Spin and charge transport in graphene devices in the classical and quantum regimes
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Chapter 2

Electronic properties and charge transport in graphene

Abstract

One of the reasons graphene is widely studied is due to its interesting electronic characteristics such as the linear electronic dispersion and the high mobilities. In this chapter I will introduce the basic electronic properties of graphene needed for the understanding of this thesis. I start by describing graphene’s crystal lattice and Brillouin zone and then introduce the tight-binding procedure to obtain the electronic dispersion. After discussing the effect of the edges on the electronic properties, a brief review on the electronic transport in graphene is given. The concepts of quantum confinement and quantum Hall effect will be introduced and, using a semi-classical explanation, I will explain how the transition from one regime to the other happens. At the end of the chapter I introduce the basic concepts used to calculate the conductance of a system using a tight-binding approach, which will later be applied to graphene nanostructures.
2. Electronic properties and charge transport in graphene

2.1 From graphite to graphene

Graphite is known by humankind already for thousands of years. It’s early applications range from decorative painting to marking sheep, and more recently in pencils and lubricants. Having been studied already for decades, the atomic and electronic structure of graphite is very well described and understood [1, 2]. Graphite is composed by several layers of carbon atoms in a sp² hybridization arranged in a honeycomb lattice, with the layers held together by van der Waals forces. Since the interlayer forces are weak, one graphite layer can slide over another. Maybe the most famous and remarkable demonstration of this fact was the development of the so-called “Scotch tape technique” by Novoselov et al. [3] to easily obtain single layer graphite on a substrate.

Single layer graphite, or graphene, has several outstanding electronic and structural properties [4–6], such as high mechanical strength, thermal conductivity, charge carrier mobility, and current carrying capabilities.

2.2 Lattice structure and Brillouin zone

As previously said, graphene is composed by carbon atoms in a sp² hybridization arranged in a honeycomb lattice, forming a one-atom-thick 2D sheet. The unit cell is composed by two atoms in inequivalent triangular sublattices: A and B, depicted in grey and black in Fig. 2.1(a).

![Graphene lattice structure](image)

Figure 2.1: Graphene lattice structure showing the sublattice A in grey and B in black, the unit vectors $\vec{a}_1$ and $\vec{a}_2$, and the unit cell in light grey. The two main edge orientations, armchair and zigzag, are indicated.
2.3. Band structure

The unit vectors can be defined as:

\[ a_1 = \left( \frac{\sqrt{3}}{2}, \frac{a}{2}, 0 \right), \]  
\[ a_2 = \left( \frac{\sqrt{3}}{2}, -\frac{a}{2}, 0 \right), \]

where \( a = |a_1| = |a_2| = a_{C-C}\sqrt{3} = 0.246 \text{ nm} \) is the lattice constant and \( a_{C-C} = 0.142 \text{ nm} \) the carbon-carbon bond length.

As its real space lattice, graphene’s Brillouin zone is 2D and hexagonal, but rotated by 90° (Fig. 2.2a). The reciprocal vectors \( b_j \) can be obtained by the relation \( a_i \cdot b_j = 2\pi \delta_{ij} \):

\[ b_1 = \left( \frac{2\pi}{a\sqrt{3}}, \frac{2\pi}{a}, 0 \right), \]
\[ b_2 = \left( \frac{2\pi}{a\sqrt{3}}, -\frac{2\pi}{a}, 0 \right), \]

The Brillouin zone has two important inequivalent, but energy degenerate points at the corner of the hexagon called K and K’. At these points the valence and the conduction band touch, therefore graphene is a zero-bandgap semiconductor. By symmetry \[7\] it can be shown that the band structure can be fully mapped by obtaining the electronic dispersion along the triangle \( \Gamma KM \) as depicted in Fig. 2.2 (a).

2.3 Band structure

In order to obtain the band structure for graphene we can resort to several different techniques. The tight binding method is one of the most used due to its simplicity. More complicated methods, such as the density functional theory (DFT) can give more precise results, since it considers the interaction of several atomic orbitals at once, which is often neglected in the tight binding approach. However, the tight binding method has the advantage that the underlying physics can be easily understood, therefore it is still widely used. Below I show how this approach can be used to obtain the electronic structure of graphene.

The tight binding approach

The tight binding model applied to graphite \[8\] has been used for more than 70 years to describe its electronic properties \[1\]. This model uses the approximation
Electronic properties and charge transport in graphene

that only the valence electrons are sufficient to describe the electronic properties of the system.

Carbon atoms in a sp\(^2\) hybridization have four valence electrons in the orbitals: 2s 2p\(_x\) 2p\(_y\) and 2p\(_z\). For the main electronic properties in graphene it is sufficient to ignore the first three orbitals which compose the \(\sigma\)-bonds between the carbon atoms and consider only the delocalized \(\pi\)-electrons in the p\(_z\) orbitals. Therefore, we will use p\(_z\) orbitals of the A and B atoms \(|\phi_A\rangle\) and \(|\phi_B\rangle\) as the basis for our tight binding wavefunctions:

\[
\Phi_j(\vec{r}, \vec{k}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \phi_j(\vec{r} - \vec{R}),
\]

where the sum is over all unit cells, \(N\) is the number of unit cells in the crystal, \(j=A,B\), and \(\vec{R}\) is the position of the atom.

