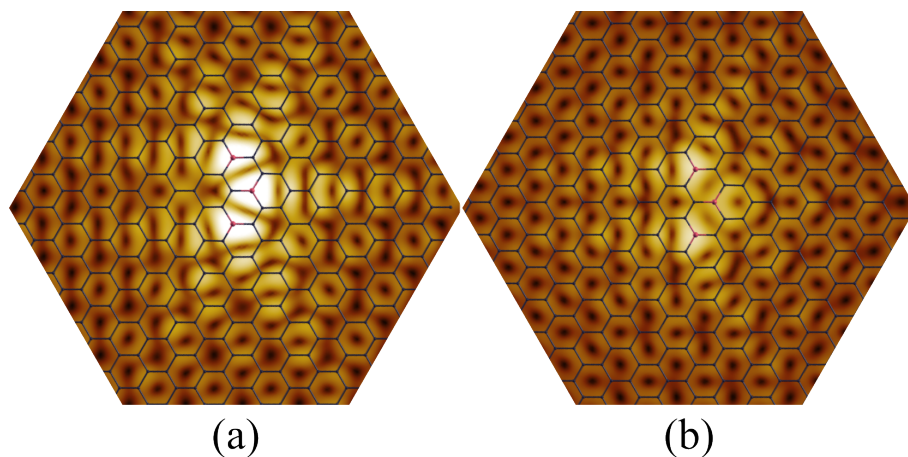


Fig. 4.15 - Simulated STM images for three boron atoms in the croissant configuration at -300 mV (a) (from M. Pan, ORNL.) and 300 mV (b) tip bias.

---

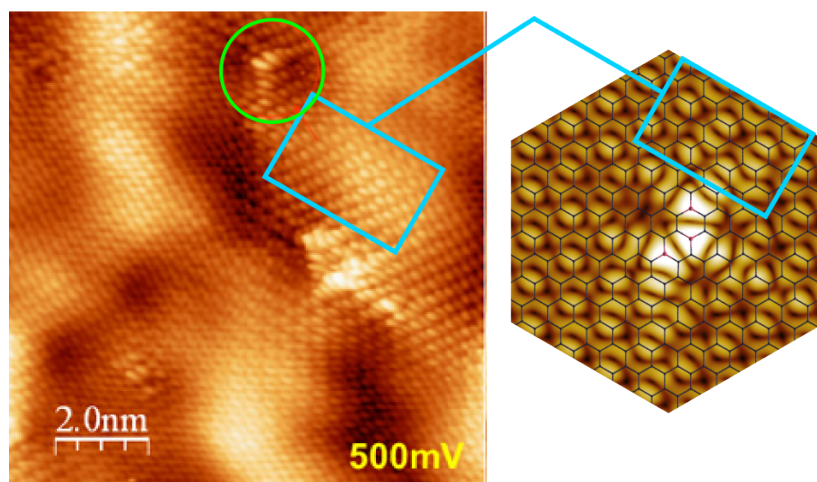


Fig. 4.16 - *Left.* Experimental image for the chevron defect. From M. Pan, ORNL. *Right.* Simulated STM images for three boron atoms in the croissant configuration for an energy window going from -200 meV to -100 meV. The green circle highlight the chevron defect. The blue rectangles highlight the pattern reproduced by the simulated images.

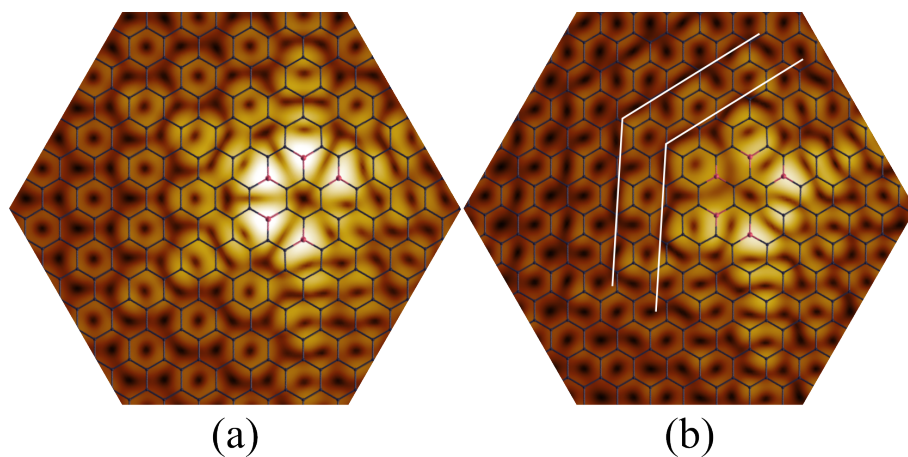
---

most promising candidates for the chevron defect. A smaller, 100 meV energy window (compared to the 300 meV for previous figures), highlights another similarity with the experimental image (Fig. 4.16). The depicted feature is observed to be related to the interaction between defects (Fig. 4.12), which agrees with the simulated image in which the defect is repeated periodically. Note also how, by comparing the three images for the croissant configuration (Figs. 4.15 and 4.16), a small change in the energy window can change the resulting image. This image exhibits bean-like satellite peaks having a shape and a size close to the ones from the chevron defect. Moreover, the symmetry of the defect is respected. The angle ( $120^\circ$ ) between the two main satellite axes is reproduced (see the white lines in Fig. 4.13(a)). The number of main peaks is also coherent with the experimental images. A close look at the upper part of Fig. 4.13(b) shows a modification of the number of main peaks associated with the defect (two or three depending on the voltage of the tip). Fig. 4.15(b) shows the quenching of the main peak centered on the central boron atom leading to two main peaks. The other images exhibit three peaks. The croissant defect can therefore reproduce the switching effect between two and three main peaks.

Fig. 4.17 is an extension of the croissant defect. Two more boron atoms are added in order to give a “C” shape to the defect, keeping the  $\text{BC}_3$  structure. This defect shares some features with the previous defect making it a good candidate too. Indeed, as seen on the right panel, three main peaks are almost invisible at some energies, leaving only two bright peaks. For the same energy window, the satellite peaks are well reproduced as well (shape, size, orientation). Another more subtle feature of the chevron defect is the presence of a secondary shell of peaks that follows closely the behavior of the main and satellite peaks.

#### 4. BORON AND NITROGEN DOPING OF GRAPHENE

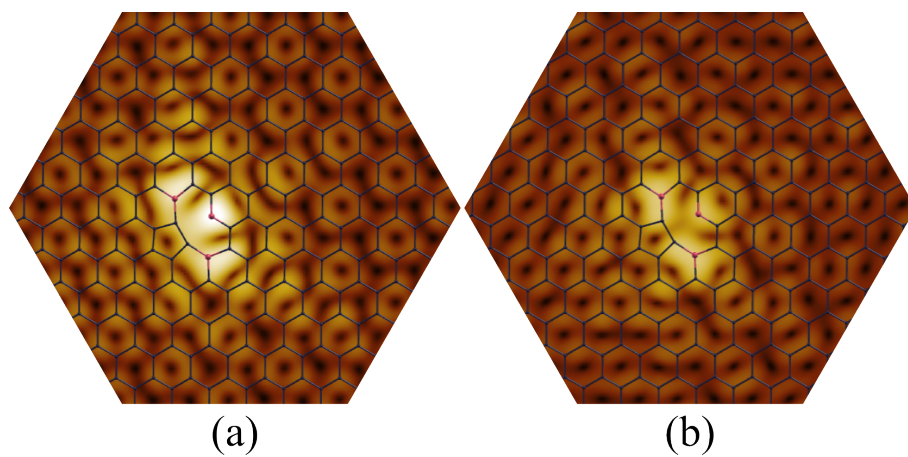
---



---

Fig. 4.17 - Simulated STM images for five boron atoms in a BC<sub>3</sub> configuration at -300 mV (a) and 100 mV (b) tip bias. The white lines highlight the secondary shell of peaks.

---



---

Fig. 4.18 - Simulated STM images for three boron atoms and a single vacancy in the croissant configuration at -300 mV (a) and 300 mV (b) tip bias.

---



This can be observed between the white lines and the brightest peaks of Fig. 4.13(a). A similar feature is seen on the right image of Fig. 4.17. White lines are there to compare with the experimental image. The only flaw with this defect is the appearance of more than three bright peaks at different biases (left panel). However, since the experimental doping level is not known, these peaks might lie outside the experimental energy windows. Bigger defects are also investigated but not presented here. They are composed of six, seven, eight, nine, and ten boron atoms. The  $BC_3$  ratio and the symmetries of the chevron defect are respected. With the increasing number of atoms, different structures are possible which fulfill all the criteria. They are also investigated. A common feature however is the ability to light on and off some of the main peaks for each of these defects.

To see if another defect can get closer to the experimental chevron defect, structural point defects are combined with the boron defects. Vacancies are very common topological defects in graphene. The  $c$  defect in Fig. 4.11 corresponds to the signature of a vacancy [69] and proves the presence of vacancies in the sample. Therefore, combinations of boron atoms and vacancies are also investigated. Fig. 4.18 represents a single vacancy with three boron atoms (similar to the croissant defect). Here again, the main features of the chevron defect are present. The left panel of Fig. 4.18 exhibits satellite peaks at the right angle with the right bean-like shape. However, no simulated image has been found yet that exhibits only two peaks as the chevron defect does.

While the single boron atom does not fit the symmetry of the chevron defect, one boron atom combined with a vacancy does. Two configurations of such specific defects are studied. The first one has a boron atom on the pentagon of the single vacancy (Fig. 4.19). The second

#### 4. BORON AND NITROGEN DOPING OF GRAPHENE

---

configuration has the boron atom on the nonagon of the single vacancy (Fig. 4.20). The green bond on Figs. 4.19 and 4.20 corresponds to a bond that is larger than the usual 1.42 Å carbon-carbon distance in graphene. Both cases exhibit satellite peaks at the right angle. The main peaks, however, show some discrepancies with the experimental image. The boron atom on the pentagon exhibits a bright peak. The resulting image displays a main peak too prominent from the satellite peaks. No single energy window is found to quench the main peak and to keep the satellite peaks at the same time. The second case exhibits a smoother angle, closer to the experimental pattern. However, apparently a third satellite branch (although dimmer) seems to originate from the pentagon of the single vacancy, leading to the wrong symmetry. Moreover, no energy window presents other main peaks than the central one. Finally, the nonagon case is found to be 2.3 eV lower in energy than the pentagon case. The former should therefore be more present than the latter (if present at all). More defects including structural defects are depicted in the Figs 4.21-4.24. Here, one boron atom is added to a  $t5t7$  divacancy. Four different inequivalent positions are studied. Tab. 4.4 shows the difference between the energy of the different cases and the configuration where the boron atom is the farthest away from the divacancy ( $E_{\text{Sep.}}$ ). The different positions for the boron atom are : at the center of the divacancy, at the 1<sup>st</sup>, 2<sup>nd</sup>, and 3<sup>rd</sup> nearest neighbor (NN) position to the central atom of the divacancy. The 1<sup>st</sup> NN case is clearly the most stable (at least 440 meV lower than the second most stable case), while the case where the divacancy and the boron atom are far apart is the less stable by far (more than 1 eV higher). As a conclusion, if divacancies and boron atoms are present in the sample, the energetics point of view highly favor the case where boron lies on

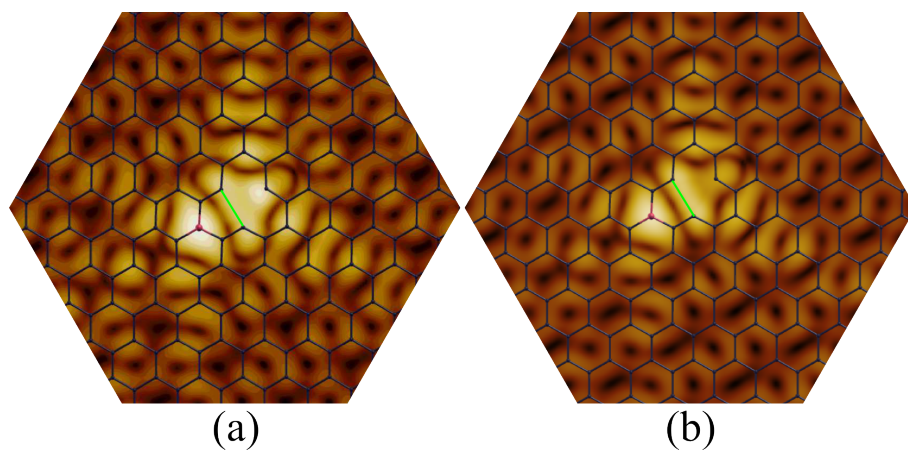


Fig. 4.19 - Simulated STM images for one boron atom on the pentagon-site of a single vacancy at -300 mV (a) and 300 mV (b) tip bias.

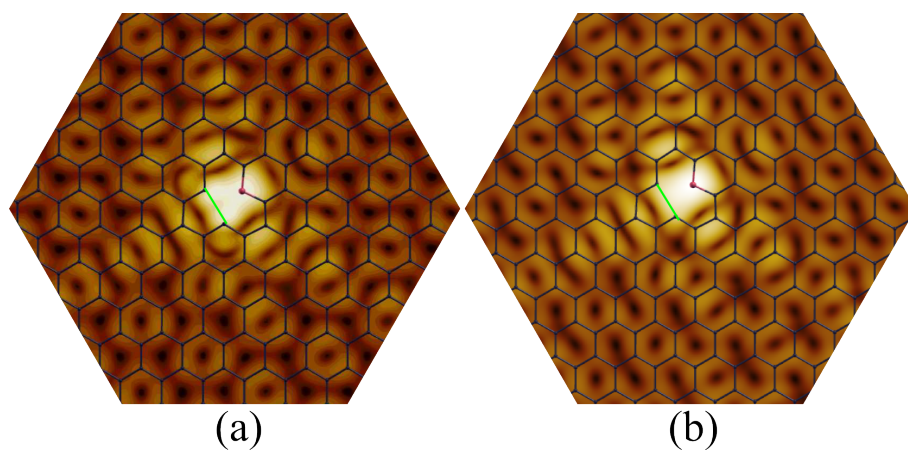


Fig. 4.20 - Simulated STM images for one boron atom on the nonagon-site of a single vacancy at -300 mV (a) and 300 mV (b) tip bias.

#### 4. BORON AND NITROGEN DOPING OF GRAPHENE

| $\alpha$                          | Center | 1 <sup>st</sup> NN <sub>c</sub> | 2 <sup>nd</sup> NN <sub>c</sub> | 3 <sup>rd</sup> NN <sub>c</sub> | Sep.  |
|-----------------------------------|--------|---------------------------------|---------------------------------|---------------------------------|-------|
| $E_\alpha - E_{\text{Sep.}}$ (eV) | -1.655 | <b>-2.095</b>                   | -1.023                          | -1.133                          | 0.000 |

Table 4.4 - Energy difference between  $E_\alpha$  and  $E_{\text{Sep.}}$ , where  $\alpha$  corresponds to the location of the boron atom. The most stable structure is the one where the boron atom is the 1<sup>st</sup> nearest neighbor to the center atom of the divacancy.

a site of the divacancy. The final geometry of the sample, however, is not only governed by the thermodynamics. Kinetic processes certainly play an important role too. Therefore, STM images are calculated for the four cases with the boron atom on a site of the divacancy. Figs. 4.21,

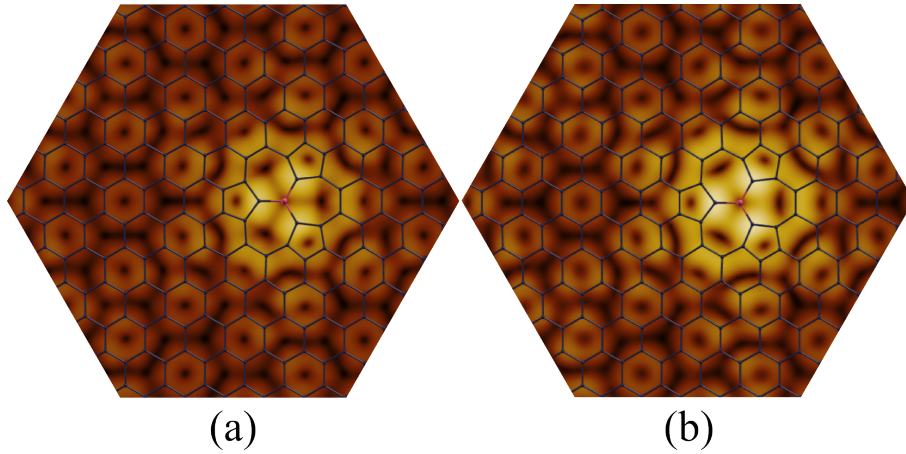
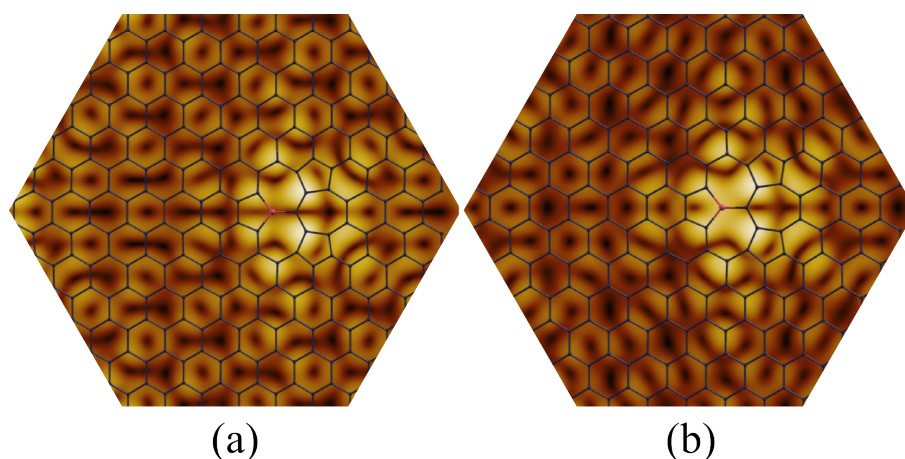


Fig. 4.21 - Simulated STM images for one boron atom and a  $t5t7$  divacancy at -200 mV (a) and 300 mV (b) tip bias. The boron atom is at the center of the divacancy.

4.22, 4.23, and 4.24 depict the images for the boron atom on the center of a  $t5t7$  divacancy, at the 1<sup>st</sup>, 2<sup>nd</sup>, and 3<sup>rd</sup> nearest neighbor (NN) position to the central atom of the divacancy, respectively. Different

features appear as for example bigger lobes than the structures seen so far. Another interesting characteristic is the different orientations of the peaks with respect to the graphene lattice. These cases might therefore be good candidates for the  $b$  defect in Fig. 4.11. This last point of view has not yet been fully applied to the experimental images to screen candidates for other defects. It is interesting to note that the right panels of Figs. 4.22 and 4.24 exhibit very similar STM patterns. The only difference is the orientation of this pattern. It looks like this signature is characteristic of the divacancy and that the orientation is fixed by the position of the boron atom.




---

Fig. 4.22 - Simulated STM images for one boron atom and a  $t5t7$  divacancy at -200 mV (a) and 200 mV (b) tip bias. The boron atom is at the first nearest neighbor to the center of the divacancy.

---

A clear identification of the experimental defects is possible but it would require scanning tunneling spectroscopy (STS) images close to the defect. STS consists of I-V curves measured very locally on and in the

#### 4. BORON AND NITROGEN DOPING OF GRAPHENE

---

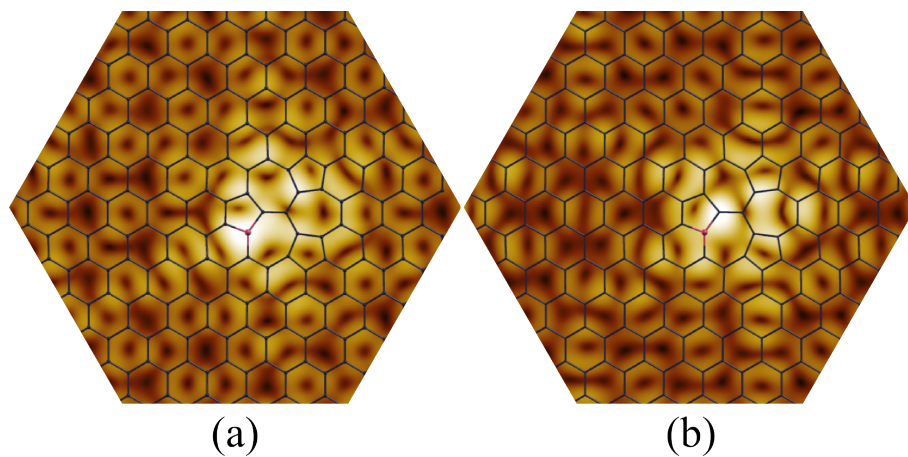


Fig. 4.23 - Simulated STM images for one boron atom and a  $t5t7$  divacancy at -200 mV (a) and 300 mV (b) tip bias. The boron atom is at the second nearest neighbor to the center of the divacancy.

