ELECTRIC TRANSPORT THROUGH C-NANOTUBES AND GRAPHENE NANORIBBONS DOUBLE QUANTUM DOTS COUPLED BY A SUPERCONDUCTOR

JUAN MANUEL GUERRA CASTRO
código 01835299
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JUAN MANUEL GUERRA CASTRO
código 01835299

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DIRECTOR
DOCTOR EN FISICA WILLIAM HERRERA

UNIVERSIDAD NACIONAL DE COLOMBIA
FACULTAD DE CIENCIAS
DEPARTAMENTO DE FISICA
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CHAPTER 1

INTRODUCTION

Graphene has become a promising material for technological applications and research in fundamental physics due to its rich physical properties. A detailed study of its hexagonal crystalline structure has been performed and has revealed its unusual electronic properties of great interest in nanotechnology and quantum electronics[1, 2, 3]. Charge carriers excitations with energies near the Fermi can be approximated by an effective Weyl-Dirac Hamiltonian thus implying relativistic behavior. As a consequence, chiral or Klein tunneling is present in transport in which electrons can tunnel a barrier with unit probability. We will review the physical properties of bulk graphene, but we will concentrate in graphene nanoribbons and carbon nanotubes in zigzag configuration and their electronic properties[4].

While ideal nanoribbons are always metallic, a band gap arises as a consequence of the curvature in nanotubes due to overlap of perpendicular orbitals and spin-orbit coupling, thus manifesting semi-metallic and semiconducting regimes according to geometry parameters[5]. These curvature effects raise valley and spin degeneracies present in graphene therefore becoming a more suitable material for quantum control applications. In nanotubes, periodicity along circumferential direction implies quantization of transverse momentum and thus to 0-dimensional energy channels available for transport. Chiral tunneling reduces electronic confinement in metallic materials, but as the energy gap increases, separated regions of the same material can be decoupled by means of a electrostatic barrier, such as a series double quantum dot. In practice, transport through single-channel carbon nanotubes double quantum dos coupled in series and tunable in-situ has been measured and has revealed the processes involved in normal- to super-current conversion. Non-local components of transport, i.e., Andreev processes at separated regions, evidence the possibility of producing entangled electronic states in a 2-level molecular system (qubit), fundamental for quantum computation[6]. A minimal model of transport thorough this device has shown that there under certain physical configurations the system can reach a
splitting efficiency of about unity[7].

Transport through \( NS \) junctions for graphene has been studied in the so called semiconductor model[8] in which current is written in terms of transmission and reflection coefficients[9]. As well, a Hamiltonian approach has been considered in which the interaction Hamiltonian between regions describes transitions between adjacent states, and mean values can be represented by means of Green’s functions. Then, the coupling between regions can be treated as a perturbation and solved using the non-equilibrium Keldysh formalism in order to compute physical observables. In the present work, we consider clean - ballistic - samples at \( T = 0 \), without magnetic scatterers, in which spin-coherent transport is approximated using a Green’s functions formalism with enough information about electronic structure and transport[10]. We develop a transport model in the tunnel limit to describe conversion from normal- to super-current through double quantum dots coupled by a superconducting electrode acting as a Cooper pairs beam splitter and a series system. We consider single-channel nanotubes to characterize the system, and then we increase the number of available quasi-bound states up to consider the infinite (continuous) case: graphene. Results are presented in terms of conductance maps or stability diagrams in the external gates voltage (\( V_L \) y \( V_R \))- space for determining resonances and between the dots, contribution of modes in transport and for representing the splitting efficiency. So, the aim of this thesis is twofold: on one hand, to determine the configurations under which non-local Andreev processes are enhanced, and, on the other hand, to derive a transport model in which processes are obtained by a perturbative approximation.

Experiments have been performed reporting conductance measurements in nano-structured devices, such as carbon nanotubes, graphene nanoribbons and nanowires, in double quantum dots configurations coupled by superconducting electrodes and biased by lateral electrodes. Transport properties of these devices have been modelled for a single-channel situation using multiple theoretical approaches. We want to extend this model up to consider transport through multiple conduction channels for the nanostructured device based on carbon nanotubes and graphene nanoribbons and carbon nanotubes. We also want to extend the Hamiltonian model of transport for the particular situation in which a central system - composed by the coupled double quantum dots - are coupled, at any perturbation order, and taking into account the underlying honeycomb structure. Thus, in the present thesis we introduce such a model and preliminary results in the lowest perturbation order.
In the present chapter, we present the physical and geometrical properties of carbon based materials - graphene and carbon nanotubes - from the atomic point of view, together with a quick review of its history. Both materials are promising for fundamental and applied research in a wide range of applications due to their rich electronic and mechanic properties. The geometry of the system defines its electronic properties. Nanoribbons are graphene stacks bounded in some rectangular way, usually with zigzag and armchair edges, and nanotubes are obtained by wrapping nanoribbons in its chiral direction. We describe the physics of graphene by means of a tight-binding Hamiltonian which represent electrons. Low-energy excitations behave like massless Dirac fermions traveling with an effective Fermi velocity about hundredths of speed of light. Relativistic effects arise as consequence, so that chiral or Klein tunneling are present in transport in which electrons tunnel a potential barrier with unit probability. Chiral direction of nanotubes determines its electronic properties: it can be either metallic or semiconducting. We considere here pure and ballistic samples of nanoribbons and nanotubes. We adopt a complete description of states in graphene by means of a spinorial representation of functions which obey Schrödinger equation of the system. This chapter is organized as follows. Section 2.1 contains the geometric and crystallographic description of the hexagonal lattice and its reciprocal space. Section 2.2 presents the energy band structure of bulk and clean graphene using the tight-binding model. In section 2.3 we present the discrete electronic spectra of graphene nanoribbons. Section 2.4 contains a discussion about relativistic properties of low-lying excitations. In section (2.5) we shall review the physics and geometry of carbon nanotubes and their conceptual relationship with graphene.
2.1 Graphene: geometry

Graphene is a two-dimensional single atomic layer of carbon atoms arranged in an hexagonal lattice. Carbon atoms can form many different allotropes by means of chemical bonding of their valence electrons[11]. Among the possibilities of hybridization of C-atoms, three \( sp^2 \) orbitals are formed thus involving the \( 2s \) orbitals hybridizing with two \( 2p \) orbital which are separated on the same plane by an angle of 120°[12], as depicted in figure 2.1 (a). Graphene can be understood as the building block of other allotropic forms of carbon, such as graphite, nanotubes and buckminsterfullerene (\( C_{60} \)). Graphite can be understood as the stacking of graphene sheets bounded by van der Walls potentials [2], and its electronic properties can be understood from graphene as well. Hexagonal lattice is not Bravais since they need three basis vectors embedded in a 2D plane, thus it can be realized as the superposition of two triangular sublattices located at a single atom, labeled as \( A \) and \( B \) in figure 2.1. Note that both sublattices are specularly related. Besides of the above mentioned valence electrons in the bonds, one \( \pi^* \) electron is aligned perpendicular to the plane, which mainly accounts for transport in graphene, as illustrated in figure 2.1 (a).

In practice, graphene may include impurities, ripples, disorder, and other scatterers thus becoming a diffusive material. Nonetheless, we assume an ideal specimen of graphene such that is clean, ballistic, and ordered. We take the unit cell of graphene lattice to be formed by two basis atoms. \( A \)- and \( B \)-type, as we depict in figure 2.1 (b). The bond distance between two neighboring carbon atoms is about \( a_0 \approx 1.42 \text{Å} \). We denote the lattice vectors of \( A \) sublattice by \( \vec{a}^A_{i,2} = \frac{a}{2} (-\sqrt{3}, \pm 1) \), where the lattice constant is \( a = \sqrt{3}a_0 \approx 2.46 \text{Å} \). The reciprocal lattice vectors are given by[13] \( \vec{b}^A_{i,2} = \frac{2\pi}{\sqrt{3}a} (-1, \pm \sqrt{3}) \), which satisfy \( \vec{b}_i \cdot \vec{a}_j = 2\pi \delta_{ij} \) for \( i, j = 1, 2 \). Each \( A \)-type carbon site has three nearest neighboring \( B \)-type atoms located at \( \vec{\delta}^A_1 = a_0(-1, 0) \) and \( \vec{\delta}^A_2,3 = \frac{a_0}{2}(1, \pm \sqrt{3}) \), as illustrated in figure 2.1 (b). The unit cell has dimensions \( a \times \sqrt{3}a \), thus its area is given by \( \Omega_0 = \sqrt{3}a^2 \approx 10.48 \text{Å}^2 \). The first Brillouin zone has area \( \Omega^*_0 = \frac{4}{\sqrt{3}} \left( \frac{2\pi}{a} \right)^2 \). Similar definitions are made for sublattice vectors of atoms at \( B \). Each nearest neighbor of \( B \)-atom is located at \( \vec{\delta}^B_\alpha = -\sigma_z \vec{\delta}^A_\alpha (\alpha = 1, 2, 3) \), where \( \sigma_z \) is the diagonal Pauli matrix and represents a reflection in the \( x \)-direction. Sublattice \( B \) vectors are obtained from \( \vec{a}^B_{i,2} = -\sigma_z \vec{a}^A_{i,2} \). Therefore, the reciprocal vectors are given by \( \vec{b}^B_{i,2} = -\sigma_z \vec{b}^A_{i,2} \). Moreover, rotational transformation on the lattice vectors can be reached by applying the operation \( \vec{a}_{1,2} \rightarrow R(\theta)\vec{a}_{1,2} \), such that \( R(\theta) = R(\theta + 2\pi/3) \). Therefore, bulk graphene can be mathematically understood as the combination of infinite unit cells
along both directions. Bravais vectors for describing each sublattice can be determined by integers \(n_1\) and \(n_2\) such that \(\vec{R}_A = n_1\vec{a}_1 + n_2\vec{a}_2\) and \(\vec{R}_B = n_1\vec{b}_1 + n_2\vec{b}_2 - \vec{\delta}_1\).

Figure 2.1: a) Orbital distribution of C-atom in \(sp^2\) hybridization. Bonding orbitals are in the same plane and separated 120°. (b) Unit cell of graphene hexagonal lattice. Solid-color atoms indicate the basis atoms together with their corresponding direct lattice vectors. (c) First Brillouin zone and hexagonal symmetric sites, and c) bulk graphene hexagonal lattice where zigzag and armchair edges are indicated. C-C atoms distance is about \(a_0 = 0.142\)nm and lattice constant \(a_0 \approx 0.246\)nm.

### 2.2 Electronic band structure

We describe graphene using a nearest neighbor Tight-Binding (TB) Hamiltonian. We assume the \(\sigma\) electronic energy bands far away from the Fermi energy, so their contribution to transport is not significant[14]. The band structure of \(\pi\) electrons in graphene was first derived by Wallace [1] in 1947 using a similar approach to that of presented here. Since then, graphene has been intensively studied due to its rich electronic properties which have been measured in lot of experiments. The pioneering experimental works are due
to K. Novoselov and A. Geim, awarded with the Nobel prize in 2010 for groundbreaking experiments regarding graphene [15, 16].

Time-independent Schrödinger equation of a single $\pi$-band electron of carbon in bulk graphene system is given by $\hat{H}\psi = E\psi$. The wavefunction $\psi = \psi(x, y)$ must reflect the rotational and translational symmetries of the underlying lattice. The translational symmetry of the system by lattice vector $\vec{R}_{A,B} = \vec{R}$ can be represented by the operator $\hat{T}_{\vec{R}_{A,B}} = e^{i\vec{k} \cdot \vec{R}_{A,B}}$, in terms of the momentum $\vec{k} = h(k, q)$, which will be restricted to the first Brillouin zone. Since the physical quantities must remain invariant under this transformation, $\hat{T}$ must commute with the full Hamiltonian $[\hat{T}, \hat{H}] = 0$. The Bloch wavefunction for the site $a$ is constructed from the orbital wavefunction $\phi^{(a)}(\vec{r} - \vec{R})$ as

$$\psi_{k}^{a}(\vec{r}) = \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \phi^{a}(\vec{r} - \vec{R}). \quad (2.1)$$

Equation 2.1 may be eigenvector of $\hat{T}$, hence $\hat{T}\psi_{k}(\vec{r}) = e^{i\vec{k} \cdot \vec{R}}\psi_{k}(\vec{r})$. Since the lattice has two atoms per unit cell, the wavefunction must be a linear combination of normalized Bloch wavefunctions in each site $A$ and $B$ on the lattice, denoted by

$$\psi_{k}(\vec{r}) = a_{k}\psi_{k}^{(A)}(\vec{r}) + b_{k}\psi_{k}^{(B)}(\vec{r}), \quad (2.2)$$

where $a_{k}$ and $b_{k}$ are complex functions of $\vec{k}$. The wavefunctions $\psi_{k}^{(A)}(\vec{r})$ and $\psi_{k}^{(B)}(\vec{r})$ are both of the form of equation 2.1, with the corresponding lattice vectors $\vec{A}$ and $\vec{B}$. The transfer integral matrix is obtained from $H_{ij} = \langle \psi_{i} | \hat{H} | \psi_{j} \rangle$ where $i, j = A, B$, which can be described using a parameter of hopping probability. The energy dispersion relation is readily obtained by solving the secular equation $\det[\hat{H} - E\hat{I}] = 0$. The TB Hamiltonian of the model is represented by

$$\hat{H} = -t \sum_{<i,j>, \sigma} \left( \hat{a}_{\sigma,i}^\dagger \hat{b}_{\sigma,j} + h.c. \right), \quad (2.3)$$

where $\hat{a}_{i,\sigma}$ ($\hat{a}_{i,\sigma}^\dagger$) annihilates (creates) an electron with spin $\sigma = \uparrow \downarrow$ on site $\vec{R}_{i}$ on sub-lattice $A$ (an equivalent definition is used for sub-lattice $B$), $t \approx 2.8eV$ is hopping energy between nearest neighbouring atoms of different sublattice. The overlap integral between nearest
atoms of the same sublattice is completely neglected; it can be found for instance in [2, 44]. It can be shown that the dispersion relation for electrons in graphene, under the above mentioned restrictions, is given by

$$\epsilon_\pm(\vec{k}) = \pm t \sqrt{1 + 4 \cos^2(\frac{qa}{2}) + 4 \cos(\frac{qa}{2}) \cos(\frac{\sqrt{3}ka}{2})},$$

(2.4)

where the plus (minus) sign represents the valence (conduction) band or the bonding $\pi$ (anti-bonding $\pi^*$) bands. Energy must be measured relative to the Fermi level, in the solid state system, thus $\epsilon \rightarrow \epsilon - E_F$. The band structure of Graphene is drawn in figure 2.2, where it can be seen that conduction (lower) and valence (upper) bands cross at six vertices in the Brillouin zone where $\epsilon_\pm(k, q) = 0$, and are spin degenerate. These vertices are given by $k = 0$, $q = \pm 4\pi/3a \equiv K_\pm$, and $k = \pm 2\pi/\sqrt{3}a$, $q = \pm 2\pi/\sqrt{3}a$. Within these points, only two are translationally inequivalent, which we take as $\vec{K}_\pm = (0, K_\pm)$ and are showed in figure 2.1 (c). These points represent the valley degree of freedom, and spectrum is degenerate nearby satisfying $\epsilon_\pm(\vec{K}_\pm) = 0$. Therefore, graphene is a semi-conductor with zero activation energy[1]. In the neighborhood of these points, dispersion is nearly conical and thus can be approximated by the continuum limit $\epsilon_\pm(\vec{k} + \vec{K}_\pm) = \pm t_g \sqrt{k^2 + q^2}$, with $t_g = \sqrt{\frac{3at}{2}}$, for $|\vec{k}|a << 1$. This approximation holds for energies $\epsilon \lesssim 0.3t \approx 0.84eV$, as we present in the inset of figure 2.1 (a) and (b). This is so due to quantum mechanical hopping between the sublattices, which lead to the formation of two cosine-like energy bands. Their intersection near each vertex of the Brillouin zone yields the conical energy spectrum.