Let us start by calculating the matrix element of the Hamiltonian \(H_{AA}\):

\[
H_{AA} = \frac{1}{N} \sum_{R=R'} \langle \phi_A(\vec{r} - \vec{R}) | H | \phi_A(\vec{r} - \vec{R}') \rangle = (1/N) \epsilon\]

where we are considering only nearest-neighbours, i.e. disregarding terms of order equal or higher than \(R = R' + a\). We also defined the self-energy term

\[
\langle \phi_A(\vec{r} - \vec{R}) | H | \phi_A(\vec{r} - \vec{R}) \rangle = \epsilon.
\]

Since we are assuming the atoms A and B as being identical, we have \(H_{AA} = H_{BB} = \epsilon\).

Next let us treat the elements \(H_{AB}\). Still considering only nearest neighbours, we have:

\[
H_{AB} = t \left(e^{i\vec{k} \cdot \vec{R}_1} + e^{i\vec{k} \cdot \vec{R}_2} + e^{i\vec{k} \cdot \vec{R}_3}\right) = tf(\vec{k})(2.5)
\]

where \(t = \langle \phi_A | H | \phi_B \rangle \approx -2.7\) eV and, using the atom coordinates according to Fig. 2.1

\[
f(\vec{k}) = e^{ik_x a/\sqrt{3}} + 2e^{-ik_x a/2\sqrt{3}} \cos \left(\frac{k_x a}{2}\right).
\]

The tight binding method comes down to solving the so-called secular equation to obtain the electronic dispersion in the system:

\[
det (H - SE) = 0
\]

where the overlap integral matrix is given by \(S_{ij} = \langle \Phi_i | \Phi_j \rangle\). \(S_{ij}\) gives the overlap between the orbitals at sites \(i\) and \(j\). Here, as a first approximation, we are going to neglect this term and substitute it for the identity matrix. With no loss of generality we shift the energy scale to \(\epsilon = 0\) eV. Therefore we have to solve:
2.3. Band structure

Figure 2.2: (a) Graphene’s Brillouin zone with the high symmetry points. (b) Electronic dispersion obtained via tight binding for the lines of the triangle $\Gamma KM$. (c) Detail of the dispersion in (b) showing the linear dispersion around the $K$ point for low energies.

\[
\begin{vmatrix}
-E & tf(\vec{k}) \\
-tf(\vec{k})^* & -E
\end{vmatrix} = 0.
\]

\[
E^2 - t^2 |f(\vec{k})|^2 = 0, \quad (2.8a)
\]

\[
E = \pm t \sqrt{|f(\vec{k})|^2}, \quad (2.8b)
\]

where:

\[
\sqrt{|f(\vec{k})|^2} = \sqrt{1 + 4\cos\left(\frac{k_x a \sqrt{3}}{2}\right) \cos\left(\frac{k_y a}{2}\right) + 4\cos^2\left(\frac{k_y a}{2}\right)} \quad (2.9)
\]

Finally we can plot the solutions (equation 2.8b) as a function of $\vec{k}$ along the high-symmetry directions of the triangle $\Gamma KM$, Fig. 2.2(b). Note that the electronic dispersion is electron-hole symmetric. In reality there is an asymmetry which is particularly visible at high energies ($|E| > 1$ eV). This asymmetry is obtained when a higher number of neighbours is used in the calculation, or with the inclusion of the the overlap matrix $S$. However, since most electronic transport and optical experiments are performed in the energy range $|E| < 1$ eV, the electron-hole asymmetry is negligible for most purposes discussed in this thesis.

A simple expression of the electronic dispersion for graphene at low energies can be obtained by expanding equation 2.9 around the K point and considering only the lower order terms. By doing so and substituting in equation 2.8b we have:

\[
f \approx \frac{a\sqrt{3}}{2} (ik_x - k_y), \quad (2.10a)
\]

\[
E \approx \pm t\frac{a\sqrt{3}}{2} \sqrt{k_x^2 + k_y^2}, \quad (2.10b)
\]

\[
E \approx \pm \hbar v_F |\vec{k}|, \quad (2.10c)
\]

where $v_F \approx 10^6$ m/s is the Fermi velocity.
Equation 2.10c shows the famous property of linear dispersion in graphene for small energies. Moreover, it can be shown that this result can also be obtained using the Hamiltonian:

$$ \mathcal{H} = \hbar v_F \vec{\sigma} \cdot \vec{k}. $$

This Hamiltonian is identical to a Dirac Hamiltonian for massless relativistic particles and velocity $v_F$. Therefore electrons in graphene are commonly referred as "Dirac particles".

### 2.4 The effect of the edges

The graphene crystal has two main crystallographic orientations in which the edge of the flakes can be terminated called zigzag and armchair (Fig. 2.1). These two edge types have different electronic properties that will be discussed below. Despite that some experiments do show flakes with a nearly perfect edge orientation \[9, 10\], transport experiments are usually performed in flakes showing heavily defected versions of these two types, or in an orientation that is between the armchair or zigzag lines. However, it is often very relevant to study and understand the electronic properties of these two edge orientations since the experimental results can usually be mapped on a combination of both \[11\].

