

Spintronics in graphene related nanostructures

An ab-initio study

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Abstract

In this report, we use first-principles methods to investigate the spin-resolved transport properties of zigzag graphene nanoribbons (ZGNRs) whose edges have been functionalized by phenyl groups. Electronic structure calculations rely on density functional theory (DFT) and transport properties are computed within the non-equilibrium Green's functions (NEGF) formalism. The computational tools used in this work are the **SIESTA** (DFT) and **TranSIESTA** (NEGF) software.

We first provide a review on the theoretical concepts behind DFT and NEGF formalism. Then, we analyse simpler systems such as pristine graphene and 6-ZGNRs. The case of a Stone-Wales defect is also treated. Finally the so-called phenyl-edge modified 6-ZGNRs (PEM 6-ZGNRs) are studied.

It is found that such defects introduce a localized state within the band-gap of the 6-ZGNRs. When multiple phenyl groups lay on the edge, the distance between them has a significant influence on the electronic properties. The spin-resolved transmission spectrum for a 6-ZGNRs/PEM 6-ZGNRs junction is analysed and reveals interesting features that may lead to efficient spin filtering.

To understand the effect of the phenyl groups on the conductance of 6-ZGNRs, 13 different edge topologies are computed within **TranSIESTA**. Common features appear for most of the structures. One of the most remarkable one is the appearance of enhanced back-scattering at the energy $E = -0.48$ eV in the $\uparrow\downarrow$ edge polarization. When one of the edge is left pristine, it is found that this back-scattering only occurs for one spin channel and not the other.

For the other polarization ($\uparrow\uparrow$), extinction of the conductance of one of the spin channel around the Fermi energy suggests a possible spin filter.

Keywords: DFT, NEGF, graphene, nanoribbons, quantum transport

Preface and Acknowledgements

Since my very young age, I have always admired scientists for their huge contribution to progress so that I wanted to be part of such community. Even though starting university at the younger age of 16, I was already convinced that research could bring me the fulfilment that I, like all other human beings on this planet, was looking for.

I was impatiently waiting for the master thesis and the associated research work which requires us, students, to show that during all those years we have not only acquired a solid amount of knowledge but also sharpened our skills like autodidaxy, self-management and critical thinking.

Quantum mechanics and its weird predictions has always amazed me by its accuracy to describe the nano-world with concepts that may sometimes be beyond our imagination. So, it was not a real surprise when I found myself totally fascinated by ab-initio quantum simulation methods.

In the area where theory fails to deliver practical descriptions and experiment stays out of reach (for technological or economical reasons), computational physics succeeds at providing us an accurate enough picture with a limited number of hardware requirements: computers. Numerical simulations possess the feature to behave as a bridge between theory and experiment as it delivers not only prediction capabilities but also a unique probe to understand the underlying physics of complex systems.

As I was studying abroad in the Norwegian University of Science and Technology the year before, I was not able to follow an atomistic simulation course that sets the foundation for a materials simulation related master thesis. However, as I knew that such topics were raising in me a growing interest, I poured a lot of efforts in self-learning. Professor Jean-Christophe Charlier, who would become my supervisor for this work, accepted to coach me, regularly exchanging e-mail from Belgium. I deeply thank him for the trust and help he provided me. None of this would have been possible without his help.

I would like to express my gratitude to all the researchers from the Nanoscopic Physics department of the *Institute of Condensed Matter and Nanosciences* I interacted with. Especially, I would like to thank Aurélien Lherbier who was closely following my work. He was always available to answer spontaneous questions. Also, I would like to thank Samuel Dechamps, a former master student of my faculty and now PhD student, who kindly shared with me tips that turned out to be particularly useful.

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Finally, I would like to thank *you*, the reader that took an interest in reading this report. I sincerely hope that the work I have done with the help of the aforementioned people will not disappoint you.

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1

The development of electronics in the past decades has allowed for smaller and faster devices. One of the most well-known prediction in this field is probably the one attributed to Gordon Moore who predicted in 1965 a doubling of components per integrated circuit every year [1]. Although this law¹ has been quite nicely followed since then (see Fig. 1.1), saturation has been observed few years ago and a physical limit is predicted to be reached within the next decades [2].

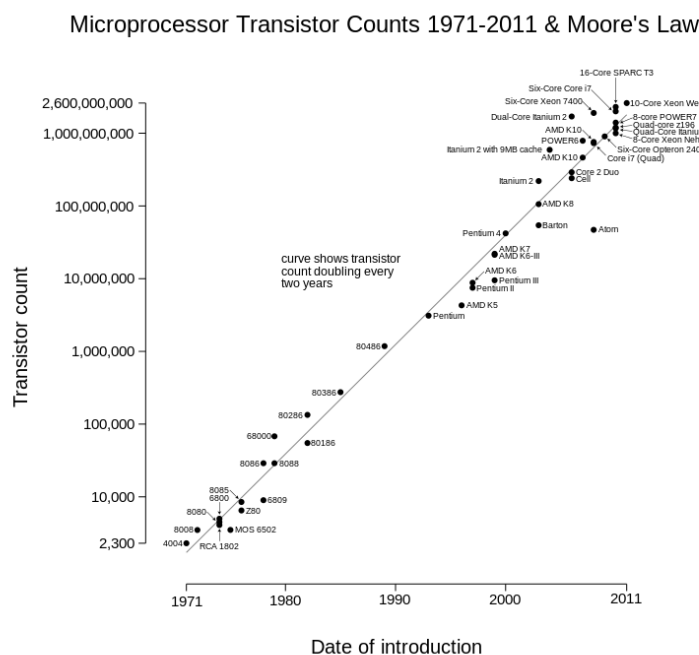


Figure 1.1: Number of transistors on an integrated circuit (transistor count) from 1971 to 2011. The vertical axis is in a logarithmic scale. Doubling of the number of transistors occurs every year. Adapted from [3].

The end of Moore's law is mainly due to the granularity of matter which limits the scaling down of transistors. Indeed, once the atomic scale will be reached, no further miniaturization is *a priori* possible. Moreover, at this scale, quantum effects, such as tunnelling, make the conception of such devices a true technological challenge. Of course, even if Moore's law applies more specifically to integrated transistors, other components follow the same trend.

¹Moore's law is an observation and *not* a physical law.

In this conventional electronics, the charge of the electron is being taken into account while its spin degree of freedom is totally disregarded. This additional information carried by the electron might actually be the essence of future electronics. This paradigm, where devices use the spin, is called *spintronics*. In this case, the spin information can either be added to the conventional charge-based devices or be used alone to create new devices.

As mentioned by S.A. Wolf et al. [4], spintronics offers nonvolatility, increased data processing speed, decreased electric power consumption, and increased integration densities compared to conventional semiconductor devices. The range of application of spintronics can be quite wide. For instance, Rudolph et al. [5] demonstrated that the use of spin-polarized electrons in laser operation could reduce the threshold by up to 50% compared to conventional non-polarized cases.

Spintronics is actually already used in our everyday life since metal-based devices, such as tunnel magnetoresistance, are an integral part of our technology. However, further development of spintronics requires to face tough challenges such as spin coherent transport, manipulation of spins on short time scales, ...

One of the promising candidates to answer those issues is to be found in graphene. Graphene was theoretically known before this century but it was not later than in 2004 that the first few atomically thick layers of graphene (including monolayers) were obtained using mechanical exfoliation on graphite [6]. This showed that graphene was not only a theoretical material but a real, feasible one. Since then, the commitment of the scientific community to this new material has never ceased to increase.

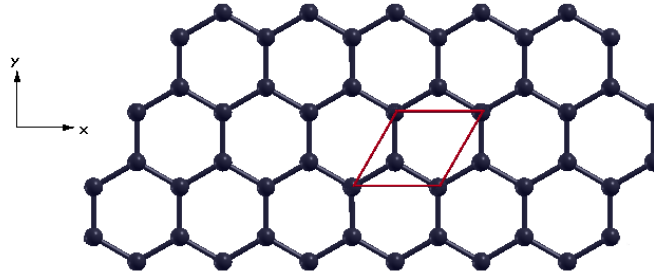


Figure 1.2: Geometrical structure of graphene with the unit cell represented by the red parallelogram. The so-called honeycomb lattice appears clearly.

The popularity of graphene is mainly due to its peculiar electronic properties such as high Fermi velocity ($v_f \approx c/300$) and high mobility ($\mu = 350\,000\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ has been obtained with CVD-grown graphene [7]). Actually, not only electronic properties but also mechanical properties make graphene a material of particular interest [8].

Nevertheless, major challenges have still to be faced to use graphene in electronic devices. For instance, its zero band gap greatly limits its use. Under those circumstances, several routes have been explored in order to open a finite band gap in graphene [9] [10] [11] [12]. One of the possibilities lays in the dimensionality of graphene-related nanostructures as graphene nanoribbons (GNRs) are found to exhibit band gaps [13] [14] [15].

In this thesis, we will explore the spin resolved transport properties of graphene nanoribbons using first-principle methods. Our computational study will rely on density functional theory (DFT) and non-equilibrium Green's functions (NEGF) as respectively implemented in **SIESTA** [16] [17] [18] and **TranSIESTA** [19]. DFT calculations are performed under the GGA, within the PBE parametrization with a norm-conserving pseudo-potential. As **SIESTA** enforces 3D periodic calculations, a supercell formalism with a distance of at least 30 Å between periodic images is used. Structures are relaxed using a conjugated gradient algorithm until the forces fall below 0.01 eV/Å.

This thesis can be broken down into three articulated steps. The first step focuses on the theoretical and computational tools required to perform electronic structure and quantum transport simulations. This will be covered by chapter 2 and 3 which will respectively present the theories (DFT and NEGF) and their practical implementation (**SIESTA** and **TranSIESTA**).

In the second step, we will consider the simple case of pristine graphene and GNRs. This will allow for a smooth transition between the first step and the third step which extensively uses DFT and NEGF to predict spin-resolved electronic properties. This step will be covered by chapter 4.

Finally, the last step of this work will rely on DFT and NEGF formalism to study what we will refer to as phenyl-edge modified graphene nanoribbons. Interesting properties of such structures will be discussed in chapter 5 and 6.

Throughout this work, we developed a post-processing tool named **SIESTAndro** written in C++. This program has been made available under the GNU General Public License v3.0 at the following address: <https://github.com/salemileandro/SIESTAndro>.

2

Theoretical Tools

In this chapter, we will review the two main theories which lay the foundation of our computational work: the density functional theory (DFT) and non-equilibrium Green's functions (NEGF).

As this work focuses on the computational study of materials and not on the development of the methods, we will only provide an introduction to important theoretical concepts. For the new comers interested in atomistic simulations, we hope that this chapter will offer a smooth introduction to the field. Further information is to be found in the references provided throughout the text.

For the experienced readers, we recommend to skip this chapter as it does not provide any crucial information to understand the main aim of this work.

2.1 Density Functional Theory

A quantum system, in its non-relativistic approximation, is fully described by the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{R}_1, \dots, \mathbf{R}_M, t) = \hat{H} \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{R}_1, \dots, \mathbf{R}_M, t) \quad (2.1)$$

where Ψ is the wavefunction, a complex-valued function of $3N + 3M + 1$ real variables. The number of electrons is given by N while M is the number of nuclei. The vector $\mathbf{r}_i$ is associated with the i^{th} electron and $\mathbf{R}_j$ with the j^{th} nucleus.

For simplicity, the spin degree of freedom is disregarded. However, it would be trivial to extend our definition, going from the position $\mathbf{r}$ ($\mathbf{R}$) to an extended 4 dimensional variable $\mathbf{x} = \{\mathbf{r}, \sigma\}$ ($\mathbf{X} = \{\mathbf{R}, \Sigma\}$) where σ (Σ) denotes the spin of electrons (nuclei).

In a simple picture where only the Coulomb interaction is taken into account, the Hamiltonian $\hat{H}$ reads

$$\hat{H} = - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + \frac{1}{4\pi\epsilon_0} \sum_{i < j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \frac{1}{4\pi\epsilon_0} \sum_{I,i} \frac{e^2 Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} + \frac{1}{4\pi\epsilon_0} \sum_{I < J} \frac{e^2 Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \quad (2.2)$$

where the first term is the kinetic energy of the nuclei, the second the kinetic energy of the electrons, the third the Coulomb interaction between electrons, the fourth the Coulomb interaction nuclei-electrons and the last the Coulomb interaction between the nuclei.

Assuming a time-independent Hamiltonian, the wavefunction Ψ can be expanded

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{R}_1, \dots, \mathbf{R}_M, t) = \psi(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{R}_1, \dots, \mathbf{R}_M) \phi(t) \quad (2.3)$$

so that ψ obeys the time-independent Schrödinger equation

$$\hat{H} \psi(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{R}_1, \dots, \mathbf{R}_M) = E \psi(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{R}_1, \dots, \mathbf{R}_M) \quad (2.4)$$

2.1.1 The Born-Oppenheimer Approximation

Eq. 2.4 considers full coupling between electrons and nuclei as the wavefunction ψ explicitly depends on both. To simplify our problem, one can use the well-known *Born-Oppenheimer approximation*. This approximation consists on decoupling the movements of electrons with the movements of nuclei. Hence, the electronic Hamiltonian is set to depend *parametrically* on the nuclei positions. The electronic problem reads

$$\left[-\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_i V_{\{\mathbf{R}\}}(\mathbf{r}_i) + \sum_i \sum_{j<i} U(\mathbf{r}_i, \mathbf{r}_j) \right] \psi_e(\mathbf{r}_1, \dots, \mathbf{r}_N) = E_e \psi_e(\mathbf{r}_1, \dots, \mathbf{r}_N) \quad (2.5)$$

where the first term into brackets is the kinetic energy of the electrons, the second term the one-body potential and the third one the two-body potential. The one-body potential $V_{\{\mathbf{R}\}}(\mathbf{r}_i)$ is the quantity in which the effect of the nuclei will be taken into account¹. The two-body potential $U(\mathbf{r}_i, \mathbf{r}_j)$ is the one describing electron-electron interactions.

It is important to understand that the electronic problem still depends on the atomic positions. However, the Born-Oppenheimer approximation allows us to treat the nuclei's positions as parameters of the electronic Hamiltonian. This means that for a given set of atomic positions $\{\mathbf{R}\}$, we can compute the electronic eigen-energies. This approximation takes source in the fact that nuclei are thousand times heavier than electrons (the mass of one proton is ~ 2000 times the mass of one electron) so that the electrons are said to adapt *instantaneously* to a change in nuclei's positions.

If the electronic problem needs to be treated within the quantum mechanical picture, the nuclei could be dealt using Newton's laws such that

$$M_I \frac{d^2 \mathbf{R}_I}{dt^2} = -\nabla_{\mathbf{R}_I} \left[\frac{1}{4\pi\epsilon_0} \sum_{I<J} \frac{e^2 Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} + E(\mathbf{R}_1, \dots, \mathbf{R}_M) \right] \quad (2.6)$$

In this equation, the influence of the electronic cloud is hidden in the quantity $E(\mathbf{R}_1, \dots, \mathbf{R}_M)$.

For atomistic simulations, one needs to solve both the atomic and electronic problem. The atomic problem is being addressed in the so-called *structural relaxation*. The equations behind this will not be treated explicitly in this work as we will focus on electrons.

We can rewrite the electronic Schrödinger equation without the cumbersome subscript which yields

$$\left[-\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_i V(\mathbf{r}_i) + \sum_i \sum_{j<i} U(\mathbf{r}_i, \mathbf{r}_j) \right] \psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = E \psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \quad (2.7)$$

From now on, we will assume the Born-Oppenheimer approximation to be valid.

2.1.2 Fundamental Theorems

The equation to be solved is a second order partial differential equation (Eq. 2.7). Assuming the expression of the Hamiltonian to be fully known, one could *at first sight* consider to solve it using a brute force algorithm such as finite differences. However, the high dimensionality is preventing us to do so. To illustrate our assertion, let's consider the case of one carbon atom.

One atom is surrounded by 6 electrons so that the wavefunction $\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$ is a multi-variate function which takes 18 real values as input. Using finite differences, one would need a grid along

¹Note that this consideration is absolutely not restrictive and other external effects could be taken into account.

each dimension and if we consider 20 points along each direction, one would get 20^{18} points to be computed. If we assume that each grid-point is one fundamental computing operation, a CPU clocked at 3 GHz would need more than $2 \cdot 10^6$ years to solve this problem !

This computational disaster is mainly due to the high dimensionality of the wavefunction. However, the wavefunction in itself is not often the main quantity of interest. The DFT simplifies the problem as it focuses its formalism around another quantity : the electronic density $n(\mathbf{r})$, defined as

$$n(\mathbf{r}) = N \int \dots \int \psi^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_2 \dots d\mathbf{r}_N \quad (2.8)$$

so that

$$\int n(\mathbf{r}) d\mathbf{r} = N \quad (2.9)$$

which is the relation between the electron density $n(\mathbf{r})$ and the number of electrons N . Note that we have considered a normalized ψ .

Simply speaking, the DFT says that the quantity $n(\mathbf{r})$ is sufficient to describe the ground-state of our system. This assertion is a direct consequence of the so-called Hohenberg-Kohn theorems which read

- The ground state density $n(\mathbf{r})$ of a many-electron system determines uniquely the external² potential $V(\mathbf{r})$ up to a constant.
- We can obtain the ground-state energy variationally: the density which minimizes the total energy is the exact ground-state density.

The proof of the theorems mainly follows what is presented in the second chapter of [20] and is to be found in appendix A.

Simply speaking, the Hohenberg-Kohn theorems tell us that the Schrödinger equation can be treated as a functional minimization problem. If we write

$$\hat{H} = \hat{F} + \hat{V} \quad (2.10)$$

where $\hat{F}$ contains the electronic kinetic operator and the two-body potential, then the energy functional can be written (see appendix A)

$$E[n(\mathbf{r})] = \langle \psi[n(\mathbf{r})] | \hat{F} | \psi[n(\mathbf{r})] \rangle + \int V(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \quad (2.11)$$

Solving the Schrödinger equation reduces then to a minimization problem

$$E = \min_{\psi \rightarrow n(\mathbf{r})} \left(E[n(\mathbf{r})] \right) = \min_{\psi \rightarrow n(\mathbf{r})} \left(\langle \psi | \hat{F} | \psi \rangle + \int V(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \right) \quad (2.12)$$

where $\psi \rightarrow n(\mathbf{r})$ means that the wavefunction chosen has to correspond to the density $n(\mathbf{r})$ under the constraint

$$\int n(\mathbf{r}) d\mathbf{r} = N \quad (2.13)$$

The energy functional can be written in a more common way as

$$E[n(\mathbf{r})] = F[n(\mathbf{r})] + V[n(\mathbf{r})] \quad (2.14)$$

²The qualifier "external" refers, *inter alia*, to the effect of the atomic cores which are indeed external compared to the electronic system.

Conceptually, the simplification DFT allows for is really remarkable. Indeed, the quantity $n(\mathbf{r})$ has been proven to be sufficient to describe *exactly* our system. However, this formalism possesses a considerable weakness: the theorems do not give us any clue on the form of $F[n(\mathbf{r})]$ and thus $E[n(\mathbf{r})]$ remains mainly unknown. As a result, without any further considerations, however beautiful our results can be, no practical calculations could be made.

2.1.3 Kohn-Sham Equations

In 1965, Kohn-Sham proposed a simple approach to tackle this problem [21]. Roughly speaking, the Kohn-Sham approach consists on going from a fully interacting problem to a non-interacting one. For this, a non-interacting electron kinetic operator is introduced.

The non-interacting one-particle wavefunctions are referred to as $\phi_i^\sigma(\mathbf{r})$ (the index i represents the i^{th} electron and the superscript σ its spin). The density of such a system is given by

$$n(\mathbf{r}) = \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} |\phi_i^\sigma(\mathbf{r})|^2 \quad (2.15)$$

where we have defined N_σ as the number of electrons of spin σ . Obviously, since electrons are two-spin particles, we have

$$N = N_\uparrow + N_\downarrow \quad (2.16)$$

We can thus now define a spin- $\uparrow$ /spin- $\downarrow$ density

$$\begin{aligned} n_\downarrow(\mathbf{r}) &= \sum_{i=1}^{N_\downarrow} |\phi_i^\downarrow(\mathbf{r})|^2 \\ n_\uparrow(\mathbf{r}) &= \sum_{i=1}^{N_\uparrow} |\phi_i^\uparrow(\mathbf{r})|^2 \end{aligned} \quad (2.17)$$

with $n(\mathbf{r}) = n_\uparrow(\mathbf{r}) + n_\downarrow(\mathbf{r})$.

The kinetic energy for this non-interacting system is

$$\begin{aligned} T_{KS} &= -\frac{\hbar^2}{2m} \sum_{\sigma} \sum_i^{N_\sigma} \langle \phi_i^\sigma(\mathbf{r}) | \nabla_{\mathbf{r}_i}^2 | \phi_i^\sigma(\mathbf{r}) \rangle \\ &= -\frac{\hbar^2}{2m} \sum_{\sigma} \sum_i^{N_\sigma} \int |\nabla_{\mathbf{r}_i}^2 \phi_i^\sigma(\mathbf{r})|^2 d\mathbf{r} \end{aligned} \quad (2.18)$$

It is important to note that the kinetic energy T_{KS} is different from the kinetic energy of the interacting system

$$T = -\frac{\hbar^2}{2m} \sum_i^N \langle \psi(\mathbf{r}_1, \sigma_1, \dots, \mathbf{r}_N, \sigma_N) | \nabla_{\mathbf{r}_i}^2 | \psi(\mathbf{r}_1, \sigma_1, \dots, \mathbf{r}_N, \sigma_N) \rangle \quad (2.19)$$

since the wave-functions ϕ_i are associated with a non-interacting system while ψ is associated with the fully interacting one. We can now write the ground-state energy as

$$E_{KS}[n(\mathbf{r})] = T_{KS}[n(\mathbf{r})] + \int V(\mathbf{r})n(\mathbf{r})d\mathbf{r} + \frac{1}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[n(\mathbf{r})] \quad (2.20)$$

where the first term T_{KS} is a functional of the density through the wave-functions ϕ_i , the second term the effect of the external potential, the third term the Coulomb interaction between electrons

(Hartree term) and the last one the so-called *exchange-correlation* energy. Using a compact notation, one can write

$$E_{KS}[n(\mathbf{r})] = T_{KS}[n(\mathbf{r})] + E_{pot}[n(\mathbf{r})] + E_{Ha}[n(\mathbf{r})] + E_{xc}[n(\mathbf{r})] \quad (2.21)$$

where we identified E_{pot} to be the energy functional associated to the external potential $V(\mathbf{r})$ and E_{Ha} the averaged Coulomb interaction.

$E_{xc}[n(\mathbf{r})]$ contains the correction to the non-interacting kinetic energy and corrections to the electronic interactions (which are not only described by E_{Ha}). If we were to know the exact form of $E_{xc}[n(\mathbf{r})]$, we would be able to find the exact solution of our Hamiltonian. However, this remains the main obstacle in DFT as no exact functional is known. Models, whose adequacy will greatly determine the accuracy of our computations, will have to be used.

If we assume $E_{xc}[n(\mathbf{r})]$ to be known and apply the variational principle, we get

$$\frac{\delta E_{KS}}{\delta \phi_i^{\sigma*}(\mathbf{r})} = \frac{\delta T_{KS}}{\delta \phi_i^{\sigma*}(\mathbf{r})} + \left[\frac{\delta E_{pot}}{\delta n(\mathbf{r})} + \frac{\delta E_{Ha}}{\delta n(\mathbf{r})} + \frac{\delta E_{xc}}{\delta n(\mathbf{r})} \right] \frac{\delta n(\mathbf{r})}{\delta \phi_i^{\sigma*}(\mathbf{r})} = 0 \quad (2.22)$$

After some functional analysis algebra (see appendix B.1), the variational equation reduces to

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) + \frac{1}{2} \int \frac{n(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' + V_{XC}(\mathbf{r}) \right] \phi_i(\mathbf{r}, \sigma) = 0 \quad (2.23)$$

Using the constraint of number of electrons

$$\int n(\mathbf{r}) d\mathbf{r} = N \quad (2.24)$$

and introducing a Lagrange multiplier for each orbital (i, σ)

$$\epsilon_i^\sigma \left(\int n(\mathbf{r}) d\mathbf{r} - N \right) = 0 \quad (2.25)$$

we get that the constrained variational equation becomes

$$\frac{\delta}{\delta \phi_i^{\sigma*}(\mathbf{r})} \left(E_{KS} - \epsilon_i^\sigma \left(\int n(\mathbf{r}) d\mathbf{r} - N \right) \right) = 0 \quad (2.26)$$

and we obtain

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) + \frac{1}{2} \int \frac{n(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' + V_{XC}(\mathbf{r}) \right] \phi_i^\sigma(\mathbf{r}) = \epsilon_i^\sigma \phi_i^\sigma(\mathbf{r}) \quad (2.27)$$

This describes the Kohn-Sham equivalent Hamiltonian

$$\hat{H}_{KS} = -\frac{\hbar^2}{2m} \nabla^2 + V_{KS}(\mathbf{r}) \quad (2.28)$$

with

$$V_{KS}(\mathbf{r}) = V(\mathbf{r}) + V_{Ha}(\mathbf{r}) + V_{XC}(\mathbf{r}) \quad (2.29)$$

where we defined $V_{Ha}(\mathbf{r}) = \frac{1}{2} \int \frac{n(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}'$. The attentive reader will realize that for this to be possible, one has to assume that the exchange-correlation functional can be written as

$$E_{XC}[n(\mathbf{r})] = \int V_{XC}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \quad (2.30)$$

where $V_{XC}(\mathbf{r})$ represents the exchange-correlation energy per electron.

In simple words, the Kohn-Scham approach states that for a fully interacting system, there exists an analogous non-interacting system whose ground-state density is equivalent to the ground-state density of the fully interacting one. Of course, limitations due to $E_{xc}[n(\mathbf{r})]$ prevent us to find the exact solution of our system. However, the Kohn-Scham formalism provides a practical way of implementing DFT codes.

The Kohn-Scham method possesses a small incoherency. Indeed, to find the ground-state single-particle wavefunctions $\phi_i^\sigma(\mathbf{r})$, one needs to know V_{KS} . In order to compute V_{KS} , one needs to know the electronic density $n(\mathbf{r})$. However, the density relies on the wavefunctions $\phi_i^\sigma(\mathbf{r})$. To solve this incoherency, we use a self-consistent method.

First, we initialize the density. Physical intuition might be required as the closer initialization is to reality, the faster our algorithm will converge. Using this density, we compute V_{KS} and solve the Kohn-Scham Hamiltonian. Once the wavefunctions $\phi_i^\sigma(\mathbf{r})$ are available, an updated electronic density is compared to the one fed at the beginning. If both are close enough, then the algorithm can be considered as converged and the energy computed. If not, we use the updated density as input to compute V_{KS} and repeat the process until convergence is reached. A flow-chart is provided at Fig. 2.1.

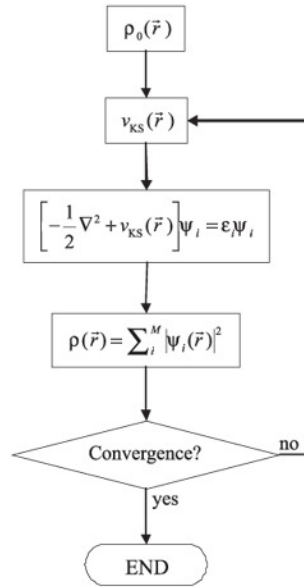


Figure 2.1: Flow-chart of the Kohn-Sham self-consistent method. Note the slight change in notations where the density is referred to as ρ on the chart. Adapted from [22].

2.1.4 Exchange-Correlation Functional

A huge variety of exchange-correlation functionals have been constructed. Every time a particular functional is used, the user should always be aware of its strengths and flaws. The two most well known classes of approximation are without any doubt the *Local Density Approximation* (LDA) and the *Generalized Gradient Approximation* (GGA).

The main idea behind the LDA is to rely upon the exchange-correlation functional of a homogeneous electron gas. The LDA considers that at each point of space $\mathbf{r}$, the exchange-correlation energy is equivalent to the one that would arise from an homogeneous electron gas of electronic

density $n(\mathbf{r})$. In this case, the exchange part of the functional can be computed analytically (see appendix B.2).

The GGA functionals take into account the density $n(\mathbf{r})$ and its gradient $\nabla n(\mathbf{r})$. At first sight, it is quite tempting to assume GGA to be more accurate than LDA. Actually, this is not necessarily the case and particular attention to which kind of approximation to use should be paid.

One of the main weakness of GGA and LDA is their locality: the functional at position $\mathbf{r}$ does not "see" what is happening at $\mathbf{r}'$ ($\mathbf{r} \neq \mathbf{r}'$). This is actually a huge problem if one wants to include van der Waals interactions as they arise from long-range, non-local correlations [23]. In this work, we will treat single layer graphene so that vdW interactions are not really to be taken into account. But for computation of other systems like graphite or bundles of carbon nanotubes, simulations would require special consideration.

2.2 Quantum Transport Theory

We will now present the basic concepts of quantum transport theory within the non-equilibrium Green's functions (NEGF) formalism. This method will allow for efficient computations of electronic transmission spectra.

Structures for which spin-resolved transport properties will be investigated are composed by two semi-infinite leads (electrodes) sandwiching a scatterer (device region). A schematic for such structures is provided at Fig. 2.2.



Figure 2.2: Schematic of a device for quantum transport. The device region (here called "scatterer") is sandwiched between two electrodes. The left and right electrodes are considered semi-infinite. Adapted from [24] .

As the main purpose of this work does not lay in the development on computational methods, we will only provide the fundamental equations of the NEGF formalism in the Landauer-Büttiker picture. The interested reader should then refer to the following references [24] [25] [26]. We also advise the online courses given by Professor Supriyo Datta which are freely available. The three aforementioned references and the online lectures of Professor Supriyo Datta will be extensively used throughout the following sections.

2.2.1 Equilibrium Green's Functions

The first challenge lays in the dimensionality of our system. Indeed, the electrodes of our quantum device are considered as semi-infinite. However, while computers can be used to represent finite systems, infinity is a unintelligible concept for such machines. Therefore, the first step of our development will consists on getting rid of the infinite feature of the leads.

Green's functions are a mathematical tool which allows for the resolution of inhomogeneous linear differential equations. A given Green's function (or operator) is associated to a given differential operator which describes the system.

Considering a differential operator $\hat{D}$ relating the response R to its source S

$$\hat{D}R = S \quad (2.31)$$

the Green's function³ $\hat{G}$ is defined such that

$$R = \hat{G}S \quad (2.32)$$

To put it simply, the Green's function can be seen as the inverse of the differential operator, $\hat{G} = \hat{D}^{-1}$. This also means that $\hat{G}$ is the impulse response of the system

$$\hat{D}\hat{G} = \hat{I} \quad (2.33)$$

with $\hat{I}$ the identity operator.

A naive approach to our quantum problem would be to consider the three parts (left electrode, device region and right electrode) as non-interacting. This would give the following system of equations

$$\begin{cases} \hat{H}_1|\psi_1\rangle = E|\psi_1\rangle \\ \hat{H}_d|\psi_d\rangle = E|\psi_d\rangle \\ \hat{H}_2|\psi_2\rangle = E|\psi_2\rangle \end{cases} \quad (2.34)$$

where the first equation describes the left electrode, the second the device region and the third the right electrode. The Hamiltonians $\hat{H}_1$, $\hat{H}_d$ and $\hat{H}_2$ are the Hamiltonians of the isolated parts.

If we consider non-interacting electrons, the Hamiltonians are of the form

$$\hat{H} = \frac{\hbar}{2m} \sum_i \hat{\nabla}_i^2 + \hat{V}_i \quad (2.35)$$

Obviously, a model where the electrodes and the device are seen non-interacting with each other cannot capture the physics of our problem. We then introduce coupling through the following coupling operators:

- τ_{1d} : couples the wavefunction of the device region to the left electrode.
- τ_{d1} : couples the wavefunction of the left electrode to the device region.
- τ_{2d} : couples the wavefunction of the device region to the right electrode.
- τ_{d2} : couples the wavefunction of the right electrode to the device region.

Note that no coupling is considered between the two electrodes.

Since Hamiltonians are hermitian, the 4 coupling operators reduce to $\tau_1 = \tau_{1d} = \tau_{d1}^\dagger$ and $\tau_2 = \tau_{2d} = \tau_{d2}^\dagger$ so that the Schrödinger equations for our system become

$$\begin{cases} \hat{H}_1|\psi_1\rangle + \hat{\tau}_1|\psi_d\rangle = E|\psi_1\rangle \\ \hat{\tau}_1^\dagger|\psi_1\rangle + \hat{H}_d|\psi_d\rangle + \hat{\tau}_2^\dagger|\psi_2\rangle = E|\psi_d\rangle \\ \hat{H}_2|\psi_2\rangle + \hat{\tau}_2|\psi_d\rangle = E|\psi_2\rangle \end{cases} \quad (2.36)$$

With this set of three equations, it is possible to express the wavefunctions of the electrodes in terms of $|\psi_d\rangle$. Using the first and last line of Eq. 2.36, we get

$$|\psi_1\rangle = [E\hat{I} - \hat{H}_1]^{-1} \tau_1|\psi_d\rangle$$

³Actually, $\hat{G}$ is the Green's function operator but one could easily associate this operator with the function using an appropriate basis set (e.g. $G(\mathbf{r}, \mathbf{r}') = \langle \mathbf{r} | \hat{G} | \mathbf{r}' \rangle$).

$$|\psi_2\rangle = [E\hat{I} - \hat{H}_2]^{-1} \tau_2 |\psi_d\rangle \quad (2.37)$$

The quantities $[E\hat{I} - \hat{H}_1]^{-1}$ and $[E\hat{I} - \hat{H}_2]^{-1}$ are nothing but the Green's function for the isolated leads, respectively denoted as $\hat{g}_1$ and $\hat{g}_2$. Injecting this in the second line of Eq. 2.36 yields

$$\hat{\tau}_1^\dagger \hat{g}_1 \hat{\tau}_1 |\psi_d\rangle + \hat{H}_d |\psi_d\rangle + \hat{\tau}_2^\dagger \hat{g}_2 \hat{\tau}_2 |\psi_d\rangle = E |\psi_d\rangle \quad (2.38)$$

We now define the electrodes self-energies $\hat{\Sigma}_1 = \hat{\tau}_1^\dagger \hat{g}_1 \hat{\tau}_1$ and $\hat{\Sigma}_2 = \hat{\tau}_2^\dagger \hat{g}_2 \hat{\tau}_2$ such that the equation for the device region reads

$$[\hat{H}_d + \hat{\Sigma}_1 + \hat{\Sigma}_2] |\psi_d\rangle = E |\psi_d\rangle \quad (2.39)$$

This is an important result since our problem reduces now to $|\psi_d\rangle$ which lays in the finite part (device region) of our quantum system. The semi-infinite characteristic of the electrodes has been bypassed. Of course, the effect of the leads is still being into account but this is done through the self-energies $\hat{\Sigma}_1$ and $\hat{\Sigma}_2$. Those self-energies can be computed quite easily relying on the periodicity of the electrodes.

2.2.2 Non-Equilibrium Green's Function

In the previous section, we managed to get rid of the infinities of our system thanks to the so-called electrodes self-energies. This was done by contacting the leads with the scatterer, without introducing any out-of-equilibrium phenomena. In this section, we will now consider a non-equilibrium situation with in-going and out-going flows of electrons.

To simplify our notations, we rewrite Eq. 2.40 as

$$[\hat{H}_d + \hat{\Sigma}] |\psi_d\rangle = E |\psi_d\rangle \quad (2.40)$$

where $\hat{\Sigma}$ contains the effect of the two electrodes.

Actually, there is no reason which enforces $\hat{\Sigma}$ to contain only the electrodes effect on the device and other interactions could be considered through $\hat{\Sigma}$ (e.g. electron-electron interaction, electron-phonon interactions). This will not be addressed this in our work.

The time-dependent Schrödinger equation reads

$$i\hbar \frac{d}{dt} |\Psi_d\rangle = \hat{H} |\Psi_d\rangle + \hat{\Sigma} |\Psi_d\rangle + |S\rangle \quad (2.41)$$

where $|\Psi_d\rangle = |\psi_d\rangle e^{-iEt/\hbar}$ is the time-dependent wavefunction and $|S\rangle$ a source term. Note that just as for $|\Psi_d\rangle$, one can define $|S\rangle = |s\rangle e^{-iEt/\hbar}$. Injecting the expressions for $|\Psi_d\rangle$ and $|S\rangle$, one can find the time-independent Schrödinger equation

$$[\hat{H} + \hat{\Sigma}] |\psi_d\rangle = E |\psi_d\rangle - |s\rangle \quad (2.42)$$

2.2.2.1 Current Operator

We now derive an expression for the current operator $\hat{I}_{op}$. This operator will allow for the computation of the flow of given quantities like spins, momentum, charges, ...

An observable O (e.g. spin, momentum) is associated with its quantum mechanical operator $\hat{O}$ such that its expectation value $\langle O \rangle$ is given by

$$\langle O \rangle = \langle \Psi_d | \hat{O} | \Psi_d \rangle \quad (2.43)$$

Since the expectation value is a scalar number, we can trace it ⁴

$$\begin{aligned}\langle O \rangle &= \text{Tr} \left[\langle \Psi_d | \hat{O} | \Psi_d \rangle \right] \\ &= \text{Tr} \left[\hat{O} | \Psi_d \rangle \langle \Psi_d | \right]\end{aligned}\tag{2.44}$$

The time derivative of $\langle O \rangle$, which describes the flow of O , is given by

$$\frac{d}{dt} \langle O \rangle = \frac{d}{dt} \text{Tr} \left[\hat{O} | \Psi_d \rangle \langle \Psi_d | \right]\tag{2.45}$$

If the operator $\hat{O}$ does not depend on time, then one can write

$$\frac{d}{dt} \langle O \rangle = \text{Tr} \left[\hat{O} \frac{d}{dt} (| \Psi_d \rangle \langle \Psi_d |) \right]\tag{2.46}$$

We now notice that the quantity $\frac{d}{dt} (| \Psi_d \rangle \langle \Psi_d |)$ does not depend on the expression of $\hat{O}$. This quantity is the aforementioned current operator $\hat{I}_{op}$

$$\hat{I}_{op} = \frac{d}{dt} (| \Psi_d \rangle \langle \Psi_d |)\tag{2.47}$$

With such results, finding the current for any quantity O (e.g. spin, momentum) becomes straightforward. Indeed, one can compute, once and for all, the current operator $\hat{I}_{op}$. Then, providing that the operator $\hat{O}$ is known, we just need to multiply it by $\hat{I}_{op}$ and trace it.

In order to work out an expression for $\hat{I}_{op}$, we recall that $| \Psi_d \rangle$ respects the time-dependent Schrödinger equation

$$i\hbar \frac{d}{dt} | \Psi_d \rangle = \hat{H} | \Psi_d \rangle + \hat{\Sigma} | \Psi_d \rangle + | S \rangle\tag{2.48}$$

Using the chain rule, $\hat{I}_{op}$ can be rewritten as

$$\hat{I}_{op} = | \Psi_d \rangle \left(\frac{d}{dt} \langle \Psi_d | \right) + \left(\frac{d}{dt} | \Psi_d \rangle \right) \langle \Psi_d | \tag{2.49}$$

We now make use of Eq. 2.48 which, after some cumbersome algebra, allows us to write

$$\hat{I}_{op} = \frac{\hat{H} | \Psi_d \rangle \langle \Psi_d | - | \Psi_d \rangle \langle \Psi_d | \hat{H}^\dagger}{i\hbar} + \frac{\hat{\Sigma} | \Psi_d \rangle \langle \Psi_d | - | \Psi_d \rangle \langle \Psi_d | \hat{\Sigma}^\dagger}{i\hbar} + \frac{| S \rangle \langle \Psi_d | - | \Psi_d \rangle \langle S |}{i\hbar}\tag{2.50}$$

The operator $| \Psi_d \rangle \langle \Psi_d |$ is linked to a key quantity of quantum mechanics called the correlation operator $\hat{G}^n$ ⁵

$$| \Psi_d \rangle \langle \Psi_d | = \frac{\hat{G}^n}{2\pi}\tag{2.51}$$

Simply speaking, $\hat{G}^n$ is the quantum generalization of the concept of number of electrons. The total number of electrons N is given by the trace of $\hat{G}^n/2\pi$.

We recall that the time-independent Schrödinger equation reads

$$\left[\hat{H} + \hat{\Sigma} \right] | \psi_d \rangle = E | \psi_d \rangle - | s \rangle\tag{2.52}$$

so that $| \psi_d \rangle$ is related to $| s \rangle$ by

$$| \psi_d \rangle = \hat{G}^R | s \rangle\tag{2.53}$$

⁴We used cyclic permutation inside the trace ($\text{Tr}[ABC] = \text{Tr}[CAB] = \text{Tr}[BCA]$).

⁵Note that $| \Psi_d \rangle \langle \Psi_d |$ is also linked with the widely used concept of *density matrix*.

where $\hat{G}^R$ is the so-called *retarded Green's function* ($\hat{G}^R = [E\hat{I} - \hat{H} - \hat{\Sigma}]^{-1}$). In a similar way, we have

$$\langle \psi_d | = \langle s | \hat{G}^A \quad (2.54)$$

where $\hat{G}^A$ is the *advanced Green's function* ($\hat{G}^A = [\hat{G}^R]^\dagger$).

Injecting those results in the expression of $\hat{I}_{op}$, we find

$$\hat{I}_{op} = \frac{\hat{H}\hat{G}^n - \hat{G}^n\hat{H}^\dagger}{i\hbar} + \frac{\hat{\Sigma}\hat{G}^n - \hat{G}^n\hat{\Sigma}^\dagger}{i\hbar} + \frac{|s\rangle\langle s|\hat{G}^A - \hat{G}^R|s\rangle\langle s|}{i\hbar} \quad (2.55)$$

The quantity $|s\rangle\langle s|$ is defined as $\hat{\Sigma}^{in}/2\pi$ such that

$$\hat{I}_{op} = \frac{\hat{H}\hat{G}^n - \hat{G}^n\hat{H}}{i\hbar} + \frac{\hat{\Sigma}\hat{G}^n - \hat{G}^n\hat{\Sigma}^\dagger}{i\hbar} + \frac{\hat{\Sigma}^{in}\hat{G}^A - \hat{G}^R\hat{\Sigma}^{in}}{i\hbar} \quad (2.56)$$

with $\hat{H} = \hat{H}^\dagger$ as Hamiltonians are hermitian.

A simple physical picture of Eq. 2.56 can be drawn: while the second and third term respectively represent out-flow and in-flow, the first term describes the generation of the interest quantity inside the device region. For instance, if the channel is magnetic, spin could be generated as electrons would flow across it. If our development is correct, the first term should disappear in the case of the electrical current (electrons are not allowed to suddenly appear/disappear inside the device).

The electrical current I is given by the number of electrons flowing such that the operator $\hat{O}$ is just the charge q of an electron. We can thus write

$$\begin{aligned} I &= Tr[q\hat{I}_{op}] \\ &= qTr\left[\frac{\hat{H}\hat{G}^n - \hat{G}^n\hat{H}}{i\hbar} + \frac{\hat{\Sigma}\hat{G}^n - \hat{G}^n\hat{\Sigma}^\dagger}{i\hbar} + \frac{\hat{\Sigma}^{in}\hat{G}^A - \hat{G}^R\hat{\Sigma}^{in}}{i\hbar}\right] \end{aligned} \quad (2.57)$$

Using cyclic permutations, one gets that the first term disappears so that

$$I = qTr\left[\frac{\hat{\Sigma}\hat{G}^n - \hat{G}^n\hat{\Sigma}^\dagger}{i\hbar} + \frac{\hat{\Sigma}^{in}\hat{G}^A - \hat{G}^R\hat{\Sigma}^{in}}{i\hbar}\right] \quad (2.58)$$

which does not contain, as expected, the generation term. Note this first term does not necessarily disappear as $Tr[\hat{O}\hat{H}\hat{G}^n]$ is in general different from $Tr[\hat{O}\hat{G}^n\hat{H}]$.

