Electronic Transport in Single Wall Carbon Nanotubes

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Preface

The work presented in this thesis is obtained during three years of Ph.D. studies at the Nano-Science Center, Niels Bohr Institute, University of Copenhagen, Denmark, where I have been part of the experimental nanophysics group of professor Poul Erik Lindelof. The main interest and expertise of this group is mesoscopic electron transport at cryogenic temperature of low-dimensional systems. An excellent candidate for such a system is the single wall carbon nanotube (SWCNT), which has been under intense investigation by the scientific community for more than a decade. The studies of the electronic transport properties of SWCNTs are continued in this thesis, where new results as well as a review of existing relevant research will be presented. An outline of the thesis follows below with the highlights of each chapter.

Chapter 1 gives a basic introduction to SWCNTs and their fascinating electronic properties, where important length and energy scales are introduced. The band structure of SWCNTs due to quantization of the wave vector around its circumference is shortly reviewed. Furthermore, the size and charge quantization of small systems are introduced and special emphasis is given on the quantization of the lowest lying energy bands in finite (small) length SWCNT systems. Such analysis has to our knowledge not been rigourously presented before. Finite zigzag SWCNTs are shown always to have four-fold degenerate levels, while finite armchair SWCNTs are found to have either four-fold degeneracy or an orbital splitting (of 1/3 of level spacing). This is analogous to the quantization of the zigzag SWCNTs being either metallic or semiconducting, respectively. The above is only true for ideal atomically sharp boundary condition and does not take other effects into account, which might perturb this ideal picture.

In chapter 2 the fabrication and technical methods are explained. First the recipe for fabricating two terminal SWCNT devices is presented. Furthermore, the experimental techniques to cool and measure SWCNT devices at cryogenic temperature are described in detail.

A review on transport in SWCNTs with normal contacts is given in chapter 3 based on measurements of our own devices. It includes three transparency
regimes, identified by Coulomb blockade, Kondo effect and Fabry-Perot interference. Some effort is given to describe the transition from Fabry-Perot interference to Coulomb blockade in the same terminology.

Chapter 4 gives an introduction to superconductor-normal metal-superconductor junctions in the context of the normal metal being a SWCNT. It provides some idea of the phenomena to be presented in the following chapters.

Chapter 5 is the first of three experimental chapters on SWCNTs coupled to superconducting leads (S) starting with the poorest coupling to the leads. In this regime the S-SWCNT-S junctions are in the Coulomb blockade regime (closed quantum dot) in which tunnel-like behavior revealing the density of states of the superconductors is observed for lowest transparency. Improving the transparency leads to an observable sub-gap structure in terms of multiple Andreev reflections (MAR). The MARs are seen to have very strong dependence on the electron filling for a four-fold degenerate shell structure. Close to each Coulomb blockade resonance the MARs shift, but the shift is additionally pronounced for every fourth Coulomb blockade diamond. These data are only partly understood at the moment and the latter has to our knowledge not been presented elsewhere.

When the coupling to the leads is further improved the Kondo effect can be observed. Chapter 6 examines the interplay between a noise smeared supercurrent and Kondo effect/Coulomb blockade, where a zero bias conductance peak is interpreted as a noise smeared supercurrent.

In chapter 7 the S-SWCNT-S devices in the Fabry-Perot regime are analyzed (no charge quantization effects). As in the Kondo regime a zero bias peak is observed and the estimated value and behavior of the critical current are shown to be consistent with existing theory. Furthermore, an excess current is extracted and shows good agreement with theory for superconducting quantum point contacts. This chapter also ends the tour of S-SWCNT-S weak links in different transparency regimes.

Chapter 8 returns to closed SWCNT quantum dot devices with normal contacts, but in the context of quantum information. Focus is on measurements to extract the relaxation time between the excited and ground state in SWCNT quantum dot, which involve technically more demanding measurements with high frequency pulse signals. These measurements were done at NTT Basic Research Laboratories, Atsugi, Japan under supervision of Dr. Fujisawa on devices made in the laboratories at the Nano-Science center, Niels Bohr Institute, University of Copenhagen, Denmark. Unfortunately the quality of the fabricated SWCNT devices for this purpose was not high enough to obtain the desired result. However, the chapter presents the idea and details about the techniques used in pulse measurements of quantum
dots. A short introduction to another quantum information experiment involving electron spin resonance is given.

Finally a conclusion of the results presented above together with an outlook of the field is given in chapter 9.

The results shown in this thesis (most of chapter 3 and 5-7) have been obtained together with Ph.D. student Henrik Ingerslev Jørgensen.

Now with this outline of the thesis in mind we are ready to enter the fascinating world of mesoscopic electronic transport through carbon nanotube. Please enjoy!
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Chapter 1

Introduction

In the field of mesoscopic physics the wave nature of the electron and quantum effects become important. It lies between the macroscopic and the microscopic regime and started in the 1980ies with the discovery of conductance quantization, quantum Hall effect, weak localization, Aharonov-Bohm effect and universal conductance fluctuation [1, 2]. These effects were identified to belong to different regimes, where the relation between the following length scales determines the nature of the physics observed.

- $L$: Length of sample
- $l_m$: Mean free path
- $l_\phi$: Single electron phase coherence length

The mesoscopic regime requires that the electron can be considered as a wave which is true when the single electron phase coherence length is longer than the device $l_\phi > L$. This length is normally determined by inelastic scattering caused by phonon-electron or electron-electron interaction. On the contrary, the elastic scattering does not affect the phase of the electron wave, but only changes the momentum. If an electron travels through a device being elastically scattered, the device is in the phase coherent diffusive regime ($l_\phi > L \gg l_m$). On the other hand, when the mean free path is longer than the length of the device the transport is in the phase coherent ballistic limit ($l_\phi, l_m \gg L$). The mesoscopic effects above can be explained considering non-interacting electrons, but as we shall see in more detail below, interactions change the transport properties dramatically.

In small conducting regions (islands) defined in two-dimensional electron gases interaction between the electrons leads to so-called quantum dots or artificial atoms [3]. The electrons are here forced to tunnel only one by one
to and from the island due to interactions. The single wall carbon nanotube, a nanometer sized molecule, is in the mesoscopic regime at low temperature and it also behaves as a quantum dot [4, 5]. It is smaller than the relatively big structure defined in two-dimensional gases. Still, it is a much bigger molecule compared to the bottom-up approach where transport is investigated on molecules synthesized by chemists.

The physics of quantum dots becomes more complicated and fascinating, when superconductors are connected to the mesoscopic region, entering the field of mesoscopic superconductivity. Additional energy scales are needed to define and explain the effects which will be treated in chapters 4-7.
1.1 Carbon nanotubes

Carbon nanotubes (CNTs) were discovered by Iijima [6] in 1991\(^1\). Since then they have attracted tremendous interest due to their unique mechanical and electronic properties [8]. They can be either metals or semiconductors and are one-dimensional conductors (four channels). At low temperature they behave as phase coherent ballistic conductors (wave guides) [9] or single electron transistors [4, 5, 10] depending on the contacts as will be explained below.

The single wall carbon nanotube (SWCNT) [11, 12] is a hollow cylinder-shaped molecule with a diameter in the order of 1 nm. The best way to imagine the arrangement of the carbon atoms is to think of the SWCNT as a rolled up graphene sheet as sketched in Fig. 1.1. A graphene sheet is a honeycomb lattice with a carbon atom in each vertex (Fig. 1.1a).

\(^1\)Previously they might have been seen by Endo, but the impact on the physics society came after 1991 [7].

Figure 1.1: (a) A layer of graphite (graphene), where the carbon atoms are arranged in a honeycomb lattice. (b) The example of folding a (4,4) armchair single wall carbon nanotube (SWCNT) from the graphene sheet. \(C_h\) and \(T\) are the chiral and the translation vectors of the SWCNT, respectively, spanning the nanotube real space unit cell (colored rectangle). This unit cell differs from the graphene lattice unit cell spanned by the unit vectors \(a_1\) and \(a_2\). (c) A zigzag SWCNT. Note, it is different from the one sketched in (b).
A specific SWCNT is defined by two integers \((n,m)\) with \(n \geq m \geq 0\) related to the chiral vector \(\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2\), where \(\mathbf{a}_1\) and \(\mathbf{a}_2\) are the basis vectors of the graphene lattice. Figure 1.1b shows the chiral vector for a so-called \((4,4)\) armchair nanotube, where the SWCNT is made by joining the ends of the chiral vector, \(i.e.,\) dashed blue lines. Three categories of SWCNT are now defined: The armchair \((n,n)\), the zigzag \((n,0)\) and the chiral nanotube \((n,m)\) with \(n > m > 0\). The two former are named after the armchair- or zigzag-like pattern of the atoms around the tube circumference (see Fig. 1.1c and Fig. 1.2a,b). In case of a chiral nanotube the atomic arrangement seems to spiral looking along the axis direction as shown in Fig. 1.2c. Quite remarkably the electronic properties crucially depend on the exact folding of the graphene sheet. The SWCNT will either be metallic, a small band gap semiconductor or a large band gap semiconductor.

For completeness it should be mentioned that the CNTs do not only exist as SWCNT but also come in other species as ropes of SWCNT [13] or multiwall carbon nanotube (MWCNT). The rope has many SWCNTs \((\sim 100)\) arranged in a triangular lattice, while the MWCNT consists of concentric shells of SWCNTs. These two types of CNTs are not the subject of this
The dispersion relation of graphene. All the states in the lower tent-shaped part (valence band) are filled due to two atoms in unit cell, each contributing with one electron. The Fermi energy is thus in the plane of the blue hexagon. The conduction and the valence band only touch in 6 points marked by red dots at the corners of the 1st Brillouin zone (light blue hexagon). Only two points are linearly independent called the K and K' point, i.e., K and K' cannot be reached by a reciprocal lattice vector of the graphene sheet. Note, that this makes graphene semi-metallic.

thesis, which is on SWCNTs, even though some of the physics introduced here can be found in ropes and MWCNTs as well. It is not easy to distinguish two SWCNT in a small rope from a SWCNT by topographic measurements, but when the transport characteristics resemble those for one SWCNT, we assume that only one SWCNT is dominating the transport.

The electronic structure of a SWCNT is deduced from the energy dispersion of graphene shown in Fig. 1.3. The 1st Brillouin zone is marked by the light blue hexagon. Graphene has the peculiar property that the conduction and the valence band only touch each other in six points at the Fermi energy marked by red dots. Such behavior makes graphene a so-called semi-metal. Only two of these points are linearly independent with respect to a reciprocal lattice vector and will be named K and K'.

The band structure of the SWCNT is found by imposing periodic boundary conditions around the circumference of the tube, i.e., the wave function has to be single valued (only the plane wave part of the Bloch wave function written here) \( e^{i\mathbf{k} \cdot \mathbf{r}} = e^{i\mathbf{k} \cdot (\mathbf{r} + \mathbf{C}_h)} \), where \( \mathbf{k} \) is a wave vector and \( \mathbf{r} \) is a real space lattice vector of the graphene lattice. This leads to periodic boundary condition in momentum space

\[
\mathbf{k} \cdot \mathbf{C}_h = 2\pi p \tag{1.1}
\]
where \( p \) is an integer. In other words, the \( k \)-vector projected onto the chiral vector \( k_{\perp} \) (along the circumference) becomes quantized, while the \( k \)-vector \( k_{\parallel} \) along the tube axis is continuous for an infinite nanotube. The 1D dispersion or band structure of a SWCNT is thus made of the energy bands related to different quantized values \( p \) as a function of \( k_{\parallel} \). Whether or not these quantization lines cross a \( K \)-point makes the SWCNT a metal or a semiconductor. Based on the electrical properties of SWCNTs three groups can be defined, however, a little different than above.

The first group contains the armchair SWCNTs. These nanotubes are truly metallic and have two bands crossing at the Fermi level. Figure 1.4a shows the band structure for a (5,5) armchair nanotube\(^2\). First note that two bands are crossing the Fermi level (or the valence and conduction band touch at the Fermi level) making it a metal. The bands stem from the quantization lines drawn in Fig. 1.4c in the reciprocal lattice. The corners of the hexagons are the \( K \)-points, where the conduction and the valence band of the graphene dispersion touch. One of the quantization lines (thick purple dashed line) passes through two \( K \)-points making the tube metallic. Note, that the degeneracy of all bands is double, except the top conduction band, the bottom valence band (black dashed quantization line) and the two bands crossing the Fermi energy (purple quantization line).

Figure 1.4b shows the band structure for a (9,0) zigzag tube which is metallic judging from the (degenerate) band crossing the Fermi level. The bands stem from the quantization lines drawn in Fig. 1.4d. It is seen that the bands touching at the Fermi level are two times degenerate (blue thick dashed lines). However, the band structure is calculated from the dispersion of a sheet of graphene, while the nanotube has a curvature around the circumference of the tube. The curvature slightly modifies the band structure by moving the \( K \)-points [14].

In the armchair case the SWCNTs are still metallic because the shift of the \( K \)-points happens along the quantization lines. Figure 1.4e (left) shows the new positions of the \( K \)-points by red dots. This is not the case for the metallic zigzag nanotube. The shift of the \( K \)-points is not along quantization lines and thus turns the metallic zigzag nanotube into a small band gap semiconducting nanotube. Note, that the \( K \)-points are located at different sides of their respective quantization line in Fig. 1.4 (right). The two lowest lying subbands are still degenerate, but the slope of the dispersion on the two quantization lines with respect to the perpendicular \( k \)-vector \( k_{\perp} \) has opposite sign. Similar transitions to a small band gap semiconductor happens for

\(^2\)This small diameter SWCNT was taken to limit the number of bands for clarity. A (10,10) armchair nanotube is more likely to be found having a diameter of 1.4 nm.
1.1. CARBON NANOTUBES

Figure 1.4: (a) The band structure of a (5,5) armchair nanotube. The purple bands crossing the Fermi energy stem from the quantization line in (c), which crosses the K-points and makes this SWCNT metallic. (b) The band structure of a (9,0) zigzag nanotube. It has a doubly degenerate band crossing the Fermi level stemming from the two blue thick dashed lines in (d). (c) The dashed quantization lines in reciprocal space of a (5,5) SWCNT showing that one line crosses the K-points. The colors are related to the bands in (a). (d) Similar figure for a (9,0) zigzag tube. (e) When the curvature effects are taken into account the K-points move from the corners of the hexagon to the red dots. Armchair nanotubes thus stay metallic (left), while metallic zigzag nanotubes become small band gap semiconductors (right). (f) Some tubes are semiconducting with a bigger band gap as the (8,0) zigzag tube.
other metallic zigzag tubes and chiral metallic tubes for which $n - m \cong 0$ mod 3. The effect is the strongest for small diameter tubes due to their bigger curvature. The gap will be in the order of tens of meV.

The last category of tubes is the semiconducting as seen in Fig. 1.4f, which shows a (8,0) zigzag SWCNT. In the reciprocal space the quantization lines do not cross the K-points (not shown). It has a band gap in the order of $\sim 1$ eV and no available state at the Fermi level. Curvature effect also modifies the band gap obtained by quantization of the graphene sheet, but at a much smaller energy scale.

In conclusion, the armchair SWCNTs are a group of truly metallic conductors with two bands crossing the Fermi level. The initially metallic zigzag and chiral SWCNTs ($n - m \cong 0 \text{ (mod 3)}$) without curvature effects turn into small band gap semiconductors, when curvature effects are included. Typical band gaps are in the order of tens of meV. Finally, a group of zigzag and chiral SWCNTs is semiconducting ($n - m \neq 0 \text{ (mod 3)}$) with bigger band gaps. The band gap of these tubes are in the order of $\sim 1$ eV and scales as $E_{\text{gap}} \sim 1/d$, where $d$ is the diameter of the SWCNT [8].

This truly amazing band structure is observed in transport measurements, where some SWCNTs behave as metals defined by not being able to deplete the structure. Others have a region with no conduction due to a big band gap. Finally a group of SWCNTs with small band gap, where transport through both the valence or the conductance band can be achieved.

Normally SWCNT are slightly p-type due to the environment, so the Fermi level is slightly shifted into the valence band.
1.2 Magnetic field dependence of the band structure

A magnetic field along the axis of the SWCNT also modifies the band structure. One way to see this is to add an Aharonov-Bohm flux term to the quantization condition, so it now reads \[ k \cdot C_h + \frac{e}{\hbar} \Phi = 2\pi p \] (1.2)

where \( \Phi \) is the flux through a cross-section of the nanotube. The magnetic field basically shifts the quantization lines perpendicular to their direction \((k_\perp)\). Because of the small diameter of the nanotubes the period to shift one quantization line to the next \((p \rightarrow p + 1)\) by the field is several thousands Tesla! However, effects due to the modification (small shifts) of the band structure with common laboratory accessible fields as \( B < 10 \text{ T} \) can easily be observed in low temperature experiments [17, 18].

A metallic armchair SWCNT can thus be made semiconducting by applying a magnetic field. For semiconducting SWCNT, the two lowest subbands are shifted in opposite directions by the field. The quantization lines corresponding to these two bands lie at different sides of the K and K’-point as shown in Fig. 1.4e (right) for a small band gap semiconductor. At zero field the distance from the quantization lines (for lowest lying bands) to the K(K’) point is identical thus making the bands degenerate. When applying a field the quantization lines shift perpendicular to their direction, which makes one quantization line move closer to the K-point while the other moves away from the K’-point. This splits the degeneracy of the two bands.

A semiclassical explanation for this effect is that a semiconducting nanotube has a magnetic moment due to the electrons orbiting around it in a helical manner. The velocity \( v_\perp \) of the electron in a state \( k_\parallel \) around the circumference is given by the slope of the (graphene) dispersion perpendicular to the quantization line. For the two bands (closest to the Fermi energy) of a semiconducting SWCNT the velocity around the circumference \( v_\perp \) has different sign, i.e., clockwise and counter clockwise motion. These helically orbiting electrons thus have oppositely oriented magnetic moments and one gains energy in the magnetic field while the other ”loses” energy. It should be emphasized that the magnetic field has to be along the tube axis. A magnetic field perpendicular to the tube axis only creates a Zeeman splitting due to the spin, i.e., no orbital effects.

Similarly, the band structure is modified by stretching the SWCNT [16], but it will not be treated here.
1.3 Conductance quantization

One of the fundamental discoveries of mesoscopic physics is the breakdown of Ohm’s law, when transport becomes ballistic \((l_m > L)\). According to Ohm’s law, the conductance \(G = \sigma A/L\) of a conductor goes to infinity as the distance between the leads becomes shorter, where \(\sigma\) is the conductivity, \(A\) the cross-section and \(L\) the length of the conductor. At some length scale \(l_m\) of the conductor, no scattering takes place in the device and the conductor becomes ballistic. However, the conductance still remains finite (in contrast to Ohm’s law) given by an integer times the quantum of conductance \(e^2/h\), where the integer is the number of one-dimensional (1D) channels inside the conductor. The related resistance of the 1D channel is the so-called contact or quantum resistance\(^3\). At low temperature, SWCNTs behave as (phase coherent) ballistic systems [19, 9]. The quantization of conductance can easily be derived and applied to SWCNTs as follows.