**Armchair edges** are composed of both sublattices A and B. As a consequence of the boundary conditions for this edge \[12\] the degeneracy of the two valleys K and K’ is lifted at the edge. Graphene nanoribbons with armchair edges were shown to be composed of 3 families characterized by the number of dimer lines $N$ in their widths \[11, 13\]. In a tight-binding approximation, for a positive integer $p$, if $N = 3p + 2$ the ribbons is metallic. If $N = 3p$ or $N = 3p + 1$ the ribbon is semiconductor. The electronic dispersion of these three families calculated using tight binding is shown in Fig. 2.3(a). However, it was later shown that all armchair ribbons appear to be semiconducting when a more accurate calculation, using DFT, is performed \[13\]. This can be understood by the tightening of the bonds of the atoms at the edge, which changes the hopping elements between them. If these hopping elements are differentiated, the correct result is obtained \[13\].

Opposed to armchair edges, **zigzag** edges are composed of only one sublattice. When the electronic dispersion for nanoribbons with zigzag edges is calculated using tight binding, the ribbons are found to be metallic with a high density of states at the Fermi level \[11\] independent of their widths $N$, where $N$ is the number of zigzag lines in the ribbon, Fig. 2.3(b). The high density of states is due to edge states and results in an instability in the electronic structure \[14\]. This instability can be resolved by allowing for spin polarization in the system \[13, 15\]. It is known that, for bipartite lattices like graphene’s, when the number of atoms of one sublattice is larger than for the other, the ground state of the system is expected to be ferromagnetic \[16\]. Indeed it was theoretically shown that the ground state of zigzag graphene nanoribbons is antiferromagnetic \[15\]. These ribbons can be tuned to a semi-metallic state by the application of an external electric field, indicating that it would be possible to generate a pure spin current using zigzag graphene nanoribbons. The antiferromagnetism appears due to the mutual interaction of the edges and, as the width of the ribbon increases, the ribbon can become ferromagnetic \[14\]. However, the spin polarization at the edges of a zigzag ribbon is not very robust to disorder \[17\], and disappears even for relatively smooth edges with one defect per nm.
2.5 Electronic transport in graphene

In this section I am going to review a few basic concepts of electronic transport in nanostructures and apply those concepts to the specific case of graphene. Let us start by defining a few relevant length scales. However, no mathematical definition of the length scales will be given yet. I will get to that later in this chapter.

The first length scales are the sample dimensions, which for a 2D conductor are: the width $W$ and length $L$. Depending on the relation between the sample dimensions and the distance

Figure 2.3: Electronic dispersion for graphene nanoribbons for (a) armchair and (b) zigzag edges with widths $N = 4, 5,$ and $6$. Adapted from Ref. [11].
that the charge carriers travel before being scattered, called the mean free path $l_{mfp}$, we can have different transport regimes. The most usual case is $l_{mfp} \ll W, L$, which is called the diffusive regime. In this regime the carriers scatter several times, randomizing their momentum while they travel through the conductor.

Most of the studies in graphene are done in the diffusive regime and the transport of the carriers can be well described by the semi-classical diffusive formulas discussed in the next section. When the mean free path becomes comparable to, or larger than, the sample dimensions we enter the ballistic regime. This regime started to be accessible for graphene researchers with the development of high quality graphene devices such as suspended graphene [18, 20] and hexagonal Boron Nitride (hBN) supported graphene [21, 22]. For these types of samples, $l_{mfp}$ can be in the order of $\mu$m [23], which makes the ballistic regime more accessible than the regular devices of graphene on Si/SiO$_2$ substrates, in which $l_{mfp} \approx 10$ nm.

Until now we discussed the effects of momentum scattering on charge transport. However, electrons can carry information not only through their charge and momentum but also its phase and spin. Each one of the characteristics of the total electron wavefunction - i.e. momentum, phase and spin - gets randomized during transport over its own characteristic length scale: the momentum over the mean free path $l_{mfp}$, the phase over the phase coherence length $\lambda_\phi$, and the spin over the spin relaxation length $\lambda_s$.

The rest of this chapter will treat more in depth the transport of carriers in the diffusive and ballistic regime, including the effect of a magnetic field in the charge transport, and will end with a brief introduction to phase coherent effects. The spin coherent transport and the techniques used to measure it will be discussed in the next chapter.

### 2.5.1 Graphene Field-Effect Transistors

A basic field-effect transistor (FET) is composed of three electrodes: source, drain and gate. The source and drain are connected by a conducting channel, graphene in our case, and the gate electrode is isolated from the channel by an insulator, in most cases SiO$_2$, Fig. 2.4(a).

![Graphene FET Diagram](image)

**Figure 2.4**: (a) Cartoon of a graphene FET including the circuit diagram. The source (S), drain (D) and gate (G) electrodes are indicated. (b) Sketch of the conductivity as a function of the gate voltage for a graphene FET. The band diagram with the Fermi energy ($E_F$) as a function of the gate voltage is also shown.