Since the trace allows cyclic permutations, one can actually write the current as

$$I = \frac{q}{i\hbar}Tr\left[\hat{G}^n(\hat{\Sigma} - \hat{\Sigma}^\dagger) + \hat{\Sigma}^{in}(\hat{G}^A - \hat{G}^R)\right] \quad (2.59)$$

We now define two important quantities

$$\hat{\Gamma} = i(\hat{\Sigma} - \hat{\Sigma}^\dagger) \quad \text{and} \quad \hat{A} = i(\hat{G}^R - \hat{G}^A) \quad (2.60)$$

so that the expression for the current reduces to

$$I = -\frac{q}{\hbar}Tr\left[\hat{G}^n\hat{\Gamma} - \hat{\Sigma}^{in}\hat{A}\right] \quad (2.61)$$

In this expression, $\hat{G}^n$ is linked to the occupation of the states inside the channel, $\hat{\Gamma}$ to the out-flow rate of the electrons, $\hat{\Sigma}^{in}$ to the in-flow rate of the electrons and $\hat{A}$ to the distribution of states inside the channel. Actually, in the same way $\hat{G}^n$ is a generalization of the concept of number of particles, $\hat{A}$, commonly called the *spectral function*, is the generalization of the concept of density of states.

Up to now, we have derived a general expression which can be used in a wide range of applications. In the next section, we will restrict our discussion to what we will refer to as *Fermi contacts*. This restriction will exclude complex interaction inside the channel (e.g. electron-electron, electron-phonon) but will allow for the formulation of the concept of transmission (as the one in the Landauer-Büttiker formalism).

2.2.2.2 Fermi Contacts

We will now assume a multi-terminal device. The current due to contact p can be written as

$$I_p = -\frac{q}{h} \text{Tr} [\hat{G}^n \hat{\Gamma}_p - \hat{\Sigma}_p^{in} \hat{A}] = \frac{q}{h} \text{Tr} [\hat{\Sigma}_p^{in} \hat{A} - \hat{G}^n \hat{\Gamma}_p] \quad (2.62)$$

For a contact described by a Fermi function, the following relation holds

$$\hat{\Sigma}_p^{in} = \hat{\Gamma}_p f_p \quad (2.63)$$

where f_p is the Fermi function for contact p . This relation is the one preventing straightforward modelling of interactions within the device.

To model interactions, one would normally use the concept of "conceptual contacts", introducing the quantities $\hat{\Sigma}_0$ and $\hat{\Gamma}_0$. Here, $\hat{\Sigma}_0$ and $\hat{\Gamma}_0$ do not represent an in-flow/out-flow but the changes of states within the channel caused by the interactions. Obviously, the out-flow and in-flow must counterbalance so that no net currents arise from those conceptual contacts.

In general, conceptual contacts can not be assumed to behave like Fermi contacts and thus Eq. 2.63 does not necessary hold. From now on, we will assume that all our contacts are Fermi contacts so that the current can be written as

$$I_p = \frac{q}{h} \text{Tr} [\hat{\Gamma}_p f_p \hat{A} - \hat{G}^n \hat{\Gamma}_p] = \frac{q}{h} \text{Tr} [\Gamma_p (\hat{A} f_p - \hat{G}^n)] \quad (2.64)$$

We now use the relations proven in appendix B.3

$$\hat{G}^n = \hat{G}^R \hat{\Sigma}^{in} \hat{G}^A \quad (2.65)$$

$$\hat{A} = \hat{G}^A \Gamma \hat{G}^R = \hat{G}^R \Gamma \hat{G}^A \quad (2.66)$$

Since we can decompose $\hat{\Sigma}^{in}$ and $\hat{\Gamma}$ for each electrode⁶, using Eq. 2.63 and the two previous equations, we write

$$\hat{G}^n = \hat{G}^R (\hat{\Gamma}_1 f_1 + \hat{\Gamma}_2 f_2 + \hat{\Gamma}_3 f_3 + \dots) \hat{G}^A \quad (2.67)$$

$$\hat{A} = \hat{G}^R (\hat{\Gamma}_1 + \hat{\Gamma}_2 + \hat{\Gamma}_3 + \dots) \hat{G}^A \quad (2.68)$$

so that

$$\hat{A} f_p - \hat{G}^n = \hat{G}^R \left(\sum_q \Gamma_q (f_p - f_q) \right) \hat{G}^A \quad (2.69)$$

where q runs over all the contacts.

⁶It simply means that we decompose the total in-flow/out-flow to the sum of each electrode contribution.

Injecting this in the expression for the current one finds

$$I_p = \frac{q}{h} \sum_q (f_p - f_q) \text{Tr} [\Gamma_p \hat{G}^R \Gamma_q \hat{G}^A] \quad (2.70)$$

The quantities we have been manipulating until now are per unit of energy so that one should actually write

$$I_p(E) = \frac{q}{h} \sum_q (f_p(E) - f_q(E)) \text{Tr} [\Gamma_p(E) \hat{G}^R(E) \Gamma_q(E) \hat{G}^A(E)] \quad (2.71)$$

which is the expression of contribution to the current between E and $E + dE$. To find the total current, one would need to integrate over the whole range of energy.

The reader experienced with the Landauer-Büttiker formalism will immediately notice that the transmission probability can be extracted from Eq. 2.71

$$T_{pq}(E) = \text{Tr} [\Gamma_p(E) \hat{G}^R(E) \Gamma_q(E) \hat{G}^A(E)] \quad (2.72)$$

In the simple case of a two channel electron, the probability for an electron of energy E coming from the left electrode to be transmitted to the right electrode is then given by

$$T(E) = \text{Tr} [\Gamma_1(E) \hat{G}^R(E) \Gamma_2(E) \hat{G}^A(E)] \quad (2.73)$$

so that the total current in our device reads

$$\begin{aligned} I &= \int_{-\infty}^{+\infty} I(E) dE \\ &= \frac{q}{h} \int_{-\infty}^{+\infty} (f_1(E) - f_2(E)) \text{Tr} [\Gamma_1(E) \hat{G}^R(E) \Gamma_2(E) \hat{G}^A(E)] dE \\ &= \frac{q}{h} \int_{-\infty}^{+\infty} \left(\frac{1}{e^{\frac{E-\mu_1}{kT}} + 1} - \frac{1}{e^{\frac{E-\mu_2}{kT}} + 1} \right) \text{Tr} [\Gamma_1(E) \hat{G}^R(E) \Gamma_2(E) \hat{G}^A(E)] dE \end{aligned} \quad (2.74)$$

In the case of spin degenerated states, each state of energy E holds two electrons so that the charge q is given by $q = 2e$ (and not $q = e$). If we consider explicitly currents for both spin channels, one can then write

$$I^\uparrow = \frac{e}{h} \int_{-\infty}^{+\infty} (f_1(E) - f_2(E)) \text{Tr} [\Gamma_1^\uparrow(E) \hat{G}^{R\uparrow}(E) \Gamma_2^\uparrow(E) \hat{G}^{A\uparrow}(E)] dE \quad (2.75)$$

$$I^\downarrow = \frac{e}{h} \int_{-\infty}^{+\infty} (f_1(E) - f_2(E)) \text{Tr} [\Gamma_1^\downarrow(E) \hat{G}^{R\downarrow}(E) \Gamma_2^\downarrow(E) \hat{G}^{A\downarrow}(E)] dE \quad (2.76)$$

Such consideration yields to the definition of two distinct conductance quantum. The first one is $G_0 = \frac{2e^2}{h}$ and is to be considered when spin-polarization is disregarded and the second one is $g_0 = \frac{e^2}{h}$ which has to be used when one considers explicitly the spin degree of freedom.

3

Computational Tools

In this chapter, we will present the practical implementation of DFT and NEGF, respectively **SIESTA** and **TranSIESTA**. We will discuss the main features of the codes and clarify their approximations. The aim is neither to provide a complete description of the codes nor tutorials which are widely available on the internet.

The information provided for **SIESTA** and **TranSIESTA** are respectively based on the references [27] and [28]. More instructions can be found in the official **SIESTA** manual.

3.1 SIESTA

The *Spanish Initiative for Electronic Simulations with Thousands of Atoms*, a.k.a **SIESTA**, is a DFT code which is based on numerical pseudo-atomic orbitals (NPAOs) of finite range. The name **SIESTA** defines both a method and its implementation.

The Kohn-Sham formalism relies on non-interacting single electron wavefunctions $\phi_i(\mathbf{r}, \sigma)$. In **SIESTA**, such wavefunctions are expanded as

$$\phi_i(\mathbf{r}, \sigma) = \sum_l c_{il} \varphi_l(\mathbf{r}, \sigma) \quad (3.1)$$

where $\varphi_l(\mathbf{r}, \sigma)$ are NPAOs of finite range.

NPAOs are conceptually quite close to atomic orbitals as they both describe the atomic Hamiltonian. However, while the latter is an exact solution, the former is only an approximation. Practically speaking, a **SIESTA** calculation starts with the NPAOs being initialized by solving the Kohn-Sham Hamiltonian of the isolated pseudo-atom within the same framework as the full system (same exchange-correlation potential, same pseudo-potential, ...).

The basis functions are defined as

$$\varphi_{lmn}(\mathbf{r}) = R_{ln}(\mathbf{r}) Y_{lm}(\mathbf{r}) \quad (3.2)$$

with R_{ln} the radial part and $Y_{lm}(\mathbf{r})$ the spherical harmonics. The spherical harmonics are well known objects which depict the shape of the orbital (e.g s-orbital, p-orbital) while the radial part is the degree of freedom we have in **SIESTA**. This radial part is found using the equation

$$\left[-\frac{1}{2r} \frac{d^2}{dr^2} r + \frac{l(l+1)}{2r^2} + V_l(r) \right] R_l(r) = (\epsilon_l + \delta\epsilon_l) R_l(r) \quad (3.3)$$

where $\delta\epsilon_l$ is the energy-shift, a parameter that controls the confinement of the NPAOs. The energy-shift can be explicitly defined by the user. A value of 100 – 200 meV is advised.

Another type of well-known basis expansion uses plane-waves as basis set. This is not implemented in **SIESTA**. Compared to a plane-waves basis, the main advantage of NPAOs is that they

offer a high efficiency as the basis size is usually quite small. This allows for a reduction of CPU time and memory requirement. Moreover, as they are based on orbitals, a more straightforward physical and chemical interpretation is possible. However, NPAOs also have drawbacks such as a higher complexity for the equations and implementation, and a lack of systematic convergence (enlarging the basis set does not ensure a better convergence).

The main feature of the **SIESTA** method is its $\mathcal{O}(N)$ complexity, N being the number of atoms in one unit cell. This efficient complexity (plane-wave DFT codes are $\mathcal{O}(N^3)$) is achieved through locality: the NPAOs are strictly equal to zero beyond a given cut-off radius. This means that if two orbitals are sufficiently far away

$$\begin{aligned} S_{\nu\mu} &= \langle \phi_\nu | \phi_\mu \rangle = \int \phi_\nu^*(\mathbf{r}) \phi_\mu(\mathbf{r}) d\mathbf{r} = 0 \\ H_{\nu\mu} &= \langle \phi_\nu | \hat{H} | \phi_\mu \rangle = \int \phi_\nu^*(\mathbf{r}) \hat{H} \phi_\mu(\mathbf{r}) d\mathbf{r} = 0 \end{aligned} \quad (3.4)$$

with $S_{\nu\mu}$ the matrix elements of the overlap matrix and $H_{\nu\mu}$ the matrix elements of the Hamiltonian matrix. The overlap matrix and the Hamiltonian matrix are thus sparse : this is the key to high efficiency computation.

In **SIESTA**, users have the freedom to tune the basis set. This can be done in two ways: either we tune finely the parameters and describe specifically each type of atom or we rely on pre-implemented type of basis sets. The latter is the one used in this work.

At the present time, **SIESTA** implements single- ζ (SZ) and double- ζ (DZ) basis sets, each of which can be extended considering polarization orbitals (SZP and DZP). As DZP leads to errors similar to the one induced by the DFT exchange-correlation functional or by the pseudo-potential, a DZP basis set is used in this work.

Since **SIESTA** implements fully 3D periodic boundary conditions, the unit cell of the system has to be defined. This cell is then virtually reproduced along the three dimensions. The atoms contained by the cell must also be defined. Periodicity allows for Bloch's formalism.

For 3D non-periodic systems (e.g. molecules, surfaces, wires, defects, ...), a supercell approach has to be adopted. This approach relies on larger cells so that our system does not interact with its periodic replica. For instance, if one wants to compute a water molecule, a cubic cell whose edges are 60 Å long can be defined and one water molecule put inside. The water molecule being far away from its replica, it can be considered as independent. Graphene is another example where replica planes can be considered as non-interacting if the size of the unit cell along the normal direction is high enough.

The low dimensionality of the systems treated within this work justifies the use of a software like **SIESTA**. Indeed, plane-waves calculations would become too computationally intensive as such functions also consider vacuum (plane-waves are extended throughout the whole volume). Here again, the locality in the **SIESTA** method is the key to efficient calculations.

3.1.1 Convergence

When we perform a computational study, we must be aware of all the approximations introduced in our method. The non-exactness takes root in the facts that the exact form of E_{XC} is unknown (modelling is necessary) and that computational methods requires discretization of the real and reciprocal space. Within **SIESTA**, higher accuracy can be achieved through to following routes:

- Completeness of the basis set: the basis set must contain enough functions to describe accurately the wavefunction. For plane-waves, this can be systematically improved by increasing the energy cut-off. However, since **SIESTA** relies on localized numerical orbitals, optimization is non-trivial.
- Sampling of the real space: the grid in the real space must be dense enough so that the resolution of Poisson's equation is reliable.
- Sampling of the reciprocal space: the grid in the reciprocal space must be dense enough so that the integration over the Brillouin zone is reliable.

The case of the completeness of the basis set will not be addressed as we will directly on DZP. For the two other conditions, convergence will have to be ensure. This will be considered in the following chapter.

Note that the pseudo-potential used must always be checked within simple case to ensure a correct description of the atoms. This will also be considered in the following chapter.

3.2 TranSIESTA

The **TranSIESTA** method describes non-equilibrium electronic transport and is designed to work with **SIESTA**. The calculation is done within the Landauer-Buttiker formalism, through NEGF. The equations have been derived in the previous chapter.

As shown at Fig. 3.1, typical systems for **TranSIESTA** calculations rely on structures composed by two semi-infinite leads (electrodes) sandwiching a device region.

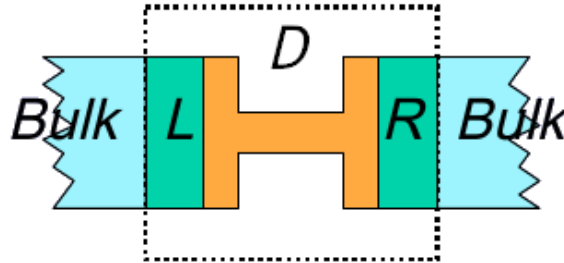


Figure 3.1: Typical system of a **TranSIESTA** run. The system is non-periodic along the z direction. L (left) and R (right) denotes the electrodes (leads) while D is the device region. The region inside the dotted box is called the scattering region. Adapted from [28]

By default, the transport direction in **TranSIESTA** is defined to be the z -direction and is treated within the NEGF formalism. The other two directions are treated through Bloch's formalism, just like in **SIESTA**.

Even though our system is conceptually infinite, a **TranSIESTA** run is performed on a well defined finite system. As explained in the previous chapter, the influence of the semi-infinite electrodes is taken into account through the self-energy they produce. Therefore, a typical **TranSIESTA** run consists on two main steps:

- First, an electrode calculation (ELC) is performed for each electrode. The ELC is an usual **SIESTA** run for fully periodic electrodes. This run will produce the usual output of **SIESTA** and a file of *.TSHS* extension which contains the data needed to compute the self-energies of the electrodes. Note that if the right and left electrodes are identical, only one run is needed.

- Then, a scattering region calculation (SRC) is performed for the device sandwiched between the electrodes. This runs starts with a classical **SIESTA** calculation to initialize the density matrix and use it as input for the Green's functions calculation.

For the ELC, the user must ensure that the unit cell interact, at most, with the nearest-neighbour cell. This condition can easily be checked and enforced. Indeed, it is possible to recover the cut-off radii¹ for the different atoms used in the output file. The interest quantity here is the largest cut-off radius R_C . To ensure the non-interacting condition, we must impose that the distance between a cell and its second-nearest-neighbour is bigger than $2R_C$. In other words, the dimensions of the cell must be larger than $2R_C$. If the condition is not enforced, then one needs to use a larger cell.

For the SRC, the user must define a system which, from left to right, contains at least one layer of left electrode, the device region and at least one layer of right electrode. The use of "*at least*" in the previous sentence is not accidental. Indeed, as the electrodes need to behave as much as possible as in the ELC run, buffer layers between the device region and the electrodes might be necessary.

If one is interested in the conduction properties of pristine materials, then there is no need to include buffer layers as the device region is identical to the electrode. However, when the device region is physically different than the electrodes, buffer layers will become required to screen what is seen by the electrodes as a "defect".

In the NEGF model we developed earlier, we considered that the left and right electrodes do not interact with each other. Therefore this condition must be enforced by defining a device region whose length along the **z**-direction is at least $2R_C$.

We attract the attention of the reader on the terminology used here. Actually, in the **TranSIESTA** run, one could define buffer layers of electrodes for the **SIESTA** part of the run. This is **not** the same as the buffer layers we discussed here. The ones discussed in the previous paragraphs are necessary to ensure physically coherent results. If the screening is not effective, one might get non-physical results which can be extremely dangerous. The buffer layers that we can define for the **SIESTA** part of the run are buffer layers used in the initialization of the density matrix and allow for better convergence. Convergence problems might be encountered as the initialization of the density matrix holds a fully periodic system. The problem particularly arises when the left and right electrodes are different.

The initialization of the density matrix holds the resolution of the system displayed at Fig. 3.2. The light blue regions B_L and B_R respectively represent the left and right buffers which are the one defined to ease convergence. The electrode buffer layers attached to the device are not explicitly depicted on Fig. 3.2 and are integrally part of the device region (D).

¹The cut-off radius is the radius beyond which the electronic density is strictly equal to zero.

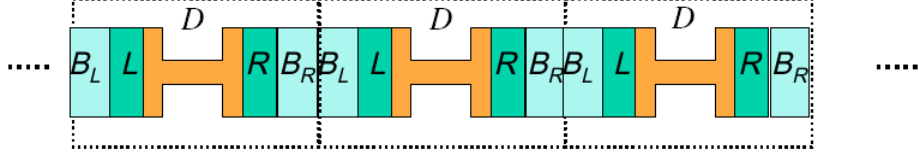


Figure 3.2: To initialize the density matrix elements, a **TranSIESTA** calculation first relies on a fully periodic **SIESTA** run. The labels B_L and B_R indicate the left/right buffer regions (more on this in the text). Adapted from [28].

Once the **TranSIESTA** run is completed, the matrix elements for the different quantities needed to compute the transmission are available. However, the transmission spectrum is not yet given. To access it, one needs to use post-processing tools. In this work we used the **TBTrans** utility which is provided in the **SIESTA** distribution package.

3.2.1 Route Sheet

Here, we provide a general recipe for the calculation of quantum transport properties with **TranSIESTA**.

1. Relax the left electrode in a fully periodic fashion ensuring that only interaction between nearest-neighbour cells are allowed. Do the same for the right electrode if it is different.
2. Using the executable "transiesta", run a **SIESTA** calculation for each of the electrodes (the variable `SolutionMethod` must be set to "diagon"). This run produces one ".TSHS" file per electrode.
3. Relax the device region including few buffer layer of electrodes. To know whether the buffer layers are thick enough, check whether the geometry changes when adding electrode layers.
4. Stick together the electrodes and the device region (which contains buffer layers) and run the **TranSIESTA** calculation (the variable `SolutionMethod` must be set to "transiesta"). For this run, include the ".TSHS" files of the electrodes.
5. Once the **TranSIESTA** calculation has succeeded, retrieve the newly generated ".TSHS" file and along with the ".TSHS" files of the electrodes, use them in **TBTrans**. The transmission can then be obtained.

Obviously, this simple route sheet is too general to prevent all existing issues and fine tuning might be required to achieve well-converged and physically coherent results. However, as this is highly dependent on the quantum system considered, we cannot provide general comments.

4

Graphene and Graphene Nanoribbons

In the present chapter, we will investigate simpler systems such as pristine graphene and zigzag graphene nanoribbons (ZGNRs). The effect of a Stone-Wales defect on the conductance of 6-ZGNRs will also be investigated.

The upcoming discussion will allow not only for a first contact with **SIESTA** and **TranSIESTA** but also for a convergence study on graphene related nanostructures. The pseudo-potential on which relies this work will be tested by comparing our results to state-of-the-art scientific literature.

For convergence, we will first impose basic criteria on the total energy and the geometry. For the energy, a maximum deviation of 5 meV/atom/cell with respect to the asymptotic value will be tolerated. For the geometry, the maximum tolerated deviation will be 0.2% on relevant lengths, always with respect to the asymptotic value.

Such criteria are only a minimal requirement and we will actually build a more stringent framework.

4.1 Graphene

We start our discussion with graphene. As displayed at Fig. 4.1, graphene's geometry is defined by a honeycomb lattice which can be seen as two inter-penetrating triangular lattices. The unit cell contains two carbon atoms and the carbon-carbon distance is 1.42 Å.

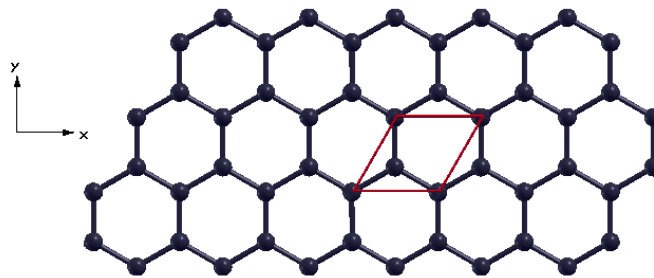


Figure 4.1: Geometrical structure of graphene with the unit cell represented by the red parallelogram. The so-called honeycomb lattice appears clearly.

We first perform systematic convergence studies. Since **SIESTA** implements fully 3D periodic boundary conditions, a vacuum of 60 Å is set in the normal direction to ensure that periodic replica planes are not interacting with each other. The convergence studies performed on the

total energy and the geometry are respectively displayed at Fig. 4.2 and Fig. 4.3.

The reciprocal space is sampled by a $k_x \times k_y \times 1$ Monkhorst-Pack grid under the constraint $k_x = k_y$ and structural relaxation is performed through coordinate optimization by conjugate gradients. Relaxation is achieved when forces fall below 0.01 eV/Å and the stress below 0.001 GPa.

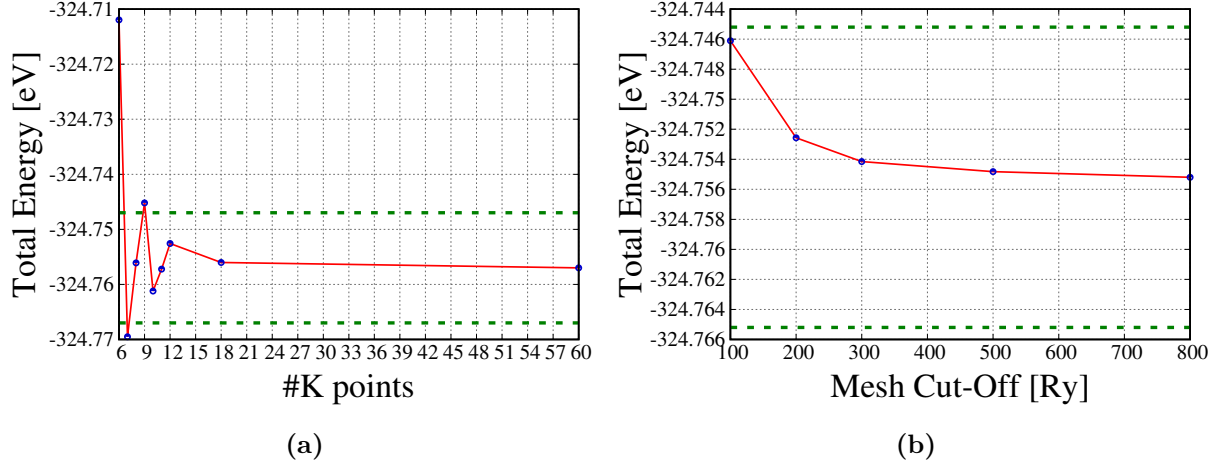


Figure 4.2: Convergence study for the total energy with respect to (a) the reciprocal space sampling and (b) the real mesh cut-off. The two horizontal lines (green) represent the tolerance: data that fall in between can be considered as converged. In our case, a $10 \times 10 \times 1$ Monkhorst-Pack grid and a real mesh cut-off of 100 Ry seem sufficient.

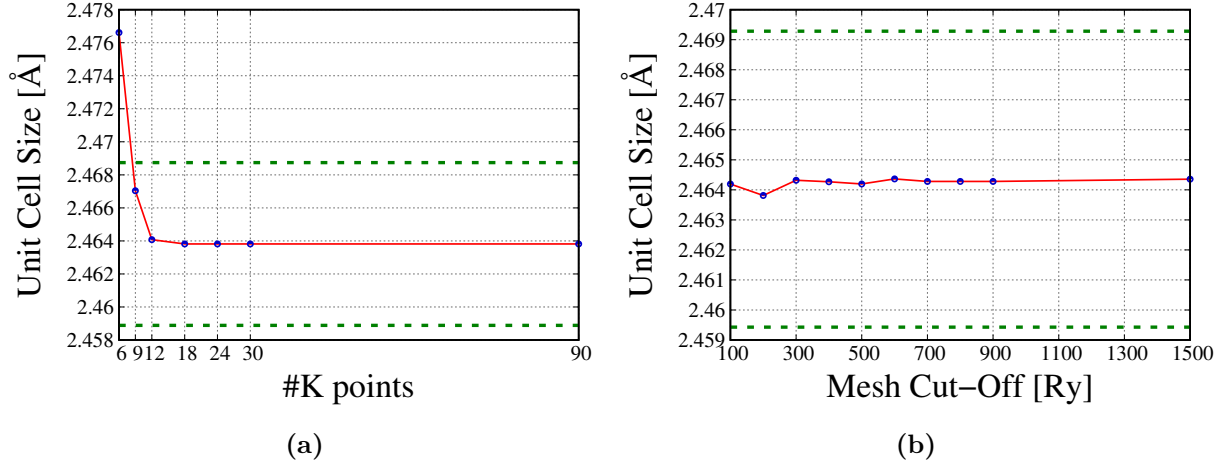


Figure 4.3: Convergence study for the structural relaxation with respect to (a) the reciprocal space sampling and (b) the real mesh cut-off. The two horizontal lines (green) represent the tolerance: data that fall in between can be considered as converged. In our case, a $9 \times 9 \times 1$ Monkhorst-Pack grid and a real mesh cut-off of 100 Ry seem sufficient.

For the total energy convergence with respect to the k-space sampling (Fig. 4.2 a), we notice an odd behaviour: local maxima when k_x, k_y are multiple of 3 appear. This peculiar behaviour is due to the fact that, when k_x, k_y are multiple of 3, the reciprocal space high-symmetry $\mathbf{K}$ and $\mathbf{K}'$ points are sampled. Since those points are particularly important for the description of the electronic states, one should ensure that the grid contains them. Therefore, a $12 \times 12 \times 1$ Monkhorst-Pack grid should at least be used to respect our basic criterion on the energy. For the mesh cut-off, the minimum value within our scope (100 Ry) seems sufficient.

Converged structural relaxation is achieved for a $9 \times 9 \times 1$ Monkhorst-Pack grid and a real mesh cut-off of 100 Ry.

To respect both criteria, a $12 \times 12 \times 1$ Monkhorst-Pack grid and a mesh cut-off of 100 Ry are to be used. Of course, this is just the minimum requirement and is actually unsatisfactory if one wants to describe properties like electronic transmission spectra. As general rule, one should always perform a convergence study with respect to the investigated property.

In our case, we are interested in spin dependant electronic transport properties. Therefore, a good description of the electronic band structure of our system is required. Consequently, we run calculations for different k-space samplings. The mesh cut-off is fixed at 200 Ry and the structure is allowed to relax for each run.

We first note that there exists a reciprocal space sampling beyond which an finer sampling does not lead to the appearance of atomic forces above $0.01 \text{ eV/\AA}$. In other words, the structure relaxed at accuracy $k_x^1 \times k_y^1 \times 1$ does not experience structural relaxation at the accuracy $k_x^2 \times k_y^2 \times 1$ ($k_x^1 = k_y^1 > k_x^2 = k_y^2$). Such situation is reached for a $18 \times 18 \times 1$ Monkhorst-Pack grid.

We now look at the electronic band structure of graphene. As convergence around the Dirac zone is the most critical, Fig. 4.4 presents a zoom around this zone.

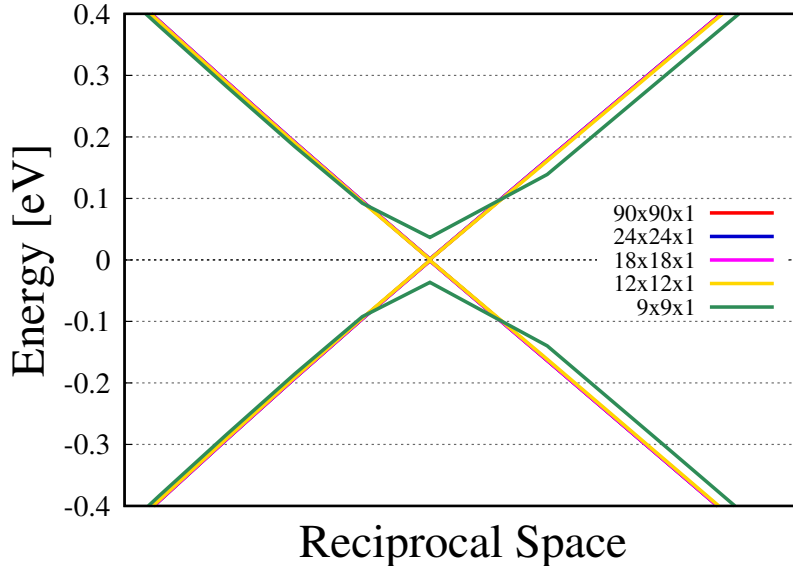


Figure 4.4: Convergence of the electronic band structure of graphene around the Dirac cone with respect to the reciprocal space sampling. A low density of k-points grid leads to an inaccurate description of the Dirac cone which can be dramatic if one wants to describe electronic properties. The Fermi energy was set to zero as reference.

We clearly notice that a too coarse k-space grid ($9 \times 9 \times 1$) leads to a totally inaccurate

description of the Dirac cone. For finer grids, convergence seems to be well achieved. One might aim at the $90 \times 90 \times 1$ Monkhorst-Pack grid but if for basic calculation this might be feasible, larger systems and/or more complex properties will not allow for a reasonable computational time. Therefore, we will set the $24 \times 24 \times 1$ Monkhorst-Pack grid to be the minimum requirement as it offers a good trade-off with excellent accuracy and reasonable computational time.

Since the length of a real space lattice vector is $2.46 \text{ \AA}$ and $k_x = k_y = 24$, we can establish a rule of thumb for graphene related nano-structures:

The product between the length of the real space vector and the number of k-points should be at least equal to ~ 60 .

Note that this is a rule of thumb: it does not ensure that our calculations are perfectly converged. However, it should provide a reliable starting point.

Having converged our calculation, we can now provide the electronic band structure of graphene. To obtain a well converged electronic structure and a fine enough density of states (DOS), we ran a calculation at a high-density $300 \times 300 \times 1$ Monkhorst-Pack grid and 800 Ry mesh cut-off. The Brillouin zone path for the electronic structure is shown at Fig. 4.5 while the electronic band structure and DOS are displayed at Fig. 4.6.

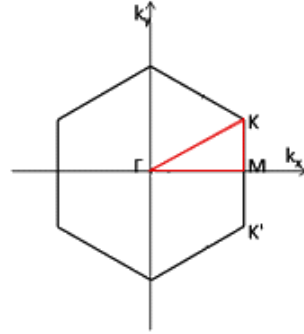


Figure 4.5: Brillouin path for the computation of the electronic band structure of graphene. The electronic band structure of graphene is displayed at Fig. 4.6

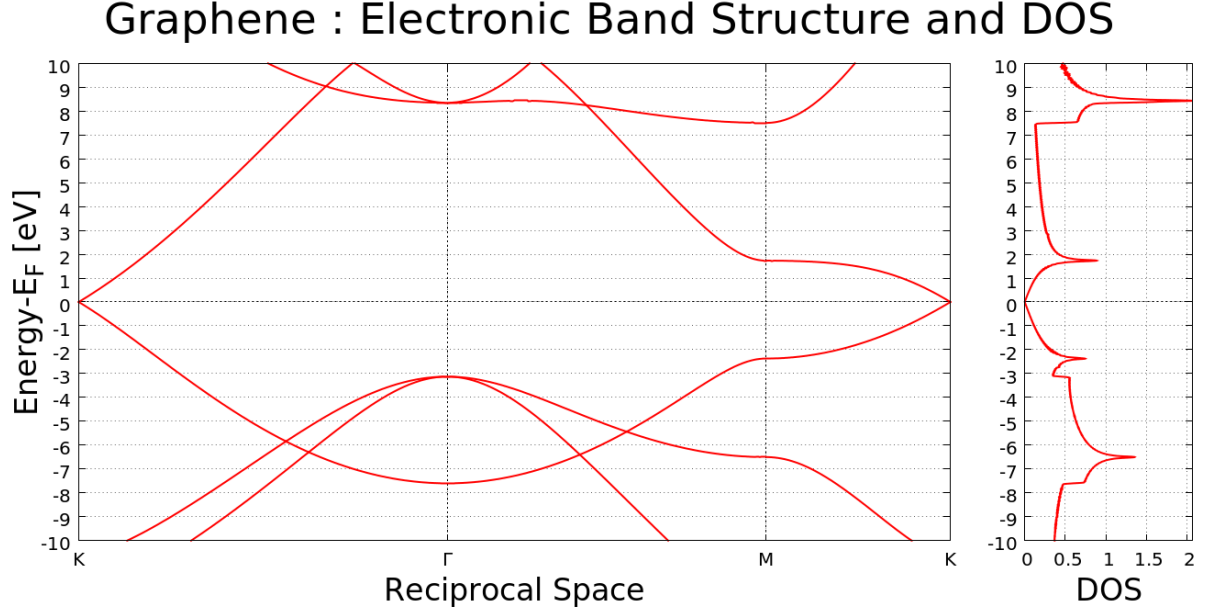


Figure 4.6: Electronic band structure (left) and density of states (right) of graphene computed with high accuracy ($300 \times 300 \times 1$ Monkhorst-Pack grid and 800 Ry mesh cut-off). Linear dispersion can be observed around $\mathbf{K}$. At the Fermi energy, the zero band gap feature of graphene is observed as the DOS goes to zero.

The zero band-gap characteristic of graphene is recovered and the relation dispersion exhibits the expected linear behaviour around the $\mathbf{K}$ -points.

4.2 Graphene Zigzag Nanoribbon

We will now address the case of graphene nanoribbons (GNRs). To be more accurate, the 6-zigzag graphene nanoribbon (6-ZGNR) will be considered as this structure will later be at the center of our study. The geometrical structure of 6-ZGNRs is displayed at Fig. 4.7.

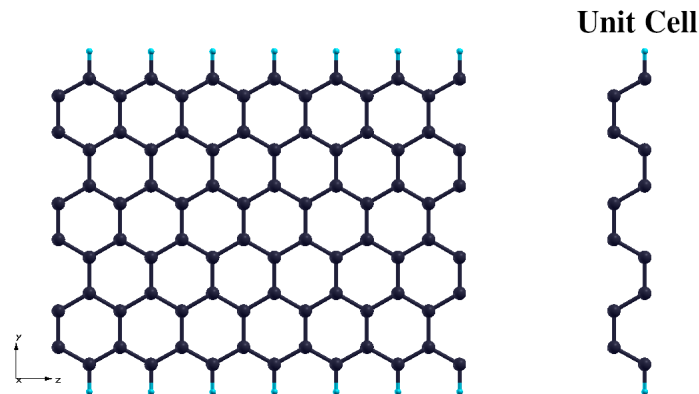


Figure 4.7: Geometrical structure of pristine 6-ZGNR. The black spheres represent the carbon atoms while the light blue one represent the hydrogen atoms. The periodic direction is defined to be along the $\mathbf{z}$ -direction while the $\mathbf{x}$ and $\mathbf{y}$ direction will respectively be referred as the normal and transversal directions. The periodic direction is also the transport direction.

We computed the converged electronic band structure of the 6-ZGNR (see Fig. 4.8). In

accordance to what have been found in the literature [29], we found that flat bands appear around the Fermi energy. This suggests possible magnetic ordering when electron-electron interactions are turned-on.

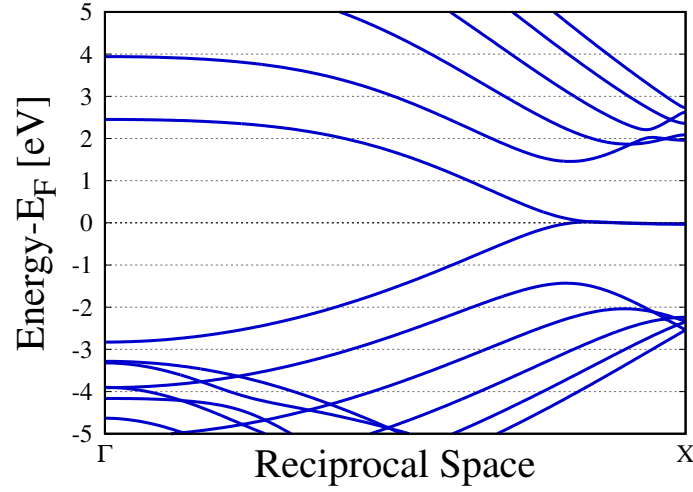


Figure 4.8: Electronic band structure of 6-ZGNR in a non-polarized calculation. Flat bands appear around the Fermi energy, suggesting magnetic ordering when spin polarization is explicitly taken into account.

Up to this point, we have disregarded the spin information in our calculations. We will now consider spin polarized systems. Two different configurations will be considered:

- The $\uparrow\downarrow$ configuration where ferromagnetic ordering is achieved along a given edge and the edges in an anti-parallel configuration.
- The $\uparrow\uparrow$ configuration where ferromagnetic ordering is achieved along a given edge and the edges in a parallel configuration.

We will refer to spin-polarized electrons as spin- $\uparrow$ and spin- $\downarrow$ electrons. Majority electrons will be defined as spin- $\uparrow$ and minority as spin- $\downarrow$ ¹. In cases for which systems do not exhibit spin imbalance, the appellation spin- $\uparrow$ and spin- $\downarrow$ will be used to distinguish between one type of electrons or the other.

We first perform a basic convergence study on spin polarized 6-ZGNRs. This will allow for the assessment of the aforementioned rule of thumb. Note that since ZGNRs are 1D structures a $1 \times 1 \times k_z^2$ Monkhorst-Pack grid is used. Vacuum layers are set in the transversal and longitudinal directions.

4.2.1 Convergence Study

Since the methodology has been previously explained, we directly present the results of convergence studies for the 6-ZGNRs in the $\uparrow\downarrow$ edge configuration. The convergence on the total energy and on the geometry are respectively displayed at Fig. 4.9 and Fig. 4.10.

¹This definition is totally arbitrary !

²The periodic direction is defined as the z -direction because **TranSIESTA** uses by default this direction for NEGF transport.

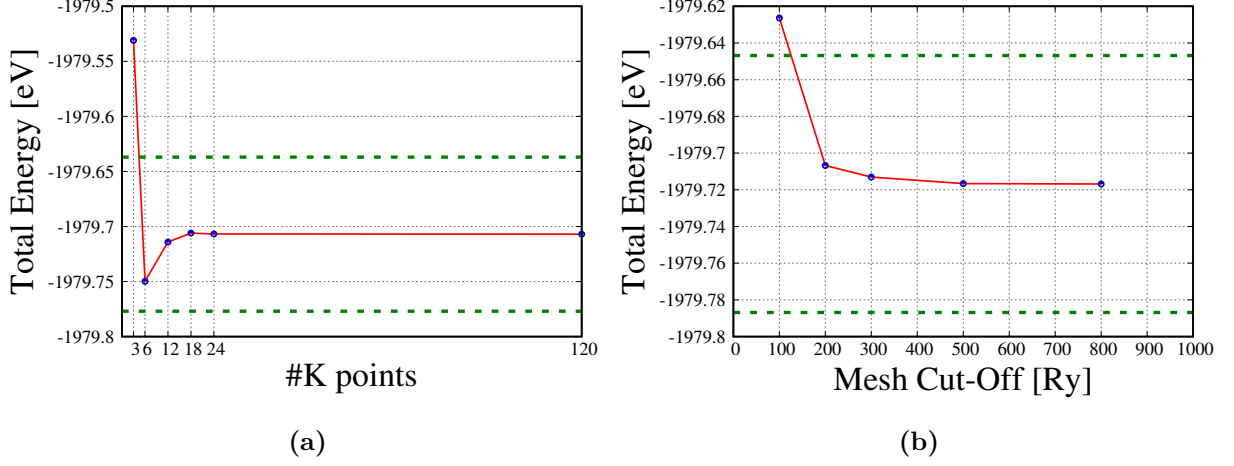


Figure 4.9: Convergence study for the total energy of the 6-ZGNR in the $\uparrow\downarrow$ spin configuration with respect to (a) the reciprocal space sampling for graphene and (b) the real mesh cut-off. The two horizontal lines (green) represent the tolerance: data that fall in between can be considered as converged. In our case, a $1 \times 1 \times 6$ Monkhorst-Pack grid and a real mesh cut-off of 200 Ry seem sufficient.

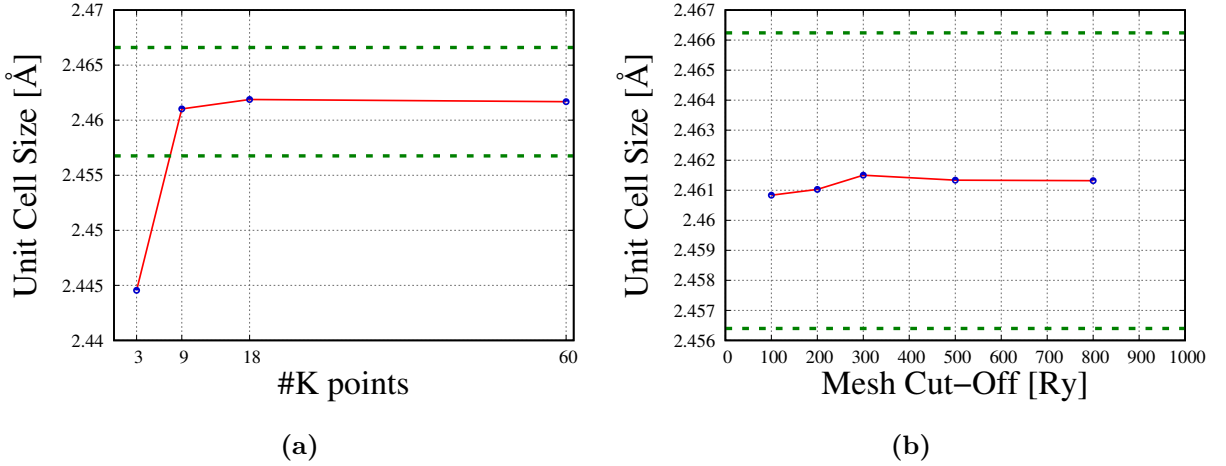


Figure 4.10: Convergence study for the structural relaxation of the 6-ZGNR in the $\uparrow\downarrow$ spin configuration with respect to (a) the reciprocal space sampling for graphene and (b) the real mesh cut-off. The two horizontal lines (green) represent the tolerance: data that fall in between can be considered as converged. In our case, a $1 \times 1 \times 9$ Monkhorst-Pack grid and a real mesh cut-off of 200 Ry seem sufficient.

Table 4.1: Summary for the basic convergence criteria for the 6-ZGNR in the $\uparrow\downarrow$ spin configuration. Both criteria are respected for a $1 \times 1 \times 9$ Monkhorst-Pack grid and a mesh cut-off of 200 Ry.

	Total Energy	Unit Cell Size
K-grid	$1 \times 1 \times 9$	$1 \times 1 \times 9$
Mesh cut-off	200 Ry	100 Ry

To respect both criteria, it seems that a $1 \times 1 \times 9$ Monkhorst-Pack grid and a mesh cut-off of 200 Ry are sufficient. However, as explained previously, those criteria are very basic and further considerations should be made. For instance, we can look at how the increase in accuracy can

influence the forces felt by the atoms (see Tab. 4.2).

Table 4.2: Convergence on the geometry of 6-ZGNR in the $\uparrow\downarrow$ spin configuration. The first column is the accuracy at which the input geometry is obtained. The second column is the accuracy at which the run is performed. The third column is the maximum force in our system before relaxation is performed. If the maximum force is over $0.01 \text{ eV/\AA}$, then the structure will automatically be relaxed.