Figure 1.5a shows the energy diagram for a 1D ballistic conductor contacted by two contacts. Assuming \(T = 0\) K for simplicity the states in the left and the right contact are occupied up to the chemical potentials \(\mu_L\) and \(\mu_R\), respectively, shifted by the applied bias \(eV_{sd} = \mu_L - \mu_R\). Below \(\mu_R\), the current contribution from the electrons originating from the left contact traveling towards the right (right-movers) and the electrons from the right contact traveling to the left (left-movers) cancel, assuming no reflections at the contact (i.e., reflectionless contacts). On the contrary, in the bias window \(\mu_L > E > \mu_R\) only right-movers are present and give the following current contribution.

\[
I = e \int_{\mu_R}^{\mu_L} v(E) \left[ \frac{1}{2} d_{1D}(E) \right] dE \tag{1.3}
\]

where \(v(E)\) is the velocity of the electrons, \(d_{1D}(E)\) is the density of state (DOS) per energy and unit length in 1D including spin and the factor of \(\frac{1}{2}\) originates from the fact that only right-movers are present in the bias window. The DOS can be found from the number of states per unit length

\[ n = 2 \times \frac{1}{2\pi} \times 2k \text{ in } 1D \text{ within a wave vector } |k| \]

as \(d_{1D}(E) = dn/dE = \frac{2}{\pi} dk/dE = 2/|\pi \hbar v(E)|\), where \(v(E) = \frac{1}{k} dE/dk\) is the group velocity. The current thus becomes

\[
I = e \int_{\mu_R}^{\mu_L} v(E) \frac{1}{2} \frac{2}{\pi \hbar v(E)} dE = \frac{2e}{\hbar} (eV_{sd}) \tag{1.4}
\]

\(^3\)The contact resistance is the resistance of the device with perfect transmission. It bears the name because the resistance of the ballistic part is zero and the resistance is in the interface between the ballistic region and the contacts.

\(^4\)The factors are as follows \((n = \text{spin } \times \text{DOS in k-space per unit length } \times \text{"area" within vector } |k|)\).
1.3. CONDUCTANCE QUANTIZATION

Figure 1.5: (a) Diagram for derivation of quantized conductance in a ballistic one-dimensional channel. In the bias window only right moving electrons contribute to the current, while the current contributions from right and left-movers cancel below $\mu_R$. For perfect (reflectionless) contacts the conductance is given by $G_0 = 2e^2/h$ for one spin-degenerate 1D channel. (b) Dispersion of a semiconducting band structure with the chemical potentials in the conduction bands. The thick lines indicate the occupied $k$-states, where the bias causes a shift of the occupation to a configuration with more occupied right moving states than left moving states. For a metallic band structure a similar shift happens.

Finally the conductance $G = I/V_{sd}$ of a one-dimensional spin-degenerate channel can be found as

$$G_0 = \frac{2e^2}{h} \quad (1.5)$$

This result is quite remarkable and thus gives an upper limit to the conductance of a 1D channel, illustrating the breakdown of Ohm’s law.

Figure 1.5b shows the dispersion of a semiconducting band structure related to Fig. 1.5a. The bias applied across the device shifts the occupation of the states to a non-equilibrium situation with more right-movers ($dE/dk_|| > 0$) than left-movers ($dE/dk_|| < 0$). The Fermi level is chosen to be in the conduction band in equilibrium. A 1D band crossing the Fermi level having a right and a left moving branch as shown in the Fig. 1.5b is called a 1D channel or mode. Each 1D spin-degenerate channel gives a maximum contribution of $G_0$ to the conductance. For a zigzag SWCNT the band is orbitally double degenerate and the maximum conductance is thus $G = 2G_0 = \frac{4e^2}{h}$.

The band structure of a metallic armchair SWCNT is shown in Fig. 1.6. Also in this case two spin-degenerate bands (blue and red) are crossing the
Figure 1.6: The dispersion of a metallic armchair nanotube which can be viewed as two spin-degenerate bands (red and blue) crossing the Fermi level (here at higher energy than equilibrium for clarity). An applied bias shifts the distribution of the carriers and thus gives a maximum conductance of $G = 4e^2/h$ for a metallic nanotube (see text). Thick lines correspond to occupied states. The same conductance is found if the band structure is viewed as a conduction and a valence band touching in two points. Even though only the conduction band crosses the Fermi level, an applied bias shifts the carrier distribution in the band identically. Thus the same two sets of a right moving and a left moving branches as shown exist, i.e., two spin-degenerate one-dimensional channel. The dispersion of a metallic tube is approximately linear at the crossings and often only this part is shown. Here the whole band structure is included to address the point above.

Fermi level. In contrary to the semiconducting tubes, these bands are only spin-degenerate (no double orbital-degeneracy as in zigzag tubes) and the maximum conductance is likewise $G = 2G_0$. The armchair dispersion can also be viewed as the conduction and valence band touching in two points at the Fermi energy. In this case only one band, namely, the conduction band is crossing the Fermi level. However, it crosses twice the number compared to the blue/red band giving the same number of right and left moving branches, i.e., two spin-degenerate channels!

For all types of nanotubes (metallic or semiconducting), two 1D channels exist at the Fermi level. A SWCNT thus has a maximum conductance of $G = 4e^2/h$. In case of a semiconducting tube it is assumed that the Fermi level is either in the conductance or the valence band.

This ideal maximum value of conductance has been confirmed in experiments in many laboratories (see chapter 3), where the conductance reaches close to $G = 4e^2/h$ [9]. Furthermore, quantization of conductance by tuning
further subbands into the bias window have been investigated with anomalous results [20].

In the case of non-perfect contacts, where the transmission related to the i’th subband is $T_i$, the conductance is given by the Landauer formula [1].

$$G = \frac{2e^2}{h} \sum_i T_i$$

(1.6)

where the sum runs over all 1D subbands crossing the Fermi level.
1.4 Quantum effects in finite single wall carbon nanotube systems

Before presenting results of measurements on SWCNTs, two quantum effects that will dominate all transport measurements shown in this thesis will be introduced. The first effect is due to the wave nature of the electron and thus phase coherence \( l_\phi > L \), while the second comes from the finite size of the electronic charge \( e \). Both effects require small systems to be observed and scale as \( 1/L \) as will be shown below.

The active region of a two terminal SWCNT device is defined by the two contacts separated by a distance of typically less than a micron. The device can be engineered to probe three transparency regimes defined by the coupling between the contact and the SWCNT. For all three regimes, Coulomb blockade, Kondo and Fabry-Perot regime\(^5\), the SWCNT is phase coherent, which gives rise to a quantum effect known as size quantization.

Instead of having a continuum of states inside the SWCNT, the continuum becomes quantized in discrete levels separated by \( \Delta E \), the well known particle in a box problem \([21]\). The underlying assumption for size quantization to happen is that the electron can travel phase coherently in the region \([22]\). The importance of phase coherence is clearly revealed considering that part of an electron wave in the SWCNT is reflected at the interfaces and will interfere with itself. This sets up resonances (also called bound states or levels). The condition for resonance is that the wave length times an integer is equal to twice the length of the device. Bound states are thus due to the wave nature of the electron. A system where transport takes place through discrete energy levels is called a resonant tunneling junction.

Size quantization happens for all transparencies of the device and as the device becomes shorter the levels become more separated. The width of the levels is given by the openness of the contacts defined by the lifetime broadening \( \Gamma = \Gamma_1 + \Gamma_2 \) related to the transmission of each barrier by \( \Gamma_i = \hbar \nu T_i, \ i = 1, 2 \). Here \( \nu = v/(2L) \) is the attempt frequency which tells how often the electrons with group velocity \( v = dE/d(\hbar k) \) tries to escape the device of length \( L \). Throughout this thesis we express the lifetime broadening of a level \( \Gamma \) as an energy except in chapter 8, where it is more convenient to be expressed as a frequency.

Figure 1.7 shows the band structure for a semiconducting SWCNT with the energy gap symmetric at \( k_{||} = 0 \). The finite length of the device leads to quantization of the longitudinal wave vector \( k_{||} = (\pi/L)n \), where \( n = \)

\(^5\)These regimes are equivalent to the closed quantum dot, Kondo and open quantum dot regime.
1.4. QUANTUM EFFECTS IN FINITE SWCNT SYSTEMS

The finite length of the SWCNT leads to quantization of the wave vector $k_{||}$ along the tube axis by $k_n = (\pi/L)n$, $n = 1, 2, 3, ...$. The traveling waves related to the states $\pm k_n$ (opposite directions) set up a standing wave with energy $E_n$. Each level is ideally four times degenerate due to spin and orbital degrees of freedom. Note, that the level spacing for a semiconducting SWCNT is not constant versus energy due to the non-linear dispersion.

The traveling waves from the states $\pm k_n$ (group velocity in different direction) set up a standing wave having energy $E_n$. The discrete wave vectors and the corresponding energies are shown for both the conduction and the valence band. In the shown case of a zigzag SWCNT, the band structure has two degenerate subbands/orbitals indicated by the blue and red bands. The energy levels thus consist of two spin-degenerate orbitals giving a four-fold degeneracy of each level/shell. Often the two orbitals (red and blue lines) are drawn beside each other as indicated in Fig. 1.7 to take into account an orbital splitting (see below). The black oval illustrates that a total of four states is available in each level/shell, two in each orbital (red and blue line). The maximum conductance through the level exactly at resonance (and equal coupling to the leads) is $G = 4e^2/h$. The equal spacing between the allowed $k_{||}$-vectors and the non-linear dispersion give an increasing spacing between the energy levels as seen in Fig. 1.7.

Figure 1.8 shows the longitudinal quantization for a metallic armchair.

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6The wave vectors for $n$ negative do not give new linearly independent states, while the wave function for $n = 0$ is 0, i.e., no state.
Figure 1.8: Size quantization for a metallic nanotube (armchair). The dispersion for the band crossing at the Fermi level at positive wave numbers is shown. The wave number $k_{||}$ along the tube axis is quantized by $k_n = (\pi/L)n$, $n = 1, 2, 3, ...$ The traveling waves related to the states $\pm k_n$ (opposite directions) set up a standing wave with energy $E_n$. A set of energy levels separated by $\Delta E$ from each band/orbital (red/blue) is formed. The two sets can be degenerate or orbitally split, which seems to depend on the length of the device through the above quantization condition. Here $\delta = \Delta E/3$.

SWCNT [23]. The two band crossings at the Fermi energy at finite $k_{||}$ are symmetric around $k_{||} = 0$ (not shown, see Fig. 1.6) and approximately linear at the crossing. Each band is only spin-degenerate (no orbital degeneracy) in contrast to the zigzag semiconducting tube above. The wave vector is quantized and the travelling waves related to $\pm k_n$ set up corresponding bound states. Thus we only need to focus on one of the metallic crossings as shown in Fig. 1.8.

The quantized energies originating from the same band are separated by the level spacing $\Delta E$ (blue or red levels). This is seen more easily from the plot on the right side of the figure, where the quantized energy levels from each band are shown. The distance between two blue levels is thus marked by $\Delta E$. However, the red set of levels might be shifted relative to the blue set of levels by an orbital splitting $\delta$ depending on the exact position of the allowed $k_{||}$-vectors $k_n$ and $k_{n+1}$ relative to the band crossing. The levels/shell would be four-fold degenerate, if the band crossing is in the middle of two allowed k-vector or coincide with one. For the example shown in Fig. 1.8 this is not the case. Here the band crossing is situated in ratio 1:2 between $k_n$ and $k_{n+1}$. This problem will be treated in more detail below.
Let us first try to estimate the level spacing for a metallic SWCNT. The linear dispersion near the Fermi level is given by
\[ E(k_\parallel) = \pm \hbar v_F k_\parallel, \]
where \( v_F \) is the Fermi velocity in graphene. Size quantization as explained above leads to bound states and quantization of the wave vector \( k_n = (\pi/L)n \), where \( n \) is a positive integer. The level spacing for a metallic tube is given by
\[ \Delta E = D_{1D}(E)^{-1} = \frac{dE}{dN} = \hbar v_F \frac{dk}{dN} = \frac{\hbar v_F \pi}{L} \]  
where \( D_{1D}(E) \) is the DOS (per energy) in 1D and \( N = L/\pi \times k \) is the number of states in \( k \)-space of a 1D box (with hard wall boundary conditions). We have also used the linear dispersion relation for a metallic SWCNT. No spin and orbital degeneracy are assumed in the calculation. If the degeneracies are included, the level spacing is still the same, however, each level can be filled with four electrons. Often the orbital degeneracy will be lifted and for \( \delta = \Delta E/2 \) the average level spacing is half of the above \( \Delta E = \frac{\hbar v_F \pi}{2L} \) [24]. For zigzag nanotubes the levels are ideally four-fold obtained from the quantization of the band structure (Fig. 1.7), but the question is whether this is also true for armchair SWCNT. For four-fold degeneracy the allowed \( k_\parallel \)-vectors should appear symmetrically around the crossing. From the quantization condition it does not seem to be the case, since the allowed wave vector scales with the length. That implies that the orbital splitting is length dependent.

The following part thus describes quantization of armchair nanotubes and is thought as a discussion, since there might be flaws in the arguments. However, a thorough treatment of finite length SWCNTs have to our knowledge not been presented elsewhere. The reader is thus encouraged not to follow the line of thought blindly but question every step.

It should be mentioned that an orbital splitting might be due to scattering or imperfect interfaces leading to coupling of the orbitals and level repulsion [22]. Furthermore, different gate coupling to the orbitals also lead to orbital splitting [25].

We want to make the most simple analysis. The armchair SWCNT is assumed to be perfect and the boundary condition atomically sharp. Furthermore, it is assumed that the length of the nanotube is compatible with the periodicity of the SWCNT, \( L = wT \), where \( T \) is the length of the translation vector (see Fig. 1.1b) and \( w \) is a (positive) longitudinal quantization integer. A finite SWCNT is thus defined by three integers
\[ (n, m, w), \quad n, w > 0, \quad m \geq 0 \]  
where \((n, m)\) are given by the usual definition of a SWCNT.
First we consider very small SWCNTs with respect to circumference and length to simplify the number of quantization lines due to periodic and hard wall boundary conditions. We furthermore ignore effects due to curvature.

Figure 1.9 shows the quantization lines in k-space and the resulting band structure for three different lengths of the \((4, 4, w)\) armchair SWCNT. In Fig. 1.9a the first Brillouin zone in the extended zone scheme (marked by a green box) of a \((4, 4, 7)\) SWCNT is shown similar to Fig. 1.4c. The eight dashed horizontal lines are the quantization lines due to periodic boundary condition around the circumference of the nanotube. The number of lines stems from the number of primitive graphene unit cells (here 8) in the real space nanotube unit cell (see Fig. 1.1b) and gives a total of \(N_{1D} = 2 \times 8 = 16\) bands due to two atoms per graphene unit cell. The finite length of the SWCNT gives rise to hard wall boundary condition and quantization of the wave vector \(k_{||}\) along the nanotube axis. The allowed wave vectors are indicated by the vertical blue lines spaced by \(\Delta k_{||} = \pi/L = \pi/(wa)\), where \(w = 7\) in the first example shown (Fig. 1.9a-b). Note, that the direction of quantization along the axis of an armchair SWCNT is actually very similar to making a zigzag tube, \(i.e., (w,0)!\)

Two important points should however be kept in mind. The hard wall quantization lines are spaced closer than in the case of periodic boundary condition (\(\pi/L\) versus \(2\pi/L\), respectively) and the number of quantization lines are given by \(w\), the number of unit cells along the tube axis. The latter can also be seen from the number of zero-dimensional states (levels) available for a \((4, 4, 7)\) SWCNT. The number of graphene unit cells according to the above is \(N_{0D} = 2 \times 8 \times 7 = 112\) (seven \((4, 4)\) armchair units cells with \(2 \times 8\) bands), which has to correspond to the number of levels obtained from the crossings in the grid defined by the dashed and blue lines. Since each crossing point \((k_{||}, k_{\perp})\) has two energies due to the dispersion of graphene, we get \(N_{0D} = 8 \times 7 \times 2 = 112\).

Figure 1.9b shows the corresponding dispersion of the \((4, 4)\) armchair nanotube with the allowed longitudinal wave vectors \(k_{||}\) given by the blue vertical lines. The crossing between a blue line and a band gives rise to a level. The important point to notice is the position of the two quantization lines closest to the crossing at the Fermi energy of the armchair bands (in the red circle). This crossing is exactly spaced in such a way, that the quantization line is \(\frac{2}{3}\Delta k_{||}\) and \(\frac{1}{3}\Delta k_{||}\) away from the crossing for the closest left and right quantization line, respectively. This is also seen in the extended zone-scheme in Fig. 1.9a relative to the relevant K-point.

\(^7\)If this is unclear look at Fig. 1.4c and 1.4d, where the direction along the axis \(k_{||}\) of the armchair tube (a) is equivalent to the quantized direction \(k_{\perp}\) for a zigzag (c) with respect to the graphene dispersion. Thus making a finite armchair tube is in some sense analog to folding a zigzag tube.
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Figure 1.9: The effect of finite length on a (4,4) armchair nanotube with length \( w = 7 \) (a-b), 8 (c-d) and 9 (e-f) nanotube units cells. (a, c, e) show the quantization lines in k-space due to periodic (horizontal dashed lines) and hard wall boundary (vertical blue lines) conditions. The crossings between these lines give 0D levels. (b, d, e) The dispersion of the nanotube with the quantization lines (blue) due to the finite length shown. The thick green line marks the first Brillouin zone. For a length \( w \) dividable by 3 an allowed \( k_{||} \) vector coincides with the band crossing at the Fermi energy (f), while this is not the case for a length not dividable by 3 (b, d). Here \( a \) is the length of the real space graphene lattice vectors and \( |\gamma_0| \sim 3 \epsilon \text{V} \).
In Fig. 1.9c-d the same is shown for the (4,4,8) SWCNT. The longer length of the tube gives rise to one more quantization line. In the dispersion it is seen that the armchair band crossing at the Fermi energy is again between two quantization lines. However, the distance to the left and the right quantization line is switched, \( \frac{1}{3} \Delta k_{||} \) to the left and \( \frac{2}{3} \Delta k_{||} \) to the right.

Fig. 1.9e-f shows the quantization for a (4,4,9) SWCNT. In contrary to the above cases, a quantization line traverses exactly at the armchair band crossing at the Fermi energy. In other words, two quantization lines, one around the circumference and one along the length both cross the same K-point (see Fig. 1.9e).

This is actually not surprising, since the longitudinal quantization "corresponds" to making a zigzag nanotube. It is well established that every third zigzag tube ideally is metallic due to the quantization lines crossing the K-points. Thus every third finite armchair SWCNT \((n,n,w)\) will have a quantization line ("metallic") traversing the band crossing, while for the other 2/3 of the nanotubes the quantization lines are spaced in the ratio 2:1 or 1:2 around the band crossing at the Fermi energy ("semiconducting").

We now turn to a more realistic case of a \( L \sim 300 \text{ nm} \) long armchair SWCNT and deduce the consequences in terms of degeneracy of the levels. Figure 1.10a-c show three nanotubes \((10,10,1219), (10,10,1220)\) and \((10,10,1221)\) around the band crossing (zoom) at the Fermi energy, where the dispersion is linear. The length of the three armchair SWCNTs are 299.81 nm, 300.06 nm and 300.31 nm, respectively. Here \( L = wa = w \sqrt{3} a_{C-C} \), where \( a_{C-C} = 1.42 \text{ Å} \) is the interatomic distance in graphene. The choice is analogous to the three examples shown in Fig. 1.9 except for the many quantization lines (~1200). It is thus not surprising that exactly the same behavior is seen, \( i.e. \), the two first (a-b) have "semiconducting" behavior, while the third (c) has "metallic" behavior.

We now define the level spacing \( \Delta E \) as the distance between the levels in one band and the orbital splitting as the offset (shortest distance) between the two sets of levels stemming from the two bands as in Fig. 1.8. Thus in the case of \( w \) being dividable by three \((w \equiv 0 \mod 3)\) the orbital splitting will be zero due to the symmetric arrangement around the band crossing. Two levels, one from each band, have the same energy and give the four-fold degeneracy counting spin. In the two other cases of \( w \) not dividable by three the orbital splitting \( \delta \) is related to the level spacing by \( \delta = \Delta E/3 \) due to the linear dispersion and the definition of the orbital splitting as the smallest difference between the set of levels. The two cases correspond to the "zigzag quantization" being "metallic" or "semiconducting", respectively, as pointed out above.