---

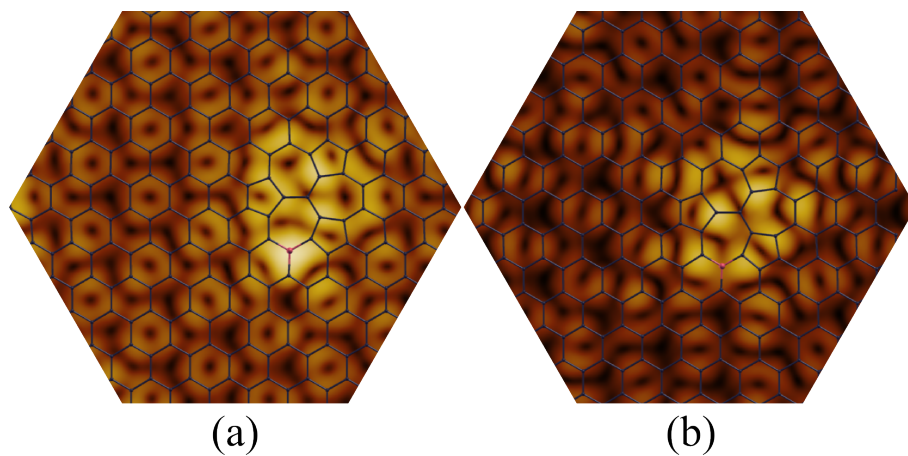


Fig. 4.24 - Simulated STM images for one boron atom and a  $t5t7$  divacancy at -200 mV (a) and 300 mV (b) tip bias. The boron atom is at the third nearest neighbor to the center of the divacancy.

---

neighborhood of the defect. It is a detailed map of the local electronic tunneling behavior. It is a way to focus on the defect itself, highlighting the differences with the pristine graphene properties. They are particularly interesting since they attribute specific fingerprints to each defect. Such measures can also be simulated with SIESTA by the combination of projected DOSs on each atom of the defect. Fig. 4.25 represents the simulated STS curve on the three boron atoms of the croissant defect. Other curves can be computed on the neighboring carbon atoms in order to have STS curves along a given path. Experimental STS images along the same path would definitely validate (or discard) the croissant defect as the right candidate for the chevron defect.

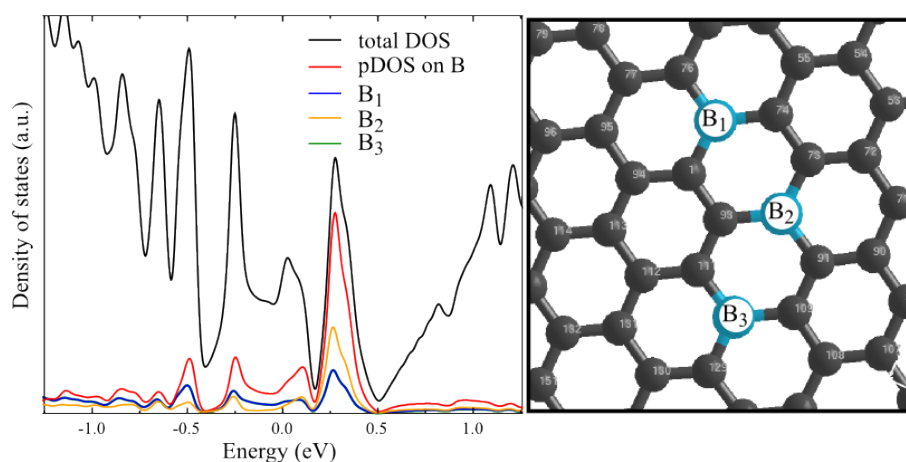


Fig. 4.25 - Simulated STS curves for a tip centered on the boron atoms of the croissant defect (labeled by B<sub>1</sub>, B<sub>2</sub>, and B<sub>3</sub>). In addition, the pDOS on the boron atoms (in red) is plotted along with the total DOS (in black).

### 4.3 Conclusion

To conclude this part, more images are shown in the appendices on p.187. These figures illustrate  $BC_3$  defects as well as boron atoms combined with structural defects (divacancies and Stones-Thrower-Wales defects). These last ones might also be good candidates for the defects such as defect *b* of Fig. 4.11. However, the defects depicted here are representative of the range of features which are found. Some of them exhibit interesting features compared to experiment. The main candidates for the chevron defect are the small  $BC_3$ -like defects with three or five boron atoms. The addition of structural defects results in other interesting candidates, such as the single vacancy with three boron atoms. Other structures (not  $BC_3$  anymore) are investigated and might be candidates for other experimental defects than the chevron one. This last point should be investigated more thoroughly though.

The combination of experimental and simulated STS images is a good way to cross-check the results and to validate or invalidate the theoretical model. Unfortunately, in the present case the lack of experimental STS measures does not allow such analysis.

The next chapter will combine graphene and boron nitride in the same sheet. The electronic properties as well as the quantum transport properties will be presented.



## Chapter 5

# Graphene-boron nitride nanoribbons and composites

As mentioned in the introductory chapter, boron nitride shares a lot of its structure with graphene. Both diamond and graphite have an analogue made of boron nitride (cubic boron nitride c-BN, and hexagonal boron nitride h-BN, respectively). The electronic properties however are different. Boron nitride always exhibits an insulating behavior which is also conserved in BN-based nanostructures.

A single sheet of boron nitride has been synthesized, identical to graphene, by using the same exfoliation technique [100]. One-dimensional boron nitride systems include mainly nanotubes and nanoribbons. Since the fabrication techniques for graphene and boron nitride are similar, graphene-composites have been synthesized and studied theoretically as a new way to tailor graphene's properties [26]. Stacked composites can be distinguished from mixed composites. The former is a stacking of graphene and single sheet(s) of boron nitride,

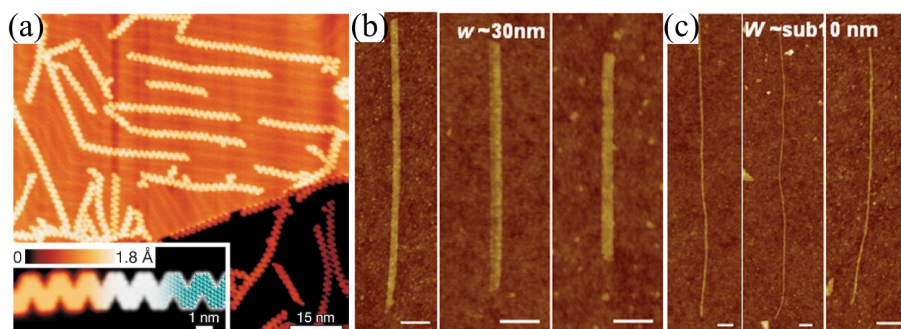
## 5. G-BN NANORIBBONS AND COMPOSITES

---

while the latter is a plane with boron nitride and graphene areas. This chapter focuses on this latter case. Before focusing on composite ribbons, the properties of pure graphene and boron nitride ribbons are detailed.

### 5.1 Graphene nanoribbons

One of the modifications that can be brought to graphene is the reduction of its dimensionality. Starting from the infinite two-dimensional plane, the confinement to one dimension leads to nanoribbons (GNRs) or nanotubes (CNTs). Fig. 5.1 presents experimental images evidencing different kinds of GNRs. Different geometries and sizes can be produced.



---

Fig. 5.1 - Experimental evidence of GNRs. (a) is extracted from [101], (b) and (c) from [102]. The synthesis method is different, leading therefore to different geometries.

---

In a honeycomb lattice, two preferred directions exist to cut a ribbon. They are highlighted in red and green in Fig. 5.2. These directions de-

fine zigzag and armchair edges, respectively. There are therefore zigzag GNRs (zGNRs) and armchair ones (aGNRs). To define the width of the ribbons, a number is put in front of the abbreviations N-zGNR/N-aGNR. For the zGNRs, this number corresponds to the number of tilted carbon-carbon bonds along the width of the ribbon, while for the aGNRs it is the number of carbon-carbon dimers parallel to the axis of the ribbon that lies across the width of the ribbon. When not specified, GNRs' edges are considered to be passivated with one hydrogen atom per edge atom. This applies to the rest of this section.

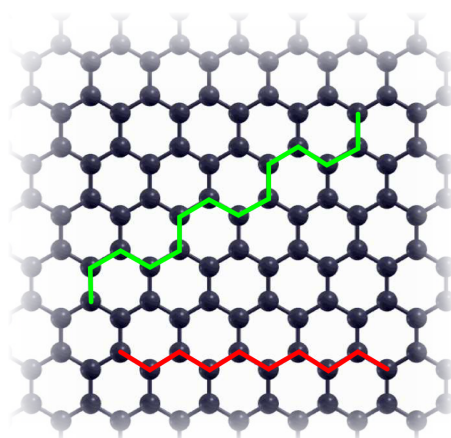


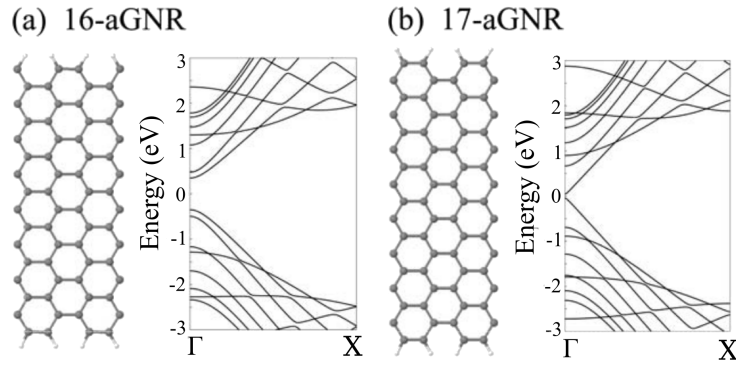
Fig. 5.2 - Preferred directions for the edges of GNRs: zigzag (red) and armchair (green).

The electronic picture is very different for these two kinds of ribbons. Next figures (Figs. 5.3 and 5.4) summarizes the behavior of the electronic properties [103]. The aGNRs are always semiconducting. However, the gap of these ribbons does not vary monotonically. The aGNRs can be splitted in three groups, each exhibiting a monotonic decrease

## 5. G-BN NANORIBBONS AND COMPOSITES

---

in the energy gap [104]. Therefore, the decrease of the energy gap in Fig. 5.3 when going from a 16-aGNR to a 17-aGNR does not reflect the general trend.



---

Fig. 5.3 - Atomic structures and electronic band structures of two aGNRs : (a) a 16-aGNR, and (b) a 17-aGNR.

---

Without including any spin freedom, the zGNRs are metallic and present flat bands at the Fermi level, as seen on Fig. 5.4(a). These almost-flat bands are known to allow spontaneous spin polarization of the zGNRs [104–108]. This polarization is mainly localized on the edges. The two cases with the lowest energy have almost the same total energy, therefore preventing the clear identification of one of them as the ground state. The first spin polarization case is the parallel one, also called ferromagnetic case ( $\uparrow\uparrow$ ) and the second is the antiparallel, or antiferromagnetic case ( $\uparrow\downarrow$ ). The corresponding band structures are represented in Figs. 5.4 (c) and (b), respectively. The latter is a semiconductor and the corresponding band structure is fully degenerate, while the former is metallic and exhibits a spin-dependent band structure. So far,

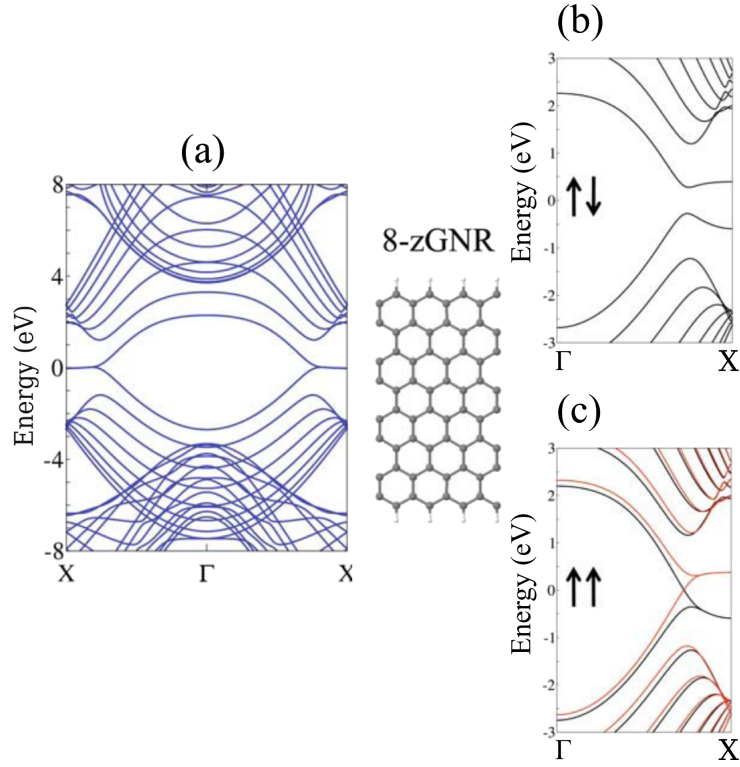
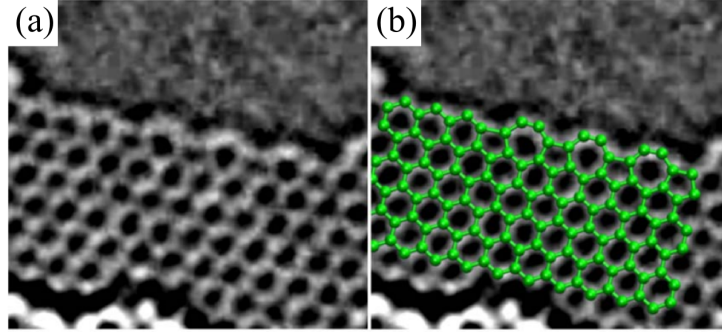


Fig. 5.4 - Atomic structures and electronic band structures for a 8-zGNR : (a) with non-magnetic spin ordering, (b) and (c) with antiparallel spin alignment ( $\uparrow\downarrow$ ) and parallel spin alignment between edges ( $\uparrow\uparrow$ ), respectively. In (c), red and black colors are used for both spin polarizations.

ribbons are either semiconducting, either metallic with two conducting channels at equilibrium. After the study of armchair and zigzag edges, other kinds of edges were experimentally evidenced [109]. Fig. 5.5 taken from [110] (which is an enhanced snapshot of a video from [109]) shows this reconstruction. It is called the zz57 reconstruction. It was

## 5. G-BN NANORIBBONS AND COMPOSITES

---



---

Fig. 5.5 - Experimental evidences of zz57 reconstruction along with zigzag edges. Images extracted from Koskinen, *et al* [110].

---

proposed as an alternative to the less stable bare zigzag edge. The chemical reactivity of the edges is lower than compared to the zigzag edge. It is therefore referred to as self-passivation of the zigzag edge. This reconstruction is composed of alternating pentagons and heptagons (see Fig. 5.6(a)). The shape at the edge is closer to the armchair geometry. Along with the self-passivation of the edges, the electronic properties of the reconstructed zGNR are modified in two ways : the spin polarization effects are lost and only one electronic band structure is found with each band doubly degenerate, for the two spin orientations, and second, one more channel is available for electronic transport at equilibrium (see Figs. 5.6(b) and (c)).

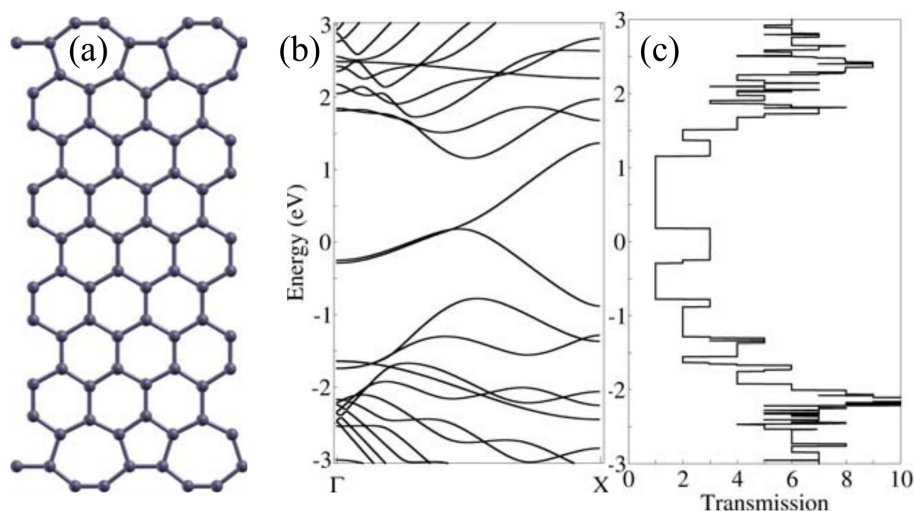


Fig. 5.6 - Atomic structure (a), electronic band structure (b) and quantum conductance (c) of an 8-zGNR with a reconstructed edge containing pentagons and heptagons (zz57).

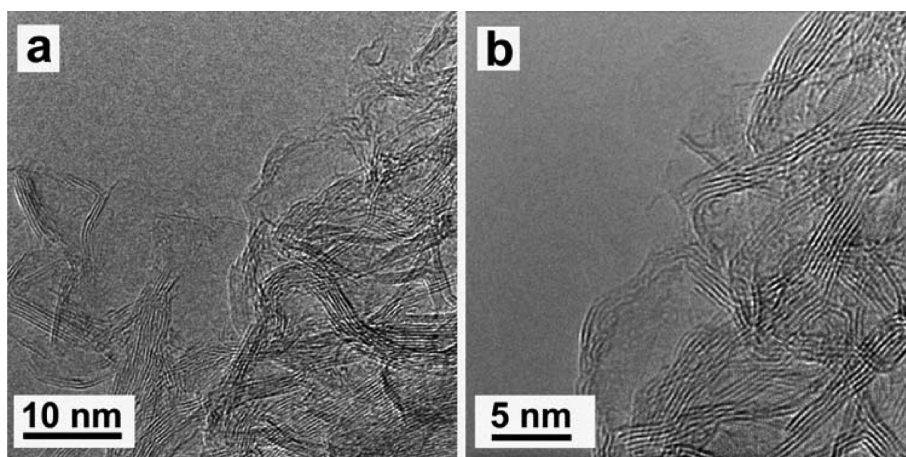
## 5.2 Boron nitride nanoribbons

As for GNRs, boron nitride nanoribbons (BNNRs) have also been synthesized through different methods [111–114] (Fig. 5.7). Depending on their size, edge geometry, and edge termination, they exhibit a whole range of properties [111, 114–116]. In addition, the energy gap of a BNNR with hydrogen passivated edges (h-BNNR) can be modulated by a transverse electric field [117–119]. Zigzag BNNRs (zBNNRs) without passivated edges exhibit a metallic behavior, independently of their spin polarization, unlike GNRs which are either metallic or semi-conducting. zBNNRs might therefore be of high interest in situations requiring a stable metallic state such as connections in nanodevices for

## 5. G-BN NANORIBBONS AND COMPOSITES

---

example. The origin of the metallic behavior of zBNNRs is the presence of localized dangling bonds, induced by edge atoms. When passivated, the zBNNR loses the dangling bonds and the metallic behavior disappears. Hydrogen-passivated ribbons are thus insulators. For armchair BNNRs (aBNNRs) the non-passivated edges experience strong atomic reconstruction, therefore reducing the localization of the edge states. Therefore, independently of the passivation or not of the edges, aBNNRs are always semiconducting. The zBNNR metallic case exhibits, as for graphene, different spin polarization cases, as illustrated in the present section.



---

Fig. 5.7 - HRTEM experimental images at different magnification of a complex BN structure (so-called nano-urchins). Some BN layers protrude from this structure, exposing their bare edges. Images extracted from [111].