Input Accuracy	Relaxation Accuracy	$F_{\max} [\text{eV/\AA}]$
$1 \times 1 \times 9$	$1 \times 1 \times 18$	0.077770
$1 \times 1 \times 18$	$1 \times 1 \times 24$	0.017123
$1 \times 1 \times 24$	$1 \times 1 \times 30$	0.006819
$1 \times 1 \times 24$	$1 \times 1 \times 36$	0.007662
$1 \times 1 \times 24$	$1 \times 1 \times 42$	0.007501
$1 \times 1 \times 24$	$1 \times 1 \times 120$	0.007645

From the data displayed at Tab. 4.2, we see that a $1 \times 1 \times 24$ Monkhorst-Pack is sufficient to ensure well relaxed structures.

Before proceeding to transport properties of such systems, we need to check whether the electronic band structure is converged enough. At Fig. 4.11, the comparison between several Monkhorst-Pack grids is done.

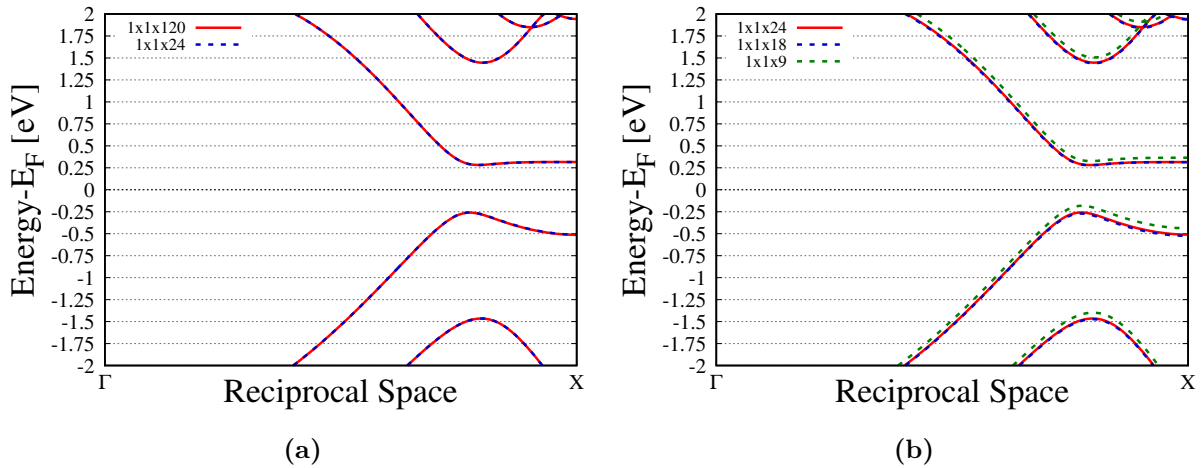


Figure 4.11: Convergence of the electronic band structure of 6-ZGNR in the $\uparrow\downarrow$ spin configuration (a) for high resolution grids, (b) for low resolution grids. Structures are fully relaxed. In (a), we notice the excellent agreement between the $1 \times 1 \times 24$ and the $1 \times 1 \times 120$ grid. As the geometry does not relax beyond $1 \times 1 \times 24$, both structures are identical. In (b), we notice discrepancies, especially for the $1 \times 1 \times 9$ grid which is obviously too coarse. The geometries in those cases are different.

The excellent agreement between the $1 \times 1 \times 24$ and $1 \times 1 \times 120$ grids (Fig. 4.11 a) confirms that 24 k-points along the periodic direction is enough to describe accurately the electronic band structure. This supports the aforementioned thumb-rule.

4.2.2 The $\uparrow\downarrow$ and $\uparrow\uparrow$ configurations

Now that we have considered convergence thoroughly, we are going to perform computations on 6-ZGNRs in both $\uparrow\downarrow$ and $\uparrow\uparrow$ spin configurations. The band structures have been computed and are displayed at Fig. 4.12.

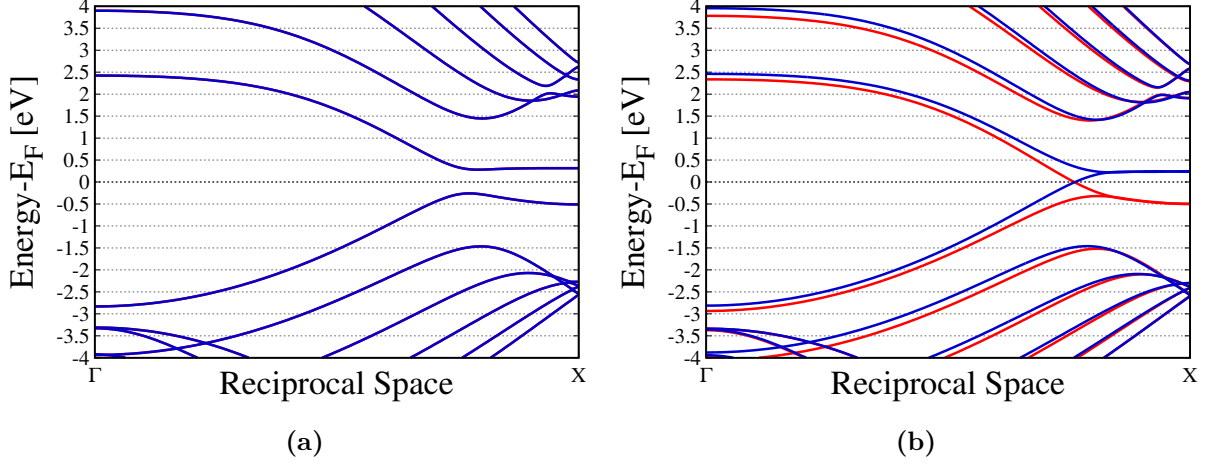


Figure 4.12: Electronic band structure for 6-ZGNRs in spin polarized calculation for (a) the $\uparrow\downarrow$ case and (b) in the $\uparrow\uparrow$ case. In the $\uparrow\downarrow$ configuration, the band structure is spin degenerated while in $\uparrow\uparrow$ the degeneracy is lifted. The red (blue) curve describes the states for the majority (minority) electrons. Note that in (a), there is *no* majority/minority electrons since the states are spin degenerated.

In the $\uparrow\downarrow$ spin configuration (Fig. 4.12 a), the electronic states are spin degenerated and the total magnetic moment is zero. In the $\uparrow\uparrow$ spin configuration (Fig. 4.12 b), the spin degeneracy is lifted and a total magnetic moment of $0.44 \mu_B$ per unit cell appears.

Both magnetic states are stable with respect to the minimization algorithm used. In other words, self-consistency cycles naturally reach such states (depending on the initial spin polarization fed into SIESTA). For the $\uparrow\downarrow$ case, the polarization at the edges was set to its maximum value while both edges were initialized in an anti-parallel fashion. In the $\uparrow\uparrow$ polarization, the initialization is similar but the edges were initialized in a parallel fashion.

We define $\Delta E_{NP-\uparrow\downarrow}$ to be the energy difference between the non-polarized calculation and the $\uparrow\downarrow$ run. We also define $\Delta E_{\uparrow\uparrow-\uparrow\downarrow}$ to be the energy difference between the $\uparrow\uparrow$ calculation and the $\uparrow\downarrow$ run. Using converged value, we find

$$\Delta E_{NP-\uparrow\downarrow} = 308 \left[\frac{\text{meV}}{\text{nm}} \right]$$

$$\Delta E_{\uparrow\uparrow-\uparrow\downarrow} = 57 \left[\frac{\text{meV}}{\text{nm}} \right]$$

Such values suggests that 6-ZGNRs naturally exhibit magnetic ordering. However, that range of energy is comparable to the thermal energy at 300 K so that stabilization of one magnetic phase over the other might be difficult. As we will see later, such states are essentially localized around the edge and are thus expected to be sensitive to edge roughness and interactions with the substrate.

Actually, some argue that such magnetic states might not exist in real system because of edge reconstruction, passivation and closure and that, even if such magnetic edges could be made, the thermal energy at room temperature would render them non-stable [30]. However, recent experimental works from Wang et al. support the existence of magnetic edge states as they uncovered edges states using scanning tunnel spectroscopy [31]. In another experimental work of Ruffieux et al. [32], they succeeded at synthesising atomically precise 6-ZGNR and showed the existence of edge-localized states using scanning tunnel spectroscopy. Techniques involving edge

engineering and interactions with the substrates might provide a way to stabilize further those magnetic edge states at room temperature [33].

Comparing Fig. 4.12 with Fig. 4.8, we see that the flat band around the Fermi energy has disappeared. In the $\uparrow\downarrow$ configuration, we notice the opening a direct band-gap of 540 meV while in the $\uparrow\uparrow$ case we observe a band splitting with the two spin channels exhibiting metallic behaviour.

The wavefunction associated with this magnetic edge states is expected to decreases exponentially when going towards the center of the ribbon [34]. Using a Mulliken population analysis, we showed that magnetization especially occurs on the edges (see Fig. 4.13). For the $\uparrow\downarrow$ case, edge carbons carry a magnetic moment of $0.262 \mu_B$ while in the $\uparrow\uparrow$ case this moments slightly shrink to $0.234 \mu_B$.

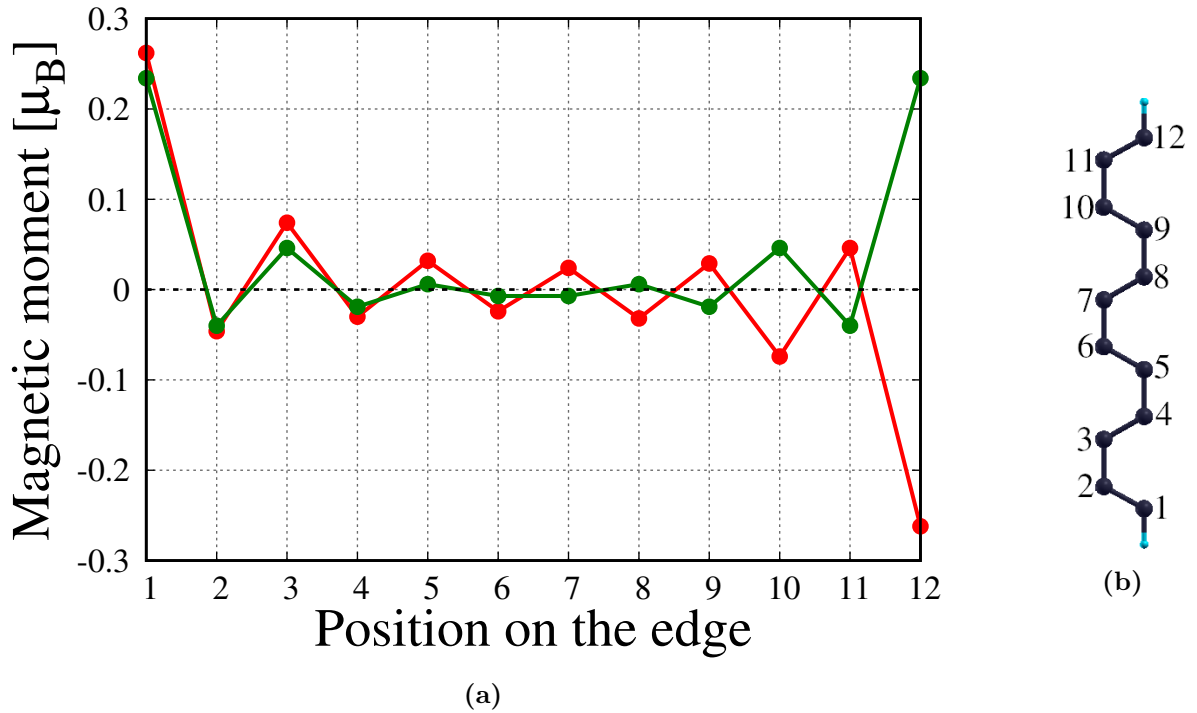


Figure 4.13: In (a), local magnetic moments on the carbons along the transversal direction of the 6-ZGNRs in both $\uparrow\downarrow$ (red) and $\uparrow\uparrow$ (green) spin configuration. In (b), the numbering used to label the carbon atoms is displayed.

In general, nearest-neighbour carbon atoms tend to interact antiferromagnetically. This is respected for all carbon atoms in the $\uparrow\downarrow$ case. However, in the $\uparrow\uparrow$ spin configuration, the carbons at position 6 and 7 experience magnetic frustration due to an even number of carbons along the transversal direction. This frustration may be one of the reasons why the $\uparrow\uparrow$ configuration is less stable than the $\uparrow\downarrow$ one. As this frustration takes roots in the even numbers of carbons along the y -direction and since all the ZGNRs possess an even number of carbons in their unit cell, the $\uparrow\downarrow$ configuration is expected to be the more stable, irrespectively to the size of the ribbon.

Actually, the frustration at the center of the ZGNRs should become vanishing as the width of the ribbon increases since magnetic states are localized around the edge. Hence, $\Delta E_{\uparrow\uparrow-\uparrow\downarrow}$ should become negligible for wider ribbons. We ran several calculation for several ribbons width. Results are displayed at Fig. 4.14.

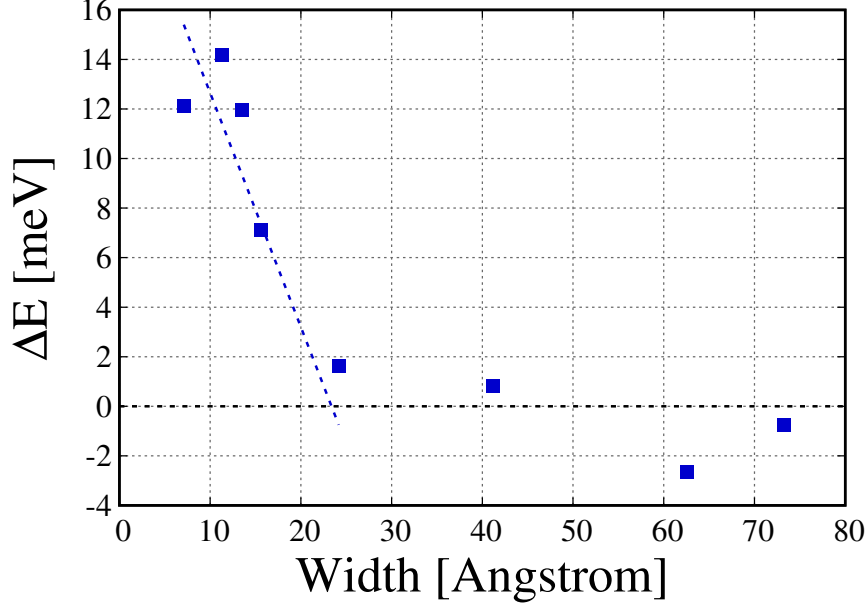


Figure 4.14: Influence of the ribbon's width on the relative stability of the two edge configurations ($\Delta E_{\uparrow\uparrow-\uparrow\downarrow}$). For ribbon wider than $\sim 20\text{\AA}$, $\Delta E_{\uparrow\uparrow-\uparrow\downarrow}$ becomes irrelevant as accuracy of DFT calculation falls within few meV.

The energy difference is per unit cell. The width of the ribbon is defined to be the transversal distance between the carbon atoms of opposite edges.

We observe that for ZGNRs whose width is bigger than $20\text{\AA}$, $\Delta E_{\uparrow\uparrow-\uparrow\downarrow}$ is too small to be relevant. Indeed, the accuracy of DFT is within few meV. Moreover, the error on an energy difference is twice as big as the error on the energy. Therefore, only narrow width ribbons are found to possess an energy barrier between the $\uparrow\downarrow$ and $\uparrow\uparrow$ configuration. However, as discussed earlier, this energy stays small compared to thermal energy at room temperature.

4.2.3 Band Gap/Width Relationship

State-of-the-art computational works suggest that the band gap of the ZGNRs is highly dependent on the width of the ribbon with a band-gap following a $\propto 1/w$ relationship, w being the width of the ribbon [13] [14].

The electronic band structures of several ZGNRs have been computed in the $\uparrow\downarrow$ configuration and are displayed at Fig. 4.15. From qualitative observation, we notice that the direct band gap decreases as the width of the ribbon increases while the gap at $k = X$ stays mostly uncorrelated to w .

Attention must be paid when one discusses band gap within DFT calculation. Indeed, DFT calculations have without any doubt greatly contributed to the prediction and explication of physical properties in materials for the last decades. Nevertheless, a serious issue about materials band gap still remains as approximations like LDA or GGA drastically underestimate its value. This so-called *band gap problem*, can be partially resolved using many-body perturbation theory and one of its practical approximation: the GW approximation. For instance, while silicon's band gap is known to be around 1.1 eV, it is seriously underestimated within LDA and GGA (respectively 0.60 and 0.71 eV) [35]. GW approximation allows for computational results way closer to experimental ones [36]. In general, many-body calculations are more computationally intensive.

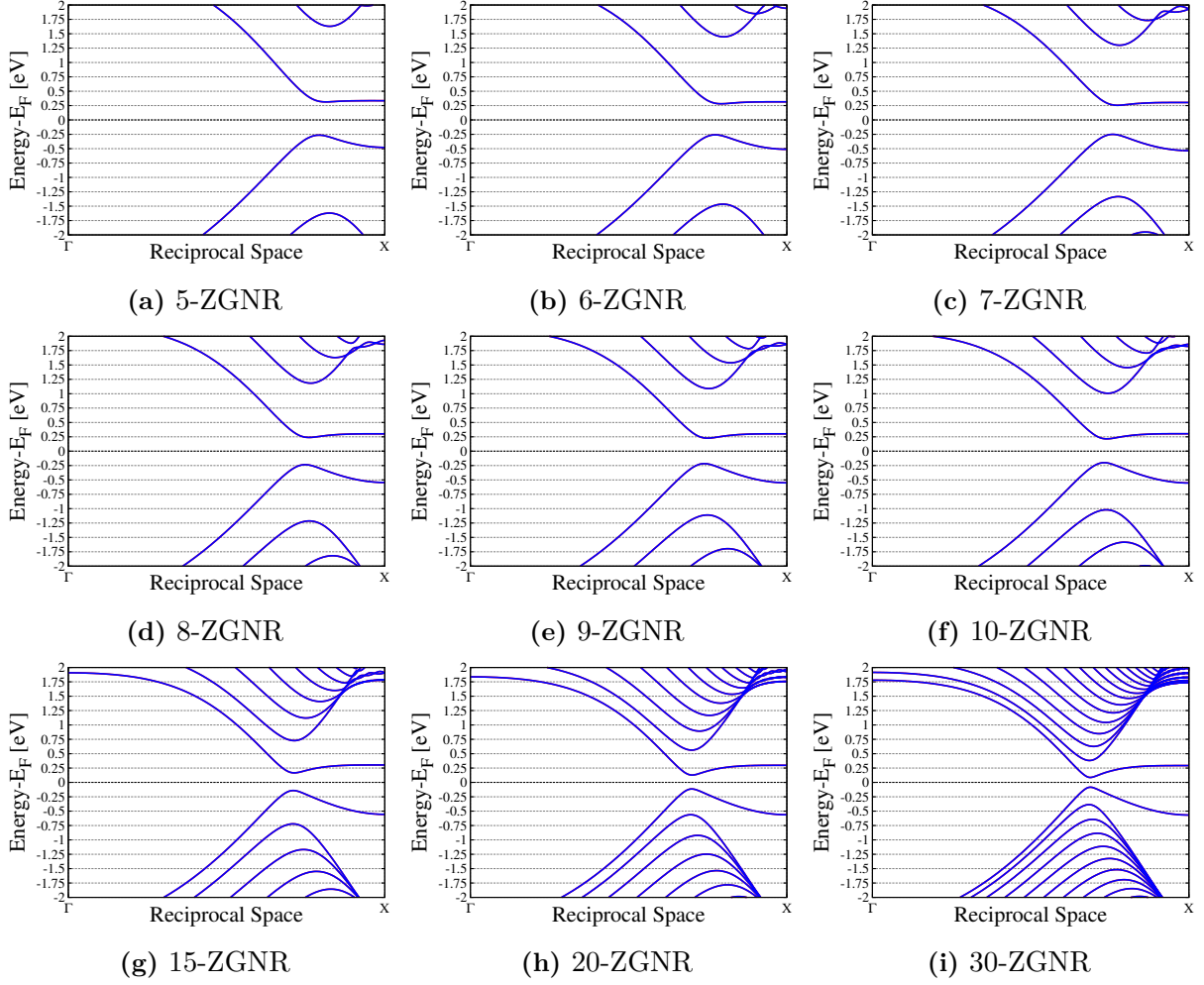


Figure 4.15: Electronic band structure of (a) 5-ZGNR, (b) 6-ZGNR, (c) 7-ZGNR, (d) 8-ZGNR, (e) 9-ZGNR, (f) 10-ZGNR, (g) 15-ZGNR, (h) 20-ZGNR, (i) 30-ZGNR in the $\uparrow\downarrow$ configuration. The direct band gap decreases as the width of the ribbon increases while the band gap at $k = X$ is mostly uncorrelated to the width.

The band gap problem being inherent to the approximations used within DFT, ZGNRs are not an exception. While, experimental results suggest that ZGNRs with a width of about 1 nm exhibit a band gap on the order of 1 eV [15], a value of around 540 meV is found in this work. This represents an underestimation of more than 40%.

We compared the results obtained for the band gap-width relationship with those reported in the work of Yang et al. [13]. The width of the ribbon is defined disregarding the hydrogen atoms. Results of our computations are displayed at Fig. 4.16.

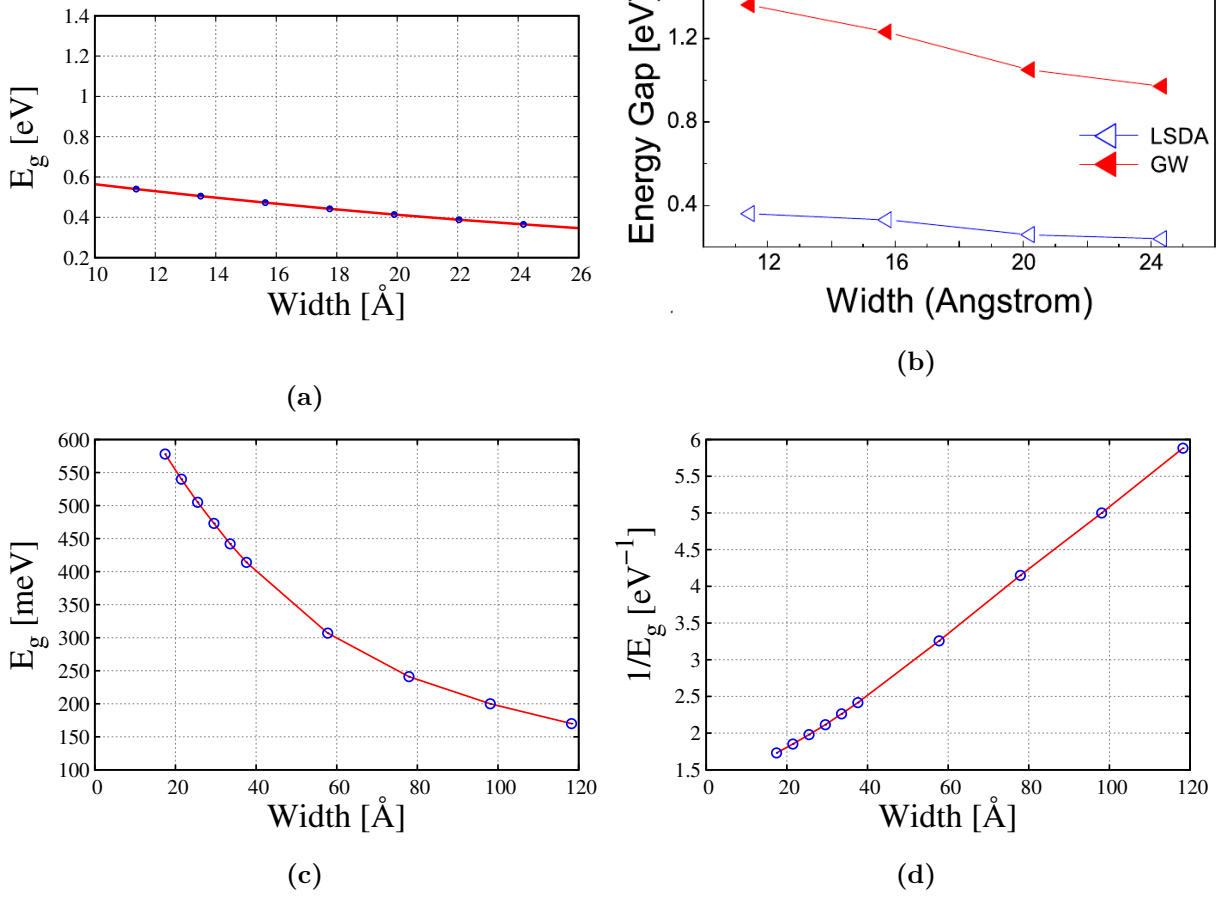


Figure 4.16: Band gap/width relationship in ZNGRs. In (a), results of this work for width between 10 and 26 Å are displayed. In (b), results for LDA (blue) and GW (red) from Yang et al. [13]. Our results follow the same tendency as the one from (b). In (c) and (d), results for a larger range of width are presented. The $\propto 1/w$ behaviour of the band gap is clear in (d). Subfigure (b) is adapted from [13].

Our results are in good agreement with what have been reported by Yang et al. [13]. In our case, the value of the band gaps are slightly higher than what they have found using LDA³. This increase in the value of the band gap is believed to be due to the use of GGA as it often gives a higher value for the gap than LDA [35].

The relationship in $1/w$ can clearly be observed on Fig. 4.16 where the inverse of the band gap is plotted with respect to the width of the ribbon.

³In their work, Yang et al. [13] used the terminology "LSDA" where the "S" explicitly states that spin polarized calculations have been performed. This is totally equivalent to saying LDA with spin polarization.

4.3 Quantum Transport Properties of 6-ZGNRs

In this section, we will explore transport properties of 6-ZGNRs and provide practical examples of well-defined **TranSIESTA** calculations. We will also explicitly show what happens when badly defined system are computed.

4.3.1 Spin Non-Polarized Calculation

First, we disregard the spin degree of freedom. Such calculations are less computationally intensive and the extension to spin polarized systems is trivial. We will consider spin-resolved transport later in this work.

As explained in the previous chapter, **TranSIESTA** requires the user to ensure the structure to respect several properties:

- 1 In the ELC, the unit cell should interact, at most, with neighbouring cells.
- 2 In the SRC, the contact region should be large enough so that the left electrode does not interact with the right electrode.
- 3 In the SRC, the device region should contain enough electrode buffer layers to ensure that the electrodes behave as bulk-like electrode⁴.

If such properties are not respected, non-physical results might be obtained.

We recall that a sufficient condition to enforce the first property is to take a cell whose dimensions are at least of $2R_C$, where R_C is the largest cut-off radius in our NPAOs (R_C is available in the output of any **SIESTA** run). For the second property, the condition is similar since using a device region bigger than $2R_C$ provide a system with non-interacting electrodes. We will now illustrate this with a practical example with the transport properties of pristine 6-ZGNRs.

In our case, the biggest cut-off radius is given by $R_C = 5.12$ Bohr ($R_C = 2.71$ Å). To ensure a well defined system, one would then need cells whose dimensions are bigger than $2R_C = 5.42$ Å. As the unit cell of a 6-ZGNRs is 2.46 Å wide, using a cell three times bigger than the basic one ensure the first property. The same reasoning can be applied for the device region which should be at least three times larger than the basic unit cell of 6-ZGNRs.

Following the aforementioned methodology, a well defined system would contain 9 basic units of 6-ZGNRs (see Fig. 4.17).

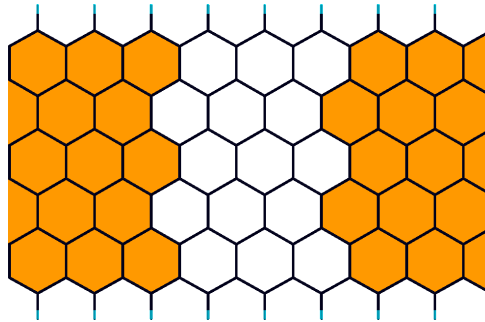


Figure 4.17: Well defined system for a SRC run using **TranSIESTA** for 6-ZGNRs. The orange zones represent the left and right electrode. For the ELC run, one of those orange zones has to be used to define the cell. Smaller cells might results in non-physical results (see Fig. 4.18).

We performed transport calculations for different sizes of cells (1, 2, 3 and 4). The one presented at Fig. 4.17 is said to be of size 3 since the cell of the electrodes and the device regions

⁴"Bulk-like" is used to describe the electrode as computed in the ELC run and has nothing to do with the dimensionality of the system

is defined by 3 times the smallest cell of 6-ZGNRs. The results of those runs are displayed at Fig. 4.18.

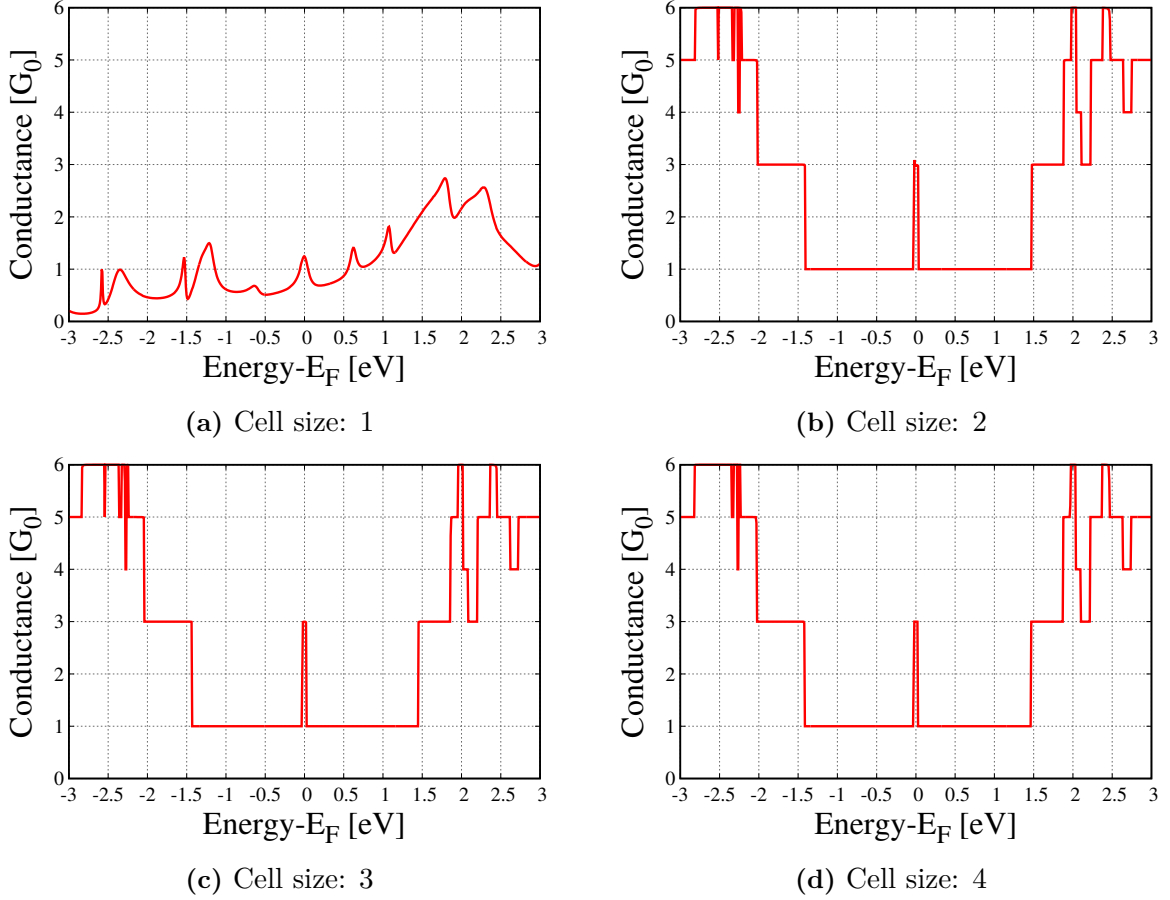


Figure 4.18: Transport simulations on pristine 6-ZGNRs with a system where electrodes and device region are as wide as (a) 1 unit cell, (b) 2 unit cells, (c) 3 unit cells and (d) 4 unit cells. In (a), non-physical results are obtained. In (b), the result is globally neat except for a small instability around $E = 0$. For (c) and (d), perfectly physical results are obtained with clear quantization of the conductance.

Looking at Fig. 4.18, we notice that when the cell is way too small (Fig. 4.18 a), absurd results are obtained. For a size 2 system (Fig. 4.18 b), the transmission spectrum is correct except for the small overshoot happening around $E = 0$. As the size increases beyond 3 (Fig. 4.18 c and d), perfect results are obtained with a neat, well-quantized conductance.

The results displayed at Fig. 4.18 emphasize on the fact that the user should always check that the considered system respects the basic properties aforementioned. This is even more critical since the **TranSIESTA** output will probably not display any warning.

4.3.2 Spin Polarized Calculation

We will now compute the spin resolved transmission spectra for the 6-ZGNRs in the $\uparrow\downarrow$ and $\uparrow\uparrow$ spin configuration. To ensure physically relevant results, a system of size 3 (see Fig. 4.17) is used.

We will first ensure the convergence with respect to the reciprocal space sampling. Usually, one has to deal with grids of the form $k_x \times k_y \times k_z$. For such systems, a convergence study for the

electrode run (which is essentially a normal SIESTA run) *and* for the scattering region calculation (TranSIESTA) has to be performed. Indeed, in TranSIESTA only the $\mathbf{z}$ -direction is treated with NEGF while the two other directions are considered within Bloch's formalism. This requires thus the user to ensure a dense enough grid along the $\mathbf{x}$ and $\mathbf{y}$ directions of the reciprocal space.

In our case, we are considering transport along one dimensional object so that $k_x = k_y = 1$. Because of this, the convergence study on the reciprocal space sampling needs to be done only for the electrode calculation.

We first focus our attention to the $\uparrow\downarrow$ configuration and compare a $1 \times 1 \times 8$ with a $1 \times 1 \times 16$ Monkhorst-Pack grid. Note that here, since a supercell equivalent to three times the unit cell of the 6-ZGNR is used, a $1 \times 1 \times 8$ Monkhorst-Pack grid used here is equivalent to a $1 \times 1 \times 24$ grid used in the previous section. This is due to the folding of the Brillouin zone as the dimensions are increased.

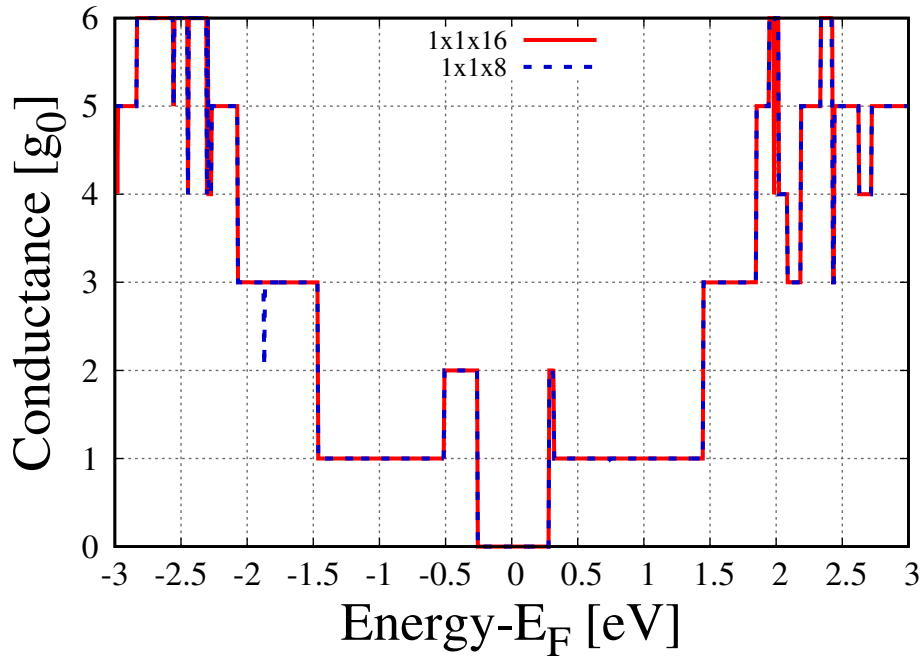


Figure 4.19: Transmission spectrum at zero bias for 6-ZGNRs at zero bias using a $1 \times 1 \times 8$ (blue dashed line) and $1 \times 1 \times 16$ (red line) Monkhorst-Pack grid for the $\uparrow\downarrow$ spin polarized case.

As shown by Fig. 4.19, the $1 \times 1 \times 8$ grid gives globally good results except for the tiny dip happening around -1.87 eV. The $1 \times 1 \times 16$ grid gives excellent results with well-quantized plateaus.

Since such electrodes will be used throughout this work, we performed the run at the higher accuracy. The result for the $\uparrow\uparrow$ configuration is then displayed at Fig. 4.20.

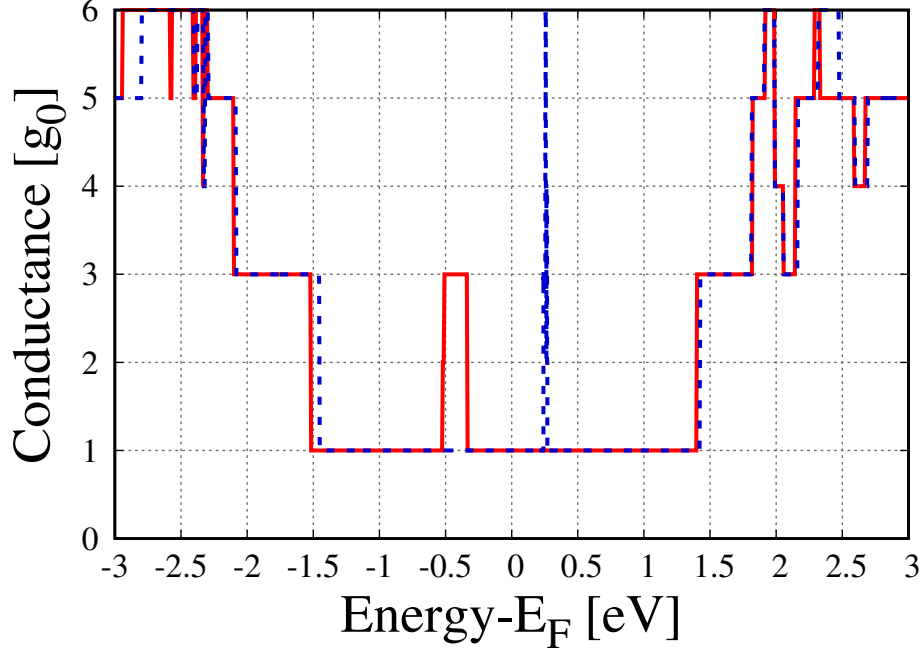


Figure 4.20: Transmission spectrum at zero bias for 6-ZGNRs in the $\uparrow\uparrow$ spin polarized case. The red (dashed-blue) line represents the majority (minority) electron channel.

The spin resolved transmission spectrum of the 6-ZGNR in the $\uparrow\uparrow$ configuration is in accordance with the Landauer-Buttiker view of quantum transport (see band structure at Fig. 4.12). In this case, we notice a strange behaviour around 0.26 eV for the minority spin channel. To check whether this is a convergence problem or not, we computed the band structure at high accuracy ($1 \times 1 \times 120$ Monkhorst-Pack grid and 500 Ry for the mesh cut-off).

As shown by Fig. 4.21, around 0.26 eV, band crossing occurs over a small range of energy so that the behaviour of the transmission spectrum does not take source in convergence problems. Actually, using the Landauer-Büttiker picture of transmission, one can easily recover the peak at $6G_0$ for $E = 0.26$ eV.

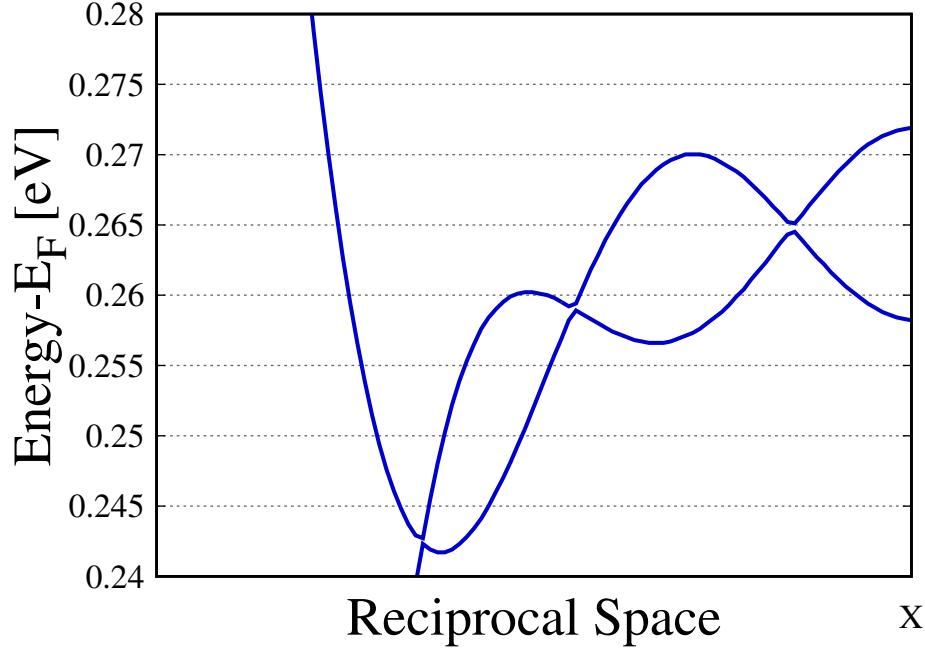


Figure 4.21: Zoom on the electronic band structure of 6-ZGNRs in the $\uparrow\uparrow$ configuration. We observe quite flat band crossings so that transmission around $E = 0.26$ is expected to vary rapidly and reach a peak of $6G_0$.

4.3.3 Effect of a Stone-Wales Defect

Transmission spectra obtained until here were described by nicely quantized plateaus as we would expect from ballistic transport theory. We now introduce a defect inside the channel. This will generate back-scattering and thus effectively reduce conductance.

The considered defect is a Stone-Wales defect which consists on a carbon-carbon bond which has been rotated by 90° . Fig. 4.22 describes such set-up.

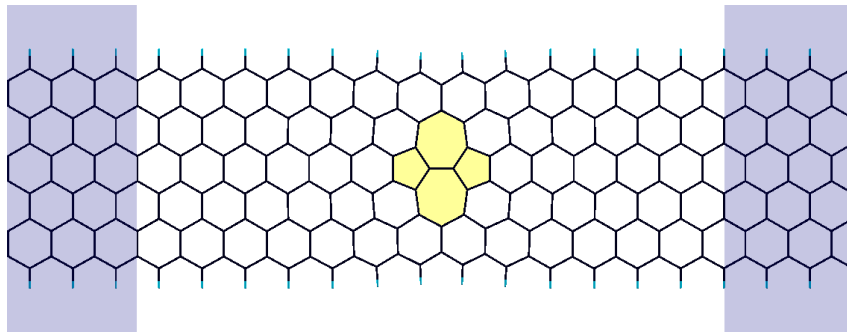


Figure 4.22: Set-up for the SRC run that will allow for the calculation of the transmission spectra for a 6-ZGNR containing a Stone-Wales defect. The Stone-Wales defect consists on a carbon-carbon bond which has been rotated by 90° and is depicted in light yellow on this picture. The light blue zones are the electrodes. We defined several layers of 6-ZGNRs between the defect and the electrodes to ensure bulk-like behaviour in the electrodes.

As a defect has been introduced in the channel, one needs to ensure that the electrodes (light blue regions in Fig. 4.22) are not influenced by the defect. Hence, layers of pristine 6-ZGNRs were put on each side of the Stone-Wales defect to screen as much as possible its influence. The

defect is located in the center of the ribbon so that symmetry is preserved. Because of this, one should not expect the spin degeneracy to be lifted in the $\uparrow\downarrow$ case.

The energy of formation of a Stone-Wales defect ΔE_{SW} defect can be computed using

$$\Delta E_{\text{SW}} = E_{\text{SW}} - N E_{\text{prist}} \quad (4.1)$$

where N is the number of pristine 6-ZGNR unit cells used to define the whole cell with the Stone-Wales defect, E_{prist} the energy of one unit cell of pristine 6-ZGNR and E_{SW} the energy of the whole cell with the Stone-Wales defect. For the non-polarized, $\uparrow\downarrow$ and $\uparrow\uparrow$ case, ΔE_{SW} is respectively given by 4.4262 eV, 4.4016 eV and 4.3554 eV.