The effect of curvature changes the above result, because the band crossing
Figure 1.10: The band structure around the band crossing at the Fermi level in the more realistic case of a ~ 300 nm long (10,10) armchair SWCNT. The blue lines spaced by $\Delta k_|| = \pi/L$ are the allowed wave vector due to the finite length of the nanotube. The length of the SWCNT is 1219 (a), 1220 (b) and 1221 (c) (10,10) nanotube unit cells. The quantization lines only intersect the band crossing, when the length (measured in unit cells) is dividable with 3 (c). Otherwise the band crossing is positioned asymmetrically between the quantization lines in relation 2:1 (a) and 1:2 (b).

at the Fermi energy (K-points) for an armchair SWCNT move outwards as sketched in Fig. 1.4e (left). In the dispersion this corresponds to a shift to bigger $|k_||$. The curvature effect increases as the diameter of the tube gets smaller, but whether the thereby introduced shift of the band crossing is dominant or just a small correction, we have not had time to examine. In the case of the curvature effects dominating, the orbital splitting is determined by this effect (and maybe additional effects). If it is a small shift $\Delta q$ compared to the distance between the longitudinal quantization lines $\Delta q \ll \Delta k$, the orbital splitting will increase and decrease for the two semiconducting cases $w \equiv 1 \mod 3$ and $w \equiv 2 \mod 3$, respectively. Thus a spread around $\delta = \Delta E/3 \pm \delta_{\text{curv}}$ depending on the effect $\delta_{\text{curv}}$ due to curvature is expected. In the
last case \( w \simeq 0 \pmod{3} \) ("metallic") a small orbital splitting is introduced.

These results are now compared to experiments on metallic SWCNTs (armchair) with an orbital splitting by Sapmaz et al. [23] and Liang et al. [26]. The experiments quite surprisingly show a good agreement with this very simple model. The orbital splitting is \( \delta \sim \Delta E/3 \) for several devices [23].

<table>
<thead>
<tr>
<th>Device</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (nm)</td>
<td>1.1</td>
<td>1.3</td>
<td>2.7</td>
</tr>
<tr>
<td>( \Delta E ) (meV)</td>
<td>9.0</td>
<td>3.0</td>
<td>8.7</td>
</tr>
<tr>
<td>( \delta ) (meV)</td>
<td>3.2</td>
<td>1.2</td>
<td>2.9</td>
</tr>
</tbody>
</table>

The discrepancy is biggest for smaller diameter tubes, which might be due to the curvature effect becoming important. For the other experiment the ratio is a little lower [26] \( \sim 0.23 - 0.35 \). No data are shown with orbital splitting zero, but these were probably not the scope of the articles and thus not included. In both articles additional parameters are extracted according to the Oreg model [25].

If this hard wall boundary condition is the explanation of these data it implies that the contact is atomically sharp and properly defined at the end of the electrode. The zigzag and the armchair nanotube real space unit cell are just a few atomic layers and thus the length is likely to consist of an integer number of the nanotube unit cells in contrast to chiral tube (see below). Whether the atomically sharp interfaces are consistent with the conclusion drawn from measurements on orbital Kondo in SWCNTs [27], where the electrons are supposed to enter the SWCNT below the contact to acquire the orbital quantum number of the SWCNT necessary for the creation of the orbital Kondo state, is not clear. However, it should be emphasized, that many other effects give rise to orbital splitting [25] and that the atomically sharp boundary condition might be unrealistic.

In our measurement we observe very clear four-fold degeneracy for small band gap semiconducting tubes at high positive voltage (see chapter 3), while no regular shell structure is seen closer to the band gap. This might also be consistent with a semiconducting dispersion symmetric around \( k_{||} = 0 \) \( (i.e. \) always four-fold) and that enough electrons on the quantum dot (high positive voltage) are needed to screen out other effects.

The above analysis has to the best of our knowledge not been presented elsewhere and further discussion to confirm the validity of the arguments is needed.

Before closing the discussion a comment on periodic versus hard wall boundary conditions will be given. Consider now a finite nanotube, but by making a torus instead of a segment (no curvature effects included). This
1.4. QUANTUM EFFECTS IN FINITE SWCNT SYSTEMS

would lead to periodic boundary condition along the tube axis as well. The four-fold degeneracy of the levels is in this case obtained both for zigzag and armchair tubes bent into a torus. This is seen from similar quantization diagrams (not shown) as the ones presented above. The same number of quantization lines are needed, but the distance between the lines is now $2\pi/L$. Thus they exceed the 1st Brillouin zone of the armchair tube and in the extended zone scheme (not shown) it is seen that they cross identically around another K-point, giving an additional spin-degenerate level from these crossings.

The above also makes intuitively sense, since it should not make a difference whether a zigzag nanotube is formed followed by an "armchair torus" by joining the ends or the other way around, i.e., periodic boundary conditions in both directions should lead to the same energy spectra independently of which is applied first. Both are subject to periodic boundary condition.

On the contrary making a zigzag nanotube finite is different from making an armchair nanotube finite due to hard wall boundary conditions, if the above analysis is correct.

Finally, the finite length quantization of chiral SWCNT devices is more complicated. The unit cells are more complex and the long translation vector makes it more realistic that the length of the SWCNT is not an integer times the translation period of the tube. The band structure of the chiral tubes furthermore have both zigzag behavior and armchair behavior. The former meaning that the band crossing/gap is centered around zero wave vector, but it might be non-degenerate band, e.g. (6,3) and the latter that the band crossings/gaps at the Fermi energy are at finite wave number $\pm k_{||}$, e.g. (7,4)). It could thus give many different values of the orbital splitting as is actually observed in experiments (also presented in this thesis). A similar analysis of chiral nanotubes to the one above will not be attempted in here.

We now turn to the quantum effect, which is related to the particle property of the electron. This effect will only be treated briefly and more thorough considerations are given in chapter 3. It introduces another energy scale called the charging energy $U_c = e^2/C$ due to electron interaction, which tells how much it costs to add one additional electron to the SWCNT. Here $C \sim L$ is the capacitance of the SWCNT [24] and the charging energy becomes $U_c \sim 1/L$ as was the case for the level spacing. Both effects are thus pronounced in small devices!

For poor contact to the SWCNT $G \ll e^2/h$ ($\Gamma \ll U_c$), the electron number on the SWCNT is well defined. Electron transport through the SWCNT consists of single electron tunneling and if it is not energetically favorable to add/extract an electron transport will be blocked. This is clearly revealed in measurements with $U_c$ as the important parameter.
Figure 1.11: Energy diagram including most of the energy scales introduced. A shell (or level if degenerate) consists of two orbitally split levels (red and blue level). The orbital splitting is $\delta$ and is shown for finite splitting. Each set of orbitals have a level spacing $\Delta E$. Furthermore, the lifetime broadening for each orbital is given $\Gamma$. For superconducting leads a gap in the DOS at the Fermi energy exists as shown.

For better contact to the SWCNT $e^2/h < G < 2e^2/h$ ($\Gamma \leq U_c$) more complicated phenomena due to cotunneling can be observed. Under certain conditions the Kondo effect is observed, which involves spin dependent cotunneling between the electrons in the leads and an electron on the SWCNT. Also this effect has a related energy scale given by the Kondo temperature $k_B T_K$. Finally when the device becomes very open $G > 2e^2/h$ $\Gamma \gg U_c$ the electron number on the SWCNT is not well defined anymore. Charge can now be added continuously giving a continuously charging of the SWCNT. The effect of size quantization is present in all three regimes, however, the levels are best defined for poor contacts as already explained.

In chapters 4-7 we present measurements with superconducting contacts to the SWCNT and the energy scale related to the superconductor is thus introduced now as well. When a metal turns superconducting, a gap of $2\Delta$ around the Fermi energy opens up in which single particle excitations are forbidden. At the Fermi energy the electrons are paired in two and form Cooper pairs consisting of a spin-up and a spin-down electron with opposite momentum wave vector. These particles are bosons and all condense in the same macroscopic quantum state.

Finally we summarize all the important energy scales introduced so far below and they are also shown in Fig. 1.11.
1.4. QUANTUM EFFECTS IN FINITE SWCNT SYSTEMS

- $\Delta E$: Level spacing
- $\delta$: Orbital/subband splitting in SWCNT
- $\Gamma$: Lifetime broadening of a bound state
- $U_c = e^2/C$: Charging energy
- $\Delta$: Superconducting energy gap
- $k_B T_K$: Binding energy related to the Kondo state

The effects related to these energy scales are observed provided that the thermal energy $k_B T$ is lower. Furthermore, the energy related to an applied bias $eV_{sd}$ across the samples should also be taken into account.
Chapter 2

Experimental methods

In this chapter we describe different routes of sample fabrication for making single wall carbon nanotube (SWCNT) devices. The procedures of growing nanotubes and defining contacts of desired choice by optical and electron beam lithography are described. Furthermore, the experimental techniques to cool down the samples to cryogenics temperatures and the electrical measurements setups will be presented.

2.1 Device fabrication

The SWCNT devices are made on a thin layer of 300 nm to 500 nm SiO$_2$ with a highly n-doped silicon substrate used as a back gate. The donors are arsenic (As) or antimony (Sb) and the gate works down to (min.) 30 mK.

Three main techniques exist to produce carbon nanotubes material: Arc discharge, laser ablation and chemical vapor deposition (CVD). In arc discharge an arc between two carbon electrodes creates a carbon vapor in which CNTs are made, while a carbon target is hit by a high power laser beam to produce CNTs by laser ablation [8]. Carbon nanotubes produced by these methods are commercially available. One of the disadvantages of the two mentioned techniques is that the nanotubes come in bundles of for instance SWCNTs. These then have to be separated to make SWCNT devices of only one tube. Separation of the bundle into single tubes is done in ultrasound, a process, which might introduce defects and degrade the electrical properties of the device. The first electrical measurements on SWCNT [5, 28, 4, 29] were made on tubes made by laser ablation (Smalley) with rather good quality. However, nowadays most groups studying transport properties of SWCNT use the third method of CVD due to the very high quality of the nanotubes produced (explained in further detail below). This growth technique has the
additional advantage that it is relatively easy to implement in the laboratory. Furthermore, it allows to control the positions of the nanotubes to some degree as well as the possibility to scale-up the production.

We have used three different ways of making devices, which can be categorized as follows. No alignment, aligning to an individual tube and aligning to catalyst islands. In the case of no alignment, SWCNTs are grown randomly by CVD on the sample with an appropriate density (about 1 per 10 $\mu$m x 10 $\mu$m) and pairs of contacts are then placed without any alignment to the SWCNTs on the samples. The hope is to have only one nanotube bridging two contacts. It can be tested electrically and/or measured by Atomic Force Microscope.

This procedure is rather simple, but good control of the density is required. The SWCNTs are grown from iron nitrate particles Fe(NO$_3$)$_3$ by chemical vapor deposition (CVD) [30]. The particles are dispersed in IPA ($\sim$ 1 mg per 20 ml IPA, the solution appears slightly yellow) and the sample is dipped for $\sim$ 10 s in the solution followed by a 5 s dip in n-hexan and finally dried in air. In the microscope the particles give a bluish shine at highest magnification (x100) in an optical microscope. The growth of the nanotubes is done in a commercial Carbolite MTF furnace connected to three sources of gasses, hydrogen (H$_2$), argon (Ar) and methane (CH$_4$).

The furnace is shown in Fig. 2.1, where the gasses are led through the furnace by a tube at temperatures of $\sim$ 900 °C in the center of the furnace. Three flow controllers, one for each gas, control the flow rate of the gasses\footnote{The flow controllers are Brooks Digital Thermal Mass Flow Meter & Controllers 5850S and the rates are controlled by a Brooks ”Gas and Liquid Mass Flow Secondary Electronics,}. During
2.1. DEVICE FABRICATION

heating the furnace is kept under an argon and hydrogen atmosphere, while growth takes place either with a mixture of all three gasses (Ar: 1 L/min, H₂: 0.1 L/min, CH₄: 0.5 L/min) or only hydrogen and methane. The growth is initiated when the desired temperature of 850-950°C is reached. Argon is used to dilute the two former to slow down growth rates (we speculate) and the slower rate might produce better quality tubes (less defect). The high temperature decomposes the methane molecules, which supply carbon for the growth of the nanotubes while hydrogen reduces the catalyst particle. The growth takes place from the catalyst particle (Fe). After ~15 minutes of growth, cooling is started in an argon flow only. Often the furnace is cooled by air (on the outside) to shorten cool down time. Good reproducibility of SWCNT quality has been achieved by using a mixture of all three gasses. High temperatures yield SWCNTs or ropes of SWCNTs, while lower temperatures give multi wall carbon nanotubes [31].

We have mostly used the third processing procedure, where the contacts are aligned to a catalyst island from which the tubes grow [32]. The catalyst (liquid form) is more complex and consist of iron nitrate Fe(NO₃)₃·9H₂O, molybdenum acetate and alumina (support) particles.

First alignment marks are defined by electron beam lithography (EBL) as shown in Fig. 2.2e. The resist used is a double layer consisting of 6% copolymer followed by 2% PMMA (see Fig. 2.2a). Both layers are spun at 4000 rpm, 45 s and baked on a hotplate at 185°C for 90 s. The EBL is done on a JEOL JSM-6320F scanning electron microscope (SEM) with Elphy software at 30 keV with a sensitivity of 200 µC/cm² and currents of ~20 pA and ~150 pA for small and big patterns, respectively. We have also used single layer 4% PMMA, 4000 rpm, 40 s, baked at 185°C for 3-5 min. The pattern is developed in MIBK:IPA (1:3) for 60 s stopped by 30 s in IPA. The sample is ashed for 20-40 s in an oxygen plasma prior to deposition of 60-70 nm Cr. Lift-off is done in acetone.

The same EBL procedure is used to make the pattern for catalyst islands schematically shown in 2.2b. The catalyst liquid is then spun on the sample at 4000 rpm for 150 s and baked at 185°C for 3 min. to ensure that the catalyst sticks to the substrate (Fig. 2.2c). Lift-off is made in acetone and ultrasound if necessary. Figure 2.2d shows a schematic of a catalyst island defined on top of the substrate. The sample is now transferred to the CVD tube furnace, where SWCNTs are grown (Fig. 2.2d) in a mixture of argon, hydrogen and methane as explained above. The optimal growth temperature depends on the thickness and the area of the catalyst islands. Typically, the temperature used is in the range of 850 – 960°C. After each growth the
CHAPTER 2. EXPERIMENTAL METHODS

Figure 2.2: (a) Silicon substrate with double layer resist. Alignment marks have already been made by electron beam lithography (EBL) as shown in (e). (b) EBL and developing make a pattern for the catalyst. (c) Deposition of catalyst. (d) After lift-off the catalyst is only present in the predefined areas (see (e-f)). (e) Top view of the alignment marks used to align the EBL mask for the catalyst islands and electrodes. In the black rectangle, catalyst islands have subsequently been defined. (f) Zoom-in on the catalyst islands in (e). (g) Micrograph of a catalyst island after CVD-growth. Only one or a few SWCNTs reach further than 1 µm from the catalyst island, which makes it likely to have only one SWCNT between the electrodes to be defined at some distance from the catalyst island.

sample is examined in a SEM on a test area, which might appear similar to the picture shown in Fig. 2.2g. Sometimes several trials are needed changing the temperature to achieve an appropriate density of tubes. The test area ensures that the SWCNTs in the regions for devices are not exposed to the
2.1. DEVICE FABRICATION

Figure 2.3: (a) Schematic picture of the metallization for contacting a SWCNT after an additional EBL step. (b) After lift-off, two electrodes spaced by the distance defined by lithography remains (typically 300-500 nm). In the ideal case one SWCNT is bridging the contacts. (c) Image of a sample showing nine SWCNT devices (gaps). The catalyst islands are clearly visible in two cases and placed between the gaps. (d) Zoom-out of a final device showing the electrodes from the bonding pads defined by optical lithography. The center EBL pattern is 200 µm × 200 µm (area within the 16 metal pads). Four of these pads in the top right are in this geometry shorted to measure the transition temperature of the superconducting electrodes.

electron beam, which might damage the SWCNT [33]. On the catalyst island and within a micron, the nanotubes grow rather densely. However, one or a few tubes "escape" to distances of several microns. The contacts are aligned relative to the catalyst island and placed some microns away. Thus it is likely that only one SWCNT lies in the gap between the two electrodes.

The procedure to define the contacts is shown schematically in Fig. 2.3a, where another EBL step with alignment is necessary. After developing the desired EBL pattern, the contact material is evaporated thermally or by electron beam gun. The pressure prior to evaporation is typically < 10⁻⁶ torr. Au/Cr (e.g. 50 nm/10 nm) for mostly high resistive contact to the device, Ti for medium contact and Au/Pd or only Pd (e.g. 50 nm/10 nm) for good con-

2For superconducting niobium contacts sputtering of a niobium target in an argon atmosphere has been used.

3This notation means Cr evaporated followed by Au.
contacts (see chapter 3). After lift-off, a schematic picture of the device is shown in Fig. 2.3b and a real device (topview) in 2.3c. A final step including optical lithography is needed to make large bonding pads as shown in Fig. 2.3d. Normally Au/Cr is used as bonding pads (150 nm/15 nm). Now the device is ready to be probed electrically and thus determine how many gaps have one or more tubes bridging the electrodes. If some of the gaps are insulating the remaining conducting gaps are likely to have only one SWCNT due to low density. Whether a single tube is present and its quality can be tested by different methods as low temperature transport measurement, AFM imaging and measuring the current saturation value $I_{\text{max}}$ at room temperature (one tube $I_{\text{max}} \sim 25 \text{nA}$) [31].

Both catalysts introduced above (iron nitrate and iron nitrate, molybdenum acetate with aluminum support particles) have produced good quality nanotubes, but the latter has yielded more reproducible result over a long period. Most of the measurements to be shown are thus made by the alignment procedure explained above.

Finally some devices have been made by aligning to individual tubes. This is a rather cumbersome procedure. First alignment marks have to be defined followed by growth of SWCNTs. Individual SWCNTs then have to be identified relative to the alignment marks by AFM and a unique EBL mask should be designed for the contacts. This is followed by metallization and an
optical lithography step to define bonding pads. Figure 2.4a shows a typical set of alignment marks used for aligning electrodes to a specific nanotube, while Fig. 2.4b shows four aligned contacts and a side gate to a nanotube (different device than in Fig. 2.4).

The alignment to the catalyst islands has proved to be a good compromise between the processing time and the yield. Many samples are made in a relatively short time and this increases the chances of finding interesting SWCNT devices.

2.1.1 Electron spin resonance and relaxation devices

Chapter 8.1 describes the effort to measure the relaxation time between the excited and the ground state in a single wall carbon nanotube quantum dot. The samples were made on conducting substrates due to the more experience in using back gated devices. However, the preferred substrate to use for these devices would be insulating and gating the SWCNT by side gates due to fast response (rise time) of the side gates. The back gate also works as a short for the rf-signal in case of electron spin resonance devices (see chapter 8.2). Finally, the side gates have not been reproducibly working at the same time as the back gate.

The next generation of devices will be on sapphire substrates. The use of EBL on sapphire does not work using only conventional PMMA due to the build up of charges on the insulating substrate. The pattern will be distorted even at very low acceleration voltage (5 keV). This problem can be solved by placing a thin metallic layer on top of the PMMA before EBL. Here we have used a conducting liquid called ESPACER that prevents charging effect. It is spun on the sample at 2000 rpm, 150 s after the baking of the PMMA. It is removed easily in DI after EBL exposure and before development. We have furthermore tested that nanotubes can be grown on the sapphire substrate by the same methods as explained above. The SEM can also be used to look at them afterwards in the control areas with only limited problems due to charging of the surface.
2.2 Cryogenics

The physical phenomena of interest in this thesis require low temperatures to be observed. The charge and size quantization in carbon nanotube quantum dots typically have energies in the order of $U_c \sim 10 \text{meV}$ and $\Delta E \sim 1 \text{meV}$. These will be smeared out by temperatures higher than $\sim 35 \text{K}$ and $\sim 3.5 \text{K}$, respectively. Furthermore, the Kondo effect (chapter 3.2) and superconductivity are typically seen at temperatures in the order of 1 K. A fundamental part of basic research in this field is thus access to cryogenic equipment based on liquid helium.

The easiest measurements are performed at 4.2 K in a liquid helium transport dewar, where the sample is dipped directly in the liquid. The temperature can be varied between 4.2 K and 300 K by controlling the distance of the sample to the liquid helium surface.