In addition, expansion of equation 2.4 in an infinitesimal neighbourhood of $K_\pm$ points, represented by $\delta\vec{k}_\pm = \vec{k} - \vec{K}_\pm$ the displacement relative to each valley, we find the limit

$$E_\pm \approx \pm \hbar v_F \left| \delta\vec{k} \right| + \mathcal{O}(k^2),$$

(2.5)

where $v_F = 3ta/2\hbar$ is effective the Fermi velocity in graphene ($v_F \approx 10^6 m/s$). This velocity $v_F = |\partial E/\hbar \partial k|$ is energy independent - as if electrons and holes were massless particles moving at the speed of light - and holds for low energy excitations[18]. Therefore, these electron excitations (filled states in the conduction band) and hole excitations (empty states in the valence bands) have zero effective mass. The linearity of this spectrum nearby these $K_\pm$ points, equation 2.5, is succesfully suited by a Weyl-Dirac type equation.
\[ \hat{H}_\pm \Phi_\pm(x, y) = E_\pm \Phi \pm(x, y), \] for the wave function close to the valleys. The Hamiltonian term is given by \( \hat{H}_\pm = -i\hbar v_F (\sigma_x \partial_x \pm \sigma_y \partial_y) - V \), including the scalar potential \( V \), and \( \sigma_{x,y} \) represent the Pauli matrices acting on sublattice space, and \( \epsilon > 0 \) is the electron-like quasiparticle excitation energy. Points \( \vec{K}_\pm \) are referred to as Dirac-points (DP) in literature, due to the above mentioned Hamiltonian representation.

Since graphene lattice is divided into two triangular sublattices, a degree of freedom arises and must be handled appropriately. Thus, wavefunctions of quasi-particles must be represented by a spinorial function \( \Phi_\pm(x, y) = [\phi_A^\pm(x, y), \phi_B^\pm(x, y)]^T \) which contains such a sub-lattice information, for each \( \vec{K}_\pm \) point. In addition, by including the valley degree of freedom, these spinors are combined into a 4-vector \( \Phi(x, y) = (\Phi_+(x, y), \Phi_-(x, y))^T \). This spinor represents a complete description of a Dirac electron, and satisfies \( \hat{H} \Phi(x, y) = E \Phi(x, y) \), where \( E = E_F + \epsilon \) and the Dirac Hamiltonian is given by

\[ \hat{H} = \begin{pmatrix} \hat{H}_+ & 0 \\ 0 & \hat{H}_- \end{pmatrix}. \] (2.6)

Wave functions of electrons lying near the Fermi level are approximated via the so called \( \vec{k} \cdot \vec{p} \) scheme\[4\). The density of states (DOS) per unit area per unit energy of bulk graphene

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\[1\] In what follows, we will use the notation \( \ddot{\cdot} \) for 4x4 matrices and \( \ddot{\cdot} \) for 2x2 matrices.
is presented in figure 2.3. An analytical expression of the DOS is obtained in reference [2], which shows that for low energy excitations, the DOS is proportional to the energy bands, and given by [21]

$$\rho(\epsilon) = \frac{1}{\Omega_0} \sum_{\pm, \mathbf{k}} \delta(\epsilon - \epsilon_{\pm}(\mathbf{k})) = \frac{|\epsilon_{\pm}|}{2\pi t_g}.$$  

Note that its conical dispersion is conserved [5], and vanishes at $\epsilon \rightarrow 0$.

![Density of states per unit cell.](image)

**Figure 2.3:** Density of states per unit cell. Figure modified from [2].

### 2.3 Graphene nanoribbons

As already mentioned, bulk graphene is idealized as a collection of infinite unit cells along the plane. It can be narrowed in any desired shape, and the corresponding wave functions for charge-carriers in that *flake* must carry these boundary conditions. In the present work, we consider the so-called nanoribbons which are obtained by imposing constriction in some direction, $x$ or $y$ according to the orientation given in figure 2.1. Here we consider the $x$-axis direction to be constricted, and therefore the remaining $y$-axis to be boundless, as we illustrate in figure 2.4. The orientation of the first Brillouin zone depends on the orientation of the direct lattice, which we take as $\theta = 0$ and $\theta = \pi/2$. The structure presented in the left-hand-side of figure 2.4 corresponds to a *zigzag* nanoribbon due to the triangular shape of this $x$-axis edge. On the other hand, right-hand-side of this figure is referred to as *armchair* nanoribbon, which contains atoms of both $(A$ and $B)$ sublattices.

In the $\mathbf{k} \cdot \mathbf{p}$ scheme, the 4-spinorial wavefunction $\Phi(x, y)$ satisfies the full Schrödinger equation given by the Hamiltonian of equation 2.6 and describes bound states in the
system. Vertical momentum ($\hbar q$) is therefore a conserved quantity since $y$-axis is translationally invariant. Therefore, wave function is written as $\Phi(x, y) = e^{iqy}\phi(x)$, where $\phi(x) = [\phi_+(x), \phi_-(x)]^T$ and $\phi_\pm(x) = (\phi^A_\pm, \phi^B_\pm)$. Now, if we solve the Hamiltonian system using definition 2.6, the following linear solutions are obtained for each valley as

$$
\begin{align*}
\phi_+(x) &= c_1^+ e^{ikx} \varphi_1 + c_2^+ e^{-ikx} \varphi_2 \\
\phi_-(x) &= c_2^- e^{-ikx} \varphi_2 + c_1^- e^{ikx} \varphi_1
\end{align*}
$$

with

$$
\varphi_{1,2} = \begin{pmatrix} e^{\mp i\alpha/2} \\ \pm s e^{\pm i\alpha/2} \end{pmatrix},
$$

where $s = \text{sgn}(E)$ and $e^{\mp i\alpha} = \hbar v_F(k \pm iq)/E$. Constants $c_i^\pm (i = 1, 2)$ are determined by boundary conditions on the wave function spinor $\phi(x)$. The term $s$ is regarded as a band index ($s = +1$ for the conduction band and $s = -1$ for valence band). A complete description of low lying electron excitations in graphene is obtained by superposing solutions at each individual valley, each modulated by the corresponding term $e^{iK_{\pm} \cdot \vec{r}}$, as

$$
\Phi(x, y) = e^{iqy}\phi(x) = e^{iqy} \left[ e^{iK_x^\pm} \phi_+(x) + e^{-iK_x^\pm} \phi_-(x) \right].
$$
This equation corresponds to an eigenfunction of full Schrödinger equation. Discrete spectrum is found in both - zigzag and armchair - nanoribbons, as presented in figure 2.5. While zigzag nanoribbons are always metallic (zero energy gap), armchair nanoribbons can be either metallic or semiconducting according to its width. These features are presented in figure 2.5.

Figure 2.5: Energy bands for graphene nanoribbons, where \( k \) is the wave vector along the nanoribbon edge measured relative to Dirac points. (a) Metallic zigzag edge and its dispersionless confined surface states. (b) and (c) present band structure for armchair metallic and semiconducting nanoribbon. Figure modified from [4]
2.3.1 Zigzag edges

This geometry is presented in figure 2.1 (d) for left and right edges, as well as in figure 2.4 where the system is bounded at left \((x_L)\) and right \((x_R)\) boundaries. The orientation of the first Brillouin zone is also presented, thus manifesting that valleys lie in vertical direction, thus no mixing is required and they are degenerate. As a consequence, no matter the width of the ribbon, Dirac points are always allowed wave numbers. Note, as well, that at each edge only one type of atom is present, say \(A\) for \(x_L\) and \(B\) for \(x_R\). Discrete energy bands are obtained by finding the eigenstates of the Dirac Hamiltonian at an individual valley and appropriate boundary conditions: setting the wavefunction to vanish at \(x = x_L\) and \(x = x_R\) at \(A\)- and \(B\)-sublattices, respectively. Energy bands are presented in figure 2.5 (a) which manifests the zero-gap activation energy. There are two degenerate and dispersionless bands of localized surface states that occur between \(K_+\) and \(K_-\). According to Dirac-Hamiltonian equation 2.6, the \(x\)-axis wavefunctions for each sub lattice and valley \(\phi^{A,B}_\pm\) are coupled by

\[
\tilde{\epsilon}\phi^B_+ = (i\partial_x - iq)\phi^A_+ \\
\tilde{\epsilon}\phi^A_- = (-i\partial_x + iq)\phi^B_-,
\]  

or decoupled as,

\[
(-\partial_x^2 + q^2)\phi^B_+ = \tilde{\epsilon}\phi^A_+ \\
(-\partial_x^2 + q^2)\phi^A_+ = \tilde{\epsilon}\phi^B_-,
\]  

where \(\tilde{\epsilon} = \epsilon/\hbar v_F\). The general solutions are given by

\[
\phi^{A,B}_\pm(x) = Ae^{zx} + Be^{-zx},
\]  

with \(z = \sqrt{q^2 - \tilde{\epsilon}^2}\) real or complex. Boundary conditions are given by

\[
\phi^A_\pm(x = x_L) = \phi^B_\pm(x = x_R) = 0,
\]  

leading to a transcendental equation for the allowed values of \(z\), given by

\[
\frac{q - z}{q + z} = e^{-2Wz},
\]
where \( W = (x_R - x_L) = \sqrt{3}Na, N \) a positive integer. Equation 2.15 holds for real values of \( z \equiv k \) for \( q > \tilde{\epsilon} \), which correspond to surface states. These have energies \( \pm \sqrt{q^2 - k^2} \), and are linear combinations of states localized at the edges. For large values of \( q \), as \( k \to q \), surface states become decoupled. For \( q < 0 \) there are no states with real \( z \) that can meet the boundary conditions, so surface states are absent. For pure complex \( z = ik_n \), the transcendental equation becomes

\[
k_y = \frac{k_n}{\tan(k_n L)},
\]

and for each solution \( k_n \) there are two confined states with energies \( \tilde{\epsilon} = \pm \sqrt{k_n^2 + q^2} \) and wavefunction

\[
\begin{pmatrix}
\phi_A \\
\phi_B
\end{pmatrix} = \begin{pmatrix}
\sin(k_n x) \\
\pm \frac{i}{\tilde{\epsilon}} (-k_n \cos(k_n x) + q \sin(k_n x))
\end{pmatrix},
\]

where \( n \) indicates the number of nodes of the confined wavefunction.

### 2.3.2 Armchair edges

The geometry of armchair edges is illustrated at top and bottom edges of figure 2.1 (d), and figure 2.4 (right), as well as the orientation of the reciprocal space. The electronic band structure can be metallic and semiconducting according to its width; it depends on whether the valleys, \( K_+ \) and \( K_- \), in the Brillouin zone are included [5]. Band structures have been studied thus revealing the spectral properties of this ribbon: it can be either metallic or semi-conducting according to its geometry[4]. In general, armchair ribbons of width \( W = 3Ma \) are metallic if \( M \) is integer, whereas otherwise are semiconducting.

As in the case of zigzag nanoribbons, this behavior can be understood in terms of eigenstates of the Dirac Hamiltonian with appropriate boundary conditions. It can be seen in armchair edge of figure 2.1 (a) that both sublattices are present at each edge, thus the wavefunction must vanish on both sublattices simultaneously at \( x = x_L \) and \( x = x_R \). To do this, valleys must be admixed, and require

\[
\begin{align*}
\phi^A_B(x = x_L) &= \phi^A_B(x = x_L) \\
\phi^A_B(x = x_R) &= \phi^A_B(x = x_R)e^{ik\Delta KL},
\end{align*}
\]

(2.18a) (2.18b)
with $\Delta K = \frac{4\pi}{3a}$ and $L = Ma$, $M$ integer. Within these conditions, the general solutions of the Dirac equation are plane waves of the form

$$\phi^B_\pm(x) = e^{\pm ikx},$$

(2.19)

where $k$ may accumulate phase factors. Wavefunctions on the $A$ sublattice may be obtained via equation 2.12. The wavevector $k_n$ satisfies the condition $e^{2ik_nL} = e^{i\Delta KL}$, so that $2k_nL - \frac{4\pi}{3}M = 2\pi n$, for $n$ integer. We make $n \rightarrow 2n$, thus $k_n = \frac{2\pi}{L}(\frac{M}{3} + n)$. Now, if $M = 3m + \nu$, where $\nu = 0, \pm 1$, then for the $\pm$ valley we have

$$k_{\mu} = \frac{2\pi}{L} \left( \mu \pm \frac{\nu}{3} \right),$$

(2.20)

with $\mu = m + n$. Note that the allowed values of $k_{\mu}$ have energy $E_{\mu}(q) = \pm \hbar v_F \sqrt{k_{\mu}^2 + q^2}$, which splits the valley degeneracy. In this case, in contrast to the zigzag case, the values of $k_n$ doesn’t depend on $q$. Moreover, ribbons with width that is multiple of $3a$ the allowed values of $k_n = \frac{2\pi n}{L}$, allow a zero energy state when $q \rightarrow 0$, and create a doubly degenerate state. Ribbons with width that are not multiple of 3 have nondegenerate states and do not include a zero energy mode. Thus these ribbons are band insulators, and the bandgap can be readily computed from $E_g(L) = \hbar v_F \frac{2\pi}{3L}$, which decays as $L \rightarrow \infty$ (Bulk limit).

### 2.4 Chiral tunneling (Klein paradox) and spin-orbit effects in graphene.

The Klein paradox refers to the transparent tunneling of relativistic particles through potential barriers. This approximation holds if the height of the barrier exceeds the electron’s rest energy, $V_0 >> E = mc^2[2, 19]$ ($m$ is the electron’s mass and $c$ is the speed of light), thus depending weakly on the barrier height. This phenomena can be explained from the coupling between electrons and their conjugate holes (positrons) due to sublattice symmetry of graphene. This fact is suggested by the spinorial description of a Dirac electron, and has been measured in graphene [2] as well as in carbon nanotubes [20]. In figure 2.6 this process is illustrated. Incoming particles from the left are in the chiral $\sigma$ direction in the conduction band in sublattice $A$ (red line). The red and green lines
Figure 2.6: (a) Conical energy spectrum of particles in the three regions of the barrier. Red and Green lines indicate the crossing between energy bands associated with sublattices A and B, respectively. Dotted line indicates the position of the Fermi level across the barrier. (b) Square-like potential barrier.

indicate the origin of the linear spectrum, which correspond to the crossing between the bands associated with each sublattice A and B[19]. The dotted line in the figure indicates that the electron’s energy lies in the conduction band outside the barrier, whilst inside it lies in the valence band; the pseudospin is parallel (antiparallel) to the direction of motion of electrons (holes). The direction of motion of an electron depends on the band index: the chirality of the electron is the projection of pseudospin onto the direction of motion, i.e., $\hat{C} = \vec{k} \cdot \hat{\sigma}$. This quantity is conserved thus commuting with $\hat{H}$ in absence of external potential. Eigenvalues of chirality operator gives the band index $s = \pm 1$. Moreover, the velocity operator is defined by $\hat{v} = -i[\vec{r}, \hat{H}] = \hat{\sigma}$. Thus, average group velocity of a plane wave is given by $\vec{v} = s\vec{k}/k$. As a result, an electron and hole propagating in the valence band have the same velocity and move in the same direction. But, their electric current is opposite. A consequence of that is the absence of backscattering. The reflection probability vanishes for two electron states in opposite direction, thus opposite chirality. It is important to notice that transport of particles in graphene through a potential barrier must represent the coupling of two isolated finite regions, or quantum dots; Quantum confinement is the key ingredient for understanding the physics of quantum dots [21]. Let
us consider the case in which the potential is

\[
V(x) = \begin{cases} 
V_0 & \text{for } 0 \leq x \leq D, \\
0 & \text{otherwise}
\end{cases},
\]  

(2.21)

as presented in figure 2.6 (b), and that the Fermi wavelength (\(\lambda_F\)) is much larger than lattice constant. Thus, the scattering problem can be solved by matching the boundary conditions of wave function for each region and finding the transmission and reflection coefficients. Since Hamiltonian is linear, no derivatives are needed as boundary conditions for solving the equation. Figure 2.7 shows the transmission amplitude as function of the incidence angle, in reciprocal space, and the barrier. In the limit \(|V| >> |E|\), transmission coefficients are given by

\[
T(\theta) \approx \frac{\cos^2 \theta}{1 - \cos^2(Dk) \sin^2 \theta}.
\]  

(2.22)

for \(\theta = \arctan(q/k)\) as the transmitted angle, and 

\[
k = \sqrt{(V - E)^2/(\hbar v_F)^2 - q^2}.
\]  

This equation holds for confined modes in the strip connected to heavily doped contacts. Equation 2.22 implies that under resonance conditions \(kD = N\pi, \; N \in \mathbb{N}\), the barrier becomes transparent \((T = 1)\) and thus transport is nearly transparent.