---

The calculations of this section use LSDA as implemented in both ABINIT and SIESTA. Norm-conserving pseudopotentials are used for both cases. ABINIT is used for the smallest unit cells (unitary unit cells). A 10 Å vacuum is used to ensure no interaction between neigh-



boring ribbons. Convergence studies prove this to be enough to avoid influence between different unit cells. A 30 Ha cutoff energy is used to expand the plane-waves basis set in ABINIT. A summation over 40  $k$  points is used to replace the full integration on the 1D Brillouin zone. The SIESTA calculations are done with a DZP basis set. The cell stud-

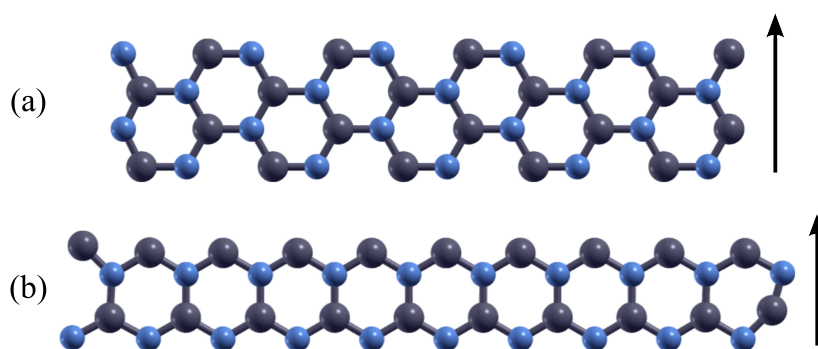


Fig. 5.8 - Optimized atomic structures of two infinite BNNRs with (a) zigzag and (b) armchair non-passivated edges. The 10-zBNNR is  $\sim 2$  nm wide and its unit cell contains 20 atoms (40 atoms in the present double unit cell) (a). The 20-aBNNR is  $\sim 2.3$  nm wide and its unit cell contains 40 atoms (b). Blue and grey circles denote nitrogen and boron atoms, respectively. The direction of the periodicity is perpendicular to the represented unit cells.

ied here is two times bigger than the unit cell. The reason for the use of this double unit cell will become clear later in this section. A 550 Ry mesh cutoff is used. The energy levels are populated according to the Fermi-Dirac distribution with an electronic temperature of 300 K. Only 14  $k$  points are needed to converge the results of the double cells. The forces on atoms and on the unit cell are reduced after relaxation to values as low as 0.01 and 0.05 eV/Å, respectively.

## 5. G-BN NANORIBBONS AND COMPOSITES

---

A first calculation is performed on an ideal BN sheet. Its lattice constant is found to be 2.49 Å and it exhibits a direct band gap at the K point of 4.7 eV (p.19). These results are in agreement with previous calculations [31] but for one detail : the band gap is indirect after inclusion of GW corrections to the LDA band structure, while it is direct for LDA calculations. ABINIT is used to check SIESTA's results only for the armchair and zigzag ribbon without inclusion of the spin. Fig. 5.8 illustrates the unit cells that are used for the SIESTA calculations. The unit cell for the zBNNR is twice as big as the one used for ABINIT. The two ribbons studied are : a 10-zBNNR (width  $\sim 2$  nm) with ten inclined B-N bonds along the width of the ribbon ; and a 20-aBNNR (width  $\sim 2.3$  nm) with twenty parallel B-N bonds along the width of the ribbon. The length of the unit cell is 2.48 Å and 4.30 Å for the 10-zBNNR (the single cell) and the 20-aBNNR, respectively. These values are very close to the ones for a single BN sheet. There is only a slight reconstruction of the edges of the 10-zBNNR. The bond at the center of the ribbon is 1.43 Å long while at the edges it is only of 1.38 Å. The 20-aBNNR, however, experiences a much larger reconstruction. Indeed, the edge bond has a 1.29 Å length. In addition, the angles on the edges are significantly modified, as seen on the right side of Fig. 5.8(b).

Fig. 5.9 depicts the band structures for the two ribbons without spin. It confirms the metallic properties of the 10-zBNNR, as well as the large indirect band gap (4.2 eV) semiconductor character of the 20-aBNNR. Moreover, the edge states (ES) and dangling bonds (DB) are indicated by arrows. Fig. 5.10 illustrates the shape of these states. As their name suggests, edge states are localized on the edge atoms, exhibiting a strong  $p_z$  type. Dangling bonds are  $sp^2$  bonds lacking an electron due to the finite width of the ribbon and the missing neighbor

atoms at the edge. The flat band around Fermi level associated with the dangling bonds are supposed to give rise to magnetism [107]. Therefore, spin polarized calculations are conducted on the 10-zBNNR to study the possible spin polarization cases. In addition to the two spin

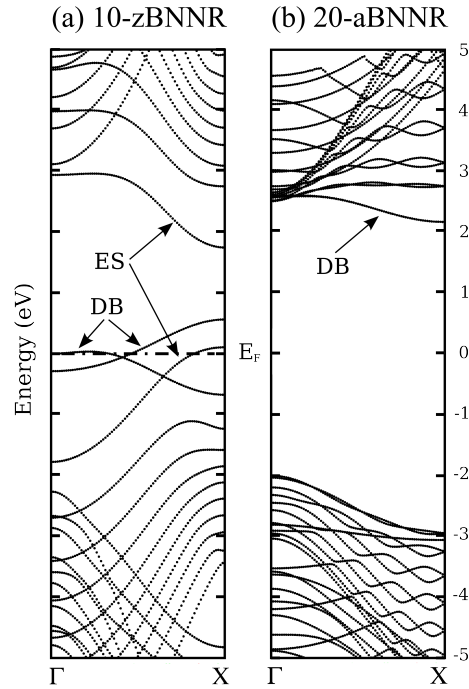


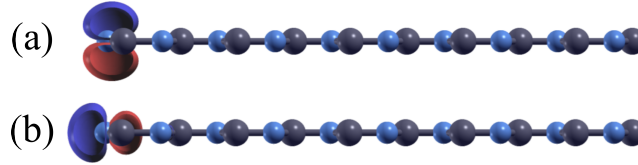
Fig. 5.9 - Band structures of a 10-zBNNR (a) and a 20-aBNNR (b), displaying metallic and semiconducting behaviors, respectively. The Fermi energy is positioned at 0 eV. Both edge (ES) and dangling bond (DB) states are indicated by arrows.

polarization cases existing for GNRs, more cases are expected in BN-NRs. A double unit cell is therefore used. Five cases can be considered in this double unit cell. One edge of the ribbon is only terminated by

## 5. G-BN NANORIBBONS AND COMPOSITES

---

nitrogen, the other by boron. Therefore, the following notation is used :  $N_{\uparrow\uparrow} - B_{\downarrow\downarrow}$ . This stands for the situation where the nitrogen-terminated edge has a ferromagnetic up polarization and the boron one has a fer-




---

Fig. 5.10 - Edge (a) and dangling bond (b) states on the nitrogen edge of a 10-zBNNR. Analogous states are also present on the corresponding boron edge (not shown here).

---

romagnetic down polarization. The five possible cases are :  $N_{\uparrow\uparrow} - B_{\uparrow\uparrow}$ ,  $N_{\uparrow\uparrow} - B_{\downarrow\downarrow}$ ,  $N_{\uparrow\uparrow} - B_{\uparrow\downarrow}$ ,  $N_{\uparrow\downarrow} - B_{\uparrow\downarrow}$ , and  $N_{\uparrow\downarrow} - B_{\uparrow\uparrow}$ . Of these five configurations, the three first are predicted to be 200 *meV* lower in energy. These results compare well with previously obtained ones [120]. The energy differences between the three lower states are lower than a few *meV*. This energy is not significant enough to draw a clear conclusion on the ground state [121,122]. One expects the three lowest polarization cases to be accessible at room temperature. The spin polarization density for these three cases is represented in Fig. 5.11.

Fig. 5.12 presents the band structures for the three cases illustrated in Fig. 5.11. It confirms the metallic behavior of bare-edge zBNNRs, regardless of the spin polarization case. As for the non-polarized spin case, strongly localized states can be identified. The different spin polarization cases can be explained by carefully counting the filled bands that correspond to ESs and DBs. On one hand, the edge state on the

nitrogen edge ( $N^{\text{ES}}$ ) is fully occupied by up electrons and only partially by spin down electrons ( $n_{\text{occ}} \sim 3/4$ ), giving rise to a  $1/4\mu_{\text{B}}$  contribution to the total spin polarization. Moreover, the dangling bond on the nitro-

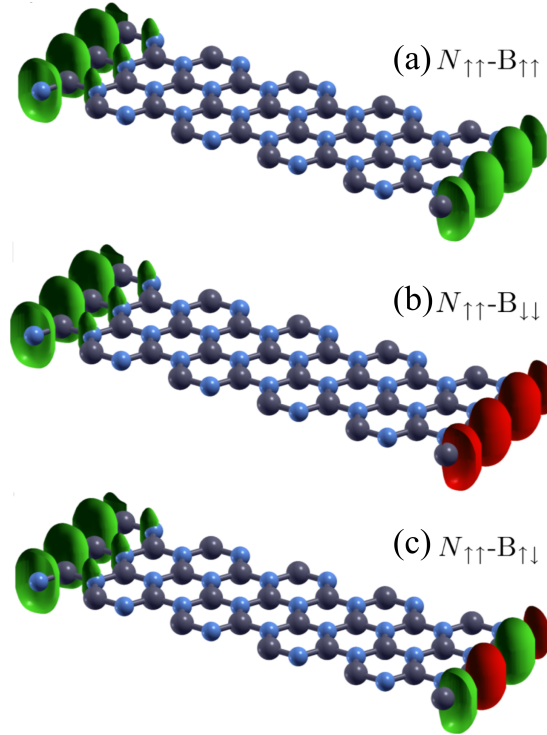


Fig. 5.11 - Spin polarization density for (a) the  $N_{\uparrow\uparrow} - B_{\uparrow\uparrow}$ , (b) the  $N_{\uparrow\uparrow} - B_{\downarrow\downarrow}$ , and (c) the  $N_{\uparrow\uparrow} - B_{\uparrow\downarrow}$  spin polarization cases. The nitrogen edge is on the left, the boron one on the right. Red and green colors correspond to a positive and negative charge density of  $0.005 \text{ e}^-/\text{Bohr}$ .

gen edge ( $N^{\text{DB}}$ ) is fully occupied by spin up atoms and filled up to  $1/4$  for the spin down electrons, leading to a  $3/4\mu_{\text{B}}$  up polarization. Therefore, the total spin polarization on the nitrogen edge is of  $1\mu_{\text{B}}$ . On the

## 5. G-BN NANORIBBONS AND COMPOSITES

other hand, for the boron edge only the dangling bond is filled for spin down electrons. The sum of the boron and nitrogen edge gives the total spin polarization case  $N_{\uparrow\uparrow} - B_{\downarrow\downarrow}$  as depicted in Fig. 5.12(a). The same

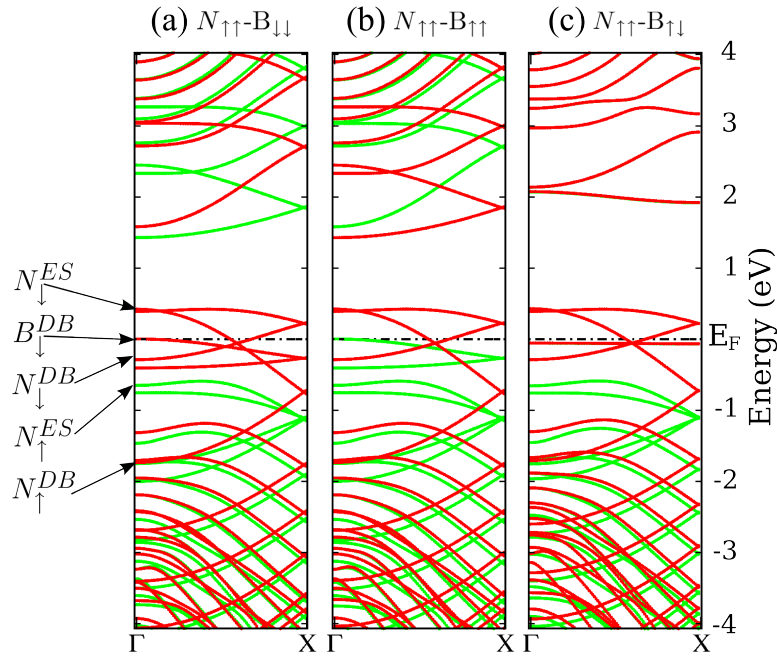


Fig. 5.12 - Spin-dependent band structure for (a) the  $N_{\uparrow\uparrow} - B_{\downarrow\downarrow}$ , (b) the  $N_{\uparrow\uparrow} - B_{\uparrow\uparrow}$ , and (c) the  $N_{\uparrow\uparrow} - B_{\uparrow\downarrow}$  spin polarization cases. The localized states (edge states and dangling bonds) are indicated by arrows on the first band structure. Green and red stands for the two spin orientations.

argument applies to the two other cases. For the  $N_{\uparrow\uparrow} - B_{\uparrow\uparrow}$  case, the dangling bond on the boron edge is filled by spin up electrons. Because of the higher number of spin polarization configurations compared to GNRs, their close total energy, and the role played by edge states in

the polarization, one can conclude that in contrast to what happens in GNRs, ES and DB are easily screened in zBNNRs.

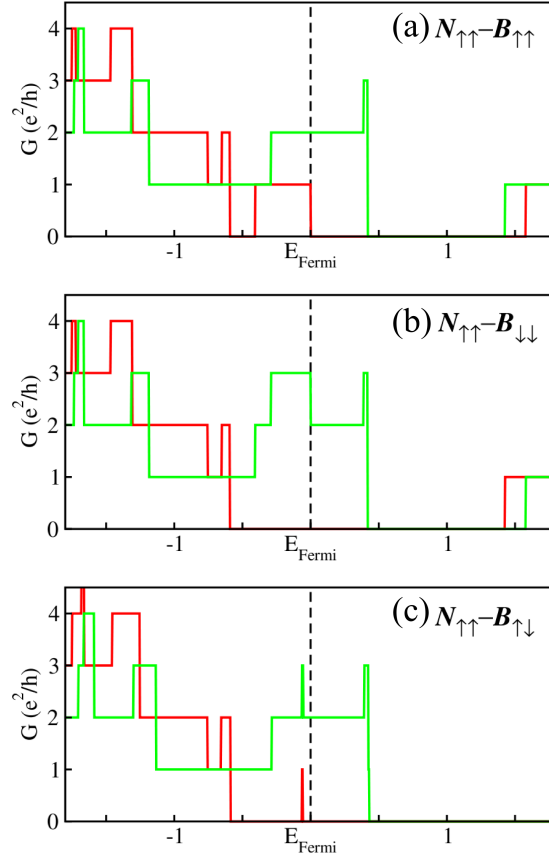


Fig. 5.13 - Conductance at equilibrium for (a) the  $N_{\uparrow\uparrow} - B_{\uparrow\uparrow}$ , (b) the  $N_{\uparrow\uparrow} - B_{\downarrow\downarrow}$ , and (c) the  $N_{\uparrow\uparrow} - B_{\uparrow\downarrow}$  spin polarization cases. Green and red stands for the two spin orientations.

To end this section, transport properties are calculated based on the Green's functions formalism which reduces to Landauer-Büttiker for

equilibrium properties. The scattering region, left and right leads are all the same 10-zBNNR. Fig. 5.13 represents the conductance for the three spin polarization cases. To analyze the results, one can compare them to the case of graphene. The antiferromagnetic spin configuration of the zGNR is semiconducting (Fig. 5.4(b)). There is a zero conductance at Fermi level. The ferromagnetic spin configuration is metallic (Fig. 5.4(c)) and the conductance has a value of  $2G_0$  with  $G_0$  the quantum of conductance :  $G_0 = e^2/h$ . Interestingly and as mentioned before, the conductance is never equal to zero for the bare-edge zBNNR. Its value at Fermi level is either  $2G_0$  or  $3G_0$  depending on the case. Moreover, while for graphene the spin up and spin down conductances are symmetric, it is not the case for the zBNNRs. This asymmetry is maximum for the  $N_{\uparrow\uparrow} - B_{\downarrow\downarrow}$  and  $N_{\uparrow\uparrow} - B_{\uparrow\uparrow}$  cases which exhibit single spin transport at Fermi level ( $G^\downarrow = 0$  and  $G^\uparrow \neq 0$ ). This suggest a possible use of zBNNRs as passive spin filters in spintronics, where the spin is used as a way to realize logic operations, in the same way that the electronic charge is used in electronics.

### 5.3 Graphene - boron nitride interface

This section investigates the interplay between graphene and boron nitride mixed in the same sheet. More precisely, focus is held on a ribbon made by the junction of a zBNNR and a zGNR of the same atomic width : a 10-zBNNR and a 10-zGNR (width  $\sim 2$  nm). The interface is thus of armchair type, which is predicted to be the most stable one [123]. The ground-state properties are investigated with DFT. The unit cell for these calculations,



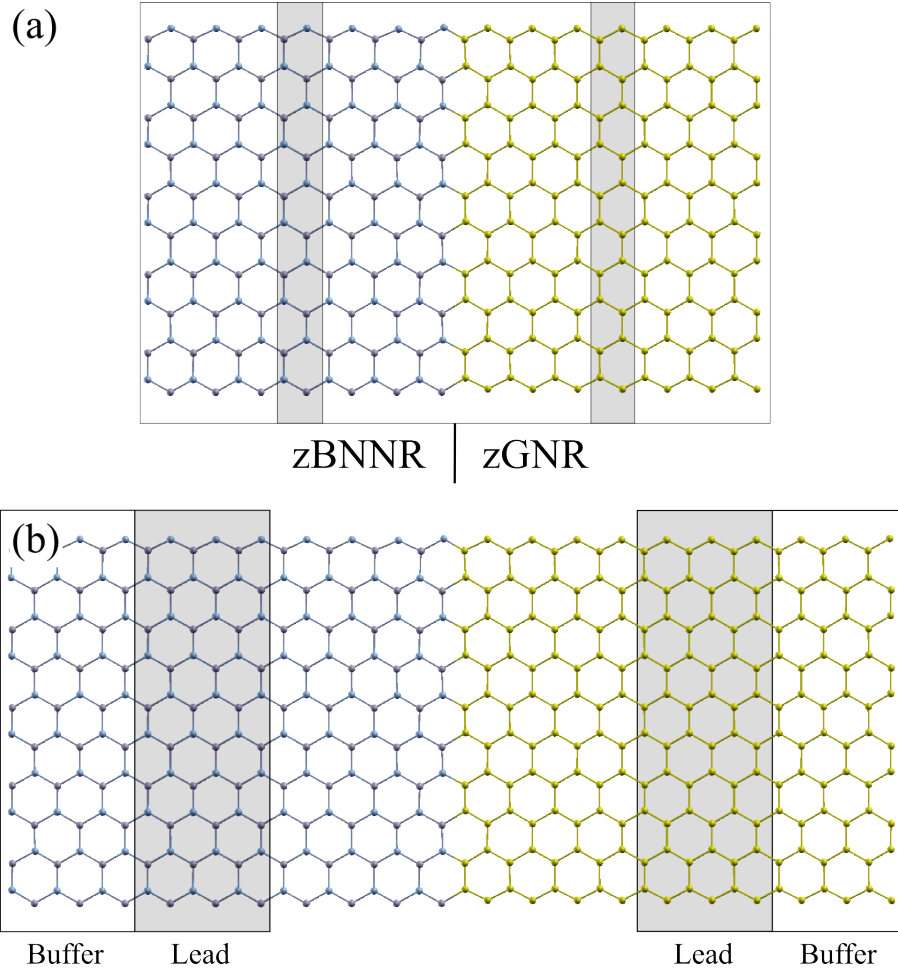


Fig. 5.14 - (a) Ball and stick representation of the supercell used for the full structural optimization of the zBNNR-zGNR interface. The 4<sup>th</sup> zBNNR and zGNR unit cells (highlighted in the picture) have been used respectively as references for the construction of the zBNNR and zGNR lead geometries. (b) Ball and stick representation of the transport setup.

## 5. G-BN NANORIBBONS AND COMPOSITES

---

represented in Fig. 5.14(a), is composed of two times seven unit cells (the unit cell is the shaded area (a)). As in the previous section, LDA is used (within the Ceperley-Alder parametrization). Both the ions and the unit cell are optimized to reach stresses and forces lower than 0.01 GPa and 0.01 eV/Å. The geometry is only altered slightly. Graphene is dilated by less than 0.2%, with very little difference between the interface and the middle of the graphene part. The boron nitride part is more peculiar. Close to the interface, it is dilated as well, while in the middle of the BN part of the ribbon, it is very slightly compressed (below 0.1%). Three  $k$  points are used along the longitudinal direction of the ribbon (equivalent to forty for one single unit cell).

The periodic system is used to extract the optimized geometry for the interface. The central part of the periodic cell is kept, up to the 4<sup>th</sup> unit cells to the left and to the right of the interface. These last unit cells are then used as the principal layers defining the leads (it is repeated semi-infinitely to the left and to the right). The final geometry used in the transport calculation is depicted in Fig. 5.14(b).

It has to be reminded that both the zBNNR and the zGNR experience spontaneous spin polarization. Moreover, multiple spin polarization cases exist for each ribbon. In this study however, only the ferromagnetic case is considered ( $\uparrow\uparrow$  or  $\downarrow\downarrow$ ), for which the two edges (where the spin polarization is localized) possess the same spin orientation. This is motivated by a magnetic field which can be experimentally applied. Indeed, a slight magnetic field will align the spin on both edges in the same orientation. It is difficult to conceive a magnetic field confined in a way that the spin polarization on one edge is opposite to the spin polarization on the other edge, only 2 nm apart. Reducing the allowed polarizations to the ferromagnetic case for each ribbon still leads to two

polarization cases for the graphene-BN composite ribbon. Indeed, the ferromagnetic alignment can be parallel for the two ribbons or antiparallel. These two cases are represented by  $\text{zBNNR}(\uparrow\uparrow)\text{-zGNR}(\uparrow\uparrow)$  and  $\text{zBNNR}(\uparrow\uparrow)\text{-zGNR}(\downarrow\downarrow)$ , respectively.