Lower temperatures can be reached by the Oxford Instruments Heliox insert, which contains a closed system with $^3\text{He}$ gas/liquid. The whole insert is immersed in liquid $^4\text{He}$ and reaches a base temperature of around 300 mK. The operation principle is briefly outlined as follows.

First, the $^3\text{He}$ gas is condensed by using the cooling power of a thermally connected $^4\text{He}$ pumped chamber (1 K pot) on the insert. Base temperature is obtained and maintained by pumping on the $^3\text{He}$ liquid until no more liquid is left. The closed circuit allows for another condensation and base temperature can be reached again. The temperature can be controlled and the insert is equipped with a 2 T superconducting magnet. For a more detailed description and operational instructions of this relatively simple cryostat, the reader is referred to the Heliox manual and related literature [34, 35].

For even lower temperatures ($\sim 30 \text{mK}$) a $^3\text{He}/^4\text{He}$ dilution refrigerator is used. The basic cooling mechanism is shown in Fig. 2.5. An internal circuit contains a mixture of the two helium isotopes $^3\text{He}$ and $^4\text{He}$. Below a critical temperature the condensed mixture separates into two phases, where one is called the concentrated phase consisting of mainly $^3\text{He}$, while the heavier diluted phase is $^4\text{He}$ diluted by around $\sim 6\%$ of $^3\text{He}$. This mixture is condensed in the mixing chamber. The cooling is achieved by pumping on the diluted phase removing mostly the light $^3\text{He}$ elements, which leads to the transfer of $^3\text{He}$ from the concentrated phase to the diluted phase to uphold the right concentration of $^3\text{He}$. In other words, $^3\text{He}$ is evaporated from the concentrated to the dilute phase thereby cooling the system. The evaporated $^3\text{He}$ is through a rather complex system of heat exchangers and flow impedances pumped back and condensed in the concentrated phase by a $^4\text{He}$ cooled 1 K pot. The cooling process can thus be sustained and measurement can be performed for months. By applying power to a heater close to the mixing
Figure 2.5: Schematic view of the dilution cooling system. A rotary pump drives the mixture around in the circuit shown. The mixture is condensed by the 1K-pot, which is cooled by liquid $^4$He, and led through a flow impedance. In the mixing chamber the mixture exists in two phases, the condensed phase of $^3$He and the diluted phase of $^3$He/$^4$He. Mostly $^3$He is pumped from the diluted phase and recondensed in the condenser line. The cooling mechanism is obtained from $^3$He traversing the phase boundary from the concentrated to the dilute phase to uphold a certain percentage of $^3$He in the diluted phase.

chamber the temperature can easily be controlled. The cryostat setup has a 7T superconducting magnet. In appendix A a checklist for running the KelvinOx cryostat at the Nano-Science center is found.

A theoretical and practical approach to cryogenics is given by references [35, 34].
2.3 Electrical measurement setups

A number of experimental setups have been used depending on the sample to be measured. The most used setup is standard DC-voltage controlled measurements as sketched on Fig. 2.6 (left). This is good for high impedance samples like carbon nanotubes devices (above kΩ). Here the DC-voltage from the DAC-card connected to the computer is reduced by a voltage divider and the current through the sample is detected by a current to voltage amplifier. All the data are controlled and collected by a LabView program. The opto-couplers are introduced to have an isolated ground in the experiment from net, which often lowers noise.

Current controlled measurements are preferred for low resistive devices and especially to measure the supercurrent of a superconductor or Josephson junction. Figure 2.6 (right) shows a DC-current controlled setup, where the resistor $R = 10 \text{ MΩ} \gg R_{\text{sample}}$ ensures a constant current through the sample. A voltage-amplifier detects the voltage across the sample and all data are collected by a LabView program.

Some samples are made to have four probe geometry to exclude the resistance of the wiring. However, the number of devices and thus the yield is decreased in this way since only half the number of devices can be cooled down compared to the two-probe configuration.

For more sensitive voltage controlled measurements standard lock-in techniques can be applied as shown in Fig. 2.7. A small AC voltage signal is superposed on the DC-bias voltage (same configuration as above for the DC-voltage). This signal is sent through the sample and detected by a current-voltage amplifier. The signal from the amplifier is multiplied by the original AC-signal and passed through a low pass filter in the lock-in amplifier. This effectively narrows the bandwidth to just around the frequency of the original AC signal. Very low noise measurements can thus be made.

For pulsed experiments to measure the relaxation time from the excited
state to the ground state in a quantum dot a different measurement setup was used requiring a high quality pulse generator. Furthermore, the wiring includes rf-cables. It will be explained in some more detail in chapter 8.

![Schematic setup for AC voltage controlled measurements. A small AC-voltage is superposed on a DC-signal and the differential conductance dI/dV versus bias is detected by lock-in techniques (ADC1).](image)

The noise in the setup can be monitored by an oscilloscope and we use opto-couplers to disconnect the ground from the setup. We place the voltage divider and preamplifier as close as possible to the cryostat. We have no cryogenic amplifiers, which clearly would lower the noise level significantly for dilution fridge measurement, but the sample holder is connected with thermocoax cables to lower noise. Measurements are normally performed in a room being a Faraday cage.
Chapter 3

Single wall carbon nanotubes contacted to normal contacts

This chapter describes electronic transport through single wall carbon nanotubes (SWCNT) contacted by (two) normal electrodes. The measurements shown are mostly taken at low temperatures (< 4 K), where quantum effects are important. All the phenomena presented have been observed and reported in the literature. The chapter serves to introduce the basic language used in the following chapter as well as to demonstrate the reproducible high quality SWCNT devices, we are making. A somewhat more intuitive explanation of the high transparency devices (Fabry-Perot regime) will be given as well as more emphasis on the transition from Coulomb blockade to Fabry-Perot interference.

Figure 3.1 shows the gate dependence of the linear conductance for two different types of SWCNTs, which defines whether the tube is semiconducting or metallic. Figure 3.1a displays the behavior of a semiconducting SWCNT characterized by its strong gate dependent linear conductance [28]. On the contrary the behavior shown in Fig. 3.1b corresponds to a metallic SWCNT due to its relatively constant linear conductance as a function of gate voltage. The semiconducting SWCNT is a p-type semiconductor where the conduction for negative gate voltages is due to hole transport through the valence band. For positive gate voltages \( V_{\text{gate}} > 4 \text{ V} \) the Fermi energy of the leads is inside the band gap and no conduction occurs. Thus a semiconducting SWCNT can be used as a field effect transistor. The SWCNT shown in Fig. 3.1a has a relative large band gap, while conduction in a smaller band gap semiconductor would reappear for positive gate voltage due to electron transport through the conduction band, \( i.e., \) a bipolar [36, 37, 38] (see below). Note, that the resistance between the two devices differ by an order of magnitude due to different coupling to the leads. In general the coupling
Figure 3.1: Two different types of SWCNT. (a) A semiconducting SWCNT identified by its strong dependence of the linear conductance on the gate voltage. It is a p-type semiconductor with a relatively large band gap. The inset shows the band structure with the electrochemical potential in the valence band. Oscillations of the conductance at low temperature in the p-type region is due to single hole transport (Coulomb blockade). (b) Metallic SWCNT identified by its weak gate voltage dependence at high temperature. At low temperatures oscillations in the conductance versus gate voltage are seen due to Coulomb Blockade.

can be to some extent controlled by choice of electrode material.

Good contact is achieved to both metallic and semiconducting SWCNTs with Pd and Rh giving $G > 2e^2/h$ [39, 40]. For semiconducting SWCNTs the contact resistance depends on the gap and thus the diameter $d$ of the tube $E_{gap} \propto 1/d$ [40]. For these well contacted tubes, open quantum dots will be defined between the electrodes. This leads to the observation of a Fabry-Perot interference pattern, first observed in metallic SWCNTs contacted by Pd electrodes [9]. Since then it has been observed in small band gap semiconducting tubes with transport through the valence band [41]. The Schottky barrier between the metal contact and the SWCNT is in this case low. The Fabry-Perot interference pattern has been calculated using a scattering matrix approach [9, 42]. For worse coupling to the SWCNT the discrete nature of the electronic charge is seen superposed on the Fabry-Perot pattern (chapter 3.3) [41, 38]. Relatively poor contacts to SWCNTs are obtained using Au/Cr and Al contacts by which a closed quantum dot is formed, while Ti and Au are known to yield better contact resistances [31] often in the Kondo regime. The above is only a rule of thumb and requires that the quality of the SWCNTs is high. Normally we observe a wide range of contact resistances in the same device fabrication.

Figure 3.1a-b also shows the temperature dependence, where the gate de-
pendence of the linear conductance for both devices evolve into regular oscillations at low temperature. These oscillations are due to Coulomb blockade, which happens for SWCNT weakly coupled to the leads as will be explained in the next section.

The regularity of the Coulomb oscillations indicate whether good quality of the SWCNT has been obtained or if more than one SWCNT is bridging the electrodes. For high quality SWCNTs regular oscillations should persist through a gate region of $|V_{\text{gate}}| < 10\,\text{V}$ as shown. On the contrary if the SWCNT has defects only small regions of gate voltage might have well behaved oscillations.

Finally, it should be mentioned that the temperature dependence of the conductance from room temperature to the Coulomb blockade regime has been used to determine whether metallic SWCNT are Luttinger liquids as predicted due to their one-dimensionality (breakdown of Fermi liquid theory) [43]. This has been indicated by a number of experiments on SWCNT devices [44, 24], where the conductance drops as a power law as a function of temperature and bias as expected for Luttinger liquids. Despite these experimental findings the issue of metallic SWCNTs being Luttinger liquids is still debated.
CHAPTER 3. SWCNTS CONTACTED TO NORMAL CONTACTS

3.1 Coulomb blockade and shell structure

When the coupling to the quantum dot (QD) is weak $G < e^2/h$ no fluctuations of the charge on the dot are possible. It leads to oscillatory behavior of the conductance as seen in Fig. 3.1a-b at low temperature. The energy related to a single electron charge fluctuation is the charging energy $U_c = e^2/C$. We do not want to give a rigorous derivation, but present the important parameters and sketch how they are derived.

Consider a model of a quantum dot as shown in Fig. 3.2 [45, 46, 24]. The quantum dot is coupled to source and drain electrodes modeled by a capacitor and a resistor in parallel. Furthermore, a third terminal called a gate is coupled only capacitively. The source is here defined as a source for electrons for positive voltages. Furthermore, the bias is applied asymmetrically, i.e., the voltage is controlled on drain, while source is held at ground.\(^1\)

We assume that all interactions to the environment is taken care of through the total capacitance $C = C_S + C_D + C_{gate}$. The minimum energy needed to add the $N+1$ electron to a QD having $N$ electrons is called the addition energy and is related to charge quantization and size quantization. It is given by the difference between the electrochemical potential $\mu_{N+1}$ and $\mu_N$ of having $N+1$ and $N$ electrons on the QD, respectively

$$E_{add} = \mu_{N+1} - \mu_N = U_c + \Delta E_{N+1,N} \quad (3.1)$$

\(^{1}\)This will be equal to a symmetric biasing for equal capacitances to source and drain and a relative small capacitance to the gate. It will be assumed as an approximation in the following.

Figure 3.2: Circuit model of a quantum dot that could represent a single wall carbon nanotube coupled poorly to the electrodes. Source (drain) electrodes are connected to the quantum dot modeled by a capacitor $C_S (C_D)$ and a resistor $R_S (R_D)$, while the gate electrode is connected by a capacitor $C_{gate}$. 
where $\Delta E_{N+1,N} = E_{N+1} - E_N$ is the difference between the single-particle levels obtained from size quantization. Note, that $\Delta E_{N+1,N} = 0$, if the $N+1$ and $N$ single-particle levels are degenerate. Therefore two important energy scales determine the electron transport through the QD, the charging energy $U_c$ and the level spacing $\Delta E$.

The electrochemical potential is derived from the ground state energy $F(N)$ as

$$\mu_{N+1} = F(N + 1) - F(N) \quad (3.2)$$

The ground state energy consists of an electrostatic and a chemical part $F(N) = F_{el}(N) + F_{ch}(N)$. The electrostatic energy contribution is calculated from classical electrostatics $F_{el}(N) = \frac{(Q_{ex}(N))^2}{2\varepsilon}$, where the excess charge stems from a discrete number of electrons on the QD and a continuously charging by the gate $Q_{ex}(N) = -|e|(N - N_0) - C_{gate}V_{gate}$. Here $N_0$ is the number of electrons for $V_{gate} = 0$ V. The chemical part $F_{ch}(N) = \sum_{i=1}^{N} E_i$ is due to the filling of single-particle levels.

We will now explicitly state the (ideal) sequence of addition energies for three cases observed in experiments [26, 47, 23]. For some SWCNT a so-called odd/even filling pattern is seen. This describes the filling of a series of spin degenerate levels, where odd filling corresponds to one electron in a level and even filling to two electron in a level. The spacing between the spin degenerate levels is $\tilde{\Delta}E = \delta = \frac{1}{2}\Delta E$ to follow the syntax used in chapter 1. The sequence of addition energies thus becomes

$$[U_c + \delta, U_c], \ [U_c + \delta, U_c], \ldots \quad (3.3)$$

In the case of four-fold shell structure with two completely degenerate orbitals in each shell the addition energy sequence is given by

$$[U_c + \Delta E, U_c, U_c, U_c], \ [U_c + \Delta E, U_c, U_c, U_c], \ldots \quad (3.4)$$

corresponding to adding the first electron into a new shell and so forth. Finally, if a splitting between the two orbitals is present, the following sequence of addition energies is expected\(^2\)

$$[U_c + \Delta E - \delta, U_c, U_c + \delta, U_c], \ [U_c + \Delta E - \delta, U_c, U_c + \delta, U_c], \ldots \quad (3.5)$$

These three kinds of addition energy spectra are observed in different devices, that will be presented in this chapter. Two more parameter are introduced, if exchange interaction ($J$) and excess Coulomb interaction ($\delta U$) are taken into account [25, 26, 23]. This will not be part of this thesis.

\(^2\)For orbital splitting $\delta = 1/2\Delta E$ Eq. (3.3) is obtained.
Figure 3.3: (a-d) Energy diagrams for transport through a SWCNT quantum dot (QD). The levels are four-fold degenerate to model the two spin degenerate orbital states of the SWCNT. (a) Below the chemical potential of the leads the levels are filled and separated by the level spacing \( \Delta E \), except the top level with one electron. An electron cannot tunnel onto the QD (Coulomb blockade), because the next available level (dotted line) is above the chemical potential of the leads due to the charging energy \( U_c \) (red arrow). The lower dotted level is three times degenerate. The energy corresponds to position A in (e). (b-c) The potential of the levels can be tuned by the back gate which align the empty level(s) with the chemical potential in the leads. Electrons can now tunnel one by one through the dot giving rise to the Coulomb peaks in the conductance versus gate voltage (see (f)). When the electron tunnel onto the QD the electrostatic potential of the QD is lifted by \( U_c \) and an energy gap due to charging to the next level appears as shown in (c). Corresponds to position BC in (e). (d) The excited states can be probed by increasing the bias across the junction. Here shown for negative bias on drain probing the \((N+1)\) excited state marked by the blue double arrow. (e) Bias spectroscopy plot at 4K of a SWCNT QD showing four-fold degenerate shell structure, where \( N + 4 \) corresponds to a filled shell. White: Zero \( dI/dV \), black: High \( dI/dV \). The relevant energy scales are shown by arrows. (f) Zero bias CB peaks.

Quantum dots are typically characterized by bias spectroscopy, where the differential conductance \( dI/dV_{sd} \) is plotted in color scale as a function of
bias and gate voltage as shown in Fig. 3.3e. The white color corresponds to zero differential conductance, while black is finite differential conductance. The zero conductance diamonds (e.g. position A) can be understood from the energy diagram for a quantum dot here with four-fold degenerate levels (shell) (Fig. 3.3a). The levels below the Fermi level of the leads are filled with the highest shell only having one electron. The energy of these levels can be controlled by the gate, while the energy of the electrons in the leads are tuned by the bias across the QD. In the diagram, the electrons in the leads can not enter the quantum dot due to the cost of the charging energy to add one electron, a phenomenon called Coulomb blockade. The number of electrons on the QD is thus constant in each diamond, i.e., the charge state is well defined.

At position BC in the bias spectroscopy plot the QD can be in two charge states as sketched in Fig. 3.3b-c. By tuning the gate voltage it is now energetically allowed for an electron in the leads to enter and leave the QD. Current thus passes through the dot one electron at the time, when applying a small bias.

For bias voltages higher than the charging energy the discrete level structure of the dot can be probed giving rise to the high bias grid of lines in the bias spectroscopy plot. The relevant energy diagram to probe an excited state (ES) is sketched in Fig. 3.3d (blue vertical line), where an additional current contribution due to an ES entering the bias window is expected. This leads to a peak in the differential conductance and the level spacing can be deduced as shown in Fig. 3.3e. Similarly the charging energy can be estimated shown by the red vertical arrow. This device has very clear excited states even at high bias, where these normally are smeared out in SWCNT devices probably due to heating.

The distance between the conductance peaks in Fig. 3.3f along the gate voltage is scaled by the coupling of the gate to the SWCNT

$$\Delta V_{\text{gate}} = E_{\text{add}}/(e \alpha)$$

with $\alpha = C_{\text{gate}}/C$. We note that this SWCNT is coupled with different capacitances to the source and the drain and/or strongly coupled to the gate because of the asymmetric shaped of the diamond with respect to the zero bias line [48], but it will not be treated in details. This example resembles the filling sequence ($U_c$, $U_c$, $U_c$, $U_c + \Delta E$) as stated in Eq. (3.4) with $U_c \sim 11 \text{ meV}$, $\Delta E \sim 5 \text{ meV}$ and $\alpha \sim (11 \text{ meV})/(e \times 35 \text{ mV}) = 0.34$, where the gate voltage $\Delta V_{\text{gate}} \sim 35 \text{ mV}$ is extracted from the width of diamond $N+3$. The first three diamonds are of the same height $U_c$, while the last is taller ($\sim 16 \text{ meV}$) by $\Delta E$ because the addition of the next electron is in the following
shell. The level spacing estimated in this way is consistent with the value obtained from the change in gate voltage (14 mV) as indicated by an arrow yielding $\Delta E \sim 4.8 \text{meV}$. The four-fold pattern continues for higher gate voltages beyond the range measured $V_{\text{gate}} < 10 \text{V}$.

This behavior (Fig. 3.3f) is like a transistor where the current can be turned on and off. However, in contrast to conventional transistors the current is turned on and off repeatedly as the electron number on the quantum dot is changed, i.e., a single electron transistor.

Figure 3.4: (a) Bias spectroscopy plot at 0.3 K of a SWCNT QD device showing four fold shell structure with orbital splitting. A relative electron number is shown for filled shells. (b) Linear conductance versus gate voltage. The peaks are spaced into pairs (blue and red bars) indicating that the electrons fill up orbital consecutively. Each orbital is coupled differently to the leads.

Figure 3.4a shows a bias spectroscopy plot of another SWCNT device. Here the addition energy is also clearly dependent on the electron filling and the bigger diamonds for every fourth indicate the four-fold degeneracy.

In Fig. 3.4b the linear conductance is shown as a function of gate voltage. The Coulomb peak seems to be spaced into two, where two Coulomb peaks have higher amplitude followed by two peaks with lower amplitude. Red and blue bars are placed below the pairs of peaks originating from the same band. This behavior has been observed in many devices (see chapter 5) and is probably due to different coupling to the two orbitals (bands). The two
Orbitals stem from quantization of the two different bands. It is also clearly visible in the bias spectroscopy plot, where the ground state lines for one set of orbitals are clearly seen. However, in contrast to other devices the peak height related to the coupling changes at $V_{\text{gate}} \sim -3\,\text{V}$ in this device, where two pairs of orbitals with low height follow each other (blue pairs become taller than red pairs for $V_{\text{gate}} > -3\,\text{V}$). At the same gate voltage the pronounced horizontal inelastic cotunneling lines (see next chapter 3.2) at finite bias switch from negative bias to positive bias as the gate voltage is increased. This behavior is not understood at the moment.