So far, the spin of the electron has not represented a remarkable property for the model. However, the spin is not inert at all[17]. The motion of an electron in some external field leads to a relativistic spin-orbit (SO) effect in which an electron changes simultaneously its spin and angular momentum[2]. This effect leads to a potential proportional to the scalar product of the electron’s spin magnetic moment with the vector product of its velocity and the external (electric) field. In absence of SO coupling, disorder and Coulomb blockade, the state of electrons in graphene is four-fold degenerated, manifesting thus spin (\(\uparrow \downarrow\)) and valley (\(K_{\pm}\)) degrees of freedom. SO effect leads to a gap at the Dirac points thus implying an spin dependent shift of the orbitals at each sublattice. Nonetheless, in graphene SO effect is expected to be weak since carbon is a light atom, thus favoring spin currents without dissipation in graphene[22]. We model SO effects as in reference [23], from the Hamiltonian term

\[
\hat{H}_{SO} = \Delta_{SO} \psi^\dagger \hat{\sigma}_z \hat{\tau}_z \hat{\delta}_z \psi,
\]  

(2.23)
Figure 2.7: Transmission probability through a square barrier as a function of incident angle for two different barrier heights. The central region length is $D = 110\text{nm}$ (top) and $D = 50\text{nm}$ (bottom). Figure taken from [2]

where $s_z$ is a Pauli matrix representing the real spin of the electron. This term respects all the symmetries of the honeycomb lattice in graphene[22]. Furthermore, it may arise an extrinsic SO term which break the specular symmetry about the plane, i.e., a Rabshe term of the form $(s \times p) \cdot \hat{z}$. Therefore, the SO interaction leads to a finite energy gap $2\Delta_{SO}$ with $E(q) = \pm \sqrt{(\hbar v_F q)^2 + \Delta_{SO}^2}$. In graphite, this interaction is also known [24], where it is shown that SO lifts all band degeneracies mentioned above, and affects the graphite Fermi-surface topology. In general, SO interaction will be modelled by the expression $\hat{H}_{SO} = \hat{L} \cdot \hat{\sigma}$, where $\hat{L} = \hbar/(4m^2c^2)(\nabla V \times \hat{p})$, and $V(r)$ represents the atomic (or external) potential, and $\hat{p}$ is the momentum operator, as can be seen in reference [36].

2.5 Carbon nanotubes

Carbon nanotubes (CNs) were discovered about in the 60’s decade, but it was in 1991[25] when Iijima recognized that CNs were made up of concentric rolled graphene sheets with a large number of potential helicities and chiralities [11]. It was further determined that the distance between concentric tubules is smaller than nearest neighbor atoms, thus electronic properties are mainly dominated by those of graphene[5, 20]. Currently there exists a vast of experimental routines to produce both, single-walled CNs (SWCNs) and multi-walled CNs (MWCNs), with a high crystalline quality[11]. The materials approaches
the theoretical predictions for electrical properties, as will be the main topic of the present thesis. CN’s can behave as either metallic or semiconducting according to its geometry, and therefore the band structure of graphene sheet wrapped up. Quantization is found in circumferential direction, where periodicity must be imposed.

Figure 2.8: (a) 2D Graphene honeycomb structure indicating chiral ($\vec{C}_h$) and translational ($\vec{r}_T$) vectors. This layer is rolled up onto the chiral direction thus connecting different equivalent sites to form a nanotube, and vector $\vec{r}_T$ indicates its length. (b) Curved graphene sheet rolled up into a zigzag nanotube in the direction of $\vec{C}_h$, for $\eta = 0$

So, as in the case of graphene, transport properties of charge carriers can be well represented in the $\mathbf{k} \cdot \mathbf{p}$ scheme. However, curvature opens a small gap due to overlap of wave functions which manifests in Hamiltonian as a mass term $[23]$. In figure 2.8 we present the geometric structure of a graphene sheet (a) as the basis of a carbon nanotube (b). The primitive lattice translation vectors of graphene were introduced in section 2.1. For convenience, from now on we will assume the primitive lattice vectors to be given by

$$\vec{a}_i = \frac{a}{2}(\sqrt{3}, \pm 1), \quad i = 1, 2$$

(see figure 2.8 (a)). Every structure of a SWCN can be created from the single layer graphene by connecting equivalent lattice sites, one at the origin and the other at the chiral direction, given by

$$\vec{C}_h = m_1 \vec{a}_1 + m_2 \vec{a}_2 = \frac{a}{2}(\sqrt{3}(m_1 + m_2), m_1 - m_2), \quad (2.24)$$

where $m_1 + m_2 = 2N$ and $m_1 - m_2 = 2M$, for $M, N$ integers. Chiral vector points in circumferential direction and its magnitude is its periphery. In particular, zigzag CNs are given by the condition $m_2 = 0$ ($0 \leq |m_2| \leq m_1$), while armchair nanotubes correspond to
the case \( m_1 = m_2 \). The chiral vector for a zigzag CN is then given by

\[ \vec{C}_h = aM(1, 0), \quad (2.25) \]

for a fixed number \( M \) of unit cells in that direction. The circumference of the radius is of magnitude \( C_h \equiv |\vec{C}_h| = aM \), thus its radius is given by \( R(M) = aM/2\pi \). Orthogonal to that chiral vector is the translational vector \( \vec{r}_T \) which points in axial direction of the tube, given by \( \vec{r}_T = n_1\vec{a}_1 + n_2\vec{a}_2 \), for integers \((n_1, n_2)\) which satisfy \( \vec{C}_h \cdot \vec{r}_T = 0 \). Therefore

\[ \vec{r}_T = \sqrt{3}aN(0, 1), \quad (2.26) \]

whose magnitude is the length of the tube. The first Brillouin zone of the CN is given by the region \(-\pi/C_h \leq \theta \leq \pi/C_h\). The number of atoms in the unit cell can be found from

\[ 2\frac{|\vec{C}_h \times \vec{r}_T|}{\Omega_0} = 2MN. \quad (2.27) \]

Wave-function must be periodic in the circumferential direction, so that \( \psi(\vec{r} + \vec{C}_h) = \psi(\vec{r}) \), which leads to quantization of transverse vector, similar to that of obtained in 2.20, given by

\[ e^{i\vec{k} \cdot \vec{C}_h} = 1, \quad (2.28) \]

while longitudinal wave vector remain continuous, for infinite large tubes. For the zigzag case, condition 2.28 leads to \( \theta \to \theta_n = 2n\pi/aM \), for \( n \equiv m_1 \) integer. The actual value \( \tilde{k} \) within the 1D first Brillouin zone \(-T/\pi \leq \tilde{k} \leq T/\pi\) is obtained from equation

\[ \exp(i\tilde{k} \cdot \vec{r}_T) = \exp(i\tilde{k}r_T). \quad (2.29) \]

Thus the number of bands in the first Brillouin zone is given by the total number of carbon atoms in a unit cell determined by 2.27.

The band structure of a SWCN depends critically on whether Dirac points are included in the allowed wave vectors. This can be understood by considering the phase component
Figure 2.9: (a) Examples of the band structure of CNs for semiconducting (lateral) and metallic (central) cases. (b) Quantization of energy bands in a metallic CN. Figure modified from [5]

so that whenever \( \exp(i\vec{K}_\pm \cdot \vec{C}_h) = 1 \) \((M = 3n)\), no phase is accumulated in \( q \) direction, thus no energy gap is present (metallic case). Otherwise, if \( M = 3n \pm 1 \), a non-zero gap arises in the spectrum, thus semiconducting behavior is found. Note that

\[
\exp(i\vec{K}_\pm \cdot \vec{C}_h) = \exp(\pm 4\pi i \frac{M}{3}),
\]

so that whenever \( M = 3n \), valence and conduction bands cross at the Fermi level \( \vec{K}_\pm \). Thus, energy bands relationship for continuous \( k \) yields

\[
E_n(k) = \pm \hbar v_F \sqrt{k^2 + q_n^2} = \pm \hbar v_F \sqrt{k^2 + \left( \frac{2\pi}{L} (n + \frac{\nu}{3}) \right)^2},
\]

for \( \nu = \pm 1 \), and where we have used 2.20. Figure 2.9 (a) shows the energy bands for both, metallic and semiconductin cases, where each band gap becomes evident. In the semiconducting regime, \( \nu = \pm 1 \), the energy gap between bands is about \( E_g = E_g(M) = \hbar v_F/(3R_T(M)) \), thus decaying as \( R_T \) increases. For \( R_T \approx 1nm \), this gap between the conduction and valence bands is \( 2E_g \), where \( E_g \approx 180meV \). In graphene, \( \pi \) orbitals weakly interacts with planar \( p_{x,y} \) orbitals of the neighboring atoms (about dozens of \( \mu eV \) only). In contrast, the curvature of nanotubes enhances such interaction leading to the so-called curvature effects. These effects and spin-orbit coupling induce a small gap even in nominally metallic nanotubes, of about \( 45meV \).
This finite bandgap favors confinement of electrons and creation of quantum dots, otherwise not possible due to Klein tunneling. For CNs with a large diameter, effects of the curvature can be neglected and therefore electronic states in the vicinity of the Fermi level are determined by states near the $\vec{K}_\pm$ points in graphene. Ab-initio measurements showed that electronic properties can be modified for tubes with an extremely small diameter because of the hybridization of $\pi$ states with $\sigma$ bands which lie well above the Fermi level in 2D graphene. Curvature effects can lead to a quantized transverse momentum given by $q_n \rightarrow q_n + q_{\text{curv}}$, where $q_{\text{curv}} \propto 1/R_T^2$ and the induced gap $E_{\text{curv}} = \hbar v_F q_{\text{curv}} \propto 1/R_T^2$. The gap which opens up due to curvature is estimated as

$$E_{\text{curv}}(\theta) = \left| \frac{V_{pp\pi} a^2 \cos(3\theta)}{4R^2} \right| \approx 10\text{meV}. \quad (2.32)$$

where $\theta = 0$ (for this case) is the chiral angle, and the overlap integral between $p_z$ orbitals is measured $V_{pp\pi} = -3.03eV$ for a $R = 1nm$ radius nanotube. Here we model $|V_{pp\pi}| \approx t$.

SO effects in CNs can be modelled in a similar way to that of presented in equation 2.23[23].

The generalized SO Hamiltonian near the DPs is $\hat{H}_{SO} = \Delta_1 \hat{\tau}_3 \hat{\sigma}_3 + \Delta_0 \hat{s}_3 \hat{\tau}_3$, with $\hat{s}_3$ being a diagonal Pauli matrix acting in the spin-space with eigenvalues $\pm 1$. According to $\hat{H}_{SO}$, spin of the electrons is still a good quantum number for the single particle problem since degeneracy is now splitted. The coupling constants $\Delta_0$ and $\Delta_1$ depend on the type of tube. Both are inversely proportional to the radius $R_T$. The remaining quantity, $\hat{\tau}_3$, is the diagonal Pauli matrix with eingenvalues $\tau = \pm 1$ acting in the $\vec{K}'(\cdot)$-isospin space. Thus, the last term in $\hat{H}_{SO}$ is diagonal, and thus it shifts the spectrum of electrons (holes) by a constant amount up (down). From the experimentally found gaps for electrons and holes, $E^e_g = 0.37meV$ and $E^h_g = 0.22meV$, the values are estimated as $\Delta_1 \approx (E^e_g - E^h_g)/2 = 0.16meV$ and $\Delta_0 \approx (E^e_g + E^h_g)/2 = 0.58meV$. Therefore, the combination of curvature, quantization of transverse momentum and SO effects, gives a final expression for the free electron dispersion relation

$$E^{s,\tau}_n(k) = \pm \hbar v_F \sqrt{k^2 + q^2} + \Delta_0 \tau s, \quad (2.33)$$

where $q = \tau q_n + s\Delta_1/\hbar v_F$ is spin and isospin dependent. The four fold degeneracy due to spin and valley degree of freedom present in graphene is splitted by spin-orbit (SO)
coupling, thus spin and valley can be discerned. First introduced by Ando ([36]), the theory shows that the SO coupling depends on the inverse of the radius of curvature and originates from the intra-atomic SO coupling in a carbon atom. Klein tunneling and absence of back-scattering in CNs has been reported (see for instance [20, 37]).
CHAPTER 3

GREEN’S FUNCTIONS FORMALISM, SUPERCONDUCTIVITY AND TRANSPORT.

In this chapter we describe the theoretical formalism that we use to derive Green’s functions (GFs) for bulk graphene, and therefore for nanoribbons and nanotubes. First, we derive the Green’s functions for zigzag graphene nanoribbons, and periodic conditions boundary conditions along abscissa (or circumferential) for nanotubes. There we find functions for isolated materials which can be perturbatively coupled by means of a Dyson equation. For the superconducting case, the Bogoliuvob de-Gennes equations will be suitable to model the edges at microscopic level, as well as the superconducting and external potentials. The Green’s functions formalism will allow us to model transport by means of the Keldysh formalism which will be roughly mentioned below, together with the semiconductor approach to transport in graphene and the Hamiltonian approach. Then we will derive an approximate model to electric transport: a current formula in the tunnel limit for the processes in a double quantum dot coupled by a superconducting electrode.

The chapter is organized as follows: in section 3.1 we determine the Green’s functions for the graphene nanoribbons. Section 3.2 contains a review of the superconducting state in graphene, and low-energy quasi-particles pairing. The next section 3.3, contains the calculation of the density of states of different systems, including the effects of boundaries in graphene nanoribbons, and the relativistic and SO effects introduced in the last section. In section 3.4 we concentrate in determining the algebraic Dyson equation which represents a perturbed hybrid system. In section 3.5 we introduce electronic transport through a point-contact junction using a Hamiltonian approach to get GFs which is extrapolated for a double contact system in section 3.6.
3.1 Green’s functions formalism: graphene and CNs

A Green’s function (GF) is defined as the solution of an inhomogeneous differential equation [26, 27], such as the Schrödinger equation of electronic states in graphene given by Hamiltonian 2.6. Within this formalism we compute electronic and transport properties, since GFs have information about the quantum system. For the case of the graphene - honeycomb - structure, GFs have been derived analytically using the same method we will use here[10], and we will extend the results for nanotubes. Spinorial representation of electronic states suggests that GFs may be written in sublattice and valley space as tensorial products. In the superconducting state, moreover, the space must be extended up to consider the quantum spin degree of freedom and particle/hole description is demanded as well. Wavefunctions of low-lying states in graphene are determined by the Dirac Hamiltonian given by 2.6, \( \hat{H} \Phi(x, y) = E \Phi(x, y) \) for \( \Phi(x, y) = (\Phi_+(x, y), \Phi_-(x, y))^T \) and \( \Phi_\pm(x, y) = e^{iqy} \psi_\pm(x) \). The 4-component Green’s function in valley space (+, −) denoted by \( \hat{G}_\psi^{++}(x, x'; y) = \int \hat{G}_\psi^{++}(x, x'; q)e^{iqy}dq \), for the ++ valley combination, must satisfy

\[
\begin{bmatrix}
\hat{H}(q) - E \hat{I} \\
\hat{H}_+ - E & 0 \\
0 & \hat{H}_- - E
\end{bmatrix}
\begin{bmatrix}
\hat{G}_\psi^{++} \\
\hat{G}_\psi^{+-} \\
\hat{G}_\psi^{-+} \\
\hat{G}_\psi^{--}
\end{bmatrix}
= \delta(x - x') \hat{I}
\]

(3.1)

where \( \hat{I} \) is the 4–dimensional identity matrix and \( \hat{H}(q) \) is the Hamiltonian in momentum representation, and superscripts + or − indicate valley projection. Retarded an advanced components of GFs are obtained by considering \( E \to E + i\eta \) as \( \eta \to 0^\pm \), respectively. A complete GF must be a superposition of each valley projection component GF \( \hat{G}_\psi \), as seen in equation (2.10), so that

\[
\hat{G}_\psi(x, x', y, y') = \int dq e^{i(q(y-y'))} \sum_{\mu, \nu = +, -} e^{i(\vec{K}_\mu \cdot \vec{r} - \vec{K}_\nu \cdot \vec{r}')} \hat{G}_{\psi}^{\mu \nu}(x, x'; q).
\]

(3.2)

The phase factor \( \exp \{ i(\vec{K}_\mu \cdot \vec{r} - \vec{K}_\nu \cdot \vec{r}') \} \) allow to consider boundary conditions on atomic scale, so the edges and thus interfaces will be well-defined in that scale and valley is a conserved quantity, so intervalley scattering can be neglected[10]. The method we implement to determine the GF is based on the asymptotic solutions of the differential equation (3.1).
So, the full GF in valley and sublattice space is written as

\[
\tilde{G}_\psi(x, x'; q) = \begin{cases} 
\sum_{\mu, \nu = +, -} A_{\mu, \nu}^\mu \psi^\mu_<(x) \cdot \tilde{\psi}^\nu T(x') \cdot \gamma; & x < x' \\
\sum_{\mu, \nu = +, -} A'_{\mu, \nu}^\mu \psi^\mu_<(x) \cdot \tilde{\psi}^\nu T(x') \cdot \gamma; & x > x'
\end{cases}, \quad (3.3)
\]

where \(\mu\) and \(\nu\) denote valley projections of the asymptotic solutions. The Green’s functions are built using tensor products between asymptotic solutions, \(\tilde{G}(x \lesssim x') \propto \psi^\mu_<(x) \cdot \tilde{\psi}^\mu T(x')\), where \(\psi^\mu_<(x)\) and \(\psi^\mu_>(x)\) must fulfil the boundary conditions at each edge. In (3.3), the matrix element \(\gamma\) in order to keep invariant the product \(\tilde{\psi} \tilde{G} \psi\) under Lorentz transformations, and \(\tilde{\psi} = \psi^\dagger \gamma\) is the adjoint Dirac spinor. The remaining term \(A\) is related to the Wronskian of the functions \(W(\varphi_<, \varphi_>) (x) \equiv W = (i\hbar v_F W)^{-1}\).