We computed the spin density using a Mulliken population analysis. The results are presented at Fig. 4.23.

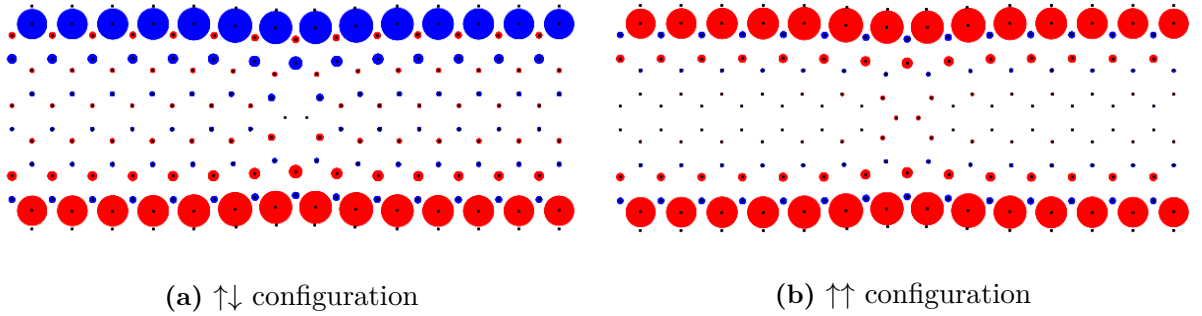


Figure 4.23: Spin density obtained through Mulliken population analysis for a 6-ZGNR with a Stone-Wales defect in the (a) $\uparrow\downarrow$ and (b) $\uparrow\uparrow$ configuration. A red (blue) circle means that locally, the spin density is dominated by spin $\uparrow$ ($\downarrow$) electrons. The bigger the circle, the stronger the spin polarization. As for pristine 6-ZGNRs, spins are mostly confined toward the edges of the structure.

Globally, the Stone-Wales defect does not change the localization of the spins along the ribbon as polarization especially occurs along the edges. Since our ribbon is quite narrow, the influence of the Stone-Wales defect on the edges is far from being negligible. The introduction of the Stone-Wales defect has reduced $\Delta E_{\uparrow\uparrow-\uparrow\downarrow}$ to the value of 41 meV/nm (for pristine 6-ZGNR, $\Delta E_{\uparrow\uparrow-\uparrow\downarrow} = 57$ meV/nm) while it did not really affect $\Delta E_{NP-\uparrow\downarrow}$. The weakening of $\Delta E_{\uparrow\uparrow-\uparrow\downarrow}$ may be linked to the magnetic frustration induced in the $\uparrow\downarrow$ case.

The conductance has been computed for the non-polarized case and for the two different edge configurations. The results of our computations are displayed at Fig. 4.24.

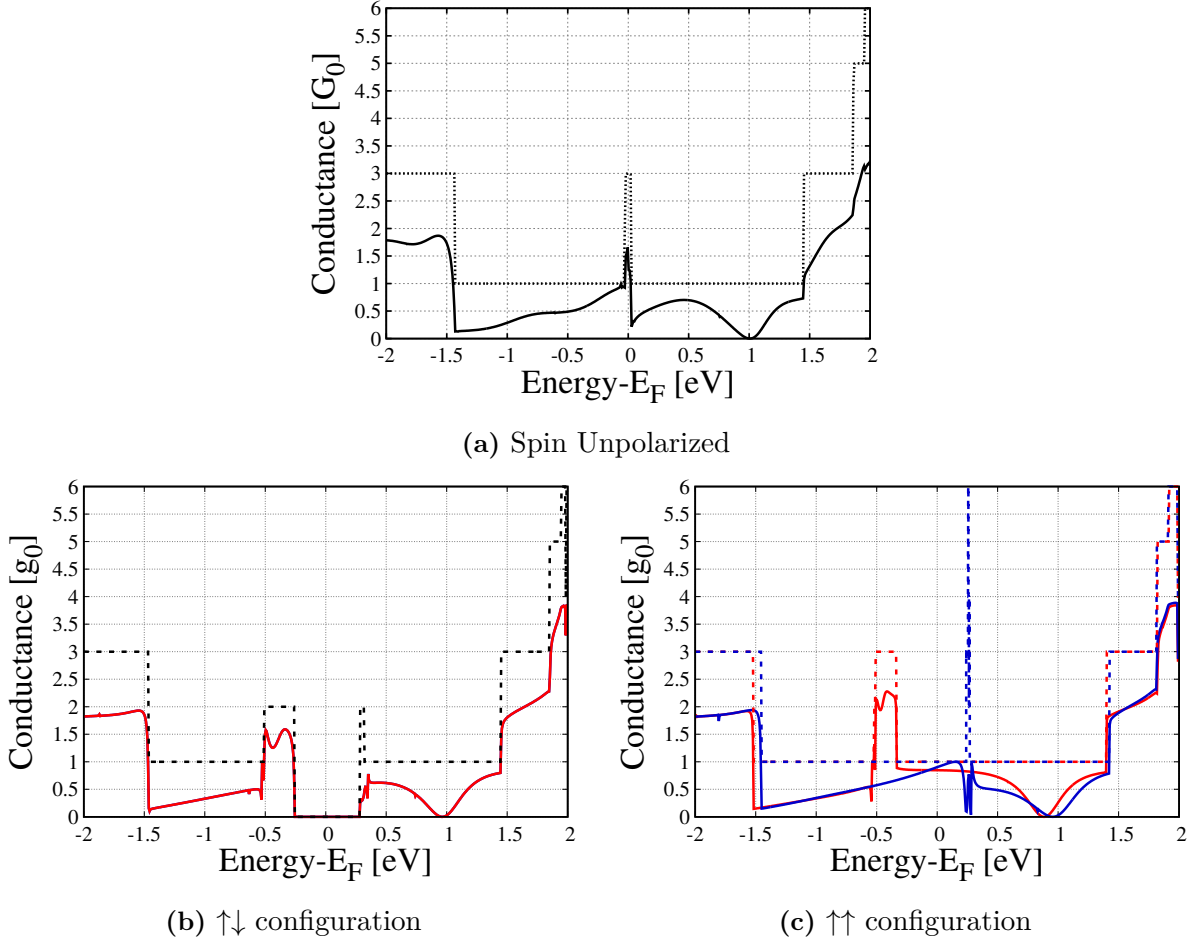


Figure 4.24: Transmission spectrum at zero bias for a 6-ZGNR with a Stone-Wales defect (see Fig. 4.22) for the (a) non-polarized, (b) $\uparrow\downarrow$ and (c) $\uparrow\uparrow$ case. The red (blue) curve represents the spin up (down) electrons. The dotted lines stand for the transmission spectra of the 6-ZGNR. For the $\uparrow\downarrow$ configuration (a), the spin channels are degenerated.

As expected, the introduction of a defect has led to back scattering in our channel as transmission is globally lowered. The transmission profile obtained in the non-polarized case (Fig. 4.24 a) is in accordance with what has been found in the literature [37].

For the $\uparrow\downarrow$ configuration, both spin channels are degenerated which agrees with the symmetry of the system. Since the leads are semiconducting, the device can not operate around the Fermi energy. In the $\uparrow\uparrow$ case, spin degeneracy is lifted. Except in the energy window $[-1 : 1]$ eV, both spins channel are globally affected in the same way.

A peculiar behaviour arises around 0.26 eV. This is probably linked with the peak in the conductance of pristine 6-ZGNRs.

5

Phenyl Edge-Modified 6-ZGNRs

In this chapter, we will study 6-ZGNRs whose edges have been functionalized by phenyl groups. Such structures will be referred to as *phenyl edge-modified 6-ZGNRs* (PEM 6-ZGNRs). Since such edge-defects are structurally similar to fluoranthene groups, they will also be referred to as "fluoranthene-like edges". PEM 6-ZGNRs structures were recently synthesized by Ruffieux et al. [32].

5.1 Experimental Structures

As explained in [32], the method to produce atomically precise 6-ZGNRs and PEM 6-ZGNRs relies on surface-assisted polymerization. First, U-shape monomers are being adsorbed by a (111) gold surface (see Fig. 5.1). Then, as the surface is held at the temperature of 475 K, the monomers are activated and undergo radical polymerization. Finally, the atomically precise 6-ZGNR is obtained through annealing at the temperature of 625 K. The method to produce PEM 6-ZGNRs is conceptually the same.

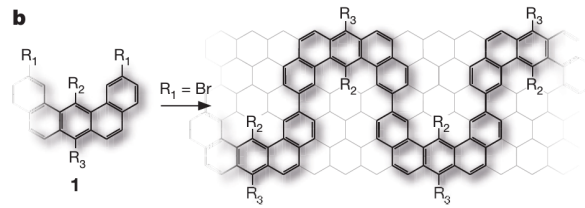


Figure 5.1: Schematic of the U-shaped dibenzo[a,j]anthracene monomer (1). The groups R_1 denote halogen functions which enable surface-assisted aryl-aryl coupling to form a polymer in a snake-like shape. The polymerization follows the zigzag direction. Adapted from [32]

The groups R_1 are halogen functions which enable thermally induced aryl-aryl coupling. This creates the snake-like shape of the polymeric structure. The group R_2 has to be designed correctly to allow completeness of the ZGNR, as shown in Fig. 5.2.

If the choice of the groups R_1 and R_2 is quite constrained, the choice of R_3 remains *a priori* unconstrained and allows us to choose between perfect 6-ZGNRs ($R_3 = H$) or edge-functionalized 6-ZGNRs. In [32], a phenyl group was put at the R_3 position (see Fig. 5.3).

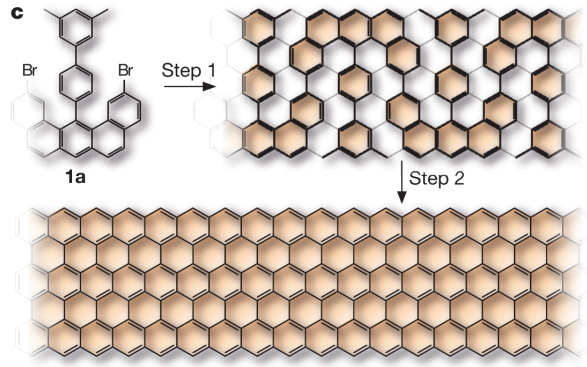


Figure 5.2: Schematic of the U-shaped monomer where a dimethyl-biphenyl group is explicitly placed at the R_2 position (see Fig.5.1). This monomer is designed to produce atomically precise 6-ZGNRs. Two steps are necessary to produce the nanostructure : (1) surface-assisted polymerization and (2) cyclization. Adapted from [32]

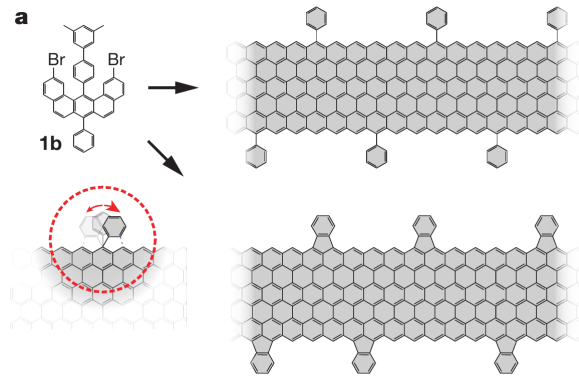


Figure 5.3: Modified monomer that contains the additional phenyl group at the R_3 position (up-left). A polymerization where the phenyl is fixed would yield a fully periodic structure (up-right). However, at the cyclodehydrogenation temperature of 573 K, the phenyl group undergoes a ring closure either on its left or its right (bottom-left). This gives a non-periodic structure where fluoranthene-type edges are separated by either 3, 4 or 5 perfect zigzag cusps (bottom-right). Adapted from [32]

At the temperature of 573 K, the extra phenyl groups undergo ring closure. Since ring closure yields a *a priori* 50%-50% to occur towards one side or the other, the probability to obtain a fully periodic structure approaches zero.

Taking two neighbouring phenyl groups, we notice that three different topological geometries arise:

- If the ring closure happens so that both phenyl groups fall towards each other, they are separated by 3 perfect zigzag cusps.
- If the ring closure happens so that both phenyl groups fall towards the same direction, they are separated by 4 perfect zigzag cusps.
- If the ring closure happens so that both phenyl groups fall avoiding each other, they are separated by 5 perfect zigzag cusps.

5.2 Systematic Approach

To study structures which display randomness, we will develop a systematic approach that will allow us to study them in a periodic fashion. Our approach relies on the fact that periodicity is

conserved as long as ring closure has not happened (see Fig. 5.4).

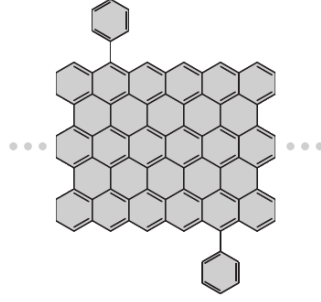


Figure 5.4: Basic unit for phenyl-edge modified 6-ZGNRs. This structure yields periodicity in the longitudinal direction. Ring closure of the phenyl groups at the edges breaks down the periodicity as the direction of the ring closure is *a priori* random. Adapted from [32]

We will refer to the unit cell displayed at Fig. 5.4 as the *basic unit*. In this basic unit, an upper phenyl group and a lower phenyl group can be defined, each of these groups being free to fall either on the right or on the left.

In our approach, we consider a unit cell which is one or several juxtaposed basic units, yielding a finite amount of periodic structures. The size N of the unit cell will be defined as the number of basic units used to define it. As each phenyl group holds two possible ring closure sites and since a basic unit contains 2 phenyl groups, 2^{2N} different topologies are to be expected for size N structures.

We quickly notice that this formalism could eventually lead to a tremendous number of different structures. For instance, taking a unit cell defined by 6 basic units, 64 different structures would arise. Fortunately, symmetries systematically bring the number of structures down. In the next section, we will develop a useful nomenclature to define those structures and look into symmetry operations.

5.3 Symmetries

Structures of size N contain $2N$ phenyl groups and will be labelled as $[a_1, \dots, a_N, a_{-1}, \dots, a_{-N}]$ where a_i with $i > 0$ ($i < 0$) represents the state of the i^{th} phenyl group of the upper (lower) edge. The numbering for each edge starts from the left so that the correspondence between the nomenclature and the structure follows the conventional western reading direction. The $\{a_i\}$ can take two distinct values: if the phenyl group fell on the right (left) then its a_i takes the value of 1 (-1).

The symmetries that will interest us are the 2-fold rotation whose axis is either in the normal direction or in the transversal direction of the ribbon and cyclic permutations.

5.3.1 Two-fold Rotation in the Normal Direction

The two-fold rotation in the normal direction is an operator $\hat{R}_n$ which acts on the structure $[a_1, \dots, a_N, a_{-1}, \dots, a_{-N}]$ such that

$$\hat{R}_n[a_1, \dots, a_N, a_{-1}, \dots, a_{-N}] = [-a_{-N}, \dots, -a_{-1}, -a_N, \dots, -a_1]$$

In simple words, it reverses the order of the $\{a_i\}$ while taking the opposite value for each a_i .

5.3.2 Two-fold Rotation in the Transversal Direction

The two-fold rotation in the transversal direction is an operator $\hat{R}_t$ which acts on the structure $[a_1, \dots, a_N, a_{-1}, \dots, a_{-N}]$ such that

$$\hat{R}_t[a_1, \dots, a_N, a_{-1}, \dots, a_{-N}] = [-a_N, \dots, -a_1, -a_{-N}, \dots, a_{-1}]$$

In simple words, it reverses the order and take the opposite for each half of the a_i 's but does not alter the order between those two half.

5.3.3 Cyclic Permutations

For a structure of size N , there exists N distinct cyclic permutations. We define the order of the cyclic permutation as j ($j = 0, \dots, N - 1$).

The cyclic permutation of order j is an operator $\hat{C}_j$ which acts on the structure $[a_1, \dots, a_N, a_{-1}, \dots, a_{-N}]$ such that

$$\begin{aligned} a_i &\rightarrow a_{(i+j) - \lfloor \frac{i+j-1}{N} \rfloor N} \\ a_{-i} &\rightarrow a_{-(1+j) - \lfloor \frac{1+j-1}{N} \rfloor N} \end{aligned}$$

where $\lfloor \cdot \rfloor$ is the floor operator. The symbol $\rightarrow$ is to be read as "becomes".

Note that the cyclic permutation of order 0 is equivalent to the identity operator.

5.4 Phenyl Edge-Modified 6-ZGNRs of size N=1

Considering $N = 1$ holds the simplest case of PEM 6-ZGNRs where one basic unit gives the unit cell of our structure. As shown in Fig. 5.5, this PEM structure possesses 2 distinct phenyl groups.

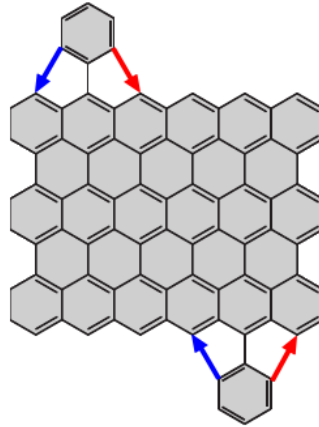


Figure 5.5: Unit cell of the PEM 6-ZGNR of size $N=1$ before ring closure. The randomness in the ring closure events is symbolized by the red and blue arrows. Each group is as likely to fall on its right than on its left. Adapted from [32].

Since the size of our unit cell is $N = 1$, there is a priori 4 different structures which are $[1, 1]$, $[1, -1]$, $[-1, 1]$ and $[-1, -1]$. Even if the number of structures is ridiculously small, symmetry considerations can bring this number further down. The symmetry analysis of those structures is summarized at Tab. 5.1.

Table 5.1: Summary of the symmetry analysis of PEM 6-ZGNRs structures where $N=1$. The first column lists the structures, the second structures which are equivalent under the two-fold rotation with respect the normal axis and the third structures which are equivalent under two-fold rotation with respect to the transversal axis. Note that in this case, cyclic permutation has not to be taken into account since only the identity cyclic permutation exists.

Structure	$\hat{R}_n$	$\hat{R}_t$
$[1, 1]$	$[-1, -1]$	$[-1, -1]$
$[1, -1]$	$[1, 1]$	$[-1, 1]$
$[-1, 1]$	$[-1, 1]$	$[1, -1]$
$[-1, -1]$	$[1, 1]$	$[1, 1]$

Using the results displayed at Tab. 5.1, we can conclude that only two structures are non-equivalent : the $[1, 1]$ and the $[1, -1]$ structures. Actually a simpler argument would have yield the same result: the first structure is obtained when both phenyl groups fall towards the same direction while the second one is obtained when the phenyl groups fall in opposite direction. The two structures are displayed at Fig. 5.6.

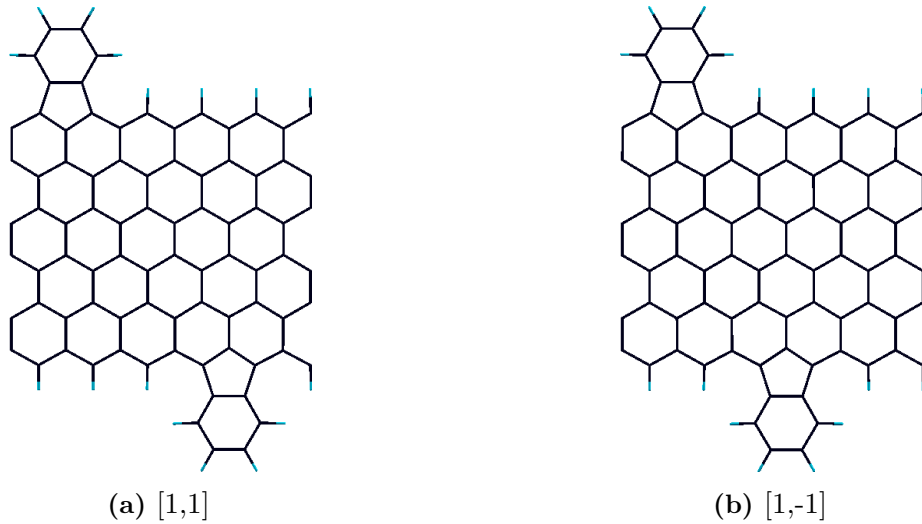


Figure 5.6: Unit cell of the PEM 6-ZGNR of size $N=1$ after ring closure. Even if size 1 PEM structures yields 4 configurations, only two of them are non-equivalent. Those non-equivalent structures are the (a) $[1,1]$ and (b) $[1,-1]$ structures.

As done previously, we will investigate those structures under two different spin polarization: the $\uparrow\downarrow$ and the $\uparrow\uparrow$ configuration.

For a given spin configuration, the energy difference between the two structures is smaller than 1 meV so that it cannot be asserted that one structure is more stable than the other. Actually, this was to be expected as both edges exhibit the same topology. Indeed, in ZGNRs, edges states play an important role and are exponentially vanishing towards the interior of the ribbon.

In both structures, the energy difference between the different spin configurations is given by $\Delta E_{\uparrow\uparrow-\uparrow\downarrow} \sim 21$ meV/nm (57 meV/nm in the pristine case). This means that the defects at the edges have decreased the relative stability of the $\uparrow\downarrow$ configuration over the $\uparrow\uparrow$ by more than 60%. The same observation can be done for $E_{NP-\uparrow\downarrow}$ whose value has decreased of approximatively 50% (from 308 meV in the pristine case to 150 meV here).

The electronic band structures are displayed at Fig. 5.7. We do not notice any outstanding difference between the $[1, 1]$ and the $[1, -1]$ structures.

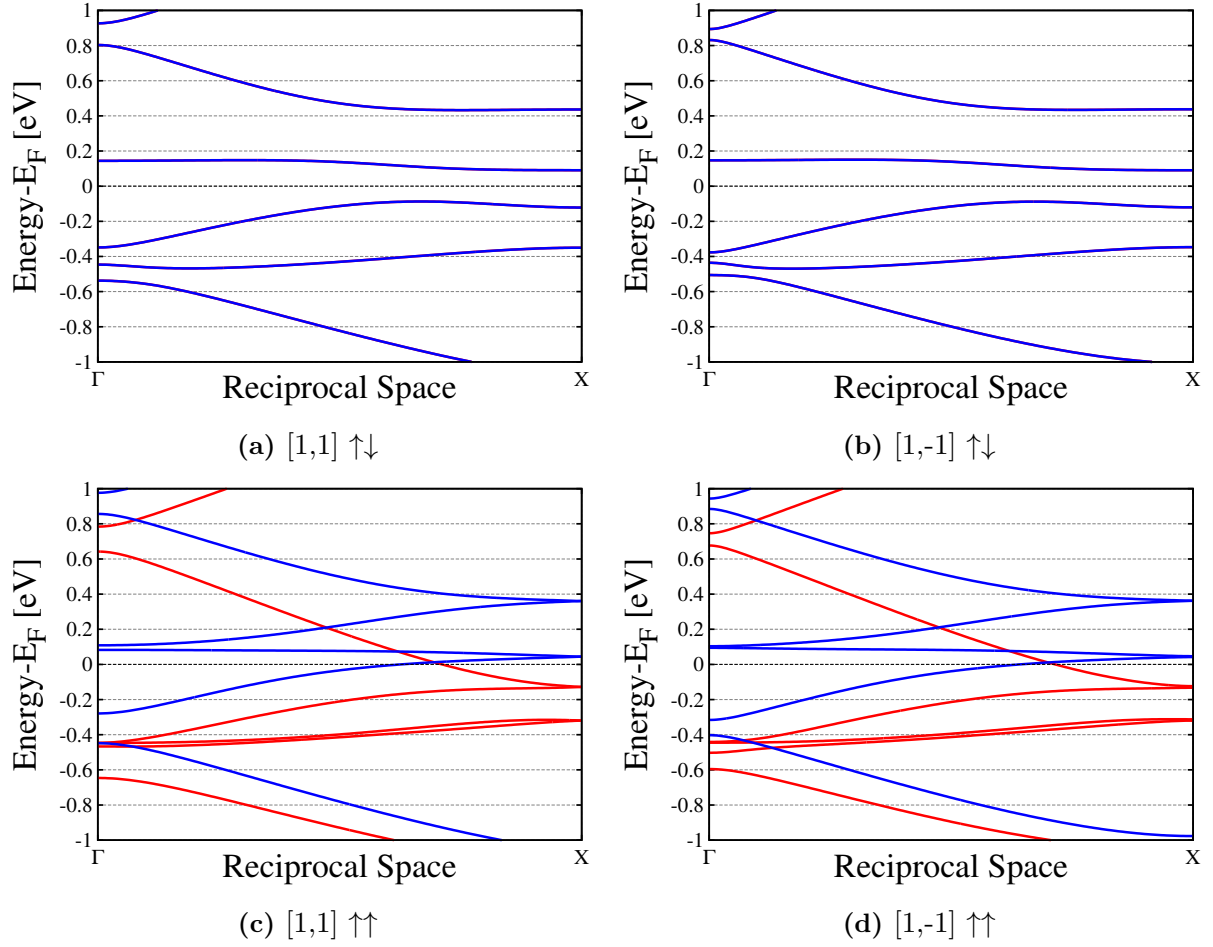


Figure 5.7: Electronic band structure of PEM 6-ZGNRs of size $N=1$ for the $[1, 1]$ and $[1, -1]$ structures in the $\uparrow\downarrow$ and $\uparrow\uparrow$ configurations. The red (blue) curve stands for the majority (minority) electrons.

For the $\uparrow\downarrow$ case, spin degeneracy is kept and a localized state appears around 90 – 150 meV above the Fermi energy. Omitting this state, the band gap of both structures is around 520 meV, respecting the band gap-width relationship of ZGNRs. In the $\uparrow\uparrow$ case, spin degeneracy is lifted and both spin channels exhibit metallic behaviour.

In the $\uparrow\downarrow$ configuration, a localized state around 90 – 150 meV appears for both structures. Omitting this state, the band gap of our systems is around 520 meV, which globally respects the band gap-width relationship of ZGNRs. Since this state lays above the Fermi energy, one could say that the ribbon is p-doped by phenyl edge defects. Both edges are topologically equivalent and structures are symmetrical so that spin degeneracy is preserved.

In the $\uparrow\uparrow$ configuration, spin degeneracy is lifted and both spin channels exhibit metallic behaviour. A net magnetic moment of $\sim 2.52 \mu_B$ appears for both structures¹ while a pristine 6-ZGNR of this length would hold a magnetic moment of $2.6 \mu_B$. This decrease of magnetic moment has to be imputed in the spin population depletion caused by the fluoranthene-like edges

¹The difference between the two structures is minuscule ($\sim 8 \cdot 10^{-3} \mu_B$) and is suspected to be due to the vanishing interaction between the two opposite edges.

(see Fig. 5.9).

The electronic band structures showed that a localized state around 0.1 eV appeared in the $\uparrow\downarrow$ configuration. To understand the nature of this state, we computed the wavefunction. A iso-surface plot is presented at Fig. 5.8.

We see that edge functionalization has created a localized state along the edges with a tendency of localization around the phenyl groups. The fact that phenyl groups are quite close to each other (only 4 cusps between neighbouring phenyl groups) allows for delocalization along the edges. We expect stronger localization around the defect for isolated phenyl. This will be addressed in the next chapter.

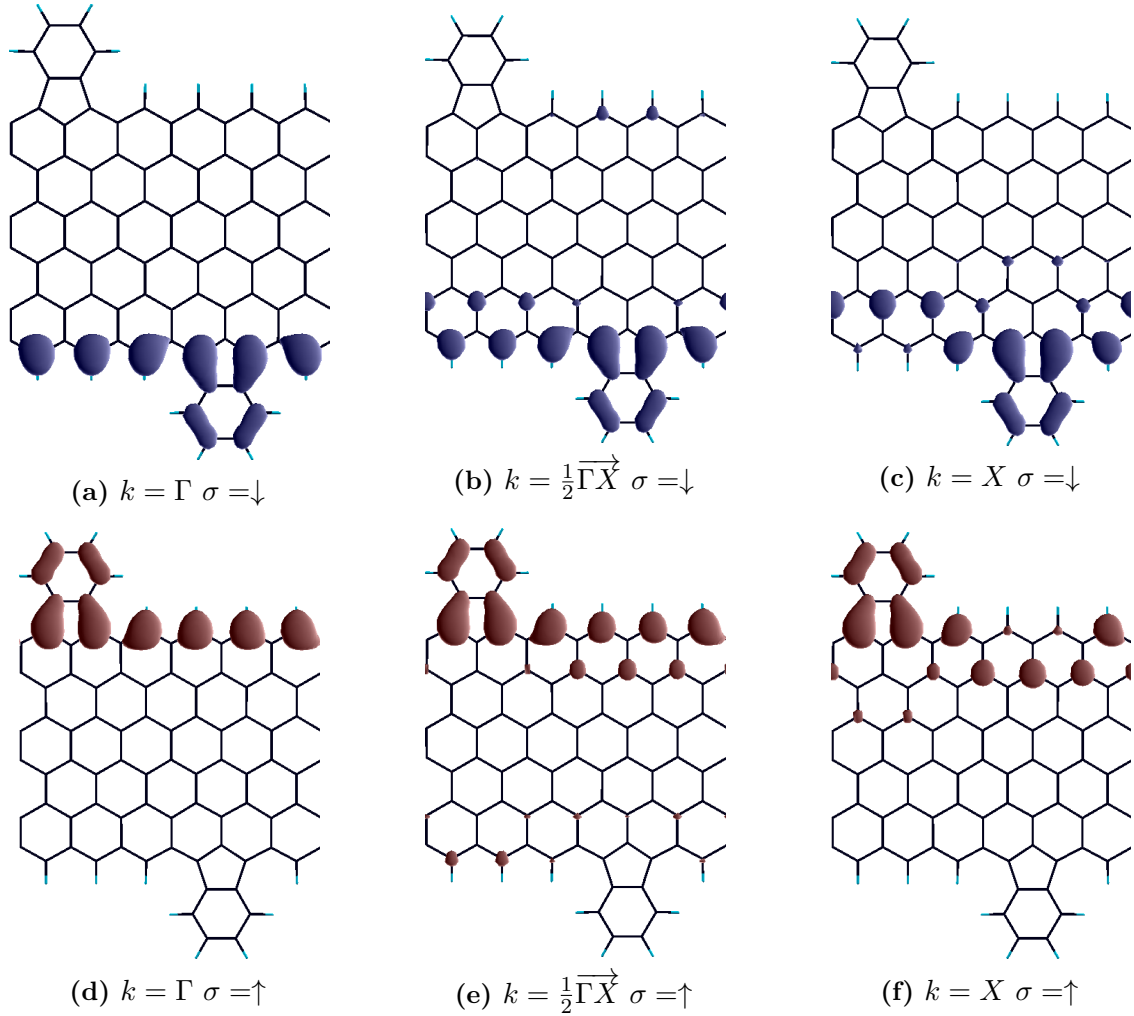


Figure 5.8: Wavefunctions for the PEM 6-ZGNR [1,1] structure ($\uparrow\downarrow$) for the localized state around 0.1 eV (see Fig. 5.7 a and b). The wavefunction has been computed for three different k-points: at Γ , at X and halfway between Γ and X ($\frac{1}{2}\overline{\Gamma X}$). The red (blue) iso-surface represents the spin $\uparrow$ ($\downarrow$) electrons.

As shown by Fig. 5.9, the spin density is found to be diminished around the phenyl groups. Globally, the polarization still occurs along the edge but a small fraction of magnetic moments is now localized around the phenyl rings. We note that the carbon atoms of a phenyl ring are all polarized in the same direction as the edge on which lays the defect.

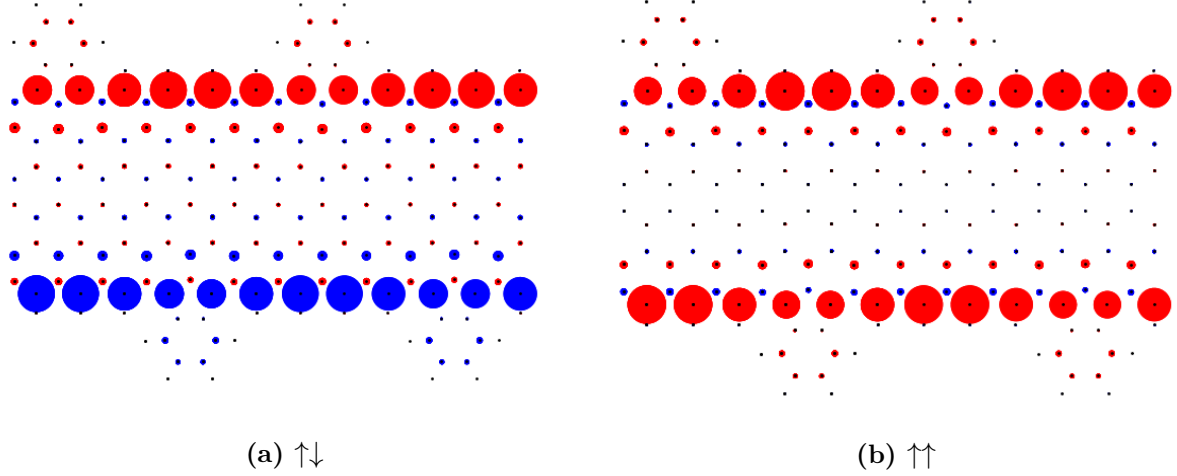


Figure 5.9: Spatial distribution of the spin population for the [1,1] structure in (a) the $\uparrow\downarrow$ configuration (b) the $\uparrow\uparrow$ configuration. The spin population difference is presented. If the circle is red (blue), then $\uparrow$ ($\downarrow$) spins are majority. The larger the circle, the bigger the population. Near phenyl groups, the spin polarization is reduced.

By comparing Fig. 5.8 and Fig. 5.9, we notice a surprising feature about those localized states. Indeed, the acceptor state for spin $\uparrow$ ($\downarrow$) electrons lays on the edge which is polarized by spin $\downarrow$ ($\uparrow$) electrons.

The density of states (DOS) has been computed. As shown in Fig. 5.10, we notice the appearance of a sharp peak around 90 meV and one around 150 meV ($\uparrow\downarrow$ configuration). Those peaks are the signature of the localized state induced by the phenyl groups, respectively for $k = X$ and $k = \Gamma$.

In the $\uparrow\uparrow$ case, the DOS for the minority electrons (blue curve) exhibits a peak around 90 meV whose intensity is comparable to the peak around 90 meV of the $\uparrow\downarrow$ configuration. As both edges are spin $\uparrow$ polarized and since the accepting states are anti-parallel to the polarization of the edge on which they lay, we believe this state to be due to the electron accepting character of the phenyl groups. This would explain why no peak is observed at this energy for the spin $\uparrow$ electrons.

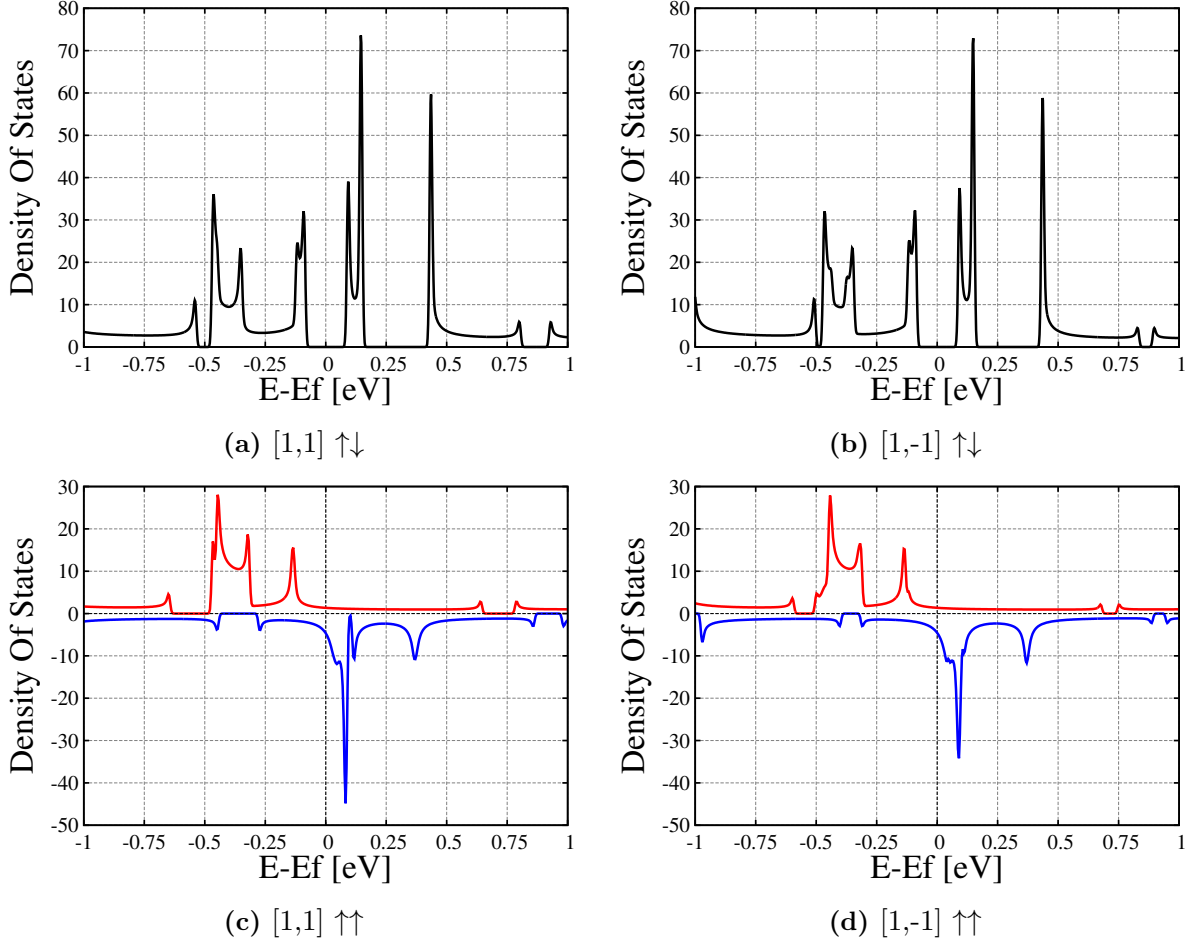


Figure 5.10: Density of states of PEM 6-ZGNRs of size $N=1$ for the $[1, 1]$ and $[1, -1]$ structures in the $\uparrow\downarrow$ and $\uparrow\uparrow$ configurations. For the $\uparrow\downarrow$ case, as spin degeneracy is lifted, the total density of states is plotted. For the $\uparrow\uparrow$ configuration, the red (blue) curve stands for the majority (minority) electrons.

Since the spin degeneracy is lifted in the $\uparrow\uparrow$ configuration, we can quantify the spin polarization at a particular energy. For this, we define the spin polarization $\mathcal{P}(E)$ as

$$\mathcal{P}(E) = \frac{N_{\uparrow}(E) - N_{\downarrow}(E)}{N_{\uparrow}(E) + N_{\downarrow}(E)} \quad (5.1)$$

where $N_{\uparrow}(E)$ ($N_{\downarrow}(E)$) is the number of states available between the energy E and $E + dE$ for a spin $\uparrow$ ($\downarrow$) electron. If $\mathcal{P}(E)$ is equal to 100% (−100%), then only states for spin $\uparrow$ ($\downarrow$) electrons are available in the energy window $[E; E + dE]$. In this case, the system is said to be fully polarized. The polarization for the $[1,1]$ and $[1,-1]$ structures is displayed at Fig. 5.11.

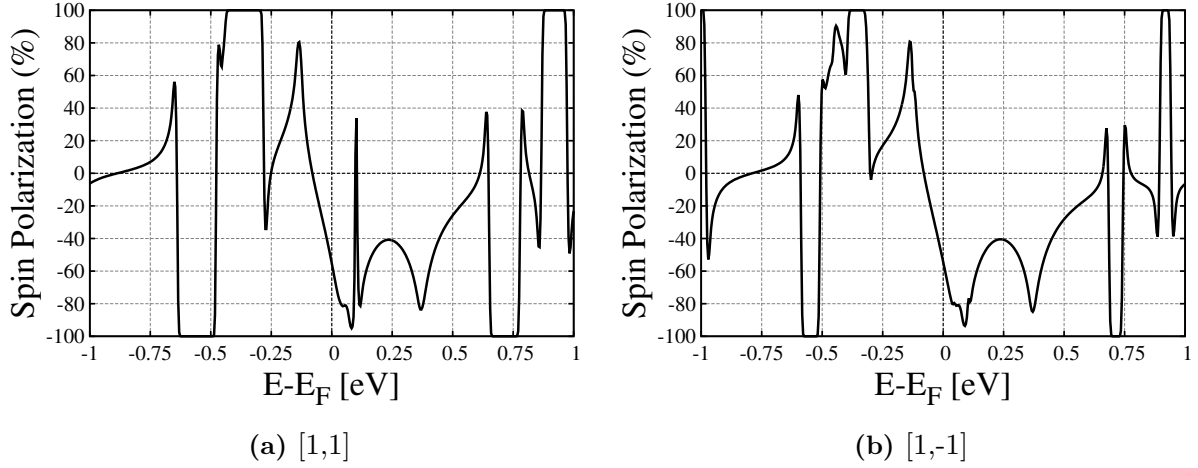


Figure 5.11: Spin polarization $\mathcal{P}(E)$ as defined in Eq.5.1 for the phenyl edge-modified $[1, 1]$ and $[1, 1]$ 6-ZGNRs in the $\uparrow\uparrow$ configuration. Both structures exhibit the same global behaviour but some differences are to be noticed. More on this in the text.

As shown in Fig. 5.11, there exists some ranges of energies for which a fully polarized system occurs. This happens around an energy $E = -0.5$ eV and $E = 0.75$ eV. Such behaviour suggests that those structures might exhibit spin filtering characteristics. The spin polarization around $E = -0.5$ eV is especially interesting as the system switches quite abruptly from fully $\uparrow$ -polarized to fully $\downarrow$ -polarized. Note that this transition is cleaner for the $[1, 1]$ structures than for the $[1, -1]$ structures

5.4.1 Spin Resolved Transmission Spectra

We computed the spin resolved transmission spectra for the $[1, 1]$ and $[1, -1]$ structures in both edge configurations. The results are displayed at Fig. 5.12.

The most interesting feature appears in the $\uparrow\uparrow$ configuration where, around $E = -0.5$ eV, both spin channels undergo extinction while the other stay conducting. The extinction for the $\uparrow$ channel occurs below $E = -0.5$ eV while the one for the $\downarrow$ channel occurs right above $E = 0.5$ eV. Such feature can be used to generate fully polarized currents.

For the $\uparrow\downarrow$ edge configuration, we discussed earlier the effect of the phenyl groups on the band gap, the later being slightly reduced. The edge defects also affect all electronic states by shifting them of roughly 0.2 eV towards higher energies. This is attributed to the modification of the electronic chemical potential.