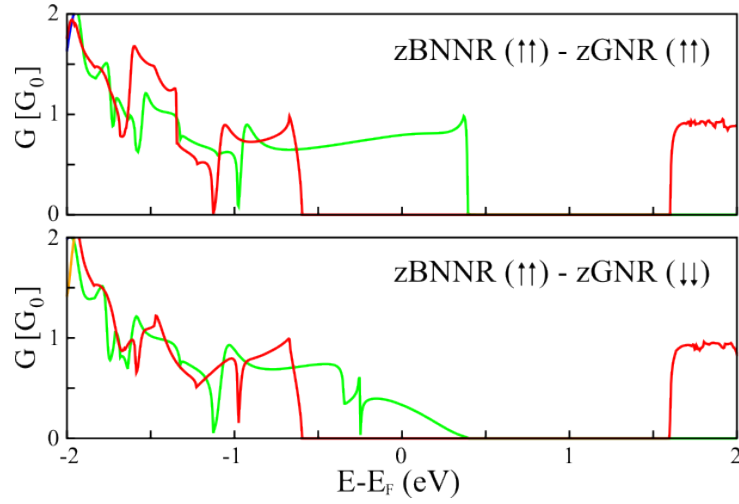


Fig. 5.15 - Electronic transmission functions for the two transport configurations :  $\text{zBNNR}(\uparrow\uparrow)\text{-zGNR}(\uparrow\uparrow)$  (top panel) and  $\text{zBNNR}(\uparrow\uparrow)\text{-zGNR}(\downarrow\downarrow)$  (bottom panel). Green and red curves correspond respectively to the majority and minority spin components.

Fig. 5.15 represents the electronic transmission (expressed as a multiple of the quantum of conductance  $G_0$ ) as a function of the energy of the charge carriers, for both spin orientations. The two colors stand for the two spin orientations ( $\uparrow$  and  $\downarrow$ ). At Fermi level (the zero of the graph) only the majority spin contributes to the electron transmission. Moreover, a quenching of two thirds of the transmission is observed when switching from  $\text{zBNNR}(\uparrow\uparrow)\text{-zGNR}(\uparrow\uparrow)$  to  $\text{zBNNR}(\uparrow\uparrow)\text{-zGNR}(\downarrow\downarrow)$ .

zGNR( $\downarrow\downarrow$ ), which should be measurable experimentally. Independently of the polarization case, spin filtering properties are observed, which might be of particular interest in spintronics.

In order to explain the presented transmission, a more detailed analysis of the local electronic properties is performed. Fig. 5.16 compares the band structures for the perfect 10-zBNNR and 10-zGNR. The bands contributing to the transmission at the Fermi level are highlighted and their shape is depicted in Fig. 5.16 (right panel). These simple elements allow to explain qualitatively the behavior of the transmission function (Fig. 5.15). Only the states of the same spin orientation can couple. For the zBNNR( $\uparrow\uparrow$ )-zGNR( $\uparrow\uparrow$ ) case, the states labelled *a* and *b* in Fig. 5.16 (right panel), although not localized on the same region of the ribbon, share the same bonding symmetry. As a consequence, the coupling between these two states is efficient and the transmission is close to  $1G_0$ . For the other polarization case (zBNNR( $\uparrow\uparrow$ )-zGNR( $\downarrow\downarrow$ )) the picture changes. The *b* state is populated by minority spin electrons and therefore does not couple with the *a* state anymore. The *c* state, however, is occupied by majority spin electrons. Its symmetry has an antibonding character. Therefore, the coupling between the *a* and *c* states is far less efficient. The resulting transmission is therefore lower ( $\sim G_0/3$ ).

Another way to look at the transmission picture is by looking at the transmission eigenchannels. Fig. 5.17 represents these eigenchannels at Fermi level. The two polarization cases are considered, as well as the transmission eigenchannels for left-incoming and right-incoming states. For the zBNNR( $\uparrow\uparrow$ )-zGNR( $\uparrow\uparrow$ ) polarization case, the eigenchannel is located on the nitrogen-terminated edge of the zBNNR and is delocalized on the whole width of the zGNR. The integral of the part of the

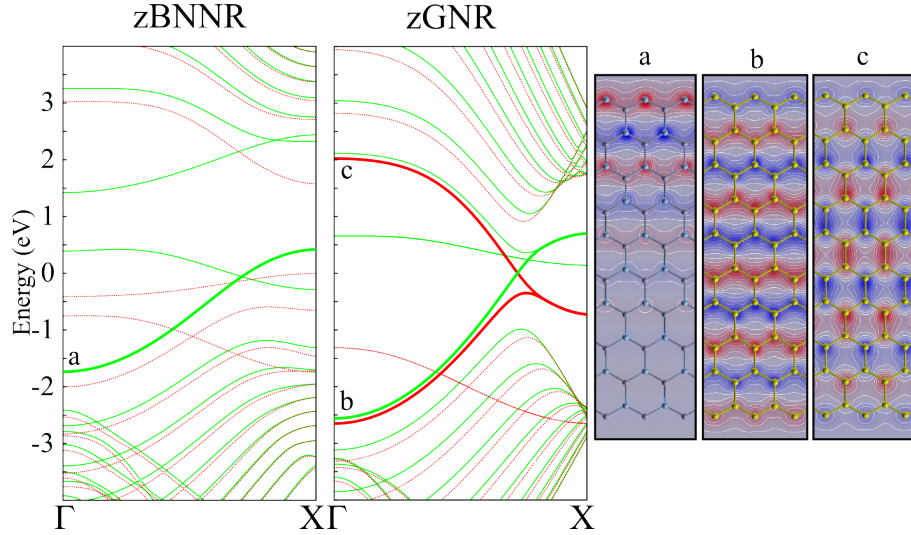


Fig. 5.16 - Band structures of the bare BN (*left*) and graphene (*center*) nanoribbons within the  $\uparrow\uparrow$  magnetic configuration. The green and red curves correspond respectively to the majority and minority spin components. The electronic bands contributing to the electronic transmission at the Fermi level are highlighted. *Right*. Spatial representation at  $\Gamma$  of the wave functions corresponding to the electronic bands highlighted in the left pannel. The color scale is obtained from the value of the eigenstate within the plane corresponding to the maximum density of  $\pi - \pi^*$  electrons. Blue and red isocurves correspond respectively to positive and negative values of the wave function.

eigenchannel on the zBNNR is equal to the integral of the part of the eigenchannel on the zGNR. For the zBNNR( $\uparrow\uparrow$ )-zGNR( $\downarrow\downarrow$ ) case, the localization of the eigenchannel is similar to the previous case. The integral however is different on the BN and on the graphene side, corresponding to the quenching of the transmission observed previously. Finally, in order to investigate the details of the interface, projected DOSs are calculated at different positions of the ribbon. Fig. 5.18 repre-

## 5. G-BN NANORIBBONS AND COMPOSITES

sents the DOS projected on each unit cell composing the central region. For comparison, the DOSs of the leads are also presented. These spectra are in good agreement with the band structures illustrated above,

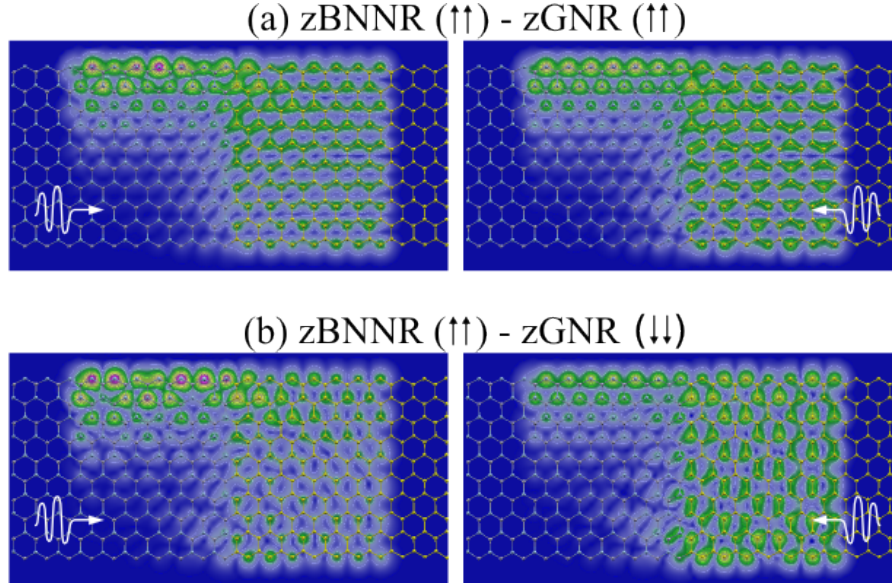


Fig. 5.17 - Spatial representation of the left and right incoming transmission eigenchannels for the two transport configurations : zBNNR( $\uparrow\uparrow$ )-zGNR( $\uparrow\uparrow$ ) (a) and zBNNR( $\uparrow\uparrow$ )-zGNR( $\downarrow\downarrow$ ) (bottom panel). The color scale is obtained from the real part of the transmission eigenstate in the plane (parallel to the ribbon) corresponding to the maximum density of  $\pi - \pi^*$  electrons.

indicating that the leads recover the ideal ribbon properties. The energy window spanned by the dangling bonds (DB) in graphene and BN are marked with arrows on the top and bottom of Fig. 5.18. The other bands seen in the DOS of the graphene leads are associated with  $\pi - \pi^*$  bands. The cells just before the leads ( $C_4$  and  $BN_4$ ) recover the bands

associated with the DB, assuring the persistence of the metallic character of the BN part of the graphene-BN ribbon. The other bands, however, are more perturbed, due probably to the higher mobility of the  $\pi$ -electronic wave functions. In addition the DOSs of Fig. 5.18 exhibit two particularly sharp peaks, identified by black arrows, and labelled

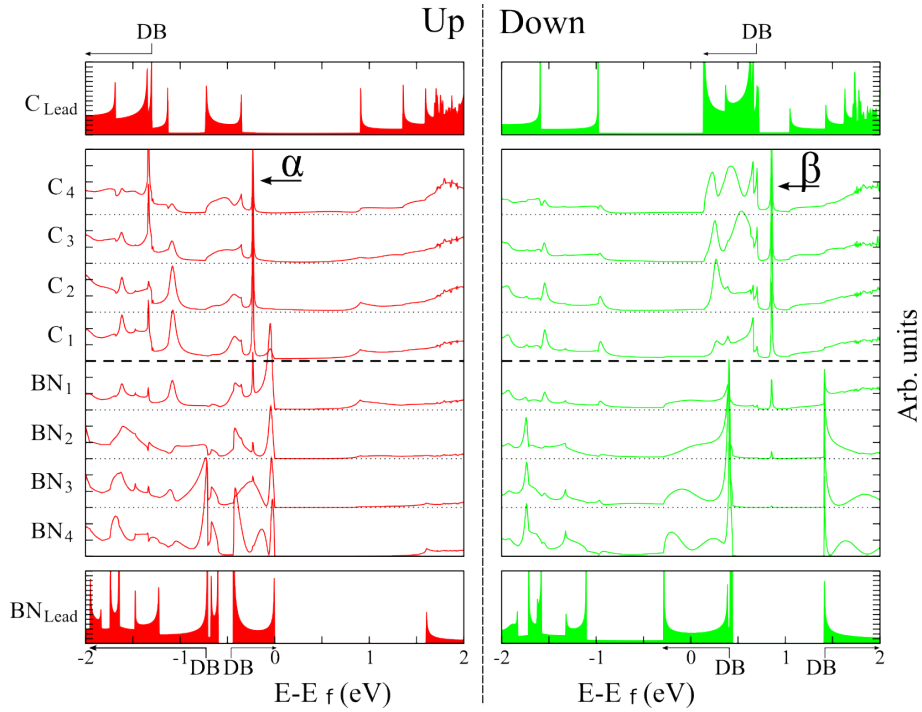
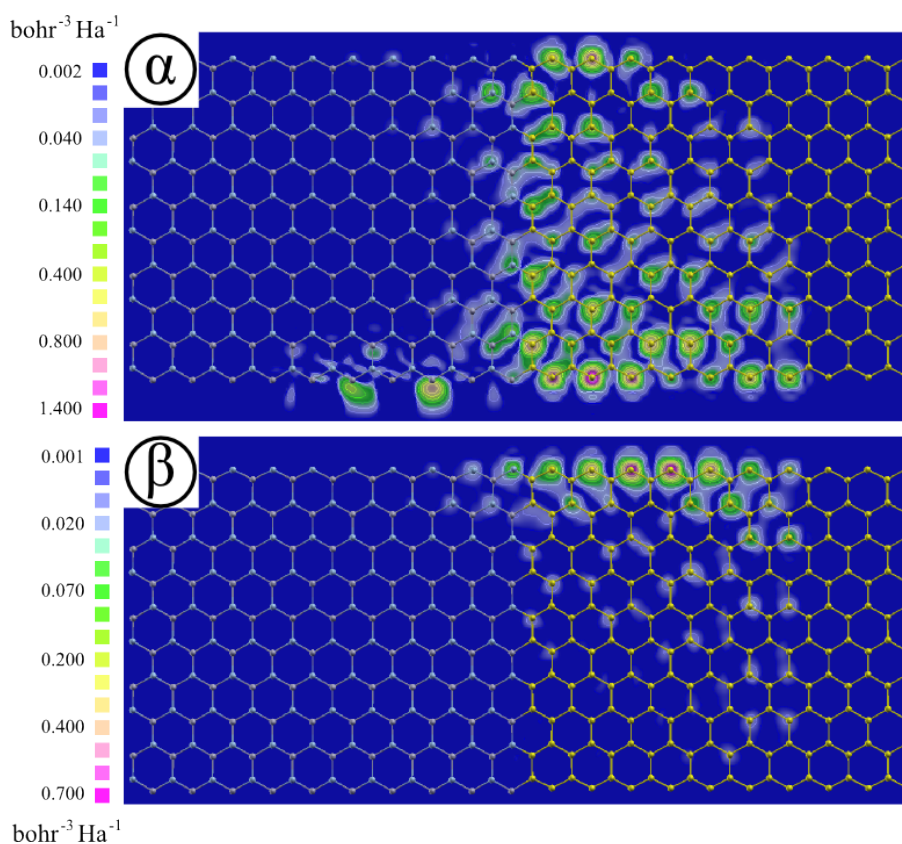


Fig. 5.18 - Electronic density of states of zBNNR-zGNR junction projected on various subsets of atoms. The symbols  $C_{1,2,\dots}$  and  $BN_{1,2,\dots}$  designate respectively the zGNR and zBNNR unit cells counted from the zBNNR-zGNR interface.  $C_{\text{Lead}}$  and  $BN_{\text{Lead}}$  refer respectively to the carbon and BN atoms within the leads. The green and red curves correspond respectively to the majority and minority spin components.

## 5. G-BN NANORIBBONS AND COMPOSITES

---

$\alpha$  and  $\beta$ . They are mainly seen in the graphene part of the graphene-BN composite. These peaks are also observed on the BN side. They are smaller and quickly fade after a few BN cells. These peaks being absent from the DOS of the leads, they ought to be associated with the interface. Fig. 5.19 depicts the  $\alpha$  and  $\beta$  localized states, seen from a



---

Fig. 5.19 - Representation of the  $\alpha$  and  $\beta$  localized states (indicated in Fig. 5.18) corresponding to the sharp peaks observed in the DOS projected on different cells of the central region.

---



top view. The  $\alpha$  state corresponds to occupied states while the  $\beta$  one is empty. Both of them share a triangular shape. The explanation of their structure is easily understood based on a feature observed in the ideal zBNNRs. One edge of the zBNNR is made of boron, the other of nitrogen. As a consequence, an internal transverse electrical field is produced (pointing from boron to nitrogen). This electric field applied to graphene at the interface creates an accumulation of electrons on the graphene edge on the same side as the boron one. This accumulation becomes smaller when going further away from the interface, leading qualitatively to the pattern of the  $\alpha$  state (see Fig. 5.19). The  $\beta$  state shares the same symmetry. It is therefore very likely originating from the internal electric field. It is probably the counterpart of the  $\alpha$  state but for holes instead of electrons.

## 5.4 Conclusion

To conclude, GNRs are studied. Zigzag GNRs are found to be metallic or semiconducting, depending on their polarization state. The armchair ribbons are always semiconducting. A reconstruction of the zigzag edge is also studied (zz57). No spin polarization is observed, but the transmission at Fermi level is calculated to be higher in this reconstructed case. The non-passivated zBNNRs are demonstrated to be metallic independently of the spin polarization cases they adopt. The polarization is linked to the presence of both dangling bonds and edge states. The transport properties of zBNNRs exhibit spin-filtering. After combination with a zGNR, two spin polarization cases are studied : zBNNR( $\uparrow\uparrow$ )-zGNR( $\uparrow\uparrow$ ) and zBNNR( $\uparrow\uparrow$ )-zGNR( $\downarrow\downarrow$ ). Each ribbon is polarized in a

ferromagnetic state. This state is either parallel for the two parts of the ribbons, or antiparallel. Independently of the polarization case, spin-filtering properties are predicted. However, a quenching of the transmission at equilibrium is seen for the zBNNR( $\uparrow\uparrow$ )-zGNR( $\downarrow\downarrow$ ) compared to the zBNNR( $\uparrow\uparrow$ )-zGNR( $\uparrow\uparrow$ ). This phenomenon is explained qualitatively based on the symmetries of the states at Fermi level. The particular transport properties could be of interest in electronics or even in spintronics due to the spin valve effect. Moreover, the details of the interface are studied. DOSs are calculated for different layers of the central part of the composite ribbon. The DBs are found to be quickly recovered away from the interface. The  $\pi - \pi^*$  states, more mobile in graphene than the DB are perturbed more strongly due to the interface. Finally, two peaks appear, mainly localized in the graphene part of the composite (and not seen in the leads) which are linked to the presence of the transverse internal field in zBNNRs.

## Chapter 6

# Graphene and boron nitride multilayers

The previous chapter focused on boron nitride (BN) and graphene mixed in the same plane. However, an easier way to build BN-graphene composites is to stack them. This idea has been first demonstrated experimentally and shows promising perspectives as dielectric material in electronics applications [25, 124], more generally as a substrate for graphene [21, 24], or to add interesting electronic features to graphene [125]. BN has numerous advantages over the more common silicon dioxide ( $\text{SiO}_2$ ) substrate.  $\text{SiO}_2$  is a three-dimensional bulk material. Therefore, its surface has localized charges due to the presence of dangling bonds. Moreover, its roughness has a root mean square of 250 pm. BN on the other hand exhibits almost perfect flatness (50 pm root mean square) since this material can be easily cleaved along one plane. Because of its insulating behavior, no charges are accumulated at its surface. For these reasons, BN allows to lay graphene

on a substrate, as flat as it can get, and avoids degrading graphene's electronic properties due to charge trapping at the surface of the substrate. The measured mobilities for graphene on  $\text{SiO}_2$  are of the order of  $\sim 10000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  [73, 126] while they are of  $\sim 100000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  [127] for suspended graphene (at room temperature). More recently, the mobility of graphene on boron nitride has been measured and found to be similar to the value for suspended graphene [12]. Therefore, the h-BN substrate is expected to influence only slightly the electronic properties of graphene. The following calculations will investigate the precise effect of the BN substrate on the graphene properties, by including van der Waals interactions.

### 6.1 Graphene/boron nitride moiré patterns

Since BN shares the same structure with graphene, there are two ways of stacking graphene on a single BN sheet. Either one stacks them by keeping the atoms aligned between the two layers (the layers are called commensurate), or one stacks them allowing the two layers to be misaligned (the stacking is called incommensurate). A commensurate alignment will induce a breaking of the symmetry between the A and B sublattices of graphene. Consequently, a band gap opens in graphene depending on the stacking [128, 129]. Moreover, from an experimental point of view, this arrangement is more difficult to realize, although it has been realized [130]! The more common technique relies on successive transfer techniques of graphene and BN separately. As a consequence, the orientation between the two layers is usually random. The simulation of commensurate systems has already been studied

[128,129]. This thesis however focuses on the incommensurate stacking of graphene and BN. The case of misoriented bi- and trilayer graphene has already been studied [131]. It was shown that the massless character is conserved with misoriented layers. The case of commensurate stacking is more rich and can lead to different electronic properties. The random orientation of graphene-boron nitride bilayer is a huge obstacle to the simulation. Indeed, the majority of simulation codes rely upon the periodic character of the simulated systems. Luckily, there is a way to simulate quasi-random systems in a periodic way. When rotating one sheet relatively to the other, some angles will cause the two lattices to define a moiré pattern<sup>1</sup>. A moiré pattern is a pattern for which the alignment of atoms between layers is repeated periodically. At a certain position, one atom of one sheet lies on top of an atom of the other sheet. Further away, one atom of one sheet lies exactly on top of a bond of the other sheet, or on top of a hexagon. Between these two positions, the alignment varies continuously. An example of a moiré pattern is illustrated in Fig. 6.1.