We now will confine our attention in the case of zigzag graphene nanoribbons where valley degeneracy is present, so that the problem is simplified by considering single valley representation. Let us consider a nanoribbon bounded at left by \(x_L\) and at right by \(x_R\), as illustrated in figure 2.4 (left); the conserved momentum along vertical direction is still denoted as \(\hbar q\) and is regarded as a good quantum number. Hereon, we will set the left edge of the nanoribbon to be formed by \(A\)-type atoms whilst right one is formed by \(B\)-type \(C\)-atoms. Asymptotic solutions are readily obtained from a single valley representation from 2.8. They correspond to linear combination of propagating plane waves into the boundary and a reflection towards infinity,

\[
\phi_<(x) = e^{-ikx} \varphi_2 + r_L e^{ikx} \varphi_1, \quad (3.4)
\]
\[
\phi_>(x) = e^{ikx} \varphi_1 + r_R e^{-ikx} \varphi_2, \quad (3.5)
\]

Note that equations 3.4 can be obtained from 2.8 by matching \(c_2^+ = 1\), \(c_1^+ = r_L\), \(c_2^- = 1\) and \(c_2^- = r_R\). As presented in section 2.3.1, boundary conditions on spinorial wavefunctions are chosen as \(\phi_<(x_L)|_B = \phi_>(x_R)|_A = 0\). Hence, reflection amplitudes are determined by

\[
r_L = -e^{i\alpha} e^{-2ikx_L}, \quad r_R = -e^{i\alpha} e^{2ikx_R}, \quad (3.6)
\]

whose product is \(r_L r_R = e^{2i\alpha} e^{2ik(x_R-x_L)}\). Whenever there is no valley mixing present in 3.1, the terms corresponding to ++ and -- vanish. Hence, single valley GF \((\tilde{G}_\psi^{++} \equiv \tilde{g}_\psi)\)
is given by

\[
\hat{g}_{\psi}^{r,a}(x, x') = \begin{cases} 
A\phi_<(x) \cdot \phi_T^T(x') \cdot \gamma; & x < x' \\
A'\phi_>(x) \cdot \phi_T^T(x') \cdot \gamma; & x > x'
\end{cases}
\]  
(3.7)

where superscripts \( r \) and \( a \) denote the retarded and advanced components of the GFs. In a single valley representation (say valley \(+\)), \( \gamma \) is equivalent to \( \sigma_z \). Thus, the graphene nanoribbon GF for the edges given by 3.6 yields

\[
\hat{g}_{\psi}^{r,a}(x, x') = \frac{-i}{2\hbar v_F \cos \alpha (1 - r_{LR}^{-1})} \left( e^{ik(x'-x)} \varphi_2 \varphi_1^\dagger + r_{LR}A_{LR}B_{LR} e^{-ik(x'-x)} \varphi_1 \varphi_2^\dagger 
+ r_{RL}^B e^{ik(x'+x)} \varphi_1 \varphi_2^\dagger + r_{RR}^B e^{-ik(x'+x)} \varphi_2 \varphi_1^\dagger \right)
\]  
(3.8)

for \( x < x' \), and

\[
\hat{g}_{\psi}^{r,a}(x, x') = \frac{-i}{2\hbar v_F \cos \alpha (1 - r_{LR}^{-1})} \left( e^{ik(x-x')} \varphi_1 \varphi_2^\dagger + r_{LR}A_{LR}B_{LR} e^{-ik(x-x')} \varphi_2 \varphi_1^\dagger 
+ r_{RL}^A e^{ik(x+x')} \varphi_1 \varphi_2^\dagger + r_{RR}^A e^{-ik(x+x')} \varphi_2 \varphi_1^\dagger \right)
\]  
(3.9)

for \( x > x' \). For the opposite valley, a similar equation is obtained with the change \( \varphi_{1,2} \leftrightarrow \varphi_{1,2} \). Bulk graphene GF are obtained by taking \( x_L \to -\infty \) and \( x_R \to \infty \), therefore \( r_L = r_R = 0 \). The band spectrum is obtained from poles of the GF leading to the bulk dispersion relation \( \cos \alpha = 0 \), and \( 1 - r_{LR}^A r_{RL}^B = 0 \) for a finite width \( W \) the spectrum gets discrete leading to 2.15. With solutions given by 3.4 and 3.5, and the amplitudes by 3.6, the resulting GF associated to \( \phi \) for the \( K_- \) valley is given by

\[
g^{r,a}_\phi(x, x') = \frac{-i}{2\hbar v_F \cos \alpha (1 - e^{2i\alpha} e^{2ikW})} \left( e^{ik(x'-x)} \varphi_2 \varphi_1^\dagger + e^{i\alpha} e^{-2ikx_L} e^{ik(x+x')} \varphi_1 \varphi_2^\dagger 
- e^{i\alpha} e^{2ikx_R} e^{-ik(x'+x')} \varphi_1 \varphi_2^\dagger + e^{2i\alpha} e^{2ik(x_R-x_L)} e^{-ik(x'-x)} \varphi_1 \varphi_2^\dagger \right)
\]  
(3.10)

for \( x < x' \), and

\[
g^{r,a}_\phi(x, x') = \frac{-i}{2\hbar v_F \cos \alpha (1 - e^{2i\alpha} e^{2ikW})} \left( e^{ik(x'-x)} \varphi_1 \varphi_2^\dagger + e^{i\alpha} e^{-2ikx_L} e^{ik(x+x')} \varphi_2 \varphi_1^\dagger 
- e^{i\alpha} e^{2ikx_R} e^{-ik(x'+x')} \varphi_1 \varphi_2^\dagger + e^{2i\alpha} e^{2ik(x_R-x_L)} e^{-ik(x'-x)} \varphi_2 \varphi_1^\dagger \right)
\]  
(3.11)
for $x > x'$. Green’s functions given by equations 3.10 and 3.11 describe quasi-particles in graphene nanoribbon with zigzag boundary conditions in the $x$-direction thus occupying discrete energy states in that bounded system. Note, as well, that GFs for carbon nanotubes can be readily obtained from that of graphene by imposing circumferential boundary - periodic - conditions thus implying quantization of transverse momentum and 0-dimensional bands.

### 3.2 Bogoliubov de-Gennes equations: superconducting graphene

Graphene is not a natural superconducting material, though it can acquire superconductivity by proximity effect with a superconductor[28]. In graphene, quasi-particles acting as Cooper pairs correspond to time-reversed electronic states with opposite spin[29]. We assume homogeneous $s$–wave pairing in the superconducting region and step-like varying potential in space, with real-valued gap $\Delta$ ($\Delta(x) = \Delta$ and $\Delta = \Delta^*$). Quasi-particle excitations are therefore represented in the Nambu (electrons/holes) and sublattice space, given by the Bogoliubov de Gennes-Dirac (BdGD) equation[30]:

$$
\begin{pmatrix}
\hat{H}_s - E_F^s \\
\Delta^*
\end{pmatrix}
\begin{pmatrix}
\phi_e^s \\
\phi_h^s
\end{pmatrix} = E
\begin{pmatrix}
\phi_e^s \\
\phi_h^s
\end{pmatrix},
$$

(3.12)

where electrons are in $K_\pm$ valley whilst holes are in $K_\mp$, with energy $E > 0$. Spinors $\phi_{e,h}^\pm$ represent electron- ($e$) or hole-like ($h$) excitations for the corresponding valley, in sublattice space. Energy dispersion relation of equation 3.12 is found to be

$$
E = \sqrt{\Delta^2 + (E_F^s - \hbar v_F \sqrt{k^2 + q^2})^2},
$$

(3.13)

for plane wave solutions, so transverse momentum is $k_{e,h}^s = \sqrt{(E_F^s \pm \Omega)^2 - (\hbar v_F q)^2}/\hbar v_F$, $\Omega(E) = \sqrt{E^2 - \Delta^2}$. Solutions of BdG-D equation 3.12 are given by direct product of graphene bulk solutions and the usual BCS solutions[30], written as

$$
\begin{pmatrix}
\phi_{e(h)}(x) \\
\end{pmatrix} = \begin{pmatrix}
\phi_e^{\pm k_{e,h}^s,x} \varphi_{2\epsilon(1h)} + r_L^{A,e(h)} \phi_{e,h}^{\pm k_{e,h}^s,x} \varphi_{1\epsilon(2h)} \\
u(v) \otimes \phi_e^{\pm k_{e,h}^s,x} \varphi_{2\epsilon(1h)} + r_L^{A,e(h)} \phi_{e,h}^{\pm k_{e,h}^s,x} \varphi_{1\epsilon(2h)} \end{pmatrix}
$$

(3.14)
\[
\phi^{e(h)}(x) = \left( e^{\pm ik_{e,h}^S x \varphi_{1e(2h)}(x)} + r_{B,e(h)}^B e^{+ik_{e,h}^S x \varphi_{2e(1h)}} \right) \otimes \begin{pmatrix} u(v) \\ v(u) \end{pmatrix}
\] (3.15)

for \( \varphi_{ie(h)} \) given by 3.4 and 3.5, \( e^{i\alpha_S^{e(h)}} = \pm \frac{\hbar v_F (k_{e,h}^S + i q)}{|E_F^S \pm \Omega|} \), and \( u^2(v^2) = (1 \pm \Omega/E)/E \).

Reflections coefficients given by 3.6 with the substitution \( \alpha \to \alpha_S^{e} \) for electronic excitations, while \( \alpha \to \alpha_S^{h} \) for hole excitations. In a similar way as the GF for normal-state graphene 3.10 and 3.11 were derived, for superconducting state we will proceed. Components of single-valley GFs, say \( K_+ \), in superconducting graphene nanoribbons are denoted by \( \hat{G}_S^{\alpha \beta} \), for \( \alpha, \beta = \text{electrons, holes} \), and obey

\[
\begin{pmatrix} \hat{H}_F^S - E_F^S & \Delta \\ \Delta^* & \hat{H}_F^S \end{pmatrix} \begin{pmatrix} \hat{G}^{S}_{ee} & \hat{G}^{S}_{eh} \\ \hat{G}^{S}_{he} & \hat{G}^{S}_{hh} \end{pmatrix} = \delta(x - x') \hat{I}
\] (3.16)

and must be such that the normal-state GFs must be recovered as \( \Delta \to 0 \), given by 3.10 and 3.11. In practice, this can be done by using external magnetic fields or increasing the temperature. Off-diagonal components of the \( 4 \times 4 \) GF given by equation 3.16 contain information about electron-hole coupling due to pairing, while diagonals describe single-particle excitations. The Green’s functions for diagonal elements are of the form

\[
\hat{G}_S^{\alpha}(x,x') \propto g^{<,>}_{\psi \alpha}(x,x') \otimes M_\pm(E) \cdot \hat{\sigma}_x,
\]

where

\[
M_\pm = \frac{1}{E^2} \begin{pmatrix} E \pm \Omega & \Delta \\ \Delta^* & E \mp \Omega \end{pmatrix},
\] (3.17)

and hole-components are obtained by taking into account band index and valley. On the other hand, off-diagonal GFs are of the form

\[
\hat{G}_{eh(he)}(x,x') \propto \varphi^{e(h)}(x) \cdot \varphi^{h(e)}(x') \cdot \sigma_z \propto \phi_<(x) \cdot \phi_>(x') \cdot \hat{M}_\pm \cdot \sigma_x,
\]

where

\[
\hat{M}_\pm = \frac{1}{E^2} \begin{pmatrix} \Delta & E \pm \Omega \\ E \mp \Omega & \Delta^* \end{pmatrix},
\] (3.18)

thus resulting proportional to normal-state solutions 3.4 and 3.5.
3.3 Density of states

As a test of formalism introduced above, we compute the local density of states \((L-DOS)\) for isolated regions, and we will compare it with that of presented in the last section. The electronic local density of states can be obtained at a distance \(x = x' = d\) from the equation

\[
\rho(E, d) = \frac{-1}{\pi} \int_{-\infty}^{\infty} dq \text{Im}[\text{Tr}\{\hat{G}_L^{ee}(q, E; d, d)\}], \tag{3.19}
\]

or for holes by taking the \(hh\) component of the GF. We will compute electronic DOS for graphene nanoribbons and carbon nanotubes in normal state.

3.3.1 Graphene nanoribbons and carbon nanotubes

Local density of states in graphene depends in its geometry, hence each type of edge - armchair or zigzag - has its effects. While electrons in as zigzag nanoribbons always present metallic behavior, armchair can be either metallic or semiconducting. Figure 3.1 shows a \(N = 51\) zigzag nanoribbon for the doped (a) and undoped (B) case. This result can be compared to that of presented in figure 2.5 thus manifesting their similarity.

In figure 3.2 we present the LDOS for metallic \((M = 24)\) and semiconducting \((M = 25)\) armchair nanoribbons. The distance between bands is about \(E_g \approx 0.01\text{meV}\).

![Figure 3.1: Energy bands for a zigzag graphene nanoribbon for the (a) undoped and (b) n-doping case. The width is about \(W \approx 97\text{nm}\), and the Fermi level for the (b) case is \(E_F \approx 0.14\text{eV}\). The dispersionless states between valleys correspond to confined surface states.](image)

On the other hand, band structure of CNs is presented in figure 3.3 for several cases, and can be compared to results presented in figure 2.9. In (a) left and right, bands for \(M = 45\)
Figure 3.2: Energy bands for undoped armchair graphene ribbons. (a) Metallic nanoribbon for $N = 24$. (b) Semi-conducting $N = 25$ nanoribbon. Energy gap of the semi-conducting case is $E_g \approx -0.14\text{meV}$.

Figure 3.3: Energy bands of CNs for (a) a semiconducting $M = 25$ CN, where curvature effects are neglected (left) and considered (right). (b) A metallic $M = 24$ CN for curvature effects neglected (left) and considered (right). And (c), energy bands for the same metallic CN of part (b). Spin-orbit and curvature effects are considered, and the bands split becomes evident for spin ($s$) and valley ($\tau$) degrees of freedom.
CNs are presented without and with curvature effects included, respectively. Energy gap is of the same order of that of armchair graphene nanoribbon.

In (b), left and right plots show metallic tubes where curvature effects are neglected and considered, respectively, and in part (c) the energy bands of a CN are illustrated where spin-orbit as well as curvature effects are considered, and 4-fold degeneracy is lifted.

