

**ELECTRON TRANSPORT THROUGH
GRAPHENE STRUCTURES**

By

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Intrinsic graphene is the first atomic monolayer structure produced experimentally. Its unique two dimensional geometric structure along with its electronic structure (Dirac cone) make it an ideal system for the fundamental exploration of novel physics as well as a promising candidate for nanoelectronic applications. In this thesis, we present theoretical studies on electronic transport properties of different graphene structures, including monolayers, bilayers, mono-bilayers and junctions between mono-bilayers and monolayers. These structures can be viewed as a graphene monolayer covered by another layer of different width. Their transport properties are calculated by the Landauer-Buttiker formalism combined with density functional theory. Our results show that, in such a structure, the electronic transport property of the graphene monolayer can be changed considerably if the other layer is a nanoribbon with finite width; however the change is less significant if the other layer is infinite or even semi-infinite. We further show that the difference of the effects between infinite and finite coverage can be attributed to antiresonance in the electronic transmission, which is caused by interlayer interference between the wavefunctions.

Resumen de Disertación Presentado a Escuela Graduada
de la Universidad de Puerto Rico como requisito parcial de los
Requerimientos para el grado de Maestría en Ciencias

TRANSPORTE ELECTRONICO A TRAVEZ DE STRUCTURAS DE GRAFENO

Por

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2012

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Grafeno es de lejos la primera estructura mono-atómica fabricada en el laboratorio. Esta única estructura bidimensional posee una estructura electrónica (Cono de Dirac) que hace de esta un sistema, ideal para exploración en física básica y un prominente candidato para aplicaciones en nano electrónica. En esta tesis se hizo un estudio teórico de las propiedades de transporte electrónico para diferentes estructuras de grafeno como grafeno monocapa, bicapa y aleaciones de grafeno mono -bicapa. Estas estructuras pueden ser consideradas como configuraciones de monocapas de grafeno con un recubrimiento de otra capa de diferentes anchos. En nuestro estudio las propiedades de transporte fueron calculadas combinando el formalismo de Landauer-Buttiker con “Density Functional Theory”. Nuestros resultados muestran que las propiedades electrónicas de transporte en una monocapa de grafeno pueden ser cambiadas considerablemente cuando se añade una capa de ancho finito; sin embargo el efecto es menor cuando el recubrimiento es infinito o semi infinitamente. Esta reducción en la transmisión electrónica es atribuido a fenómenos de antirresonancia entre las funciones de onda de ambas capas.

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Daniel A. Valencia Hoyos

I would like to dedicate this thesis to God, who has supported me throughout my masters

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CHAPTER 1

INTRODUCTION

1.1 QUANTUM TRANSPORT: SMALL IS DIFFERENT

Electron flow through a material has been one of the most important topics in condensed matter physics. One of the first and most well known theories is the Drude model, in which electron flow in a material is considered to be a gas of moving electrons. This theory considers electrons as identical solid spheres that move in straight lines until they collide with one other or with fixed nuclei. The time taken up by a single collision is assumed to be negligible and except for the forces coming momentarily into play during each collision, no other forces are assumed to act on the particles [1]. In general we can say that electrons flow in a random walk through a material with width W and length L . This kind of electron transport is called diffusive transport figure 1–1. in which the conductance G is given by:

$$G = \frac{\sigma W}{L} \quad (1.1)$$

where σ is the electric conductivity that depends on the material and is independent of the dimensions, and W and L the width and length of the sample respectively. However, if the length is reduced to zero, the conductance cannot be modelled by the expression 1.1. This is exactly the case for the nano-transistors on which we will focus in this work.

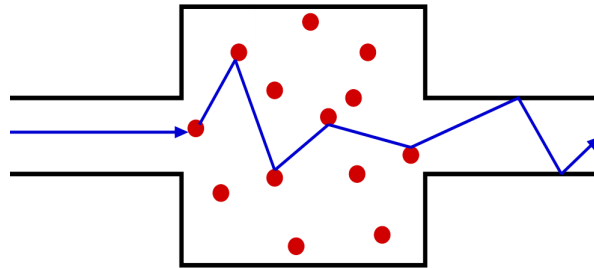


Figure 1–1: Diffusive electronic transport [2].

The field effect transistor was discovered by William Shockley at Bell Labs in 1947. It has opened a new human age called the “Transistor Age” in which the transistor has been the base for the construction of all our electronic devices that have impacted many fields of our society. We constantly want smaller, more powerful and faster electronic devices which implies that transistors have to be miniaturized to fit more into less space. In general, electrons in a transistor flow from the source to the drain through a channel as shown in the figure below, and can be controlled by a potential gate that allows or restricts the electron flow. If the potential difference between the source and the drain is greater than that of the gate potential, electrons flow from source to drain. However, if the potential between the source and drain is less than gate potential, the electrons cannot flow from the source to the drain.

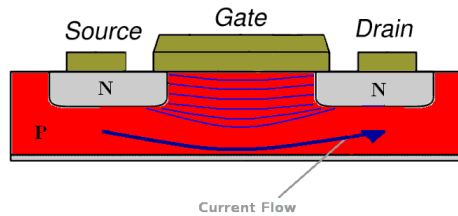


Figure 1–2: Transistor schematic.

High-tech devices have millions of transistors which may be switched on and off in billionths of a second [2]. Twenty years ago computers were less powerful because there were only a million transistors in each. In addition, they switched more slowly. In a few short years, transistors have been reduced to sizes less than $1\ \mu m$, and at these sizes electron flow cannot be considered as diffusive because the free path from the source to the drain is on the order of the electron path. Therefore equation 1.1 cannot apply to these situations. On such a small scale, electrons flow directly without experiencing scattering (“ballistic flow”) and quantum effects that may be neglected in macroscopic models must be considered. The tool introduced to understand ballistic flow is “Quantum Transport Theory” in which quantum phenomena are taken into account using a ballistic electron flow model.

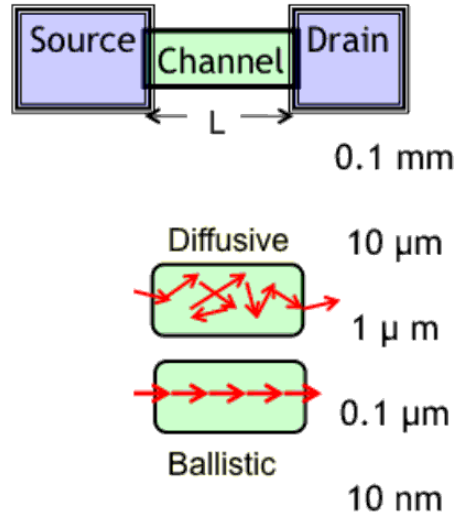


Figure 1–3: Scales of electrons flow [2].

Quantum transport theory was first introduced in the middle of the last century. Since R. Landauer proposed the subtle concept of reservoir, it was named the Landauer formula [3]. Later in 1980s, M. Buttiker developed the Landauer-Buttiker approach [4], which views “conductance as transmission” [5]. This has been very successful and is now the standard approach to quantum transport. The details of the Landauer-Buttiker approach will be discussed in Chapter 3.

1.2 GRAPHENE: THE 2-D MATERIAL THAT SHOULD NOT EXIST

One of the most important elements for life on earth is carbon. Pure carbon only exists naturally in three forms: diamond, carbon black, and graphite. Fortunately carbon is one of the most abundant elements. All life forms are constantly reusing it, creating an infinite cycle that allows life on earth to continue. Carbon has an atomic number of 6, and atomic weight of 12.11 u. Carbon is usually found in combination with other elements in substances such as carbon dioxide, limestone, coal, and petroleum.

Graphite has two crystalline structures alpha (hexagonal) and beta (rhombohedral), both of them with very similar physical properties [6]. The hexagonal graphite may

be either flat or buckled. The alpha form can be converted to the beta form through mechanical treatment, and the beta form reverts to the alpha form when it is heated above 1300 C [7]. Graphite alpha is formed in planar layers, which contributes to its lower density. This material is frequently considered a semimetal. In each layer, the carbon atoms are arranged in a hexagonal lattice with a separation of 142 pm, and a distance between planes of 335 pm [8] (see figure 1–3).

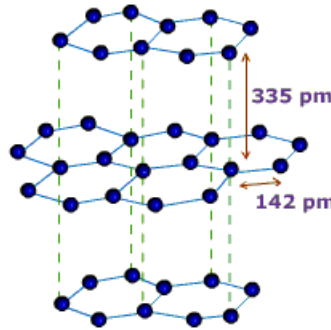


Figure 1–4: Graphite structure.

Our work will focus on a two dimensional, one-atom-thick planar sheet of graphite called “**Graphene**”, a configuration that theoretical physicists believed to be impossible for many years.

Peirles and Landau argued 70 years ago that two dimensional structures cannot exist because they would be thermodynamically unstable [9, 10]. Their theory predicted that thermal fluctuations in low dimensional crystal lattices would generate a displacement of the lattice’s atoms comparable to inter-atomic distances at any finite temperature thereby inducing a unstable configuration. Moreover experimental observation confirmed that the melting temperature of thin films decreases with decreasing thickness, making them unstable and so that they segregate into islands or decompose at a thickness of dozens of atomic layers [11].

For those reasons, the physics community rejected the idea of finding 2D structures. Therefore, isolated structures that are one atom thick were considered impossible until 2004, when a curious 2D structure called graphene was observed in Manchester and

Chernobologka. Professor Geim and his postdoc Novoselov made one of the the biggest discoveries of the decade [12]. From England and Russian institutions, they reported their observation of *“monocrystalline graphitic films, which are a few atoms thick but are nonetheless stable under ambient conditions, metallic, and of remarkably high quality. The two-dimensional structure found presented a semimetal configuration with a tiny overlap between valence and conductance bands.”*

Some images of the first reported graphene structure are shown in Figure 1–5. Geim and his group made this material by mechanical exfoliation of small mesas of highly oriented pyrolytic graphite. By this process they could prepare few-layer graphene films which were placed on top of an oxidized material, generally a silicon oxide substrate (SiO_2). Silicon dioxide has a bandgap larger than 9 eV, so it electrically isolates the graphene and interacted weakly with the graphene, providing nearly charge-neutral graphene layers.

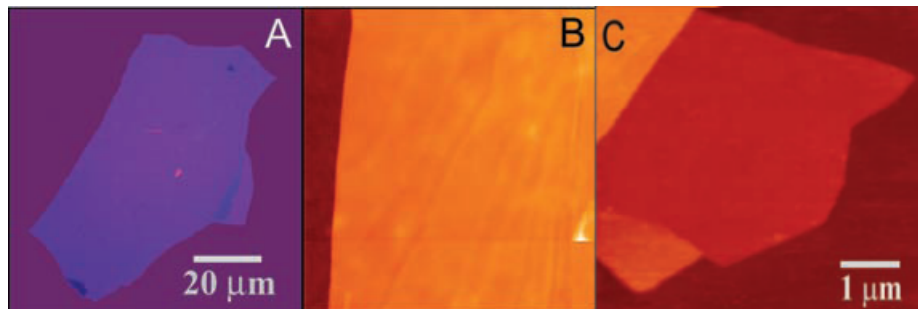


Figure 1–5: Graphene films. (A) Photograph (in normal white light) of a relatively large multilayer graphene flake with thickness 3 nm, (B) Atomic force microscope (AFM) image of $2\mu\text{m}$ by $2\mu\text{m}$ area of this flake near its edge, (C) AFM image of single-layer graphene [15].

The existence of two dimensional structures can be reconciled with the theory due to strong interatomic bonds in graphene atoms which avoid the thermal fluctuations leading to the generation of dislocations or other crystal defects even at elevated temperature. Furthermore 2D crystals are intrinsically stable under weak crumpling in the

third dimension. This three dimensional warping permits the whole system to gain elastic energy and suppress part of the energy of thermal vibrations, making the existence of our two dimensional structure possible[13, 14].

In general, electrons may flow through graphene in two different directions (armchair and zigzag) as seen in figure 1–6. Where one is a 90 degree rotation from the other. It is important to mention that both directions have different electronic transport properties that we are going to study in this work.