Figure 3.5: The addition energies as a function of electron filling extracted from the difference between the Coulomb blockade peaks along the gate axis. The shaded region corresponds to Fig. 3.4a, where a filled shell is marked with red squares. The red oval indicates a gate range with four-fold degenerate levels. For the other shells shown an orbital splitting is present.

Figure 3.5 shows the addition energies for the above device in a wider gate voltage range. For most shells an orbital splitting is present in the order of $\delta \sim 0.5 - 2\,\text{meV}$ depending on the shell except for the two shells marked by a red oval, where the levels are almost degenerate. From these the level spacing is easily estimated as $\Delta E \sim 4 - 4.5\,\text{meV}$. This SWCNT QD mostly follows the addition energy sequence Eq. (3.5), i.e., for electron filling $< 24$. The charging energy $U_c \sim 4\,\text{meV}$ is estimated from the addition energy for filling the first or third electron in a shell. The conversion from gate voltage to energy is $\alpha \sim 0.05$. It is found from the addition energy along the source direction $E_{\text{add}} \sim 7.5\,\text{meV}$ and the peak spacing $\Delta V_{\text{gate}} \sim 0.15\,\text{V}$ for filling number 12. At higher gate voltages than shown, the addition energy is more irregular. The orbital splitting in this device is probably not determined by perfect boundary conditions alone.
3.2 Kondo effect in SWCNTs

For SWCNT devices with relatively strong coupling to the leads, but still in the Coulomb blockade regime, higher order tunneling processes through virtual states become possible. According to Heisenberg’s uncertainty principle an energy uncertainty is allowed for a time $\Delta t < \hbar/U_c \sim 0.1 \text{ ps}$, where the energy uncertainty related to a charge fluctuation is determined by the typical charging energy $U_c \sim 10 \text{ meV}$. Thus an electron can tunnel onto the quantum dot even though it is energetically forbidden provided that it stays a short time (or another tunnels off).

These processes are known as cotunneling and two kinds of cotunneling processes are defined based on energy considerations [49]. The first is elastic cotunneling where the quantum dot is left in its ground state. An electron enters the quantum dot having the same energy with which it (or another electron) tunnels out. On the contrary in the case of inelastic cotunneling, an electron enters the quantum dot with higher energy than another electron tunnels out, leaving the quantum dot in an excited state.

Cotunneling taking spin flip processes into account gives rise to the Kondo effect. The Kondo effect in different forms has been studied extensively both experimentally and theoretically in many years [50]. We will only treat the effect briefly from an experimental point of view. In chapter 6 the Kondo effect is revisited in connection with superconductivity, which makes the physics even more interesting and complicated.

Originally, the Kondo effect explains the temperature dependence of the resistivity of non-magnetic metals (Cu, Ag, Au, etc.) diluted with magnetic impurities (Mn, Fe). When the temperature is lowered a minimum followed by a logarithmic increase of the resistivity is observed. The minimum occurs at a temperature defined as the Kondo temperature $T_K$. The low temperature increase is due to scattering (through exchange interactions) of the electrons on magnetic impurities, i.e., the Kondo effect [51]. This behavior is in contrast to metals without magnetic impurities, where the resistivity diminishes as temperature is lowered due to the freeze out of phonons, but becomes temperature independent at low temperature (scattering on non-magnetic impurities).

However, in a quantum dot the ”modern” Kondo effect can be observed, where the conductance increases (logarithmically) as the temperature is lowered [3]. A qualitative idea of the effect as well as experimental data will be presented. For a more detailed discussion the reader is referred to the following Ph.D. theses and text books [52, 24, 53].

In a quantum dot an uncoupled spin on the dot acts as a magnetic impurity for the conduction electrons in the leads. This system thus gives the possi-
3.2. KONDO EFFECT IN SWCNTS

Figure 3.6: Exchange cotunneling processes leading to the Kondo state. One process is illustrated in (a-c) involving a spin flip of the spin on the quantum dot. (d) These kind of processes leads to the formation of a many-body ground state with a peak in the DOS locked to the Fermi level of the leads and having a width $T_K$.

bility to examine the effects of a single magnetic impurity on the conduction electrons in the leads instead of many impurities as explained above for bulk systems. Furthermore, the important parameters for the Kondo effect can be tuned in the case of a quantum dot, i.e., the coupling to the leads $\Gamma$, the energy difference between the impurity level and the Fermi level of the leads $\epsilon_0$, the charging energy $^3U_c$ and the Fermi energy and the total spin $S$. Quantum dots therefore represent ideal systems for investigation of the Kondo effect.

Figure 3.6 shows one of the spin flip (exchange) cotunneling processes that leads to formation of a new state called the Kondo state or resonance. We want to consider one spin-degenerate level in a quantum dot (Anderson model). In Fig. 3.6a a localized spin on the quantum dot is trapped on a spin degenerate level $\epsilon_0$ below the Fermi level of the leads because single electron tunneling is forbidden due to the energy cost of adding a new electron on the dot $\sim U_c$. However, cotunneling processes allow for an electron from the lead to tunnel onto the energetically forbidden (originally degenerate) level provided that the electron on the dot tunnels out in a sufficiently fast time to fulfill the Heisenberg uncertainty relation. This is illustrated in Fig. 3.6b with a spin flip involved. The final state on the quantum dot now consists of an opposite spin than the initial state with a spin up electron in the lead. These spin flip processes involve conduction electrons in the leads and the localized spin on the dot and form a many-body problem. The many-body ground state leads to formation of a peak in the DOS at the Fermi level

$^3$The charging energy is to some extent controlled by the length of the device, but the charging energy often varies experimentally as a function of gate voltage for the same device as well.
as shown in Fig. 3.6d. The width is given by the Kondo temperature $T_K$. The Kondo temperature is related to the parameters of the spin 1/2 Kondo problem as [50]

$$k_B T_K = \frac{1}{2}(\Gamma U_c)^{1/2} e^{-\pi a (\epsilon_0 + U_c)}$$ (3.7)

where $k_B$ is Boltzmann’s constant, $\Gamma$ is the normal level line width, $U_c$ is the charging energy and $\epsilon_0$ is the energy difference (negative value) between the Fermi level of the leads and the level as already introduced. An idea of the magnitude of the quantities is obtained by considering the Kondo temperature in the center of a resonance ($\epsilon_0 = -U_c/2$) of a typical SWCNT QD with charging energy $U_c = 5 \text{ meV}$. The Kondo temperature interval [250 mK, 2 K] corresponds to $\Gamma$ in the interval [1 mV, 1.82 mV]. Due to the resonance at the Fermi energy current passes through the dot around zero bias as such the Kondo effect has overcome the Coulomb blockade.

The Kondo effect breaks down at finite bias and is affected by a magnetic field as will be shown in connection with experimental data below.

The modern Kondo effect has been measured in many systems during the last decade, GaAs/AlGaAs 2DEG quantum dots [54, 55], SWCNTs [56] and small molecules [57].

We now present measurements of the spin 1/2 Kondo effect in SWCNTs and will end this section by a discussion of other kinds of Kondo resonances. Figure 3.7a shows a bias spectroscopy plot of a SWCNT at 300 mK with relatively good coupling to the leads. Electron charging effects are still observed and each diamond corresponds to an integer number of electrons on the SWCNT QD. In contrast to the above measurements with poorly coupled contacts, new features appear at zero and finite bias in the plot due to cotunneling. The zero bias ridge at every second diamond is due to the spin 1/2 Kondo effect. The even/odd (E/O) structure can now be identified as indicated above the plot, where an odd number of electrons are present on the SWCNT QD in the Kondo diamonds. All the electrons couple in pairs giving a zero net spin except the uncoupled electron, which is the reason for the Kondo effect leaving the SWCNT QD in a $S = 1/2$ state. For even number of electrons on the quantum dot (in the simplest case) the total spin is $S = 0$ and no zero-bias Kondo effect is observed.

The even diamonds are truncated at finite bias due to inelastic cotunneling through the next level [49]. The level spacing can be estimated by the related energy (bias) as $\Delta E \sim 4 \text{ meV}$. Assuming that the addition energy to add an odd numbered electron is $U_c + \Delta E$ and to add an even numbered electron is only $U_c$, the charging energy is of the same order $U_c \sim 4 \text{ meV}$. It thus appears as the orbital splitting is $\delta \sim \Delta E/2$. The reason for this is not clear, but it has often observed in the Kondo regime [56].
Figure 3.7: (a) Bias spectroscopy plot at 300 mK of a SWCNT quantum dot device with an even (E)/odd (O) filling of the levels indicated by white letters. For odd filling a high conductance ridge is seen around zero bias, which is a manifestation of the Kondo effect. (b) A Kondo ridge from another sample for odd filling. The dashed red line indicates the position of the bias sweep in the middle of the Kondo ridge as shown in (c). The width of the Kondo peak is $\sim 2T_K$. (d) The Kondo peak is split by a magnetic field. Note, that the low field splitting is due to superconductivity in the leads. (e) Linear conductance versus gate voltage for the Kondo ridge in (b). (f) The temperature dependence of the linear conductance in the middle of three Kondo ridges (green squares correspond to (e)).
The Kondo temperature $T_K$ can be estimated from the width of the Kondo ridge (non-equilibrium) and deduced from the temperature dependence of the center of the Kondo ridge. Figure 3.7b shows a Kondo ridge for another device at 30 mK cooled in a dilution fridge. The bias dependence along the dashed red line is plotted in Fig. 3.7c, which gives a Kondo temperature in the order of $T_K \sim 2$ K.

Figure 3.7d shows the splitting of the Kondo ridge in a magnetic field. This splitting is twice the Zeeman splitting, where the latter is given by $\Delta E_Z = 2g\mu_B m_s B = g\mu_B B$ with $m_s = 1/2$ being the spin of an electron. The Kondo splitting thus becomes

$$e\Delta V_{sd} = 2g\mu_B B \quad (\sim 230 \text{ } \mu eV/T)$$

(3.8)

Here $g = 2$ is the expected $g$-factor for the SWCNT [58, 59], $\mu_B = 9.2 \times 10^{-24}$ J/T the Bohr magneton and $\Delta V_{sd}$ is the splitting of the peak. At $B = 5$ T the splitting is expected to be $\Delta V_{sd} = 1.15 \text{ } meV$ roughly consistent with the estimated splitting from the measurement of $\sim 1 \text{ } meV$. This indicates that the zero bias ridge is due to the spin 1/2 Kondo effect.

The temperature dependence of the linear conductance as a function of gate voltage is shown in Fig. 3.7e for the Kondo ridge in Fig. 3.7c. The value of conductance in the middle of the Kondo ridges for each temperature is plotted in Fig. 3.7e by the green points together with two other Kondo ridges (same sample). This temperature dependence can be used to extract the Kondo temperature by fitting to the following interpolation

$$G(T) = \frac{G_0}{1 + (2^{1/s} - 1)(\frac{T}{T_K})^2}$$

(3.9)

where $s = 0.22$ for a spin 1/2 Kondo [60]. The fit yields a Kondo temperature of around $T_K \sim 3 - 4$ K, which is not in so good agreement with the Kondo temperature extracted from the width of the peak. The discrepancy is not understood. However, the temperature dependence of two other Kondo ridges shown gives a better correspondence between the Kondo temperature extracted in the two independent ways as seen in the figure.

In the so-called unitary limit (equal coupling to the leads) the saturation conductance of the Kondo effect is $G_0 = 2e^2/h$. Lower values of $G_0 = \frac{2e^2}{h} \frac{4\Gamma L\Gamma R}{(\Gamma L + \Gamma R)^2}$ is due to asymmetry according to the resonant junction formula [1]. Asymmetric coupling is for instance the case of the Kondo ridge in 3.7b.

The last two odd filling Kondo ridges (black and red squares in Fig. 3.7f) are actually from a SWCNT device, where the four-fold degeneracy is observed. In such system the Kondo effect can be more complicated. An observation of the orbital and spin Kondo effect (SU4) was shown by Jarillo-Herrero et
3.2. **KONDO EFFECT IN SWCNTS**

Figure 3.8: Bias spectroscopy plot at 300 mK of a SWCNT quantum dot with four fold degenerate level (shell). A finite magnetic field $B = 180 \text{ mT}$ is applied to suppress the superconductivity in the leads. The numbers indicate the relative hole filling and the big diamonds corresponds to filled shells. The red arrows point to the Kondo for half filling, *i.e.*, two electrons in the shell.

The authors show that the orbital degeneracy (two orbitals with different magnetic moment) also leads to a Kondo effect in similar way as two degenerate spin levels (spin up and down).

Babic *et al.* examined the Kondo effect at half filling (electron number 2) in SWCNTs where a four period structure was observed [61, 33]. At half filling different ground states are expected. If the first electron has spin up and the next spin down the ground state is the singlet state and no Kondo effect is observed ($S=0$) as above. However, when the ground state is a spin triplet state degenerate with the singlet the Kondo effect can be observed at half filling [62]. A pure triplet Kondo should have a very low Kondo temperature and will be difficult to observe experimentally [61].

We have also observed Kondo effect in many devices. Some of them come in even/odd structure as shown in Fig. 3.7a, but we have also observed Kondo effect at filling 1 and 3 in SWCNT with four-fold degeneracy (see measurements in chapter 6). Furthermore, an interesting Kondo effect at half filling is observed without Kondo effect in 1 and 3 as shown in Fig. 3.8. This is merely to illustrate the variety of phenomena observed in SWCNT quantum dot and the data still need to be analyzed and understood in more detail. The numbers indicate the relative hole filling and the big diamonds correspond to filled shells. This quantum dot thus has a four-fold degeneracy probably with a small orbital splitting corresponding to the low bias horizontal line in the odd diamonds. The red arrows points to the half filling Kondo effect, which
seems to consist of three peaks instead of just one. It should be mentioned that a finite field of \( B = 180 \text{ mT} \) is applied to suppress superconductivity in the Ti/Al/Ti leads of this device. The reason for the Kondo effect only to appear at half filling is not clear. It could be due to a spin triplet degenerate with the singlet, which should have larger \( T_K \) than the respective spin half Kondo [62]. The measurement is taken at \( T = 300 \text{ mK} \), which in that case indicates a quite low \( T_{K,S=1/2} \). However, inelastic cotunneling lines are seen at filling 1 and 3 and could be due to a split up Kondo. More analysis in the line of Babic *et al.* is needed [61].
3.3 Fabry-Perot interference in small band gap semiconducting SWCNTs

We will now focus on small band gap semiconducting SWCNTs, where the band gap is so small that transport can be tuned from hole transport through the valence band to electron transport through the conduction band by the gate [36]. The two situations are shown in Fig. 3.9. In (a) the bands are bending in such a way that holes can tunnel from the contact into the valence band and out in the contact. The Schottky barrier for hole transport is small by choosing proper contact material (for instance Pd) leading to high conductance [41]. Transport can be changed to electron transport through the conduction band (b) by the applying positive voltage to the gate. The Schottky barrier is in this case significant leading to poorly coupled SWCNT to the contacts. Between these two transport regions no transport is allowed when the electrochemical potential in the leads is in the band gap of the

![Figure 3.9: Schematic band diagrams of a small band gap single wall carbon nanotube contacted to leads, where the band bending is controlled by the gate voltage. The red/blue band is the conduction/valence band. (a) The condition for hole transport through the valence band. Holes tunnel into/out of the valence band through the relative small Schottky barrier. (b) Condition for electron transport through the conduction band. Electrons tunnel into/out of the conduction band through a Schottky barrier. This barrier is bigger than in the case of the hole transport for Pd contacts. Thus high conductance is observed through the valence band in contrast to low conduction through the conduction band, i.e., Fabry-Perot versus Coulomb blockade regime.](image-url)
Figure 3.10a shows the conductance versus gate voltage at $V_{sd} \sim 1$ meV for a small band gap SWCNT at $T = 4$ K. The nature of the SWCNT is identified by the relatively high conductance region for negative gate voltages (hole transport) in contrast to the low conductance region for positive gate voltages (electron transport) as explained above. The broad oscillations for hole transport from $V_{\text{gate}}$ between $-3$ V and $0.5$ V are a manifestation of the Fabry-Perot oscillations [9], i.e., an open quantum dot. For positive gate voltages regular oscillations are observed due to Coulomb blockade. The inset shows a gate region for electron transport where relative high conductance Coulomb peaks are seen. They are spaced into four reflecting the spin orbital degree of freedom as expected (see chapter 1.4).

A bias spectroscopy plot of part of the Fabry-Perot region is shown in Fig. 3.10b. The low conductance regions (black area\(^4\)) form a mesh due to interference of the hole waves reflected back and forward. Instead of having resonances on a non-conducting background as in the Coulomb blockade case, the Fabry-Perot interference pattern consists of anti-resonances (off resonance) on a conducting background. The level spacing can be extracted as the distance from being in resonance with a level to being off resonance in similar ways as in the charging energy. This gives $\Delta E \sim 4$ meV as indicated in Fig. 3.10b consistent with the device being around $L = \frac{h\pi}{\Delta E} \sim 400$ nm (four-fold degeneracy assumed). The level spacing $\Delta E$ is identical with the characteristic voltage $eV_c$ defined in Ref. 10. The distance between two resonance peaks along the gate voltage axis is given by the level spacing but an additional energy due to charging has to be paid as well. Even though the charging is not observed directly as for Coulomb blockade the SWCNT charges continuously as the level is filled. For four-fold degenerate levels the spacing in gate voltage is thus $\alpha eV_{\text{gate}} = \Delta E + 4U_c$, where $\alpha$ is the usual coupling factor. The device has a high asymmetric (resistive) coupling, because the conductance at resonance is lower than $G = \frac{4e^2}{h}$. It can be found by $G = \frac{4e^2}{h} \frac{4\Gamma_L \Gamma_R}{(\Gamma_L + \Gamma_R)^2}$ with $G_{\text{exp, res}} \sim 2e^2/h$ and gives $\Gamma_L/\Gamma_R = 0.17$. The capacitive coupling to the source and the drain electrode is also slightly different or and the capacitive coupling to the gate is significant compared to the source and drain capacitance because of the different slope of the dip lines. It will not be pursued in further detail.

Figure 3.10c shows the differential conductance versus bias and gate voltage in the n-type region\(^5\) (also called stability diagram). Clear Coulomb

\(^4\)Note, that the grey scale is reversed compared to Coulomb blockade plots. The visibility of the important features are enhanced by choosing white for the high conductive background and black for anti-resonance lines in Fabry-Perot interference pattern.

\(^5\)Same device as shown in Fig. 3.3.
3.3. FABRY-PEROT INTERFERENCE IN SWCNTs

Figure 3.10: Measurements at 4K for a small band gap semiconductor SWCNT. (a) Linear conductance versus gate voltage. For (hole) transport through the valence band, high conductance Fabry-Perot oscillations are observed, while transport through the conduction band is dominated by Coulomb blockade due to the high Scottky barriers. Inset: Four-fold Coulomb blockade structure. (b) Bias spectroscopy plot from a small region of (a) showing Fabry-Perot interference pattern through the valence band. Note, that the color scale is reversed compared to the case of Coulomb blockade for clarity. The level spacing is $\Delta E \sim 4 \text{meV}$, while the distance between two resonances is $\Delta E + 4U_c$ due to the continuous charging of the device. (c) Single electron transport through the conduction band (from small region in (a)) with four period structure indicated by relative electron filling.
Figure 3.11: Bias spectroscopy plot at 4 K showing Fabry-Perot oscillations with the four degenerate level structure visible as 4 peak in each resonance for another small band gap semiconducting SWCNT. The level spacing is $\Delta E \sim 3-4 \text{meV}$, while the distance between two resonances is $\Delta E + 4U_c$.

blockade diamonds and excited states are observed. The numbers indicate the relative filling of the SWCNT quantum dot, where a number divisible by four corresponds to a filled shell. The shell consists of a four-fold degenerate level due to orbital and spin degrees of freedom. The charging energy can be extracted from the three small diamonds as half the height $U_c \sim 11 \text{meV}$. The orbital splitting is very small since the small diamonds are almost equal in height. Every fourth diamond is bigger (shell filled) and the additional diamond height is the level spacing yielding $\Delta \sim 3 - 5 \text{meV}$. This is consistent with the level spacing identified from the excited lines in the stability diagram.