### 3.4 Dyson equation for coupling separate regions

The above derived GFs correspond to isolated regions, thus in equilibrium. Boundaries between different regions can be treated perturbatively up to infinite order with the aid of a Dyson equation, interacting via a Dirac delta-like potential\([10]\). Separate regions can be coupled by means of a phenomenological hopping \(t\) parameter which accounts for the coupling strength\([34]\). This is achieved by solving the Dyson equation

\[
\hat{G}_\phi(x, x') = \hat{g}_\phi(x, x') + \int dx_1 dx_2 \hat{g}_\phi(x, x_1) \hat{V}(x_1, x_2) \hat{G}_\phi(x_2, x'), \tag{3.20}
\]

where \(\hat{G}_\phi\) denotes the single valley GF of the perturbed ribbon while \(\hat{g}_\phi\) represents the unperturbed GF and \(\hat{V}\) must describe the perturbative coupling appropriately. We follow the model introduced in \([10]\) in which \(\hat{V}(x, x') = \beta t a_{\text{eff}} \delta(x_1 - x_0)\delta(x_2 + x_0)\sigma_x\), which phenomenologically can be modulated by the factor \(\beta = [0, 1]\). The remaining terms, \(t a_{\text{eff}}\sigma_x\) represent the hopping between adjacent layers taking into account the sublattice flip. \(a_{\text{eff}}\) is a test-distance which must be optimized in order to get a clean and continuous system as \(\beta \to 1\). Using this potential, equation 3.20 is just algebraic as

\[
\hat{G}_\phi(x, x') = \hat{g}_\phi(x, x') + \beta t a_{\text{eff}} \hat{g}_\phi(x, x_0) \hat{\sigma}_x \hat{G}_\phi(x_0, x'), \tag{3.21}
\]

for \(x_0\) in the neighborhood of the junction, approaching from left or right. Note that the GFs evaluated at the boundary from left are given by \(\hat{g}_\phi(x_0 - 0^+, x_0 - 0^-)\) and \(\hat{g}_\phi(x_0 - 0^+, x_0 - 0^-)\), and from right \(\hat{g}_\phi(x_0 + 0^-, x_0 + 0^+)\) and \(\hat{g}_\phi(x_0 + 0^+, x_0 + 0^-)\). Local GF at the edge are given by

\[
\hat{G}_{R(L)} = \left[\hat{g}_{R(L)}^{-1} - (\beta t a_{\text{eff}})^2 \hat{\sigma}_x \hat{g}_{L(R)} \hat{\sigma}_x\right]^{-1}, \tag{3.22}
\]
where $R, L$ indicates the limit $(x, x') \to (0^\pm, 0^\pm)$ at the boundary $x_0$. Note that the perfect transparency conditions lead to $a_{eff} = \sqrt{3}a/4$. Equation 3.20 is written in reciprocal space as

$$G_{\vec{k}}(E) = g_{\vec{k}}(E) + g_{\vec{k}}(E)\Sigma(\vec{k}, E)G_{\vec{k}}(E),$$

where $\Sigma(\vec{k}, E)$ denotes the self-energy, which represents the perturbative interaction between layers.

### 3.5 Hamiltonian approach to transport: NS junction

Transport through mesoscopic and microscopic systems has been widely researched since quantum effects can be observed such as quantization of conductance and other phenomena relative to the wave nature of electrons such as tunneling[21]. In a NS junction, electronic transport has manifested the existence of an energy gap, since in the superconductor there are no single-particle states available, at low energies[31]. Transition between adjacent regions can be modelled by means of an interaction Hamiltonian that couples the states via a phenomenological hopping parameter[32], and taking into account that occupied states must $jump$ to available states and they are governed by the local density of states and the Fermi distribution function. The details of the interface can be absorbed into a phenomenological transmission matrix element between states $k$ and $k'$ of different metals, namely $T_{kk'}$, so that the transfer Hamiltonian is written as $\hat{H}_T = \Sigma_{kk',\sigma}T_{kk'}\hat{c}_{k\sigma}\hat{c}_{k'\sigma} + h.c.$, and no spin flip is considered[30]. As an ansatz, the current thus will be proportional to the square of the transmission matrix elements, such as in a BTK model for transport[8]. Note that the anztats for current from metal 1 to metal 2 can be related to the Fermi golden rule[33], which is written as

$$P_{1\to2} = \frac{2\pi}{\hbar} \sum_{kk',\sigma} |T_{kk'}|^2 n_F(\epsilon_k)(1 - n_F(\epsilon_{k'}))\delta(\epsilon_k - \epsilon_{k'}),$$

where in general $k$ is a 3–D vector, and $n_F(\epsilon) = (exp((\epsilon - \mu)/k_B T) + 1)^{-1}$ is a thermal factor corresponding to the Fermi function which determines that transport occur from occupied to empty states; $k_B$ is the Boltzmann constant. Note that energy conservation demands that $\epsilon_k = \epsilon'_{k'}$, and the current thus must be expressed as equation $I = e(P_{1\to2} - P_{2\to1}$,
which is conserved at the interface. In the NS junction problem, one have to consider that incident electrons can be normally (specularly) reflected as electrons or retro-reflected as holes. In this case, the reflected hole retraces the path of the incoming electron and thus a Cooper pair is transmitted in a process known as Andreev reflection (AR), or normal AR[8]. In the graphene case, the fermi wavelength at the Dirac level is infinite, thus the shape of the electrostatic potential profile at the interface is not important; it can be approximated by a square potential[18]. The electron-hole conversion at a NS junction of graphene presents unusual features: electron and hole states belong to different valley, Klein tunneling implies that at normal incidence the barrier is transparent, and the hole can be either retro-reflected or specularly-reflected for incidence angles away from normal[9]. These regimes between retro- and specularly-reflected holes depend on the doping of graphene. For heavily doped graphene, reflections belong to the same band and hence reflected holes retraces the path of incoming electrons. On the other hand, for weakly doped graphene, reflected hole can belong to different band, so the component of group velocity parallel to the interface is flipped; this implies an inversion of voltage dependence of the subgap conductance in the interface. Conductance through a NS junction in graphene has been studied from a “BTK”-model point of view in a paper by C. Beenaker[9] in which reflection and transmission amplitudes are computed for different regimes ($E_F \gg \epsilon$ and $E_F \ll \epsilon$) and Andreev processes by matching wave functions at the interface. In that case, Klein tunneling refers to the fact that at normal incidence Andreev reflections must be unity, i.e. $r_A = 1$, and is a consequence of conservation of chirality. Within this model, differential conductance is computed using

$$\frac{\partial I}{\partial V} = g_0(V) \int dE \left( 1 - |r(eV)|^2 + |r_A(eV)|^2 \right),$$

for $g_0(V) = 4e^2/hN(eV)$, $N(\epsilon) = (E_F + \epsilon)W/(\pi \hbar v)$. The term $g_0$ is referred to as the ballistic conductance for a graphene sheet of width $W$, which differs from the usual value $g_0 = 2e^2/h$ in a factor of 2 due to the valley degeneracy, $r(eV)$ is the amplitude probability of normal reflected electrons, while $r_A(eV)$ is the hole-reflection amplitude. On the other hand, since the coupling between regions can be modelled by a transfer Hamiltonian and its hopping parameter, a Green’s function approach will be useful for treating transport in a more sophisticated and complete way and in which processes arise in a natural way. Hence, we introduce a Hamiltonian approach to transport which can be found in reference [34] and will support our model. Let the full Hamiltonian of the system of regions, say, $L$
and $R$ be denoted by

$$
\hat{H} = \hat{H}_L + \hat{H}_R + \hat{H}_{LR},
$$

(3.26)

where $\hat{H}_\alpha$ ($\alpha = L, R$) represents the free-particle Hamiltonian at each region, given by

$$
\hat{H}(\tau) = \sum_\sigma (\epsilon_\alpha - \mu_\alpha) \hat{c}_\sigma^\dagger(\tau)\hat{c}_\sigma(\tau),
$$

(3.27)

where energy is measured relative to the chemical potential $\mu$, and the sum is taken over the spin quantum number $\sigma = \uparrow, \downarrow$. In this case, it is more convenient to represent the system into the interaction picture[27], so that time-dependent operators $\hat{A}(t)$ obey the law

$$
\text{i} \hbar \frac{d}{d\tau} \hat{A}(\tau) = \left[ \hat{A}(\tau), \hat{H}_0 \right],
$$

(3.28)

where $\hat{H}_0$ is the non-interacting Hamiltonian. Number operator is given by $\hat{N}(\tau) = \sum_\sigma \hat{c}_\sigma^\dagger(\tau)\hat{c}_\sigma(\tau)$ for a given site. Also, whenever a superconducting region is considered, the pairing correlation must be included in the Hamiltonian as a term of the form $\Delta \hat{c}_\downarrow^\dagger \hat{c}_\uparrow + \Delta \hat{c}_\uparrow \hat{c}_\downarrow \downarrow$. The transfer Hamiltonian of a point-contact between regions $L$ and $R$ is given by[34]

$$
\hat{H}_{LR}(\tau) = \sum_\sigma \left( t \hat{c}_{L\sigma}^\dagger(\tau)\hat{c}_{R\sigma}(\tau) + t^* \hat{c}_{R\sigma}^\dagger(\tau)\hat{c}_{L\sigma}(\tau) \right),
$$

(3.29)

where conduction is assumed to be carried by a single channel. This model can be expanded so that the quantum contact between regions includes a hopping parameter $p_{nn'}$ which models the transmission of particles in channel $n$ in $L$ and in channel in the metal $n'$[35]. The hopping parameter of equation 3.29 can model an arbitrary transparency or strength of the junction so that it may contains information about the tunneling regime $t \approx 0$ as well as the ballistic (contact or metallic) regime $\approx 1$. Now, conservation of energy in the transmission will require that the difference in chemical potentials between regions will be given by $\mu_L - \mu_R = eV_{LR} \equiv eV$. In this case the average current at metal $\alpha$ can be expressed as
\[ I_\alpha(\tau) = -e \left\langle \frac{d}{d\tau} \hat{N}_\alpha(\tau) \right\rangle, \]

where \( i\hbar \frac{d\hat{N}_\alpha}{d\tau} = [\hat{N}_\alpha, \hat{H}] \). Hence, by combining the Hamiltonian 3.29 and the number operator, and by considering commutation relations in the fermionic operator, it can be demonstrated that the current formula yields

\[ I(\tau) = \frac{ie}{\hbar} \sum_\sigma \left[ t \left\langle \hat{c}_{L\sigma}^\dagger(\tau) \hat{c}_{R\sigma}(\tau) \right\rangle - t^* \left\langle \hat{c}_{R\sigma}(\tau) \hat{c}_{L\sigma}(\tau) \right\rangle \right], \quad (3.30) \]

where commutation relations are given by \([\hat{c}_{i\sigma}, \hat{c}_{j\sigma'}^\dagger] = \delta_{ij} \delta_{\sigma\sigma'}\), and \([\hat{c}_{i\sigma}, \hat{c}_{j\sigma'}] = 0 = [\hat{c}_{i\sigma}^\dagger, \hat{c}_{j\sigma'}^\dagger]\). Average quantities found in 3.30 can be expressed in terms of the non-equilibrium Keldysh-Green functions \( \hat{G}^{+-} \), which, in the Nambu space, are written as

\[ \hat{G}^{+-}_{ij}(\tau, \tau') = i \begin{pmatrix} \left\langle \hat{c}_{j\uparrow}^\dagger(\tau') \hat{c}_{i\uparrow}(\tau) \right\rangle & \left\langle \hat{c}_{j\downarrow}(\tau') \hat{c}_{i\uparrow}(\tau) \right\rangle \\ \left\langle \hat{c}_{j\uparrow}(\tau') \hat{c}_{i\downarrow}(\tau) \right\rangle & \left\langle \hat{c}_{j\downarrow}^\dagger(\tau') \hat{c}_{i\downarrow}(\tau) \right\rangle \end{pmatrix}, \quad (3.31) \]

Note that the Keldysh function can be defined as follows: Let us define the spinorial operator as \( \hat{C}_{i\uparrow}(\tau) = (\hat{c}_{i\uparrow}(\tau), \hat{c}_{i\downarrow}(\tau)) \), then the general Green’s function is given by \( \hat{G}^{\gamma\delta}_{ij}(\tau_\gamma, \tau_\delta) = -i \left\langle \hat{T}[\hat{C}_{i\uparrow}(\tau_\gamma) \hat{C}_{j\uparrow}(\tau_\delta)] \right\rangle \), where \( \hat{T} \) is the Keldysh temporal ordering operator[33]. The current 3.30 in terms of Keldysh functions 3.31 is expressed as

\[ I(\tau) = \frac{2e}{\hbar} \left[ i \hat{G}^{+-}_{RL}(\tau, \tau) - \hat{t}^* \hat{G}^{+-}_{LR}(\tau, \tau) \right]_{11}, \quad (3.32) \]

where the hopping matrix \( \hat{t} \) in the Nambu space is written as

\[ \hat{t} = \begin{pmatrix} t & 0 \\ 0 & -t^* \end{pmatrix}. \quad (3.33) \]

Note that if \( t = t^* \), then \( \hat{t} = t\sigma_z \); the Pauli matrix. The problem is then reduced to find out the perturbed GFs of 3.32. The perturbed GFs \( \hat{G}^{+-}_{ij} \) can be obtained from retarded and advanced components from the integral equation

\[ \hat{G}^{+-}(\tau, \tau') = \int d\tau_1 d\tau_2 \left[ \hat{I}\delta(\tau - \tau') + \hat{G}^{\sigma}(\tau, \tau_1) \right] \hat{g}^{+-}(\tau_1 - \tau_2) \left[ \hat{I}\delta(\tau_2 - \tau') + \Sigma^a \right], \quad (3.34) \]
where perturbed advanced and retarded GFs obey the Dyson equations

\[
\hat{G}^{r,a}(\tau, \tau') = \hat{g}^{r,a}(\tau - \tau') + \int d\tau_1 \hat{g}^{r,a}(\tau - \tau_1)\hat{\Sigma}^{r,a}(\tau_1)\hat{G}^{r,a}(\tau_1, \tau'),
\]

(3.35)

and the self energies are just \(\hat{\Sigma}_{LL}^{r,a} = \hat{\Sigma}_{RR}^{r,a} = 0\) and \(\hat{\Sigma}_{LR}^{r,a} = (\hat{\Sigma}_{RL}^{r,a})^* = \hat{t}\). The unperturbed GFs, \(\hat{g}^{+-}(\omega)\) satisfy \(\hat{g}^{+-}(\omega) = 2\pi i \hat{\rho}(\omega)n_F(\omega)\), where \(n_F(\omega)\) is the Fermi function. Moreover, it is convenient to express relations 3.34 and 3.35 in a time-independent fashion by virtue of the stationary situation of model Hamiltonian 3.26. In that case, these equations are simple algebraic given by

\[
\hat{G}^{r,a}(\omega) = \hat{g}^{r,a}(\omega) + \hat{g}^{r,a}(\omega)\hat{\Sigma}^{r,a}(\omega)\hat{G}^{r,a}(\omega),
\]

(3.36)

\[
\hat{G}^{+-(-+)}(\omega) = \left[\hat{I} + \hat{G}^r(\omega)\right]\hat{g}^{+-(-+)}(\omega)\left[\hat{I} + \hat{\Sigma}^a(\omega)\hat{G}^a(\omega)\right],
\]

(3.37)

where \(\hat{g}^{-+}(\omega) = -2\pi i \hat{\rho}(\omega)[1 - n_F(\omega)]\) [34]. The current formula can be conveniently written, in components and considering the \(L\)-electrode to be in normal state, as

\[
I = \frac{2e}{h} t^2 \int_{-\infty}^{\infty} \left[ g_{LL,11}^{-+} G_{RR,11}^{++}(\omega) - g_{LL,11}^{+-} G_{RR,11}^{-+}(\omega) \right] d\omega,
\]

(3.38)

where the perturbed GFs \(G_{RR}\) are found from equation 3.36. At this point, we have to consider how to compute the perturbed Keldysh functions in order to deal with the geometry of graphene, and the remaining degrees of freedom, and to coupled a 5 fold system: double quantum dots, central region and the lateral leads. We will restrict our analysis, at first, to the tunnel limit case in which contributions of \(t\) in higher order than linear will be neglected. Nonetheless, a full model will require to solve rigorously the system and thus understanding the amount of posibilities in transport.

### 3.6 Transport through a multi-contact device

Now, from the Hamiltonian approach to quantum point contact transport, we extend to consider atomic contact leads laterally conected to a graphene nanoribbon, as illustrated
Figure 3.4: Pictorical sketch of a two-contact device made of graphene. Left edge is bounded by $A$-type atoms and right edge by $B$-type carbon atoms. (a) Graphene nanoribbon coupled by two lateral leads by means of hopping parameters $p_L$ and $p_R$. (b) Graphene double quantum dots coupled by a superconducting electrode, where regions are coupled by hopping parameters $t_L$ and $t_R$, at left and right interfaces respectively.