When a voltage $V_{sd}$ is applied between the source and drain electrodes, a current $I_{sd}$ flows...
through the channel and, knowing both $V_{sd}$ and $I_{sd}$, we can calculate the conductance $G = I_{sd}/V_{sd}$. The application of a voltage between the gate and the source electrodes changes the Fermi energy location in the bandstructure and therefore the carrier density $n$ in the channel. This changes graphene’s conductivity $\sigma$ according to Drude’s formula \cite{24}, Fig. 2.4(b):

$$\sigma = ne\mu,$$  \hspace{1cm} (2.12)

where $e$ is the electron charge and $\mu$ is the carrier mobility in the channel. The carrier mobility can be defined for graphene in terms of the mean free path using the formula: $\sigma = \frac{2e^2}{h} k_F l_{mfp}$, where $h$ is the Planck’s constant and $k_F$ the Fermi wavevector. Using the relation $k_F = \sqrt{\pi n}$ we can define the mobility as:

$$\mu = \frac{2e}{h} \sqrt{\pi n} l_{mfp}. \hspace{1cm} (2.13)$$

From equations 2.12 and 2.13 assuming that $l_{mfp}$ stays finite, we would expect that the conductivity goes to zero and the mobility to infinity at very low carrier densities. However, due to the massless Dirac fermion character of the carriers in graphene, theory shows that the minimum of conductivity for both ballistic and diffusive cases is $\frac{4e^2}{\pi h}$ \cite{25}. Nevertheless, experimental results showed $\sigma_0 \approx \frac{4e^2}{\pi h}$ \cite{25, 26}. This discrepancy between the initial theoretical predictions and experimental results is known as the mystery of the missing pi. Later it was theoretically suggested that the aspect ratio of the graphene flake might play a major role on the minimum of conductivity due to transport via evanescent waves \cite{27}, reaching the value $\sigma_0 = \frac{4e^2}{\pi h}$ for $W/L \gg 1$. The experimental verification of this fact was reported one year later \cite{28}.

At high carrier densities the conductivity is limited due to short range scatterers to a value $\rho_s^{-1}$ \cite{4, 26, 29}. Therefore, a more realistic equation for the conductivity of graphene is given by \cite{21}:

$$\sigma = \left( \frac{1}{ne\mu + \sigma_0 + \rho_s} \right)^{-1}. \hspace{1cm} (2.14)$$

It is important to highlight that even for devices with considerable inhomogeneity, graphene FET show mobilities in the order of $10^3$ cm$^2$/Vs, comparable to Si transistors used in CMOS industry. This high mobility in graphene is due to the fact that graphene has low electron-phonon coupling and, because of the chiral nature of the carriers, backscattering is forbidden due to pseudo-spin conservation\cite{26}.

Since the mobility of graphene FETs has shown to be so robust against impurities and defects, it was expected that graphene might take over silicon’s place in the CMOS industry. This high mobility in graphene is due to the fact that graphene has low electron-phonon coupling and, because of the chiral nature of the carriers, backscattering is forbidden due to pseudo-spin conservation\cite{1}.

1This means that to scatter an electron from one branch of the dispersion cone to the branch with opposite momentum ($\vec{k} \rightarrow -\vec{k}$) it has also to change valleys ($K \rightarrow K'$) in order to conserve pseudo-spin. This is difficult since it demands a scatterer with a large wavevector.
But often these results are accompanied by a degradation in the carrier mobility or a fast decrease of the on/off ratios with temperature.

Even though its future in digital electronics seems uncertain, graphene’s future in industrial applications in electronics for high-frequency devices [32], transparent touch screens [33] and pressure sensors [34] looks promising [35].

### 2.5.2 Limits on the charge transport

There are three main types of disturbance that limit charge transport in graphene: short and long range scatterers, and electron-phonon scattering. Short range scatterers constitute of scattering potentials with ranges comparable to graphene’s unit cell. They are, for example, vacancies, cracks, and edges. Since their corresponding wavevector is large, short range scatterers are the main contribution to intervalley scattering (scattering from K to K’).

Long range scatterers are due to potentials that decay slowly in space, such as charged impurities. Due to their short corresponding wavevector, they cause intravalley scattering processes. Long range scatterers seem to be the main responsible for the conductivity obtained in graphene samples on SiO$_2$ with intermediate mobilities [26]. Since they are composed in great part by Coulomb scatterers (e.g. charged impurities), their effects are large at small $n$ and reduce with increasing charge density due to screening [26]. These charged impurities can come from adatoms or hydrocarbons left on the graphene due to the sample preparation process, or due to charge trapping on the surface of the substrate. The fluctuation in the potential causes a spacial fluctuation on the position in energy of the charge neutrality point, which results in the so-called electron-hole puddles [36]. The contribution to the conductance due to charged impurities can be significantly reduced for devices where the substrate is eliminated, therefore suspending the graphene flake [19], or where a less invasive substrate is used, such as hBN [37]. In this case of high quality samples, the culprits for the upper limit on the measured conductance are short range scatterers as already mentioned.