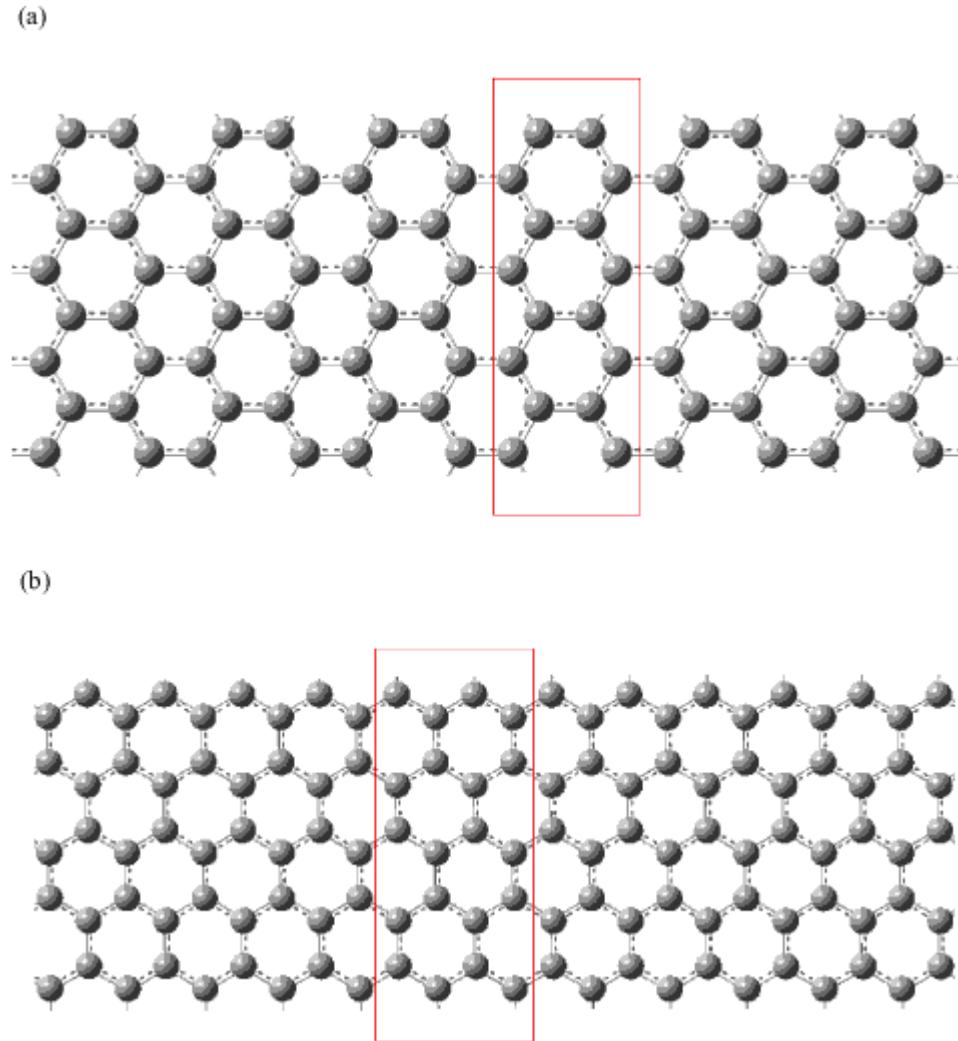


Figure 1–6: Graphene a) armchair and b) zigzag direction

1.2.1 Band Structure of graphene

The unit cell of graphene contains two atoms A and B separated by a distance a and a reciprocal lattice of magnitude $2/(\sqrt{3}a)$. The vector from A to B is constructed from the base vectors $\vec{a}_1$ and $\vec{a}_2$: $\vec{a}_1 = a(\sqrt{3}/2, -1/2)$ y $\vec{a}_2 = a(\sqrt{3}/2, 1/2)$.

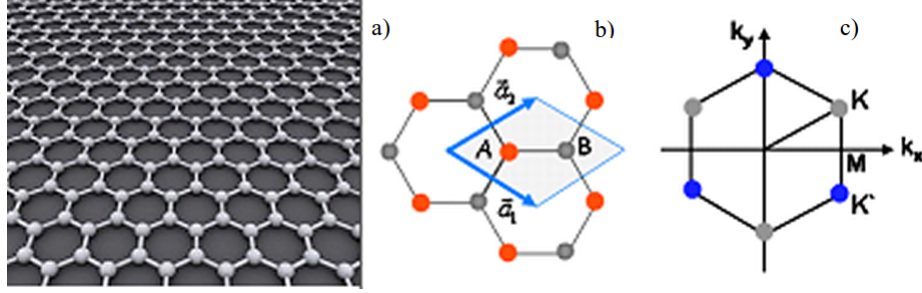


Figure 1-7: a) Graphene structure, b) Unit Cell, and c) reciprocal lattice.

The bloch wave function in the atoms A and B is defined as:

$$\Phi_j = \frac{1}{\sqrt{N}} \sum_{R_\alpha} e^{i\vec{k} \cdot \vec{R}_\alpha} \varphi_j(\vec{r} - \vec{R}_\alpha), \quad (\alpha = A, B) \quad (1.2)$$

where N is a normalizing constant, φ_j is the isolated wave function of each carbon atom, $\vec{R}_\alpha$ is the vector position of each carbon atom, and $\vec{r}$ is any point in space. In tight binding approximation, the interaction is only considered for the nearest-neighbors. In that case the wave function can be approximated as:

$$\psi = \Phi_A + \lambda \Phi_B \quad (1.3)$$

We know that the wave function ψ must satisfy the Schrödinger equation $H\psi = E\psi$. Therefore substituting 1.2 and 1.3 into the Schrödinger equation we get:

$$\begin{aligned} H_{AA} + \lambda H_{AB} &= ES \\ H_{BA} + \lambda H_{BB} &= ES \end{aligned} \quad (1.4)$$

where H_{AA} , H_{BB} , H_{AB} are equal to:

$$\begin{aligned}
H_{AA} &= \frac{1}{N} \sum_{R R'} e^{ik(\vec{R}-\vec{R}')} \langle \varphi_A(\vec{r}-\vec{R}') | H | \varphi_A(\vec{r}-\vec{R}') \rangle \\
&\approx \frac{1}{N} \sum_{R=R'} \epsilon_{2p} + \frac{1}{N} \sum_{R=R' \pm a} e^{ik(\vec{R}-\vec{R}')} \langle \varphi_A(\vec{r}-\vec{R}') | H | \varphi_A(\vec{r}-\vec{R}') \rangle \\
&\approx \epsilon_{2p} + \text{term equal or more distant}
\end{aligned} \tag{1.5}$$

Similarly for H_{BB} , making use of the same order approximation we get $H_{BB} = \epsilon_{2p}$. For the case $H_{AB} = H_{BA}^*$, considering only the three nearest-neighbors of atom B, we get:

$$\begin{aligned}
H_{AB} &= \frac{1}{N} \sum_{R R'} e^{ik(\vec{R}-\vec{R}')} \langle \varphi_A(\vec{r}-\vec{R}') | H | \varphi_B(\vec{r}-\vec{R}') \rangle \\
&\approx t(e^{\vec{k} \cdot \vec{R}_1} + e^{\vec{k} \cdot \vec{R}_2} + e^{\vec{k} \cdot \vec{R}_3}) \\
&\approx t f(k)
\end{aligned} \tag{1.6}$$

with $f(k) = e^{ik_x a / \sqrt{3}} + 2e^{-ik_x a / 2\sqrt{3}} \cos(\frac{k_y a}{2})$ and finally the term S that is usually called the overlapping between the wave function is equal to:

$$S = \langle \varphi_A(\vec{r}-\vec{R}) | \varphi_B(\vec{r}-\vec{R}') \rangle \tag{1.7}$$

Eliminating λ from 1.3 a secular equation is obtained as:

$$\begin{vmatrix} H_{AA} - ES & H_{AB} \\ H_{BA} & H_{BB} - ES \end{vmatrix} = 0 \tag{1.8}$$

Setting the overlapping equal to zero $S = 0$, the energy relation will be [15]:

$$E = \epsilon_{2p} \pm \left\{ 1 + 4\cos\left(\frac{\sqrt{3}k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) + 4\cos^2\left(\frac{k_y a}{2}\right) \right\} \tag{1.9}$$

where the symbol $\pm$ refers to the conduction (+) and the valence (-) band respectively. Since both bands are symmetric over the point ϵ_{2p} it may be neglected, and the

bands can approximated as:

$$E_{\pm} \approx 3t' \pm \hbar v_f |q| - \left(\frac{9t'a^2}{4} \pm \frac{3ta^2}{8} \sin(3\theta_q) \right) |q|^2 \quad (1.10)$$

where $q = \sqrt{k_x^2 + k_y^2}$, $v_f = 3ta/2$ is the fermi velocity, and $\theta_q = \arctan^{-1}[q_x/q_y]$ and t, t' are the nearest neighbor between lattice A-B and next nearest neighbor interlattice A-A and B-B respectively. Experimentally, the values of t, t' are approximately equal to 2.5 eV and 0.1 eV . In long wave approximation, t' is set equal to zero and for small q , the band structure will be:

$$E_{\pm} = \hbar v_f q + \delta(q/k)^2 \quad (1.11)$$

This implies that in the regions around the Fermi energy, the band structure is linear (see figure 1–8) and depends on the Fermi velocity. For $t \approx 2.5\text{ eV}$ and $a = 0.142\text{ nm}$, the Fermi velocity $v_f \approx 10^8\text{ cm/s}$. The experimental and theoretical results imply that electrons in graphene can be described as massless quasiparticles known as “Dirac-Fermions” .

The band structures were calculated many years ago, but were not experimentally confirmed until 2005 when Geim and Novoselov measured the electron rest mass at the Dirac points to be 0.06 times the rest mass. Experimentally, discovery of graphene has provided physicists with a new way to understand quantum electrodynamic (QED) phenomena by measuring graphenes electronic properties . [16]

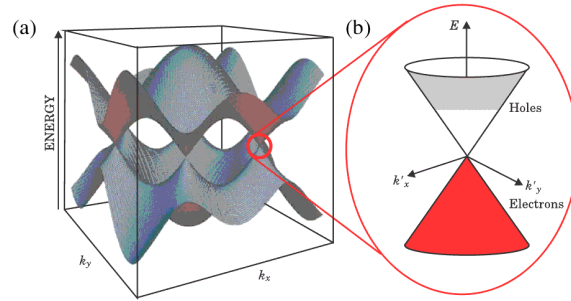


Figure 1–8: a) Graphene band structure, b) Enlargement of the band structure around the points k and k' equal to zero [12].

1.2.2 Some experimental measurements on electronic transport properties of graphene

Graphene has a unique ambipolar electric field effect, which means that it carries electrons and holes in almost the same proportions. For this reason the electric conductivity σ increases linearly with the gate voltage V_g (see figure 1-9) in almost the same proportions for both polarities. Also in regions close to $V_g = 0$, the Hall coefficient ($R_H = 1/ne$) changes its sign due to concentrations of electrons (holes) that are induced by positive (negative) gate voltages.

Away from the transition region $V_g \approx 0$, the Hall coefficient varies as $1/V_g$ and carries a density of $n = \alpha \cdot V_g$ where the value $\alpha \approx 7.3 \cdot 10^{10} \text{ cm}^{-2}/\text{V}$ is in agreement with the theoretical estimation $n/V_g \approx 7.2 \cdot 10^{10} \text{ cm}^{-2}/\text{V}$ [17]. In a similar process, the induced carrier mobility $\mu = \sigma/ne$ was found to be up to $5000 \text{ cm}^2/\text{Vs}$ for both electrons and holes. These measurement also showed a constant mobility for temperatures between 10 and 100K.

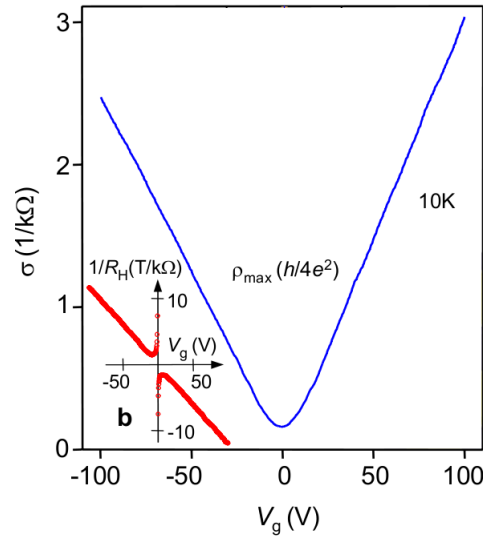


Figure 1-9: Ambipolar electric field effect in single-layer graphene and the Hall effect for different gate voltages [15].