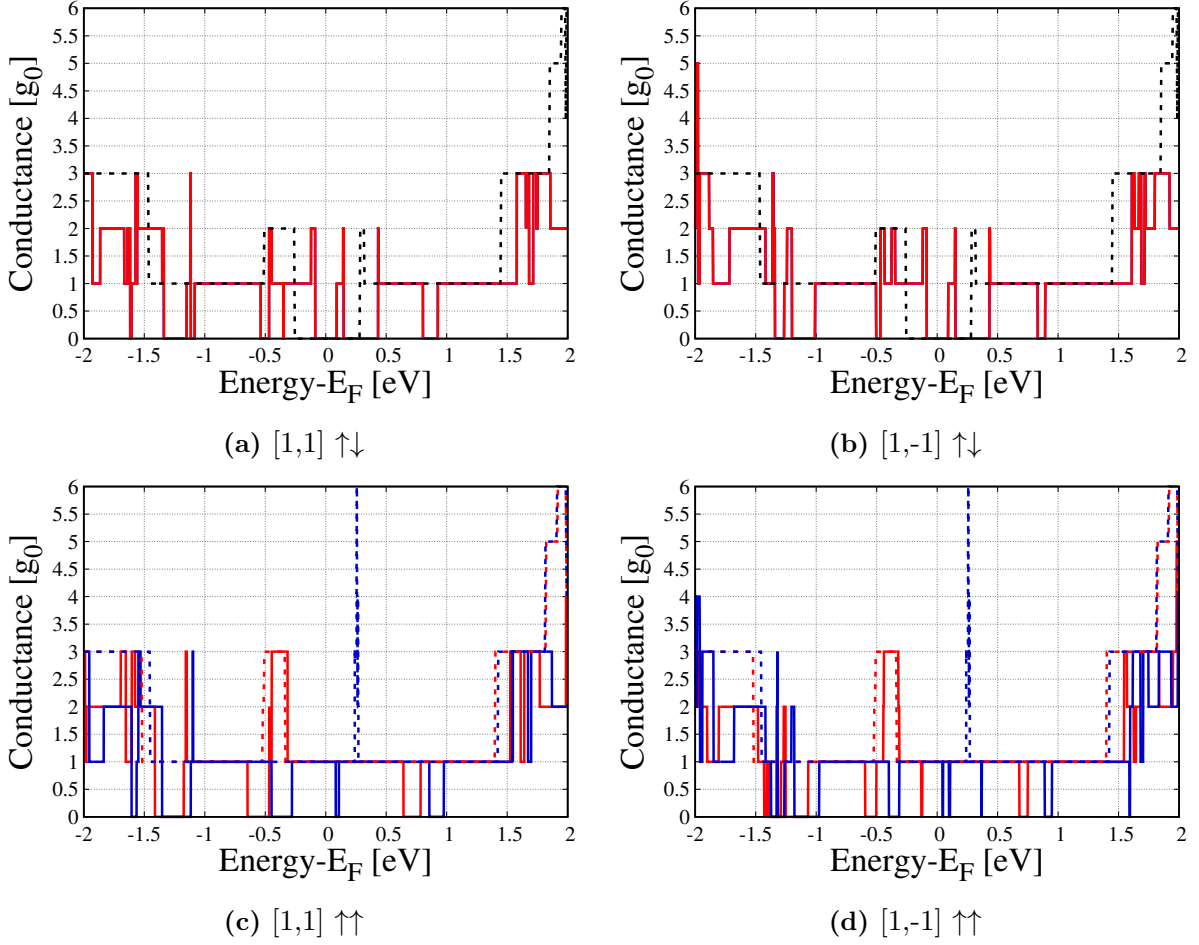


Figure 5.12: Spin resolved transmission spectra of PEM 6-ZGNRs of size $N=1$ for the $[1, 1]$ and $[1, -1]$ structures in the $\uparrow\downarrow$ and $\uparrow\uparrow$ configurations. The red (blue) curve stands for the spin $\uparrow$ ($\downarrow$) channel. Dotted lines indicate the transmission of pristine 6-ZGNR. For the $\uparrow\downarrow$ configuration, the transmission is spin degenerated so that only one spin channel is plotted.

5.5 Phenyl Edge-Modified 6-ZGNRs of size $N=2$

We will now double the size of our unit cell, considering a size $N = 2$. In this case, 16 structures are going to emerge from the randomness of ring closures. As exposed in the previous section, we first perform a symmetry analysis to bring down the number of structures to be studied (see Tab. 5.2).

Taking the set of structures which cannot be obtained by symmetries operations of others, we end up with 6 different structures : $[1, 1, 1, 1]$, $[1, 1, 1, -1]$, $[1, 1, -1, -1]$, $[1, -1, 1, 1]$, $[1, -1, 1, -1]$ and $[1, -1, -1, 1]$. Actually, this number can be brought further down since the structures $[1, 1, 1, 1]$ and $[1, 1, -1, -1]$ are just supercells of the structures of size $N=1$ studied in the previous section. The number of different structures reduces thus to 4 which are presented at Fig. 5.13.

Table 5.2: Summary of the symmetry analysis of PEM 6-ZGNRs structures where N=2. The first column lists the structures, the second structures which are equivalent under the two-fold rotation with respect the normal axis, the third structures which are equivalent under two-fold rotation with respect to the transversal axis and the third column the cyclic permutation of order 1.

Structure	$\hat{R}_n$	$\hat{R}_t$	$\hat{C}_1$
[1, 1, 1, 1]	[-1, -1, -1, -1]	[-1, -1, -1, -1]	[1, 1, 1, 1]
[1, 1, 1, -1]	[1, -1, -1, -1]	[-1, -1, 1, -1]	[1, 1, -1, 1]
[1, 1, -1, 1]	[-1, 1, -1, -1]	[-1, -1, -1, 1]	[1, 1, 1, -1]
[1, 1, -1, -1]	[1, 1, -1, -1]	[-1, -1, 1, 1]	[1, 1, -1, -1]
[1, -1, 1, 1]	[-1, -1, 1, -1]	[1, -1, -1, -1]	[-1, 1, 1, 1]
[1, -1, 1, -1]	[1, -1, 1, -1]	[1, -1, 1, -1]	[-1, 1, -1, 1]
[1, -1, -1, 1]	[-1, 1, 1, -1]	[1, -1, -1, 1]	[-1, 1, 1, -1]
[1, -1, -1, -1]	[1, 1, 1, -1]	[-1, 1, 1, 1]	[-1, 1, -1, -1]
[-1, 1, 1, 1]	[-1, -1, -1, 1]	[-1, 1, -1, -1]	[1, -1, 1, 1]
[-1, 1, 1, -1]	[1, -1, -1, 1]	[-1, 1, 1, -1]	[1, -1, -1, 1]
[-1, 1, -1, 1]	[-1, 1, -1, 1]	[-1, 1, -1, 1]	[1, -1, 1, -1]
[-1, 1, -1, -1]	[1, 1, -1, 1]	[-1, 1, 1, 1]	[1, -1, -1, -1]
[-1, -1, 1, 1]	[-1, -1, 1, 1]	[1, 1, -1, -1]	[-1, -1, 1, 1]
[-1, -1, 1, -1]	[1, -1, 1, 1]	[1, 1, 1, -1]	[-1, -1, -1, 1]
[-1, -1, -1, 1]	[-1, 1, 1, 1]	[1, 1, -1, 1]	[-1, -1, 1, -1]
[-1, -1, -1, -1]	[1, 1, 1, 1]	[1, 1, 1, 1]	[-1, -1, -1, -1]

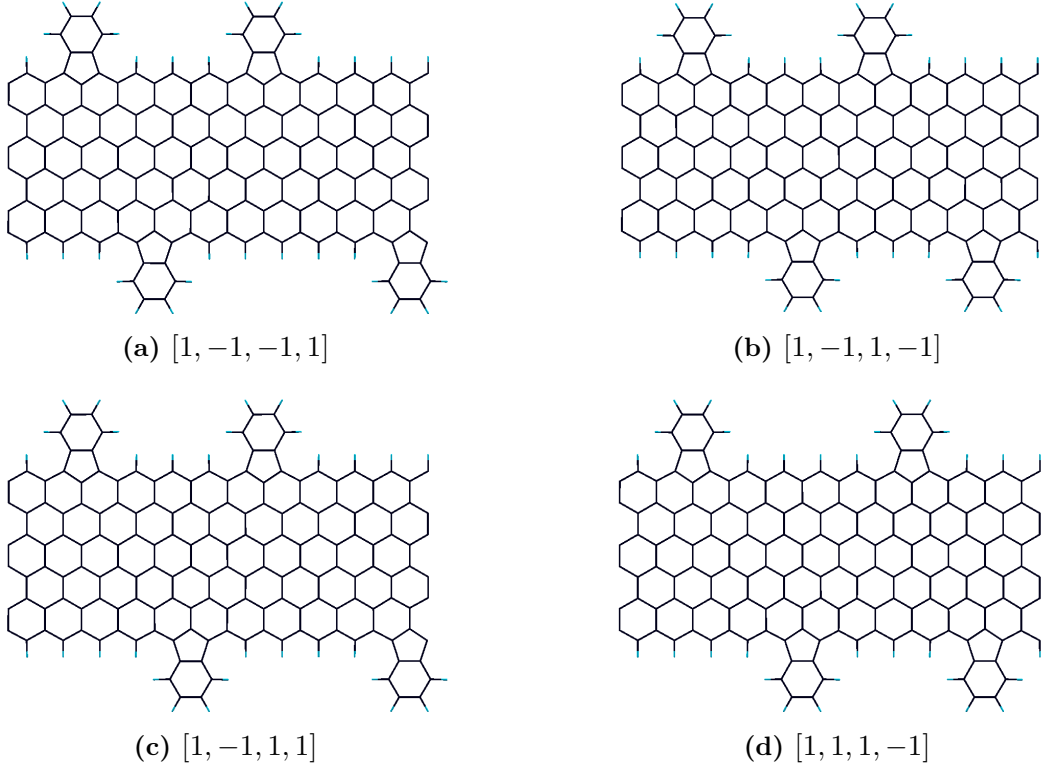


Figure 5.13: Unit cell of the PEM 6-ZGNR of size $N=2$ after ring closure. Even if size 2 PEM structures yields 16 configurations, only 6 of them are non-equivalent. Two out of those 6 were already studied in the previous section. The remaining structures are thus (a) $[1, -1, -1, 1]$, (b) $[1, -1, 1, -1]$, (c) $[1, -1, 1, 1]$ and (d) $[1, 1, 1, -1]$.

Within that set, $[1, -1, 1, -1]$ is invariant with respect to $\hat{R}_n$ and $\hat{R}_t$ and $[1, -1, -1, 1]$ is invariant with respect to $\hat{R}_t$. The edge topology for those two structures is essentially the same where phenyl groups are separated alternatively by 3 and 5 cusps. The two other structures (i.e. $[1, 1, 1, -1]$ and $[1, -1, 1, 1]$) do not exhibit any particular symmetry and their edge topology is different (one edge is composed by phenyl groups separated by 4 cusps and the other by phenyl groups separated alternatively by 3 and 5 cusps).

This geometrical consideration allows for the classification of the structures in two groups. The first group contains the $[1, -1, -1, 1]$ and the $[1, -1, 1, -1]$ structures while the second is composed by the $[1, -1, 1, 1]$ and $[1, 1, 1, -1]$ PEM 6-ZGNRs. Groups are defined by the topology of their edges:

- First group: both edges have the same edge topology where phenyl groups are alternatively separated by 3 and 5 cusps.
- Second group: one of the edge consists of phenyl groups alternatively separated by 3 and 5 cusps while the other edge is composed by groups separated by 4 cusps.

As seen in the electronic band structure for the $\uparrow\downarrow$ ordering (Fig. 5.14), the first group features spin degenerated states while spin degeneracy is lifted for the second one. Spin degeneracy lifting is due to the difference in topologies for the two edges and the symmetry breaking it implies. In this case, both structures possess a net magnetic moment of a thousands of μ_B .

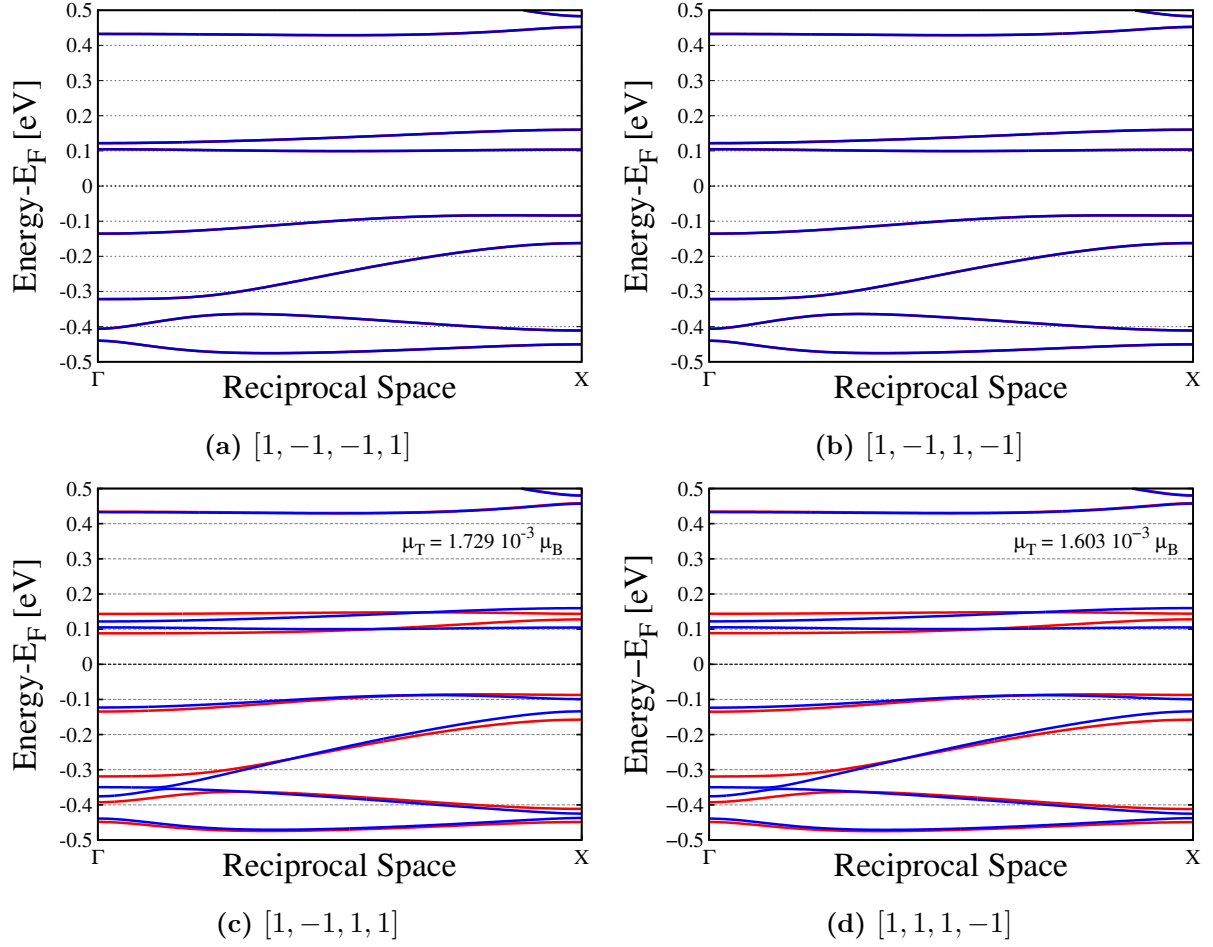


Figure 5.14: Electronic band structure of the PEM 6-ZGNRs of size $N=2$ in the $\uparrow\downarrow$ configuration for the (a) $[1, -1, -1, 1]$, (b) $[1, -1, 1, -1]$, (c) $[1, -1, 1, 1]$ and (d) $[1, 1, 1, -1]$ structures. For (a) and (b), the spin degeneracy is kept. For (c) and (d), the spin degeneracy is lifted. The red (blue) curve stands for spin majority (minority) electrons. For (c) and (d), a net magnetization per unit cell μ_T on the order of a thousandth of Bohr magneton appears.

In all structures, two localized states per spin appear around 0.1 eV. For the first group, those two states are located inside the band gap of 512 meV. The first localized state is practically not spread in energy while the second state has an energy of 122 meV at $k = \Gamma$ and 160 meV at $k = X$.

In the second group, the spin degeneracy is left and a net magnetization of a thousands of μ_B appears. The majority spin is the one associated with the polarization of the edge containing the phenyl groups alternatively separated by 3 and 5 cusps. This can be explained by the effect of the floranthene-like edges on the spin polarization of the edges.

Indeed, we saw in the previous section that phenyl groups have a tendency to suppress the spin polarization near them. In Fig. 5.15, we notice that the evolution of local magnetic moments on the edge is slightly quicker in between groups separated by 5 cusps than those separated by 3 cusps. In other words, taking 4 cusps pairs phenyl groups as reference, the loss implied by putting them closer (3 cusps) is less than the gain of putting them away (5 cusps). The excess gain in magnetization is what we measured to be on the order of a thousands of μ_B .

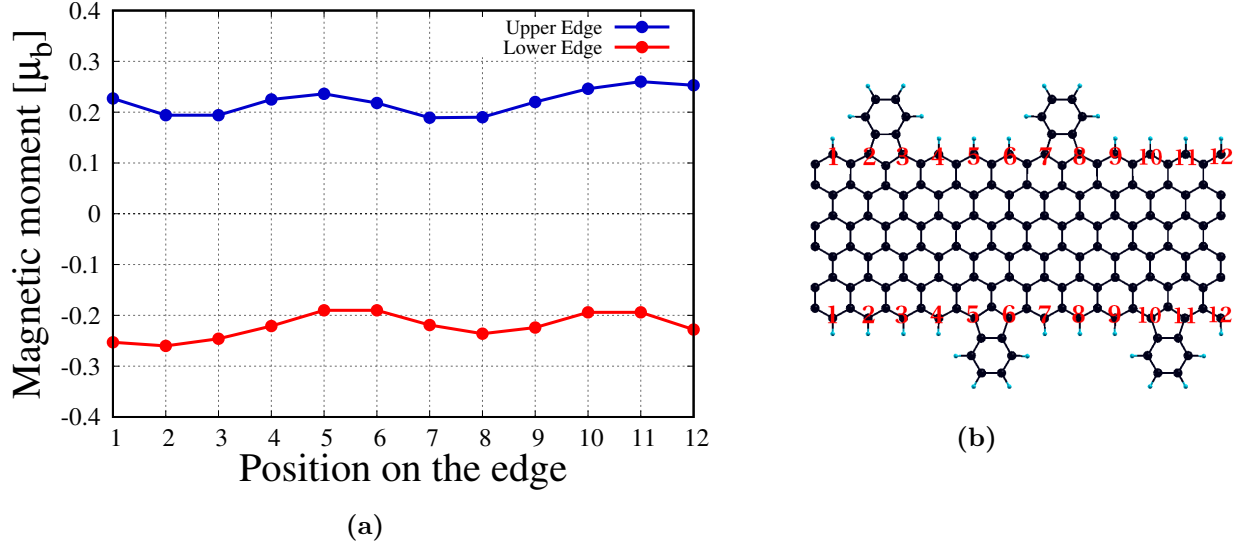


Figure 5.15: Local magnetic along the edges for the $[1, -1, 1, -1]$ structure in the $\uparrow\downarrow$ configuration (a). The numbering associated to (a) is displayed in (b).

In the $\uparrow\uparrow$ configuration, the band structure of the 4 structures are really similar and are presented in the supplementary figures of this chapter along with the DOS for both $\uparrow\downarrow$ and $\uparrow\uparrow$ configurations (see Appendix C).

As shown in Fig. 5.16, the spin polarization for the $\uparrow\uparrow$ configuration displays interesting features where fully polarized ribbon would occur for given energies. Fig. 5.16 allows for the neat distinction between the aforementioned groups separating the symmetric structures from the asymmetric ones.

The spin polarization of PEM 6-ZGNRs of size $N=2$ is similar to the one of size $N=1$. Especially, the extinction of both spin channels below and above 0.5 eV displays similar features. However, in this case, we notice an extinction of the minority channel for negative energies close to the Fermi Energy. This feature is particularly interesting because it suggests that for small bias and gate voltage, fully polarized current could occur.

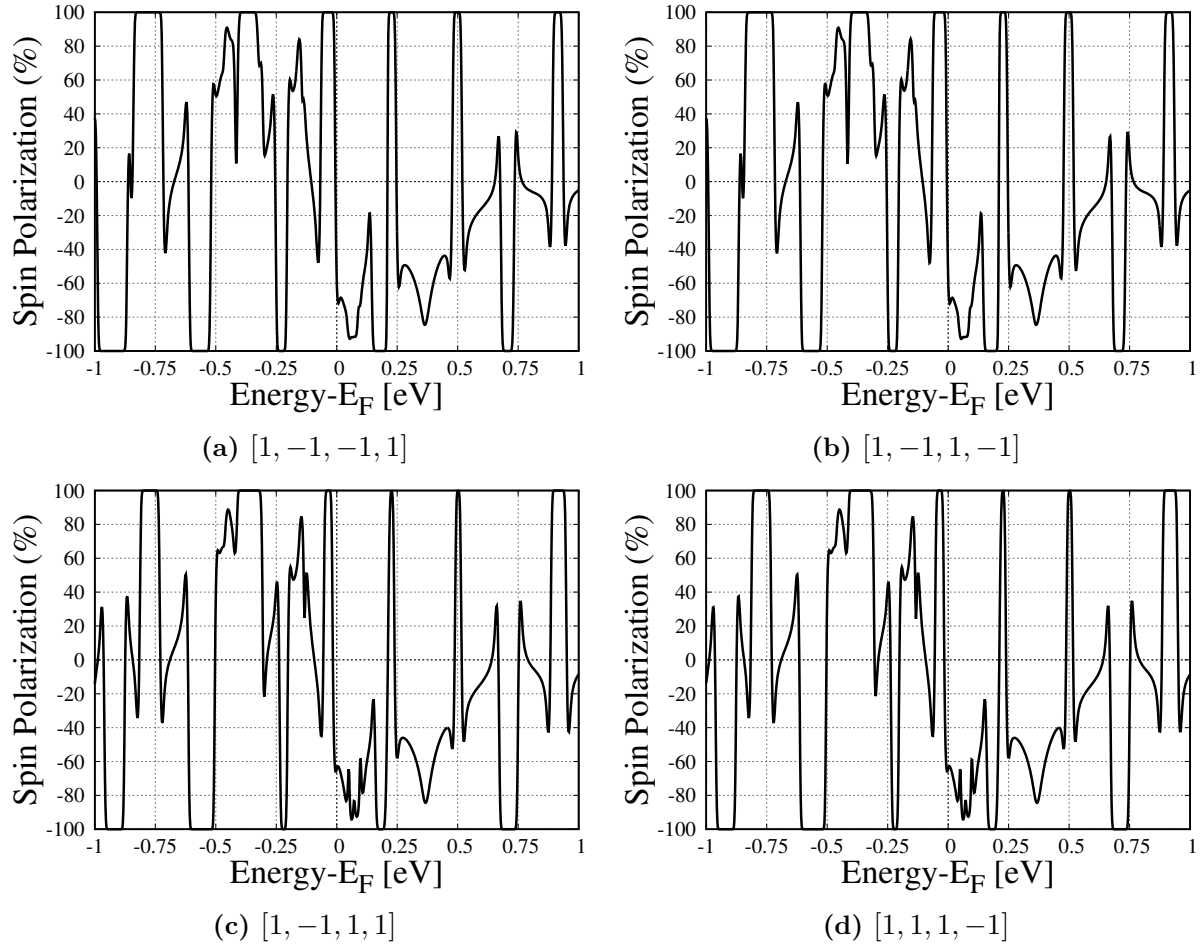


Figure 5.16: Spin polarization $\mathcal{P}(E)$ as defined in Eq.5.1 for the phenyl edge-modified $[1, -1, -1, 1]$, $[1, -1, 1, -1]$, $[1, -1, 1, 1]$ and $[1, 1, 1, -1]$ 6-ZGNRs in the $\uparrow\uparrow$ configuration.

To conclude our discussion on PEM 6-ZGNRs of size $N=2$, we considered a theoretical structure whose edges topology would be defined by phenyl separated by 2 and 6 cusps and phenyl separated by 4 cusps. Such structure will be referred as the 44-62 PEM and is displayed at Fig. 5.17.

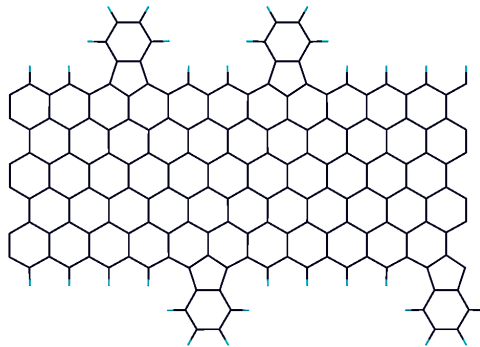


Figure 5.17: Theoretical 44-62 PEM structure. One edge is characterized by phenyl groups separated by alternatively 2 and 6 cusps while the other consists on phenyl groups separated by 4 cusps. This structure has not been yet produced.

The band structure for both spin configurations is presented at Fig. 5.18.

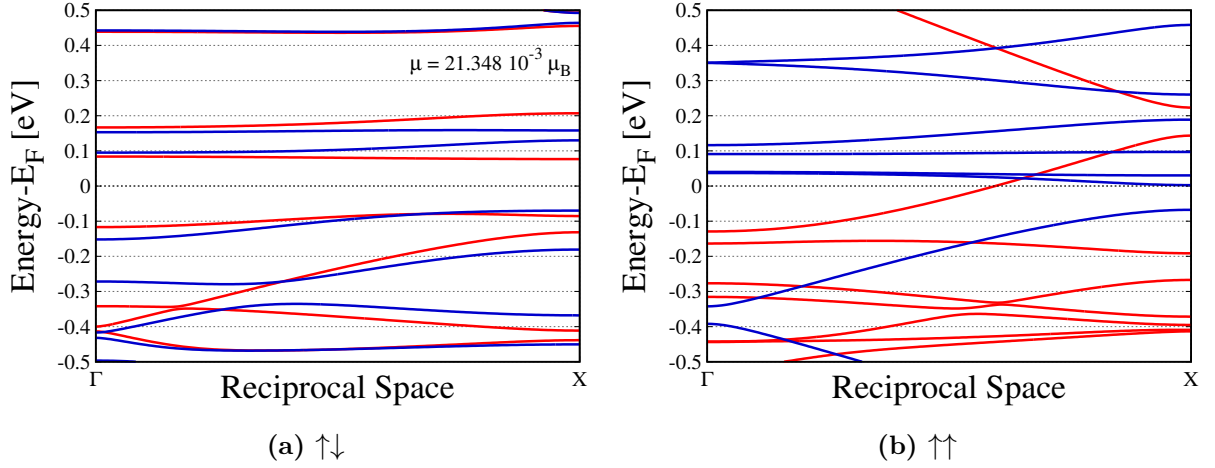


Figure 5.18: Electronic band structure of the of the theoretical 44-62 PEM structure in (a) the $\uparrow\downarrow$ and (b) the $\uparrow\uparrow$ configuration.

By shifting one phenyl groups, we get a substantially larger net magnetic moment in the $\uparrow\downarrow$ configuration ($21.348 \cdot 10^{-3} \mu_B$) leading to a band splitting way more noticeable than for the $[1, -1, 1, 1]$ and $[1, 1, 1, -1]$ structures.

Reversely to what has been found before, the majority spin is given by the polarization of the edge consisting of phenyl groups separated by 4 cusps. This means that bringing phenyl groups that close from each other diminishes spin polarization more than the gain obtained by bringing some phenyl groups apart.

5.6 Fluoranthene-like edges and asymmetry

In the previous sections, we essentially analysed structures which, based on the recent works of Ruffieux et al. [32], are experimentally feasible. Here, we consider a high asymmetry between the edges as one of the them will be clogged up with phenyl groups while the other will be left ideal. We will refer to this structure as the *one edge phenyl-edge modified 6-ZGNR* (OEP6M 6-ZGNR). The structure is displayed at Fig. 5.19.

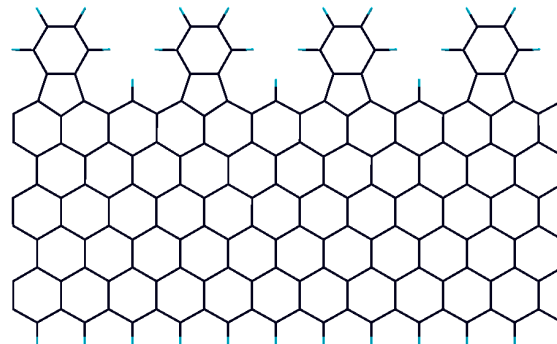


Figure 5.19: Geometrical structure of the *one edge phenyl-edge modified 6-ZGNR* (OEP6M 6-ZGNR). One of the edge is functionalized by phenyl groups while the other is kept pristine. Here, 4 unit cells are displayed.

Starting with the $\uparrow\downarrow$ configuration, we computed the spin densities using a Mulliken population analysis. As shown by Fig. 5.20, the majority electrons (red circles) lay on the lower edge and are practically unaffected by the phenyl groups while minority electrons (blue circles), located on the upper edge, see their density diminished. This imbalance leads to a net magnetization of $47.264 \cdot 10^{-3} \mu_B$.

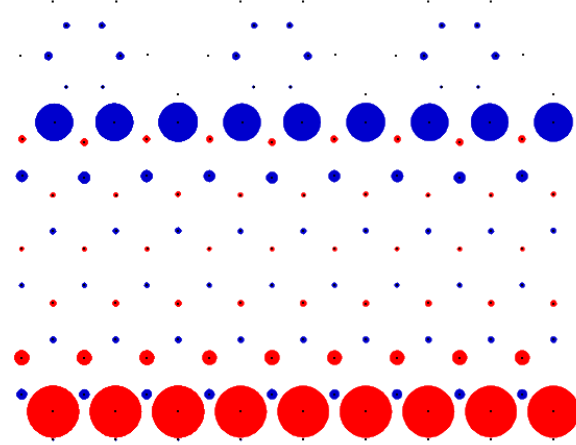


Figure 5.20: Spin density for OEPEM 6-ZGNR in the $\uparrow\downarrow$ configuration using Mulliken population analysis. In red (blue) is given the majority (minority) spin density. The larger the circle, the higher the density. Around the phenyl groups, the density is diminished while the density of the perfect edge is non-affected.

As the edge topologies are dramatically different, it is not surprising that the spin degeneracy is lifted, as shown in the electronic band structure of OEPEM 6-ZGNRs (Fig. 5.21).

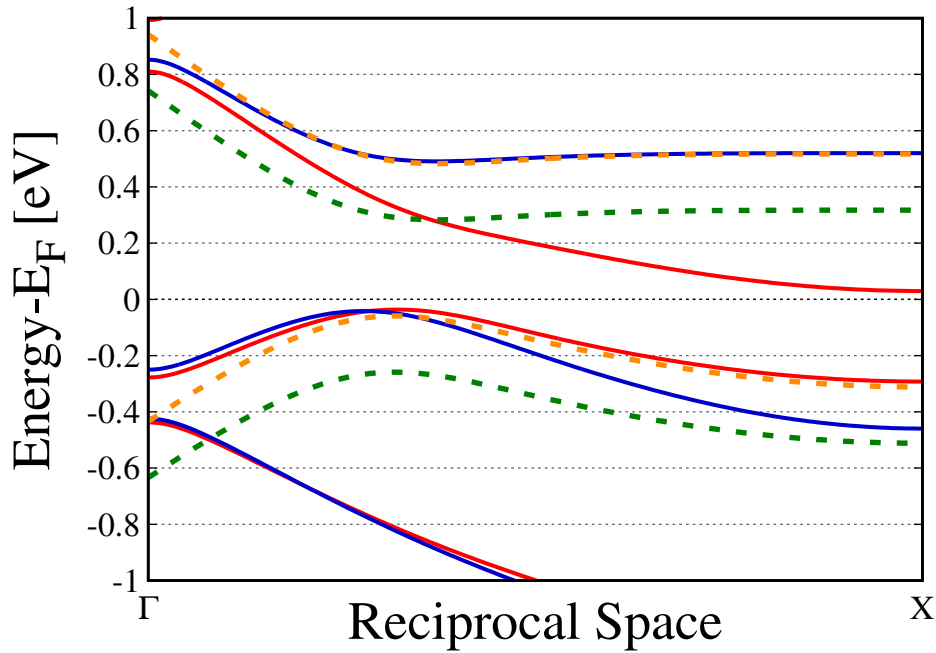


Figure 5.21: Electronic band structure of the OEPEM 6-ZGNR in the $\uparrow\downarrow$ configuration. Red (blue) curves stand for majority (minority) electrons. The green dotted line is the valence and conduction band of a pristine 6-ZGNR in the $\uparrow\downarrow$ configuration. The orange dotted line is the former shifted of 0.2 eV.

Both spin channels are still semiconducting but the band gaps are different: 66 meV for the majority electrons and 532 meV for the minority electrons. The similarity between the conduction band of pristine 6-ZGNR and the conduction band of the minority electrons and between the valence band of the majority electrons is outstanding. The resemblance is even pushed further when the valence and conduction band of pristine 6-ZGNRs is shifted by 0.2 eV. The shift is due to the change in electronic chemical potential induced by the defects.

We look at the wavefunction for the valence band and conduction band of such systems (see Fig. 5.22 and 5.23). As expected, the state which is most affected (conduction state for spin- $\uparrow$ electrons) shows a strong localization around the defected edge and more particularly around the phenyl groups.

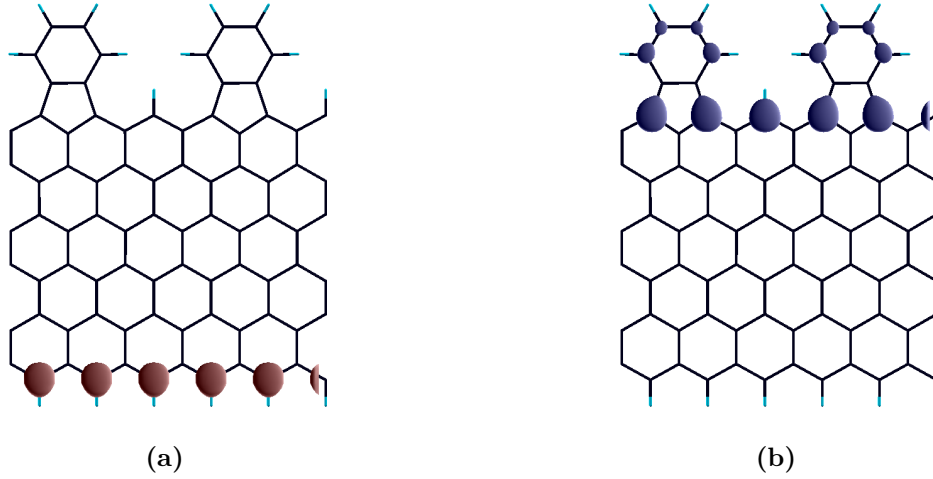


Figure 5.22: Wavefunction at $k = X$ for the valence band for (a) majority and (b) minority electrons.

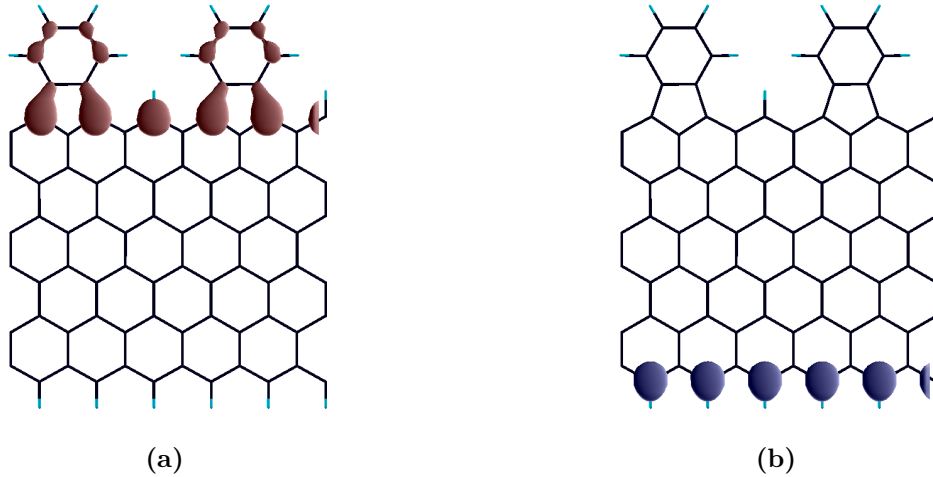


Figure 5.23: Wavefunction at $k = X$ for the conduction band for (a) majority and (b) minority electrons.

We investigated the effect of the edge functionalization on the majority electrons for a uniform distribution of phenyl groups along the edge. We focused our calculations on the bandwidth of the conduction band and on the band gap Δ (spin- $\uparrow$ electrons). The results of our computations are displayed at Fig. 5.24.

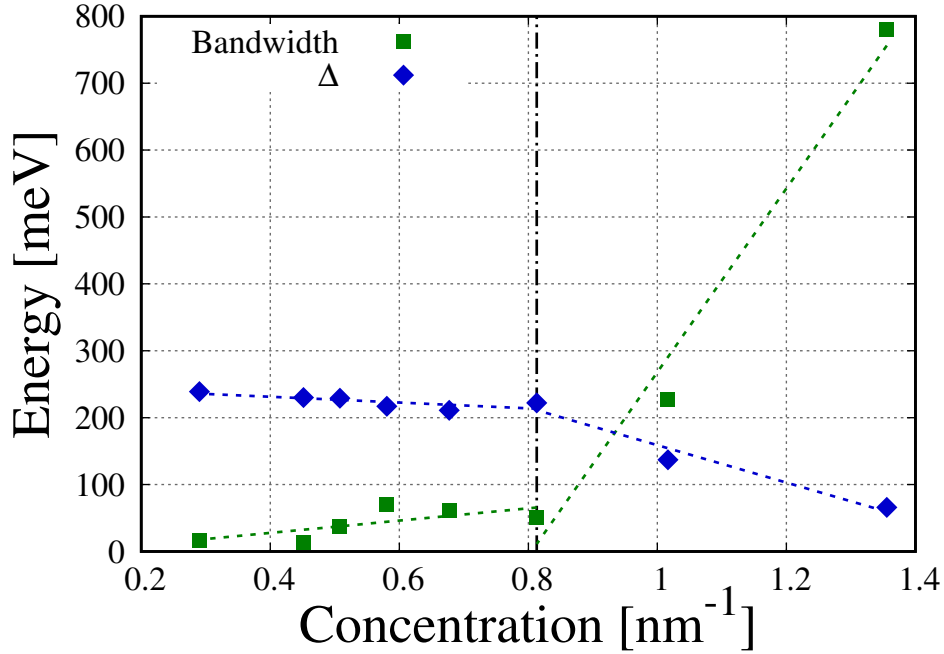


Figure 5.24: Influence of the phenyl groups concentration on the bandwidth of the conduction band and on the band gap Δ for spin- $\uparrow$ electrons. The concentration is given by phenyl group per unit length. Two regimes seem to appear with the concentration of 0.81 phenyl per nm separating them. The dotted line are only there to guide the eye.

As shown on Fig. 5.24, two distinguishable regimes seem to appear:

- For a concentration of phenyl groups lower than 0.81 per nm, the bandwidth approaches zero as the concentration decreases while Δ remains roughly independent on the concentration. This regime corresponds to a low concentration doping, where the phenyl groups are weakly interacting with each other. In this case, the ribbon can be considered as p-doped where Δ would represent the ionization energy of the impurities.
- For concentration of phenyl groups higher than 0.81 per nm, we observe the onset of a strong interaction between the phenyl groups, where a more dispersed band appears. When the concentration increases, the bandwidth increases and the gap Δ decreases linearly.

Of course, only uniform distribution was considered so that the existence of such regimes can not be asserted. For the high concentration regime, steric hindrance prevent the sampling of more concentrations as the limit is reached slightly below 1.4 nm^{-1} (1 cusp between the phenyl). Calculations for non-uniformly distributed defects would allow for finer description.

In the $\uparrow\uparrow$ configuration, the spin degeneracy is lifted and both spin channels exhibit a metallic behaviour (see Fig. 5.25).

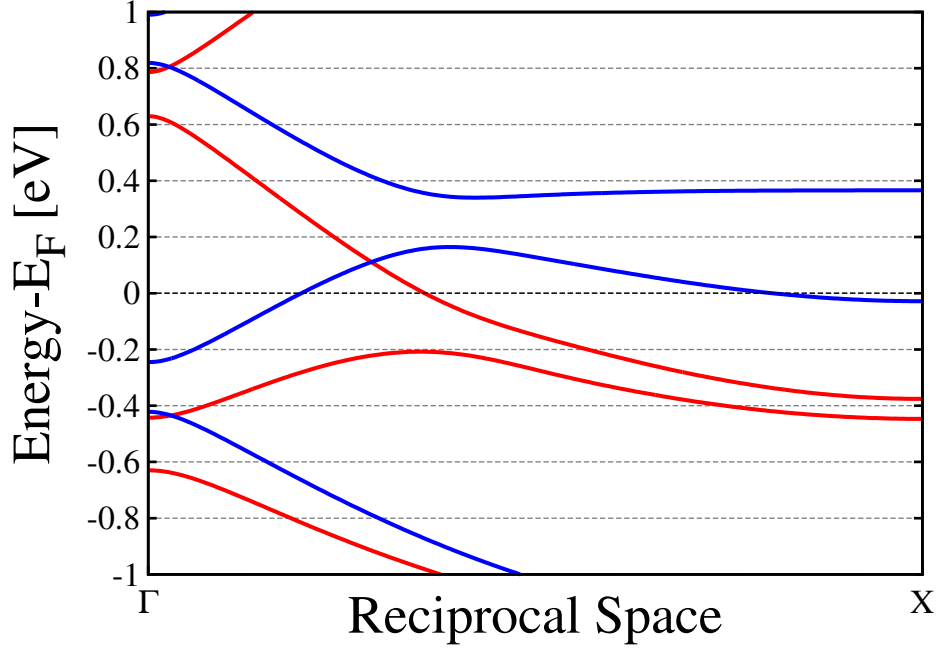


Figure 5.25: Electronic band structure of the OEPEM 6-ZGNR in the $\uparrow\uparrow$ configuration. Both spin channels exhibit a metallic behaviour. Red (blue) curves stand for majority (minority) electrons.

$\Delta E_{NP-\uparrow\downarrow}$ and $\Delta E_{\uparrow\uparrow-\uparrow\downarrow}$ are respectively given by 160 meV/nm and 8.3 meV/nm. They are thus smaller than in the case of pristine 6-ZGNR. The relative stability between the two different polarization is thus brought further down.

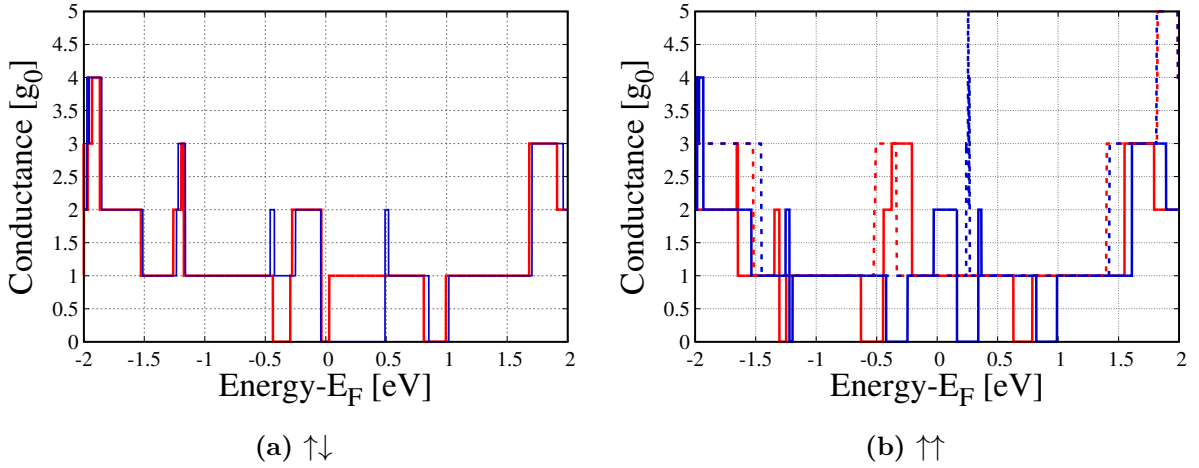


Figure 5.26: Spin-resolved transmission spectra for the OEPEM 6-ZGNRs structures in (a) $\uparrow\downarrow$ and (b) $\uparrow\uparrow$ configuration. Red (blue) curves stand for majority (minority) electrons.

The transmission for both configuration is displayed at Fig. 5.26. In the $\uparrow\downarrow$ configuration, we observe a notable spin filtering characteristic with only spin- $\uparrow$ electrons being conducting from $E = 0.03$ eV to $E = 0.49$ eV.

In the $\uparrow\uparrow$ configuration, we observe again this peculiar behaviour around $E = -0.5$ eV. This feature seems to be displayed by all the phenyl-edge modified structures. Technologically, such characteristic is particularly interesting as such devices would allow for the switch to fully $\uparrow$ /fully

↓ polarized currents for a small variation of the bias.

The density of states and spin polarization are respectively present at Fig. C.4 and Fig. C.5.

5.7 Pristine 6-ZGNR - Phenyl-edge Modified 6-ZGNR junction

We analysed the behaviour of a junction composed by pristine 6-ZGNR and PEM 6-ZGNR ([1,1]). The structure is displayed at Fig. 5.27 while the spin-resolved transmission spectra for both edge configurations are displayed at Fig. 5.28. For both spin configuration, the transmission contains the features of both part of the junction.