Coupling to surface phonons from the substrate has also shown to be important for the charge transport in graphene, specially for SiO$_2$ substrates [38]. Such contributions are eliminated in high quality devices by using less invasive substrates or by suspending the graphene flake. Experiments performed at low temperatures ($T < 150$ K) show that the electronic mobility of high quality suspended graphene samples seems to be limited due to flexural phonons [39]. It has been predicted that, similar to charge transport, spin transport in suspended samples could also be limited by flexural phonons [40], however experiments in homogeneously clean samples have to be performed in order to confirm these predictions [41].

### 2.5.3 Conductance quantization

Within the ballistic regime, we can observe quantum confinement of the carriers when the their wavelength at the Fermi energy is in the same order of the sample dimensions: $\lambda_F \geq W, L$. Here I will describe how confinement leads to quantized plateaus in conductance, and also will treat the evolution from 1D confinement to the quantum Hall state in the next section.

When we have the condition $l_{mfp} > \lambda_F \geq W$, the electrons can probe both edges of the sample before scattering. This leads to a confinement of the carriers in which, as in typical quantum well examples in quantum mechanics [42], leads to a quantization of the energy
2.5. Electronic transport in graphene

with characteristic quantum numbers \( n_x, n_y, \) and \( n_z \) for quantization in each of the three dimensions.

In the case of graphene, the carriers are already confined in the \( z \) direction. Due to the small thickness of the graphene flake, the separation of the energy levels in the \( z \) direction is so large that only the ground state for the quantum number \( n_z \) is considered. We can confine the carriers in another dimension by, for example, cutting the graphene flake along one direction (e.g. \( x \)) in order to create a ribbon. This results in additional confinement of the carriers which leads to quantization in the (quasi-) momentum in the \( y \) direction, \( k_y \), while the spectra in the \( x \) direction is continuous. The quantization in \( k_y \) leads to the formation of subbands and quantization of the conductance according to the Landauer-Buttiker formula:

\[
G = \frac{\nu e^2}{h} M, \tag{2.15}
\]

where \( \nu \) is the degeneracy of the subbands and \( M \) is the number of subbands below the Fermi level.

The conductance quantization due to lateral confinement of the carriers was first observed in 1988 by van Wees et al. \[43\] and Wharam et al. \[44\] in a GaAs 2-dimensional electron gas (2DEG). There, the confinement of the carriers was done electrically, by a pair of gate electrodes (split gates) and clear plateaus at integers of \( 2e^2/h \) as a function of the width of the channel were observed, where the factor of 2 is due to spin degeneracy.

In graphene, if the valley and spin degeneracy are both conserved, we expect quantized plateaus in steps of \( 4e^2/h \) (a factor of 2 for valley and 2 for spin degeneracies). As explained before, for an armchair graphene nanoribbon the valley degeneracy is lifted, which leads to quantized plateaus in the conductance in steps of \( 2e^2/h \).

Theoretical works indicate that conductance quantization in graphene nanoribbons is not very robust with respect to edge disorder \[45\]. It was shown that conductance quantization can be observed for a reasonable amount of defects (removing about 10% of the atoms at the edge), although the transmission for the subbands can be seriously reduced, specially at high energies. This effect get stronger for longer ribbons which causes localization of the carriers and seems to be responsible for Coulomb blockade effects in etched graphene nanoribbons \[46\].

Indication of the formation of subbands in graphene nanoribbons was observed in 2008 for etched graphene devices \[47\]. However, the transmission for each channel was very low, \( T \approx 0.01 \), most probably due to the low mean free-path in these devices.

The first observation of conductance quantization in a single layer graphene ballistic nanoconstrictions was done in 2011 for suspended graphene devices \[48\]. In this work conductance quantization in steps of \( 2e^2/h \) was observed, indicating one broken degeneracy (valley) as shown in Fig. 2.5. Semi-classically, the conductance as a function of the Fermi wavevector is given by: 

\[
G = \frac{4e^2}{h} k_F W \pi. 
\]

By fitting this linear relation to the data, a width for the constriction of \( W \approx 200 \) nm was obtained. This value for the width was also confirmed by the transition between quantum confinement to the quantum Hall state as we will see in the next section.

It is interesting to note that the plateaus in conductance shown in Fig. 2.5 have values very close to multiples of \( 2e^2/h \), which indicates a transmission close to unity for the channels.

Later works performed on etched suspended graphene nanoribbons which had a much longer channel showed electronic localization, which results in Coulomb blockade at zero
2. Electronic properties and charge transport in graphene

Figure 2.5: Conductance as a function of the Fermi wavevector $k_F$ for holes in a suspended graphene nanoconstriction. The line is the equation $G = \frac{4 e^2}{h} \frac{k_F W}{\pi}$ with $W = 200$ nm. Inset: Scanning electron micrograph of a suspended graphene nanoribbon created after the current annealing procedure. Adapted from Ref. [48].

magnetic field [49]. However, it was possible to demonstrate the high quality of the devices by the transition to the quantum Hall state at reasonably low magnetic fields. This work showed that the edges of the ribbons can strongly affect the charge transport even for high quality devices, which results in a reduction of the carrier’s mean free-path.

Works on electrical confinement in bilayer graphene devices [50, 51] also showed conductance quantization in steps of $2e^2/h$, which also indicate that the valley degeneracy has been lifted. Until now there is no clear understanding why the valley degeneracy seems to be lifted in these devices.