The band gap can not be clearly identified properly due to interaction with the substrate in close contact with the SWCNT. For very few electrons/holes on the SWCNT no screening is possible, while the transport properties seem much more regular at higher filling (more negative/positive gate voltages) where screening is possible. The observation of the first hole and electron has been observed very clearly in Ref. [36].

Figure 3.11 shows a bias spectroscopy plot in the p-type region for another small band gap semiconducting SWCNT. Fabry-Perot oscillations are also observed, but each Fabry-Perot resonance is split into four smaller peaks. These peaks are sign of Coulomb blockade and single hole tunneling, i.e., the four-fold degenerate shell is being split due the quantization of the charge.

This is even more clearly revealed in the linear conductance versus gate voltage shown in Fig. 3.12. All three curves are extracted around zero bias from the bias spectroscopy plots in the p- or n-type region of the two small
3.3. FABRY-PEROT INTERFERENCE IN SWCNTs

Figure 3.12: Linear conductance for three different "devices" at 4 K, where the behavior evolves from Fabry-Perot to Coulomb blockade resonances because of worse coupling to the leads. The red curve shows broad Fabry-Perot resonances from Fig. 3.10b with no single hole charging effects, while the four periodicity becomes visible due to Coulomb blockade for the black curve from Fig. 3.11. This structure is even more evident when the coupling is more weak. The red and blue curves are translated along the gate axis, but not scaled.

band gap semiconducting SWCNTs presented above. The most conducting device (red curve) shows broad Fabry-Perot oscillations with no sign of single hole transport consistent with the number of holes not being an integer on the SWCNT due to the relatively good coupling. When the coupling to the SWCNT weakens, the holes become more defined on the SWCNT and signs of single hole transport is observed. Each broad Fabry-Perot resonance splits up in four peaks consisting with each resonance (level) being four-fold degenerate. For even weaker coupling a quantum dot is formed (in this example electrons are the carriers). The three curves are not scaled but only shifted along the gate axis. Similar observations have been made by Cao et al. on very clean suspended small band gap semiconducting SWCNTs, where the conduction in the p-type region is related to the band gap of the SWCNT [41]. A bigger band gap leads to a bigger Schottky barrier. It is not clear on the two devices presented above, since the band gap is difficult to identify.

We have also observed Fabry-Perot like oscillations in metallic SWCNTs
with conductance around $\sim 3e^2/h$. A regular interference pattern is only visible in a small gate region, which might be due to non perfect SWCNT. However, according to Cao et al. on their very clean SWCNTs, the Fabry-Perot interference pattern is less clear in metallic SWCNTs [41]. We also present measurements on a highly conducting SWCNT device with superconducting leads in the Fabry-Perot regime in chapter 7.
Chapter 4

Introduction to SWCNT weak links

The results and theory discussed so far have been concentrated on the transport properties of single wall carbon nanotubes (SWCNTs) with normal metallic leads (N). We now turn our attention to another favorable aspect of carbon nanotubes. They provide a low-dimensional system, which is easily contacted to materials with different properties. The materials can for instance be ferromagnetic metals/semiconductors (F) or superconductors (S). This new degree of freedom creates a wealth of possible device configurations by choice of electrode material (e.g. F-SWCNT-F [63, 64, 65], S-CNT-N [66]). The nanotube bridging the contacts can be a semiconducting SWCNT, a metallic SWCNT or a multi wall carbon nanotube. The device can furthermore be examined in different transparency regimes and in a two or four terminal configuration [67]. Such systematic investigation of carbon nanotube zero- or one-dimensional systems contacted to leads with specific properties has just begun.

4.1 SNS junctions with size and charge quantization

Below we focus on superconductor-normal-superconductor junctions (SNS), where the normal part is a SWCNT [68, 69, 70, 71, 72, 73, 74, 75, 76, 77]. SNS junctions, also called weak links, have been studied extensively in the 60/70ties [78] and had a revival during the nineties due to the improved top-down fabrication methods, which carried the devices into the field of mesoscopic physics. Reflectionless tunneling [79, 80] and quantization of supercurrent [81, 82] were among the many novel effects observed in mesoscopic
superconductivity.

Before going into the physics of S-SWCNT-S junctions a short introduction to conventional SNS junctions will be given. This gives the basis for the discussions in the following chapters.

Two effects are important when considering a weak link. The most well known is probably that a dissipationless current (supercurrent) can flow through the system, *i.e.*, a current $I_s$ flows at zero bias voltage. This effect is called the DC-Josephson effect and was predicted and measured by Josephson in 1962. Its most simple form is given by [83]

$$I_s = I_c \sin(\Delta \phi) \quad (4.1)$$

where $I_c$ is the maximum supercurrent (critical current) the weak link can sustain and $\Delta \phi$ is the phase difference between the superconductors. A finite voltage across the junctions makes the phase "run" at high frequencies described by the AC-Josephson relation [83]

$$\frac{d}{dt} \Delta \phi = \frac{2e}{\hbar} V \quad (4.2)$$

The supercurrent will thus be smeared when applying a bias.

The other effect is the so-called sub-gap structure (SGS) in current (or $dI/dV$) versus bias [84, 85, 86]. Contrary to the DC-Josephson effect the SGS is observed at finite bias and is due to Andreev reflections (ARs) [87, 22]. An electron in the normal region impinging on the superconductor has a probability of being Andreev reflected as a hole, transferring two electrons to the condensate of the superconductor as a Cooper pair. This process requires energy conservation and an initial electron above the Fermi energy of the superconductor is thus reflected as a hole equally below the Fermi energy. An electron is most likely to be Andreev reflected within the gap of the superconductor provided good transparency between the normal region and the superconductor [88].

In a SNS junction, an electron has a probability to be AR on one superconductor followed by an AR of the reflected hole on the other superconductor and so forth. Such processes are called multiple Andreev reflections (MAR) and lead to the above mentioned SGS at certain voltages given by

$$V_{sd} = \pm \frac{2\Delta}{en}, \quad n = 1, 2, 3, .. \quad (4.3)$$

For $n = 1$ ($eV_{sd} = \pm 2\Delta$), quasiparticles (QPs) can tunnel from the peak in the density of states (DOS) of one superconductor to the other, while at slightly lower voltages this process is forbidden. Similarly, the bias corresponding to $n = 2$ ($eV_{sd} = \pm \Delta$) is the cutoff bias for processes involving only
one Andreev reflection. This closing of Andreev channels gives rise to a SGS at the above defined bias values. The SGS has been treated theoretically, incoherently in Refs. [84, 85] and coherently in Ref. [86].

We now want to consider, what happens in a SNS-junction, when size and charge quantization are taken into account. In this context three new energy scales are introduced that have not been part of the vast experimental and theoretical work on conventional weak links [78]. First, transport takes place through one or more discrete levels separated by \( \Delta E \) having a natural line width \( \Gamma \). Second, the electron interaction is represented by the Coulomb energy \( U_c = e^2/C \), where \( C \) is the capacitance of the quantum dot (SWCNT). Here we assume that temperature is smaller than the above mentioned energy scales, which mostly is the case for measurements at cryogenic temperature. The mutual relation between these two parameters (\( \Delta E, U_c \)) and the superconducting energy gap \( \Delta \) defines different transport regimes. In the devices presented in the following chapters the level spacing is bigger than the superconducting energy gap (\( \Delta E \gg \Delta \)) and transport within the gap can be thought of as resonant transport through one level.

For a SWCNT resonant weak link the DOS is made of resonant levels due to size quantization (phase coherence). This corresponds to a S-SWCNT-S with good contacts, i.e., an open quantum dot \( \Delta E > \Gamma \gg U_c \) or equivalent a Fabry-Perot (electron/hole) waveguide. Coulomb blockade is thus not important. Two regimes are defined called the short and long regime [89]

- Short resonant weak link: \( \Gamma \gg \Delta \)
- Long resonant weak link: \( \Gamma \ll \Delta \)

The critical current is given in terms of the Breit-Wigner transmission probability and depends on the regime [90, 89]

\[
I_{c,\text{short}} = 2\frac{e\Delta}{\hbar} [1 - (1 - T_{BW}(\epsilon))^{1/2}] \tag{4.4}
\]

\[
I_{c,\text{long}} = 2\frac{e}{\hbar} [\epsilon^2 + \frac{1}{4} \Gamma^2]^{1/2} [1 - (1 - T_{BW}(\epsilon))^{1/2}] \tag{4.5}
\]

where the Breit-Wigner formula is \( T_{BW}(\epsilon) = \Gamma_1 \Gamma_2 / (\epsilon^2 + (\Gamma/2)^2) \), \( \epsilon = 0 \) corresponds to the resonance condition and \( \Gamma = \Gamma_1 + \Gamma_2 \) with \( \Gamma_1 \) and \( \Gamma_2 \) being the coupling to the left and right lead, respectively. The factor of 2 in Eqs. (4.5) and (4.5) stems from the two spin degenerate channels (orbitals) in the case of a SWCNT. For short resonant weak links, the critical current at resonance yields \( I_{c,\text{res}} = 2e\Delta / \hbar \). This is equivalent to the value for a (two channel) superconducting quantum point contact\(^1\) [81]. Off resonance, the

\(^1\)This is true in the short regime for quantum point contacts defined in Ref. [81].
supercurrent decays differently in the two regimes according to the above equations. The critical current behaves as \( I_{c}^{\text{short}} \propto 1/\epsilon^2 \) and \( I_{c}^{\text{long}} \propto 1/\epsilon \) in the short and long regime, respectively. At resonance and equal coupling to the leads (\( \Gamma_0 \)) the two regimes can be bridged by

\[
I_{c}^{\text{res}} = 2e \frac{\Gamma_0 \Delta}{\hbar \Gamma_0 + \Delta}
\]

Coulomb blockade effects generally suppress the critical current by a factor of \( \Gamma/\Delta \) [91, 89]. However, in the short regime, when the number of electrons on the dot is odd (net spin 1/2 on the dot), the Kondo effect becomes important. The Kondo effect sets up a resonance with width \( \sim T_K \) and in some sense turns off Coulomb blockade around the Fermi energy. The Kondo temperature \( T_K \) now becomes the relevant parameter (not \( \Gamma \)). Thus a resonance exists in the CB diamond to carry the supercurrent for \( k_B T_K > \Delta \).

Note, that the Kondo temperature (width of resonance) is minimum in and symmetric around the center of an odd numbered CB diamond and changes according to Eq. (3.7). The interplay between Kondo/CB and supercurrent is the topic of chapter 6 and (has been) is under intense theoretical interest [91, 92, 93]. To our knowledge these are the first experiments addressing that regime.

We now want to consider qualitatively how the SGS is modified by size quantization based on models available in the literature. Theoretical [94, 95, 96] and experimental [72, 73] work on a resonant level contacted to superconductors have already been addressed by some groups. In the model introduced the charging energy is neglected and the relation between the different energy scales become

\[
\Delta E \gg \Delta > \Gamma \gg U_c
\]

Note, that the line width of the level is (much) smaller than the superconducting gap for the effect to be pronounced. Consider a symmetric weak link with equal capacitive coupling and tunneling rates to the left and right lead\(^2\).

Figure 4.1 shows a schematic plot of \( dI/dV \) as a function of the level position and positive bias of the SGS around a resonance deduced from Ref. [95]. The level is at resonance for \( e\alpha V_{\text{gate}} = 0 \), where \( \alpha \) is the conversion factor from gate voltage to energy. It is assumed that increasing the bias by \( V_{sd} \) shifts the resonance by \( V_{sd}/2 \) placing it midway between the chemical

---

\(^2\)It is further assumed that the junction is in the short clean limit defined for a quantum point contact as \( \xi_N \gg L, \xi_N > l_m \), where \( L \) is the length of the normal region, \( \xi_N = h\nu_f/k_B T \) and \( l_m \) are the clean limit coherence length and the mean free path in the normal region, respectively.
4.1. SNS JUNCTIONS WITH SIZE AND CHARGE QUANTIZATION

Figure 4.1: Simplified schematic of $dI/dV$ versus positive bias and gate voltage showing the SGS for a S-resonant level-S junction close to resonance deduced from Ref. [95] ($\Gamma \ll \Delta$). Coulomb blockade effects are not taken into account in this model. The dashed horizontal lines correspond to the SGS for a non-resonant junction, while the colored lines indicate the new SGS close to resonance. At resonance the even order MAR are predicted to be suppressed, while the odd order are enhanced. Close to resonance the SGS (MAR processes) are gate dependent. The solid black lines indicate the onset of quasiparticle (QP) tunneling, while a new strong resonance develops when the level is aligned to the Fermi level in one of the leads (pair current). Higher order MAR processes are also gate dependent. The length of the lines do not indicate an abrupt cut-off of the process. The lines are merely drawn to illustrate the complicated behavior of the SGS close to resonance.

Potential of source and drain due to the equal capacitive coupling.$^3$ The horizontal dashed lines mark the position $V_n = 2\Delta/e\alpha$, $n = 1, 2, 3$ for MARs in a non-resonant junction. The solid lines indicate a gate dependent SGS around the resonance (within a few $\Delta$), where only the lowest order processes have been drawn.

At $V_{sd} \geq \Delta$ a strong resonant line (red) due to resonant pair tunneling is seen. This appears when the level is aligned to the chemical potential in one of the leads allowing one AR.$^4$ The condition for pair current is identical to being in normal resonance, i.e., following the edges of a CB diamond.

The higher order odd MAR lines also shifts outward as shown giving rise to a very rich structure at low bias.

$^3$In our experimental setup, the bias is applied asymmetrically, but often we have $C_{gate} \ll C_s, C_d$ and $C_s \sim C_d$. This makes the setup approximately equal to symmetric biasing.

$^4$The resonance is actually a peak in the current and thus also shows negative differential conductance (not shown in the figure).
CHAPTER 4. INTRODUCTION TO SWCNT WEAK LINKS

Figure 4.2: Energy diagrams illustrating the gate dependence of MARs around resonance for a resonant junction. The resonant level is given by a Lorentzian function, horizontal black arrows represent electrons while red arrows are holes. (a) At resonance the onset of quasiparticle (QP) tunneling happens at $eV_{sd} = 2\Delta$. (b) Off resonance ($e\alpha V_{\text{gate}} = \phi_0$) QP tunneling is not possible at $eV_{sd} = 2\Delta$ due to no state available for tunneling. (c) At $eV_{sd} = 2\Delta + 2|e\alpha V_{\text{gate}}|$ QP tunneling through the level becomes possible again. The onset of QP tunneling is thus shifted to higher bias. (d) At resonance one Andreev reflection at $eV_{sd} = \Delta$ ($n = 2$) does not tunnel through the level and is thus suppressed (true for all even $n$). (e) For $eV_{sd} = 2\Delta/3$ at resonance, two Andreev reflections ($n = 3$) are possible, since they connect source and drain through the level (true for all odd $n$). Only ARs starting with an electron are shown for clarity.

The gate dependence of the different processes can intuitively be understood in case of the QP tunneling $n = 1$ (black line). The onset of QP tunneling at resonance is at $eV_{sd} = 2\Delta$, while the onset shifts to higher bias voltages when the level is moved away from resonance. At resonance the QPs tunnel through the level from the peak in the DOS of the source to the peak in DOS of the drain (Fig. 4.2a). However, when the level is shifted off resonance these processes are no longer allowed (only through cotunneling) as shown in Fig. 4.2b. The onset is instead shifted to higher bias voltage, since the level is aligned to the peak in the DOS of the drain by increasing the bias voltage further (Fig. 4.2c). The condition for alignment reads $eV_{sd} = 2\Delta + 2|e\alpha V_{\text{gate}}|$. If the device is rather transparent and cotunneling is allowed the $2\Delta$ line will not be shifted. In experiments the gate dependence of the MAR resonances leads to the impression that the SGS turns to lower biases close to resonance [73]. A similar behavior is seen in our measurements presented below, but whether it is due to the above effect is still to discuss. Note, that the onset of quasiparticle tunneling corresponds to the edges of the CB diamond.

At resonance, the even order MARs are theoretically predicted to be sup-
pressed while the odd order are enhanced [96, 95]. The suppression of even
$n$ processes can be qualitatively understood from Fig. 4.2d. It shows that
the $n = 2$ MAR process at resonance does not tunnel through the level and
is thus suppressed. On the contrary, odd order MARs connect the peaks in
the superconducting DOS of the leads through the level (Fig. 4.2e).

When CB is dominant $U_c \gg \Gamma$ the characteristics will be like a tunnel junc-
tion and only single particle tunneling will be possible [97]. No simultaneous
transfer of a Cooper pair is allowed. MAR processes ($n \geq 2$) will be highly
suppressed if cotunneling processes are not contributing ($\Gamma$ small), since a $n$
order MAR involves $n$ charges and the energy cost is $\sim nU_c$.

Consider now the regime $U_c, \Delta E > \Gamma$, where $\Gamma$ is increased so
cotunneling is significant and the MAR processes can happen through cotunneling.
Quasiparticle tunneling ($n = 1$) would be a second order process, while one
AR ($n = 2$) would be a fourth order process and so fourth. Part of the data
presented below will be in this regime.
Chapter 5

S-SWCNT-S weak links in the closed quantum dot regime

5.1 Tunnel-like behavior in closed SWCNT quantum dots

The main reason to include the following measurements is to display data in the "less interesting" regime with $U_c, \Delta E > \Delta \gg \Gamma$, where all higher order Andreev reflection processes are suppressed by Coulomb blockade and a tunneling characteristic is observed as expected. This regime has previously been studied with superconductors coupled to an aluminum particle [98] and to SWCNT [99]. Figure 5.1 shows a bias spectroscopy plot of a S-SWCNT-S quantum dot measured at $T = 300 \text{ mK}$ below the critical temperature of the leads\(^1\). Here the leads are made of a Pd/Nb/Pd trilayer with the layers being 4 nm, 70 nm and 10 nm from below. The device shows a clear regular Coulomb blockade diamond structure with 83 electrons added to the quantum dot in the gate range measured. No four-fold pattern is observed, but the regular pattern indicates a high quality metallic SWCNT. From the Coulomb diamonds a charging energy of $U_c \sim 5 - 7 \text{ meV}$ and a level spacing of $\Delta E \sim 1 - 3 \text{ meV}$ are deduced. The latter is estimated from the relative few excited states visible. Furthermore, a very rough estimate of the line width $\Gamma \sim 10 \mu \text{V}$ can be extracted from the current plateau of the ground state in the VI curves assuming equal coupling.

A gap in differential conductance is observed around zero bias, which is most pronounced at/close to all the resonances (charge degeneracy point). Such tunnel characteristic is consistent with the low transparency contacts

\(^1\)This chapter has been used as part of the data presented in Ref. [100].
between the SWCNT and the leads because Andreev reflections are suppressed.

In Fig. 5.1b this tunnel-like behavior is more clearly revealed in a zoom of a few Coulomb diamonds. The green arrows point to the horizontal lines attributed to the onset of QP tunneling \( V_{sd} = \pm 2\Delta \sim \pm 550 \mu V \) reflecting the peaks in the density of states of the superconductor. The onset of QP tunneling is most visible when the level in the dot is resonant with the Fermi level in the source and drain, but it is also visible in regions of Coulomb blockade. In the latter case the QPs tunnel via cotunneling. This behavior is consistent with the model of Fig. 4.1 in each resonance, where the only lines clearly distinguishable are the \( 2\Delta \)-lines corresponding to black lines in the model starting at \( eV_{sd} \sim 2\Delta \).

Figure 5.1c shows cuts at two different gate voltages. Position A is in res-
5.1. TUNNEL-LIKE BEHAVIOR IN CLOSED SWCNT QDs

onance while position B is slightly off resonance. The onset of QP tunneling is clearly visible in both cases but suppressed off resonance due to Coulomb blockade and the sharpness of the level ($\Gamma \ll U_c, \Delta E$). The peaks at higher bias voltages are due to tunneling through the ground state (GS) and the first excited state (ES) of the QD.