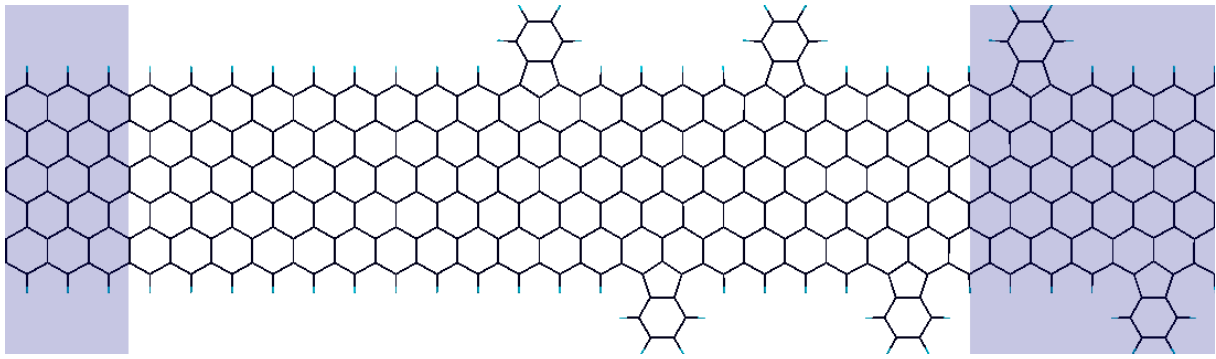


Figure 5.27: Schematic of a junction between a pristine 6-ZGNR and a phenyl-edge modified nanoribbon. This structure would be feasible, using both monomers.

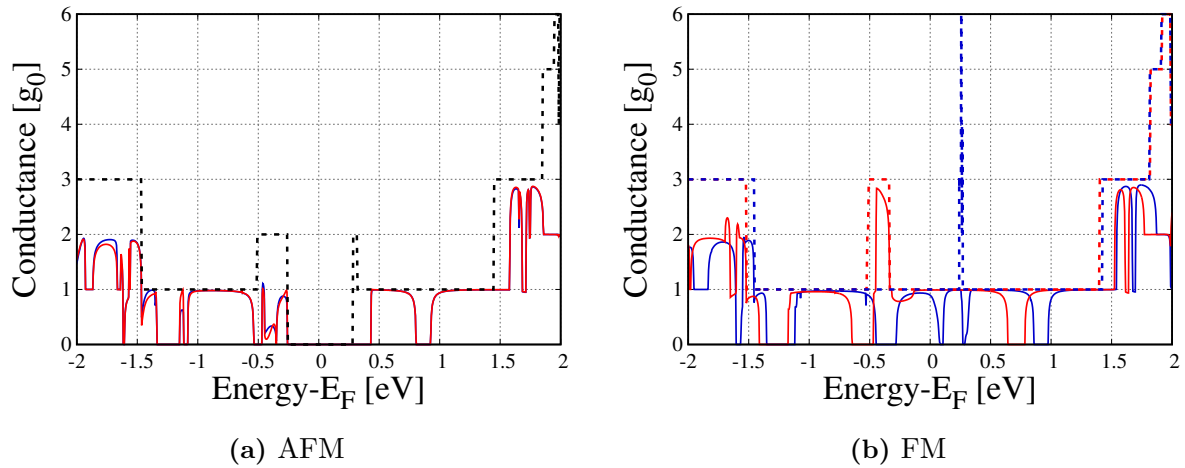


Figure 5.28: Spin polarization of the ZGNR presented at Fig.5.19 obtained (a) in the AFM calculation (b) in the FM calculation.

In the $\uparrow\downarrow$ configuration, the transmission is nearly spin degenerated which could be explained by the two edges of the device region displaying slightly different topologies. The structure is semiconducting with a band gap extending from $E = -0.26$ eV to $E = 0.43$ eV. The width of the band gap is thus of 0.69 eV. This enlargement of the band gap is due to the shift of the electronic chemical potential induced by the phenyl groups.

For the $\uparrow\uparrow$ case, the technologically interesting characteristic happening around $E = -0.5$ eV for phenyl-edge modified structures appears. From -0.64 eV to -0.47 eV, the spin- $\uparrow$ channel undergoes complete extinction while the spin- $\downarrow$ channel displays a finite conductance of g_0 . From

-0.44 eV to -0.28 eV, the opposite occurs and the conductance for spin- $\downarrow$ electrons goes to zero while the one for spin- $\uparrow$ electrons is between $2g_0$ and $3g_0$.

Such feature could lead to spin filtering device that could switch their polarization for a small variation of the bias voltage and gate voltage. Gating the system with a voltage of approximately 0.5 eV would allow for the Fermi level to be displaced. Then, by fine tuning the gate voltage to enforce the Fermi energy to locate in a zone where one of the spin channel exhibit extinction, a small bias voltage could drain a fully polarized current.

However, gating and biasing the system would affect the electronic states so that the transmission spectrum might be altered. However, 0.5 V being a reasonable voltage, there is a chance that the effect does not completely modify the transmission.

Another issue also need to be addressed. Indeed, the stability of the $\uparrow\downarrow$ is higher than the $\uparrow\uparrow$ and the difference stays small compared to the thermal energy at room temperature ($\Delta E_{\uparrow\uparrow-\uparrow\downarrow} = 30$ meV). Stabilization of the $\uparrow\uparrow$ should then be enforced, e.g. by choosing an adequate substrate. However, here again, interactions with the hypothetical substrate will obviously modify the transmission spectrum. Further investigations are thus needed.

5.8 Summary

In this chapter, we investigated the electronic properties of 6-ZGNRs whose edges are functionalized by phenyl groups. Such structures have been produced atomically precisely [32].

We saw that because of ring closure of the phenyl groups, such ribbons should be expected to exhibit randomness along their edges. However, only 3 different topologies between pairs of phenyl groups arise: a pair of phenyl groups separated by 3, 4 or 5 cusps.

Even if the number of possible structures is huge, we noticed that structures display similar features. In the $\uparrow\downarrow$ configuration, the two most noticeable is the shift of the electronic states towards higher energies and the appearance of a localized state around 0.1 eV above the Fermi energy. If this edge configuration yields spin degeneracy in symmetric structures, randomness in ring closure highly suggests that spin degeneracy is lifted in real structures (the probability for the structure to be symmetrical is quite small).

Another important feature displayed by all structures is the spin polarization around $E = -0.5$ eV in the $\uparrow\uparrow$ configuration. Below (above) this energy, only states for spin- $\downarrow$ (spin- $\uparrow$) electrons are available. This feature appears also in the 6-ZGNR/PEM 6-ZGNR ([1,1]) junction which suggests that such structures could lead to spin filtering devices.

6

Effect of Fluoranthene-like Edges on the Transport Properties of 6-ZGNRs

In this chapter, we will study the influence of the fluoranthene-like edges on the spin-dependant electronic transport properties of 6-ZGNRs. Transport properties are computed within the NEGF formalism as implemented in **TranSIESTA**. All structures are relaxed using a conjugate gradient algorithm until the forces fall below 0.01 eV/Å and the stresses below 0.001 GPa.

An example of systems we will be dealing with is displayed at Fig. 6.1. In blue are represented the electrodes in between whom lays the device region. The latter contains both the scatterer (phenyl groups) and some electrode layers to screen the defect. As edge states play an predominant role in ZGNRs, we expect a non-negligible effect of such edge functionalization on the spin-resolved transmission spectrum. The computational study will focus on both $\uparrow\downarrow$ and $\uparrow\uparrow$ edge configuration.

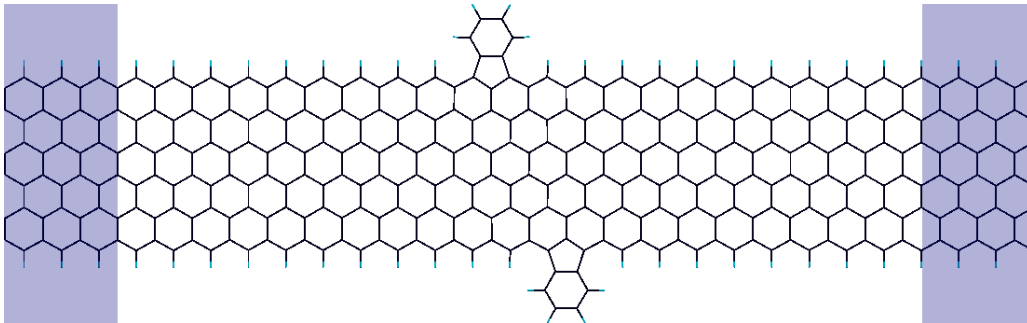


Figure 6.1: Structure as defined in the input file for a **TranSIESTA** run. In blue are represented the electrodes in between whom lays the device region which contains the defect (phenyl groups) and electrode screening layers.

The device region is first relaxed in a full 3D periodic fashion. Therefore, the influence of phenyl groups on the electronic states of 6-ZGNRs can be analysed. Since electrode layers are defined within the device region, phenyl-edge defects of neighbouring cells can be considered as non-interacting with each other.

We will consider two different topologies. The first one will consist on ribbons whose edges are both functionalized by one phenyl group. The effect of the relative displacement of one defect with respect to the other will be examined.

The second topology will introduce a high asymmetry in the structure as one edge will be kept free of impurities. For this group, we will first look at the effect of one phenyl group on the properties of the 6-ZGNRs. In a second step, we will consider two phenyl groups along the altered edge. The influence of the distance between those groups will be investigated.

6.1 Fluoranthene-like Edges on Opposite Edges

We start our discussion with the first group of structures which consists on ribbons whose edges are both functionalized by one phenyl group. The structures are displayed at Fig. 6.2.

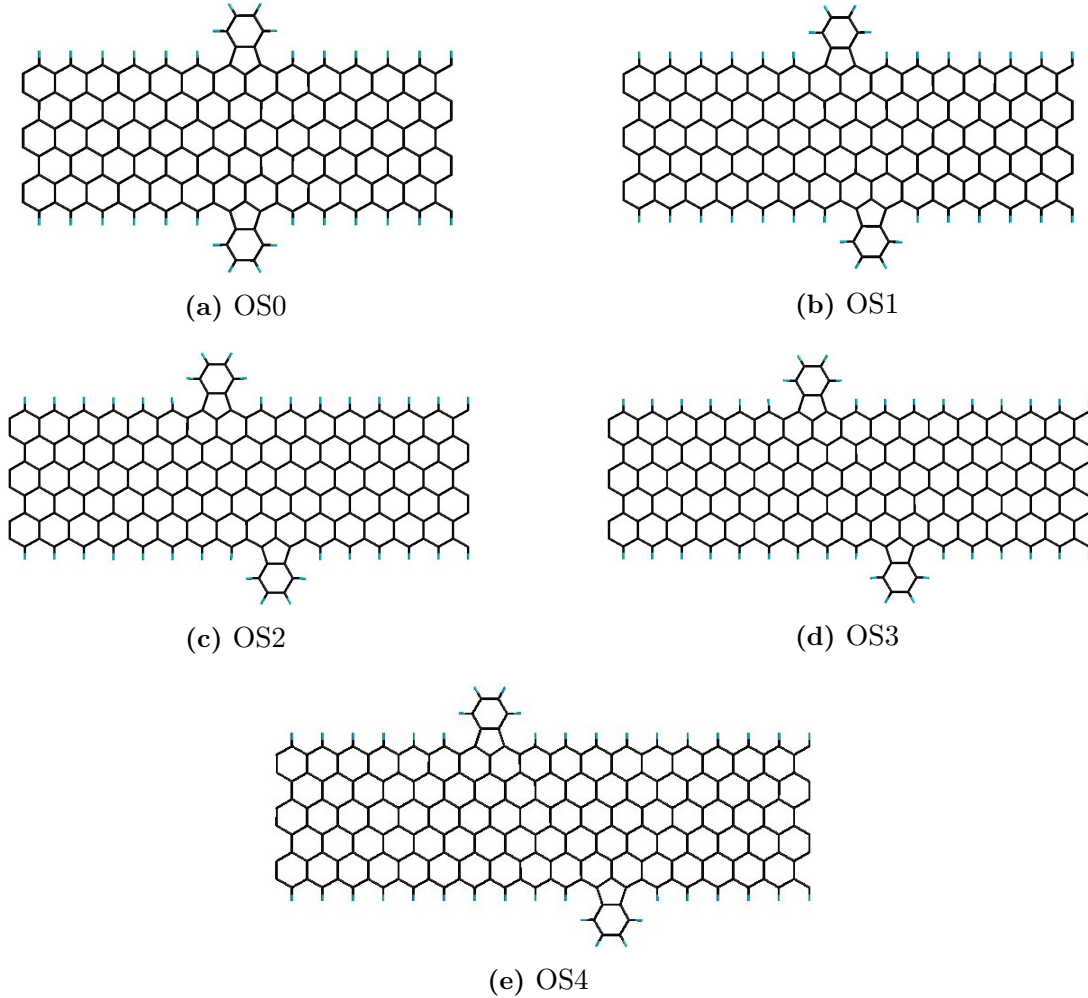


Figure 6.2: Device regions of the structures considered in this section. A given length of pristine 6-ZGNRs is set on both side of the defects so that screening is ensured. More on the nomenclature for such structures is to be found in the text.

To ease our discussion, we will designate such structures by "OSX" where "OS" stands for "Opposite Shifted" and X is an index quantifying the shift. We consider 5 different structures (OS0, OS1, OS2, OS3 and OS4). Note that OS2 and OS3 are structures which come respectively from the phenyl-edge modified [1,-1] and [1,1] PEM 6-ZGNRs.

As shown in Fig. 6.3, $\Delta E_{\uparrow\uparrow-\uparrow\downarrow}$ is smaller than in the pristine case.

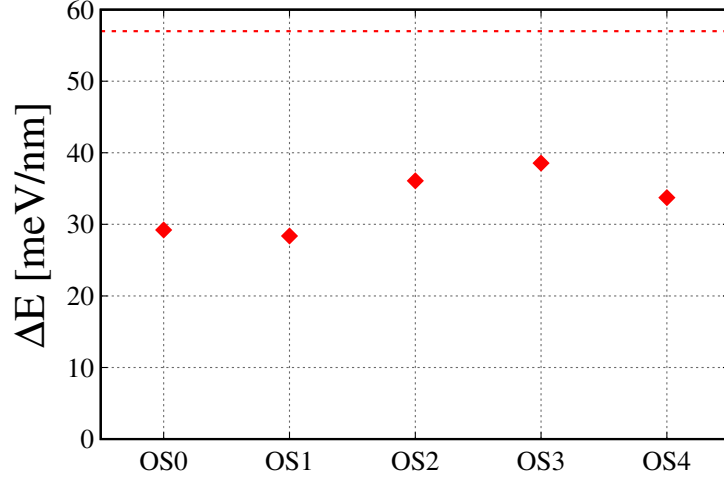


Figure 6.3: Relative stability between the two edge configurations ($\Delta E_{\uparrow\uparrow-\uparrow\downarrow}$). The red dotted line is $\Delta E_{\uparrow\uparrow-\uparrow\downarrow}$ in the pristine case as computed in this work. All structure yields lower stability.

6.1.1 The $\uparrow\downarrow$ Edge Configuration

We first discuss the $\uparrow\downarrow$ edge configuration. As shown by Fig. 6.4, the electronic states are spin degenerated. This was to be expected as the symmetry of such structures is preserved.

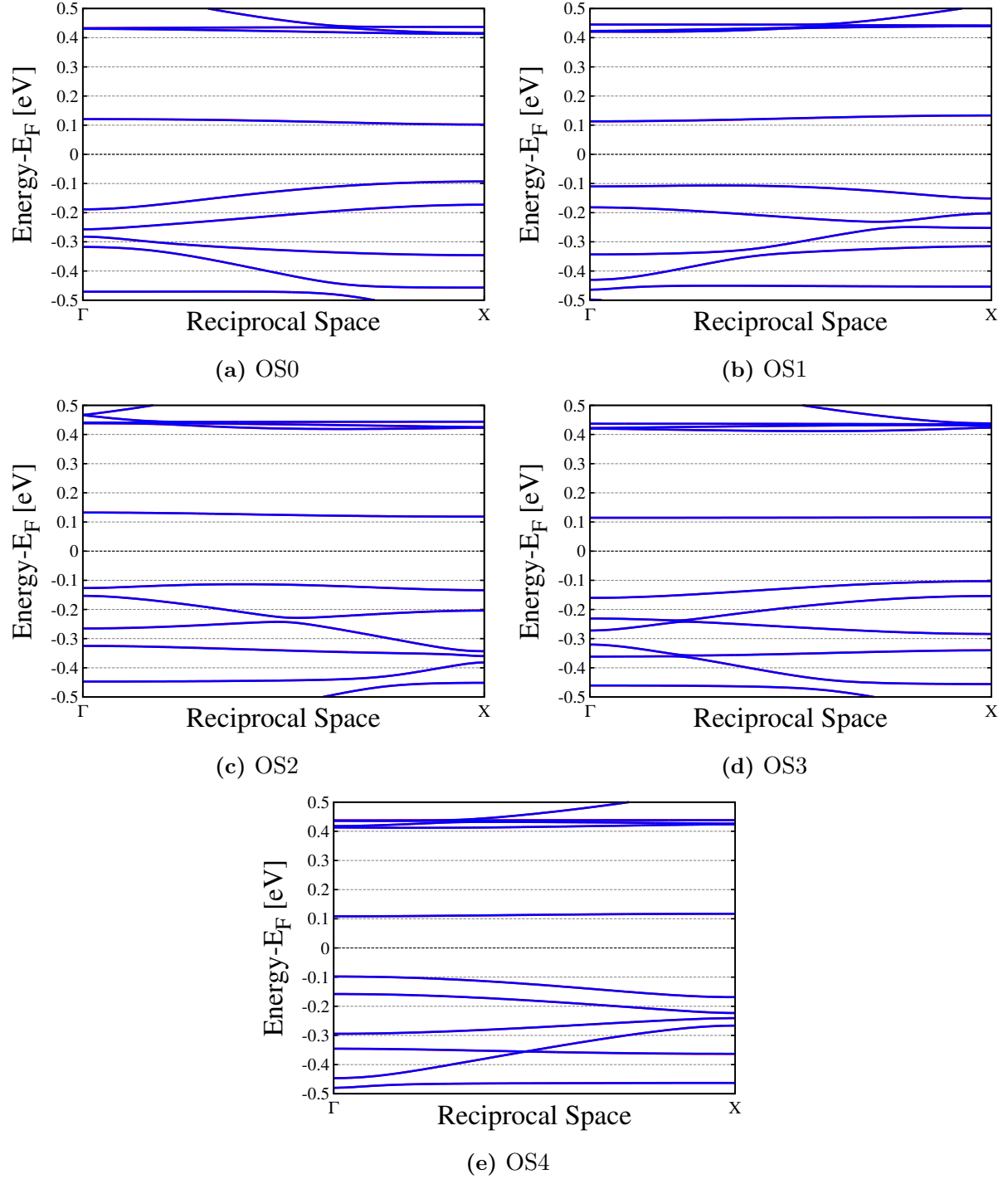


Figure 6.4: Electronic band structures of the (a) OS0, (b) OS1, (c) OS2, (d) OS3 and (e) OS4 in the $\uparrow\downarrow$ configuration. Spin degeneracy is preserved. As seen in the previous chapter, the phenyl groups introduce a localized state within the band gap. Here, since phenyl of neighbouring cells are far away from each other, they can be considered as non-interacting which explains why the localized characteristic of this state is stronger.

Similarly to what have been found in the previous chapter, phenyl groups introduce a localized state within the band gap. This state approximatively lays 0.1 eV above the Fermi energy. Disregarding this state, the width of the band gap of the ribbon is mainly unaffected by the edge defect. However, we observe a shift in the top (bottom) of the valence (conduction) band of towards higher energies. This shift is due to the change in electronic chemical potential induced

by the phenyl groups.

To understand the nature of the localized states, we computed the wavefunction at $k = \Gamma$ and $k = X$ for both spins. The results of our calculations are displayed at Fig. 6.5.

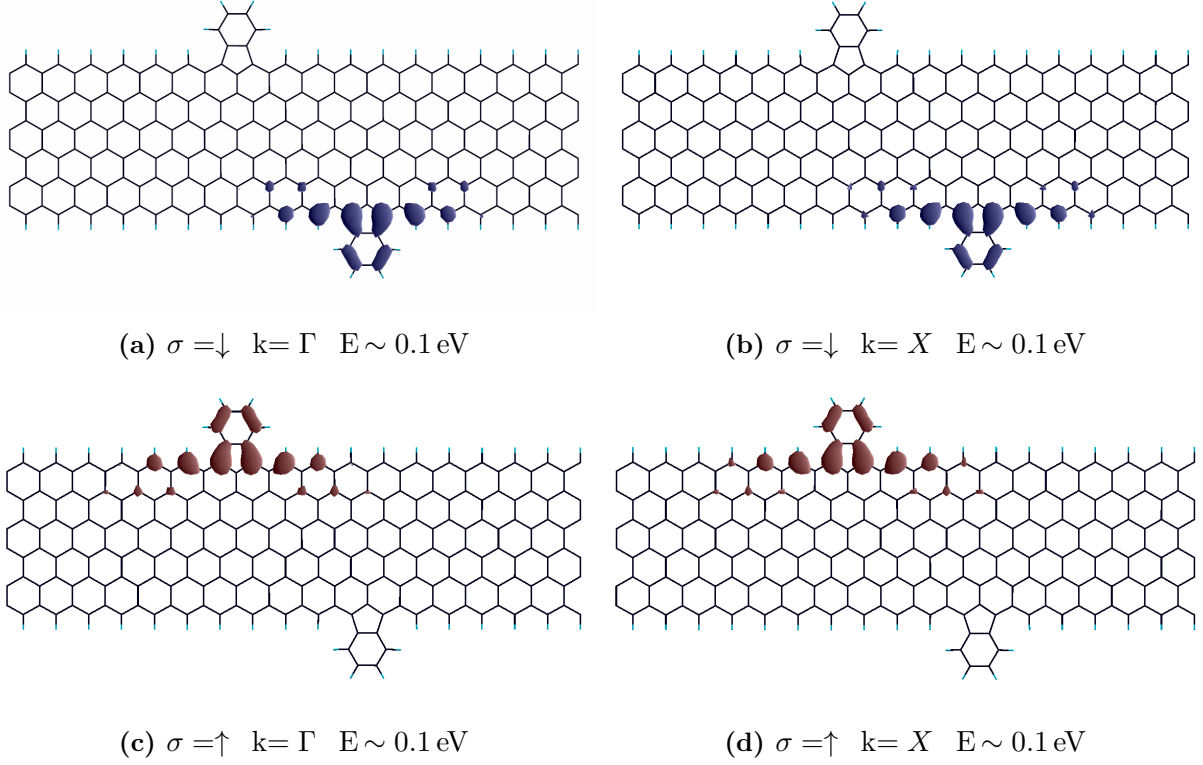


Figure 6.5: Wavefunction associated with the localized state around 0.1 eV for the OS4 structure. " σ " represents the spin, " k " the reciprocal space vector and " E " the energy. We clearly see that the state is localized around the fluoranthene-like edges.

As we expected, we notice that the localization of this state around the phenyl groups is much stronger than what has been found in the previous chapter. The reason behind this has already been discussed: as phenyl groups of neighbouring cells are sufficiently far from each other, such defects can be considered as non-interacting.

Similarly to what has been found before, the accepting states for the spin- $\uparrow$ (spin- $\downarrow$) electrons lay on the edge displaying a net spin- $\downarrow$ (spin- $\uparrow$) density.

Let's consider the lower edge to be $\uparrow$ -polarized and the upper edge $\downarrow$ -polarized. This means that the spin density at the ground-state is dominated by spin- $\uparrow$ electrons for the lower edge (and vice versa). The valence band states of spin- $\uparrow$ electrons lay on the lower edge while the conduction band states are mainly located on the upper edge. Upon excitation (e.g. thermal excitation), a spin $\uparrow$ electron would then jump from the lower edge to the upper edge where it would be localized around the phenyl defect. As a result, a spin $\uparrow$ hole would then be created on the lower edge and both edge would see their polarization diminished. The same consideration could be made for spin $\downarrow$ electrons. As the system is spin degenerated, such transitions are as likely to happen for electrons on both edge.

Since both edges are edge-functionalized by phenyl groups, spin-polarized hole conduction would then occur for the two of them. However, if only one edge was to contain phenyl groups,

spin-polarized hole conduction would then occur for one of the edge. This will be addressed in the case of structures with edge asymmetry.

We computed the spin-resolved transmission for the OSX structures in the $\uparrow\downarrow$ configuration. As shown by Fig. 6.6, the transmissions are spin degenerated.

For the OS1, OS2, OS3 and OS4 structures, it is complicated to observe any general tendency. The most remarkable feature is probably the dip in conductance around $E = -0.48$ eV. The depth of this conductance well increases as the relative distance between phenyl groups increases. This suggests an interaction between the two opposite edge which is surprising but as 6-ZGNRs are quite narrow, residual interaction was to be expected.

The OS0 structure is particular as the ribbon possesses a mirror plane located in the center. The shape of the conductance is slightly different than for the other cases. However, the same dip around $E = -0.48$ eV is still observed.

As seen earlier, the width of the band gap¹ is barely affected by the phenyl groups. However, the valence and conduction band are shifted of around 0.1 eV towards higher energies. This leads the band gap of our device to be actually larger than pristine 6-ZGNRs. Indeed, while pristine 6-ZGNRs displays a non-zero transmission spectra for $E = 0.28$ eV, the conductance is the OSX structures struggles to reach unity between $E = 0.28$ eV and $E = 0.36$ eV.

¹Omitting the localized state introduced by the phenyl groups.

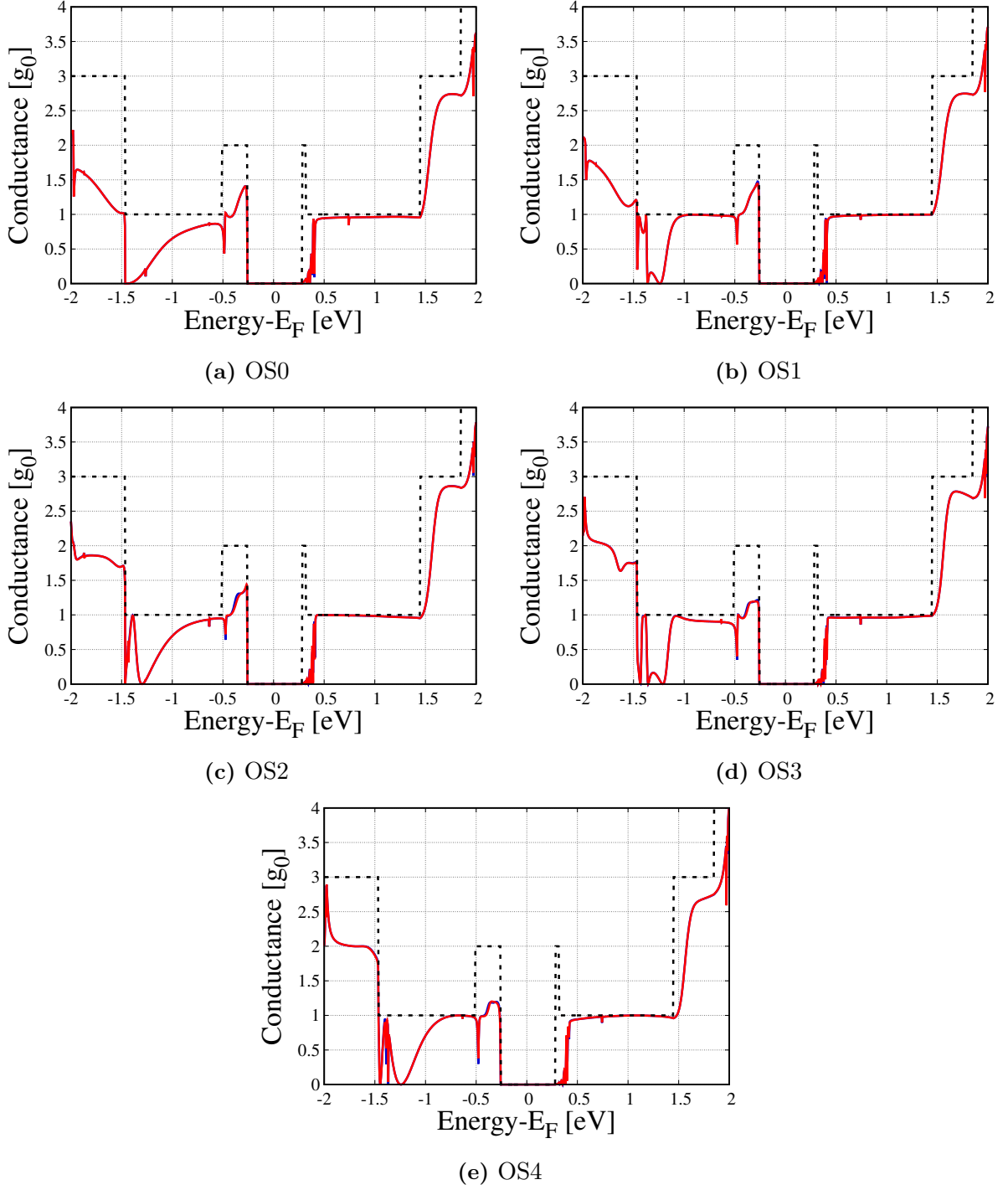


Figure 6.6: Spin-resolved transmission spectrum for the (a) OS0, (b) OS1, (c) OS2, (d) OS3 and (e) OS4 structures in the $\uparrow\downarrow$ configuration. Spin degeneracy is kept as both spin channels exhibit the same behaviour. Similarities are to be observed for all the structures. The most remarkable feature is the dip around $E = -0.48$ eV.

6.1.2 The $\uparrow\uparrow$ Edge Configuration

We now discuss the $\uparrow\uparrow$ edge configuration. As shown by Fig. 6.7, the electronic states are not spin-degenerated. It is quite hard to see any particular feature on the electronic band structures.

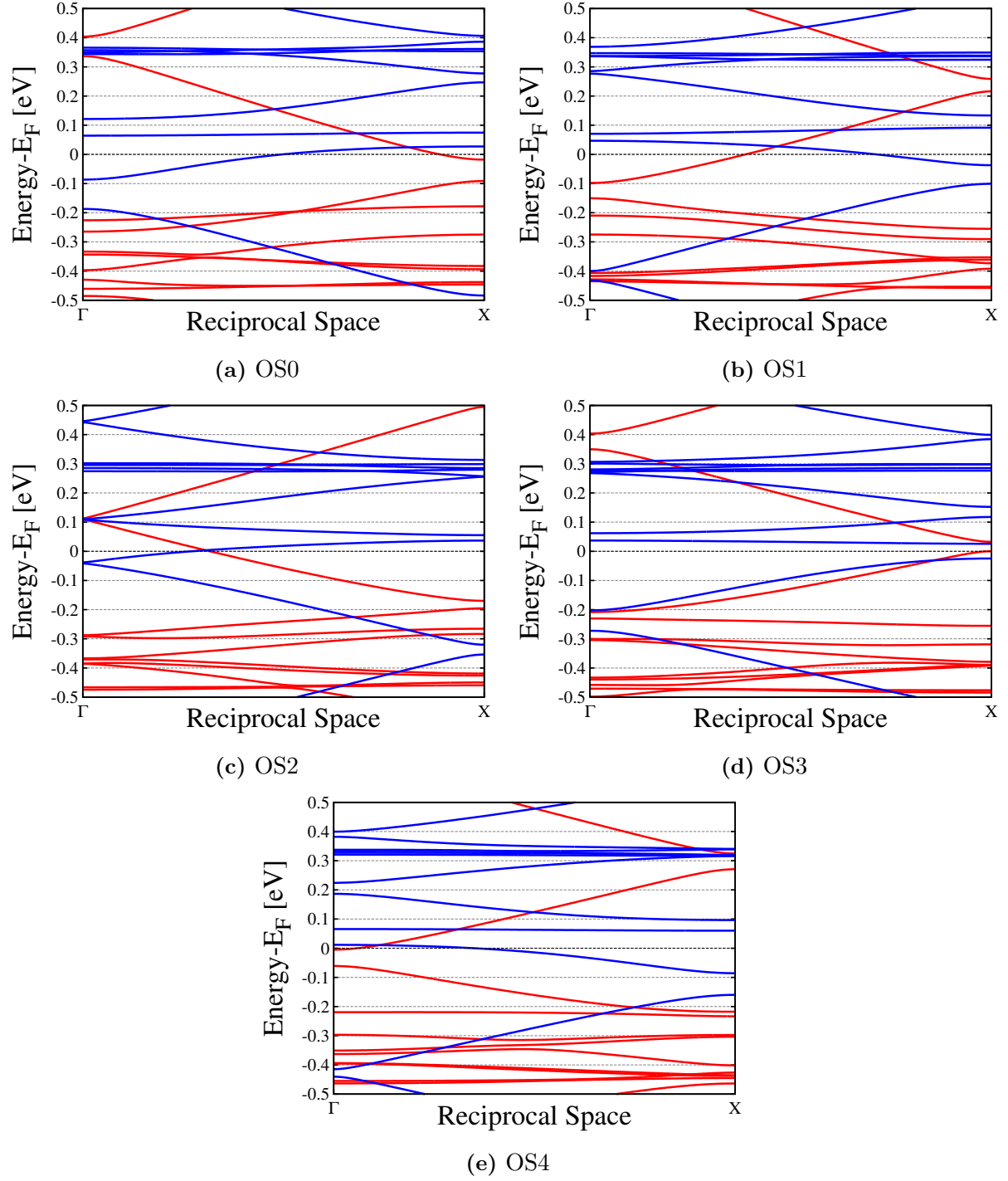


Figure 6.7: Electronic band structures of the (a) OS0, (b) OS1, (c) OS2, (d) OS3 and (e) OS4 in the $\uparrow\uparrow$ configuration. Spin degeneracy is lifted. The red (blue) curves stand for the majority (minority) electrons.

The spin-resolved transmission spectra are displayed at Fig. 6.8.

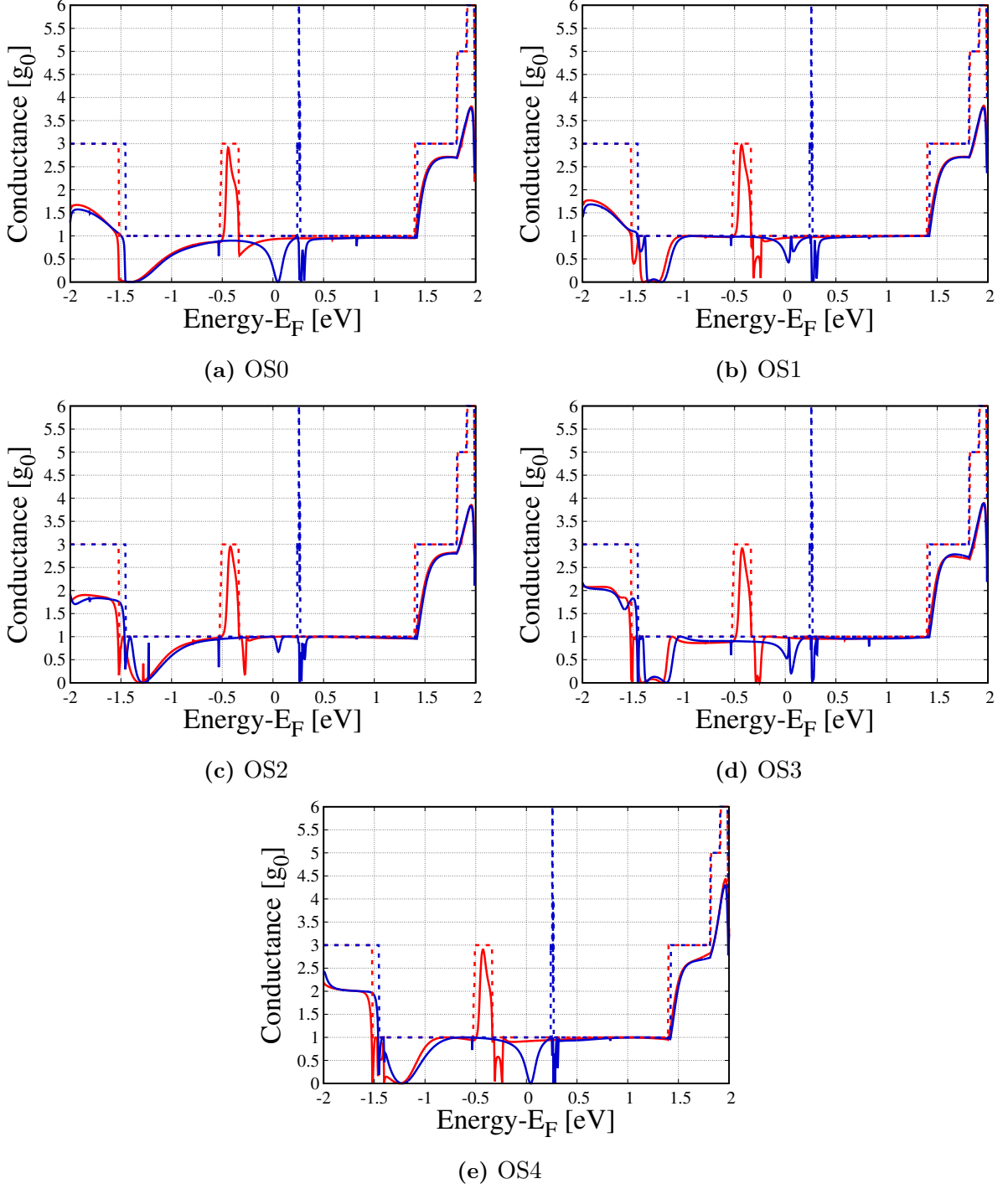


Figure 6.8: Transmission spectrum for the (a) OS0, (b) OS1, (c) OS2, (d) OS3 and (e) OS4 structures in the $\uparrow\uparrow$ configuration. The spin degeneracy is left. A substantial decrease in conductance for spin- $\downarrow$ electrons is observed right next to the the Fermi energy. The same occurs for the other spin channel below E_F . The red (blue) curves stand for the majority (minority) electrons.

Outside the range $[-1; 1]$ eV, both spin channels follow approximatively the same trends. However, inside this energy window, interesting differences are noticeable. We will focus our discussion on this range.

First, for all structures, the high conductance for spin $\uparrow$ electrons around $E = -0.4$ eV is

only slightly affected by the defects. This zone of high conductance is slightly narrower than in pristine ribbons and The nicely quantized plateau has become a relatively wide peak.

Secondly, all structures exhibit a well in the conductance for spin- $\downarrow$ electrons right above the Fermi energy. Letting apart the OS0 structure, the depth and width of the well seems to increase as the relative distance between phenyl groups increases. As in the $\uparrow\downarrow$ configuration, an odd behaviour is to be observed when one goes from OS1 to OS2. We also observe the same behaviour for spin- $\uparrow$ electrons around $E = -0.25$ eV. Again the OS2 structure seems to stand out.

At the energy of the overshoot in the conductance of spin $\downarrow$ electrons for pristine 6-ZGNRs, a strange behaviour of the spin $\downarrow$ electrons is observed as the conductance decreases and recover brutally. Further investigation is required.

The OS0 and OS4 structures exhibit a really interesting feature as transmission for spin $\downarrow$ electrons undergoes complete extinction right above the Fermi energy. Such structures might be technologically interesting as highly spin-polarized current could be obtained for a small bias.

Since the transmission spectra are different for both spin channels, one could quantify the spin polarization of the electronic current. We recall that from chapter 2, the current in the NEGF formalism with Fermi contacts can be expressed as

$$I = \frac{q}{h} \int_{-\infty}^{+\infty} \left(f_1(E) - f_2(E) \right) T(E) dE \quad (6.1)$$

with the transmission given by

$$T(E) = Tr \left[\Gamma_1(E) \hat{G}^R(E) \Gamma_2(E) \hat{G}^A(E) \right] \quad (6.2)$$

Assuming low temperature, Fermi functions can be considered as step functions so that the current reads

$$I = \frac{q}{h} \int_{\mu_2}^{\mu_1} T(E) dE \quad (6.3)$$

The electronic chemical potential of the electrons are linked to the applied bias ΔV by

$$\frac{\mu_2 - \mu_1}{q} = \Delta V \quad (6.4)$$

Setting μ_1 by reference to zero, one obtains

$$\mu_2 = q\Delta V \quad (6.5)$$

so that the current reads

$$I = \frac{q}{h} \int_{q\Delta V}^0 T(E) dE \quad (6.6)$$

Actually, one can differentiate the electrical current for spin $\uparrow/\downarrow$ electrons so that

$$I^\uparrow = \frac{q}{h} \int_{q\Delta V}^0 T^\uparrow(E) dE \quad (6.7)$$

$$I^\downarrow = \frac{q}{h} \int_{q\Delta V}^0 T^\downarrow(E) dE \quad (6.8)$$

We then define the polarization of the current $P_I(\Delta V)$ as the ratio

$$P_I(\Delta V) = \frac{I^\uparrow(\Delta V) - I^\downarrow(\Delta V)}{I^\uparrow(\Delta V) + I^\downarrow(\Delta V)} \quad (6.9)$$

$P_I(\Delta V)$ has been computed and the results are displayed at Fig.6.9.

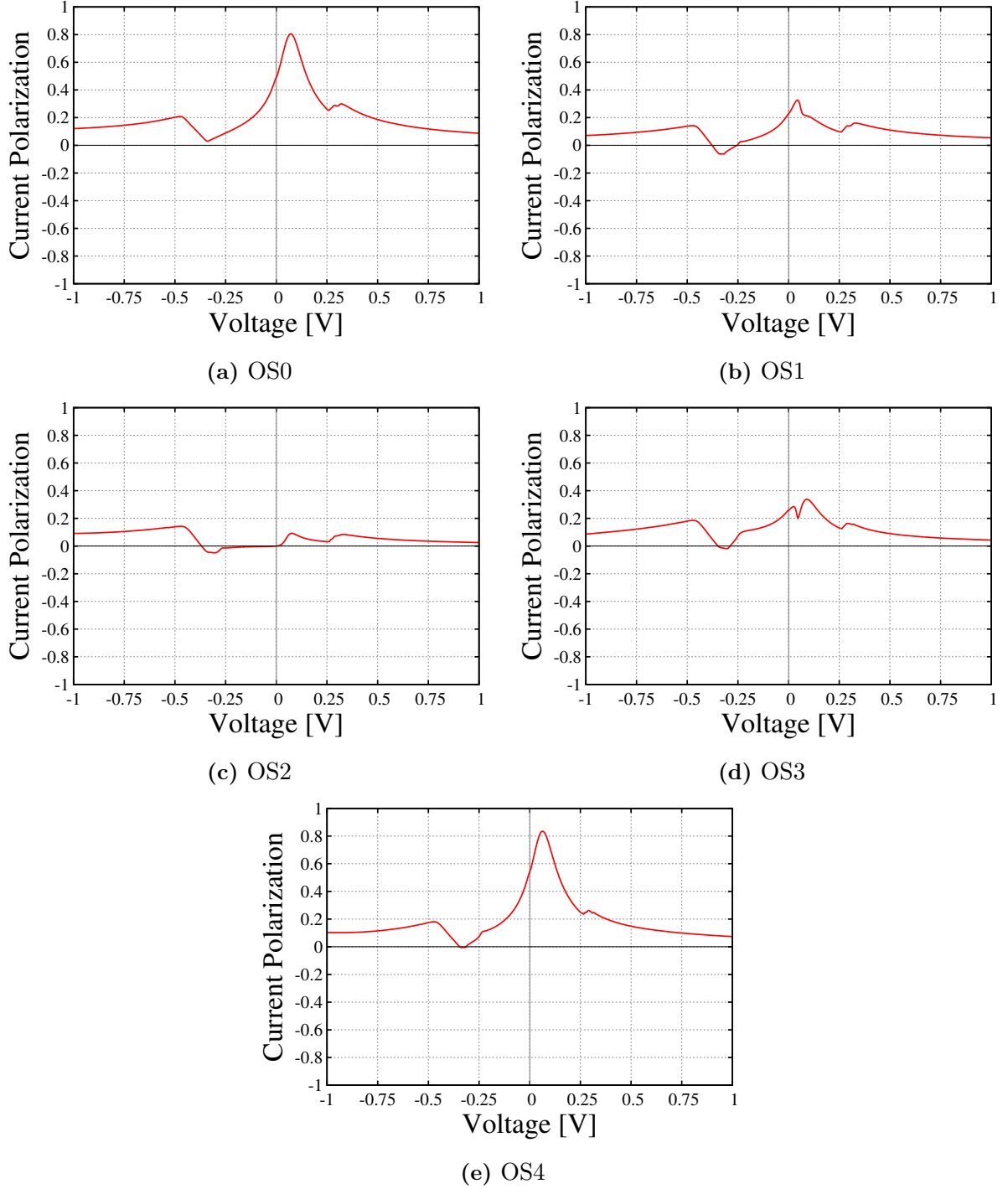


Figure 6.9: Current polarization curve in the low-bias approximation with no gate voltage for the (a) OS0, (b) OS1, (c) OS2, (d) OS3 and (e) OS4 structures in the $\uparrow\uparrow$ configuration.