2.5.4 Quantum Hall effect

When a 2DEG is subjected to a perpendicular magnetic field the carriers experience a Lorentz force while travelling through the device. At low magnetic fields the carriers are deflected to the edges of the sample, which results in a voltage difference between the edges (Hall voltage) given by [24]: $V_H = IB/en = \mu I B/\sigma$, where $I$ is the applied current. At high enough magnetic fields the carriers are forced to move in closed loops and quantum effects start to play a role. Adopting a semi-classical approach, due to the wave nature of the electrons, the circumference of the loops has to be an integer number of the de Broglie wavelength (and the inclusion of a phase factor). Using a quantum mechanical approach, it can be shown [24] that the Schrödinger equation for the carriers under a magnetic field is equivalent to the equation for a harmonic oscillator with frequency $\omega_c = eB/m^*$, known as the cyclotron frequency, where $m^*$ the effective mass. This results in a quantization in the allowed energies, called Landau Levels (LL), and is given by:

$$E_N = (N + 1/2) \hbar \omega_c.$$  \hspace{1cm} (2.16)

\[\text{For single layer graphene the cyclotron mass is used instead.}\]
This quantization in energy is the origin of the quantum Hall effect.

The closed orbits result in a "localization" of the carriers which do not contribute to the conductance of the device. However, at the edges of the sample the energy for the LL goes up and eventually crosses the Fermi energy (Fig. 2.6). This causes the electrons to flow through channels close to the edges of the sample. These channels, called edge channels, propagate at opposite directions in opposite edges of the sample. In a classical picture the electrons "skip" at the edges creating channels from one end of the sample to the other and with opposite directions as in the edge channel picture (Fig. 2.6).

\[
E_N = \pm v_F \sqrt{2e\hbar B(N + 1/2 \pm 1/2)},
\]

(2.17)

where the first \( \pm \) sign refers to electron (+) and holes (−) and the last \( \pm 1/2 \) term is due to the chiral nature of the carriers. The resulting Hall resistance is quantized and given by (Fig. 2.7):

\[
\rho_{xy} = V_H / I = \frac{\hbar}{4e^2} \frac{1}{(N \pm 1/2)}.
\]

(2.18)

This is the half-integer quantum Hall effect which is a consequence of the linear dispersion in graphene \[52\]. The longitudinal resistance \( \rho_{xx} \) shows peaks when a LL is being occupied and drops to zero when the Fermi energy is between two LL (Fig. 2.7).

The Hall and longitudinal resistances are most often measured directly in a Hall bar geometry. For a 2-probe device, the conductance \( G \) measured when in the quantum Hall state depends on the aspect ratio of the device \[53\]: for long devices \( G \approx \sigma_{xy} \) while for short devices \( G \approx \sigma_{xx} \).
Figure 2.7: Quantum Hall effect in a graphene FET showing the plateaus in Hall conductance ($\sigma_{xy}$ in red) in steps of $4e^2/h$ and starting from $2e^2/h$. The longitudinal resistivity $\rho_{xx}$ (green) shows peaks when the Fermi energy crosses a Landau Level. Adapted from Ref. [52]. Inset: A graphene Hall bar showing the circuit diagram for the measurement of the transversal and longitudinal resistances.

Transition from quantum confinement to the quantum Hall effect

An interesting case that will be relevant for chapter 5 is the transition between the conductance quantization in long ballistic devices, where the quantized conductance in steps of $2e^2/h$ slowly evolves to the Hall conductance $3$. At zero magnetic field the carriers coming from one electrode are specularly reflected at the edges of the sample until they reach the other contact. As we saw in the previous section, since the device is ballistic, with $W < l_{mfp}$, the conductance is quantized in steps of $2e^2/h$. When a small perpendicular magnetic field is applied, the carriers’ paths will bend a little, but they can still bounce from the edges and the plateaus in conductance stay at the same energy values. When the cyclotron radius $l_c$ of the carriers is half the sample width there is the possibility of closed orbits in the device, meaning that we entered the quantum Hall state. This happens at a critical magnetic field $B_c$ given by:

$$l_c = \frac{W}{2} = \frac{\hbar k}{eB_c}.$$  \hspace{1cm} (2.19)

At higher magnetic fields the LL follow the same energy dependence as a regular sample. The evolution from conductance quantization due to size confinement to the quantum Hall state with increasing magnetic field is shown in Fig. 2.8.

This effect was measured in the suspended graphene constrictions presented before (from Ref. [48]) by following the back gate voltage corresponding to the centre of the first plateau in conductance $G = 2e^2/h$ as a function of the applied magnetic field (Fig. 2.9). It was shown that at very low fields, $B < 60$ mT, the centre of the plateau does not change its corresponding back gate voltage (energy). After the critical field $B \approx 60$ mT the plateau follows the quantum Hall behaviour expected for single layer graphene (Eq. 2.17). This critical field corresponds

\hspace{1cm} \footnote{Here we are assuming broken valley degeneracy.}
Figure 2.8: Semi-classical electronic trajectories for a ballistic device as a function of the magnetic field. For low fields the electron suffers specular reflection at the edges of the sample keeping the same value for $k_y$. As the field goes up the trajectories get bent due to the Lorentz force. At a critical magnetic field $B_c$ the cyclotron orbit is about the size of the device’s width and it enters the quantum Hall state.

to a constriction width of $W \approx 300$ nm, which is in reasonable agreement with the previously estimated value (Fig. 2.5).