Another interesting result found for the conductivity of graphene (σ) is that it remains finite even as the charge carrier concentration n tends to zero; moreover, its value

approaches quantum conductivity $4e^2/\hbar$. Furthermore, most theories predict a minimum conductivity which is lower than the experimentally observed value by a factor of π . This contradiction is known as the mystery of the missing π and it is still unclear if this is a consequence of theoretical approximations or stems from the limited parameters of experimental procedures.

CHAPTER 2

MOTIVATION

As we mentioned in the section 1.2; graphene is a two-dimensional, one-atom-thick structure that has emerged as an exotic material and received a great deal of scientific attention due to its exceptional physical properties. This material and its derivatives are being studied in nearly every field of science and engineering in applications such as electronic devices, chemical sensors, nanocomposites, and energy storage [18]. The enormous research interest generated by graphene has brought the exploration of different methods of synthesis such as mechanical exfoliation [19], thermal CVD [20], and thermal decomposition on different substrates [21, 22].

In this thesis, our attention will be focused on the electronic transport properties of graphene for applications in nanoelectronic devices. The ability to make graphene-based devices depends on our ability to change or manipulate electronic transport properties of graphene. Unfortunately, a recent study showed that a graphene monolayer will have perfect transmission of charge carriers near the Fermi energy which cannot be changed or controlled by a local electrostatic barrier applied by a gate.[23] This phenomenon is called as Klein paradox or Klein tunneling, which is theoretically interesting as it is related to the chiral nature of the Dirac cone band structures; however it creates application disadvantage as the perfect tunneling may limit the performance of graphene-based electronic devices like diodes and transistors [24]. Recently, a change the electron flow in graphene bilayers has been observed when a gate voltage perpendicular to the structure is introduced [23]. Furthermore, it has been demonstrated that applying an electric field along transverse direction of a bilayer can break symmetry between the two layers and hence change its electronic transport properties.[25]

2.1 Klein tunneling in graphene monolayer

From quantum mechanics, it is well known that electron transmission through a barrier potential V_0 decays exponentially as the potential is increased. However, in 1929 Klein showed that if the barrier potential is higher than the electron rest energy $V_0 > mc^2$, the electron reflection is almost zero and that when the potential V_0 approaches infinity, the barrier becomes totally transparent [26]. The origin of this phenomena is the fact that the electron and the positron are highly correlated particles and are described by different components of the same spinor wavefunction.

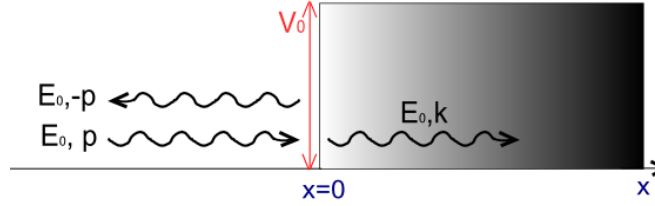


Figure 2–1: Electrons penetrating through barrier potential V_0

This effect has never been observed experimentally because of the huge electronic field required ($V_0 > 10^{16} \text{V/cm}$). Nevertheless, graphene provides an adequate medium in which the perfect transmission postulated by the Klein paradox can be tested, because at low energies graphene has a linear dispersion energy $E = \hbar k v_f$ and relativistic quasi-particles called Dirac Fermions with rest mass equal to zero (Section 1.2.2). Moreover, since quasiparticles are massless, they can directly penetrate the barrier potential in any electric field.[23]

2.2 Graphene bilayer with applied voltages or fields

Similar to a monolayer, a graphene bilayer is a gapless semi-metal, the difference being a parabolic energy dispersion and charge carriers described by an off-diagonal Hamiltonian given by

$$\hat{H}_0 = -\frac{\hbar^2}{2m} \begin{pmatrix} 0 & (k_x - ik_y)^2 \\ (k_x + ik_y)^2 & 0 \end{pmatrix} \quad (2.1)$$

where m is the effective mass for electrons and holes in graphene.

Now applying a potential barrier by an electric field V_0 perpendicular to the graphene bilayer, a perfect electron reflection is achieved with less energy than the potential barrier $E < V_0$. This effect is completely different from the massless Dirac Fermions in the graphene monolayer, which are completely transmitted through the barrier potential[23] and normal quasiparticles, which have a probability greater than zero of tunneling through barrier. Furthermore, in 2009, Feng Wang and his group in Berkeley [25] experimentally obtained that an electric field perpendicular ($E_\perp$) to a graphene bilayer can continuously control a tunable bandgap up to 250 meV (see figure 2–2).

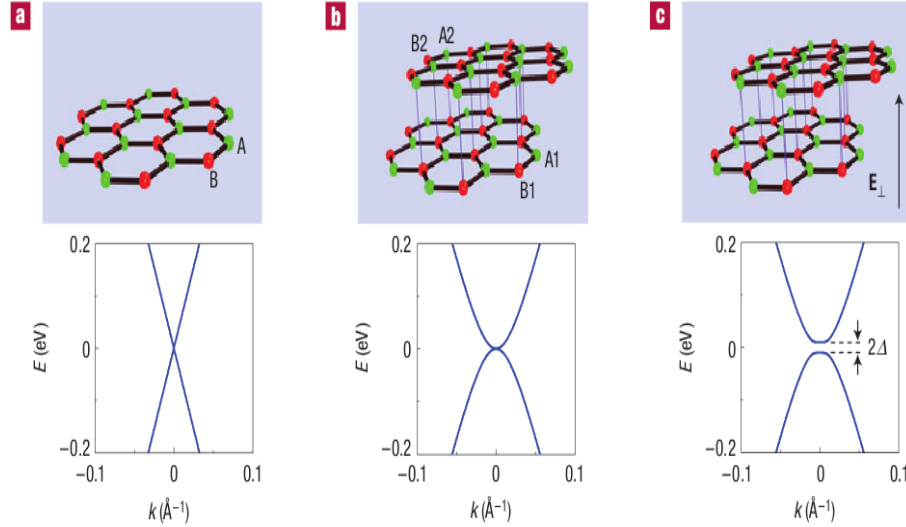


Figure 2–2: Breaking the symmetry at Dirac point in a graphene bilayer [23].

In this thesis, we demonstrate a method to change the electronic transport property of a graphene monolayer by depositing another layer with finite size on top of it. We illustrate our idea by calculating electronic transport property of a graphene monolayer when it is covered by another layer with infinite or finite size. Our results show that, though change of electronic transport property of a monolayer is insignificant when covered by an infinitely large layer or even a semi-infinite one; the change can be more considerable when covered by a nanoribbon of finite width. Furthermore, we show that

the different effects from infinite and finite coverage can be attributed to antiresonance in electron transmission due to interference between the wavefunctions in the two layers. The novel method described in this thesis has not been reported before and no experimental work has explored this possibility. Therefore the spirit of this thesis work gives a new approach to allow experimental physicists to use graphene in nanodevice applications.

CHAPTER 3

THEORETICAL BACKGROUND AND METHODOLOGY

3.1 TRANSMISSION SPECTRUM

The transmission spectrum in nanodevices is a direct measurement of how easily electrons can flow in a two contact system. In order to get an expression for the transmission, a relation for the electric current in the system must be found first, after which we can easily calculate the transmission.

In this work a nanodevice will be formed by two electrodes (a source and a drain) and a central region or channel in which electron scattering is present (see figure 3–1). If this system is connected to a battery, the chemical differential creates an electron flow.

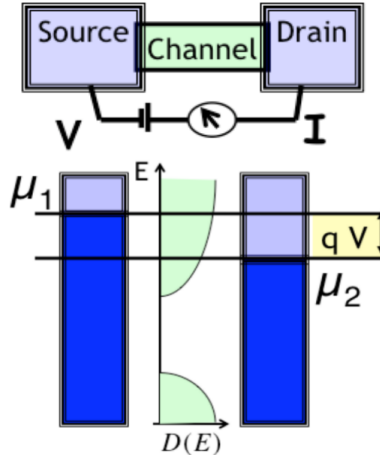


Figure 3–1: Nano-device at a voltage V [2].

If the contact is considered infinitely large and isolated (see figure 3–2 a)), the electrons cannot flow into the channel. From a quantum point of view, the contact is described by the Schrödinger equation [27] as:

$$[EI_R - H_R]\{\Phi_R\} = 0 \quad (3.1)$$

where H_R is the Hamiltonian for the contact that is represented by a matrix of $(R \times R)$ terms and I_R is the identity matrix. Now if the electrode is connected to the channel (see figure 3-2 b)) a term ($i\eta\{\Phi_R\}$) that models the extraction of electrons from the contact should be introduced. Similarly, it is necessary to introduce a second term to model the reinjection of electrons from external sources(S_R). In this case, the channel and contact wave function will be coupled, giving a Hamiltonian with electrons transmitted and reflected from the contact to the channel :

$$\begin{pmatrix} EI_R - H_R + i\eta & -\tau^+ \\ -\tau & EI - H \end{pmatrix} \begin{Bmatrix} \Phi_R + \chi \\ \psi \end{Bmatrix} = \begin{Bmatrix} S_R \\ 0 \end{Bmatrix} \quad (3.2)$$

where $\{\psi\}$ and $\{\Phi_R\}$ are the wave functions of electrons in the channel and the contact respectively, H is the Hamiltonian of the channel and is represented by a matrix of $(d \times d)$ terms, $\{\chi\}$ is the excitation in the contact when electrons flow from it, and τ is the coupling between the contact and the reservoir.

Assuming that the coupling is known and the reinjection of electrons from the external source remains unchanged ($\{S_R\} = 0$), we can derive the following expression from equation 3.2

$$(EI_R - H_R + i\eta)\{\chi\} - \tau^+\{\psi\} = 0 \quad (3.3)$$

$$(EI - H)\{\psi\} - \tau\{\chi\} = \tau\{\Phi_R\} \quad (3.4)$$

where the matrix $\{\chi\}$ can be expressed in terms of $\{\psi\}$ as:

$$\{\chi\} \equiv G_R \tau^+ \{\psi\} \quad (3.5)$$

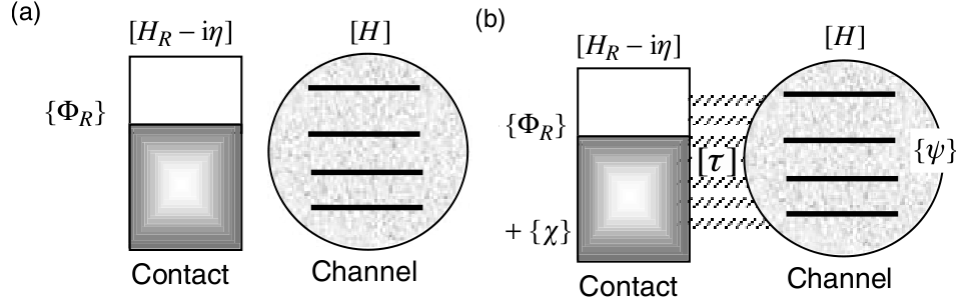


Figure 3-2: a) The contact and channel are not coupled b) The channel and the contact are connected giving rise to an electron flow from the contact to the channel, generating a scattered wave $\{\chi\}$ in the contact [25].

where $G_R = (EI_R - H_R + i\eta)^{-1}$ is the Green function of the reservoir represented by a matrix of $(R \times R)$ terms. Substituting this term into the equation 3.4 we get

$$(EI - H - \Sigma)\{\psi\} = \{S\} \quad (3.6)$$

where $\Sigma \equiv \tau G_R \tau^+$ and $S \equiv \tau \Phi_R$. Since G_R is expressed as an infinitely large matrix $(R \times R)$ it is almost impossible to calculate. However, this may be truncated by only taking into account the interaction of the nearest neighbors between the contacts and the channels. This gives a smaller matrix of r terms which is renamed the compact Green function. It is also important to mention that the matrix Σ , called self-energy matrix, represents the boundary effect between the contact and the channel. This is expressed as a matrix of $(d \times d)$ terms as:

$$\begin{aligned} \Sigma &\equiv \tau G_r \tau^+ \\ (d \times d) &= (d \times r) (r \times r) (r \times d) \end{aligned} \quad (3.7)$$

In general, a nanodevice is composed by a channel and two contacts (a source and a drain) at different chemical potentials μ_1 and μ_2 (see figure 3-3). This system is quite similar to case described before 3.2, but this time it includes the effects of the two contacts by the self energy terms Σ_1 and Σ_2 and the two different couplings τ_1 and τ_2

as:

$$\begin{pmatrix} EI_R - H_1 + i\eta & -\tau_1^+ & 0 \\ -\tau_1 & EI - H & -\tau_2 \\ 0 & -\tau_2^+ & EI_R - H_2 + i\eta \end{pmatrix} \begin{pmatrix} \Phi_1 + \chi_1 \\ \psi \\ \Phi_2 + \chi_2 \end{pmatrix} = \begin{pmatrix} S_1 \\ 0 \\ S_2 \end{pmatrix} \quad (3.8)$$

Making use of the same argument presented for one contact channel, we get:

$$\{\chi_1\} = G_1 \tau_1^+ \{\psi\} \quad \text{with} \quad G_1 = (EI - H_1 + i\eta)^{-1} \quad \text{and} \quad (3.9)$$

$$\{\chi_2\} = G_2 \tau_2^+ \{\psi\} \quad \text{with} \quad G_2 = (EI - H_2 + i\eta)^{-1} \quad (3.10)$$

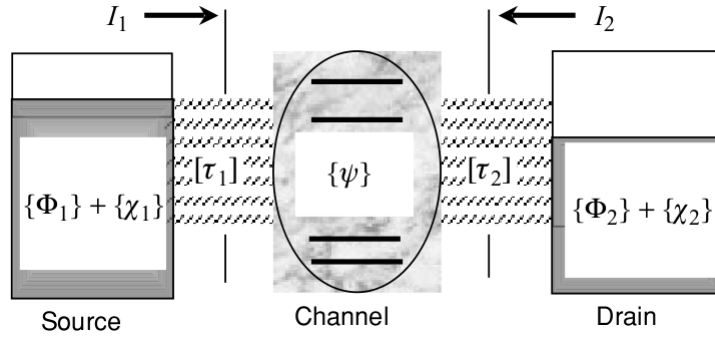


Figure 3–3: Two contact system and a channel [25].