The transmission spectra have actually been computed at zero bias. Biasing the system implies an effect on the electronic states which obviously modifies the transmission spectra. If one wants to get the $I - V$ curve of such ribbons, then a calculation at different voltages should be done. However, for sufficiently low bias, one can assume the transmission spectra to be mostly unaffected (low-bias approximation).

Looking at Fig. 6.9, we notice that the OS0 and OS4 structures exhibit the highest polarization at zero bias. For the OS0 structure, 80 % of polarization is reached for a voltage of 70 mV while

83 % is reached for the OS4 structure for 62 mV.

6.2 Fluoranthene-like Edges on the Same Edge

We will now focus our discussion on the second group of structures which consists on ribbons containing phenyl groups only along one edge. The structures are displayed at Fig. 6.10.

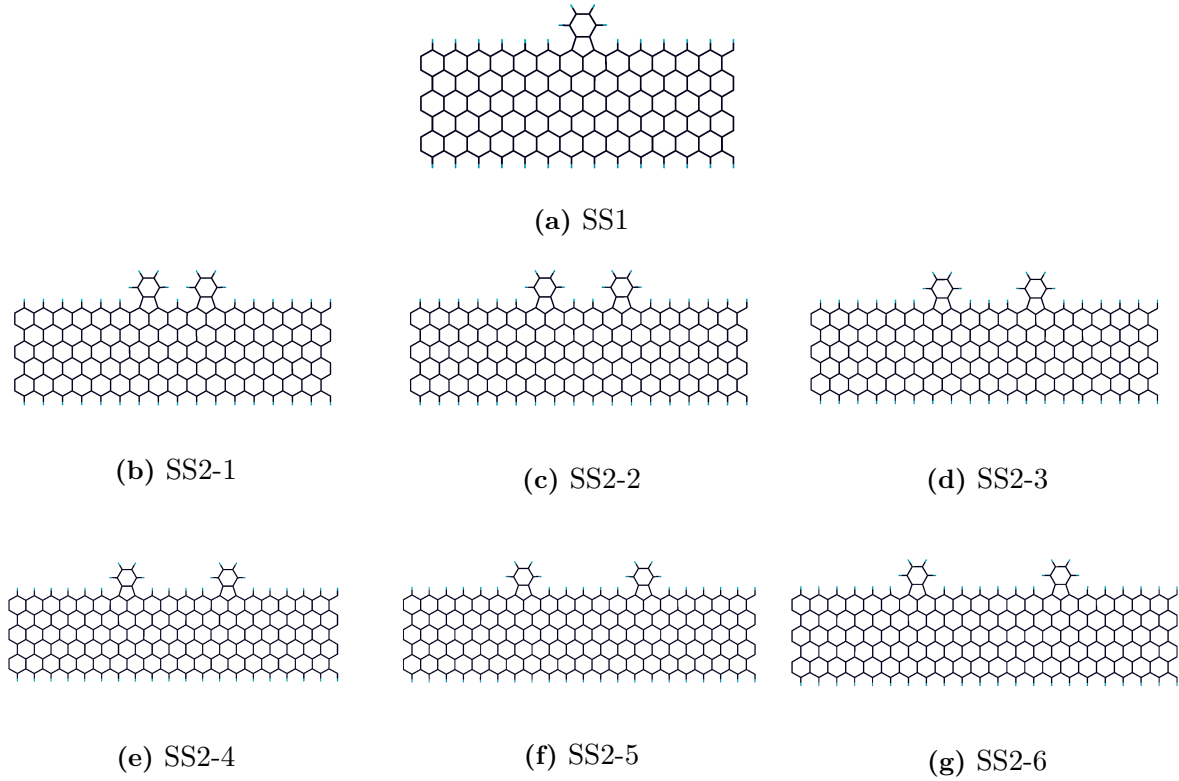


Figure 6.10: Device regions of the structures considered in this section. A given length of pristine 6-ZGNRs is set on both side of the defects so that screening is ensured. More on the nomenclature for such structures is to be found in the text.

To ensure coherence in our nomenclature, we will call those structures $SSX-Y$ where "SS" stands for "Same Side", X is the number of phenyl groups and Y the spacing between them. Obviously, SS1 yields the simplest structure with its unique phenyl group. Since it does not carry any other groups, this structure allows for the analysis of the effect of one phenyl group on 6-ZGNRs.

6.2.1 SS1 Structure

We start our discussion by looking at the electronic band structure for the SS1 structure in the $\uparrow\downarrow$ and $\uparrow\uparrow$ configuration (see Fig. 6.11).

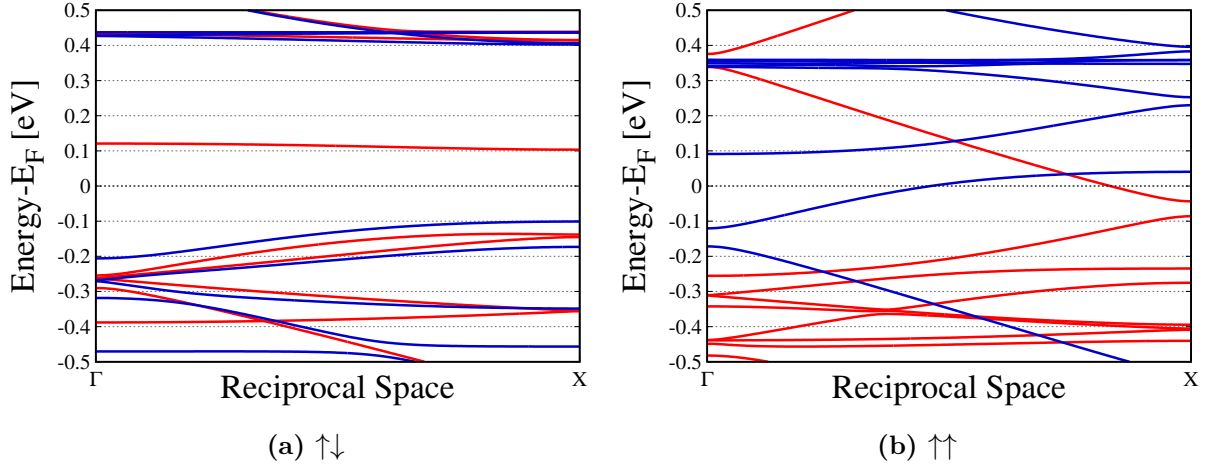


Figure 6.11: Electronic band structure of the SS1 structure in both $\uparrow\downarrow$ and $\uparrow\uparrow$ spin configurations. For the $\uparrow\downarrow$ case, the asymmetry in the structure breaks the spin degeneracy and a net magnetic moment $\mu = 0.02\mu_B$ appears. The red (blue) curves stand for the majority (minority) electrons.

The radically different topology of the two edges lifts the spin degeneracy, even for the the $\uparrow\downarrow$ case. In this configuration, the net polarization of the perfect edge is associated with the majority electrons while the one for the defective is associated with the minority electrons (see Fig. 6.12). Hereafter, majority (minority) electrons will be referred to as "spin- $\uparrow$ " ("spin- $\downarrow$ ") electrons.

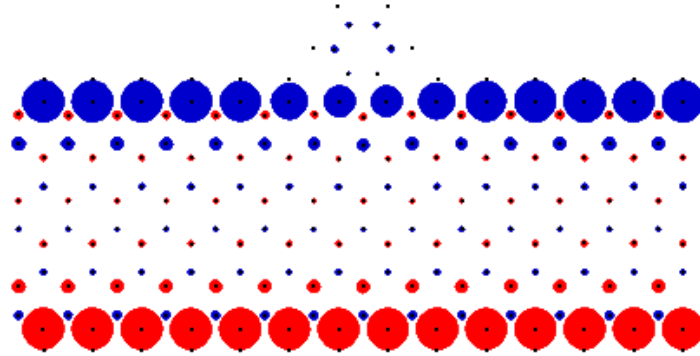


Figure 6.12: Spin density for the SS1 structure within the Mulliken population analysis in (a) the $\uparrow\downarrow$ and (b) the $\uparrow\uparrow$ configuration. A red (blue) circle indicates a majority of spin- $\uparrow$ (spin- $\downarrow$) electrons. The bigger the circle, the stronger the polarization.

The $\uparrow\downarrow$ configuration exhibits a net magnetic moment $\mu = 0.02\mu_B$ whose direction is given by the polarization of the perfect edge. This is due to the fact that the phenyl group depleted the spin density of the edge on which it lays.

Similarly to the OSX structures (see Fig. 6.4), we notice the appearance of a localized state around 0.1 eV above the Fermi energy. However, since the structure contains only one phenyl group, this state only exists for spin- $\uparrow$ electrons.

As discussed previously, such accepting state can be populated if sufficient energy is supplied to electrons. Here, the excitation is highly asymmetrical. Indeed, only spin- $\uparrow$ electrons, which mainly lay on the perfect edge, will be able to migrate to this localized state. As a result, both edges will see their polarization reduced *and* a charge imbalance between the two edges will arise. Spin-polarized hole conduction only happens along the perfect edge.

In the $\uparrow\uparrow$ configuration, no outstanding feature appear and the system stays metallic for both spin channels.

Since even the $\uparrow\downarrow$ configuration exhibits spin degeneracy lifting, spin resolved transmission spectra for such structures are different for both spin channels, as shown by Fig. 6.13.

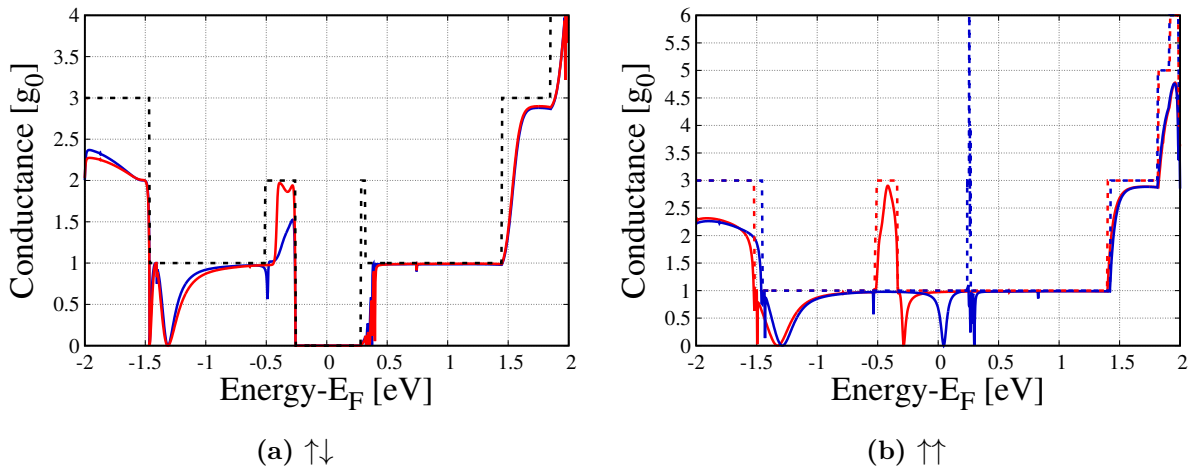


Figure 6.13: Transmission spectra for the SS1 structure in both $\uparrow\downarrow$ (a) and (b) $\uparrow\uparrow$ spin configurations. In the $\uparrow\downarrow$ case (a), even if the leads do not exhibit spin degeneracy lifting, the transmission spectrum is not spin degenerated. The most remarkable feature lays between -0.5 and -0.2 eV where spin- $\downarrow$ electrons are more affected than the others. In the $\uparrow\uparrow$ case (b), we see two extinctions of the transmission, one for the spin majority channel below the Fermi energy and the other for the spin minority channel above the Fermi energy. The red (blue) curves stand for the majority (minority) electrons.

For the $\uparrow\downarrow$ configuration, the behaviour displayed by the spin- $\downarrow$ channel is similar to what has been observed for the OSX structures (see Fig. 6.6). The similarity is especially noticeable around $E = -0.48$ eV where the sharp decrease in conductance suggests back-scattering has been enhanced. This resonant energy is only relevant for electrons whose spin is associated with the polarization of the defected edge (i.e. the spin- $\uparrow$ conduction channel does not experience enhance back-scattering at this energy). For this reason, we believe that this resonant energy is characteristic to edges exhibiting phenyl-groups functionalization. We can thus expect the SS2-Y structures to exhibit stronger back-scattering at $E = -0.48$ eV.

For spin- $\uparrow$ electrons, the plateau at $2g_0$ between $E = -0.5$ and $E = -0.26$ is nearly preserved. However, we note that the width of is slightly reduced (it starts at $E = -0.4$). Actually, this effect is due to the shift in electronic chemical potential induced by the phenyl group. Indeed, the band structure is globally shifted towards higher energies, meaning that the top of the valence band inside the device region is slightly higher than the top of the valence band inside the leads. However, since the leads are non-conducting for energies between $E = -0.26$ eV and $E = 0.28$ eV, the plateau for spin- $\uparrow$ electrons is truncated. The shift in electronic chemical potential is also observable for energies higher than the Fermi energy. Indeed, for pristine 6-ZGNRs, the ribbon

starts to be conducting at $E = 0.28$ eV while the conductance for both spin channel in our SS1 device reaches g_0 around $E = 0.38$ eV.

In the $\uparrow\uparrow$ configuration, both spin channels follow the same trends outside the range $[-1; 1]$ eV. Inside this energy window, we notice two specific energies at which conduction for one spin or the other goes towards zero. For the spin- $\uparrow$ electrons, extinction happens at $E = -0.286$ eV while for the spin- $\downarrow$ channel, this happens around $E = 0.046$ eV. Such features is of technological interest as small voltages might lead to highly polarized currents.

The current polarization, as introduced in the previous section, has been computed for both edge polarization configurations and is presented at Fig. 6.14. Note that here, since $\uparrow\downarrow$ edges yield lifting of spin degeneracy, current polarization can be computed.

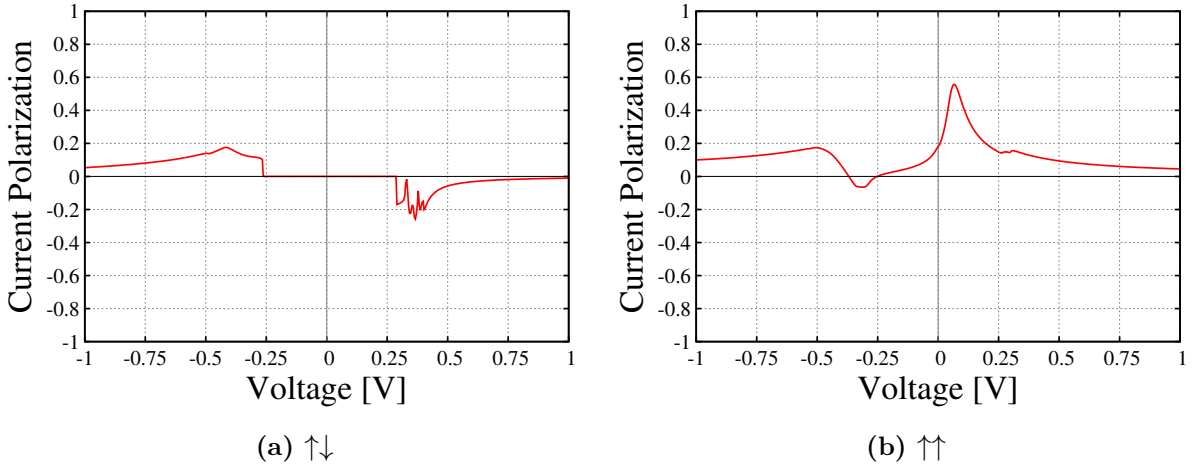


Figure 6.14: Current polarization at zero gate-voltage for the SS1 structure in in both (a) $\uparrow\downarrow$ and (b) $\uparrow\uparrow$ spin configurations. For the $\uparrow\uparrow$ case (b), we notice a non-zero current polarization around $V = 0$.

In the $\uparrow\downarrow$ configuration (Fig. 6.14 a), current polarization is achieved when the system starts to be conducting but stays relatively small (below 20%). However, depending on the sign of the bias, one polarization or the opposite can be obtained.

In the $\uparrow\uparrow$ configuration (Fig. 6.14 b), the system is conducting and for infinitesimal voltages the spin polarization reaches 20 %. Polarization peaks at 55% for a small bias $V = 66$ mV.

6.2.2 SS2-Y Structures

We will now discuss the effect of two phenyl groups on the conductance of 6-ZGNRs by looking at the SS2-Y structures. We expect the parameter Y to be crucial as close phenyl groups would hold strong interactions.

6.2.2.1 The $\uparrow\downarrow$ Edge Configuration

In the $\uparrow\downarrow$ configuration, spin degeneracy is lifted (see Fig. 6.15). We observe the appearance of two spin- $\uparrow$ polarized states within the ribbon's band gap.

As the distance between phenyl groups increases from $Y = 1$ to $Y = 3$, we notice that the two energy levels get closer to each other. This is probably due to the decreasing interaction between the defects. Actually, the distance $Y = 3$ corresponds to the spacing between uniformly

distributed edge-defect phenyl of concentration 0.81 nm^{-1} . At this concentration (or lower), we noticed in the previous chapter (see Fig. 5.24) that electronic states introduced by the phenyl groups were quite localized in energy. This suggests and confirms that phenyl separated by less than 3 cusps tends to interact strongly.

When we look at the transition from $Y = 1$ to $Y = 6$, we actually notice an odd behaviour. If the two localized states get closer from $Y = 1$ to $Y = 3$, the SS2-4 structure exhibits more spaced localized states than SS2-3. Moreover, while the electronic band structure of SS2-5 resembles the one of SS2-4, SS2-6 presents characteristics closer to SS2-3 than any other structures. The peculiar behaviour of the SS2-3 and SS2-6 structures seems to display a period of 3 in terms of phenyl group spacing. Using analytical solution of tight-binding model, this periodicity of 3 in the wavefunction was actually predicted in armchair graphene nanoribbon along the zigzag direction [38]. Further investigation is required.

The spin-resolved transmission spectra are displayed at Fig. 6.16. As we see, the conductance for energies higher than the Fermi energy does not really depend on the spacing between phenyl. For those energies, the transmission is nearly spin degenerated as both channels exhibit similar behaviour.

We notice that most of the structures exhibit the dip at $E = -0.48 \text{ eV}$ for the transmission of spin- $\downarrow$ electrons. The dip is stronger than for the SS1 structure. This supports the hypothesis according to which phenyl groups would be responsible for this enhanced back-scattering. Nevertheless, we notice that SS2-1 and SS2-6 display a different behaviour. For the SS2-1 structure, the distinction probably originates from the strong interaction between the defects. For SS2-6, the discrepancy with the general behaviour stays unexplained.

For SS2-4 and SS2-5, we notice an overshoot at $E = -0.44 \text{ eV}$ where the conductance peaks respectively at the value of $1.67g_0$ and $1.49g_0$. Such enhancement of conductance at this particular energy might be the signature of quantum resonant tunnelling.

The spin- $\uparrow$ conductance between -0.5 eV and -0.28 eV approaches the plateau of pristine 6-ZGNR as the distance between phenyl groups increases. The narrowing of the width of the plateau is due to a shift in electronic chemical potential, as explained before. Increasing the parameter Y also leads to general decrease in the conductance of spin- $\downarrow$ electrons in the energy window $[-0.5; -0.28] \text{ eV}$. Our interpretation for this behaviour is the following.

For phenyl groups close enough, the two defects strongly interact and can actually be seen as one bigger defect. The effect on the conductance is then not simply "twice" the effect of one phenyl group. However, for defect which are far enough, the effect on the conductance can be pictured as "twice" the effect of one phenyl group. Spin- $\downarrow$ electrons can thus be seen as experiencing twice the back-scattering of one phenyl group. This physical picture is of course way too simple as basic quantum physics tells us that a double-well system is not simply twice a simple-well system (e.g. resonant tunnelling).

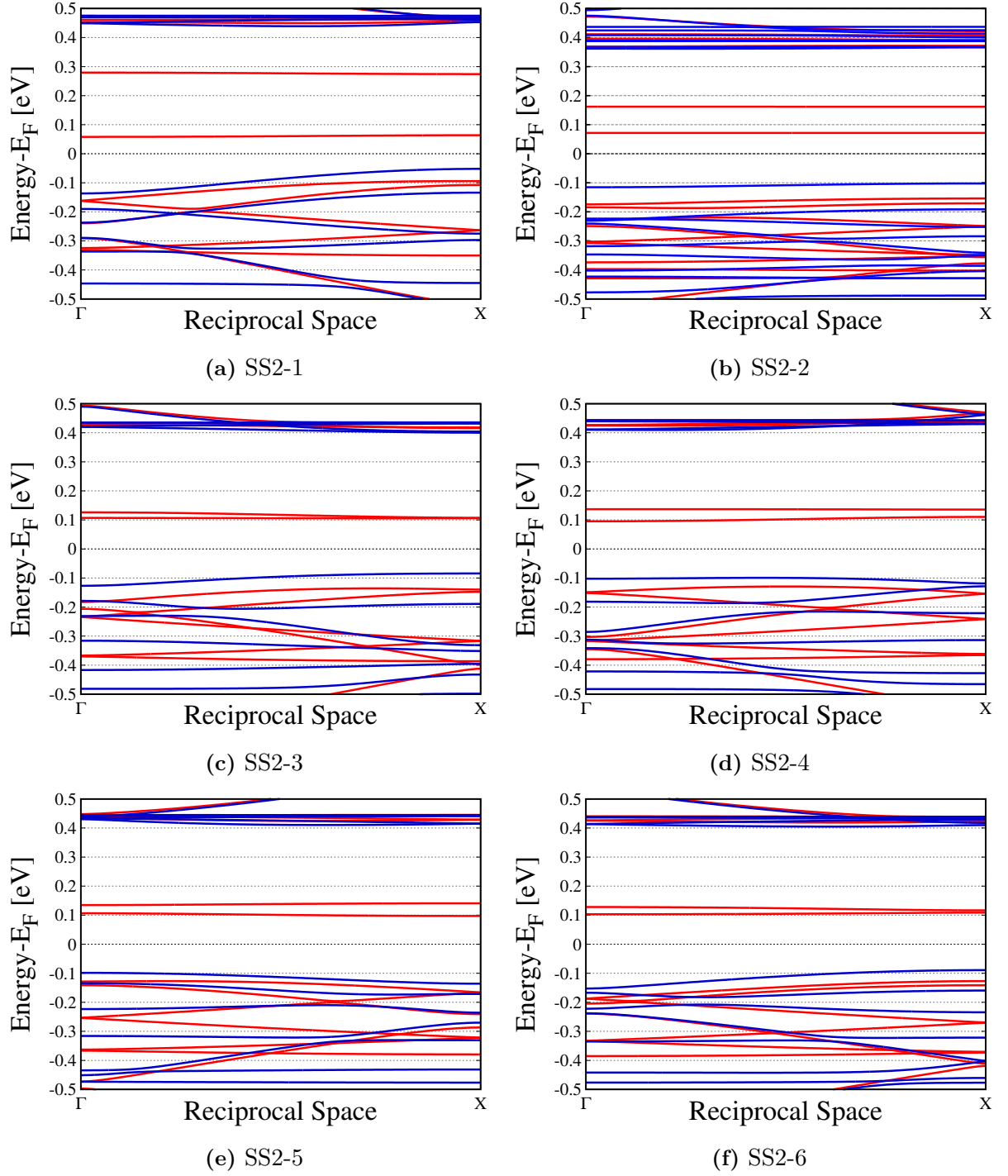


Figure 6.15: Electronic band structures of the (a) SS2-1, (b) SS2-2, (c) SS2-3, (d) SS2-4, (e) SS2-5, (f) SS2-6 in the $\uparrow\downarrow$ configuration.

Spin degeneracy is lifted. As seen previously, localized states are introduced within the band gaps by the phenyl groups. Here, two spin-degenerated states appear. The spacing between those states is highly dependent on the spacing between the phenyl groups. The red (blue) curves stand for the majority (minority) electrons.

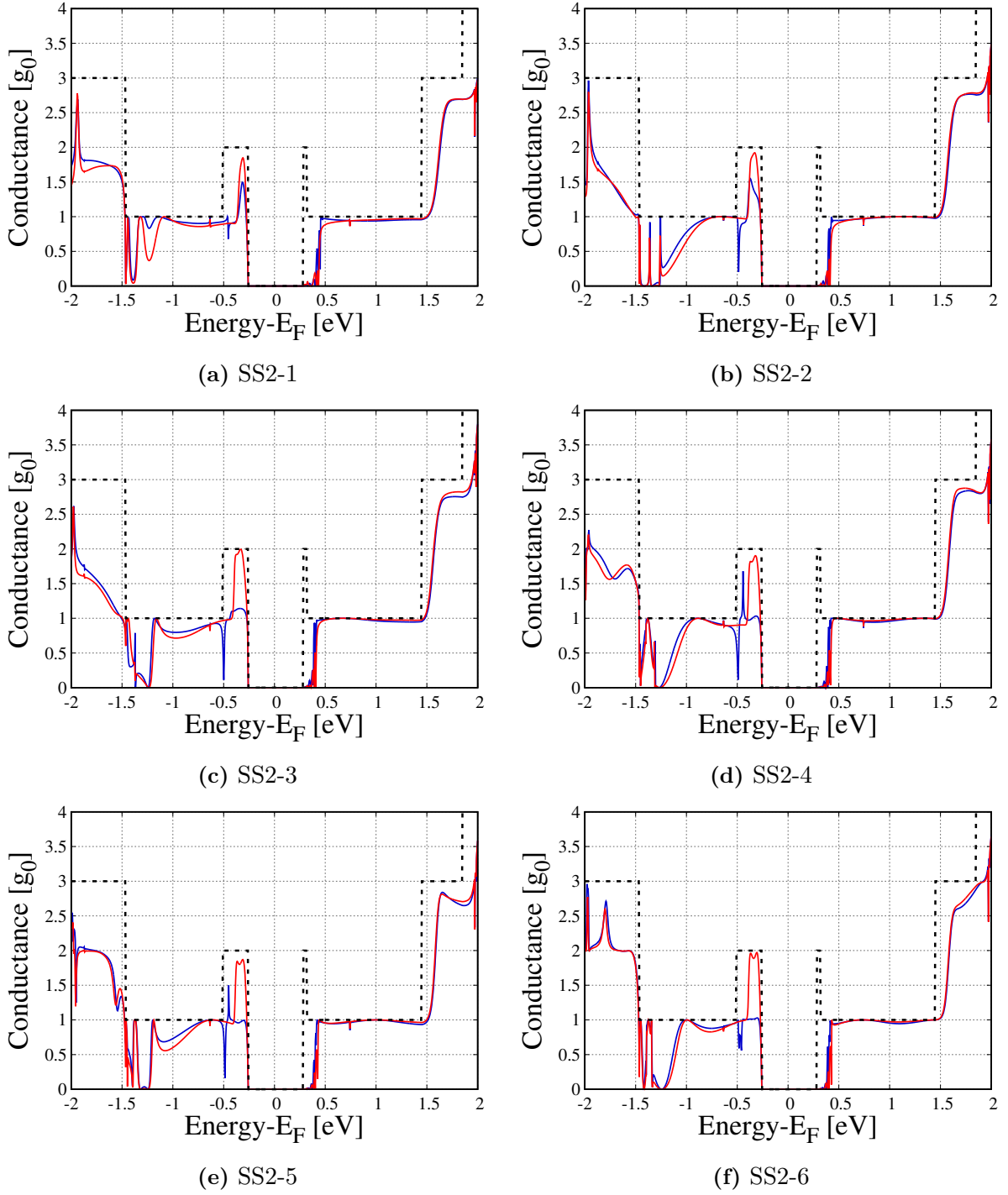


Figure 6.16: Spin-resolved transmission spectra of the (a) SS2-1, (b) SS2-2, (c) SS2-3, (d) SS2-4, (e) SS2-5, (f) SS2-6 in the $\uparrow\downarrow$ configuration. In red (blue) is represented the conductance of spin- $\uparrow$ (spin- $\downarrow$) electrons. A complete discussion on those graphs is to be found in the text.

6.2.2.2 The $\uparrow\uparrow$ Edge Configuration

We now discuss the structures the $\uparrow\uparrow$ configuration. The band structures are provided in the appendix (see Fig. D.1) and we focus directly on the transmission spectra displayed at 6.17.

The conductance for the SS2-Y structures is quite similar to the one displayed by the OSX structures (see Fig. 6.8). As observed before, the high conductance around -0.4 eV is mostly unaffected. The nice quantized plateau that displayed pristine 6-ZGNRs has not taken the shape of a wide peak. Except SS2-3, all structures display an extinction in the conduction for spin- $\downarrow$ electrons right above the Fermi energy. The same observation can be done for spin- $\uparrow$ electrons at an energy below E_F but, in this case it is SS2-1 and SS2-6 that does not yield complete extinction.

As shown by Fig. 6.18, the most outstanding feature is obtained for the SS2-6 structure for which a current polarization of 80.9 % is reached at $V = 78$ mV. The low value of this voltage is quite encouraging as the current polarization was obtained within a low-bias approximation

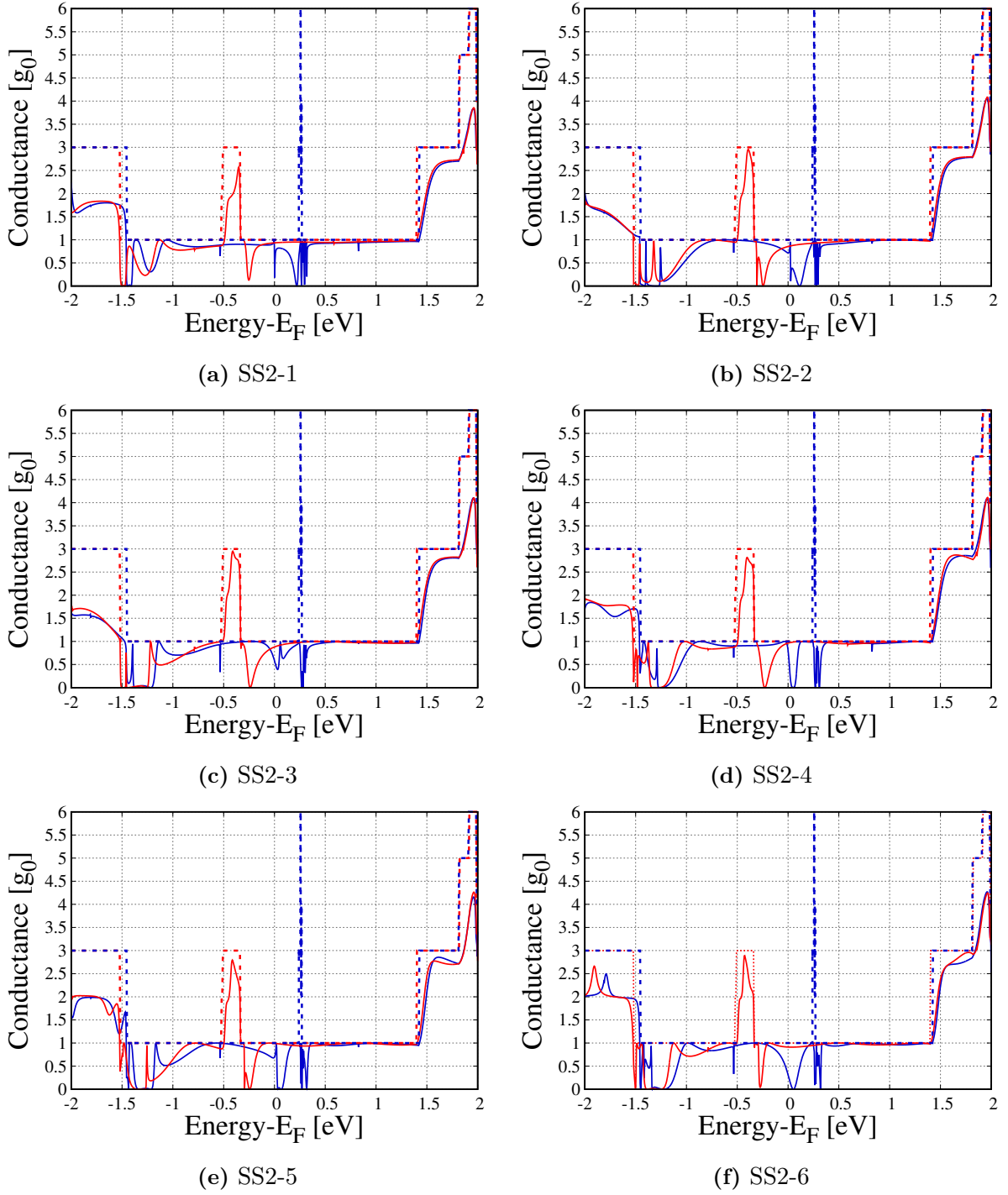


Figure 6.17: Spin-resolved transmission spectrum of the (a) SS2-1, (b) SS2-2, (c) SS2-3, (d) SS2-4, (e) SS2-5, (f) SS2-6 structures in the $\uparrow\uparrow$ spin configuration. The red (blue) curves stand for the majority (minority) electrons.

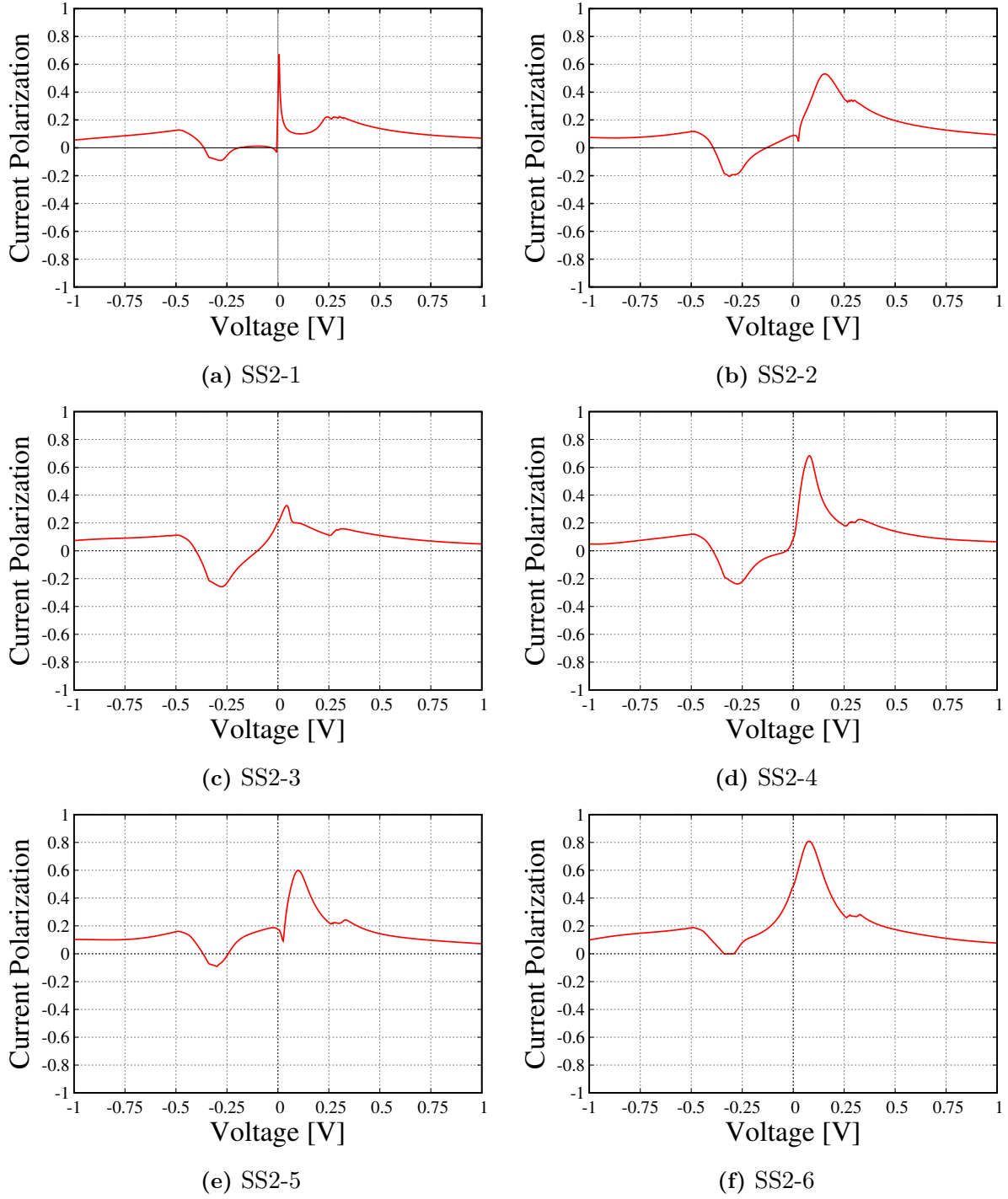


Figure 6.18: Current polarization for the (a) SS2-1, (b) SS2-2, (c) SS2-3, (d) SS2-4, (e) SS2-5, (f) SS2-6 structures in the $\uparrow\uparrow$ spin configuration.

6.3 Summary

We hereby summarize the results of this chapter.

In the $\uparrow\downarrow$ configuration:

- A resonant energy at $E = -0.48$ eV where back-scattering is enhanced by the phenyl groups appears. The strength of back-scattering is increased when one considers several phenyl groups.
- For the SS2-Y structures, the two localized state (one per phenyl) are more spaced as Y is small. We saw that below a distance of 3 cusps between the defects, interaction can be considered as strong. This is to be related with the previous chapter.
- For the SS1, the plateau at $2g_0$ of pristine 6-ZGNRs laying between -0.5 and -0.26 eV is barely affected for spin- $\uparrow$ electrons. The decrease in the width of this plateau is due to the shift in electronic chemical potential. For the SS2-Y structures, the closer the phenyls groups are, the stronger the effect on the conductance in this range of energy. For all structure, the spin- $\downarrow$ electrons are more severely impacted.
- For the SS2-4 and SS2-5 a positive peak in the conductance around -0.44 eV might be the signature of resonant tunnelling.

In the $\uparrow\uparrow$ configuration:

- Slightly above the Fermi energy, the spin minority channel undergoes either a partial or complete extinction. Whether the conductance reaches zero or not is highly dependent on the geometry of the edges. The same observation can be held for spin majority electrons at energies below E_F .
- Few defects on one edge could lead to highly spin-polarized current. For instance, a current polarization of 80.9 % is reached at $V = 78$ mV for the SS2-6 structure.

7

Conclusion

In this work, we investigated the properties of graphene related nanostructures using *ab-initio* methods. Electronic structures calculations were performed through DFT as implemented in the SIESTA software. Spin-resolved electronic transport properties were computed with TranSIESTA, an *ab-initio* quantum transport simulation software which relies on the NEGF formalism within the transmission picture of Landauer-Büttiker.

We first looked at rather simple systems like pristine graphene and ZGNRs. For graphene, we recovered the zero band-gap property and the linear energy dispersion at $\mathbf{K}$ and $\mathbf{K}'$. For the nanoribbons, we studied the nature of the electronic states which have been found to be confined around the edges. In this case, two edge configurations were considered: $\uparrow\downarrow$ and $\uparrow\uparrow$. We predicted that the band gap of ZGNRs were expected to follow a $\propto 1/w$ trend, which is in total accordance with what has been reported in the literature [13]. The effect of a Stone-Wales defect on the conductance of 6-ZGNRs was analysed. As a defect is introduced in the channel, electrons start to experience back-scattering and the transmission spectrum loses its well-quantized characteristic.

The existence of the magnetic edge states in ZGNRs and their stability at room temperature are actually quite controversial. Some argue that such magnetic states might not exist in real systems because of edge reconstruction, passivation and closure and that, even if such magnetic edges could be made, thermal energy at room temperature would render them non-stable [30]. However several experiments using scanning tunnel microscopy showed in 2016 that graphene nanoribbons host localized magnetic edge states along their zigzag edge [31] [32].

The advances in bottom-up synthesis have enabled the production of atomically precise graphene nanoribbons. If a significant amount of those methods produces armchair type of ribbons [39] [40] [41], Ruffieux et al. [32] recently provided an experimental bottom-up method which yields atomically precise 6-ZGNRs. In their work, they also managed to produce 6-ZGNRs with phenyl defects along their edge. Those structures were at the center of this work and were referred to as phenyl-edge modified 6-ZGNRs (PEM 6-ZGNRs).

The synthesis of PEM 6-ZGNRs yields random ring closure of the phenyl groups along the edge so that periodic structures virtually do not exist. However, the topology between two neighbouring phenyl groups was found to be described by a small set since they are allowed to be separated by 3, 4 or 5 cusps. We saw that such structures would see the relative stability of the two edge-configurations ($\Delta E_{\uparrow\uparrow-\uparrow\downarrow}$) diminished. In the $\uparrow\downarrow$ configuration, the effect of the phenyl groups is to shift the electronic states towards higher energies. They also introduce spin-polarized accepting states which are roughly located 0.1 eV above the Fermi energy. Such structures would then allow for spin-polarized hole conduction along their edges.

We investigated the influence of structures that would exhibit phenyl edge defects only along one edge. It was found that, for the highest concentration of phenyl groups, outstanding spin filtering characteristic were obtained in the $\uparrow\downarrow$ configuration. It was also found that when phenyl

are close to each other (3 cusps or closer), they strongly interact and introduce a state quite spread in energy. However, for lower concentrations, a doping regime with a more localized state would be reached.

PEM 6-ZGNRs were found to exhibit an interesting feature in the $\uparrow\uparrow$ configuration around $E = -0.5$ eV as the polarization $P(E)$ would reach $\pm 100\%$. This characteristic was found to be displayed by all the structures studied, suggesting that randomness along the edge does not drastically affect this feature. We thus contacted a pristine 6-ZGNR with a [1,1] PEM 6-ZGNR structure to yield a junction. The transmission spectrum of such junction displays hybrid characteristics and the spin filtering could be obtained if one could displace the Fermi energy of 0.5 towards negative energies. This could be done by gating the system.

In the last part of the work, we analysed the impact of fluoranthene-like edges by looking at 13 different topologies for the channel. Within those, we created two groups: the first one containing structures with 1 phenyl group on each edge (OSX) and the second one exhibiting phenyl-edge defects only along one of the two edges (SSX – Y). In the first group, the spin degeneracy was found to be preserved in the $\uparrow\downarrow$ configuration. The relative distance between the groups, do yield a non-negligible influence on the transport properties which suggests weak interactions between opposite edge. In the $\uparrow\uparrow$ configuration, the OS0 and OS4 structures were found to exhibit the best spin-filtering characteristic.

For SSX – Y structures, we first analysed SS1 which yields only one phenyl along one edge. We saw that in this case, only spin- $\uparrow$ electrons possess a localized state around 0.1 eV. In the $\uparrow\downarrow$ configuration, spin degeneracy was unsurprisingly lifted. The effect on the majority channel is far from being negligible but minority electrons exhibit the highest decrease in conductance. In the $\uparrow\uparrow$ configuration, it was found that the spin- $\uparrow$ conductance shows an extinction at $E = -0.286$ eV. The spin- $\downarrow$ channel also experiences such feature at $E = 0.046$ eV. This suggests that low gating voltage and bias may lead to spin filtering devices.

Finally, we increased the number of phenyl groups along the given edge to two, looking at the SS2–Y structures. It was found that when the phenyl were close, the spin- $\uparrow$ channel would be affected in a greater way than before. Reversely, when they are sufficiently driven apart, the spin- $\uparrow$ channel tends to recover, especially between -0.5 and -0.26 eV where it nearly reaches the plateau of $2g_0$. This plateau is found to be narrower than in the pristine case. However, this is probably due to the shift in electronic chemical potential and not to the introduction of back-scattering center.

As a general rule, we saw that spin channels associated with a given edge¹ would experience strong back-scattering at a resonant energy of $E = -0.48$ eV. The more the phenyl groups along this edge, the stronger back-scattering electron would experience.

For the $\uparrow\uparrow$ configuration of SS2–Y structures, we observed that similarly to SS1, the spin- $\uparrow$ (spin- $\downarrow$) channel experiences a diminution of its conductance below (above) the Fermi energy. Extinction of the conductance happens for both spin channels in most of the structures (except SS2-1 for the spin- $\uparrow$ electrons and SS2-3 for the spin- $\downarrow$ electrons). Globally, those "conductance wells" were found to be wider as the number of phenyl groups was brought from 1 to 2.

¹A spin channel is said to be associated with a given edge when the polarization of the edge is parallel to the spins.

In the body of this thesis, we discussed briefly about the shortcoming of DFT. We especially considered the band-gap underestimation problem. It is also worth to discuss about the limitations of our quantum transport model. Indeed, **TransSIESTA** does not implement complex interactions such as electron-electron or electron-phonon interactions. Does that mean that our results are meaningless ? We ought to believe the answer to be "no" and think that even if our computational methods do not capture the whole physics, they do expose some realistic features.