2.5.5 Phase coherent effects

Between the ballistic and diffusive regimes there is an intermediate transport regime called quantum diffusive transport. Here we have the condition: $l_{mfp}, \lambda_F < L, W < \lambda_{\phi}$, meaning that the momentum of the charge carriers gets randomized while travelling through the system, but their phase is conserved. The phase relaxation length is related to the charge diffusion constant $D_c$ and the phase relaxation time $\tau_{\phi}$ by: $\lambda_{\phi} = \sqrt{D_c \tau_{\phi}}$.

As in optics, phase coherence gives rise to quantum interference effects which results in a modulation of the device transmission (and therefore electronic conductance). There are two main phenomena in phase coherent electronic transport: Universal Conductance Fluctuations (UCF) and Weak (Anti) Localization [54].

Universal Conductance Fluctuations

Electrons travelling through the device can take different paths (Fig. 2.10h), which causes the electrons to interfere constructively or destructively at certain places. The interference pattern leads to deviations from the classical value for the conductance of the device (which excludes
interference effects). It can be shown that the root-mean-square magnitude of the conductance fluctuations around the mean value $G_{\text{mean}}$ is [54]:

$$
\delta G = \sqrt{\langle (G - G_{\text{mean}})^2 \rangle} \approx \frac{g_v g_s e^2}{2 \hbar},
$$

(2.20)

for a valley (spin) degeneracy $g_{v(s)}$. Since for graphene $g_v = g_s = 2$, we have: $\delta G \approx 2e^2/h$.

In optics, the interference pattern can be modulated by changing the wavelength or the optical path. Using this analogy, we expect that the interference effects can be modulated by changing the carriers wavelength $\lambda_F$ or their trajectory. The wavelength can be changed by changing the Fermi energy, e.g. by using a gate voltage, and the carriers trajectory by applying a small perpendicular magnetic field. Therefore, by changing the gate voltage or a perpendicular magnetic field we expect the conductance to fluctuate around a mean value with a rms amplitude of about $2e^2/h$ (Fig. 2.10b).

The phase coherence length decreases with temperature ($T$) due to, for example, energy averaging due to temperature and electron-phonon scattering. The current flow takes place at an energy range a few $k_B T$ around the Fermi energy, where $k_B$ the Boltzmann constant. When $k_B T > \hbar/\tau_\phi$, the energy range given by the temperature broadening can be viewed as $N$ uncorrelated channels in parallel [24], with each channel having an energy width $\hbar/\tau_\phi$:

$$
N = \frac{k_B T}{\hbar/\tau_\phi} = \left(\frac{\lambda_T}{\lambda_T}\right)^2, \quad \text{where } \lambda_T = \sqrt{\hbar D e / k_B T} \text{ is the thermal length. This effect results on the reduction of the fluctuations by a factor } N^{-1/2} = \lambda_\phi / \lambda_T \quad [24, 54].
$$

---

**Figure 2.9:** (a) Conductance of a suspended graphene nanoconstriction as a function of the gate voltage $V_g$ for different values of magnetic field. The distance in gate voltage of the centre of the first conductance plateau from the charge neutrality point is indicated as $\Delta V_{N=1}$. (b) $\Delta V_{N=1}$ as a function of the magnetic field $B$. The dashed black line indicates the expected position of the Landau Level. The critical field $B_c \approx 60$ mT is also indicated.
2.5. Electronic transport in graphene

Figure 2.10: (a) Two possible trajectories for an electron to go from one electrode to the other. (b) Fluctuations of the conductance around an average value $G_{\text{mean}}$ as a function of energy or magnetic field. (c) Two closed trajectories related to each other by time reversal symmetry. If a perpendicular magnetic field is applied there is a magnetic flux $\Phi$ through the loop. (d) Conductivity as a function of magnetic field showing a characteristic weak localization dip.

Weak localization and weak antilocalization

Another interference effect that takes place in the quantum diffusive regime is an effect called coherent backscattering. To explain this effect we start by writing the probability amplitude for an electron to travel from a point A to a point B in a trajectory $i$ as $a_i e^{i\phi_i}$. Since there are many indistinguishable trajectories, the total probability to travel from A to B can be written as [26]:

$$P(A \rightarrow B) = \sum_i |a_i|^2 + \sum_{i \neq j} a_i a_j e^{-i(\phi_i - \phi_j)}. \quad (2.21)$$
If the trajectories are open, i.e. \( A \neq B \), the trajectories are uncorrelated and the second term of the equation is washed out, leaving only the classical result which is the sum of the probabilities of all possible trajectories. For closed trajectories (\( A = B \)), if two paths \( i \) and \( j \) are related by time reversal symmetry (Fig. 2.10(c)) we have: \( a_i = a_j \) and \( \phi_i = \phi_j \) and therefore
\[
P(A \rightarrow A) = 2 \sum |a_i|^2.
\]
This means that the probability of return is enhanced when comparing to the classical result. The increase in the probability of backscattering results in a decrease in \( D_c \), therefore a reduction of the conductance.