Slightly off resonance (black curve) no higher order Andreev reflection processes are visible for $|V_{sd}| < 2\Delta$ as expected due to suppression by Coulomb blockade. One AR would be a fourth order process in the CB region and is thus highly suppressed. At resonance some structure is visible at low bias, which could be due to higher order ARs. In fact all the even order (n) MAR processes should be suppressed at resonance [96, 95, 94, 73], while the odd MARs are enhanced. The features (red arrows) at $|V_{sd}| \sim 110\, \mu V$ might stem from higher order MAR. It is also seen that the $2\Delta$ lines seem to be at slightly higher bias off resonance than in resonance. Even though a supercurrent through a quantum dot has been predicted theoretically [91], we observe no sign of it in these measurements.

A remark on the superconducting trilayer is necessary. The Pd/Nb/Pd leads do not have the same critical temperature throughout the different layers. The niobium layer has a transition temperature around 9 K measured on a four terminal device. However, the lower palladium layer has much lower transition temperature measured by the temperature dependence of the SGS in the bias spectroscopy plot of the SWCNT device. We believe this behavior is due to an interface between the Nb and the Pd layers that limits the proximity effect of the Nb into the Pd layer below. Similar effects have been observed in Ti/Nb/Ti trilayers.

The maximum magnetic field that can be applied in this setup is 2 T. At this field the superconductors are not driven normal. A small supercurrent is observed on a four terminal reference device.
5.2 Sub-gap structure in closed SWCNT QDs

Below we present data from another device in the Coulomb blockade regime (closed quantum dot), where the SWCNT is slightly better coupled to the leads. The coupling is typically $\Gamma \sim 200 - 400 \mu$eV estimated from the width of the Coulomb blockade peaks. Thus some SGS due to MARs is present. Figure 5.2a shows a bias spectroscopy plot of a SWCNT coupled to superconducting Ti/Nb/Ti electrodes at 6 K above the critical temperature.

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Note, that the estimate is made in the superconducting state, since the superconducting electrodes are not driven normal by the magnetic field $B = 2\, \text{T}$ available in the setup.

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Figure 5.2: (a) Bias spectroscopy plot of a metallic SWCNT device coupled to Ti/Nb/Ti electrodes at $T \sim 6\, \text{K}$. The device has regular Coulomb oscillations in the whole measured range $|V_{\text{gate}}| < 10\, \text{V}$, but only a part of the positive gate voltage is shown. In this region a four-fold shell filling is indicated with relative electron numbers. For negatives gate voltage the device has even/odd filling. (b) When the leads are superconducting a sub-gap structure appears at low bias ($T \sim 0.3\, \text{K}$). The sub-gap structure changes in each resonance and for every fourth diamond it is squeezed as pointed to by the vertical green arrows. At higher bias $V_{sd} \sim \pm 2\, \text{mV}$ gate dependent features probably due to inelastic cotunneling is seen.
of leads $T_c \sim 1.6$ K. The layers are 4 nm, 70 nm and 10 nm starting from the bottom Pd-layer and Nb is deposited by Ar-sputtering technique. Clear Coulomb blockade diamonds are observed and arranged in a four-fold shell structure, where a number dividable by four corresponds to a filled shell. A charging energy of $U_c \sim 12$ meV and a level spacing of $\Delta E \sim 6$ meV are extracted in the same way as chapter 3.1. A gate coupling factor of $\alpha \sim 0.058$ is also deduced (see chapter 3.1). Furthermore, the two orbitals are split by a small energy $\delta \sim 1$ meV much smaller than the other energies (see below). The whole gate range (not shown) is well behaved and the counting of electrons added to the quantum dot starts at $V_{\text{gate}} \sim -10$ V. For negative gate voltages the shell structure changes to be even/odd filling, i.e., large orbital splitting.

Figure 5.2b shows a bias spectroscopy plot for the same gate range, but at relatively small bias voltages at 0.3 K, when the leads are superconducting. A clear SGS is seen throughout the gate voltage range, which is attributed to QP tunneling and MARs. Up to six distinct horizontal lines are observed in some of the diamonds (e.g. diamond 63). The lines at $V_{\text{sd}} \sim \pm 0.5$ mV are due to the onset of QP tunneling, while the lower bias lines are believed to involve ARs. The overall gate voltage dependence of the low bias lines, which shift slowly to higher bias and fade increasing the gate voltage is not understood. No such gate dependence has been observed for negative bias voltages.

Furthermore, an interesting behavior is observed for every fourth diamond (green arrows), where the SGS is very gate dependent and pronounced around the respective resonances. For some of these diamonds it seems like the SGS is squeezed to lower bias voltages.

Finally, the blue arrows point to gate-dependent features at higher bias voltages above the superconducting gap in the differential conductance. Note, that these are absent when the shells are filled.

We first focus on the low bias features and the diamonds with very pronounced gate dependence of the SGS structure. Figure 5.3a shows a bias spectroscopy plot with addition of 10 electrons for negative gate voltages, where the characteristic features for this device are particular strong. In the range shown a strong orbital splitting leads to an even/odd (E/O) filling as indicated in the bottom of the plot. Counting the number of diamonds from positive voltages (see Fig. 5.2)b, the diamonds corresponding to a filled shell (4, 8 and 12) can be identified.

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3The critical temperature is in this case determined by the horizontal lines in Fig. 5.2b identified as the onset of QP tunneling $eV_{\text{sd}} \sim \pm 2\Delta$ giving a gap of $\Delta \sim 0.25$ meV. In other devices this has been consistent with the SGS disappearing at the corresponding temperature according to BCS-like behavior.
Figure 5.3: (a) Bias spectroscopy plot for the same device as in Fig. 5.2 but for negative gate voltages, where an even/odd electron filling is observed (0.3 K). The relative electron number indicating a filled shell (but orbitally split) is extrapolated from the clear four-fold shell filling at positive gate voltage. The horizontal lines (green arrows) are attributes to MAR and show a clear gate dependence at each resonance. Especially for every fourth diamond with an odd number of electrons on the dot the effect is very pronounced. (b) Linear conductance versus gate voltage showing that the two orbitals are coupled differently, where resonance peaks are spaced. The lifetime broadening of each state is estimated in $\mu eV$). Two strong resonances appear on each side of the diamond with most squeezed MAR lines (3,7 and 11). (c) The addition energy versus electron filling $N + 1$. The energies are extracted from the gate voltage distances for filling $N$. The charging energy is thus $U_c \sim 8 - 12 \, \text{meV}$ and level spacing between spin degenerate levels $\delta E \sim 6 \, \text{meV}$ (5-10 meV). Red circles and black squares correspond to two different measurements (bias spectra).

The bias voltages corresponding to the gate dependent horizontal lines off resonance are $V_{sd} \sim \pm 500 \, \mu V$ and $V_{sd} \sim \pm 190 \, \mu V$ (green arrows). The two outermost lines are assigned to the onset of QP tunneling at $V_{sd} = \pm 2\Delta$. However, it is less clear whether the lower bias lines are due to one or two Andreev reflections. For non-resonant junctions, MAR lines appear at $V_{sd} =$
with $n = 2$ and $n = 3$, respectively. The corresponding bias voltages are $V_{sd} = \pm 250 \mu V$ and $V_{sd} = \pm 167 \mu V$ inconsistent with the above value.

It should also be taken into account that the MAR processes are suppressed by Coulomb blockade as mentioned above. An MAR process of order $n$ (i.e., $n - 1$ ARs) involves a $n$th order tunneling process. Thus a process involving one AR ($n = 2$) is a second order process. Off resonance (e.g. center of diamond), the MAR tunneling processes happen via cotunneling and one AR becomes a fourth order process.

In a resonant junction without Coulomb blockade the even order MAR processes are theoretically predicted to be suppressed at resonance [95], but this should not be the case off resonance. We thus can not explain the absence of the $n = 2$ MAR process and assign the lower lying lines (with the present understanding) as the $n = 2$ process due to its much higher probability than $n = 3$. The discrepancy between theory and experiment is not understood. To our knowledge no theory exists that incorporate MARs in a Coulomb blockaded resonant system for relatively low transparency.

Another characteristic feature in Fig. 5.3a is that the SGS (MAR lines) turns inwards at all resonances, which (at first sight) seems consistent with the behavior predicted for a resonant junction shown in Fig. 4.1 [95, 96]. However, this turning is much more pronounced for every fourth diamond. These diamonds correspond to an odd electron filling (filling of 3 electrons in a shell) on the quantum dot. Furthermore, the peak conductance of the resonances around these diamonds is generally broader than the following two resonances seen from the linear conductance versus gate plotted in Fig. 5.3b. This indicates that the two orbitals originating from different bands are coupled differently to leads. The numbers indicate the lifetime broadening of the orbitals (in the superconducting state).

Furthermore, the SGS inside every fourth diamond (3, 7 and 11) is squeezed to lower bias voltage. The strength of this shift varies but the effect is strongest for electron filling 3. This behavior is at present not understood. It seems to happen for the better coupled orbital, when the orbital is occupied with only one electron. The MAR lines are due to cotunneling, but it is not clear why cotunneling with one electron in the orbital in this context is fundamentally different from having two electrons. The most clear distinction between these two states (one or two electron in the orbital) is that for odd filling the quantum dot has a net nonzero spin $S = 1/2$, i.e. Kondo effect. Whether this is important for the shown squeezing effect is a subject for further discussions.

Similar to above, the inward turning of the SGS is very dependent on the particular resonance. When the resonances have a high linear conductance, the energy scales for the turning is enhanced.
Figure 5.4: Bias spectroscopy plot in units of $\Delta$ around charge degeneracy points. (a) Between electron filling 3 and 4, and (b) between 4 and 5 in Fig. 5.3. The sub-gap structure is gate dependent around resonance in both cases, but the turning of the MAR lines takes place over $10-15\Delta$ and $5-8\Delta$ in (a) and (b), respectively. These energy scales seem to be related to the coupling of the orbital. The discontinuity in the color scale at $V_{\text{gate}} \sim 10\Delta$ in (a) is due to a correction for a gate switch.

The addition energies shown in Fig. 5.3c are extracted from two different measurements (black squares and red circles). A charging energy of $U_c \sim 8-12$ meV and a level spacing between spin degenerate levels of typically $\Delta E \sim 6$ meV are found.$^4$

The gate dependence at resonance is now treated more quantitatively. Figure 5.4a shows the behavior of the SGS around the strong amplitude resonance for electron filling 3 and 4 on the dot. The bias and the gate voltage are plotted in units of the superconducting gap deduced from the $2\Delta$ line off resonance. The turning of MAR lines happens over an energy scale of $10-15\Delta$, which is much larger than the expected few $\Delta$, if the effect is to be explained solely by the resonant nature of the junction (see Fig. 4.1). Furthermore, as pointed out above, it is seen that the $2\Delta$ lines off resonance are at very different bias values depending on the orbital through which the cotunneling takes place, i.e., electron filling 3 and 4.

The turning of the MAR lines happens at smaller energy scales in the case of the lower amplitude resonance between electron filling 4 and 5. From Fig.

$^4$Note, that the level spacing $\Delta E$ is reserved for the level spacing between four completely degenerate levels. In this case it is more convenient to state the level spacing between the spin degenerate levels, because the orbital splitting $\Delta E \sim \delta \sim 1/2\Delta E$. 

(continued)
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Figure 5.5: Bias spectroscopy plot measured with lock-in technique showing a representative filling of one shell (81-84) for positive gate voltages. Electron filling (80 and) 84 correspond to a filled shell. Gate dependent inelastic cotunneling lines are visible for 1, 2 and 3 electrons in the shell, while they are absent for a filled shell. This is consistent with inelastic cotunneling through slightly split orbitals. The gate dependence is not understood.

5.4b it is estimated to be $5 - 8\Delta$. However, it is still larger than the range expected for a resonant junction.

This discrepancy in the energy range of the turning of MAR lines and its origin is not fully understood at the moment. However, the effect of Coulomb blockade is not included in the model to which the experiment is compared.

Due to the above mentioned discrepancy with the model of the SGS through a level (Fig. 4.1), we speculate on an alternative explanation. The turning of the SGS in resonance could be due to an inverse proximity effect, where the normal region (SWCNT) suppresses the proximity induced superconductivity and thus the superconducting gap in the thin lower Pd layer. The MAR lines would move inwards following the suppression of the superconducting gap. This would be pronounced at resonance due to the better coupling to the leads. The effect would also be strongest for the better coupled orbitals. Furthermore, the odd numbered diamonds (well coupled), where an additional squeezing of the diamond is seen (every fourth) could be due to an interplay with the Kondo effect. The Kondo temperature and thus the width of the Kondo resonance increases from the center of a diamond towards a resonance, where the overall strength is given by the width of the normal resonance. Thus for a well coupled orbital with one electron, a relatively
Figure 5.6: Energy diagrams to explain inelastic cotunneling through two split orbitals constituting one shell. Blue and red level represent the two spin degenerate orbitals split by an energy $\delta$. Coulomb blockade blocks single electron transport through the quantum dot. (a) One electron is in the shell (lowest orbital). An inelastic cotunneling event is possible when the bias is $eV_{sd} = 2\Delta + \delta$. A quasiparticle in the left lead tunnel into the orbital with highest energy, while the electron already in the shell tunnels out into the empty state above the gap in the right lead conserving energy. (b-c) Similar processes are possible with two and three electrons on the quantum dot as shown. (d) The same process is not allowed when the shell is filled. Only elastic cotunneling processes are allowed. An electron on the dot tunnels out provided that a quasiparticle tunnels into the same state. This is allowed for $V_{sd} = 2\Delta$.

strong (Kondo) resonance exists throughout the CB diamond which might allow for the inverse proximity as well. The stronger the normal resonance, the stronger the Kondo effect (higher $T_K$) qualitatively consistent with the observed behavior of Fig. 5.3. This might explain the energy scales involved and the ”selection” of every fourth diamond. Note, that no zero bias Kondo features are seen in the measurements. However, the superconductor can not be turned off and for $k_B T_K < \Delta$ the Kondo effect is expected to be suppressed by superconductivity [72]. No quantitative analysis has been made to confirm/falsify this picture yet.

Next we return to the high bias features above the superconducting gap. These are believed to be due to inelastic cotunneling through two slightly split orbitals. They are not directly related to superconductivity, but the sharp QP peaks in the DOS of the superconductors at $\pm\Delta$ represent a sensitive tool to probe for instance inelastic cotunneling.

In Fig. 5.2b inelastic cotunneling lines are not observed, when the shells are filled (60, 64,.., 84). This behavior is shown for one shell from electron
5.2. SUB-GAP STRUCTURE IN CLOSED SWCNT QDs

filling 80-84 in Fig. 5.5 (detailed lock-in measurements). The numbers 1-4 indicate the number of electrons in the shell and gate dependent lines are observed for filling 1-3.

These lines are explained by inelastic cotunneling through orbitally split levels as shown in Fig. 5.6. For one electron in the shell an inelastic cotunneling process is depicted in Fig. 5.6a. Single electron tunneling is not allowed, because the charging energy is much larger than the bias window (and the gap). However, when the bias voltage is \( eV_{sd} = 2\Delta + \delta \), a QP just below the gap in the left lead can tunnel onto the highest orbital provided that the electron in the other orbital tunnels out to an empty state above the gap in the right lead. Such a cotunneling process leaves the dot in an excited state and is therefore called inelastic. A similar process is allowed when two and three electrons are in the shell as shown in Fig. 5.6b-c.

When the shell is completely filled only elastic cotunneling processes are possible. An electron on the dot tunnels to the right lead provided that a QP in the left lead tunnels onto the dot. The only available state is the just emptied. The energy difference required in this case is only \( eV_{sd} = 2\Delta \), while it is \( eV_{sd} = 2\Delta + \delta \) for inelastic cotunneling as stated above. From the latter and the position of the features in the bias spectroscopy plot an orbital splitting of \( \delta \sim 1 \text{ meV} \) is estimated for this shell.

This inelastic tunneling picture provides a strong explanation for the absence of finite bias lines for filled shells. For negative gate voltages the inelastic cotunneling lines move to higher bias voltages consistent with larger orbital splitting (even/odd shell filling).

However, the asymmetric gate dependence of these inelastic cotunneling lines is still not understood. It is not clear whether Andreev dynamics plays a role for inelastic cotunneling and similar gate dependent structure could be expected as for a resonant junction. Another explanation could be that the orbital splitting \( \delta = \delta(V_{\text{gate}}) \) is gate dependent. More analysis (and data) are needed to understand the full behavior of the observed features.

Furthermore, the inelastic cotunneling lines seem to come in doublets or triplet (Fig. 5.5). This might be partly explained by introducing an exchange coupling as well [26]. Additional high resolution experimental data is needed prior to such analysis\(^5\).

All the features of the device presented above persist at a magnetic field of 2 T, but become blurred. This is consisting with the superconducting trilayer still being superconducting confirmed by measuring a supercurrent on a four terminal device on the same chip. Thus a very high field is needed to break

\(^5\)The bias spectroscopy plot shown is the only high resolution data (lock-in) measured on this sample.
down superconductivity in these thin films consisting of niobium. Obviously, the above features could be understood better if the superconductivity in the leads could be suppressed, but the setup only allowed for a magnetic field of 2 T. This high critical field is in contrast to the critical field of leads being made of aluminum as presented in the next chapters. The aluminum film has a critical field around 100 mT, which allows to turn off and on the superconductivity in the leads. Finally, we note that no supercurrent has been observed in this low contact regime.

In conclusion the Andreev dynamics of a SWCNT quantum dot coupled to superconducting electrodes have been examined in the regime where both the resonant nature and Coulomb blockade effects of the junction determine its transport properties. A SGS highly dependent on the electron filling is observed. The SGS between high/broad linear conductance resonances is significantly modified compared to between low/narrow linear conductance resonances. The energy scale at which the SGS ”turns inward” is not consistent with a resonant junction alone and maybe cotunneling MAR processes have to be included to describe the effects. An alternative explanation of an inverse proximity effect in combination with the Kondo effect to explain the behavior is suggested. More collaboration with theorists in the field is needed to analyze the above presented data more thoroughly. Furthermore, an experimental investigation of this device and five other promising devices showing clear Coulomb blockade structure (see appendix B) is planned in a dilution fridge. Unfortunately, the transport dewar in which the $^3$He cryostat was mounted for these measurement ran out of Helium during the measurements of the device. Finally, gate dependent inelastic cotunneling lines in the differential conductance versus bias and gate voltage is observed.
Chapter 6

S-SWCNT-S weak links in the Kondo regime

This chapter\(^1\) treats single wall carbon nanotubes (SWCNT) coupled to superconducting leads in the intermediate transparency regime \((\Gamma \sim U_c)\), where several complicated many-body effects are present at the same time. It can be viewed as an extension of previous work on MWCNTs coupled to superconductors also in the Kondo regime \([72]\). The authors examine the interplay between the Kondo effect and superconductivity by linear conductance measurements. Superconductivity (proximity of the superconducting electrodes) and the Kondo effect indeed show to have an interesting interplay. For Kondo temperatures bigger than the superconducting gap \(T_K > \Delta\), superconductivity in the leads enhances the linear conductance compared to the normal state conductance. On the other hand when \(T_K < \Delta\), the linear conductance in the superconducting state is suppressed. We have found very similar behavior in more than 10 analyzed Kondo ridges\(^2\). These data will not be presented in this thesis, where we instead focus more on the supercurrent and its interplay with Kondo resonances, quantized energy spectra and Coulomb blockade. We emphasize that this regime is very interesting but also very complicated, because of the number of effects present at the same time: Multiple Andreev reflections (MARs), supercurrent, four-fold degenerate discrete level structure, Kondo resonances and Coulomb Blockade. As briefly discussed in chapter 4 for some of these effects a complicated behavior is predicted.