If these expressions are used in the second line of the equation 3.8, the wave function of electrons in the channel including the boundary effect of the contacts is written as:

$$(EI - H - \Sigma_1 - \Sigma_2)\{\psi\} = \{S\} \quad (3.11)$$

where $\Sigma_i = \tau_i^+ G_i \tau_i$ is the self-energy matrix for each contact, S is the additive effect of the excitation in the contacts when electrons flow from contacts to channel $S = S_1 + S_2$, and $S_i = \tau_i \{\Phi_i\}$.

The equation 3.11 is perhaps the most important equation in our system, because

it allows us to calculate the wave function of electrons in the channel ($\{\psi\}$) as:

$$\{\psi\} = G\{S\} \quad \text{with } G \text{ defined as } G \equiv (EI - H - \Sigma_1 - \Sigma_2)^{-1} \quad (3.12)$$

Here G corresponds to the Green function of the whole system and will allow us to calculate the transmission spectrum in our system. As we commented before, we will first find the current I_1 and I_2 in the two contact system, considering that current can be calculated by the *Trace* of the matrix elements of the electrons wave function in the channel ψ as:

$$I \equiv \text{Trace} \left[\frac{d}{dt}(\psi^+ \psi) \right] \quad (3.13)$$

where $i\hbar d\{\psi\}/dt = H\{\psi\}$. In the time independent case, $\{\psi(t)\} = e^{-i\hat{H}t/\hbar}\{\psi_0\}$ hence the current will be equal to

$$\begin{aligned} I &= \text{Trace} \left[\frac{1}{i\hbar} \frac{d}{dt}[\psi^+(t)\psi(t)] \right] = \text{Trace} \left[\frac{1}{i\hbar} \left(\frac{d}{dt}\psi^+ \psi + \psi^+ \frac{d}{dt}\psi \right) \right] = \text{Trace} \left[\frac{1}{i\hbar} (\hat{H}\psi^+ \psi - \psi^+ \hat{H}\psi) \right] \\ &= \text{Trace} \left[\frac{1}{i\hbar} (E\psi^+ - \phi^+ \tau^+) \psi \right] - \text{Trace} \left[\frac{1}{i\hbar} \psi^+ (E\psi - \tau\phi) \right] = \text{Trace} \left[\frac{1}{i\hbar} (\psi^+ \tau\phi - \phi^+ \tau^+ \psi) \right] \end{aligned} \quad (3.14)$$

But the wave function in the contacts is excited when it is connected to the channel as $\{\phi\} = \{\phi_R\} + \{\chi\}$ therefore the current will be equal to:

$$I = \underbrace{\frac{\text{Trace}[\psi^+ \tau \phi_R - \phi_R^+ \tau^+ \psi]}{i\hbar}}_{\text{Inflow}} - \underbrace{\frac{\text{Trace}[\chi^+ \tau \psi - \psi^+ \tau^+ \chi]}{i\hbar}}_{\text{Outflow}} \quad (3.15)$$

In our case, the total current is the sum of each contact current $I = I_1 + I_2$, but each current is the outcome of a inflow and outflow given by:

$$I_i = \underbrace{\frac{\text{Trace}[\psi^+ \tau_i \phi_i - \phi_i^+ \tau_i^+ \psi]}{i\hbar}}_{\text{Inflow}} - \underbrace{\frac{\text{Trace}[\chi_i^+ \tau_i \psi - \psi^+ \tau_i^+ \chi_i]}{i\hbar}}_{\text{Outflow}} \quad (3.16)$$

Replacing the relation 3.12 and $\{S_1\} = \tau_1\{\phi_1\}$ into the inflow at I_1 we get

$$\text{Inflow} = \frac{1}{i\hbar} \text{Trace} [S^+ G^+ \tau_1 * \frac{1}{\tau_1} S_1 - \frac{1}{\tau_1^+} S_1^+ \tau_1^+ G S] \quad (3.17)$$

since $S = S_1 + S_2$ and $S_1^+ S_2 = S_2^+ S_1 = 0$. Making use of this result, the inflow will be equal to:

$$Inflow = \frac{1}{\hbar} Trace[S_1^+ A S_1] = \frac{1}{\hbar} Trace[S_1^+ S_1 A] = \frac{1}{\hbar} Trace[\tau_1^+(E) \phi_1^+(E) \tau_1(E) \phi_1(E) A(E)] \quad (3.18)$$

where $A \equiv i[G - G^+]$, and $S_1(E) = \tau_1(E) \phi_1(E)$. The total amplitude of the wave function ($\{\phi^+\}$) should be summed over the whole energy and weighted by the occupancy density distribution f_0 as:

$$\{\phi\}\{\phi^+\} = \int \frac{dE}{2\pi} f_0(E) \left(\sum_{\alpha} \delta(E - \epsilon_{\alpha}) \{\phi(E)\} \{\phi^+(E)\} \right) \quad (3.19)$$

where the delta Dirac functional can be constructed as the limit of the expression as η approaches 0

$$\begin{aligned} 2\pi\delta(EI - H) &= \left[\frac{2\eta}{(E - \epsilon_{\alpha})^2 + \eta^2} \right]_{\eta \rightarrow 0^+} = i \lim_{\eta \rightarrow 0} \left[\frac{1}{E - \epsilon_{\alpha} + \eta} - \frac{1}{E - \epsilon_{\alpha} - \eta} \right] \\ &= i[G(E) - G^+(E)] \end{aligned} \quad (3.20)$$

Making use of the relationships 3.19 and 3.20, the inflow will be:

$$Inflow = \frac{1}{\hbar} \int dE f_1(E) Trace[\Gamma_1 A] \quad (3.21)$$

since the term $\Gamma_1 = \tau_1 (i[G_1 - G_1^+]) \tau_1^+ = \tau_1 A_1 \tau_1^+$ is the imaginary part of the self energy term in equation 3.11 and $f_1(E)$ is the occupancy function of electrons in contact 1. In a manner analagous to that for inflow current, the outflow current I_1 with $\{\chi_1\} = G_1 \tau_1^+ \{\psi\}$ and 3.12 is given by

$$\begin{aligned} Outflow &= \frac{1}{i\hbar} Trace[\psi^+ \tau_1 G_1^+ \tau_1 \psi - \psi^+ \tau_1^+ G_1 \tau_1 \psi] \\ &= \frac{1}{i\hbar} \psi^+ [\tau_1 G_1^+ \tau_1 - \tau_1^+ G_1 \tau_1^+] \psi = \frac{1}{\hbar} Trace[\psi^+ \Gamma_1 \psi] \end{aligned} \quad (3.22)$$

From the expression 3.12 we have $\{\psi\} = G\{S\}$, therefore $\{\psi\}\{\psi^+\} = G(\{S\}\{S\})G^+$ with $\{S\}\{S^+\} = \tau_1\phi_1\phi_1^+\tau_1^+ + \tau_2\phi_2\phi_2^+\tau_2^+ + \tau_1\phi_1\phi_2^+\tau_2^+ + \tau_2\phi_2\phi_1^+\tau_1^+$ for a two contact system. We also assume that the wave functions of each isolated contact ϕ_i are orthonormal ($\phi_1\phi_2^+ = \phi_2\phi_1^+ = 0$). Using this expression, the amplitude wave function of the channel (ψ) is equal to:

$$\begin{aligned}
\psi\psi^+ &= (GS)(S^+G^+) = G(SS^+)G^+ \\
&= \left\{ \int \frac{dE}{2\pi} G\tau_1 f_1(E) \left(\sum_{\alpha} \delta(E - \epsilon_{\alpha}) \{\phi(E)\}\{\phi^+(E)\} \right) \tau_1^+ G^+ \right\} \\
&+ \left\{ \int \frac{dE}{2\pi} G\tau_2 f_2(E) \left(\sum_{\alpha} \delta(E - \epsilon_{\alpha}) \{\phi(E)\}\{\phi^+(E)\} \right) \tau_2^+ G^+ \right\} \\
&= \int \frac{dE}{2\pi} \left(f_1(E)A_1(E) + f_2(E)A_2(E) \right) \equiv \int \frac{dE}{2\pi} [G^{(n)}(E)] \quad (3.23)
\end{aligned}$$

Replacing 3.22 in 3.23, the outflow current is given by equation

$$Outflow = \frac{1}{h} \int dE \, Trace[\Gamma_1 G^{(n)}(E)] \quad (3.24)$$

Combining the expressions 3.21 and 3.24, the current I_1 is finally equal to:

$$\begin{aligned}
I_1 &= \frac{1}{h} \int dE \left(f_1(E) Trace[\Gamma_1 A] - [G^{(n)}(E)] \right) \\
&= \frac{1}{h} \int dE \, Trace[\Gamma_1 G\Gamma_2 G^+](f_1(E) - f_2(E)) \quad (3.25)
\end{aligned}$$

The current I_2 need not be calculated, because by physical arguments it is known that $I_1 = -I_2$, therefore the total current in the system will be

$$I = \frac{1}{h} \int dE \, T(E) (f_1(E) - f_2(E)) \quad (3.26)$$

Lastly we find the transmission spectrum for nanodevices is given by

$$T(E) = Trace[\Gamma_1 G\Gamma_2 G^+] \quad (3.27)$$

This term is interpreted in the single electron figure by Kohn and Sham as the amplitude for one electron incident in contact one in a subband or mode m to transmit to a subband n in contact two after the scattering process in the channel (see figure 3–4). This kind of interpretation is usually called the Landauer-Buttiker approach in which transmission is calculated by the transmitted wave function in the system as:

$$T(E) = \sum_m \sum_n |t_{nm}|^2 = \text{Trace}[tt^+] \quad (3.28)$$

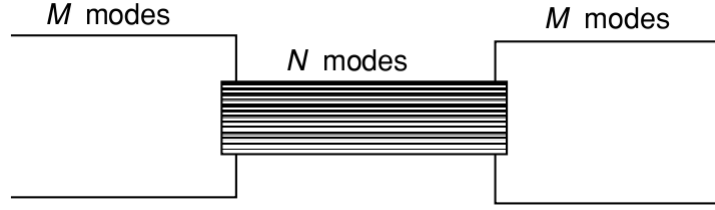


Figure 3–4: Two contact system and a channel [25].