In a magnetic field, the magnetic flux through the area of the loop enclosed by the trajectory (Fig. 2.10(c)) results in a phase difference for the two time reversed trajectories. When the magnetic field is increased the interference effects are suppressed due to the relative phase changes. Therefore, the conductivity as a function of the magnetic field \( \sigma(B) \) increases with the applied field (Fig. 2.10(d)):
\[
\sigma(B) - \sigma(B = 0) > 0.
\]
This is the core result of the weak localization effect.

Due to the presence of the Berry curvature in graphene \([55]\), the constructive interference that gives rise to the enhanced backscattering transforms into a destructive one \([26]\). Therefore the conductance increases in relation to the classical result and the "\( > \)" sign in Eq. 2.22 becomes a "\( < \)". This is known as weak antilocalization \([\text{4}]\). However, if short range scatterers are present, then intervalley scattering plays a role. Since the valleys K and K' have different chiralities the weak localization effect is recovered. The transition between localization and antilocalization in graphene was shown to depend on experimental conditions such as mobility, temperature and carrier density \([57]\).

Weak (anti)localization can be used to estimate the phase relaxation length since only paths with a length smaller than \( \lambda_\phi \) will contribute to the effect. Since weak (anti)localization does not depend on the length of the sample, it can be observed even for relatively large samples therefore it is used more often than UCF to estimate \( \lambda_\phi \).

### 2.5.6 Electronic transport via the tight-binding approach

To calculate the electronic transport properties of a graphene system we can use the tight-binding combined with the retarded Green functions formalism to obtain the transmission from one point to another in the system. The transmission through the system using the retarded Green functions formalism is explained in much detail in the book "Electronic transport in mesoscopic systems" by Supriyo Datta (pg. 132-157) \([24]\). This is the same formalism adopted in the KNIT program \([58]\) which was used to obtain the results shown in chapter 5. Here I will introduce the basic concepts of the formalism used.

We start by rewriting the Hamiltonian of the system in a similar way as described in section 2.3 considering the whole graphene system (all the atoms in the system):
\[
\mathcal{H} = \sum_{i \neq j} c_i^+ t_{ij} c_j + \sum_i c_i^+ V_i c_i,
\]
where the operator $c_i^+$ creates a particle on the $i$-th site, $t_{ij}$ defines a hopping energy between the $i$-th and $j$-th sites and $V_i$ defines the on-site energy for the $i$-th site. For simplicity we adopt the first nearest neighbours approximation: $t_{ij} \neq 0$ only for adjacent sites $i$ and $j$. This means that there is only hopping between atoms from one sublattice (e.g. A) to the other (B), which leads to electron-hole symmetry as described previously in section 2.3.

Here we only consider one degree of freedom for the system. Higher degrees of the freedom (e.g. spin or different orbital quantum numbers) can be taken into account by including another index to the operators $c_i^+$. Therefore, we are assuming that the transport through the system is spin independent.

The system is connected to the environment via semi-infinite leads. The interaction of the graphene system with a semi-infinite lead $l$ is taken into account by the use of a self-energy term $\Sigma_l$. This term can be viewed as an effective Hamiltonian arising from the interaction of the graphene with the lead.

The retarded Green function for the system contacted by semi-infinite leads as a function of the energy $E$ is:

$$G(E) = \left( EI - \mathcal{H} + \sum_i \Sigma_l(E) \right)^{-1}, \quad (2.24)$$

where $I$ is the identity matrix. The self-energy term of the leads can be calculated exactly within the tight-binding approximation [24] and uses the assumption that the leads are independent, therefore their effects are additive.

The transmission between two leads $k$ and $l$ at a certain energy $E$ can then be calculated by:

$$T_{kl} = Tr \left[ \Gamma_k G_l G_l^\dagger \right], \quad (2.25)$$

where the argument $(E)$ was omitted in favour of a more compact form for the equation. The term $\Gamma_k = Im \left( \Sigma_k \right)$ can be viewed as describing the coupling between the conductor and the leads.

The related conductance is given by the Landauer formula:

$$G_{kl} = \frac{2e^2}{h} T_{kl}, \quad (2.26)$$

where the factor 2 is added to account for spin degeneracy.

In summary, if one wants to calculate the conductance of a system connected by two leads, the protocol goes as follows:

1. Obtain the total Hamiltonian of the system (without the leads) $\mathcal{H}$.
2. Obtain the self-energies of both leads 1 and 2 ($\Sigma_{1,2}$).
3. Calculate the retarded Green function given by Eq. 2.24.
4. Calculate the transmission coefficient between leads 1 and 2 ($T_{12}(E)$).
5. The conductance as a function of the energy is given by Eq. 2.26 $G_{12} = T_{12}(E)2e^2/h$. 
2. Electronic properties and charge transport in graphene

2.6 Supplementary literature

General graphene properties


Tight binding calculation of molecules and solids


Electronic transport in graphene


Electronic transport in mesoscopic devices

References

2. Electronic properties and charge transport in graphene

p. 232104, 2011.


References