In order to define a moiré pattern between a graphene and a BN monolayer, one has to find the couple of vectors  $\mathbf{A}_1$  and  $\mathbf{B}_1$  belonging to the graphene and BN layer, respectively, that have the same length. Expressing them in their respective basis set gives :

$$|\mathbf{A}_1| = |n\mathbf{a}_1 + m\mathbf{a}_2| = |r\mathbf{b}_1 + s\mathbf{b}_2| = |\mathbf{B}_1|, \quad (6.1)$$

with  $(n, m)$  and  $(r, s)$  the components of the vectors decomposed, on the basis sets for graphene and BN :  $\{\mathbf{a}_1, \mathbf{a}_2\}$  and  $\{\mathbf{b}_1, \mathbf{b}_2\}$ , respectively. Because of the lattice mismatch between graphene and BN, the lattice

---

<sup>1</sup>Moiré patterns are well known effects caused by the optical interference of two lattices with an angle and/or a lattice mismatch.

vectors of BN are linked to the graphene lattice vectors following :

$$\mathbf{b}_{1,2} = (1 + \delta)\mathbf{a}_{1,2}, \quad (6.2)$$

with  $\delta$  the percentage of lattice mismatch between BN and graphene ( $\sim 1.80\%$  experimentally). Once this condition is satisfied, the relative rotation angle is determined accordingly. The appendix at p.191 contains a table with different values of (n,m), and the associated vector length for graphene and boron nitride. The presented method is the easiest to implement numerically. An example of this is given in the next figures. Fig. 6.2(a) shows the vector  $\mathbf{A}_1 = 2\mathbf{a}_1 + 4\mathbf{a}_2$  in the graphene lattice. Fig. 6.2(b) shows the vector  $\mathbf{B}_1 = 3\mathbf{b}_1 + 3\mathbf{b}_2$  in the BN sheet. These two vectors have the same length and define an angle with respect to their first basis vector ( $\alpha$  and  $\beta$  respectively). Rotating the BN sheet by an angle  $\phi = \alpha - \beta$  will align  $\mathbf{A}_1$  and  $\mathbf{B}_1$  and define a moiré pattern (Fig. 6.3). The notation for this particular moiré pattern is (2,4)-(3,3). Finally, one defines the angle  $\theta$  as the angle between the moiré pattern and the original graphene lattice.

The smaller the rotation angle, the bigger the unit cell. In order to browse different rotation angles, some variation in  $\delta$  is allowed to reduce the size of the unit cells. To avoid any stress on graphene, the unit cell size is fixed to the relaxed size of the graphene sheet alone. Another way to look at moiré patterns is from the reciprocal space point of view. Let  $\mathbf{k}_g$  and  $\mathbf{k}_{BN}$  be the reciprocal lattice vectors for graphene and BN, respectively. Choosing to write  $\mathbf{k}_g$  as :

$$\mathbf{k}_g = \frac{2\pi}{a}(1,0), \quad (6.3)$$

with  $a = |\mathbf{a}_{1,2}|$ , one can write  $\mathbf{k}_{BN}$  as :

$$\mathbf{k}_{BN} = \frac{2\pi}{(1 + \delta)a}(\cos\phi, \sin\phi). \quad (6.4)$$

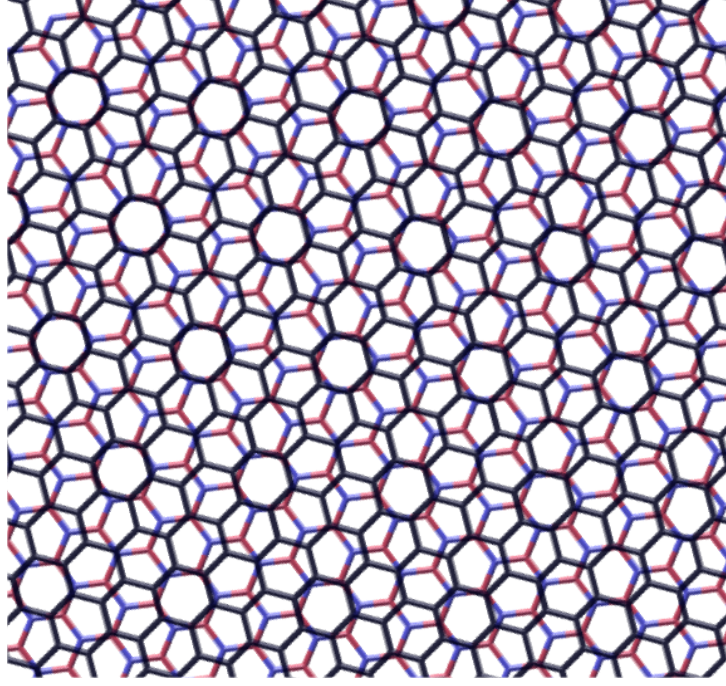


Fig. 6.1 - Example of a moiré pattern between graphene (black plane) and BN (blue-red plane).

The angle  $\phi$  is the same as defined above, the relative rotation angle between the two sheets. After rotation, the moiré pattern must connect the two reciprocal lattice vectors :

$$\mathbf{k}_m = \mathbf{k}_g - \mathbf{k}_{BN} = \frac{2\pi}{a} \left( 1 - \frac{\cos\phi}{1+\delta}, -\frac{\sin\phi}{1+\delta} \right). \quad (6.5)$$

The vector  $\mathbf{k}_m$  is the reciprocal lattice vector associated with the moiré pattern. Writing explicitly  $|\mathbf{k}_m|$  and using the relation between the wavelength  $\lambda$  and the wave vector, one can write the expression for the

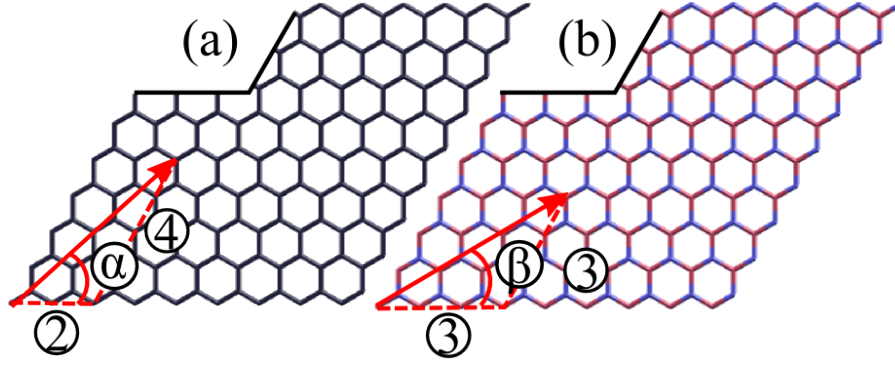


Fig. 6.2 - (2,4) vector in graphene for the formation of a moiré pattern with BN (a) and (3,3) vector in BN for the formation of a moiré pattern with graphene (b).

wavelength of the moiré pattern :

$$\lambda = \frac{(1 + \delta)a}{\sqrt{2(1 + \delta)(1 - \cos\phi) + \delta^2}}. \quad (6.6)$$

To find the rotation angle between the graphene lattice and the moiré pattern one extracts the angle  $\theta$  from the expression :

$$\tan\theta = \frac{k_{m,y}}{k_{m,x}} = \frac{\sin\phi}{(1 + \delta) - \cos\phi}. \quad (6.7)$$

Different cells corresponding to different moiré patterns are studied. A (2,4)-(3,3), a (4,3)-(6,0), and an (8,4)-(7,5). The corresponding relative rotation angles are :  $\phi = 10.893^\circ$ ,  $25.285^\circ$ , and  $-5.389^\circ$ . As for the wavelength associated to each moiré pattern,  $\lambda = 13.162 \text{ \AA}$ ,  $5.718 \text{ \AA}$ , and  $26.317 \text{ \AA}$ . The mismatch is adjusted to 1.84%, 1.38%, and 1.37%, respectively.



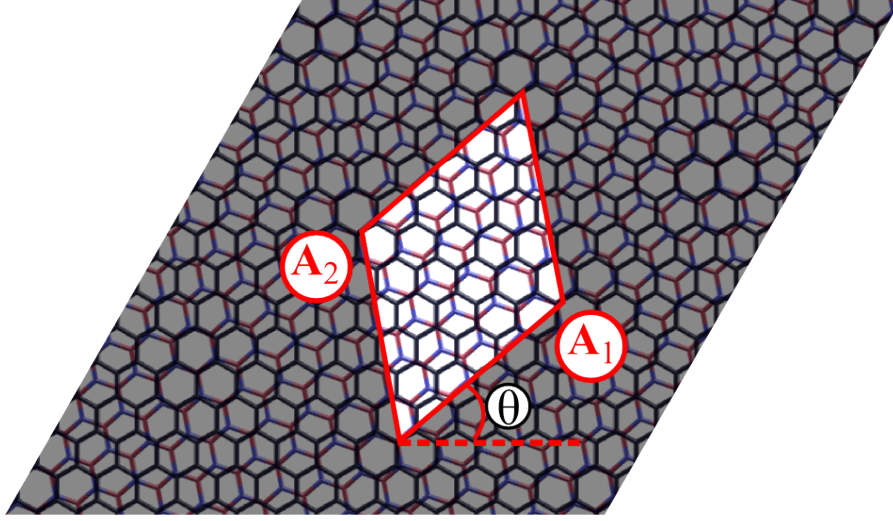


Fig. 6.3 - (2,4)-(3,3) moiré pattern created by a (2,4) vector in graphene superimposed on a (3,3) vector in BN. The angle  $\theta$  is the rotation angle between the moiré lattice and the graphene lattice. One unit cell is highlighted in red.

## 6.2 Graphite and h-BN with van der Waals interactions

The van der Waals forces are expected to have an influence on the properties of the graphene-BN multilayers. Therefore, along with the more common Ceperley-Alder LDA for the exchange-correlation approximation, the vdW-DF2 van der Waals functional [40] is used (p.28). This latter approximation is far less frequently used than the LDA. As a consequence, great care is focused on the construction of the pseudopotential as well as for the basis set. They are optimized in order to reproduce the experimental interlayer distance in h-BN and graphite. Indeed, this

## 6. GRAPHENE AND BORON NITRIDE MULTILAYERS

latter parameter is known to be influenced by vdW interactions, which are poorly reproduced with LDA and GGA. An exception is the interlayer distance of graphite (3.337 Å) as calculated with LDA [132], but this is more a coincidence since LDA does not include any van der Waals interaction term. Tab. 6.1 and 6.2 show the comparisons between the geometrical parameters obtained for graphite and h-BN with LDA, vdW-DF2, and experimental values.

| Interlayer spacing (Å) | exp. | LDA  | GGA        | vdW-DF2 |
|------------------------|------|------|------------|---------|
| graphite               | 3.35 | 3.18 | no minimum | 3.41    |
| h-BN                   | 3.33 | 3.18 | no minimum | 3.30    |

Table 6.1 - Comparison between the experimental interlayer spacing for graphite and h-BN, and the one obtained by using LDA and vdW-DF2.

| Cell parameter (Å) | exp. | LDA  | vdW-DF2 |
|--------------------|------|------|---------|
| graphite           | 2.46 | 2.47 | 2.49    |
| h-BN               | 2.51 | 2.49 | 2.54    |

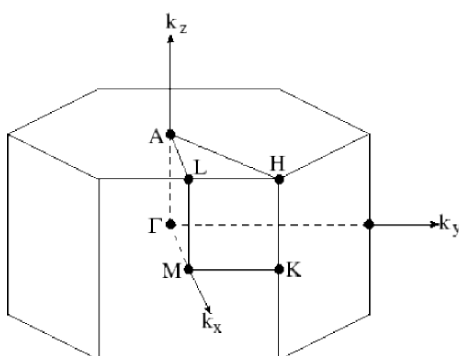
Table 6.2 - Comparison between the experimental cell parameter for graphite and h-BN, and the one obtained by using LDA and vdW-DF2.

The experimental interlayer distance is in general well reproduced with vdW-DF2 (the error is below 2%). LDA underestimates the interlayer spacing, with errors as big as 5.2%. This last figure however is particular to SIESTA. LDA is able to reproduce the graphite interlayer distance [132] but requires more extended basis sets<sup>2</sup>. The trend changes

<sup>2</sup>The basis used is a DZP which is a very good choice for simple elements such as boron, carbon, and nitrogen. As presented below, the electronic properties are well reproduced.

when comparing the cell parameter. Indeed, LDA is very close to the experimental values, whereas vdW-DF2 systematically overestimates by more than 1%. The overshooting in the covalent bond distance is a well known consequence of the use of vdW-DF2 [40]. As demonstrated in the following sections, this too large bond length will not affect the quality of the electronic properties.

The electronic band structures are represented in Figs. 6.5 and 6.6. Black and red are used for LDA and vdW-DF2, respectively. The points of the path in reciprocal space used for the plotting of the band structures are shown in Fig. 6.4. The general trend is a compression of the band structure calculated with vdW-DF2 compared to LDA. For h-BN,




---

Fig. 6.4 - Hexagonal Brillouin zone depicting the high-symmetry  $k$  points used for the band structure of Figs. 6.5 and 6.6

---

the band gap is of 3.93 eV for LDA, while it is  $\sim 0.4$  eV larger for vdW-DF2, at 4.30 eV. The value for the LDA calculation is very similar to previous ones [31]. As a reminder, the exact BN band gap value is closer to 6 eV [23]. The use of vdW-DF2 improves slightly the value of

the band gap although it remains far from the exact value. The green circles in Fig. 6.5 locate the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). Even if they lie in the same region, the exact position of the HOMO and LUMO for the LDA band structure differs from the vdW band structure. This shift is not explained but might be too small to have any physical meaning related to the inclusion of the vdW interactions. The band structure of graphite with both functionals is very similar (Fig. 6.6). Except the previously mentioned compression of the vdW-DF2 bandstructure, some divergences might be observed on the  $\pi$ - $\pi^*$  bands mainly (labelled in Fig. 6.6). The closeness of the electronic band structures for h-BN and graphite using both LDA and vdW-DF2 validates the combination of vdW pseudopotential and basis set. The main difference lies in the better description of the interlayer spacing, for which vdW was precisely used in the present case. To end the preliminary calculations on graphite, the cohesive energies between the graphite planes is computed. It is calculated as the difference between the total energy for the relaxed equilibrium structure and the total energy of the same system with a much larger interlayer distance (ten times larger). Tab. 6.3 summarizes the calculated values for LDA, vdW-DF2, and a comparison with the experimental value. The value obtained with vdW-DF2 is much closer to the experimental one, whereas LDA overestimates it, proving again the importance of vdW-DF2 for the description of the interaction between stacked layers. These results validate the pseudopotential, as well as the basis set optimized with the vdW functional. They are used for the subsequent calculations on the larger cells used to simulate the graphene-boron nitride misoriented bilayers.

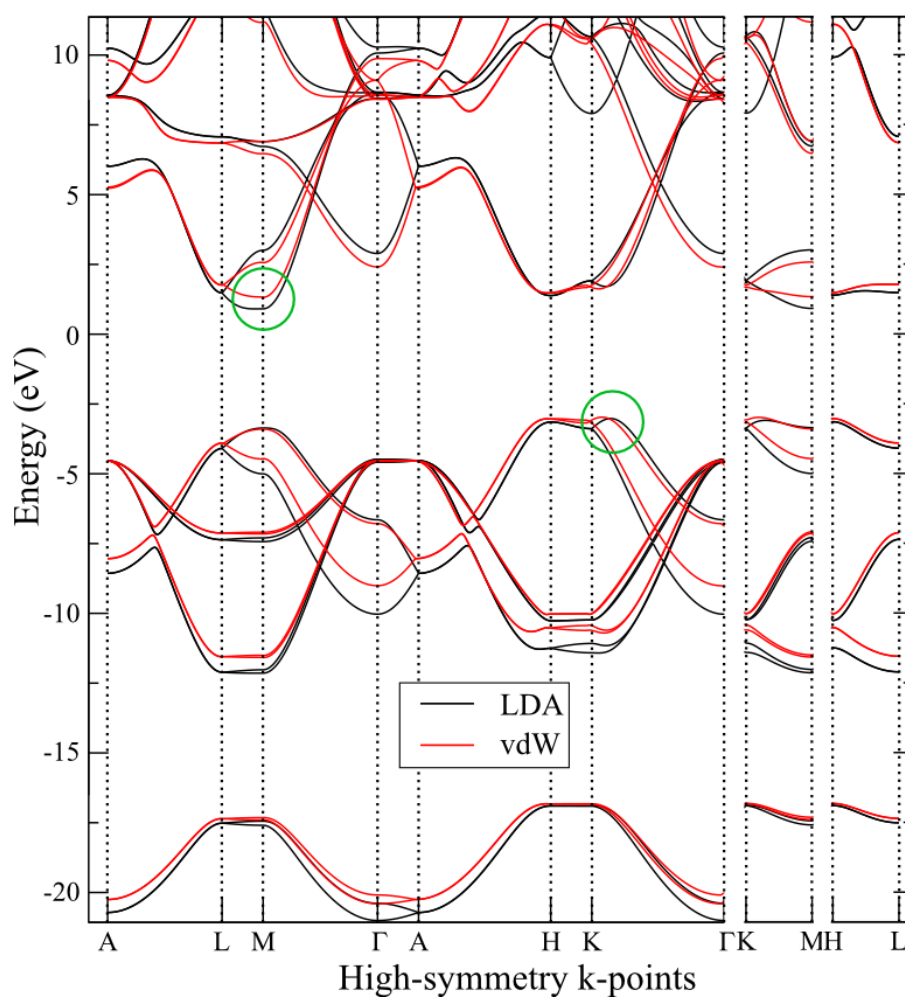


Fig. 6.5 - Electronic band structure for h-BN, calculated with LDA (black) and vdW-DF2 (red). The green circles highlight the HOMO and LUMO.

## 6. GRAPHENE AND BORON NITRIDE MULTILAYERS

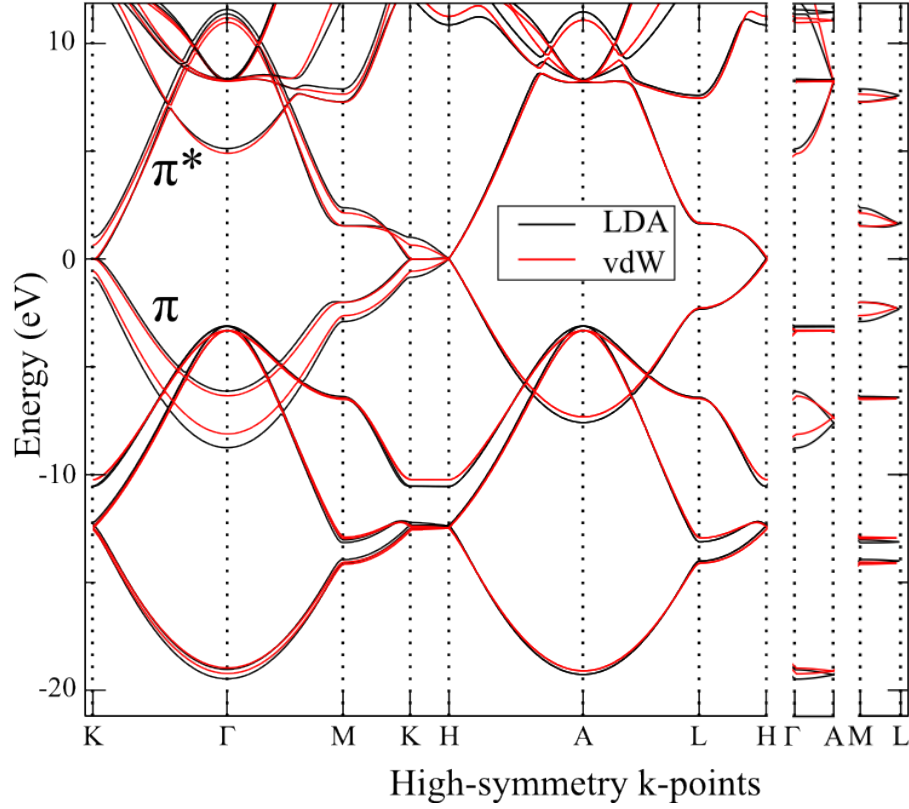


Fig. 6.6 - Electronic band structure for graphite, calculated with LDA (black) and vdW-DF2 (red).

|                       | exp. [135] | LDA | vdW-DF2 |
|-----------------------|------------|-----|---------|
| cohesive energy (meV) | $61 \pm 5$ | 111 | 57      |

Table 6.3 - Comparison between the experimental cohesive energy of graphite [135], and the one obtained by using LDA and vdW-DF2.