In our specific case the transmission spectrum calculations were carried out following the algorithm given below:

Algorithm

1. Consider the channel and the contacts as isolated systems and calculate the wave functions ϕ_1 , ϕ_2 and ψ by DFT (Section 3.2).
2. Identify the nearest neighbors between the contacts and the channel, then calculate the interaction coupling τ_1 and τ_2 as:

$$\tau_i = \int \Psi_i(r) H \Psi_{ch}^+(r) dr \quad \text{with} \quad i = 1, 2 \quad (3.29)$$

where $\Psi_i(r)$ is the wave function of each contact, Ψ_{ch} is the wave function of the channel, and they are all found via DFT (step 1)

3. Obtain the Green matrices G_i and Γ_i for $i = 1, 2$ given by the equations 3.9 and 3.21.

4. Calculate the Σ_1 and Σ_2 matrices given by 3.11 and the reduced Green function $G(E)$ by equation 3.12.
5. Compute the transmission spectrum at each energy $T(E)$ given by the trace of $[\Gamma_1 G \Gamma_2 G^+]$

3.2 DENSITY FUNCTIONAL THEORY

Several approaches may be used to understand the electronic configuration in a material and all of them depend on the scale and the application of the model. The methods most used for these purposes are: ab initio, semi-empirical and classical force field. In this work, we are going to use the first principles theory or “ab-initio” which has been widely use in recently. Under this consideration, the system will be studied from a fundamental viewpoint seeking to understand the interactions and constraints involved in a quantum physics context.

As we know, the laws that rule our universe at small dimensions are modelled by quantum mechanic physics. In that context, the formulation that every system must satisfy is the time independent schrödinger equation.

$$H|\psi\rangle = E|\psi\rangle \quad (3.30)$$

where H is the Hamiltonian of the system and $|\psi\rangle$ is the set of solutions or the eigenstate that solves the Hamiltonian. Each function $|\psi\rangle$ has an associated eigenvalue E (a real number) that satisfies the Schrödinger equation. In the case presented here, the Schrödinger equation is described by:

$$H = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \frac{1}{2} \sum_{A=1}^M \frac{1}{M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \quad (3.31)$$

where A and B run over M nuclei, while i and j denote the N electrons in the system. The two first terms in the equation correspond to the kinetic energy of the electrons and the nuclei respectively, and M_A is the mass of the nucleus in terms of the mass an electron (in atomic units $m_e = 1$). The remaining terms represent the attractive electrostatic interaction between the electrons and nuclei, and the repulsive interaction between electron-electron and nucleus-nucleus respectively. Also for this system the wave function ψ will be dependent of electrons and nucleus coordinates $\psi(\vec{r}; \vec{R})$. It is important

to mention that equation 3.31 was defined in atomic units to make the notation easier.

This equation can be simplified by making use of the physics argument that the nuclei mass is one thousand times the electron mass. In consequence, the electrons can be considered with high accuracy as charge particles moving in a positive background of statically charged nuclei. Therefore the Hamiltonian can be written as:

$$H = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} = \hat{T} + \hat{V}_{Ne} + \hat{V}_{ee} \quad (3.32)$$

which imply at the same time that the wave function of the whole system can be approached as the wave function of all N electrons coordinates $\psi(\vec{r}; \vec{R}) \approx \psi(\vec{r})$.

Until today, this wave function ($\psi(\vec{r})$) which is a function of all N electrons coordinates $\psi = \psi(\vec{r}_1, \vec{r}_2 \dots, \vec{r}_N)$ is impossible to solve for real problems. Therefore it is simplified even more by approximating it as a product of individual electron wave functions $\psi \approx \psi_1(\vec{r})\psi_2(\vec{r}) \dots, \psi_N(\vec{r})$ [28]. This last approximation of the wave function is known as the Hartree product. To this point, no restriction has been fixed on the expression $\psi_i(\vec{r})$ with $i = 1, 2 \dots, N$. Notice also that N is the number of electrons and is considerably larger than the number of nuclei M . For example, the electron wave functions of a simple molecule of CO_2 has twenty two electrons; taking into account three dimension for each electrons, the full wave function is composed of sixty six components.

In our case the eigenfunction $|\psi_i\rangle$ of the Hamiltonian matrix H itself is not observable, but a physical interpretation can be associated with the electron density $\rho(r)$ which is the probability of finding a electron at a position r which may be expressed as:

$$\rho(\vec{r}) = 2 \sum_i \psi_i^*(\vec{r})\psi_i(\vec{r}) \quad (3.33)$$

The number 2 in this last expression is due to the fact that different spins (up or down) might occupy the same state $|\psi_i\rangle$. In spite of previous approximations, the wave function for a system of $3N$ components role by schödinger equation 3.32 still remains

unsolved. However, in 1960, Kohn and Sham made it possible to solve the electronic wave function for a system of $3N$ components by postulating two mathematics theorems on which density functional theory (DFT) rests.

The first theorem proved by Hohenberg and Kohn was “*The external potential $V_{ext}(\vec{r})$ is (to within a constant) a unique function of $\rho(\vec{r})$; since in turn $V_{ext}(\vec{r})$ fixes $\hat{H}$ we see that the full many particles ground state is a unique functional of $\rho(\vec{r})$* ”. This theorem affirms that a one-to-one mapping between the ground state wave function and the ground electron density exists [29].

The second Hohenberg and Kohn theorem postulates an important property of the energy “*The electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrödinger equation.*” Making use of this postulate, the ground state of the energy can be rewritten as:

$$E_0[\rho_0] = T[\rho_0] + E_{ee}[\rho_0] + E_{Ne}[\rho_0] \quad (3.34)$$

This equation can be arranged into two terms as follows:

$$E_0[\rho_0] = \underbrace{\int \rho_0(\vec{r}) V_{Ne} d\vec{r}}_{\text{system dependent}} + \underbrace{T[\rho_0] + E_{ee}[\rho_0]}_{\text{Universally valid}} \quad (3.35)$$

This last term is independent of the system at hand, which means that it applies equally well to hydrogen atoms as to complex molecules such as DNA. The only issue is that an explicit form of this term is completely unknown. Therefore, finding an approximation of this term is currently one of the most active research areas. In the literature, this universal term is called the Hohenberg-Kohn functional and the expected value is given by:

$$F_{KH}[\rho] = \langle \psi | \hat{T} + \hat{V}_{ee} | \psi \rangle = T[\rho] + E_{ee}[\rho] \quad (3.36)$$

where the electron-electron interaction E_{ee} can be expressed as:

$$E_{ee}[\rho] = \frac{1}{2} \int \int \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + E_{nc}[\rho] = J[\rho] + E_{nc}[\rho] \quad (3.37)$$

where $E_{nc}[\rho]$ is the non-classical contribution to the electron-electron interaction that contains the self-interaction correction and all of the quantum effects. Assuming that E_{nc} is well known, the ground state of the system can be found by the second Hohenberg and Kohn theorem which postulates that the ground state ϕ_0 of the system must be generated by the electron density ρ that minimize the energy $E[\rho_0]$

$$E_0 = \min_{\rho \rightarrow N} \left(\min_{\psi \rightarrow \rho} \langle \psi | \hat{T} + \hat{V}_{Ne} + \hat{V}_{ee} | \psi \rangle \right) \quad (3.38)$$

where the energy due to the external potential V_{Ne} is determined by the density ρ , and is thus independent of the wave function so that

$$E_0 = \min_{\rho \rightarrow N} \left(\min_{\psi \rightarrow \rho} \langle \psi | \hat{T} + \hat{V}_{ee} | \psi \rangle + \int \rho(\vec{r}) V_{Ne} d\vec{r} \right) \quad (3.39)$$

or compactly

$$\begin{aligned} E_0 &= \min_{\rho \rightarrow N} \left(F[\rho] + \int \rho(\vec{r}) V_{Ne} d\vec{r} \right) \\ &= \min_{\rho \rightarrow N} \left(T[\rho(\vec{r})] + J[\rho(\vec{r})] + E_{nc}[\rho(\vec{r})] + \int \rho(\vec{r}) V_{Ne} d\vec{r} \right) \end{aligned} \quad (3.40)$$

In principle, to solve this equation we would need to use a variational principle in order to get the ground state for the whole system, however this is not possible due to the large number of unknown terms. Nevertheless, if we are less ambitious and approximate the real kinetic energy as the kinetic energy $T[\rho]$ of a non interacting system of particles, we obtain:

$$T_{ni} = -\frac{1}{2} \sum_i^N \langle \varphi | \nabla^2 | \varphi \rangle \quad (3.41)$$

Clearly the non-interacting kinetic energy is not equal to the true kinetic energy of the interacting system, even if the system shares the same density $T_{ni} \neq T$, because in

the case of non-interacting electrons, the coulomb potential vanishes. Nonetheless, the quantum effects still present in the system generate a change in the kinetic energy of a non interacting system. Under this assumption, the Hohenberg and Kohn functional presented in the equation 3.36 will be equal to:

$$F[\rho(\vec{r})] = T_s[\rho(\vec{r})] + J[\rho(\vec{r})] + E_{XC}[\rho(\vec{r})] \quad (3.42)$$

where E_{XC} is called the exchange-correlation energy defined by equation 3.42 as:

$$E_{XC}[\rho] \equiv (T[\rho] - T_{ni}[\rho]) + (E_{ee}[\rho] - J[\rho]) = T_c[\rho] + E_{nc} \quad (3.43)$$

The first term in parentheses is the effect neglected when the kinetic energy is calculated by the non-interacting particles. The second term is the quantum effect and self-interaction not considering the coulomb potential (J). Consequently the complete expression E_{XC} expresses all unknown elements in the system. Replacing this expression 3.43 in the Hamiltonian 3.40 we get:

$$\begin{aligned} E[\rho(\vec{r})] &= T_s[\rho] + J[\rho] + E_{XC}[\rho] + \int V_{Ne}\rho(\vec{r}) d\vec{r} \\ &= T_s[\rho] + \frac{1}{2} \int \int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + E_{XC}[\rho] + \int V_{Ne}\rho(\vec{r}) d\vec{r} \\ &= -\frac{1}{2} \sum_i^N \langle \varphi_i | \nabla^2 | \varphi_i \rangle + \frac{1}{2} \sum_i^N \sum_j^N \int \int |\varphi_i(\vec{r}_1)|^2 \frac{1}{r_{12}} |\varphi_j(\vec{r}_2)|^2 d\vec{r}_1 d\vec{r}_2 \\ &\quad + E_{XC}[\rho(\vec{r})] - \sum_i^N \int \sum_A^M \frac{Z_A}{r_{1A}} |\varphi_i(\vec{r}_1)|^2 d\vec{r}_1 \end{aligned} \quad (3.44)$$

We apply the equation before the variational principle in order to find the ground state that minimizes the energy using the following constraint: $\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$ getting [30]:

$$\begin{aligned} \left(-\frac{1}{2} \nabla^2 + \left[\int \frac{\rho(\vec{r}_2)}{r_{12}} d\vec{r}_2 + V_{XC}(\vec{r}_1) - \sum_A^M \frac{Z_A}{r_{1A}} \right] \right) \varphi_i &= \epsilon_i \varphi_i \\ \left(-\frac{1}{2} \nabla^2 + V_{eff}(\vec{r}_1) \right) \varphi_i &= \epsilon_i \varphi_i \end{aligned} \quad (3.45)$$

This last expression is a single set of equations originally proposed by Kohn and Sham, in which each equation involves a single electron system. The enormous power of this equation lies in that we move from a many-body problem to a single system of independent equations with an effective potential (the term in square brackets). The potential V_{XC} in this equation is simply defined as the functional derivative of E_{XC} with respect to ρ as a result of the variational principle:

$$V_{XC} = \frac{\delta E_{XC}}{\delta \rho(\vec{r})} \quad (3.46)$$

In conclusion, the Schrödinger equation can be solved approximately by the equation 3.45. To obtain a solution to Kohn-Sham equation, we must know the electron density $\rho(\vec{r})$ 3.33, but electron density is calculated by the wave function φ_i which in turn is the solution to the Kohn-Sham equation. Therefore an infinite loop exists in the solution of the Kohn-Sham equation. This loop can be broken by treating the problem in a self-consistent way by following the next algorithm:

1. Define an educated guess $\varphi_i(\vec{r})$.
2. Calculate the trial electron density $\rho(\vec{r})$.
3. Solve the Kohn-Sham equations using the trial electron density to find the single particle wave function $\varphi_i(\vec{r})$.
4. Calculate the electron density $\rho(\vec{r}) = 2 \sum_i \varphi_i^*(\vec{r}) \varphi_i(\vec{r})$.
5. Compare the computed $\rho(\vec{r})$ with the electron density proposed $\rho(\vec{r})$ in step two. If both expressions are the same, the algorithm stops and calculates the energy of the ground state. However if the two densities are different, we start the process again from the step 3 making use of the computed wave function.

At this time the question of how to calculate the exchange correlation function remains unsolved, but in the next section we will show some models to compute it.