In figure 3.4, where atomic details are included. We assume that the hopping parameters between the graphene sheet and the external normal leads are given by $p_L$ and $p_R$. It can be seen, from the geometry presented in figure 3.4 (a), that the atomic contact of leads at each side will be connected to a sublattice, say, $L$-electrode will be connected to $A$-type atoms while $R$-electrode will contact $B$-type atoms. Central region will be labeled $S$, since it can be either in normal or superconducting state. Hence, the Hamiltonian for coupling 2 different regions, at each interface, will depend on the side. A general Hamiltonian, for the interface $n = L, R$, can be written as

$$
\hat{H}_{nS}(\tau) = \sum_\sigma \left( (p_n \hat{c}_{nB,\sigma}^\dagger(\tau) \hat{c}_{SA,\sigma}(\tau) + p_n^* \hat{c}_{SA,\sigma}^\dagger(\tau) \hat{c}_{nB,\sigma}(\tau)) \delta_{nL} + (p_n \hat{c}_{nA,\sigma}^\dagger(\tau) \hat{c}_{SB,\sigma}(\tau) + p_n^* \hat{c}_{SB,\sigma}^\dagger(\tau) \hat{c}_{nA,\sigma}(\tau)) \delta_{nR} \right) (3.39)
$$

We have assumed that $L$- and $R$- electrodes are graphene-like atomic contacts since each site is connected by a different sublattice atom, as the situation represented in the middle junctions of figure 3.4 (b). Nonetheless, it can be replaced by a usual definition of normal-state metallic electrodes[30], and the substitution $\hat{c}_{nA|B} \rightarrow \hat{c}_n$, corresponding to an electron on electrode $L|R$. Let the lateral electrodes be at potential $V_{L,R}$ with respect to the central electrode (ground), thus creation/annihilation operators can be written as $\hat{c}_{L|R,n\sigma}(t) = e^{-i(E+eV_{L|R})t/\hbar} \hat{c}_{L|R,n\sigma}$, and $c_{S,n\sigma}(t) = e^{-iEt/\hbar} \hat{c}_{S,n\sigma}$. Since the hopping parameter is assumed to be a perturbation in the system and contributions to transport can be obtained perturbatively for an arbitrary order, we may consider low-order contributions in
the so called tunnel limit and the contribution of quasi-bound states to transport (single quantum dot). As before, we need Keldysh functions to describe transport, but first we have to define the operator
\[ \hat{C}_i(t) = (\hat{c}^\dagger_{iA,\uparrow}(t), \hat{c}^\dagger_{iB,\uparrow}(t), \hat{c}_{iA,\downarrow}(t), \hat{c}_{iB,\downarrow}(t)) \]
so that the Keldysh functions are given by
\[ \hat{G}_{ij}(\tau, \tau') = -i \langle \hat{T}[\hat{C}_i(t), \hat{C}_j(t')] \rangle, \]
with \( \gamma, \delta = +, - \). The current from \( n \) to \( S \) in terms of the \( 4 \times 4 \) Keldysh functions is given by
\[ I_{nS}(\tau) = \frac{e}{\hbar} Tr \left[ \left( \hat{p}_n \hat{\tau}_B \hat{G}^{+\downarrow}_{nS}(\tau, \tau) + \hat{\tau}_B \hat{p}_n \hat{G}^{-\uparrow}_{Sn}(\tau, \tau) \right) \delta_{nL} \\
+ \left( \hat{p}_n \hat{\tau}_B \hat{G}^{+\uparrow}_{nS}(\tau, \tau) + \hat{\tau}_B \hat{p}_n \hat{G}^{-\downarrow}_{Sn}(\tau, \tau) \right) \delta_{nR} \right], \tag{3.40} \]
where \( \hat{p}_n = p_n \otimes \hat{I} \), and \( \hat{\tau}_B = \tau_B \otimes \hat{I} \). \( \hat{I} \) corresponds to the \( 2 \times 2 \) identity matrix, \( p_n \) is the hopping matrix given by 3.33, and \( \tau_B \) is a sublattice-like matrix so that \( \tau_{B,bb} = 1 \), and \( \tau_B = 0 \) otherwise. Therefore the current depends on the contact, so it will be convenient to expand the space of Keldysh function up to consider both contacts, namely, the contact space [35]. Let the electrodes be denoted by greek letters \( \beta, \alpha \equiv L, R \), while preserving the notation of the direction of the current as \( nS \) or \( Sn \), with \( n = L, R \). Then, the Keldysh GFs in contact space are given by
\[ \hat{G}_{ij}(t, t') = \left( \begin{array}{cc} \hat{G}_{ij,\beta\beta} & \hat{G}_{ij,\beta\alpha} \\ \hat{G}_{ij,\alpha\beta} & \hat{G}_{ij,\alpha\alpha} \end{array} \right), \tag{3.41} \]
and the current through the interface \( \beta \) is then written as
\[ I_{n\beta} = \frac{e}{\hbar} \int dE Tr \tilde{N}_\beta \left[ \hat{p}_n \hat{\tau}_B \hat{g}^{+\uparrow}_{nn}(E) \hat{p}_n \hat{G}^{+\downarrow}_{SS}(E) - \hat{\tau}_B \hat{p}_n \hat{G}^{-\uparrow}_{SS}(E) \hat{\tau}_B \hat{p}_n \hat{g}^{-\downarrow}_{nn}(E) \right], \tag{3.42} \]
where
\[ \tilde{N}_\beta = \left( \begin{array}{cc} \hat{I}_{\beta L} & 0 \\ 0 & \hat{I}_{\beta R} \end{array} \right), \tag{3.43} \]
\( \hat{p}_n = \hat{p}_n \otimes \hat{I} \) and \( \hat{\tau} = \hat{\tau} \otimes \hat{I} \). Perturbed Keldysh GFs in contact space \( \tilde{G} \) are obtained from a similar Dyson equation of the form 3.37. In this case, Green’s functions can be either local or non-local propagators, according to the process they describe. Local GFs,

\[ ^1 \text{We denote } 4 \times 4 \text{ matrices using the } \ldots \text{ sign and } 8 \times 8 \text{ matrices using } \ldots. \]
in the central region, account for transmission at single electrodes while non-local GFs represent transport between contacts inside the central electrode. Unperturbed GFs are related to the DOS as well as the Fermi functions, so that \( \hat{g}_{nn}^{+} = 2\pi i \hat{\rho}_{nn} \hat{n}_{F,nn} \), where \( \hat{\rho}_{nn} \) is diagonal in contact space with elements \( \hat{\rho}_{nn,\beta\beta} \) which represent a \( 4 \times 4 \) matrix in the sublattice-Nambu space. Local density of states matrix in sublattice-Nambu space is given by

\[
\hat{\rho}_{nn,\beta\beta} = \begin{pmatrix}
\rho_{nn,AA}(E - eV_{\beta})\delta_{\beta R} & 0 & 0 & 0 \\
0 & \rho_{nn,BB}(E - eV_{\beta})\delta_{\beta L} & 0 & 0 \\
0 & 0 & \rho_{nn,AA}(E + eV_{\beta})\delta_{\beta R} & 0 \\
0 & 0 & 0 & \rho_{nn,BB}(E + eV_{\beta})\delta_{\beta L}
\end{pmatrix},
\]

(3.44)

and Fermi functions for electrons and holes are respectively \( n_{F}(E - eV) \) and \( n_{F}(E + eV) \). In this way, using the perturbed GFs for \( \hat{G} \), it can be demonstrated that the net current through the electrode (interface) \( L \) is given by [35]

\[
I_{L} = I_{LL} + I_{LR},
\]

(3.45)

where \( I_{LL} = I_{1,LL} + I_{2,LL} + I_{3,LL} + I_{A,LL} \) can be regarded as a *local* current, and \( I_{LR} = I_{e-h,LR} + I_{e-e,LR} + I_{e-q,LR} \) is a crossed - non local - current. Current terms can be found in reference [35] for a general point-contact case. For a tunnel contact, however, not all terms contribute to transport, i.e., some of them vanish. In this tunnel limit case, the contributions \( I_{2,LL} \approx I_{3,LL} \approx 0 \), and the remaining terms can be written as

\[
I_{1,LL} = \frac{8p_{e}^{2}e}{\hbar} \int_{-\infty}^{\infty} dE \rho_{e}(E)\rho_{SS,11}(E)(n_{F,e}(E) - n_{F}(E)),
\]

(3.46)

and corresponds to normal electronic tunneling, while

\[
I_{A,LL} = \frac{8\pi^{2}e}{\hbar} p_{L}^{2} \int_{-\infty}^{\infty} dE \rho_{e,LL}(E)\rho_{h,LL}(E) \left( n_{F,e(L)} - n_{F,h(L)} \right) \left| \hat{G}_{SS,LL,21}^{r} \right|^{2}
\]

(3.47)

corresponds to local Andreev reflections thus involving the component \( \hat{G}_{RR,LL,21}^{r} \) of the local propagator. On the other side, in the tunnel tunnel limit perturbed GFs can be
approximated by unperturbed functions, so that the non-local components of transport are given by

\[ I_{e-h,LR} \approx \frac{8\pi^2 e^2 p_\alpha^2}{h} \int_{-\infty}^{\infty} dE \rho_{e\alpha}(E) \rho_{h\beta}(E) (\hat{g}_{SS,\beta\alpha,11}(E)) \left| \hat{g}_{SS,\beta\alpha,21}(E) \right|^2, \tag{3.48} \]

\[ I_{e-e,LR} \approx \frac{8\pi^2 e^2 p_\alpha^2}{h} \int_{-\infty}^{\infty} dE \rho_{e\beta}(E) \rho_{h\alpha}(E) (\hat{g}_{SS,\beta\alpha,11}(E)) \left| \hat{g}_{SS,\beta\alpha,11}(E) \right|^2, \tag{3.49} \]

and

\[ I_{e-q,LR} \approx 0. \tag{3.50} \]

Physical interpretations of contributions to transport of each term is read according to the mathematical terms they contain. \( I_{e-h,LR} \) corresponds to the reflection of an electron at electrode \( L \) into a hole in the electrode \( R \), which is referred to as crossed Andreev reflection (CAR), thus mediated by a propagator in the superconducting region of the sort \( \hat{G}_{SS,LR,12} \). The term \( I_{e-e,LR} \) refers to electron cotunneling processes between different electrodes, thus involving a propagator in the superconducting region of the sort \( \hat{G}_{SS,LR,11} \). And the term \( I_{e-q,LR} \) is due to the transmission of an electron from the normal-state electrode \( L \) to the right \( R \) electrode as a quasiparticle. In this case, tunneling current occurs as \( p_L \approx p_R \approx 0 \) through the electrodes and corresponds to propagation of electrons thus involving unperturbed GFs.

Now we would like to distinguish two different cases: symmetric potentials in the electrodes, and a potential difference between them. In the first case, both electrodes are at the same potential, i.e., \( V_L = V_R = V \), thus the electron-cotunneling term vanishes identically \((I_{e-e,LR} = 0)\). Hence, the current is given by

\[ I_{LR} = \frac{8\pi^2 e^2 p_L^2}{h} \int_{-\infty}^{\infty} dE \rho_{eR}(E) \rho_{hL}(E) (f(E - eV) - f(E + eV)) \left| \hat{g}_{SS,LR,21}^r \right|^2. \tag{3.51} \]

We can obtain the crossed differential conductance from the definition,

\[ \sigma_{LR} = \frac{dI_{LR}}{dV_R}; \tag{3.52} \]
for $V_R = V$; so we have

$$\sigma_{LR}(V) = \frac{16\pi^2 e^2 p_L^2 p_R^2}{\hbar} \rho_{eR}(V) \rho_{hL}(V) \left| \tilde{g}_{SS,LR,21}(V) \right|^2,$$  \hspace{1cm} (3.53)

and the local differential conductance is given by

$$\sigma_{LL}(V) \equiv \frac{dI_L}{dV_L} = \frac{16\pi^2 e^2 p_L^4}{\hbar} \rho_{eL}(V) \rho_{hL}(V) \left| \tilde{g}_{SS,LL,21}(V) \right|^2.$$ \hspace{1cm} (3.54)

In the second case, we consider a potential difference between the electrodes such that $V_L - V_R = V$ and $V_R = 0$, as an arbitrary reference. In this case the crossed differential conductance yields

$$\sigma_{LR} = \frac{8\pi^2 e^2 p_L^2 p_R^2}{\hbar} \rho_{eR}(E) \left( \rho_{hL}(E) \left| \tilde{g}_{SS,LR,21}(E) \right|^2 - \rho_{eL}(E) \left| \tilde{g}_{SS,LR,11} \right|^2 \right).$$ \hspace{1cm} (3.55)

Both cases manifest their difference in which electron cotunneling contributes or not in transport. In the second case, the net crossed current is reduced by direct cotunneling between the electrodes. Unperturbed GFs for isolated electrodes can be written as

$$\tilde{g}_{nn} = \frac{1}{W} \left( \begin{array}{cc} \hat{I} & 0 \\ 0 & \hat{I} \end{array} \right),$$ \hspace{1cm} (3.56)

where $W$ is an energy scale related to the normal density of states at the Fermi level by $\rho(\epsilon_F) \approx 1/(\pi W)$. Now we consider the case of in which the central region of the device depicted in figure 3.4 (a) is divided into three different regions: two lateral electrodes in normal state (quantum dots), at external potentials $V_{gL}$ and $V_{gR}$, coupled by a superconducting (central) electrode, as depicted in figure 3.4 (b). In this case, Lateral dots will be labeled as left ($L$)- and right ($R$)-Dots, while external gate potentials will be labeled as $V_g$ and hopping parameters at interfaces will be denoted as $t_L$ for $L$-side interface and $t_R$ for the $R$-side. Now, current from the lead can be transmitted to the other lead or to the superconducting electrode by means of a NS current conversion.

In this case, it can be noticeable that current through the boundaries can be transmitted directly to the superconducting region and then to ground. In the tunnel limit, the current
is just due to local Andreev processes\cite{46}, and can be written as

\[ I_n = \frac{16e^2}{\hbar} \int dE \text{Tr} \left[ \text{Re} \left( \hat{t}_n \hat{\rho}_{nn,ee} \hat{t}_n^T \hat{G}_{eh} \hat{t}_n \hat{\rho}_{nn,hh} \hat{t}_n^T \hat{G}_{he}^a \right) \right] \hat{n}_{Fnn,ee}, \]  

(3.57)

or in components

\[ I_A = \frac{16\pi^2 e^2}{\hbar} \int dE \text{Re} \left( \rho_{eL} G_{ss,eh,21}^{r} \rho_{hl} G_{ss,LL,21}^{a} \right) N_F(E), \]  

(3.58)

where, for the graphene case, \( G_{SS,eh,11} \) corresponds to the AA sublattice component and the density of states considerations given by equation 3.44. In this way, if we assume a potential difference \( V \) between the normal leads and the superconductor, then the local differential conductance is given by

\[ \sigma_A = \frac{dI_A}{dV} = \frac{16\pi^2 e}{\hbar} \rho_{eL} \rho_{hl} \left| G_{ss,LL,21}^{r} (V) \right|^2 \]  

(3.59)

Hence, we know the contributions of transport in the tunnel regime due to local and crossed Andreev processes. The device depicted in figure 3.4 can be regarded as a series double quantum dot whenever a potential difference is applied between the reservoirs (S region connected to ground)\cite{6}, and a Cooper pair beam splitter if there is an applied potential difference between the normal leads and the superconductor\cite{7}. When acting as a series double quantum dot, total current is given by \( I = I_{LL} + I_{LR} \), and crossed conductance \( \sigma_{LR} \) is given by equation 3.55. When acting as a Cooper pairs splitter, crossed conductance is given by equation 3.53, and current contribution doesn’t include EC processes. In graphene, it wwould be possible to observe entangled electrons along different paths since electrons can be specularly-reflected\cite{9}, and they can be probed separately at each dot\cite{3}. One problem to deal with is the local Andreev processes that always are present in transport thus reducing the non-local transport. In the last chapter we will study the conditions such that local Andreev processes are reduced.
CHAPTER 4

TRANSPORT THROUGH DOUBLE QUANTUM DOTS COUPLED BY A SUPERCONDUCTOR

This chapter is mainly concerned with the results of the minimal model for describing transport in a double quantum dot. Linear conductance diagrams, in the gate-voltage space, are obtained for single-channel nanotubes which are in concordance with literature and experiments. Then, we turn superconductivity on thus implying electron/hole correlations and non-local Andreev reflections, which are measured as functions of the distance between the normal contacts (superconducting length). The contribution of non-local reflections to total transport is measured by means of an efficiency index in the linear and non-linear regimes. While single-channel nanotubes exhibit a unit efficiency (100%), it drops as the number of channels is increased therefore for graphene. We analyze the non-local contributions relative to local processes. This chapter is organized as follows: section 4.1 introduce the basic device which we model to produce non-local Andreev reflections.