### 6.3 Properties of graphene-boron nitride bilayers

Figs. 6.7 and 6.8 show the geometry of the studied moiré structures. The unit cell for the graphene-boron nitride bilayer corresponding to a (2,4)-(3,3) (Fig. 6.7(a)) contains 110 atoms while the (8,4)-(7,5) (Fig. 6.7(b)) contains 442. Fig. 6.8 highlights the moiré pattern of the (8,4)-(7,5) cell.

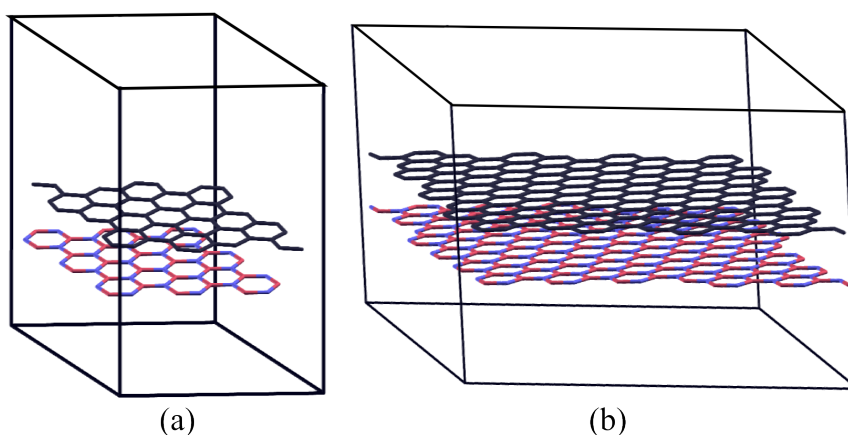
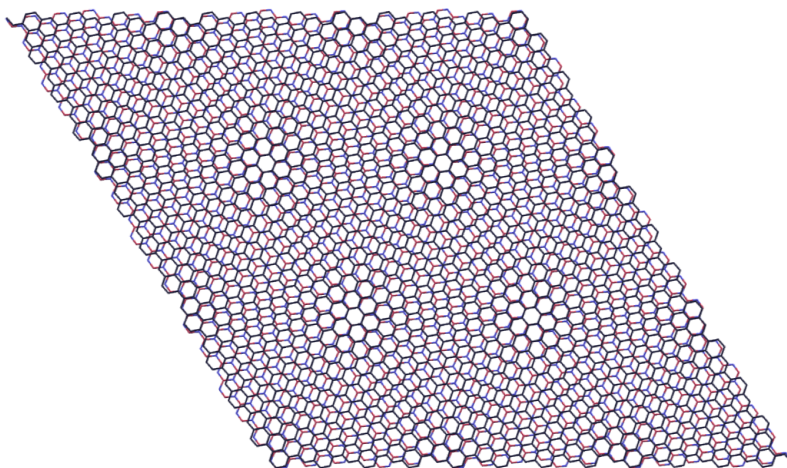


Fig. 6.7 - Unit cells for graphene-boron nitride bilayers defining a (2,4)-(3,3) (a) and an (8,4)-(7,5) (b) moiré pattern. Carbon, boron and nitrogen are depicted with black, red, and blue sticks, respectively.

The interlayer spacing is found to be equal to  $\sim 3.25$  Å and  $\sim 3.41$  Å for the calculation with LDA and vdW-DF2, respectively. This value is very close to the value for the graphite interlayer distance as calculated with vdW-DF2. For LDA, however, the value is a bit higher. Other theoretical studies present similar results [133]. It is worth mentioning an early work consisting in x-ray characterization of carbon structures de-

## 6. GRAPHENE AND BORON NITRIDE MULTILAYERS

---



---

Fig. 6.8 - Top view of a 3x3 cell corresponding to an (8,4)-(7,5) moiré pattern.

---

scribed as “random layer structures” [134]. These structures were found to have an interlayer spacing of 3.44 Å, larger than the 3.354 Å found for the pure graphitic structures. The value of 3.44 Å is attributed to random oriented graphene layers. The value found in the present thesis for the misoriented graphene-boron nitride bilayer is very close to these experimental results (although the experimental work was performed on pure carbon structures).

The band structures for the largest moiré structure ((8,4)-(7,5)) are shown below. The first one (Fig. 6.9) presents the comparison for the single graphene sheet corresponding to a (8,4)-(7,5) supercell. As noted before, the main effect of the vdW-DF2 compared to the LDA results is a compression of the bands towards the Fermi level. This compression occurs even at the Dirac cone. The result is a different Fermi velocity for the LDA calculation compared to the vdW-DF2 one. As a reminder,



the Fermi velocity is the slope of the linear dispersion near the K point :  $v_F = E/(\hbar q)$ , with  $q$  defined as  $q = |K - k|$ . The value of the Fermi velocity is  $8.04 \times 10^5$  m/s and  $7.88 \times 10^5$  m/s for the LDA and vdW-DF2 band structure, respectively. This is qualitatively good, since the experimental Fermi velocity lies around  $1.00 \times 10^6$  m/s. The vdW-DF2

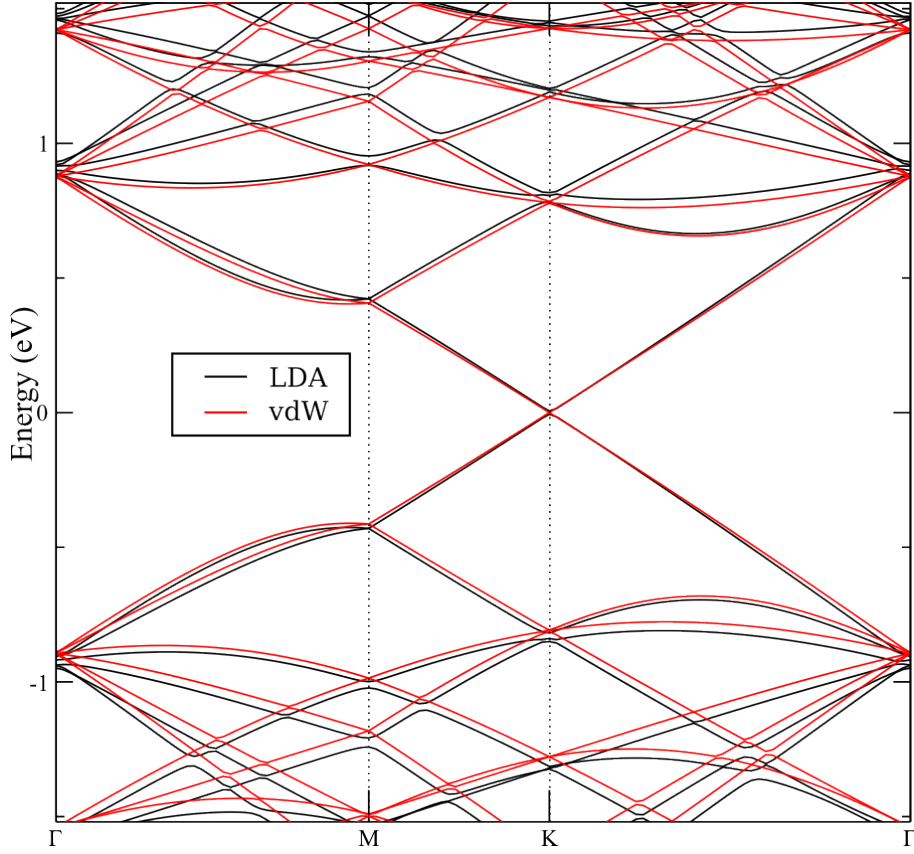


Fig. 6.9 - Electronic band structure for the (8,4)-(7,5) supercell graphene monolayer as calculated with LDA (black) and vdW-DF2 (red).

Fermi velocity is around 2% lower than the LDA one. It is probably an effect of the overestimation of the cell parameter of the vdW-DF2 calculation.

Fig. 6.11 shows the comparison between the band structures for graphene alone and for an (8,4)-(7,5) graphene-boron nitride bilayer, as calculated with vdW-DF2. Compared to Fig. 6.10 (the same configuration but obtained with LDA), the difference between the single graphene sheet and the graphene-boron nitride bilayer is more important. Consequently, the inclusion of vdW forces increases the interaction between the boron nitride sheet and the graphene one compared to LDA, although the interlayer distance is larger for vdW-DF2. For both cases, the effect is a compression of the valence bands towards the Fermi level. This compression is less important for LDA than for vdW-DF2. In addition, the boron nitride layer is supposed to impose a superlattice potential to the graphene lattice. This potential leads to the appearance of superlattice Dirac cones, as observed experimentally [125] (see Fig. 6.12 b). This new Dirac cones appear at an energy which depends on the wavelength of the potential (see Fig. 6.12 d). The bigger the wavelength, the closer the superlattice Dirac cone will be to the original Dirac point. For the (8,4)-(7,5), this superlattice should appear close to 1 eV around the Fermi level, at the M high-symmetry  $k$  point [136]. The black circle on Fig. 6.11 shows the area which supposedly contains this Dirac cone. The same area seems less dense for the image corresponding to the LDA calculation (Fig. 6.10), which might be an indication of the presence of the superlattice Dirac cones when including vdW interactions. Although containing a certain amount of atoms, the (8,4)-(7,5) cell is still too small to clearly evidence the superlattice Dirac cones. A larger cell would shift this Dirac cone closer to

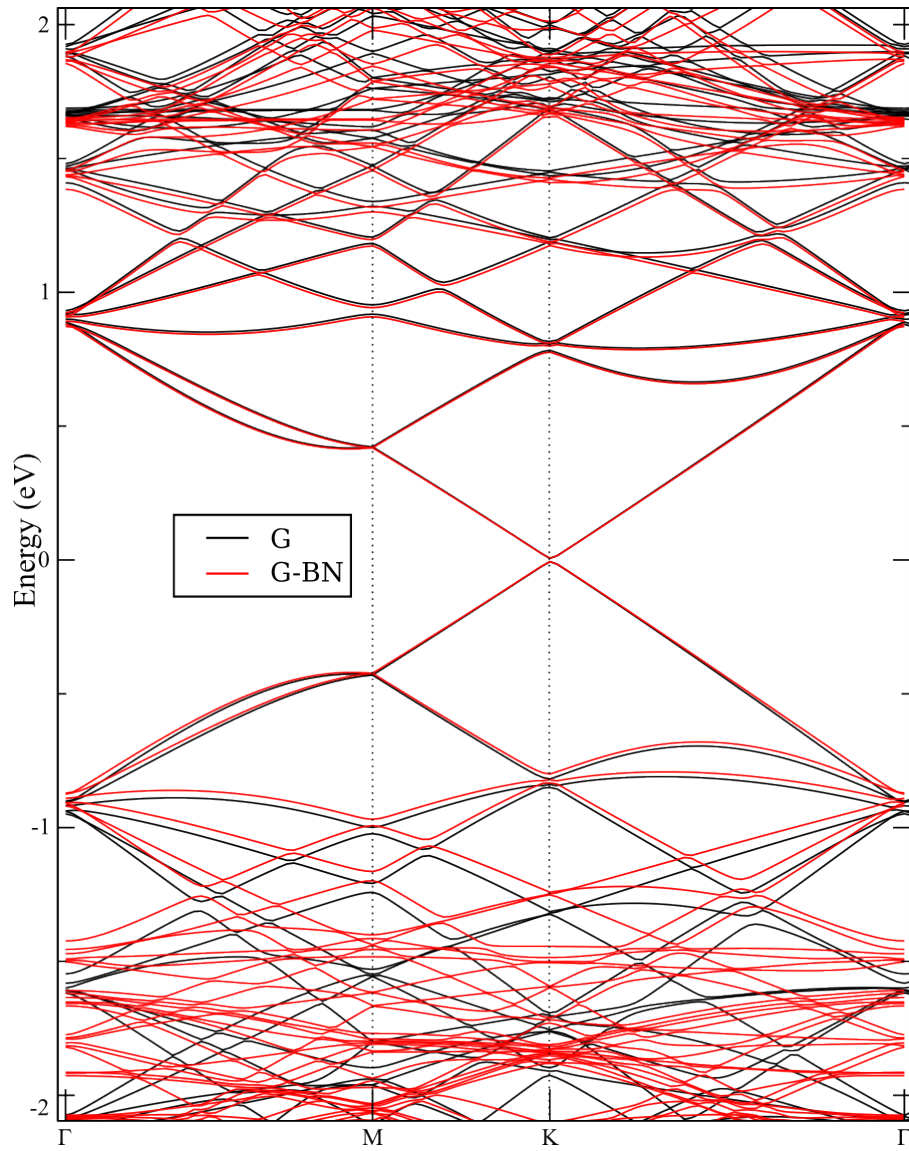


Fig. 6.10 - LDA electronic band structure for the (8,4)-(7,5) monolayer graphene (black) and the graphene-boron nitride bilayer (red).

## 6. GRAPHENE AND BORON NITRIDE MULTILAYERS

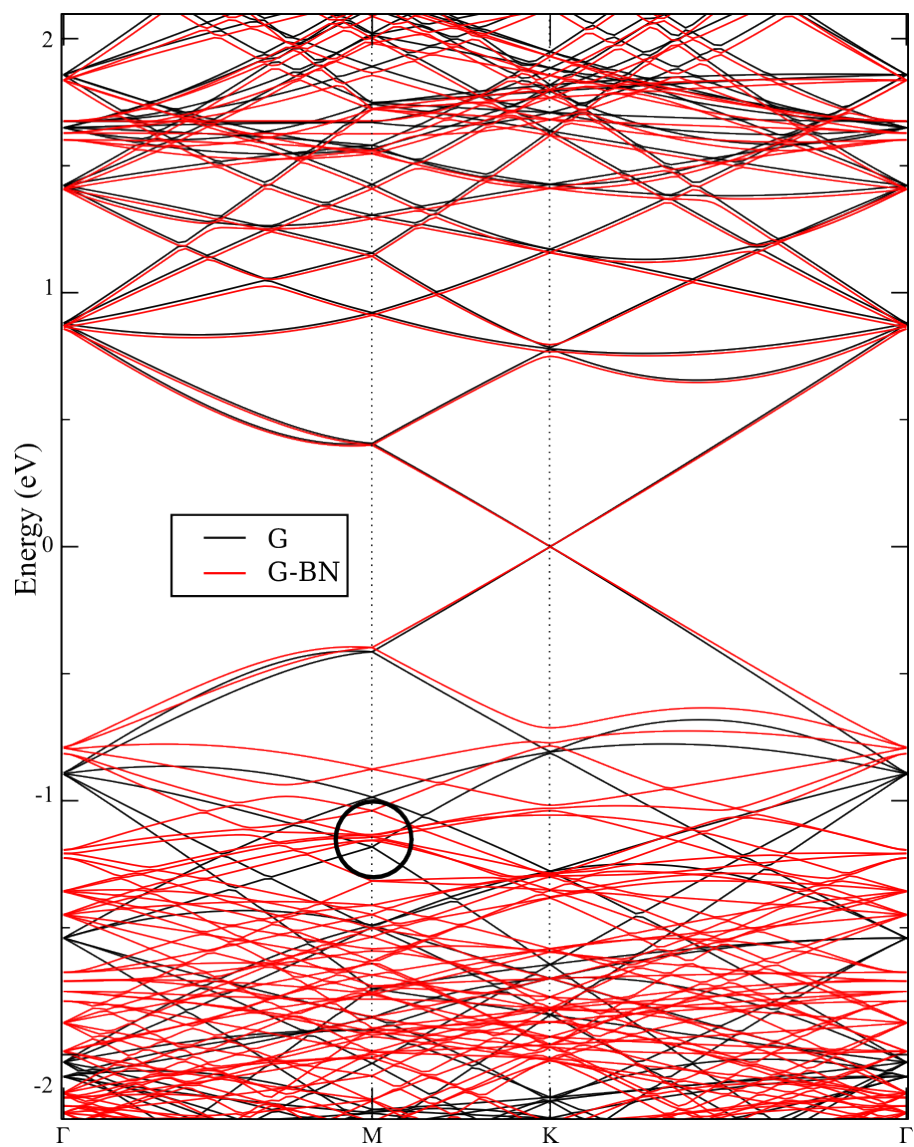


Fig. 6.11 - vdW-DF2 electronic band structure for the (8,4)-(7,5) monolayer graphene (black) and the graphene-boron nitride bilayer (red).

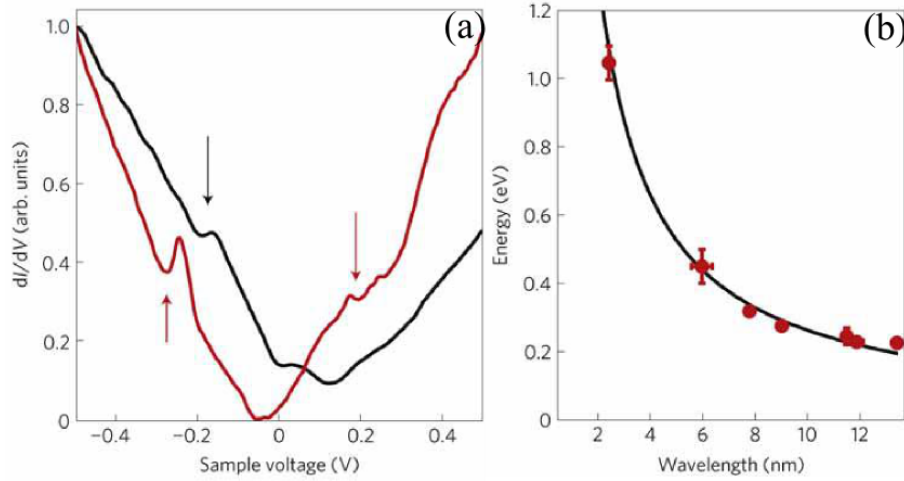


Fig. 6.12 - Experimental  $dI/dV$  curve for different moiré patterns (a). The arrows mark the signatures of the superlattice Dirac cones. The energy corresponding to the dips is a function of the moiré pattern wavelength (b). Images extracted from [125].

the Fermi level, making it easier to identify due to the lower band density in this region. The magnitude of the effect on the Fermi velocities is almost identical for the LDA and vdW-DF2 cases. A decrease of  $\sim 2\%$  on the Fermi velocity is calculated. Similar results were found in [133]. Finally, Fig. 6.13 presents the comparison between the band structure for a free and a compressed graphene-boron nitride bilayer with vdW-DF2. The compression is of  $0.5 \text{ \AA}$ , or  $\sim 15\%$ . This compression is huge but not impossible to reach experimentally if we assume the same very weak perpendicular stiffness coefficient as graphite [137]. The Fermi velocity is reduced by  $\sim 7.6\%$  due to this compression. Such a change should be possible to detect experimentally.

## 6. GRAPHENE AND BORON NITRIDE MULTILAYERS

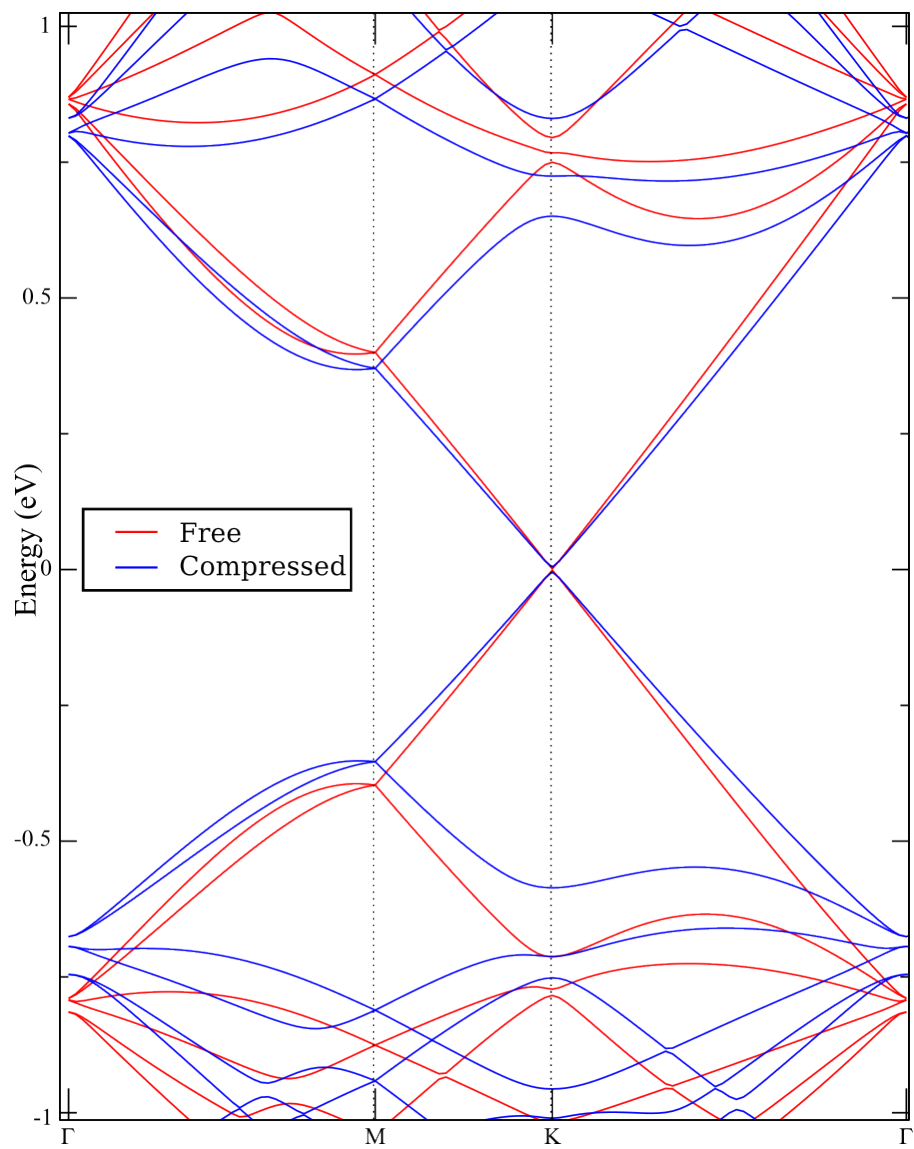


Fig. 6.13 - Electronic band structure for the (8,4)-(7,5) graphene-boron nitride bilayer without any constraints (red) and with a 0.5 Å perpendicular compression (blue).