3.2.1 Exchange correlation functional

Before introducing a model to calculate the exchange correlation function in our system we need to use the concept of electron density. In general this quantity provides information of how likely is to find one electron with spin σ within a volume element $d\vec{r}$ while all of the electrons may be anywhere. For two electrons, the probability of finding both with spin σ_1 and σ_2 simultaneously within two volume elements $d\vec{r}_1$ and $d\vec{r}_2$ is given by [31]:

$$\rho_2(\vec{r}_1, \vec{r}_2) = N(N-1) \int \cdots \int |\Psi(\vec{r}_1, \vec{r}_2, \dots)|^2 d\vec{r}_3 \dots d\vec{r}_N \quad (3.47)$$

In the literature, this probability is called the pair density probability, which contains all the directions of electron correlation. In an unambiguous manner the pair density considers electrons in a classical way so that probability of finding one of them is independent of the other. In that case, the pair probability would reduce to a simple product of individual probabilities.

$$\rho(\vec{r}_1, \vec{r}_2) = \frac{N-1}{N} \rho(\vec{r}_1) \rho(\vec{r}_2) \quad (3.48)$$

The $\frac{N-1}{N}$ factor enters, because the particles considered up to this point are identical and not distinguishable. Therefore the total pair probability will be equal to:

$$\int \int \rho(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 = \frac{N-1}{N} \left(\int \rho(\vec{r}_1) d\vec{r}_1 \right) \left(\int \rho(\vec{r}_2) d\vec{r}_2 \right) = N(N-1) \quad (3.49)$$

Although we know that electrons are fermions that satisfy Pauli exclusion principle, the electrons interact through Coulomb repulsion and stay away from each other as much as possible. The Coulomb and Pauli exclusion effects might be included in the pair density in two ways. The first one is by an exchange or “*Fermi correlation*” that restricts the pair density in the case of two electrons with the same spins being localized in the same place ($\vec{r}_1 = \vec{r}_2$) to zero $\rho_2(\vec{r}_1, \vec{r}_2 = \vec{r}_1) = 0$. In this way, the Pauli exclusion principle is satisfied.

The second effect is the “*Coulomb correlation*” that models the electrostatic repulsion between electrons, which manifests itself through the $\frac{1}{r_{12}}$ which prevents electrons from being quite close to each other. “*Fermi correlation*” and “*Coulomb correlation*”. are included in the pair density $\rho(\vec{r}_1, \vec{r}_2)$ by the exchange correlation hole h_{XC} as:

$$\rho(\vec{r}_1, \vec{r}_2) = \rho(\vec{r}_1)\rho(\vec{r}_2) + \rho(\vec{r}_1)h_{XC}(\vec{r}_1, \vec{r}_2) \quad (3.50)$$

In the case that the electrons are completely uncorrelated, $h_{XC}(\vec{r}_1, \vec{r}_2) = 0$; but if a correlation exists between electrons ($h_{XC}(\vec{r}_1, \vec{r}_2) \neq 0$) the total pair density will be equal to:

$$\begin{aligned} \int \int \rho(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 &= \int \int \rho(\vec{r}_1)\rho(\vec{r}_2) d\vec{r}_1 d\vec{r}_2 + \int \int \rho(\vec{r}_1)h_{XC}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 \\ &= \left(\int \rho(\vec{r}_1) d\vec{r}_1 \right) \left(\int \rho(\vec{r}_2) d\vec{r}_2 \right) + \int \rho(\vec{r}_1) \left[\int h_{XC}(\vec{r}_1, \vec{r}_2) d\vec{r}_2 \right] d\vec{r}_1 \\ &= N^2 - N \end{aligned} \quad (3.51)$$

In order to get a result similar to equation 3.49 $\int h_{XC}(\vec{r}_1, \vec{r}_2) d\vec{r}_2 = -1$. This implies that the exchange correlation hole contains the exact charge of one electron. Under this consideration, the energy of interaction E_{ee} will be equal to

$$\begin{aligned} E_{ee} &= \frac{1}{2} \int \int \frac{\rho(\vec{r}_1, \vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 \\ &= \frac{1}{2} \int \int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + \frac{1}{2} \int \int \frac{\rho(\vec{r}_1)h_{XC}(\vec{r}_1, \vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 \\ &= J[\rho] + E_{XC}[\rho] \end{aligned} \quad (3.52)$$

The first term corresponding to the Coulomb interaction $J[\rho]$ contains a nonphysical term of self-interaction. To observe this effect, assume that the system encloses only one charge. In this case the Coulomb energy should be zero, but the previous expression is obviously not zero.

The second term of the expression corresponds to the exchange correlation function E_{XC} that includes the correction for the self interaction in addition to all the quantum effects such as the Pauli exclusion principle that must be satisfied by electrons. An exact form for this expression is not available, but an accurate result can be obtained if the hole exchange correlation is split into the Fermi hole $h_f^{\sigma_1=\sigma_2}$ and Coulomb hole $h_c^{\sigma_1,\sigma_2}$ as:

$$h_{XC}(\vec{r}_1, \vec{r}_2) = h_f^{\sigma_1=\sigma_2}(\vec{r}_1, \vec{r}_2) + h_c^{\sigma_1,\sigma_2}(\vec{r}_1, \vec{r}_2) \quad (3.53)$$

Fermi Hole

The Fermi hole models the fact that electrons must satisfy the Pauli exclusion principle. For that reason h_f must be negative everywhere ($h_f < 0$) preventing two atoms from being in the same quantum state. For example, if two atoms with the same spin σ fixed at a position r_1 and r_2 approach each other $r_2 \rightarrow r_1$, the Fermi hole will be equal to the negative of density at r_1 :

$$h_f(r_2 \rightarrow r_1) = -\rho(\vec{r}_1) \quad (3.54)$$

Another example of how is described the Coulomb and Fermi holes is the model of the molecule of H_2 presented by Baerends and Gritsenko [32] (see figure 3-5). This work shows clearly that in regions close to the hydrogen's electrons, the Fermi hole (h_f) increases, and that it tends to zero far away from electrons. Also when the distance between the electrons is relatively small, the Fermi hole correlation is more uniform; when the electron distance is large, the Fermi hole exhibits large peaks.

Coulomb Hole

The Coulomb hole has the role of correcting the self-interaction for electrons with different spins:

$$\int h_c(\vec{r}_1, \vec{r}_2) d\vec{r}_2 = 0 \quad (3.55)$$

As we explained before for the fermi hole, the H_2 molecule displays Coulomb hole behavior. When the electrodes are separated $r_{ee} \rightarrow \infty$ the Coulomb hole cancels the effect of half an electron from the nucleus where the reference electron is positioned and builds a charge of half an electron in the other nucleus. For short distance, the electrodes are less localized and the Coulomb hole slightly reduces the effect of the Fermi hole at the reference electrode and builds up the same quantity at the other nucleus.

It is important to mention that Coulomb and Fermi holes do not have any physical meaning independently, but together the expressions accurately model the quantum effects and self interaction correction [31].

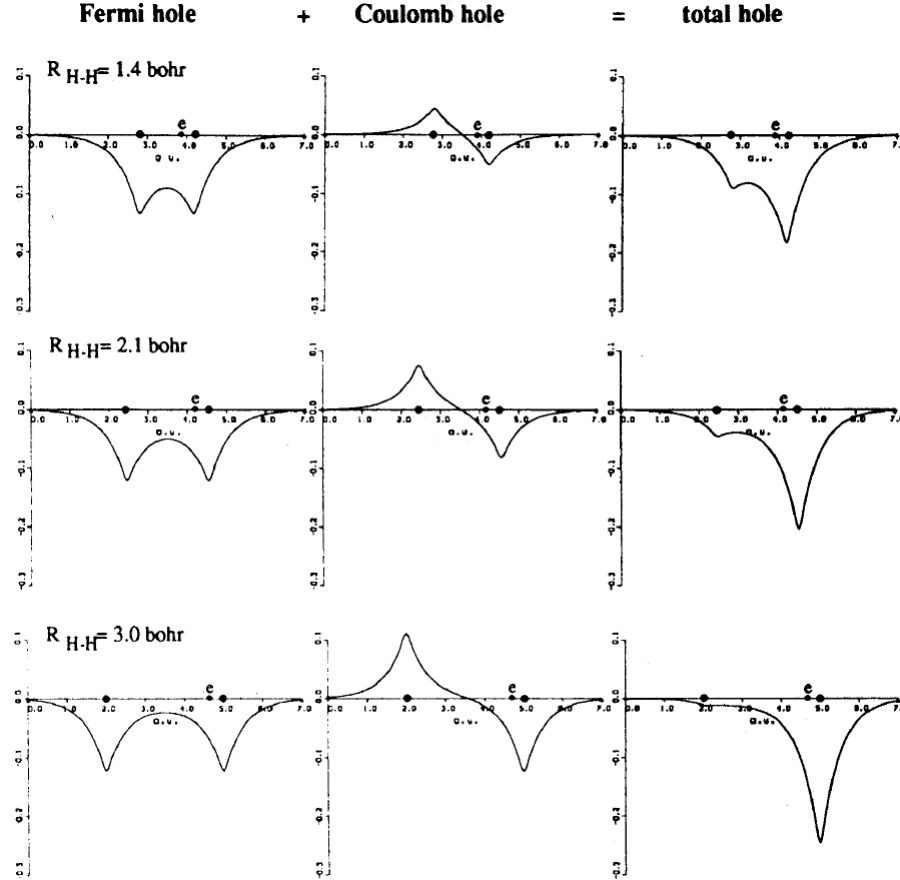


Figure 3-5: Exchange correlation hole for H_2 molecule [30].

3.2.2 Local Density Approximation.

Now we know how the exchange correlation function (E_{XC}) is represented, but an analytical expression for h_{XC} is still unknown. In the sixties, Kohn and Sham used the old Thomas-Fermi-Dirac method to formulate an exchange correlation functional that is the base of all correlational functional in DFT.

The Thomas-Fermi-Dirac model simplified all electrons to one hypothetical uniform electron gas, and assumed that electrons are moving in a positive charge distribution background, so that the whole composition in the system is kept neutral. It also assumed that the number of electrons N is on the order of Avogadro's number $N \rightarrow \infty$ within a volume $V \rightarrow \infty$ such that $N/V = n$ remains finite and has a constant value everywhere.

This model is called the local density approximation and can physically model a simple metal crystal such as sodium in which the nucleus and electrons are regularly distributed over the entire space. However this assumption is quite far from typical structures where the electrons density is usually characterized by irregular and rapid variations. Despite this, the local density approximation has been good enough for a wide range of molecular studies. In general the exchange correlation functions is expressed as:

$$E_{XC}^{LDA}[\rho] = \int \rho(\vec{r}) h_{XC}(\rho(\vec{r})) dr \quad (3.56)$$

where h_{XC} is the exchange-correlation energy per particle in a uniform electron gas with electron density $\rho(\vec{r})$ and where h_{XC} can be split into Fermi and Coulomb holes. For the particular case of an uniform electron gas, the fermi hole [33] is given by

$$h_f = -\frac{3}{4} \sqrt[3]{\frac{3\rho(\vec{r})}{\pi}} \quad (3.57)$$

This factor was found by Slater in his approximation of the Hartree-Fock exchange, but was originally derived by Bloch and Dirac in the late 1920s. Inserting this factor into 3.56 yields a factor of $\rho^{4/3}$ dependent on the Fermi hole.

In the case of the Coulomb hole, h_c is not known by an explicit expression, however it has been simulated numerically with high accuracy by quantum Monte-Carlo methods. The most referenced has been the work of Ceperly and Alder, 1980. Making use of these results, an analytical expression for the Coulomb hole has been proposed based on sophisticated interpolation schemes. The most widely used representation of h_c is the expression presented by Vosko, Wilk, and Nusair, 1980, but perhaps one of the most accurate representations was presented by Perdew and Wang in 1992.

Unquestionably the local density approximation (LDA) is a better approximation for systems with a homogeneous density (as some metals) than for systems with an inhomogeneous density of atoms. The effect produced in the latter type of system is that the exchange energy becomes too negative, causing a dramatic overbending. However, a homogeneous electron gas does in fact provide a reasonable first approximation to spherically average exchange correlation holes of real systems. Clearly, in a real system this assumption will deteriorate at larger distances between the reference electron at $\vec{r}_1$ and another $\vec{r}_2$ where the variation of ρ is considerable. In recently years, new functionals have been proposed, nevertheless in our study the exchange correlation used GGA, which has a better accuracy than LDA. In the next section we will describe GGA.