4.1 Double quantum dot in graphene and nanotubes

Quantum dots are man-made nanoscopic structures in a solid state system which may contain hundreds of atoms and discrete energy levels. Coupling of two quantum dots is useful since the coupling can be tuned by using external gates and bias potentials. This double quantum dot (DQD) circuit has been extensively studied since it can represent a two-level molecular system [43]. Here we restrict to the case of two normal-state quantum dots coupled by a central conventional superconductor, and the dots are weakly coupled to external leads. The system is defined on carbon nanotubes as illustrated in 4.1. Two external leads, namely \( \alpha \) and \( \beta \) in the figure, represent external reservoirs at potential \( V_{\alpha, \beta} \) relative to the superconducting electrode, which is regarded to be at ground. In the figure also the external gate potentials for individual dots are represented, which we assume are capacitively connected to the system. Energy levels of individual dots can be
tuned in order to enhance transport between the dots. Electronic confinement in single quantum dots has been reported [40], and experimental realizations have been performed in the normal [39] as well as in the superconducting regime [6], even when the device is considered as a nano-transistor [3].

The behavior of the stability diagram depends on the coupling between the dots [43]. The stability diagram - or linear conductance diagram - is found at very low injection energies, about zero bias, in a 2-dimensional space defined by the potential of the gates. In the minimal coupling, or maximal ionic decoupling, the stability map is nearly rectangular since quantum states of individual dots are independent. As the coupling is getting increased, the diagram turns into hexagonal and tends to be diagonal in the maximal covalent coupling. In this coupling regime, states are delocalized along the dots and thus transport is carried in a phase-coherent way. In zigzag nanoribbons, chiral tunneling avoids confinement in contrast to the case of a semiconducting nanotube. From chapters 2 and 3 we know electronic properties of individual dots made of graphene or nanotubes, as well as GFs which will help us to compute numerical quantities. The model set-up of the device we pretend to model is presented in figure 4.1, together with a representation of the square-like Fermi profile along the system; a smooth-varying potential approach can be performed in order to model a more realistic situation [7]. Tunneling through a DQD can be approached by considering wave function at each individual region and then coupling it by boundary conditions given by the Schrödinger equation [23, 3]. Therefore, transport or current will be described by transmission coefficients within the BTK model.

Allowed transport processes are depicted in figure 4.2 and the corresponding charge conversion, which is related with the components of the Green function. Part (a) of this figure we represent non-local processes. The elastic electronic transmission, or elastic cotunneling, in which an electron is directly transmitted between the electrodes. This process involves the electron-electron component of the non-local propagator. Note, moreover, that this must correspond to the \( AB \) propagation in the lattice, according to the geometry defined above. Holes can also be transmitted directly between the electrodes. A second non-local process occurs when superconductivity is on: the crossed Andreev reflection. In order to convert normal to super-current, an incoming (subgap) electron for the normal region must combine with another electron with opposite spin and momentum. This second electron must come from the same lead leaving behind a retro-reflected hole (normal Andreev reflection
Figure 4.1: Pictorial representation of the DQD device: a conventional superconducting electrode coupled by two quantum dots. The system is beased by two external leads. External gates are shown below each dot which are used to tune in/out individual quantized energy states (bottom picture). The non-local Andreev reflection is illustrated by an incoming electron coupling with a second electron from the opposite electrode. This process is equivalent, in the time-reversed case, to split a Cooper pair into separate electrode.

Figure 4.2: Illustration of (a) non-local and (b) local processes in a series DQD coupled by a superconducting electrode. Coefficients amplitudes are determined by components of the Dyson equations of the entire system and time-reversed processes are obtained in a similar way; from sublattice B to A.
- AR), or from another electrode attached to the superconductor (crossed Andreev reflection - CAR), if the separation between the electrodes is comparable to the superconducting coherence length. Non-local AR is presented in figure 4.2 as a hole reflected back to the right lead, thus transmitting a Cooper pair into the superconductor. Part (b) of the same figure represents the allowed local processes, which take place at the same lead. First, normal electron and hole reflections in which no particles are transmitted.

As we mentioned in the last section, the system will be operated in two cases according to the potential of the leads. In the symmetric case the external potentials are the same, i.e., \( V_L = V_R \equiv V \), and conductance is given by \( G_{L|R}(V) = G_0(\text{T}_{\text{CAR}}(V) + \text{T}_{\text{CAR}}(-V) + 2\text{R}_{\text{A}(L|R)}) \), where \( G_0 = 4e^2/h \) is the quantum conductance for graphene. In the asymmetric case there is a potential difference between the leads given by \( V_L - V_R \equiv V \), and the crossed differential conductance is given by \( G_{L|R} = G_0(\text{T}_{\text{CAR}}(V) - \text{T}_{\text{EC}}(V)) \). Since in the symmetric case EC components are eliminated, CAR processes become one of the transport mechanisms besides local AR. CAR processes are fundamental for producing spin-engaged electronic states at individual quantum dots, hence the symmetric case will be referred to as the beam splitter as well. The asymmetric case, on the other hand, acts as a series double quantum dot. We compute transport coefficients according to the functions in the last section: CAR transmission coefficients for a single-channel (point) contact are determined by equation 3.53, and can be written as

\[
T_{\text{CAR}}(V) = 4G_0{\tilde{p}}_L^2{\tilde{p}}_R^2 \left| \hat{\tilde{G}}_{\text{SS,LR,21}}^{\text{r}}(V) \right|^2, 
\]

where we have assumed that the normal DOS of lateral electrodes is about constant, given by \( \rho_L \approx \rho_R \approx 1/\pi W \), where \( W \) is an energy-scale related to the DOS at the Fermi level, and the terms \( \tilde{p}_{L,R} = p_{L,R}/\sqrt{W} \) correspond to normalized hopping parameters. It is important to remark that the unperturbed GF of equation 4.1 corresponds to the perturbed GF of the double quantum dot system which will be found below. Hence, we denote the GFs of the QDQ system by capital letters. For a \( n \)-channel contact, equation 4.1 must be generalized as

\[
T_{\text{CAR}}(V) = 4G_0{\tilde{p}}_L^2{\tilde{p}}_R^2 \sum_n \left| \hat{\tilde{G}}_{\text{SS,LR,21}}^{\text{r}}(V, n) \right|^2, 
\]

where\( n \) represents the channel index.
and for the continuous case

\[ T_{\text{CAR}}(V) = 4G_0 \hat{p}_L^2 \hat{p}_R^2 \int_q \left| \hat{G}_{\text{SS,LR},21}(V,q) \right|^2 dq. \] (4.3)

On the other hand, EC components are computed as

\[ T_{\text{EC}}(V) = 4G_0 \hat{p}_L^2 \hat{p}_R^2 \sum_n \left| \hat{G}_{\text{SS,LR},11}(V,n) \right|^2, \] (4.4)

for the discrete-channel case, and

\[ T_{\text{EC}}(V) = 4G_0 \hat{p}_L^2 \hat{p}_R^2 \int_q \left| \hat{G}_{\text{SS,LR},11}(V,q) \right|^2 dq. \] (4.5)

for the continuous case. Similarly, the local AR components for electrode \( n = L, R \), according to equation 3.59, are computed as

\[ A_{R(L|R)} = 4G_0 \hat{p}_{(L|R)}^4 \sum_n \left| \hat{G}_{\text{SS,LR},11}(V,n) \right|^2, \] (4.6)

for the discrete case, and

\[ A_{R(L|R)} = 4G_0 \hat{p}_{(L|R)}^4 \int_q \left| \hat{G}_{\text{SS,eh},11}(V,q) \right|^2 dq. \] (4.7)

for the continuous case. Now, as pointed out in the last section, when the device is acting as a Cooper pair beam splitter, EC components vanish and thus conductance is written as a combination of local and non-local Andreev processes. Therefore, it is convenient to introduce the splitting efficiency ratio[7], given by

\[ \eta = \frac{4G_0 \left( T_{\text{CAR}}(V) + T_{\text{CAR}}(-V) \right)}{G_L(V) + G_R(V)}, \] (4.8)

where contribution of electrons \(+V\) and holes \(-V\) have been considered. In general, \( T_{\text{CAR}(V)} \neq T_{\text{CAR}(-V)} \) for doped materials since electron/hole symmetries are broken[7]. So that whenever the local processes are reduced to zero \( G_L = G_R = 0 \), the splitting efficiency approaches unity.
4.2 Evolution of modes in carbon nanotubes

![Figure 4.3: Allowed modes as function of the unit cells in chiral direction for metallic (lower axis) and semiconducting (upper axis) CNs of length of central region. Metallic range period is of nearly $3 \times 10^5$ unit cells, and increases in pairwise numbers. Semi-conducting modes increase in integer numbers.](image)

As pointed out in chapter 2, transverse wave vector is quantized due to periodic boundary conditions, thus creating bands in the energy spectrum denoted by the band index $n$. Bound energy states correspond to real valued longitudinal wave-vectors, determined by the dispersion relation given by equation 2.31. In this work we consider tubes with length of the order of $1\mu m$ and radii near $1\mu m$ in both, metallic ($M = 11$) and semiconducting ($M = 12$) cases, as in experiments reported in reference [6]. Let the Fermi levels of metallic and semiconducting tubes to be fixed at $E_g(12)$ and $E_g(11)$ respectively. So that, as the radius is increased, the number of transverse modes must be increased as well, as depicted in figure 4.3 for both cases. Solid (red) line is a step-like function indicating that metallic modes emerge in pairs each about $3 \times 10^5$ unit cells ($77.4 nm$) due to the small gap; in general, the $n$-modes metallic CNs will be in the range $3 \times [0, 105] + 3 \times 105(n - 1)$, for $n$ odd. In contrast, semiconducting nanotubes can be either of even or odd number of modes according to its radius, and they emerges faster than in the metallic case, as indicated by the dashed (blue) line of figure. It is important to note, from equation 2.31, that the energy gap depends on the mode and as the radius is increased, lower order modes tend to be metallic like. Thus, a single nanotube may have metallic and semiconducting quasi bound states for transport.
4.3 Single-channel CN-DQDs

We begin our analysis of transport through a DQD using single-channel CNs for both cases, metallic $M = 12$ and semiconducting $M = 11$, coupled to external leads in an atomic-like contact. In order to compute the transport coefficients given above we need to determine the perturbed GF of the DQD system which can be found in appendix 6 for the local and non-local GFs. The leads will be coupled in the tunnel limit, so that the approximations given by equations 4.1 and 4.6 still hold. Normal-state conductance maps are computed in order to locate resonances between the dots, and we include spin-orbit effects in the analysis. We then turn on superconductivity in the central region and we compute conductance terms in and out of resonance in order to determine the physical conditions under which CAR processes are enhanced, and local Andreev processes are suppressed.

4.3.1 Normal state

Coupling between dots depends on several physical conditions, but we confine our attention to variation in the coupling due to the distance between the dots (width of the central region $W_S$) and the strength of the barrier $E_{FS}$, such as depicted in figure 4.1. In normal state, transport occur via direct electron cotunneling, so we compute conductance maps for this component for DQDs under the following conditions: Fermi level of metallic $M = 12$ CNs is set at $E_G(12) \approx 46\text{meV}$ and of semiconducting CNs at $E_G(11) \approx 390\text{meV}$; therefore, in what follows we will use these configurations unless otherwise stated.

Figure 4.4: Oscillations of normal-state differential conductance of a series DQD of single-channel CNs, measured relative to $\sigma_o$, as function of (a) width of the central region, and (b) Fermi level of S-region. Maxima and minimal represents the coupling between the dots.

In figure 4.4 we present the resonant oscillations of normal state differential conductance through, measured with respect to $\sigma_o$, as function of $W_S$ in part (a), and as function of the
Figure 4.5: Conductance maps in normal state of the single-channel DQD for metallic (a) and (b) and semiconducting - in log scale - (c) and (d) CNs. Left diagrams are computed in the maximal coupling between the dots, while right diagrams are in minimal coupling.

Figure 4.6: Conductance maps for metallic (a) and semiconducting (b) CNs - DQDs - in normal state. Bands are splitted due to spin-orbit effects.
Fermi level of the barrier height $E_{FS}$ in part (b). Maxima and minima can be associated to a maxima and minima coupling between dots. The overall length of the system is about $1-1.2 \mu m$, while the central region length is about $150-200 nm$, which is comparable to the BCS superconducting coherence length[6]. Conductance diagrams, for the npn region, are presented in figure 4.5 for metallic (upper diagrams (a) and (b)) and semiconducting (lower diagrams (c) and (d)). In these figures, it becomes clear that semiconducting CN-DQDs present a relative weak coupling between dots due to the energy gap, while honeycomb-like stability diagrams and triple point resonances are present in the metallic case, where energy gap is low[43]. In figure 4.6 we compute the conductance maps for metallic and semiconducting systems, in their maximal coupling, considering SO effects. Therefore, we identify resonances in diagrams so that we can configure the (in site) external gates in order to obtain any desirable regime of the system, corresponding to encircled regions in figure 4.5.

4.3.2 Superconducting state

Now, we turn-on the induced pairing potential on the central region and analyze local and crossed Andreev processes which now are non vanishing. Let the superconducting pairing potential be about $\Delta \approx 1 meV$, according to experiments[6, 7]. The oscillations of CAR probability as function of the superconducting length $W_S$ are presented in figure 4.7 for metallic and semiconducting cases, which are well known [3]. Overall CAR exponential oscillations decay on the scale $\lambda_F$, described by the $\epsilon_0 = \hbar v_F / \Delta \sqrt{1 - (\hbar v_F q / E_F(S))} \ (q = q_0 \pm \delta_1 / \hbar v_F)[7]$. Whenever the system is operated as a Cooper pairs beam splitter, efficiency maps are obtained according to equation 4.8 as function of external gates voltage in and out of resonances indicated in figure 4.5. As illustrated in figure 4.7, for both metallic and semiconducting regimes of the system, efficiency in the zero-bias oscillates with an upper bound of about 0.5 (0.4 for the semiconducting case), so that we can set the system in a configuration of maximal efficiency. Resonances are located, for the metallic case, at about $V_L = V_R = -8.2 meV$, and for the semiconducting case, at about $V_L = V_R = -2.4 meV$, both measured relative to each Fermi level in the single-channel case. In that resonance, for the metallic case, we compute local and non-local transport coefficients for a symmetric gates potential case ($V_L = V_R$), as presented in figure 4.8, where it can be seen that local Andreev processes never vanishes while CAR probability remains finite. For this reason,
Figure 4.7: Evolution of CAR probability for metallic \((N = 12)\) and semiconducting \((N = 11)\) single-channel DQDs as a function of the width \((W_S)\) of the central \(S\) region, in red solid lines. Evolution of splitting efficiency for a DQD acting as a Cooper pairs beam splitter (blue dotted line). In both cases, oscillations exhibit an exponential decay as the superconducting width is increased.

we can’t find a 100% efficient system under this configuration. Alternatively, for the anti-diagonal choice of external gates \((V_L + V_R = \text{const})\) we can find that local processes are completely suppressed thus leaving the CAR processes as the main transport mechanism, as we show in figure 4.9. Hence, we compute a full efficiency map using the anti-diagonal configuration of external gates in which we expect the efficiency to be about unity (100%). In figure 4.11 we compute differential conductance maps at resonance of a metallic single-channel CN-DQD, for the series double quantum dot (a) and the beam splitter cases (b), and we include cross-sectional plots of both, diagonal and antidiagonal cases in part (c).

Figure 4.8: Local and non-local transport coefficients: crossed Andreev reflections (red solid line), Andreev reflection at L-electrode (blue dotted line) and local AR at R–electrode (green segment line). Energy for each case is indicated, and gate voltages are taken in the diagonal \(V_L = V_R\), measured relative to the resonance location \(E_{\text{res}} \approx -8.2\text{meV}\), and Fermi level.
Figure 4.9: Local and non-local transport coefficients: crossed Andreev reflections (red solid line), Andreev reflection at L-electrode (blue dotted line) and local AR at R-electrode (green segment line). Energy for each case is indicated, and gate voltages are taken in the off-diagonal $V_L + V_R = \text{const}$, measured relative the the resonance location $E_{\text{res}} \approx -8.2\text{meV}$, and Fermi level.

Figure 4.10: Splitting efficiency maps for zero bias and biased metallic and semiconducting single-channel CNs - DQDs. (a) and (c) present the zero-biased case of metallic and semiconducting systems, respectively, as function of external gate potentials $V_L$ and $V_R$. Figures (b) and (d) show biased efficiency maps as function of external gate potentials $V_L = V_L R = V$ and injecting energy $eV$ of incident electrons.
Figure 4.11: Differential conductance plots for a single-channel metallic CN-DQD at resonance located about at $V_g \approx -8.2\text{meV}$ above the Fermi level. (a) Conductance maps for the system acting as a series DQD, (b) conductance maps for the system acting as a beam splitter, and (c) cross-section in diagonal (upper) and anti-diagonal (lower) configuration of external gate potentials.