## 6.4 Conclusion

In conclusion, the vdW-DF2 functional is used for the study of graphene-boron nitride multilayers. The geometry and energetics of graphite and h-BN are well reproduced and both close to experimental values, whereas LDA fails to do so. The electronic band structures are shown for different cases : isolated sheets, and bilayers with different incommensurate-like superlattice cells. Around the Fermi level, the electronic properties of graphene on boron nitride are dominated by the graphene properties. This is good compared to other substrates as  $\text{SiO}_2$ , which destroy the properties of graphene due to the corrugation induced by  $\text{SiO}_2$ . The excellent electronic mobilities in graphene are therefore conserved after the stacking on BN. Although a 2% decrease of the Fermi velocity is observed, the Dirac cone is still present. The superlattice Dirac cones are not clearly evidenced, but the identification of a region where they could lie is done. Moreover, this region is only present for the calculation with the vdW functional, indicating the higher interaction between planes brought by the vdW-DF2. Finally, the effect of an important compression on the electronic band structure is investigated. The main consequence is a 7.6% decrease in the Fermi velocity due to this compression. This Fermi velocity modulation might be of interest in applications as it gives a way to modify the mean free path, potentially changing from one transport regime to another. Experimentally, Raman measurements might be another tool to characterize and investigate the graphene-boron nitride multilayers, as a recent work suggests for twisted graphene bilayers [138].





## Conclusion and future perspectives

In this thesis, graphene's properties under various perturbations were investigated using *ab initio* techniques. Graphene possesses a unique combination of properties making many scientists believe in its future applications. Being a one-atom thick material its properties and manipulation are novel in many ways and have to be studied in depth before considering applications at its full potential. For example, the main problem in graphene is its zero band gap. Many applications in electronics require graphene to have an “on” and an “off” state for the transport of electrons. Therefore, intensive research has been conducted in order to find ways to tailor graphene's properties in order to have a finite band gap without destroying its exceptional electronic characteristics (high mobilities of the charge carriers). Other studies aim to study the effect of the materials which graphene is in contact with. The most obvious is the substrate on which graphene is deposited.

The present work made use of density functional theory (DFT) to study graphene. It gives access to useful ground-state properties (energetics, geometry, electronic band structure,...). To go beyond ground-state

properties and study the electronic transport characteristics two formalisms were used : the Kubo-Greenwood formalism and the Green's functions formalism for phase-coherent transport. As implemented, the former studies large systems compared to DFT and gives access to mesoscopic transport properties for two-dimensional samples, while the latter investigates the properties of a sample of smaller size, taking explicitly the contacts into account. Finally, a convenient and easy way to simulate scanning tunneling microscopy (STM) images was presented, relying on the ground-state properties only.

The modification due to structural defects was investigated using DFT and the Kubo-Greenwood formalism. The studied defects are : the Stone-Thrower-Wales defect, as well as the  $t5t7$  and 585 divacancies. The DFT band structures were calculated. The transport properties of different concentrations of a single, or of mixed defects were produced. The quenching of the transport properties were found to be different for each defect. As a result, fingerprints for each defect/combination of defects were identified. Higher dimensionality defects were studied as well. Three linear perturbations of the graphene lattice were investigated with DFT, as well as within the Green's functions formalism. STM images were computed and are in good agreement with experimental ones. Attention was driven on a particular defect which behaves like a metallic wire embedded in a graphene sheet. This latter case would be of particular interest in electronics as connects for example.

Another way to change graphene's properties is by doping. In this thesis, both nitrogen and boron dopings were studied. The experimental identification of boron-doped graphene is not straightforward. In order to ease this analysis, simulated STM images were calculated. The candidates were boron defects arranged according to the  $BC_3$  ratio only, or

---

combined with vacancies and divacancies. Three candidates were found to show many similarities with one of the most common defects observed experimentally (the “chevron” defect). However, to identify the candidate without any doubt, complementary scanning tunneling spectroscopy images, both experimental and simulated ones, are needed. Nitrogen islands were investigated as well. When present, vacancies tend to cluster with nitrogen atoms, favoring the formation of larger islands. Experimental images were not available to compare STM images and confirm the presence of defects involving more than two atoms. Nitrogen and boron can be incorporated together in graphene as well. Graphene-boron nitride composites were studied within the DFT formalism. The interface between graphene and boron nitride was investigated. The quantum transport properties of a zigzag graphene-boron nitride ribbon have been studied with the Green’s functions formalism and spin-filtering effects were evidenced, potentially interesting in graphene-based spintronics. Finally, the influence of a boron nitride substrate on graphene was investigated. The simulation was performed including van der Waals (vdW) interactions which play an important role for layered materials. Twisted graphene-boron nitride bilayers were studied to simulate the incommensurate alignment resulting from the deposition of graphene on boron nitride. The inclusion of vdW interactions reproduces the interlayer distance for graphite and hexagonal boron nitride better than conventional LDA. Graphene on boron nitride was predicted to maintain the zero band gap and the linear dispersion. A reduction of 2% in the Fermi velocity was observed compared to the single graphene sheet. The effect of compression was investigated as well. A higher reduction of the Fermi velocity was found, leading to a possible application in transport

## CONCLUSION AND FUTURE PERSPECTIVES

---

regime modulation.

More calculations could be performed to go deeper into the different studies. For the boron defects for example, other candidates could be investigated, as well as the previously mentioned STS simulations. Different interface geometries between graphene and boron nitride could be studied, or different ribbons in order to reveal the characteristics of the interfaces and their influence on the rest of the graphene and boron nitride ribbons. Finally, the study on multilayers of graphene and boron nitride could benefit from calculations on bigger cells which would highlight the effect of the interaction between the two layers. Moreover, sandwich structures could be studied as well, simulating the trilayers of graphene between a boron nitride substrate, and a protective boron nitride layer on top of it as recently synthesized experimentally [25].

# List of publications

The following list contains the different articles to which I contributed during this thesis :

- S. M.-M. Dubois, Z. Zanolli, X. Declerck, and J.-C. Charlier “*Electronic properties and quantum transport in graphene-based nanostructures*” Eur. Phys. J. B 72, 1 (2009).
- A. R. Botello-Méndez, X. Declerck, M. Terrones, H. Terrones, and J.-C. Charlier “*One-dimensional extended lines of divacancy defects in graphene*” Nanoscale 3, 2868 (2011).
- A. Lherbier, S. M.-M. Dubois, X. Declerck, S. Roche, Y.-M. Niquet, J.-C. Charlier “*Two-dimensional graphene with structural defects : elastic mean free path, minimum conductivity, and Anderson transistion*” Phys. Rev. Lett. 106, 046803 (2011).
- A. Lherbier, S. M.-M. Dubois, X. Declerck, S. Roche, Y.-M. Niquet, J.-C. Charlier “*Transport properties of graphene containing structural defects*” Phys. Rev. B 86, 075402 (2012).
- S. M.-M. Dubois, X. Declerck, and J.-C. Charlier “*Magnetoresistive junction in bare zigzag boron nitride/graphene ribbons*” in

## LIST OF PUBLICATIONS

---

preparation **2013**.

- X. Declerck and J.-C. Charlier “*Ab initio electronic properties of graphene deposited on a single BN layer*” in preparation **2013**.

## Bibliography

- [1] K. S. Novoselov, *et al.* “*Electric field effect in atomically thin carbon films*” *Science* 306, 666 (2004).
- [2] H.-P. Boehm, *et al.* “*Thinnest carbon films*” *Z. Naturforschg.* 17 b, 150 (1962).
- [3] H.-P. Boehm and E. Stumpp “*Citation errors concerning the first report on exfoliated graphite*” *Carbon* 45, 1381 (2007).
- [4] C. Schafhaeuti “*On the combinations of carbon with silicon and iron, and other metals, forming the different species of cast iron, steel, and malleable iron*” *Phil Mag* 16, 570 (1840).
- [5] H. C. Schniepp, *et al.* “*Functionalized single graphene sheets derived from splitting graphite oxide*” *J. Phys. Chem. B* 110, 8535 (2006).
- [6] L. Jiao, *et al.* “*Narrow graphene nanoribbons from carbon nanotubes*” *Nature* 458, 877 (2009).
- [7] D. V. Kosynkin, *et al.* “*Longitudinal unzipping of carbon nanotubes to form graphene nanoribbons*” *Nature* 458, 872 (2009).

## BIBLIOGRAPHY

---

- [8] C. Berger, *et al.* “*Ultrathin epitaxial graphite : 2D electron gas properties and a route toward graphene-based nanoelectronics*” J. Phys. Chem. B 108, 19912 (2004).
- [9] T. Ohta, *et al.* “*Controlling the electronic structure of bilayer graphene*” Science 313, 951 (2006).
- [10] X. S. Li, *et al.* “*Large-area synthesis of high-quality and uniform graphene films on copper foils*” Science 324, 1312 (2009).
- [11] S. Bae, *et al.* “*Roll-to-roll production of 30-inch graphene films for transparent electrodes*” Nat. Nano 5, 574 (2010).
- [12] A. S. Mayorov, *et al.* “*Micrometer-scale ballistic transport in encapsulated graphene at room temperature*” Nano Lett. 11, 2396 (2011).
- [13] J. Moser, *et al.* “*Current-induced cleaning of graphene*” Appl. Phys. Lett. 91, 163513 (2007).
- [14] C. Lee, *et al.* “*Measurement of the elastic properties and intrinsic strength of monolayer graphene*” Science 321, 385 (2008).
- [15] A. A. Balandin “*Thermal properties of graphene and nanostructured carbon materials*” Nat. Mater. 10, 569 (2011).
- [16] R. R. Nair, *et al.* “*Fine structure constant defines visual transparency of graphene*” Science 320, 1308 (2008).
- [17] D. C. Elias; *et al.* “*Control of graphene’s properties by reversible hydrogenation*” Science 323, 610 (2009).



- 
- [18] R. R. Nair, *et al.* “*Fluorographene : a two-dimensional counterpart of Teflon*” *Small* 6, 2877 (2010).
- [19] K. Novoselov, *et al.* “*A roadmap for graphene*” *Nature* 490, 192 (2012).
- [20] K. Novoselov, *et al.* “*Two-dimensional atomic crystals*” *Proc. Natl Acad. Sci. USA* 102, 10451 (2005).
- [21] J. Xue, *et al.* “*Scanning tunneling microscopy and spectroscopy of ultra-flat graphene on hexagonal boron nitride*” *Nat. Mater.* 10, 282 (2010).
- [22] S. Joshi, *et al.* “*Boron nitride on Cu(111) : an electronically corrugated monolayer*” *Nano Lett.* 12, 5821 (2012).
- [23] A. Zunger, *et al.* “*Optical properties of hexagonal boron nitride*” *Phys. Rev. B* 13, 5560 (1976).
- [24] C. R. Dean, *et al.* “*Boron nitride substrates for high-quality graphene electronics*” *Nat. Nano.* 5, 722 (2010).
- [25] L. Britnell, *et al.* “*Field-effect tunneling transistor based on vertical graphene heterostructures*” *Science* 335, 947 (2012).
- [26] L. Ci, *et al.* “*Atomic layers of hybridized boron nitride and graphene domains*” *Nat. Mater.* 9, 430 (2010).
- [27] M. P. Levendorf, *et al.* “*Graphene and boron nitride lateral heterostructures for atomically thin circuitry*” *Nature* 488, 627 (2012).

## BIBLIOGRAPHY

---

- [28] A. H. Castro Neto, *et al.* “*The electronic properties of graphene*” Rev. Mod. Phys 81, 109 (2009).
- [29] P. R. Wallace “*The band theory of graphite*” Phys. Rev. 71, 622 (1947).
- [30] M. I. Katsnelson, *et al.* “*Chiral tunnelling and the Klein paradox in graphene*” Nat. Phys. 2, 620 (2006).
- [31] X. Blase, *et al.* “*Quasiparticle band structure of bulk hexagonal boron nitride and related systems*” Phys. Rev. B 51, 6868 (1995).
- [32] X. Gonze, lecture notes [PHYS 2420] “*Formalisme de la fonctionnelle de la densité*”, 1997.
- [33] J. M. Soler, *et al.* “*The SIESTA method for ab initio order-N materials simulation*” J. Phys. Cond. Matt. 14, 2745 (2002).
- [34] X. Gonze, *et al.* “*ABINIT : first-principles approach of materials and nanosystem properties*” Computer Phys. Commun. 180, 2582 (2009).
- [35] X. Gonze, *et al.* “*A brief introduction to the ABINIT software package*” Zeit. Kristallogr. 220, 558 (2005).
- [36] M. Born and R. Oppenheimer “*Quantum theory of molecules*” Ann. Phys. 84, 0457 (1927).
- [37] P. Hohenberg and W. Kohn “*Inhomogeneous electron gas*” Phys. Rev. 136, B864 (1964).
- [38] W. Kohn and L. J. Sham “*Self-consistent equations including exchange and correlation effects*” Phys. Rev. 140, A1133 (1965).

- 
- [39] D. M. Ceperley and B. J. Alder “*Ground state of the electron gas by a stochastic method*” Phys. Rev. Lett. 45, 566 (1980).
  - [40] K. Lee, *et al.* “*Higher-accuracy van der Waals density functional*” Phys. Rev. B 82, 081101(R) (2010).
  - [41] J. Perdew and Y. Wang “*Accurate and simple density functional for the electronic exchange energy: generalized gradient approximation*” Phys. Rev. B 33, 8800 (1986).
  - [42] J. Perdew “*Electronic structure of solids '91*”. Edited by P. Ziesche and H. Eschrig, Akademie Verlag, Berlin, 1991, p. 11.
  - [43] Y. Zhang and W. Yang “*Comment on 'Generalized gradient approximation made simple'*” Phys. Rev. Lett. 80, 890 (1998).
  - [44] M. Dion, *et al.* “*Van der Waals density functional for general geometries*” Phys. Rev. Lett. 92, 246401 (2004).
  - [45] N. Troullier and J. L. Martins “*Efficient pseudopotential for plane-wave calculations*” Phys. Rev. B 43, 1993 (1991).
  - [46] L. Kleinman and D. M. Bylander “*Efficacious form for model pseudopotentials*” Phys. Rev. Lett. 48, 1425 (1982).
  - [47] M. C. Payne, *et al.* “*Iterative minimization techniques for ab initio total-energy calculations : molecular dynamics and conjugate gradients*” Rev. Mod. Phys. 64, 1045 (1992).
  - [48] S. Roche and D. Mayou “*Conductivity of quasiperiodic systems : a numerical study*” Phys. Rev. Lett. 79, 2518 (1997).

## BIBLIOGRAPHY

---

- [49] A. Lherbier, *et al.* “*Charge transport in chemically doped 2D graphene*” Phys. Rev. Lett. 101, 036808 (**2008**).
- [50] H. Ishii, *et al.* “*Charge transport in carbon nanotubes based materials : a Kubo-Greenwood computational approach*” C. R. Physique 10, 283 (**2009**).
- [51] F. Triozon, “*Diffusion quantique et conductivité dans les système a périodiques*”, Ph.D. Thesis. Laboratoire d’Études des Propriétés Électroniques des Solides - CNRS - Grenoble, **1999**.
- [52] S. Datta “*Electronic transport in mesoscopic systems*”. Cambridge University Press, Cambridge, **1997**.
- [53] M. Brandbyge, *et al.* “*Density-functional method for nonequilibrium electron transport*” Phys. Rev. B 65, 165401 (**2002**).
- [54] D. Z.-Y. Ting, *et al.* “*Multiband treatment of quantum transport in interband tunnel devices*” Phys. Rev. B 45, 3583 (**1992**).
- [55] Y. Meir and N. S. Wingreen “*Landauer formula for the current through an interacting electron region*” Phys. Rev. Lett. 68, 2512 (**1992**).
- [56] S. Sanvito, *et al.* “*General Green’s-function formalism for transport calculations with spd Hamiltonians and giant magnetoresistance in Co- and Ni-based magnetic multilayers*” Phys. Rev. B 59, 11936 (**1999**).
- [57] M. Paulsson and M. Brandbyge “*Transmission eigenchannels from nonequilibrium Green’s functions*” Phys. Rev. B 76, 115117 (**2007**).

- 
- [58] J. Tersoff, and D. R. Hamann “*Theory of the scanning tunneling microscope*” Phys. Rev. B 31, 805 (1984).
  - [59] A. V. Krashennnikov, *et al.* “*Bending the rules : contrasting vacancy energetics and migration in graphite and carbon nanotubes*” Chem. Phys. Lett. 418, 132 (2006).
  - [60] C. Gómez-Navarro, *et al.* “*Tuning the conductance of single-walled carbon nanotubes by ion irradiation in the Anderson localization regime*” Nat. Mater. 4, 534 (2005).
  - [61] B. Biel, *et al.* “*Anderson localization in carbon nanotubes: defect density and temperature effects*” Phys. Rev. Lett. 95, 266801 (2005).
  - [62] J.-H. Chen, *et al.* “*Defect scattering in graphene*” Phys. Rev. Lett. 102, 236805 (2009).
  - [63] J. Lahiri, *et al.* “*An extended defect in graphene as a metallic wire*” Nat. Nano. 5, 326 (2010).
  - [64] A. R. Botello-Méndez, *et al.* “*One-dimensional extended lines of divacancy defects in graphene*” Nanoscale 3, 2868 (2011).
  - [65] A. Lherbier, *et al.* “*Two-dimensional graphene with structural defects : elastic mean free path, minimum conductivity, and Anderson transistion*” Phys. Rev. Lett. 106, 046803 (2011).
  - [66] A. Lherbier, *et al.* “*Transport properties of graphene containing structural defects*” Phys. Rev. B 86, 075402 (2012).

## BIBLIOGRAPHY

---

- [67] R. G. Amorim, *et al.* “*Divacancies in graphene and carbon nanotubes*” Nano Lett. 7, 2459 (2007).
- [68] J. Ma, *et al.* “*Stone-Wales defects in graphene and other planar  $sp^2$ -bonded materials*” Phys. Rev. B 80, 033407 (2009).
- [69] H. Amara, *et al.* “*Scanning tunneling microscopy fingerprints of point defects in graphene : a theoretical prediction*” Phys. Rev. B 76, 115423 (2007).
- [70] H. Lee, *et al.* “*Magnetic ordering at the edges of graphitic fragments : magnetic tail interactions between the edge-localized states*” Phys. Rev. B 72, 174431 (2005).
- [71] S. M.-M. Dubois, *et al.* In preparation (2013).
- [72] S. Roche, *et al.* “*Chemically enriched graphene-based switching devices : a novel principle driven by impurity-induced quasi-bound states and quantum coherence*” Physica E 44, 960 (2012).
- [73] J. H. Chen, *et al.* “*Intrinsic and extrinsic performance limits of graphene devices on SiO<sub>2</sub>*” Nat. Nano. 3, 206 (2008).
- [74] S. V. Morozov, *et al.* “*Giant intrinsic carrier mobilities in graphene and its bilayer*” Phys. Rev. Lett. 100, 016602 (2008).
- [75] J. Bang, *et al.* “*Localization and one-parameter scaling in hydrogenated graphene*” Phys. Rev. B 81, 193412 (2010).
- [76] Y. V. Skrypnyk, *et al.* “*Metal-insulator transition in hydrogenated graphene as manifestation of quasiparticle spectrum*”

- 
- rearrangement of anomalous type*” Phys. Rev. B 83, 085421 (2011).
- [77] G. Schubert, *et al.* “*Metal-to-insulator transition and electron-hole puddle formation in disordered graphene nanoribbons*” Phys. Rev. Lett. 108, 066402 (2012).
- [78] R. Grassi, *et al.* “*Scaling of the energy gap in pattern-hydrogenated graphene*” Nano Lett. 11, 4574 (2011).
- [79] A. Bostwick, *et al.* “*Quasiparticle transformation during a metal-insulator transition in graphene*” Phys. Rev. Lett. 103, 056404 (2009).
- [80] N. Leconte, *et al.* “*Damaging graphene with ozone treatment : a chemically tunable metal-insulator transition*” ACS Nano 4, 4033 (2010).
- [81] J. Moser, *et al.* “*Magnetotransport in disordered graphene exposed to ozone: from weak to strong localization*” Phys. Rev. B 81, 205445 (2010).
- [82] N. Leconte, *et al.* “*Quantum transport in chemically modified two-dimensional graphene: from minimal conductivity to Anderson localization*” Phys. Rev. B 84, 235420 (2011).
- [83] G. Trambly de Laissardière, *et al.* “*Electronic transport in graphene : quantum effects and role of local defects*” Mod. Phys. Lett. B 25, 1019 (2011).