In conclusion to this work, we see that edge-engineering of GNRs could provide a powerful tool to tailor the properties of such nanostructures. Other works actually go towards this direction [42] [43]. For our structures, the biggest challenges probably lay in the stabilization of one magnetic state over the other. Interactions with the substrate or doping might be part of the answer.

Further investigation in the field has to be done for further understanding of such complex structures. Inside those possible paths lay the analysis of the effect of non-uniform distribution of phenyl groups on the energy and bandwidth of the localized state, the study of other edge topologies for transport properties and the investigation of interactions with substrates to stabilize magnetic ordering. Of course, this list is far from being exhaustive.

We hope that the results we presented here will contribute to pave the way to the computational and experimental study of transport properties of phenyl-edge modified ZGNRs.

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A

Hohenberg-Kohn Theorems

A.1 First Theorem

The first theorem states:

The ground state density $n(\mathbf{r})$ of a many-electron system determines uniquely the external potential $V(\mathbf{r})$ up to a constant.

We first consider two systems that only differ by their one-body potential. Note that we do not need to specify any particular analytical expression for the potentials V and U . The only consideration we make is that the ground-states are non-degenerated. Those systems are pictured by the labels "1" and "2" so that

$$\hat{H}_1 = \left[-\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N V_1(\mathbf{r}_i) + \sum_{i=1}^N \sum_{j<i} U(\mathbf{r}_i, \mathbf{r}_j) \right] \quad (\text{A.1})$$

$$\hat{H}_2 = \left[-\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N V_2(\mathbf{r}_i) + \sum_{i=1}^N \sum_{j<i} U(\mathbf{r}_i, \mathbf{r}_j) \right] \quad (\text{A.2})$$

To the ground-state wavefunction ψ_1 (ψ_2) of the first (second) system is associated a ground-state energy E_1 (E_2)

$$\begin{aligned} \hat{H}_1 \psi_1 &= E_1 \psi_1 \\ \hat{H}_2 \psi_2 &= E_2 \psi_2 \end{aligned} \quad (\text{A.3})$$

It is obvious that, since we defined the Hamiltonians to differ only by their one-body potential, the difference between $\hat{H}_1$ and $\hat{H}_2$ lays in the definition of V_1 and V_2 . Since the one-body potential defines the Hamiltonian and since the Hamiltonian defines the ground-state of the system, the one-body potential defines the ground-state and thus the ground-state wavefunction.

If we call $\mathcal{V}$ the ensemble of one-body potentials that differ more than just by a spatial constant¹ and $\mathcal{W}$, the ensemble of the ground-state wavefunctions, we can say that there exists a mapping A , such that

$$A : \mathcal{V} \longrightarrow \mathcal{W} \quad (\text{A.4})$$

A is surjective by construction since $\mathcal{W}$ collects all the ground-states wave-functions defined by the Hamiltonian, itself defined by the one-body potential. We now proof that if $\mathcal{V}$ is defined to be the ensemble of one-body potentials that differ more than just by a spatial constant, then the mapping A is also injective and thus, bijective.

¹This "up to a constant" consideration will be explained further.

Proof : We consider the Hamiltonians $\hat{H}_1$ and $\hat{H}_2$ to share a common ground-state wavefunction ψ . In that case, one can write

$$\left[-\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N V_1(\mathbf{r}_i) + \sum_{i=1}^N \sum_{j<i}^N U(\mathbf{r}_i, \mathbf{r}_j) \right] \psi = E_1 \psi \quad (\text{A.5})$$

$$\left[-\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N V_2(\mathbf{r}_i) + \sum_{i=1}^N \sum_{j<i}^N U(\mathbf{r}_i, \mathbf{r}_j) \right] \psi = E_2 \psi \quad (\text{A.6})$$

so that the difference gives

$$\left[\sum_{i=1}^N (V_1(\mathbf{r}_i) - V_2(\mathbf{r}_i)) + (E_1 - E_2) \right] \psi = 0 \quad (\text{A.7})$$

Fixing the position of electrons 2, ..., N, for "well-behaved" wavefunctions² we get

$$V_1(\mathbf{r}_1) - V_2(\mathbf{r}_1) = \left[\sum_{i=2}^N (V_1(\mathbf{r}_i) - V_2(\mathbf{r}_i)) + (E_1 - E_2) \right] \quad (\text{A.8})$$

Hence, if two (non-degenerated ground-states) Hamiltonians, that differ only by their one-body potential V , share the same ground state wave-function ψ , then

$$V_1 = V_2 + \text{constant} \quad (\text{A.9})$$

The corollary is

If $V_1 \neq V_2 + \text{constant}$, then the two ground-state wavefunctions ψ_1 and ψ_2 cannot be the same.
 $\rightarrow A$ is also injective.

Q.E.D.

The mapping A being bijective (injective and surjective), the inverse mapping exists

$$A^{-1} : \mathcal{W} \longrightarrow \mathcal{V} \quad (\text{A.10})$$

which means that for a given ground-state wavefunction ψ , we can associate one and only one one-body potential V (up to one constant).

We now define a mapping Q associating a wavefunction in $\mathcal{W}$ to a ground-state electronic density belonging to the set of the ground-state electronic densities $\mathcal{N}$.

$$Q : \mathcal{W} \longrightarrow \mathcal{N} \quad (\text{A.11})$$

By definition, Q is surjective (the set $\mathcal{N}$ is constructed exclusively thanks to the set $\mathcal{W}$). We will now proof that Q is also injective, so that Q is invertible.

Proof : We consider two systems so that they have different ground-states (as shown before, those systems have different potentials that differ more than just a simple spatial constant). Considering that our ground-states are normalized³, we have that

$$E_1 = \langle \psi_1 | \hat{H}_1 | \psi_1 \rangle \quad (\text{A.12})$$

Using the variational principle, we can write

$$E_1 = \langle \psi_1 | \hat{H}_1 | \psi_1 \rangle < \langle \psi_2 | \hat{H}_1 | \psi_2 \rangle \quad (\text{A.13})$$

²One could argue about the fact that is ψ goes to zero, then the two potential could be different.

³If the state is not normalized, the expression reads $E_1 = \langle \psi_1 | \hat{H}_1 | \psi_1 \rangle / \langle \psi_1 | \psi_1 \rangle$.

If not, we would have that ψ_2 is the ground-state of the potential V_1 , which does not respect our working hypothesis. We now develop the right hand-side of the inequality

$$\begin{aligned}\langle \psi_2 | \hat{H}_1 | \psi_2 \rangle &= \langle \psi_2 | \hat{H}_2 | \psi_2 \rangle + \langle \psi_2 | \hat{H}_1 - \hat{H}_2 | \psi_2 \rangle \\ &= E_2 + \int (V_1(\mathbf{r}) - V_2(\mathbf{r})) n_2(\mathbf{r}) d\mathbf{r}\end{aligned}\tag{A.14}$$

So that we get

$$E_1 < E_2 + \int (V_1(\mathbf{r}) - V_2(\mathbf{r})) n_2(\mathbf{r}) d\mathbf{r}\tag{A.15}$$

Symmetrically, we have

$$E_2 < E_1 + \int (V_2(\mathbf{r}) - V_1(\mathbf{r})) n_1(\mathbf{r}) d\mathbf{r}\tag{A.16}$$

We now sum the two expressions so that

$$0 < \int (V_1(\mathbf{r}) - V_2(\mathbf{r})) (n_2(\mathbf{r}) - n_1(\mathbf{r})) d\mathbf{r}\tag{A.17}$$

The end of the demonstration is pretty straightforward. Indeed, using *reductio ad absurdum*, we see that introducing $n_2(\mathbf{r}) = n_1(\mathbf{r})$ leads to $0 < 0$, which is obviously wrong. Hence, two different ground-state wavefunctions ψ_1 and ψ_2 cannot be associated with the same ground-state electronic density. Q is also injective.

Q.E.D.

The map Q is then bijective (injective and surjective) so that this mapping is invertible

$$Q^{-1} : \mathcal{N} \longrightarrow \mathcal{W}\tag{A.18}$$

Using the composition of maps, we get that

$$(AQ)^{-1} : \mathcal{N} \longrightarrow \mathcal{V}\tag{A.19}$$

is a proper bijective map.

Hence, to one given ground-state electronic density $n(\mathbf{r})$, there exists one and only one associated one-body potential $V(\mathbf{r})$ (up to a constant). We say that V is a *functional* (this is why the theory is called *Density Functional Theory*) of the ground-state electronic density and write

$$V = V[n(\mathbf{r})]\tag{A.20}$$

If we fix a condition to avoid a spatial constant ambiguity in V , then the ground-state energy become uniquely defined and the electronic energy is also a functional of the density.

$$E = E[n(\mathbf{r})]\tag{A.21}$$

Actually, having proven that the ground-state wavefunction is a functional of the ground-state electronic density, we have that for any observable O associated with its operator $\hat{O}$, the ground-state expectation value of this observable is also a functional of $n(\mathbf{r})$.

$$O[n(\mathbf{r})] = \langle \psi[n(\mathbf{r})] | \hat{O} | \psi[n(\mathbf{r})] \rangle\tag{A.22}$$

which justifies clearly

$$E[n(\mathbf{r})] = \langle \psi[n(\mathbf{r})] | \hat{H} | \psi[n(\mathbf{r})] \rangle\tag{A.23}$$

A.2 Second Theorem

The second theorem states:

We can obtain the ground-state energy variationally: the density which minimizes the total energy is the exact ground-state density.

We write our Hamiltonian as

$$\hat{H} = \hat{F} + \hat{V} \quad (\text{A.24})$$

where the operator $\hat{F}$,

$$\hat{F} = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N \sum_{j<i}^N U(\mathbf{r}_i, \mathbf{r}_j) \quad (\text{A.25})$$

contains the kinetic energy of the electrons and the electron-electron interactions. The operator $\hat{V}$ is simply $\sum_i V(\mathbf{r}_i)$.

The energy is a functional of the electronic density $n(\mathbf{r})$ so that

$$\begin{aligned} E[n(\mathbf{r})] &= \langle \psi[n(\mathbf{r})] | \hat{H} | \psi[n(\mathbf{r})] \rangle \\ &= \langle \psi[n(\mathbf{r})] | \hat{F} | \psi[n(\mathbf{r})] \rangle + \langle \psi[n(\mathbf{r})] | \hat{V} | \psi[n(\mathbf{r})] \rangle \\ &= \langle \psi[n(\mathbf{r})] | \hat{F} | \psi[n(\mathbf{r})] \rangle + \int V(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \end{aligned} \quad (\text{A.26})$$

where $n(\mathbf{r})$ is a given electronic density. In the last line, we used

$$\langle \psi[n(\mathbf{r})] | \hat{V} | \psi[n(\mathbf{r})] \rangle = \int V(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \quad (\text{A.27})$$

which is not complicated to prove yet not obvious. To prove it, we just need to develop the expression. By definition $\langle \Psi | \hat{V} | \Psi \rangle$ is

$$\langle \Psi | \hat{V} | \Psi \rangle = \int \Psi^*(\mathbf{r}_1, \dots, \mathbf{r}_N) \left[\sum_i V(\mathbf{r}_i) \right] \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) d\mathbf{r}_1 \dots d\mathbf{r}_N \quad (\text{A.28})$$

so that

$$\begin{aligned} \langle \Psi | \hat{V} | \Psi \rangle &= \sum_i \int \Psi^*(\mathbf{r}_1, \dots, \mathbf{r}_N) V(\mathbf{r}_i) \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) d\mathbf{r}_1 \dots d\mathbf{r}_N \\ &= \int \Psi^*(\mathbf{r}_1, \dots, \mathbf{r}_N) V(\mathbf{r}_1) \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) d\mathbf{r}_1 \dots d\mathbf{r}_N + \dots \\ &\quad + \int \Psi^*(\mathbf{r}_1, \dots, \mathbf{r}_N) V(\mathbf{r}_N) \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) d\mathbf{r}_1 \dots d\mathbf{r}_N \\ &= \int V(\mathbf{r}_1) d\mathbf{r}_1 \int \Psi^*(\mathbf{r}_1, \dots, \mathbf{r}_N) \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) d\mathbf{r}_2 \dots d\mathbf{r}_N + \dots \\ &\quad + \int V(\mathbf{r}_N) d\mathbf{r}_N \int \Psi^*(\mathbf{r}_1, \dots, \mathbf{r}_N) \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) d\mathbf{r}_1 \dots d\mathbf{r}_{N-1} \\ &= \sum_i \int V(\mathbf{r}_i) \frac{1}{N} n(\mathbf{r}_i) d\mathbf{r}_i \\ &= \int V(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \end{aligned} \quad (\text{A.29})$$

Using the variational principle, one can write

$$\langle \psi_0 | \hat{H} | \psi_0 \rangle < \langle \psi | \hat{H} | \psi \rangle \quad (\text{A.30})$$

which can be rewritten, using the functional characteristic of the wave-function:

$$\langle \Psi[n_0(\mathbf{r})] | \hat{H} | \Psi[n_0(\mathbf{r})] \rangle < \langle \Psi[n(\mathbf{r})] | \hat{H} | \Psi[n(\mathbf{r})] \rangle \quad (\text{A.31})$$

with $n_0(\mathbf{r})$ the electronic ground-state density and $n(\mathbf{r})$ an electronic density which is *not* the ground-state density. And thus

$$E[n_0(\mathbf{r})] < E[n(\mathbf{r})] \quad (\text{A.32})$$

We have proven that the minimum energy is obtained when, plugging different densities $n(\mathbf{r})$, the energy functional is minimized.

B

Extra Computation

B.1 Functional Analysis

We define a functional F such that

$$F[n] = \int g(\mathbf{r})n(\mathbf{r})d\mathbf{r} \quad (\text{B.1})$$

The functional derivative is defined by the variation of that functional

$$\delta F[n] = F[n + \delta n] - F[n] = \int \frac{\delta F}{\delta n(\mathbf{r})} \delta n(\mathbf{r}) d\mathbf{r} \quad (\text{B.2})$$

where $\frac{\delta F}{\delta n(\mathbf{r})}$ is the functional derivative. For our type of functional, we can apply the definition

$$\begin{aligned} \delta F[n] &= F[n + \delta n] - F[n] \\ &= \int g(\mathbf{r})(n(\mathbf{r}) + \delta n(\mathbf{r}))d\mathbf{r} - \int g(\mathbf{r})n(\mathbf{r})d\mathbf{r} \\ &= \int g(\mathbf{r})\delta n(\mathbf{r})d\mathbf{r} \end{aligned} \quad (\text{B.3})$$

so that, by identification, we find

$$\frac{\delta F}{\delta n(\mathbf{r})} = g(\mathbf{r}) \quad (\text{B.4})$$

B.2 Exchange-Correlation and LDA

In the LDA, the exchange-correlation energy E_{XC} can be computed with high precision. The expression of E_{XC} is then given by

$$E_{XC}[n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})] = \int n(\mathbf{r}) \left(\epsilon_X^{hom}[n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})] + \epsilon_C^{hom}[n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})] \right) d\mathbf{r} \quad (\text{B.5})$$

where we have assumed the axis of quantization of the spins to be the same throughout the material¹. Note that we take into account spin polarization and that the functional has been split in an exchange part and a correlation part.

We first consider the non-polarized case which is written

$$E_{XC}[n(\mathbf{r})] = \int n(\mathbf{r}) \left(\epsilon_X^{hom}[n(\mathbf{r})] + \epsilon_C^{hom}[n(\mathbf{r})] \right) d\mathbf{r} \quad (\text{B.6})$$

Looking at the exchange term, we define

$$E_X[n(\mathbf{r})] = \int n(\mathbf{r}) \epsilon_X^{hom}[n(\mathbf{r})] d\mathbf{r} \quad (\text{B.7})$$

¹When the axis of quantization of the spins is the same everywhere, we say that they are collinear. However, non-collinear spin configurations might also be possible.

From the theory of the homogeneous electron gas, we have

$$\epsilon_X^{hom}[n(\mathbf{r})] = Cn(\mathbf{r})^{1/3} \quad \text{with} \quad C = -\frac{3}{4\pi}(3\pi^2)^{1/3} \quad (\text{B.8})$$

The differential of the functional E_X is given by

$$\begin{aligned} \delta E_X[n(\mathbf{r})] &= E_X[n(\mathbf{r}) + \delta n(\mathbf{r})] - E_X[n(\mathbf{r})] \\ &= \int \left((n(\mathbf{r}) + \delta n(\mathbf{r})) \epsilon_X[n(\mathbf{r}) + \delta n(\mathbf{r})] - n(\mathbf{r}) \epsilon_X[n(\mathbf{r})] \right) d\mathbf{r} \end{aligned} \quad (\text{B.9})$$

where we have

$$\begin{aligned} \epsilon_X[n(\mathbf{r}) + \delta n(\mathbf{r})] &= C(n(\mathbf{r}) + \delta n(\mathbf{r}))^{1/3} \\ &= Cn(\mathbf{r})^{1/3} \left(1 + \frac{\delta n(\mathbf{r})}{n(\mathbf{r})} \right)^{1/3} \\ &= Cn(\mathbf{r})^{1/3} \left(1 + \frac{1}{3} \frac{\delta n(\mathbf{r})}{n(\mathbf{r})} \right) \\ &= Cn(\mathbf{r})^{1/3} + \frac{1}{3} Cn(\mathbf{r})^{-2/3} \delta n(\mathbf{r}) \end{aligned} \quad (\text{B.10})$$

so that

$$\begin{aligned} (n(\mathbf{r}) + \delta n(\mathbf{r})) \epsilon_X[n(\mathbf{r}) + \delta n(\mathbf{r})] &= (n(\mathbf{r}) + \delta n(\mathbf{r})) \left(Cn(\mathbf{r})^{1/3} + \frac{1}{3} Cn(\mathbf{r})^{-2/3} \delta n(\mathbf{r}) \right) \\ &= Cn(\mathbf{r})^{4/3} + \frac{1}{3} Cn(\mathbf{r})^{1/3} \delta n(\mathbf{r}) + Cn(\mathbf{r})^{1/3} \delta n(\mathbf{r}) \\ &\quad + \frac{1}{3} Cn(\mathbf{r})^{-2/3} \delta n(\mathbf{r})^2 \\ &= Cn(\mathbf{r})^{4/3} + \frac{4}{3} Cn(\mathbf{r})^{1/3} \delta n(\mathbf{r}) \end{aligned} \quad (\text{B.11})$$

where we took the limit where $\delta n \rightarrow 0$ so that the term proportional to δn^2 vanishes. We also notice that the first term is just $n(\mathbf{r}) \epsilon_X^{hom}[n(\mathbf{r})]$ so that the integral reads

$$\delta E_X[n(\mathbf{r})] = \int \frac{4}{3} Cn(\mathbf{r})^{1/3} \delta n(\mathbf{r}) d\mathbf{r} \quad (\text{B.12})$$

Using the basics of functional analysis, we identify

$$V_X[n(\mathbf{r})] = \frac{\delta E_X[n(\mathbf{r})]}{\delta n(\mathbf{r})} = \frac{4}{3} Cn(\mathbf{r})^{1/3} = \frac{4}{3} \epsilon_X^{hom}[n(\mathbf{r})] \quad (\text{B.13})$$

For the correlation part, we have

$$E_C[n(\mathbf{r})] = \int V_C(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \quad (\text{B.14})$$

which implies, as seen before,

$$\frac{\delta E_C[n(\mathbf{r})]}{\delta n(\mathbf{r})} = V_C(\mathbf{r}) \quad (\text{B.15})$$

in another fashion, one can write

$$E_C[n(\mathbf{r})] = \int \epsilon_C[n(\mathbf{r})] n(\mathbf{r}) d\mathbf{r} \quad (\text{B.16})$$

so that

$$\begin{aligned}
 \delta E_C[n(\mathbf{r})] &= E_C[n(\mathbf{r}) + \delta n(\mathbf{r})] - E_C[n(\mathbf{r})] \\
 &= \int \epsilon_C[n(\mathbf{r}) + \delta n(\mathbf{r})](n(\mathbf{r}) + \delta n(\mathbf{r})) - \epsilon_C[n(\mathbf{r})]n(\mathbf{r}) d\mathbf{r} \\
 &= \int (\epsilon_C[n(\mathbf{r})] + \delta \epsilon_C[n(\mathbf{r})])(n(\mathbf{r}) + \delta n(\mathbf{r})) - \epsilon_C[n(\mathbf{r})]n(\mathbf{r}) d\mathbf{r}
 \end{aligned} \tag{B.17}$$

neglecting the products of deltas, we find

$$\begin{aligned}
 \delta E_C[n(\mathbf{r})] &= \int (\epsilon_C[n(\mathbf{r})]\delta n(\mathbf{r}) + \delta \epsilon_C[n(\mathbf{r})]n(\mathbf{r})) d\mathbf{r} \\
 &= \int \delta(n(\mathbf{r})\epsilon_C[n(\mathbf{r})]) d\mathbf{r} \\
 &= \int \frac{\delta(n(\mathbf{r})\epsilon_C[n(\mathbf{r})])}{\delta n(\mathbf{r})} \delta n(\mathbf{r}) d\mathbf{r}
 \end{aligned} \tag{B.18}$$

so that we get, by identification,

$$V_C(\mathbf{r}) = \frac{\delta(n(\mathbf{r})\epsilon_C[n(\mathbf{r})])}{\delta n(\mathbf{r})} = \epsilon_C[n(\mathbf{r})] + n(\mathbf{r}) \frac{\delta(\epsilon_C[n(\mathbf{r})])}{\delta n(\mathbf{r})} \tag{B.19}$$

The exact expression of $\epsilon_C[n(\mathbf{r})]$ cannot be found analytically and numerical methods have to be used. As example, we cite the work of Perdew-Zunger [44].

B.3 Useful Relations

B.3.1 First Relation

The time-independent Schrödinger equation with the influence of the leads through $\hat{\Sigma}$ and a source term $|s\rangle$ reads

$$[\hat{H} + \hat{\Sigma}]|\psi_d\rangle = E|\psi_d\rangle - |s\rangle \tag{B.20}$$

The retarded Green's function $\hat{G}^R$ relates the wavefunction $|\psi_d\rangle$ to the source $|s\rangle$

$$|\psi_d\rangle = \hat{G}^R |s\rangle \tag{B.21}$$

with $\hat{G}^R = [E\hat{I} - \hat{H} - \hat{\Sigma}]^{-1}$. In the same way, we define the advanced Green's function $\hat{G}^A$

$$\langle \psi_d | = \langle s | \hat{G}^A \tag{B.22}$$

Therefore, $\hat{G}^n$ can be written as

$$\begin{aligned}
 \hat{G}^n &= 2\pi |\psi_d\rangle \langle \psi_d| \\
 &= 2\pi \hat{G}^R |s\rangle \langle s| \hat{G}^A \\
 &= \hat{G}^R \hat{\Sigma}^{in} \hat{G}^A
 \end{aligned} \tag{B.23}$$

where we identified $2\pi |s\rangle \langle s| = \hat{\Sigma}^{in}$.

B.3.2 Second Relation

The retarded Green's function $\hat{G}^R$ is defined by the relation

$$\left[\hat{G}^R\right]^{-1} = E\hat{I} - \hat{H} - \hat{\Sigma} \quad (\text{B.24})$$

so that

$$\left[\left[\hat{G}^R\right]^{-1}\right]^\dagger = E\hat{I} - \hat{H} - \hat{\Sigma}^\dagger \quad (\text{B.25})$$

since the Hamiltonian is Hermitian.

As the conjugate transpose of the inverse is equal to the inverse of the conjugate transpose, we can write

$$\left[\left[\hat{G}^R\right]^\dagger\right]^{-1} = \left[\hat{G}^A\right]^{-1} = E\hat{I} - \hat{H} - \hat{\Sigma}^\dagger \quad (\text{B.26})$$

so that the difference gives

$$\left[\hat{G}^A\right]^{-1} - \left[\hat{G}^R\right]^{-1} = -\hat{\Sigma}^\dagger + \hat{\Sigma} = -i\Gamma \quad (\text{B.27})$$

We now multiply this expression by $\hat{G}^A$ by the left and $\hat{G}^R$ by the right. Actually, one could also take the product with $\hat{G}^R$ on the left and $\hat{G}^A$ on the right. This gives the following double equality

$$\hat{G}^R - \hat{G}^A = -i\hat{G}^A\Gamma\hat{G}^R = -i\hat{G}^R\Gamma\hat{G}^A \quad (\text{B.28})$$

Recalling $\hat{A} = i(\hat{G}^R - \hat{G}^A)$, we can write

$$\hat{A} = \hat{G}^A\Gamma\hat{G}^R = \hat{G}^R\Gamma\hat{G}^A \quad (\text{B.29})$$

C

Phenyl Edge-Modified 6-ZGNRs: supplementary figures

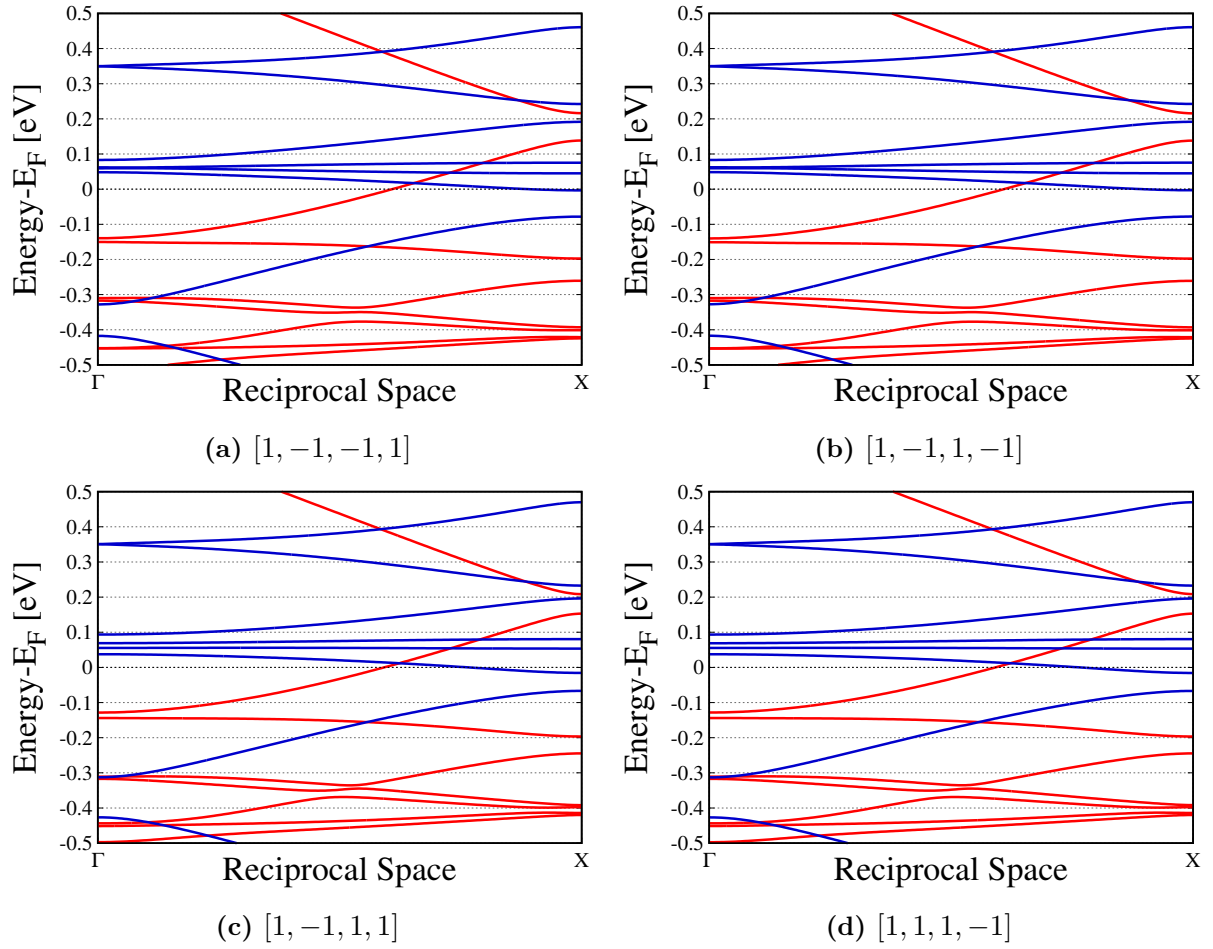


Figure C.1: Electronic band structure of the PEM 6-ZGNRs of size $N=2$ in the $\uparrow\uparrow$ configuration for the (a) $[1, -1, -1, 1]$, (b) $[1, -1, 1, -1]$, (c) $[1, -1, 1, 1]$ and (d) $[1, 1, 1, -1]$ structures. The spin degeneracy is left. The red (blue) curve stands for spin majority (minority) electrons.

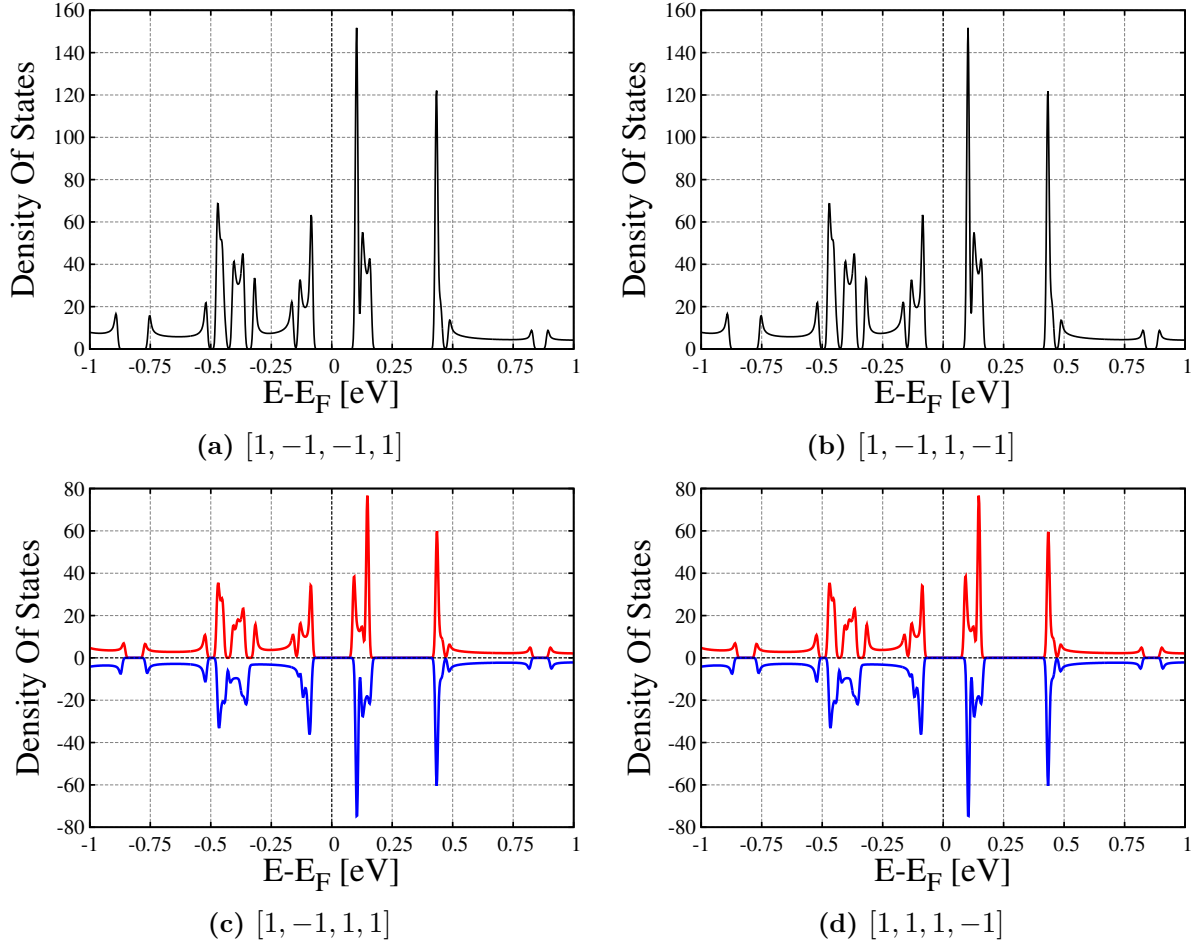


Figure C.2: Density of states of phenyl edge-modified 6-ZGNRs of size $N=2$ in the $\uparrow\downarrow$ configuration for the (a) $[1, -1, -1, 1]$, (b) $[1, -1, 1, -1]$, (c) $[1, -1, 1, 1]$ and (d) $[1, 1, 1, -1]$ structures. For (a) and (b), the spin degeneracy is kept so that the total density of state is displayed. For (c) and (d), spin degeneracy is lifted. The red (blue) curve stands for spin majority (minority) electrons.

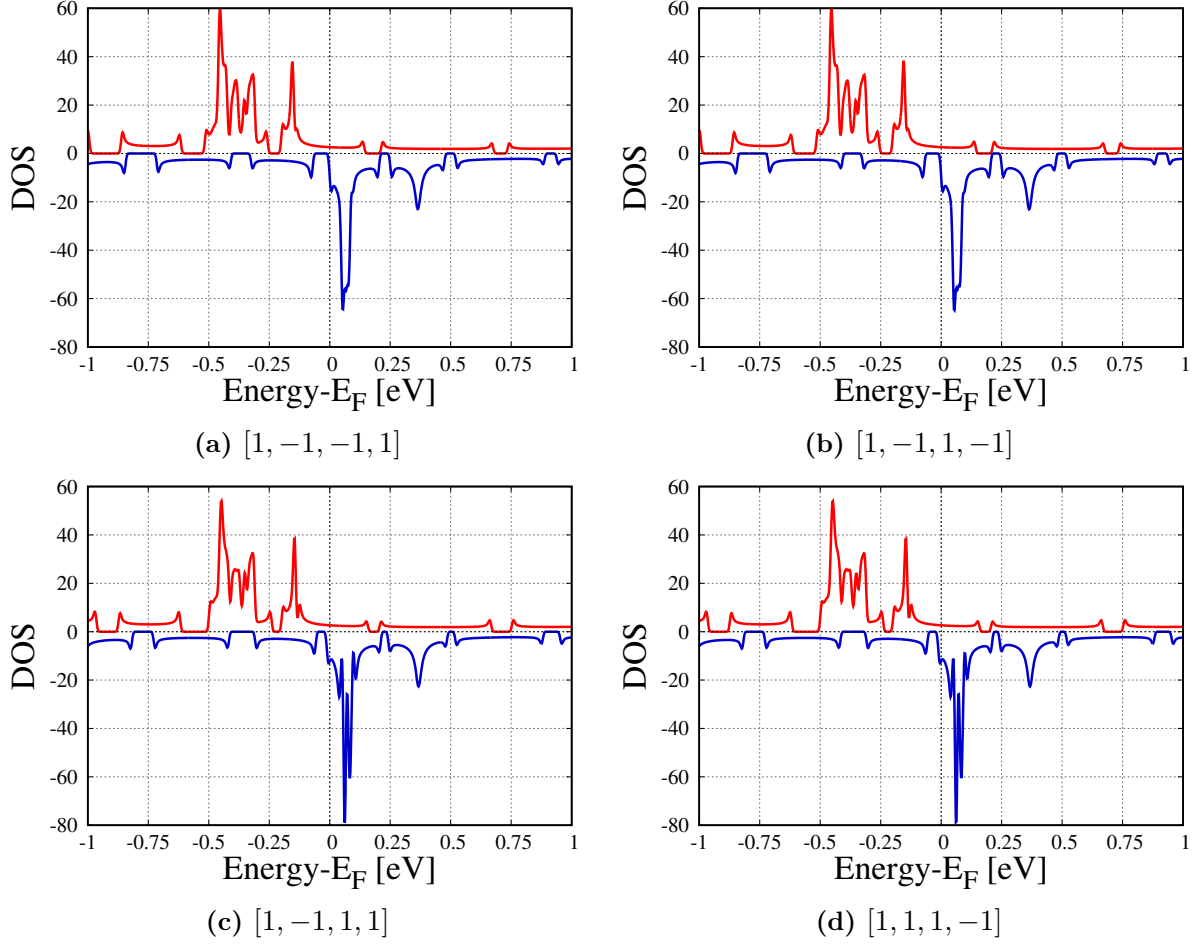


Figure C.3: Density of states of phenyl edge-modified 6-ZGNRs of size $N=2$ in the $\uparrow\uparrow$ configuration for the (a) $[1, -1, -1, 1]$, (b) $[1, -1, 1, -1]$, (c) $[1, -1, 1, 1]$ and (d) $[1, 1, 1, -1]$ structures. The red (blue) curve stands for spin majority (minority) electrons.

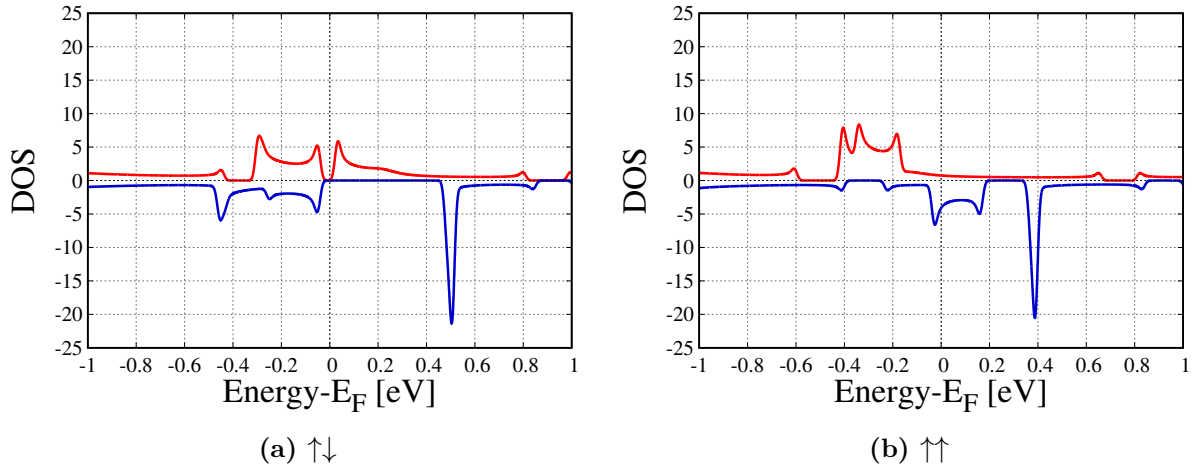


Figure C.4: DOS for the OEPem 6-ZGNRs structures in (a) $\uparrow\downarrow$ and (b) $\uparrow\uparrow$ configuration. Red (blue) curves stand for majority (minority) electrons.

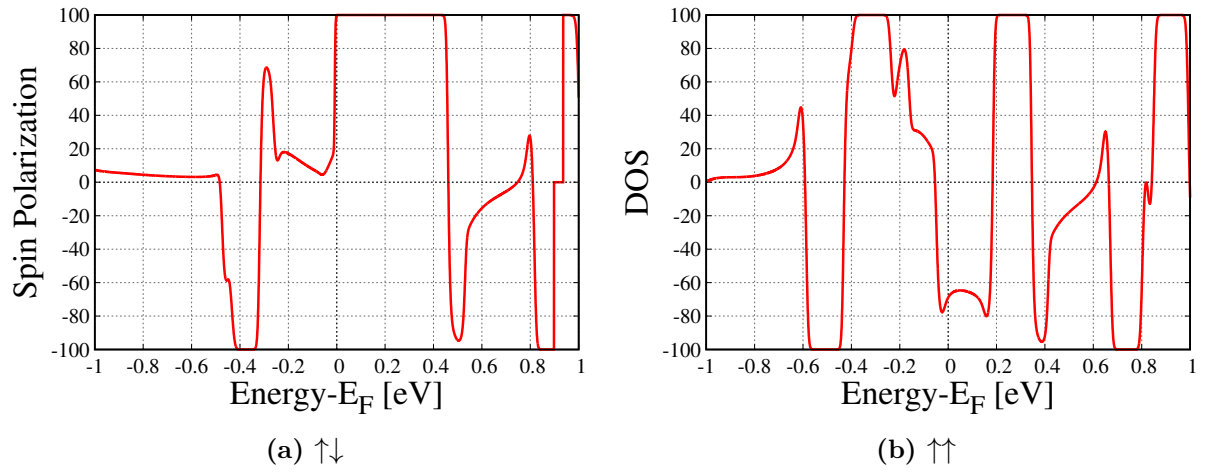


Figure C.5: Spin polarization for the OEPEM 6-ZGNRs structures in (a) $\uparrow\downarrow$ and (b) $\uparrow\uparrow$ configuration.

D

Effect of Fluoranthene-like Edges on the Transport Properties of 6-ZGNRs: supplementary figures

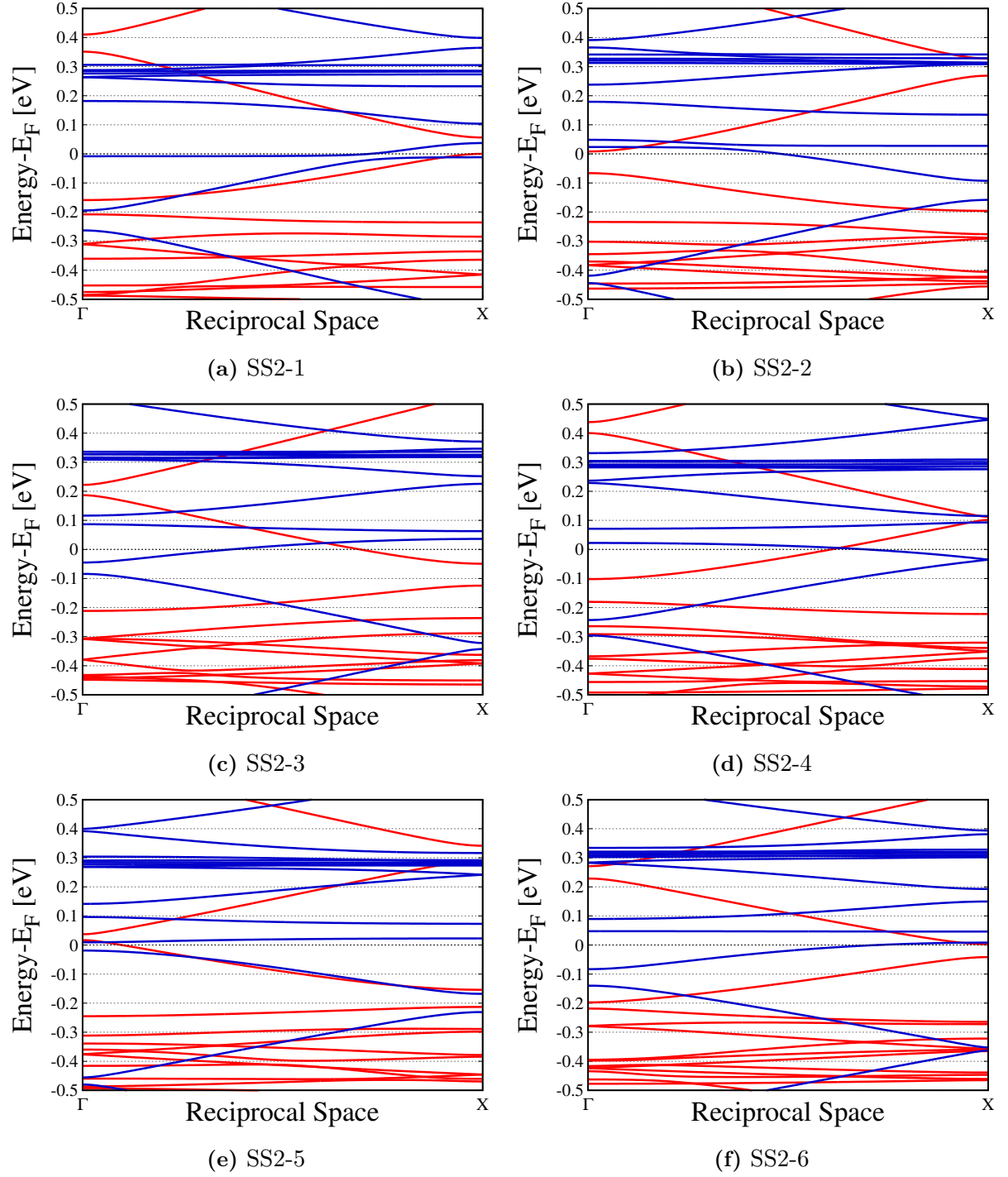


Figure D.1: Electronic band structure of the (a) SS2-1, (b) SS2-2, (c) SS2-3, (d) SS2-4, (e) SS2-5, (f) SS2-6 structures in the $\uparrow\uparrow$ spin configuration. The red (blue) curve stands for spin majority (minority) electrons.