We compute efficiency maps for the zero-bias regime in the $V_g|_{L,R}$ space, as illustrated in figures 4.10, (a) and (c), for the metallic and semiconducting case, respectively. It can be seen that efficiency can’t reach more than about 40%, but when biased in the subgap range, efficiency approaches to unity (100% efficient). It can be noticed that under certain bias configuration, efficiency can reach up to $\approx 1$ thus indicating 100% of splitting efficiency in the metallic case, for a wide range, while in the semiconducting case efficiency only reaches about 70% of efficiency. Therefore, as a numerical approximation, it can be determined the conditions under which CAR processes are enhanced and how to increase such a efficiency for single channel CNs systems. We also include the conductance for $V_g|_{L,R}$ out or resonance, thus manifesting subgap tunneling of particles into the superconductor and the relevance of local processes over no-local (see figure 4.12).

### 4.4 Multi-channel CN-DQDs: Graphene as a limit

For the multi-channel case, we will follow the same procedure executed for the single-channel case. First, we compute normal-state conductance terms and maps in order to locate resonances in the EC components. Then we turn on superconductivity and then we compute CAR probabilities as function of the separation between the dots, efficiency maps thus showing that splitting efficiency drops as the number of modes increases, and
Figure 4.12: Differential conductance for a double quantum dot in the beam splitter configuration, for anti-diagonal choice of external potentials and for $V_{gL,R}$ out of resonance. Contribution of local processes is always more significant than that of CAR processes.

Differential conductance graphs for the system acting as a beam splitter and a series double quantum dot. Our population of nanotubes is composed by well-defined $n = 3, 15, 31, 75, 301$ modes metallic CNs, according to the families defined in section 4.2. The behavior of each nanotube in each set of $n$ modes is completely different if the number of transverse unit cells changes. We will show that local processes will become more relevant as the number of modes increases thus reducing CAR efficiency. By increasing the number of modes we see that nanotubes behave like a graphene nanoribbon in the so called graphene limit. We obtain that graphene nanoribbons behave in a similar way as a $n \gg 1$, in particular, the $n = 301$ CN. We take the nominally metallic nanotubes as reference, but as the number of modes gets large, the energy gap vanishes no matter if the tube is metallic or semiconducting; graphene is always metallic.

### 4.4.1 Normal state

First, we obtain conductance maps for the above mentioned CNs with $n = 3, 15, 31, 75$ and $n = 301$ modes and corresponding radii of about $r = 45.16, 315.73, 676.62, 1243.1, 6766.2 - nm$, respectively, so that resultant conductance map is composed by superposition of indistinguishable individual contributions. It is well known that as the number of modes is increased conductance increases as well thus reducing the resistance[21]. In figure 4.13 we present the conductance maps, normalized to $\sigma_o$, of multi-channel CNs in normal state regime. In the first plot in which $n = 3$, the contribution of individual modes can be appreciated. In this case, band index for each mode corresponds to $n = -1, 0, 1$, where the lowest mode $n = 0$ is about metallic - or of zero gap thus Klein tunneling - and therefore is the most significant mode in that diagram. In the same way, as the number of modes is increased, individual channels cannot be distinguished anymore thus leading
to conductance bands corresponding to a graphene nanoribbon. Nonetheless, the resulting bands for the graphene limit are always diagonal in the external gates space thus indicating the metallic (zero gap) behavior of the material and delocalization of states along the dots due to chiral tunneling. Thus we can conclude that lower order modes are more significant in transport since the band gap vanishes as increasing the radius and new modes emerge. Note, as well, that spin-orbit effects can be negligible in the graphene limit, as well as other curvature effects. Hence, we conserve the resonance location for the subsequent analysis.

Figure 4.13: Conductance maps for (a) \( n = 3 \) (\( R \approx 45.16\,\text{nm} \)), (b) \( n = 15 \) (\( R \approx 315.73\,\text{nm} \)), (c) \( n = 31 \) (\( R \approx 676.62\,\text{nm} \)), (d) \( n = 75 \) (\( R \approx 1.24\,\mu\text{m} \)) and (e) \( n = 301 \) (\( R \approx 6.77\,\mu\text{m} \)). Superposition of modes tend to form bands in the graphene limit, as \( n \) becomes infinite.

### 4.4.2 Superconducting state

When superconductivity is turned on in the central electrode, pairing correlation induces CAR processes each system and depends on the separation between the dots, as presented in figure 4.14 for each case. The efficiency ranges between 0 and about 50% for all cases and the exponential decay is qualitatively the same, for this zero-bias case. For the \( n = 3 \)}
nanotube we compute the beam splitter and series DQD conductances for the anti-diagonal potentials case, as presented in figure 4.14. It can be noticed that resonances are now wide bands and anti-diagonal potential calibration along that resonance show that the contribution of CAR processes are more relevant.

In figure 4.16 we present the zero-bias efficiency maps for the full range of external potentials. As seen in the normal state conductance, contribution of individual channels tend to form bands in the graphene limit, as appreciated in part (e) of figure 4.16. In the biased case, we compute the efficiency maps for the same set of nanotubes in the same conditions, as presented in figure 4.17, where it can be seen that efficiency is upper bounded by about 35% for all cases. This can be understood by considering the conductance plots presented in figure 4.18 where, for a fixed location in the $V_{gL/R}$-space, local processes become more significant crossed processes thus decreasing the efficiency. Therefore, we can see that as the radius is increased in the system, and new emerging modes arise, contribution of local Andreev processes become more relevant thus exceeding the contribution of Crossed terms in conductance.

Figure 4.14: Evolution of CAR probability coefficients for multi-channel CNS-DQDs as function of their reparation ($W_S$), in red solid line. The number of modes is indicted at each figure. Evolution of splitting efficiency is presented in blue dotted lines for each case.
Figure 4.15: Differential conductance plots for a $n = 3$-channel metallic CN-DQD at resonance located about at $V_g \approx -5.2\text{meV}$ above the Fermi level. (a) Conductance maps for the system acting as a series DQD, (b) conductance maps for the system acting as a beam splitter, and (c) cross-section in diagonal (upper) and anti-diagonal (lower) configuration of external gate potentials.

Figure 4.16: Splitting efficiency maps for multi-channel CNs - double quantum dots systems - as function of external gates voltages. Efficiency maps are computed for (a) $n = 15$, (b) $n = 31$, (c) $n = 75$ and $n = 301$ conduction channels.
Figure 4.17: Splitting efficiency maps for multi-channel CNs - double quantum dots systems - as function of external gates $V_L = V_R = V$ and vias voltage $V$
Figure 4.18: Differential conductances for multi-channel carbon nanotubes - double quantum dots - coupled by a superconductor. All plots have been made in the anti-diagonal configuration of external potentials. We include in this plots the CAR probability amplitudes (red solid lines), local Andreev reflection terms at $L$ (blue-dotted line) and $R$ (green-segment line), for a fixed location in the $V_{gL/R}$ space given by the resonance indicated by the single-channel case.
In this thesis we have addressed the problem of transport in graphene-based nanostructured systems, using experimental data reported in references, and a theoretical model based on the Green’s function of the quantum system. We review the electronic properties of graphene and carbon nanotubes and roughly the theoretical models to perform numerical simulations of electronic quantities. We describe the density of states of isolated ideal samples of graphene with arbitrary Fermi level and states at interfaces between different interacting regions or with inhomogeneous external potentials. Induced superconductivity is approached at microscopic level using the Bogoliubov-de-Gennes solutions to describe quasiparticles of time-reversed electrons and holes in graphene. Then, we model interfaces using the Keldysh formalism in which electric current through boundaries can be solved perturbatively.

We model transport using the Green’s functions derived in chapter 3, and we focus on the problem of a double quantum dot made of zigzag nanoribbons and nanotubes coupled by a superconducting electrode and biased by external leads. So we calculate the differential conductance in the tunnel limit, at lowest perturbative order, of a set of systems. We begin with a single-channel nanotube, then we increase the radius and new conduction channels fill the characteristic conductance maps revealing resonances in the system. These systems are considered in two regimes according to the potential of the leads: symmetric, in which both leads are at the same potential and asymmetric when there are a potential difference between them. At resonance, the presence of crossed and normal Andreev reflections was measured with the aid of the splitting efficiency, which approaches to unity (100%) in the nominally metallic nanotube, and decreases with increasing the radius. In the graphene limit, as the number of conduction channels is large enough, we compute conductance components which manifest the metallic behavior and maximal coupling between dots due to Klein tunneling. We observe how crossed Andreev reflections are gradually reduced as the radius is increased and how to find configurations where these reflections are predominant.
We perform numerical computations and we define the doping of metallic systems at the resulting curvature gap of metallic \( N = 12 \) carbon nanotubes \((E_G(12) \approx 42 \text{meV})\), while semiconducting systems are doped at the corresponding gap of single-channel semiconducting nanotubes \( N = 11 \) \((E_G(11) \approx 390 \text{meV})\). The double quantum dot is operated in two ways according to the potendial difference between the external leads. In one case, the system operates as a Cooper pairs beam splitter, in which both leads are at the same potential \((V_L = V_R \equiv V)\), and electron cotunneling is supressed. In the second case, we define a potential difference between the leads: \( V_L - V_R \equiv V \), and electron cuttuneling contributes to transport. For both cases we compute transport components and efficiency maps, and we observe how to enhance CAR processes.

In any case, local Andreev processes are always present, together with crossed processes. Thus we find out the physical conditions under which CAR processes are enhanced, or local Andreev processes are reduced. So, we observe the processes allowed in the model in the limit tunnel. A more detailed model must be constructed in order to take into account all contributions at arbitrary order of perturbation. Likewise, for a more realistic description, the inclusion of factors such as Coulomb blockade, magnetic fieds, and so on, we have to construct a full model within the basis exposed above.

The problem addressed in this thesis can be expanded in many ways. For instance, the construction of nano-scaled transistors will require the electronic characterization of hybrid structures like a double quantum dot. The measurement of phase-currents in superconducting quantum interference devices using a two-level system, or the construction of multi-walled carbon nanotubes with considerable radius, and so on.
APPENDICE 1: DYSON EQUATION FOR A DOUBLE QUANTUM DOT

In order to compute transport coefficients for the double quantum dot, we have to find the Dyson equation for the superconducting central region perturbed by lateral electrodes. We assume that the interfaces are located at \(-W_S \leq x, x' \leq 0\) (L-interface) and \(0 \leq x, x' \leq W_R\) (R-interface), so the central region has width \(W_S\), while left and right regions have length of \(W_L\) and \(W_R\), respectively, as shown in Figure 4.1 (a). Unperturbed Green’s functions in the central (superconducting) region will be denoted by \(g_{SS}(x, x')\), even if the electrode is in normal state (as \(\Delta \to 0\)). Unperturbed GFs for lateral - normal state - electrodes will be denoted by \(g_{<,>_{L,R}}(x, x')\), and the retarded and advanced components will be, as before, labeled by a superscript \(r, a\) accordingly. The series coupling of these three regions will be represented by a double Dyson equation at each interface, so we need the local GFs evaluated at each edge. Local GF for the perturbed \(L\) region, by the remaining \(S\)-\(R\) system, is given by

\[
\hat{G}_{LL}(x, x') = \hat{g}_{LL}(x, x') + \hat{g}_{LL}(x, -W_S - 0^-)\hat{\tau}_L\hat{\Sigma}_L
\times \hat{G}_{SS}(-W_S + 0^+, -W_S + 0^-)\hat{\tau}_L\hat{g}_L(-W_C - 0^+, x')
\times \hat{\Sigma}_L' = \left(\hat{I} - \hat{G}_{SS}(-W_S + 0^+, -W_S + 0^-)\hat{\tau}_L\hat{g}_L(-W_S - 0^+, -W_S - 0^-)\hat{\tau}_L\right)^{-1},
\]

where

\[
\hat{G}_{SS}(-W_S + 0^+, -W_S + 0^-) = \hat{g}_{SS}(-W_S + 0^+, -W_S + 0^-) + g_{SS}(-W_S + 0^+, -0^-)\hat{\tau}_R
\times \hat{\Sigma}_L'\hat{g}_{SS}(-0^+, -W_S + 0^-)
\]

\[
\Sigma'_L = \left(\hat{I} - g_{RR}(0^+, 0^-)\hat{\tau}_R\hat{g}_{SS}(-0^+, -0^-)\hat{\tau}_R\right)^{-1}g_{RR}(0^+, 0^-)\hat{\tau}_R.
\]

and \(\tau_{L|R} = t_{L|R}\sigma_x, \sigma_x\) acting on the sublattice space. Note that the component \(\hat{g}_{SS}(-W_C + 0^+, 0^-)\) corresponds to the non-local component of the unperturbed GF from \(L\)- to \(R\)-
interface, and \( \hat{g}_{SS}(-0^+, -W_C + 0^-) \) corresponds to the non-local component from \( R \) to \( L \) interface in the superconducting region.

In a similar way, the perturbed GF for the \( R \) region by the remaining \( L - S \) system is given by

\[
\hat{G}_{RR}(x, x') = \hat{g}_{RR}(x, x') + \hat{g}_{RR}(x, 0^-)\hat{\tau}_R\hat{\Sigma}_R\hat{G}_{SS}(-0^+, -0^-)\tau_R\hat{g}_{RR}(0^+, x') \\
\hat{\Sigma}_R = (I - G_{SS}(-0^+, -0^-)\tau_R\hat{g}_{RR}(0^+, 0^-)\hat{\tau}_R)^{-1} \tag{6.3}
\]

where

\[
G_{SS}(-0^+, -0^-) = g_{SS}(-0^+, -0^-) + g_{SS}(-0^+, -W_S + 0^-)\hat{\tau}_L\hat{\Sigma}'_R \\
\times \hat{g}_{SS}(-W_S + 0^+, -0^-)\hat{\tau}_L\hat{g}_{LL}(-W_S - 0^+, -W_S - 0^-)\hat{\tau}_R \\
\hat{\Sigma}'_R = \left(\hat{I} - \hat{g}_{LL}(-W_S - 0^+, -W_S - 0^-)\hat{\tau}_L\hat{g}_{RR}(-W_C + 0^+, -W_C + 0^-)\hat{\tau}_L\right)^{-1}. \tag{6.4}
\]

Non-local GFs from \( L \) to \( R \) region is given by

\[
G_{LR}(x, x') = \hat{g}_{LL}(x, -W_C - 0^-)\hat{\tau}_L\hat{G}_{SS}(-W_C + 0^+, -0^-)\tau_R\hat{G}_{RR}(0^+, x') \tag{6.5}
\]

where \( x \) is in \( L \) region whilst \( x' \) belongs to \( R \) region. In this case, perturbed GF from the middle region \( \hat{G}_{SS}(x, x') \) is given by

\[
\hat{G}_{SS}(x, x') = g_{SS}(x, x') + g_{LL}(x, -W_C + 0^-)\hat{\tau}_L\hat{\Sigma}_{SL} \\
\times \hat{g}_{LL}(-W_C - 0^+, -W_C - 0^-)\hat{\tau}_L\hat{g}_{SS}(-W_C + 0^+, x') \\
\hat{\Sigma}_{SL} = \left(\hat{I} - \hat{g}_{LL}(-W_C - 0^+, -W_C - 0^-)\hat{\tau}_L\hat{g}_{SS}(-W_C + 0^+, -W_C + 0^-)\hat{\tau}_L\right)^{-1}, \tag{6.6}
\]

and perturbed GF for the \( R \) region is given by

\[
\hat{G}_{RR}(x, x') = \hat{g}_{RR}(x, x') + \hat{g}_{RR}(x, 0^-)\hat{\tau}_R\hat{\Sigma}_{RS}G_{SS}(-0^+, -0^-)\tau_R\hat{g}_{RR}(0^+, x') \\
\hat{\Sigma}_{RS} = \left(\hat{I} - \hat{G}_{SS}(-0^+, -0^-)\tau_R\hat{g}_{RR}(0^+, 0^-)\hat{\tau}_R\right)^{-1}. \tag{6.7}
\]

In a similar way, the non-local GF from \( R \) to \( L \) can be found. It is important to remark that the above derived functions correspond to the perturbed double quantum dot, but we want to couple that system to external leads. Hence, at left boundary \( x, x' = -W_L - W_C \)
the left electrode will be coupled and at right boundary \( x, x' = W_R \) the right electrode
will be coupled. When we consider the tunnel limit, low order contributions of the
coupling parameter, then the perturbed equation can be approximated as

\[ G_{LL} = (I - g_{LL} \Sigma g_{RR} \Sigma)^{-1} g_{LL}. \]
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