3.2.3 The Generalized Gradient Approximation (GGA)

As previously described, the local density approximation is certainly insufficient for most applications since it overestimates the bonding energy. However, in 1985 Perdew proposed a model that he and Yue later simplified in 1986, where the exchange correlation function $E_{XC}\{\rho(\vec{r})\}$ expands as a Fourier approximation of the density $\rho(\vec{r})$ as powers of $\rho(\vec{r})$, $\nabla\rho(\vec{r})$, and $\nabla^2\rho(\vec{r})$ as [34]:

$$E_{XC}^{GGA}[\rho] = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int \rho^{4/3} F(s) dr \quad (3.58)$$

with

$$s = \frac{|\nabla\rho(\vec{r})|}{2k_f\rho} \quad (3.59)$$

$$k_f = (3\pi^2\rho)^{1/3} \quad (3.60)$$

$$(3.61)$$

and

$$F(s) = (1 + 1.296s^2 + 14s^4 + 0.2s^6)^{1/15} \quad (3.62)$$

Based on this approximation, the density is not uniform but very slowly varying. Unfortunately GGA does not lead to the desired improved accuracy for real systems, for this reason a second class of GGA exchange functionals was implemented by Perdew, Burke, and Ernzerhof in 1996 (PBE). [\[31\]](#) This functional is a hybrid functional in which most of the parameters are obtained experimentally.

CHAPTER 4

RESULTS AND DISCUSSIONS

As mentioned in the chapter 2, we present in this chapter our results of the electronic transport properties of a graphene monolayer covered by another layer with infinite or finite widths. We will first study three structures shown in figure 4–1 (a)-(c). Figure 4–1 a) is a graphene monolayer; Figure 4–1 b) is a monolayer covered by another infinite layer or a bilayer; and Figure 4–1 c) is a monolayer covered by a semi-infinite layer. To carry out all our calculations, we use an “ab initio” simulation package Atomistix [35] with the following parameters: a double zeta polarized basic set, an exchange-correlation potential of the generalized gradient approximation with the Perdew-Burke-Ernzerhof parameterization [36], an energy mesh cutoff of 70.0 Ry, and a convergence threshold of 10^{-5} eV. All calculations use room temperature.

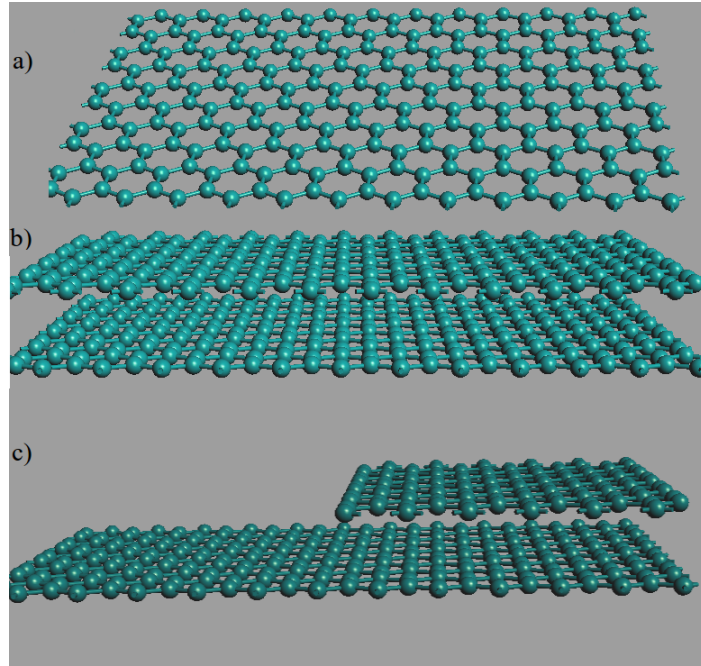


Figure 4–1: Graphene Structures

The first step in our work was the geometric optimization of the graphene bilayer. For that purpose, in addition to the aforementioned parameters, a k point sampling of (1,1,30) and a maximum force accepted between bulk atoms of $10^{-2} \text{ eV}/\text{\AA}$ were used. The results obtained by our ab initio simulator were $a_{AB} = 3.383 \text{\AA}$ and $a_{cc} = 1.4151 \text{\AA}$, respectively, which are very close to the experimental results of $a_{AB} = 3.34 \text{\AA}$ and $a_{cc} = 1.42 \text{\AA}$ [37].

4.1 Band structures of graphene monolayer and bilayer

Once the interplanar spacing and lattice constant were determined, the band structure for a monolayer and bilayer in the armchair and zigzag arrangements were calculated using the aforementioned parameters but with a k point sampling of (1, 1, 81). The results of those calculations between the directions Γ (0, 0, 0) and Z (0, 0, 1) are presented below.

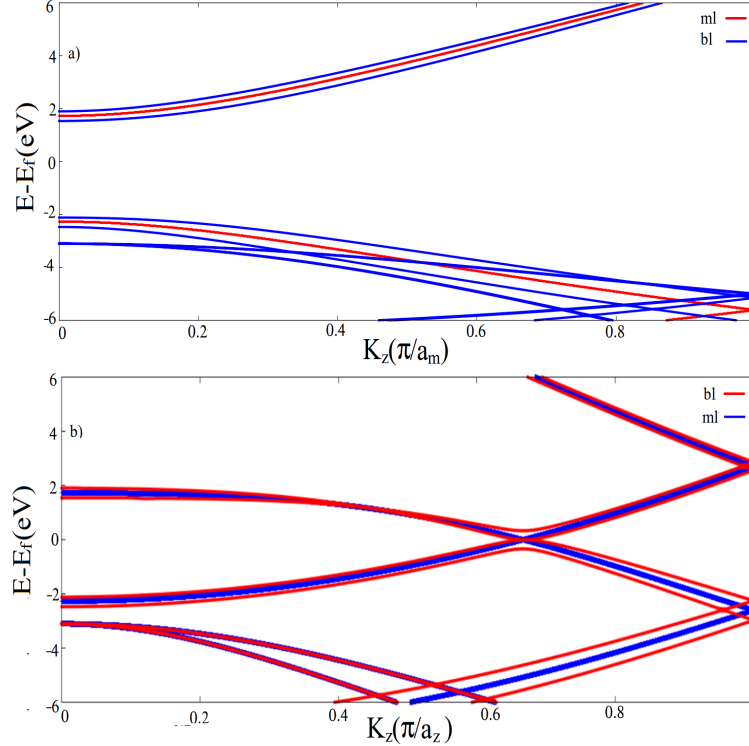


Figure 4–2: Band structure for mono and bilayer graphene in the a) armchair and b) zigzag directions

where E_f is the system's Fermi energy, K_z is the wave vector in the z axis, and a_m and a_z are the unit cell distances for armchair and zigzag respectively. The band structure gives information about how the electrons are arranged in the material. In this specific case, the structure of the graphene monolayer and bilayer in the armchair direction figure 4-2 a) shows a direct gap between the conduction and valence bands. However, when the band structure is calculated in the zigzag direction, a zero band gap is obtained figure 4-2 b). At the Fermi energy, the valence and conduction bands overlap. As was previously explained, this implies that this band structure is similar to massless particles (photons) modelled by the Dirac equation [17]. We can also conclude from these results that mono and bilayer band structure in the armchair and zigzag directions are quite similar. The reason for this effect is that interaction between the layers is weak. To confirm this argument, the coupling between the intralayer and interlayer nearest neighbor was calculated; the energies were found to be 2.661 eV and 0.256 eV respectively, which is in agreement with both experimental and theoretical results [38–40]. This means that the energy between orbitals (P_z) of different layers is less than the interaction between interlayer orbitals (P_x and P_y) by a factor of ten. These results are better demonstrated when the local density of states (LDOS) at the Fermi energy is calculated (see figure 4-3)

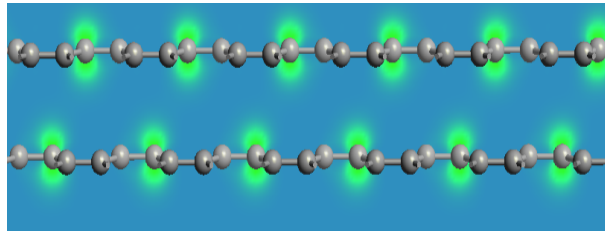


Figure 4-3: LDOS for a bilayer at the Fermi energy E_f

In this figure we observe that orbitals P_z (light green surfaces) of the top and bottom layers do not overlap at the Fermi energy, which confirms the weak interaction between layers.

4.2 Transmission spectra of different graphene structures

In order to understand how electrons flow in a mesoscopic device as defined in figure 4-1, the transmission spectrum was calculated based on the Landauer-Buttiker formalism combined with density functional theory (DFT) as explained in Chapter 3. To carry out the computations, we defined the system as being formed by two infinite contacts (a source and a drain), and a channel or scattering region, as shown in figure 4-4.

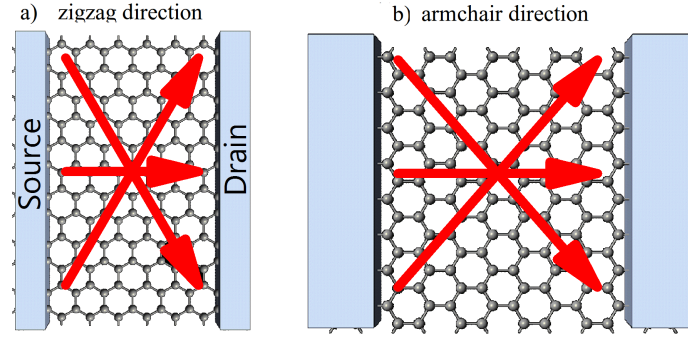


Figure 4-4: Graphene device in a) armchair and b) zigzag directions.

We calculate both electronic transport properties along armchair or zigzag direction. Please note that transport along the armchair direction means we deposit source and drain electrodes in the zigzag direction and transport along the zigzag direction means the electrodes are in the armchair direction, as shown in figure 4-4. In our transmission calculations, we use the parameters expressed before and a k point sampling of (1,81,81).

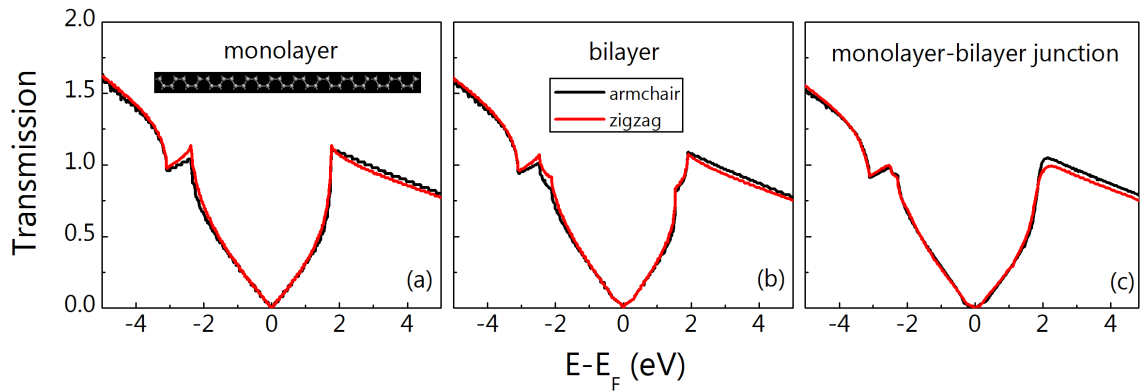


Figure 4-5: Transmission spectrum for armchair and zigzag configuration for a) monolayer, b) bilayer, and c) mono-bilayer junctions

Figure 4-5 a) plots the transmission spectrum of a monolayer, along armchair or zigzag directions. Since the structures in our calculations are periodic along the transverse direction (y-direction), the transmissions calculated are averaged and plotted per unit cell (u.c.) in figure 4-5 (a) are transmissions. The insert of figure 4-5 (a) shows a unit cell of a monolayer along the armchair direction. The transmission along zigzag direction has been multiplied by a factor of $(1/\sqrt{3})$, since the width of one unit cell along zigzag direction is $\sqrt{3}$ times of that along armchair direction. From figure 4-5 (a), we can see that both transmissions agree very well with each other. They present a linear relationship with the energy near the Fermi energy, which reflects the electronic structure of the Dirac cone.