## BIBLIOGRAPHY

---

- [84] A. Uppstu, *et al.* “*Electronic transport in graphene-based structures: an effective cross-section approach*” *Phys. Rev. B* 85, 041401(R) (2012).
- [85] J. Haskins, *et al.* “*Control of thermal and electronic transport in defect-engineered graphene nanoribbon*” *ACS Nano* 5, 3779 (2011).
- [86] S. Wu, *et al.* “*Criticality of vacancy-induced metal-insulator transition in graphene*” arXiv:1001.2057.
- [87] W. Li, *et al.* “*Electron localization in metal-decorated graphene*” *Phys. Rev. B* 84, 045431 (2011).
- [88] H. Tanaka, *et al.* “*Novel macroscopic BC<sub>3</sub> honeycomb sheet*” *Solid State Commun.* 136, 22 (2005).
- [89] A. Thomas, *et al.* “*Graphitic carbon nitride materials : variation of structure and morphology and their use a metal-free catalysts*” *J. Mater. Chem* 18, 4893 (2008).
- [90] L. Zhao, *et al.* “*Visualizing individual nitrogen dopants in monolayer graphene*” *Science* 333, 999 (2011).
- [91] F. Joucken, *et al.* “*Localized state and charge transfer in nitrogen-doped graphene*” *Phys. Rev. B* 85, 161408(R) (2012).
- [92] R. Lv, *et al.* “*Nitrogen-doped graphene : beyond single substitution and enhanced molecular sensing*” *Sci. Rep.* 2, 586 (2012).
- [93] D. Usachov, *et al.* “*Nitrogen-doped graphene : efficient growth, structure, and electronic properties*” *Nano Lett.* 11, 5401 (2011).



- 
- [94] D. Deng, *et al.* “Toward N-doped graphene via solvothermal synthesis” Chem. Mater. 23, 1188 (2011).
- [95] B. Zheng, *et al.* “Scanning tunneling microscopy simulations of nitrogen- and boron-doped graphene and single-walled carbon nanotubes” ACS Nano 4, 4165 (2010).
- [96] A. Lherbier, *et al.* In preparation (2013).
- [97] Ph. Lambin, *et al.* “Long-range interactions between substitutional nitrogen dopants in graphene : electronic properties calculations” Phys. Rev. B 86, 045448 (2012).
- [98] Y. Fujimoto and Susumu Saito “Formation, stabilities, and electronic properties of nitrogen defects in graphene” Phys. Rev. B 84, 245446 (2011).
- [99] Z. Hou, *et al.* “Interplay between nitrogen dopants and native point defects in graphene” Phys. Rev. B 85, 165439 (2012).
- [100] J. C. Meyer, *et al.* “Selective sputtering and atomic resolution imaging of atomically thin boron nitride membranes” Nano Lett. 9, 2683 (2009).
- [101] J. Cai, *et al.* “Atomically precise bottom-up fabrication of graphene nanoribbons” Nature 466, 470 (2010).
- [102] X. Li, *et al.* “Chemically derived, ultrasmooth graphene nanoribbon semiconductors” Science 319, 1229 (2008).
- [103] S. M.-M. Dubois, *et al.* “Electronic properties and quantum transport in graphene-based nanostructures” Eur. Phys. J. B 72, 1 (2009).

## BIBLIOGRAPHY

---

- [104] Y.-W. Son, *et al.* “*Energy gaps in graphene nanoribbons*” Phys. Rev. Lett. 97, 216803 (2006).
- [105] K. Wakabayashi, *et al.* “*Electronic and magnetic properties of nanographite ribbons*” Phys. Rev. B 59, 8271 (1999).
- [106] S. Okada and A. Oshiyama “*Magnetic ordering in hexagonally bonded sheets with first-row elements*” Phys. Rev. Lett. 87, 146803 (2001).
- [107] H. Lee, *et al.* “*Magnetic ordering at the edges of graphitic fragments: magnetic tail interactions between the edge-localized states*” Phys. Rev. B 72, 174431 (2005).
- [108] Y.-W. Son, *et al.* “*Half-metallic graphene nanoribbons*” Nature 444, 347 (2006).
- [109] Ç. Ö. Girit, *et al.* “*Graphene at the edge : stability and dynamics*” 323, 1705 (2009).
- [110] P. Koskinen, *et al.* “*Evidence for graphene edges beyond zigzag and armchair*” Phys. Rev. B 80, 073401 (2009).
- [111] M. Terrones, *et al.* “*Experimental and theoretical studies suggesting the possibility of metallic boron nitride edges in porous nanourchins*” Nano Lett. 8, 1026 (2008).
- [112] A. Nagashima, *et al.* “*Electronic structure of monolayer hexagonal boron nitride physisorbed on metal surfaces*” Phys. Rev. Lett. 75, 3918 (1995).

- 
- [113] D. Pacilé, *et al.* “*The two-dimensional phase of boron nitride : few-atomic-layer sheets and suspended membranes*” Appl. Phys. Lett. 92, 133107 (2008).
- [114] H. Zeng, *et al.* “*White graphenes : boron nitride nanoribbons via boron nitride nanotube unwrapping*” Nano Lett. 10, 5049 (2010).
- [115] J. Nakamura, *et al.* “*Electronic and magnetic properties of BNC ribbons*” Phys. Rev. B 72, 205429 (2005).
- [116] A. J. Du, *et al.* “*First-principle studies of electronic structure and C-doping effect in boron nitride nanoribbon*” Chem. Phys. Lett. 447, 181 (2007).
- [117] Z. Zhang, *et al.* “*Energy-gap modulation of BN ribbons by transverse electric fields : first-principles calculations*” Phys. Rev. B 77, 075403 (2008).
- [118] F. Zheng, *et al.* “*Scaling law of the giant Stark effect in boron nitride nanoribbons and nanotubes*” Phys. Rev. B 78, 085423 (2008).
- [119] C.-H. Park, *et al.* “*Energy gaps and Stark effect in boron nitride nanoribbons*” Nano Lett. 8, 2200 (2008).
- [120] V. Barone and J. E. Peralta “*Magnetic boron nitride nanoribbons with tunable electronic properties*” Nano Lett. 8, 2210 (2008).
- [121] A. J. Williamson, *et al.* “*Linear-scaling quantum Monte Carlo calculations*” Phys. Rev. Lett. 87, 246406 (2001).

## BIBLIOGRAPHY

---

- [122] B. Grabowski, *et al.* “*Ab initio study of the thermodynamic properties of nonmagnetic elementary fcc metals : exchange-correlation-related error bars and chemical trends*” Phys. Rev. B 76, 024309 (2007).
- [123] S. Jungthawan, *et al.* “*Electronic structures of graphene/boron nitride sheet superlattices*” Phys. Rev. B 84, 235424 (2011).
- [124] L. Britnell, *et al.* “*Electron tunneling through ultrathin boron nitride crystalline barriers*” Nano Lett. 12, 1707 (2012).
- [125] M. Yankowitz, *et al.* “*Emergence of superlattice Dirac points in graphene on hexagonal boron nitride*” Nat. Phys. 8, 382 (2012).
- [126] Y.-W. Tan, *et al.* “*Measurement of scattering rate and minimum conductivity in graphene*” Phys. Rev. Lett. 99, 246803 (2007).
- [127] K. I. Bolotin, *et al.* “*Temperature-Dependent Transport in Suspended Graphene*” Phys. Rev. Lett. 101, 096802 (2008).
- [128] Y. Fan, *et al.* “*Tunable electronic structure of graphene/boron nitride heterobilayers*” Appl. Phys. Lett. 98, 083103 (2011).
- [129] G. Giovannetti, *et al.* “*Substrate-induced band gap in graphene on hexagonal boron nitride : ab initio density functional calculations*” Phys. Rev. B 76, 073103 (2007).
- [130] Z. Liu, *et al.* “*Direct growth of graphene/hexagonal boron nitride stacked layers*” Nano Lett. 11, 2032 (2011).
- [131] S. Latil, *et al.* “*Massless fermions in multilayer graphitic systems with misoriented layers : ab initio calculations and experimental fingerprints*” Phys. Rev. B 76, 201402(R) (2007).

- 
- [132] J.-C. Charlier, *et al.* “*First-principles study of the electronic properties of graphite*” Phys. Rev. B 43, 4570 (1991).
- [133] B. Sachs, *et al.* “*Adhesion and electronic structure of graphene on hexagonal boron nitride substrate*” Phys. Rev. B 84, 195414 (2011).
- [134] R. E. Franklin “*The structure of graphitic carbons*” Acta Cryst. 4, 253 (1953).
- [135] R. Zacharia, *et al.* “*Interlayer cohesive energy of graphite from thermal desorption of polyaromatic hydrocarbons*” Phys. Rev. B 69, 155406 (2004).
- [136] C.-H. Park, *et al.* “*New generation of massless Dirac fermions in graphene under external periodic potentials*” Phys. Rev. Lett. 101, 126804 (2008).
- [137] A. Bosak and M. Krisch, “*Elasticity of single-crystalline graphite : inelastic x-ray scattering study*” Phys. Rev. B 75, 153408 (2007).
- [138] K. Sato, *et al.* “*Zone folding effect in Raman G-band intensity of twisted bilayer graphene*” Phys. Rev. B 86, 125414 (2012).



# Appendix A

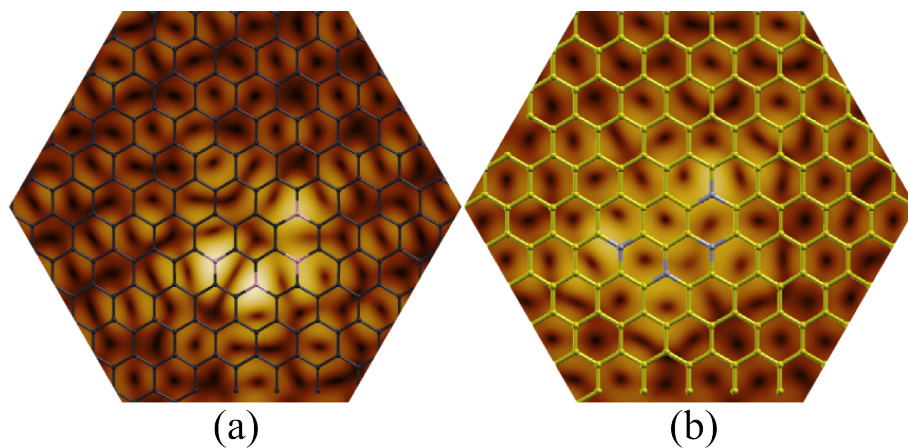
## Boron and nitrogen doping of graphene

This appendix shows complementary STM images to the ones presented in the chapter devoted to this subject (p.99). The simulation parameters are identical to the ones used before, except for the exchange-correlation functional. In the present case, GGA is used. Fig. A.1 represents the images for negative and positive bias of an arrangement of four boron atoms in a  $BC_3$  configuration (the so-called boat configuration). Fig. A.2 shows the image corresponding to two boron atoms on a  $q5q7$  divacancy. This latter defect has not been introduced before in this thesis. It is composed of a square arrangement made of four pentagons and four heptagons, with a hexagon “trapped” on the inside of the square. Fig. A.3 presents the image corresponding to two boron atoms on the previously discussed 585 divacancy. Finally, Fig. A.4 shows the image corresponding to one boron atom on a Stone-Thrower-Wales defect. These defects might be good candidates for some of the experimental

## A. BORON AND NITROGEN DOPING OF GRAPHENE

---

defects observed in Fig. 4.12. However, more calculations as well as more detailed experimental images are needed to confirm this. STS calculation might also help to validate or discard some of these candidates.

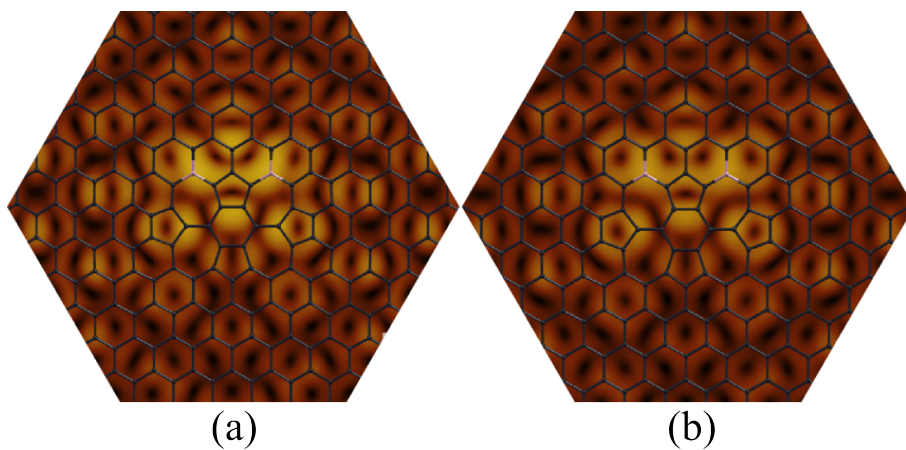


---

Fig. A.1 - Simulated STM images for four boron atoms in a  $BC_3$  configuration at -100 mV (a) and 100 mV (b) tip bias.

---

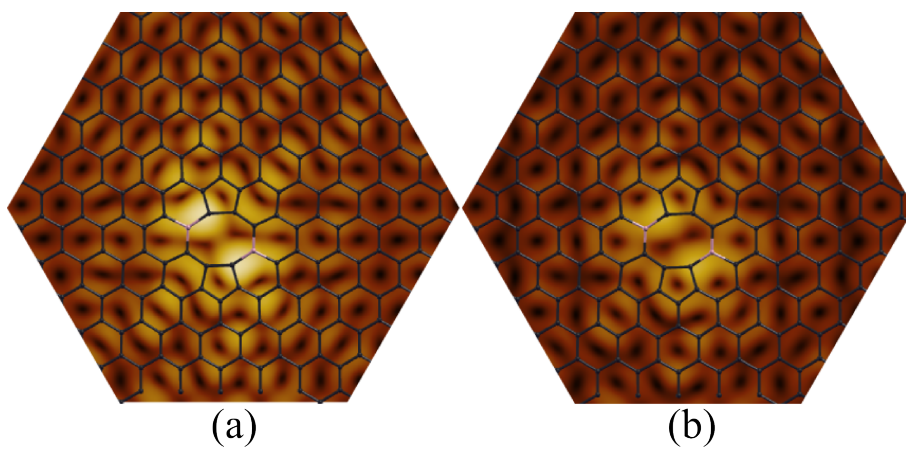




---

Fig. A.2 - Simulated STM images for two boron atom combined with a  $q5q7$  divacancy at -100 mV (a) and 100 mV (b) tip bias.

---



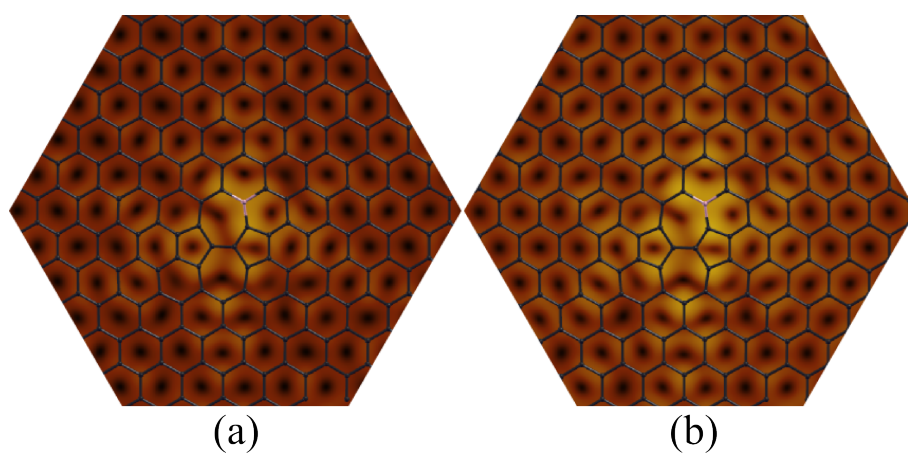
---

Fig. A.3 - Simulated STM images for two boron atom combined with a 585 divacancy at -100 mV (a) and 100 mV (b) tip bias.

---

## A. BORON AND NITROGEN DOPING OF GRAPHENE

---



---

Fig. A.4 - Simulated STM images for one boron atom combined with a STW defect at -100 mV (a) and 100 mV (b) tip bias.

---

## Appendix B

### Graphene and boron nitride multilayers

The next table (Tab. B.1) presents the length of the smallest vector  $\mathbf{A} = n\mathbf{a}_1 + m\mathbf{a}_2$  in graphene and  $\mathbf{B} = n\mathbf{b}_1 + m\mathbf{b}_2$  in boron nitride (BN). The mismatch between graphene and boron nitride is of 1.8%. The colors highlight the choices of integers that were done to define the moiré patterns used in Chap. 6 : red for the (2,4)-(3,3), blue for the (4,3)-(6,0), and green for the (8,4)-(7,5). The corresponding mismatches are 1.84%, 1.38%, and 1.37%, respectively (the experimental value is  $\sim 1.80\%$ ).

## B. GRAPHENE AND BORON NITRIDE MULTILAYERS

| n | m | graphene :<br>$ \mathbf{A} $ (Å) | BN :<br>$ \mathbf{B} $ (Å) | n | m | graphene :<br>$ \mathbf{A} $ (Å) | BN :<br>$ \mathbf{B} $ (Å) |
|---|---|----------------------------------|----------------------------|---|---|----------------------------------|----------------------------|
| 1 | 0 | 2.460                            | 2.504                      | 6 | 2 | 17.736                           | 18.055                     |
| 1 | 1 | 4.260                            | 4.337                      | 6 | 3 | 19.522                           | 19.873                     |
| 2 | 0 | 4.919                            | 5.008                      | 6 | 4 | 21.442                           | 21.827                     |
| 2 | 1 | 5.607                            | 6.624                      | 6 | 5 | 23.462                           | 23.885                     |
| 2 | 2 | 8.520                            | 8.673                      | 6 | 6 | 25.560                           | 26.020                     |
| 3 | 0 | 7.379                            | 7.511                      | 7 | 0 | 17.217                           | 17.526                     |
| 3 | 1 | 8.868                            | 9.028                      | 7 | 1 | 18.569                           | 18.903                     |
| 3 | 2 | 10.721                           | 10.914                     | 7 | 2 | 20.132                           | 20.494                     |
| 3 | 3 | 12.78                            | 13.010                     | 7 | 3 | 21.861                           | 22.254                     |
| 4 | 0 | 9.838                            | 10.015                     | 7 | 4 | 23.719                           | 24.146                     |
| 4 | 1 | 11.271                           | 11.474                     | 7 | 5 | 25.678                           | 26.140                     |
| 4 | 2 | 13.015                           | 13.249                     | 7 | 6 | 27.717                           | 28.216                     |
| 4 | 3 | 14.961                           | 15.230                     | 7 | 7 | 29.820                           | 30.357                     |
| 4 | 4 | 17.040                           | 17.347                     | 8 | 0 | 19.676                           | 20.030                     |
| 5 | 0 | 12.298                           | 12.519                     | 8 | 1 | 21.014                           | 21.392                     |
| 5 | 1 | 13.694                           | 13.940                     | 8 | 2 | 22.542                           | 22.948                     |
| 5 | 2 | 15.360                           | 15.636                     | 8 | 3 | 24.223                           | 24.659                     |
| 5 | 3 | 17.217                           | 17.526                     | 8 | 4 | 26.029                           | 26.498                     |
| 5 | 4 | 19.209                           | 19.555                     | 8 | 5 | 27.935                           | 28.438                     |
| 5 | 5 | 21.300                           | 21.683                     | 8 | 6 | 31.974                           | 30.460                     |
| 6 | 0 | 14.757                           | 15.023                     | 8 | 7 | 31.974                           | 32.549                     |
| 6 | 1 | 16.128                           | 16.418                     | 8 | 8 | 34.080                           | 34.369                     |

Table B.1 - Comparison between the length of an  $(n, m)$  vector for graphene ( $|\mathbf{A}|$ ) and for boron nitride ( $|\mathbf{B}|$ ), with 1.80% lattice mismatch. The colors highlight the pairs of vectors used to define the studied moiré patterns.