The transmission spectra of a bilayer and a monolayer-bilayer junction are plotted in figure 4-5 (b) and 4-5 (c) respectively. In figure 4-5 (b), the transmissions have been multiplied by $(1/2)$ in order to get the contribution from one layer. We can see that the transmission spectra from both figure 4-5 (b) and 4-5 (c) are very close to those in figure 4-5 (a), which indicates the transmission of a monolayer will not be changed significantly when covered by another layer with infinite or semi-infinite size. According to the transmissions, the two layers are coupled weakly and almost independent of each other.

The weak interlayer coupling leads to relative independence between the two layers in the electronic transmission, which implies that covering a monolayer will not significantly change its electronic transport property. However, we can construct a new configuration in which the electronic properties of graphene monolayer is changed. In this configuration a graphene monolayer is connected to the contacts, while the ribbon is detached from the contacts as shown in figure 4-6.

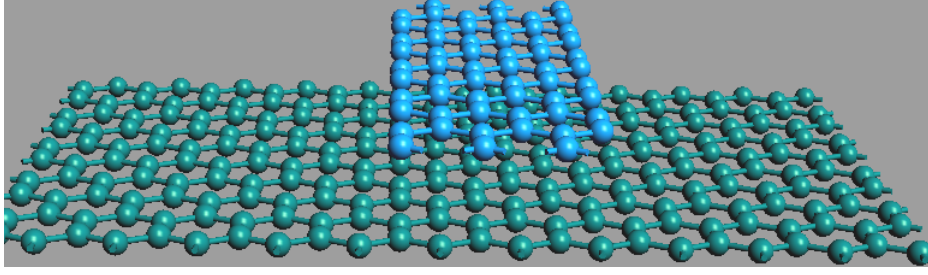


Figure 4-6: Monolayer covered by a nanoribbon (mbnr).

Figure 4-7 presents the transmission spectra of a monolayer covered by a nanoribbon with different widths. In figure 4-7 (a), the electron transport is along the armchair direction, while that in 4-7 (b) is along the zigzag direction. In both 4-7 (a) and (b), increasing of the nanoribbon width from one unit cell to four unit cells reduces the transmission of the monolayer. The changes are more significant than that of an infinite cover. Thus, electronic transport property of a monolayer can be changed by depositing a nanoribbon with finite width on top of it.

In figure 4-7 (a), though the transmission is referred to as the armchair direction, it includes contributions from all possible channels from the source electrode to the drain electrode. The same is true for the transmission in figure 4-7 (b). Different transmission channels can be identified by different wave vectors along the transverse direction (k_y).

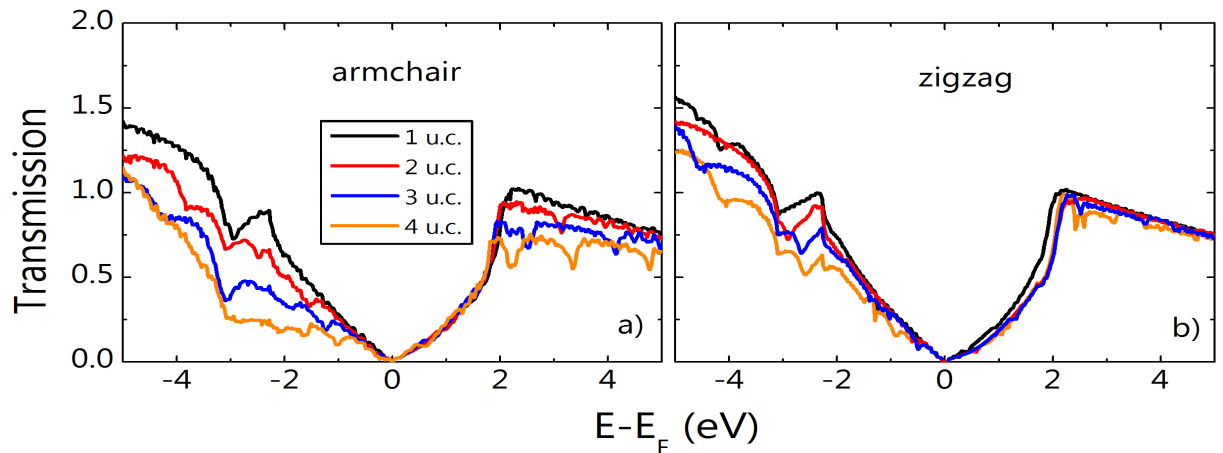


Figure 4-7: Transmission spectrum for (mbnr) structure in a) armchair and b) zigzag arrangement.

To understand the effect of a finite-width ribbon on the transmission of a monolayer, it is necessary to study the effect on individual transmission channels. Here we take the channel with $k_y = 0$ as an example. Figure 4-8 presents transmission spectra of a monolayer covered by a nanoribbon with different widths, for $k_y = 0$ only. Figure 4-8 (a) shows the transmission along armchair direction, and figure 4-8 (b) shows that along the zigzag direction. They show that the transmission for $k_y = 0$ only is reduced when presenting the finite-width nanoribbons. Moreover, the transmission is reduced to zero at certain energies. With an increase in the width of nanoribbon, the number of zeros in transmission increases and their positions are changed.

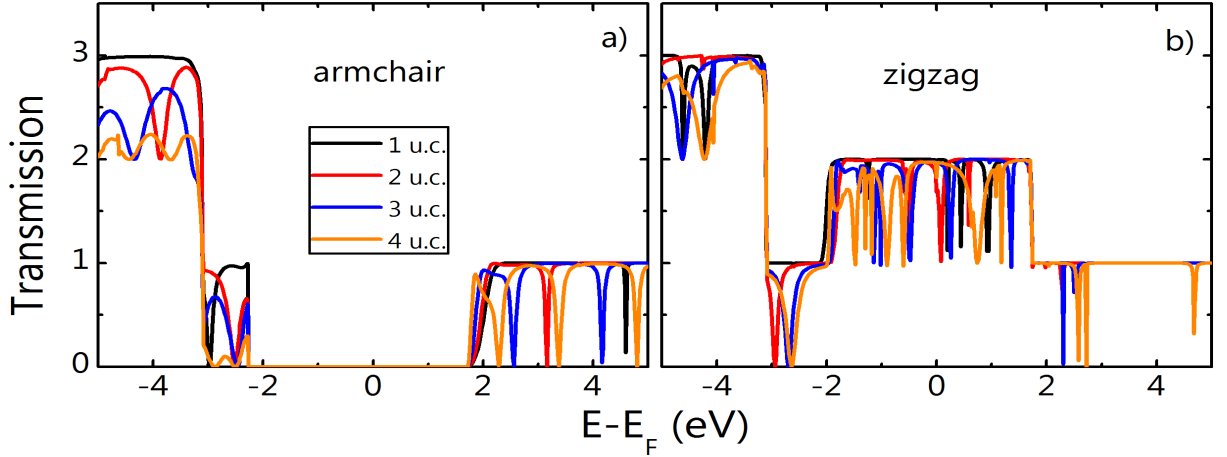


Figure 4-8: Transmission spectrum for mbnr structure to one channel ($k_y = 0$) a) armchair and b) zigzag arrangement.

The zeros in the transmission due to the presence of finite-width nanoribbons can be understood by interference between electron wavefunctions. An electron with $k_y = 0$ only has one transmission channel in a monolayer before reaching the region covered by the nanoribbon. After it reaches the covered region, the electron can go through another channel in the nanoribbon due to interlayer coupling (nonzero though small). Thus the covered region is a two-channel region for electron transmission, as shown in figure 4-9 (a). Because electron wavefunctions exist in both channels, destructive interference

between them occurs at certain wave vectors (k_z). This is the so-called antiresonance, which leads to the zeros in the transmission.

4.3 Antiresonance

The antiresonance in transmission occurs when the change of phase in the wave-function is equal to $2n\pi$. In that case, the electron travels in one closed loop through the two-channel region. Therefore

$$k_z(2l + 2l_0) = 2n\pi \quad (4.1)$$

where l is the width of nanoribbon and l_0 is an effective length used to represent interlayer hopping distance as shown in figure 4-9

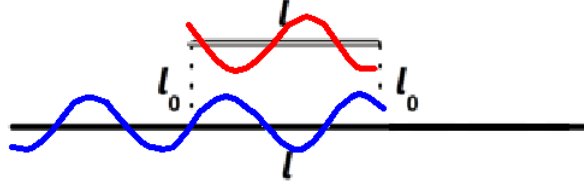


Figure 4-9: Antiresonance effect between layers.

Thus in antiresonance, the inverse of the wave vector k_z should have a linear relationship with the width of nanoribbon. This may be calculated from 4.1 as:

$$\frac{1}{k_z} = \frac{1}{n\pi}(l + l_0) \quad (4.2)$$

Now we plot the inverse of wave vector k_z at zero transmission as function of width l of nanoribbon with k_z in units of $\pi/u.c.$ and l in unit of u.c. If we do a fit with these points we get the linear relation expressed in figure 4-10 when l_0 is set equal to 0.5 and 1 u.c. for the armchair and zigzag configurations, respectively. The slope for armchair ranges between 1/2 and 1/4 when n is equal to 1, 2, 3 and 4; the slope for zigzag ranges between 1/4 and 1/11 when n ranges from 4 to 11. It is important to note that n is an integer, therefore the linear relation may be clearly observed for the armchair and zigzag arrangements. This confirms our hypothesis that antiresonance creates the zero

observed in the transmission for one channel.

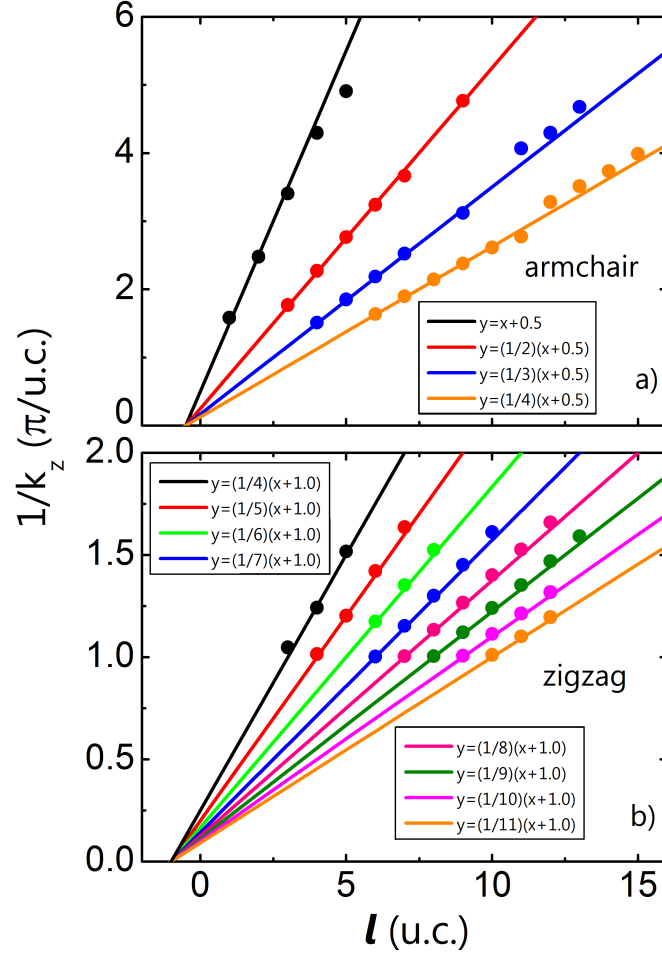


Figure 4-10: Linear relationship between $1/k_z$ and l .

Although we have described these results only for $k_y = 0$, the linear relation and the antiresonance mechanism are general for all k_y channels. Thus, we may state that antiresonance reduces the transmission of the monolayer when covered by a finite-width nanoribbon as shown in figure 4-7. In the case of infinite coverage, antiresonance will not happen since $l = \infty$.

CHAPTER 5

CONCLUSIONS

In this thesis, we studied the electronic transport properties of different graphene structures, including monolayers, bilayers, mono-bilayers and junctions between mono-bilayers and monolayers, using the Landauer-Buttiker formalism combined with density functional theory. The structures under study can be viewed as a graphene monolayer covered by another layer of varying width. The main conclusions of this study are as follows:

- 1) The band structure calculations show weak interlayer coupling in the graphene bilayer.
- 2) The change in the electronic transport properties of a monolayer is insignificant when it is covered by an infinitely large layer or even a semi-infinite one.
- 3) The change in the electronic transport properties of a monolayer can be considerable when covered by a nanoribbon with finite width. This change is due to antiresonance in the electron transmission caused by interference between the wavefunctions in the two layers.
- 4) The results presented in this thesis introduce a new method to control electron flow in graphene monolayers for future applications in nanoelectronic devices.

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