With this in mind we now present studies of MARs and a narrow zero bias

\(^1\)This chapter is available as a preprint in similar form on condmat/0601371: K. Grove-Rasmussen, H. Ingerslev Jørgensen, P.E. Lindelof , ”Interplay between supercurrent and Kondo effect in single wall carbon nanotube Josephson junctions “.

\(^2\)Some of them are from Fig. 3.7.
conductance peak interpreted as a supercurrent in a gated SWCNT quantum dot (QD) fabricated by conventional top-down fabrication methods. The supercurrent is shown to have very strong dependence on the four-fold shell filling having maxima at normal resonances (CB peaks) and sufficiently broad Kondo resonances, while being gradually and abruptly suppressed entering regions of Coulomb blockade and narrow Kondo resonances, respectively. This has to the best of our knowledge not been reported before.

SWCNTs are grown from catalyst islands consisting of Fe-oxide and Mo-oxide supported by aluminum nano-particles [32]. Growth is performed by chemical vapor deposition (CVD) at 850°C with a controlled flow of gasses Ar: 1 L/min, H$_2$: 0.1 L/min, CH$_4$: 0.5 L/min. During heating the CVD-oven is kept under an Ar and H$_2$ flow, whereas cooling is done in Ar. We reduce cooling time by air-cooling the CVD-oven. The substrate is a doped silicon wafer (used as back gate) with a 500 nm SiO$_2$ layer on top. Superconducting electrodes of Ti/Al/Ti (5/40/5 nm) are defined directly on top of the SWCNT by electron beam lithography followed by optical lithography to define the bonding pads. The first titanium layer of the metallic trilayer ensures good contact to the SWCNT, whereas the thick middle aluminum layer is the actual superconductor in the device. Finally the top layer of Ti is intended to stop oxidation of the aluminum.

The gap between the source and drain electrode is around 0.5 µm. In the same evaporation process a four-probe device is made next to the S-SWCNT-S devices, which we use to measure the transition temperature $T_c = 760$ mK and the critical field around $B_c = 100$ mT of the superconductor. From BCS theory we deduce the superconducting energy gap $\Delta = 1.75k_BT_c = 115\mu eV$.

We cool the devices in a $^3$He-$^4$He dilution fridge with a base temperature of 30 mK. The measurements are made with DAC-cards, opto-couplers and lock-in amplifiers (AC-excitation voltages 5-10 µV).

At room temperature the current through the device is gate dependent, which shows that the SWCNT is semiconducting. Figure 6.1a shows a bias spectroscopy plot at $T = 30$ mK of the SWCNT in the QD regime. It is measured at negative gate voltages and thus the transport takes place through the valence band. The superconductivity in the leads is here suppressed by a relative weak magnetic field of 180 mT (> $B_c$). The plot shows Coulomb blockade diamonds with a total of 11 holes added to the SWCNT QD (dashed lines are guidelines to the eye). Each diamond has a fixed number of holes on the QD. The Coulomb blockade diamond structure exhibits a four-fold degenerate shell structure due to the spin and orbital degrees of freedom and signifies a high quality nanotube [41]. The filled shells are marked by the relative number of holes on the SWCNT QD. We estimate the charging energy as half the source-drain height of the small diamonds $U_c \sim 4 \mu eV$, and the
Figure 6.1: (a) Bias spectroscopy plot of the SWCNT device showing four fold Coulomb blockade diamonds. The numbers indicate the additional hole filling. The device is measured at 30 mK and in a magnetic field of 180 mT to suppress the superconductivity in the leads. (b) Bias spectroscopy plot for the same gate range as (a) but with a zoom-in around $|V_{sd}| \leq 0.5$ meV. (c) Same plot as (b), but with the leads in the superconducting state, i.e. no magnetic field. A rich sub-gap structure emerges due to MAR. The solid arrows point to the most pronounced supercurrent peaks.
level spacing as the extra height of the large diamonds $\Delta E \sim 4 \text{meV}$ (orbital splitting small) [23]. The horizontal lines at finite bias in the large diamonds are due to inelastic cotunneling through the levels in the following shell [49], while we attribute the lines at very low finite bias in some of the small diamonds as inelastic cotunneling through the two not completely degenerate orbitals in each shell with orbital splitting $\delta \sim 0.3 - 0.4 \text{meV}$. We note that these lines are not related to superconductivity.

Three Kondo resonances are identified in this plot based on their temperature and magnetic field dependence. The three Kondo resonances are in diamond number 3, 5, and 7, with respective Kondo temperatures of $T_K \sim 2 \text{K}$, $T_K \sim 6 \text{K}$, and $T_K \sim 5 \text{K}$.

Figure 6.1b and 6.1c show a low bias region with the leads in the normal and the superconducting state, respectively. A rich sub-gap structure (SGS) appears for $|V_{sd}| \leq 2\Delta/e$ when the leads turn superconducting. Horizontal lines are observed at $V_{sd} \sim \pm 230 \mu\text{V}$ and $V_{sd} \sim \pm 115 \mu\text{V}$ corresponding to $\pm 2\Delta/e$ and $\pm \Delta/e$, respectively. Furthermore we observe a clear narrow peak in the conductance at zero bias for some ranges in gate voltage. This peak is especially pronounced at some of the normal resonances indicated by arrows in Fig. 6.1c and is not unique for this device but also observed in other devices.

The peaks at $\pm 2\Delta/e$ in the differential conductance are attributed to the onset of quasi-particle tunneling. At lower bias the transport is governed by Andreev reflections due to the relative high transparency between the SWCNT and the superconducting leads [87]. Features at biases $V_n = \frac{2\Delta}{en}$, $n = 2, 3, 4, \ldots$ are expected due to the opening of higher order MAR processes as the bias is lowered [85, 86].

The SGS of a resonant level coupled to superconductors is gate dependent and thus depends on whether a level in the SWCNT-QD is in or off resonance [95, 96] as experimentally shown by Buitelaar et al. on MWCNT [73]. Thus the $\pm 2\Delta$ peaks are more pronounced off resonance than in resonance as expected (Fig. 6.1c). Narrowing of the MAR lines is observed in Fig. 6.1c both for normal and Kondo resonances. In the case of normal resonances, the effect is strongest when $\Gamma < \Delta$ [95] and is therefore less clear in the here reported device ($\Gamma \sim 1 \text{meV} > \Delta \sim 0.1 \text{meV}$, where $\Gamma$ is estimated from the current through the ground state). Similarly, narrowing of the MAR lines in the Kondo resonances is observed to become more pronounced as the line width of the Kondo resonance ($k_B T_K$) decreases and is thus especially pronounced in diamond 3 where $k_B T_K \sim 150 \mu\text{eV} \sim \Delta$. The narrowing of MAR lines in the Kondo resonances has to the best of our knowledge not been reported before.

Figure 6.2a shows a cut through Fig. 6.1c at position A, where the black
Figure 6.2: (a) $dI/dV$ versus $V_{sd}$ at position A in Fig. 6.1c, where a level in the dot is aligned with the chemical potential in the leads. The black and red curve are with the leads in the superconducting ($T = 30 \text{ mK}$) and the normal state ($T = 800 \text{ mK}$), respectively (coincide at $V_{sd} \gg \Delta$). Features due to multiple Andreev reflections and a zero bias supercurrent peak are seen. (b) $dI/dV$ versus $V_{sd}$ at position A (Fig. 6.1c) at different temperatures. The black curve is at 30 mK while the curves at 100, 250, 300, 400, 500, 600, 700, 800 mK are offset for clarity. (c) The zero bias peak area (supercurrent) as a function of temperature at a normal resonance (from (b), diamond 12/13) and in Kondo resonance (diamond 3, $k_B T_K \sim \Delta$). Inset: The $\pm 2\Delta$ peaks follow the BSC-like temperature dependence obtained from (b).
and the red curve correspond to the leads being in the superconducting ($T = 30 \text{ mK}$) and normal state ($T = 800 \text{ mK}$), respectively. The dashed green vertical lines are the expected voltages for MAR in a non resonant junction. Clear features are observed corresponding to $\pm 2\Delta$ and $\pm \Delta$. At resonance the MAR processes for even $n$ are expected to be suppressed, but features are still visible due to the high transparency of the device [95]. The structures at even lower bias can not be clearly related to a specific MAR process. Furthermore the narrow peak around zero bias is visible, which we interpret as a small supercurrent running through the SWCNT. In the following chapter a similar zero bias peak observed in the Fabry-Perot regime is being analyzed as a supercurrent in good agreement with theory [75] thus supporting the interpretation of the zero bias peak being a supercurrent. An order of magnitude estimate of the critical current is made by integrating the area of the peak (not the whole area under the peak), which yields $I_C = 0.4 \text{ nA}$. 

We briefly discuss another possible origin of the zero bias peak [72] in the differential conductance [101]. It might also appear because high order MARs are cut off by an inelastic scattering length/time giving rise to a linear regime in quasiparticle current (MARs current) versus bias [86]. We estimate this cutoff by the HWHM of the peak $V_{HWHM} \sim 8 \mu eV$, which relates to a MAR process of $n \sim 2\Delta/(eV_{HWHM}) \sim 29$ much higher than the observed features in the data indicating that the zero bias peak is not likely to be due to quasiparticle current.

A supercurrent is normally measured in a four-terminal arrangement, where the SNS junction is current controlled. This allows elimination of the series lead resistance from the wiring and ensures that the supercurrent at zero bias is resolved (phase difference between superconductors is constant). Our device is two terminal with a series resistance of around $\sim 100 \Omega$. We have not seen a dissipationless branch in the IV characteristics probably due to insufficient noise shielding of our cryostat (our cryostat is only shielded with thermal coax cables). Bias controlled lock-in measurements are therefore needed to resolve the structures below the superconducting energy gap. The Josephson energy $E_J = I_C h/2e$ yields $1 \mu eV \sim 10 \text{ mK}$ for a critical current of $0.4 \text{ nA}$, which is somewhat lower than temperature of the cryostat and probably much lower than the noise temperature $^3$. Therefore thermal fluctuations in the phase smear the supercurrent into a peak in $dI/dV$ versus bias [102].

Figure 6.2b shows the temperature dependence of the differential conductance versus bias at position A. The zero bias peak is seen to diminish with

$^3$The noise temperature is $\sim 80 \text{ mK}$ obtained from other experiments.
higher temperatures while the voltage position \( V_n \) of the different MAR processes move towards lower biases as the gap gets smaller according to the BCS theory. At \( T_c = 760 \text{ mK} \) all features due to superconductivity have disappeared.

This effect is more clearly displayed in Fig. 6.2c, where the zero bias peak area is shown as a function of temperature up to the critical temperature of the superconducting leads. The peak area clearly increases by lowering the temperature consistent with a supercurrent dependence.

The inset shows the average of the \( \pm 2\Delta \) peak positions (from Fig. 6.2b) normalized by the superconducting energy gap as a function of the normalized temperature \( T/T_c \). When the temperature is raised the position of the averaged \( 2\Delta \) peaks follows the BCS theory as expected.

Assuming our S-SWCNT-S device can be modeled as a series of resonant levels (\( \Gamma \ll \Delta E \)) coupled to superconductors, two regimes can be defined as in chapter 4 [89]. The short \( \Gamma \gg \Delta \) and the long limit \( \Gamma \ll \Delta \), which determines the behavior of the supercurrent induced in the device. For equal couplings to the leads \( \Gamma_0 \), the zero temperature supercurrent through the device is given by \( I_c = 2e \frac{\Delta \Gamma_0}{\Gamma_0 + \Delta} \) at resonance valid for all \( \Gamma_0 \) and \( \Delta \). The factor of two stems from the two spin degenerate channels of the SWCNT (assuming that the orbital splitting \( \delta \) is small \( \delta < \Gamma \ll \Delta E \)). This expression reaches the so called universal limit in the short regime \( I_c = 2e\Delta/\hbar \). Since it is a resonant system the supercurrent is energy (gate) dependent and falls off as \( I_c \propto \frac{1}{\epsilon} (\epsilon \gg \Gamma_0) \) and \( I_c \propto \frac{1}{\epsilon} (\Delta \gg \epsilon \gg \Gamma_0) \) in the short and the long regime, respectively. Here \( \epsilon \) is the energy measured relative to resonance.

The effect of Coulomb interactions is very different in the two limits [91]. In the short limit \( (U_c, \Gamma \gg \Delta) \), the Coulomb blockade does not suppress the supercurrent when a Kondo resonance is present \( (k_B T_K \sim \Delta) \), while in the long regime \( (U_c, \Delta \gg \Gamma) \) the supercurrent is suppressed by a factor of \( \Gamma/\Delta \). The device reported here is in the short limit \( (\Delta \sim 115 \mu V< \Gamma \sim 1 \text{ meV}) \).

Figure 6.3 shows the gate dependence of the zero bias peak area. The three charge degeneracy points A-C (normal resonances) correspond to the positions marked in Fig. 6.1c. The data points are extracted from high resolution data (Fig. 6.3 inset). The numbers indicate the relative shell filling of holes as in Fig. 6.1a. The zero bias peak area clearly has a maximum at normal resonance for all three positions (A-C) as expected [90, 89]. We note that the zero bias peak does not originate from the Kondo effect due to the appearance of a finite zero bias peak area for filled shells (big diamonds, i.e. 4, 8 and 12), where the net spin on the SWCNT QD is zero. The off resonant decay in diamond 2, 4 and 12 falls off gradually consistent with the SWCNT device being a resonant junction. However, the magnitude of the zero bias peak area is much smaller than the expected zero temperature
Figure 6.3: Zero bias peak area (supercurrent) versus gate voltage at $T = 30$ mK. The peak is pronounced at normal resonances (A-C) and Kondo resonances (5 and 7) provided $k_B T_K \gg \Delta$. Otherwise ($k_B T_K < \Delta$) the zero bias peak area is suppressed. The hole filling is given by relative numbers. Inset: High resolution bias spectroscopy plot where the zero bias peak is clearly visible with an area given below in the main figure.

The critical current $I_c = 2e \frac{\Delta \Gamma_0}{\hbar (\Gamma_0 + \Delta)} \sim 50$ nA with $\Gamma \sim 1$ meV and $\Delta = 115 \mu$eV. The reason for this is probably due to the interactions of the Josephson junction with the external circuit (see chapter 7) [75]. Furthermore, the temperature dependence indicates that the saturated value of the peak area has not yet been reached.

The gate dependence of the zero bias peak area is highly asymmetric across the normal resonances, which is due to an interplay with the Kondo effect [91, 92, 93]. In the weak coupling regime ($k_B T_K \ll \Delta$) the critical current is suppressed, while a supercurrent coexists with the Kondo effect in the strong coupling regime ($k_B T_K \gg \Delta$). This is qualitatively seen in Fig. 6.3. For hole filling with a narrow Kondo peak of $k_B T_K \sim 1.5\Delta$ (diamond 3), the zero bias peak area abruptly drops to zero, while it coexists for Kondo diamonds with a high Kondo temperature of $k_B T_K \sim 3.7\Delta$ (diamond 7) and $k_B T_K \sim 4.5\Delta$ (diamond 5). We note that the crossover is not in full quantitative agreement
with theory.

At the center of the Kondo resonance of hole filling 3 \( (k_B T_K \sim 1.5\Delta) \) we see a quite peculiar temperature dependence of a zero bias peak. At base temperature (30 mK) no zero bias peak is present, but when the temperature is increased a zero bias peak emerges. The extracted zero bias peak area as a function of temperature is shown in Fig. 6.2c by red squares. We speculate that changing the temperature might influence the competition between the Kondo effect and the supercurrent, but further experimental and theoretical work is needed to confirm and understand this effect.

In conclusion SWCNTs have been contacted to superconducting Ti/Al/Ti leads with conventional processing techniques creating a SWCNT weak link. The superconducting proximity effect manifests itself as MAR as well as a narrow zero bias conductance peak. We interpret the narrow zero bias peak as a noise smeared proximity induced supercurrent with a maximum estimated magnitude of \( \sim 0.7 \text{nA} \). The small magnitude is probably due to the interaction of the Josephson junction with its environment. This zero bias peak area depends strongly on the shell filling and is suppressed/observed for Kondo resonances in the weak/strong coupling regime qualitatively consistent with theory.
Chapter 7

S-SWCNT-S weak links in the Fabry-Perot regime

This chapter continues the discussion on single wall carbon nanotubes (SWCNT) contacted to superconducting leads (S), but now with rather high transparency. As discussed in chapter 3, a well contacted SWCNT acts as a one-dimensional waveguide where the electron waves set up (Fabry-Perot) resonances, i.e., an open quantum dot $\Delta E > \Gamma > U_c$. Charging effects are not significant due to the continuous charging of the device instead of in quanta of the electronic charge $e$ (Coulomb blockade).

The transparent regime of S-SWCNT-S junctions was addressed before by several groups, but only very recently in the clearly identified Fabry-Perot regime [75]. We now briefly summarize the earlier attempts. SWCNTs and ropes of SWCNT weak links have been fabricated with a non-conventional laser welding technique with rather good transparency where anomalously large proximity induced supercurrents were observed [68, 69, 103]. The drawback of this welding technique is that no gating of the SWCNT is available. The SWCNT was identified by microscopy, but no bias spectroscopy plot $(dI/dV_{sd}$ versus gate voltage and bias) could be presented to confirm the quality nor the regime (Fabry-Perot regime) of the devices.

Gated SWCNT weak links with probably a few SWCNT bridging the gap between niobium electrodes have also been fabricated [70]. It was shown that the devices could be tuned from poor contacts with tunnel-like behavior to good contacts with Andreev-like behavior. No bias spectroscopy plots were shown probably due to several SWCNTs in the gap.

1This chapter is available as a preprint in similar form on condmat/0510200: H. Ingerslev Jørgensen, K. Grove-Rasmussen, T. Novotný, Karsten Flensberg, and P.E. Lindelof, "Electron transport in single wall carbon nanotube weak links in the Fabry-Perot regime" and Ref. [100].
Since these early attempts to fabricate well contacted S-SWCNT-S weak links better quality of the SWCNTs and understanding of the contacts to SWCNT have been achieved, making it possible to routinely observe clean bias spectroscopy plots in different regimes.

As mentioned previously multi wall carbon nanotubes (MWCNTs) have also been contacted to superconducting contacts where bias spectroscopy plots identified the MWCNT device to be in the Kondo regime \[10, 72, 73\]. MWCNT devices with higher transparency superconducting contacts have also been examined by the same group, where an interference pattern in the bias spectroscopy plot was attributed to universal conductance fluctuations \[104\]. In contrast to the Fabry-Perot interference pattern in SWCNT, irregularity in the pattern due to scattering in the MWCNT as well as conductance above \[4e^2/h\] was observed. Finally, good contacts to MWCNTs have been achieved by contacting many vertically aligned MWCNTs, and observation of a proximity induced supercurrent through the structure was reported \[74\].

This chapter presents experimental results on gated SWCNTs produced by conventional processing techniques. Bias spectroscopy identifies the S-SWCNT-S device to be in the Fabry-Perot regime. The focus will be on the excess current and the supercurrent, where an estimate of the latter is deduced from a zero bias peak. During the reviewing process of the below results on the excess current, Jarillo-Herrero et al. \[75\] published their work on similar SWCNT weak links in the Fabry-Perot regime. Clear observation of a supercurrent was reported and analyzed thoroughly. This approach has been adopted here and the treatment of the supercurrent in our SWCNT weak links supports the zero bias peak as being a supercurrent and confirms the picture given by Ref. \[75\].

The SWCNTs are grown by chemical vapor deposition (CVD) from catalyst islands made by electron beam lithography and positioned relative to predefined alignment marks. The details of the CVD-growth procedure are described in chapter 2 and 6 and as well as Ref. \[32\]. After growth, source and drain electrodes consisting of superconducting trilayers are positioned next to the catalyst islands to contact the SWCNT. The gap between the source and drain trilayer films is approximately 500 nm. The superconducting trilayers consist of 5 nm titanium to make good contact to the SWCNT, then of 40 nm aluminum to raise the transition temperature, and finally 5 nm titanium to stop oxidation of the aluminum.

Our devices are made on a highly doped silicon wafer with a 0.5 \(\mu m\) thermally oxidized SiO\(_2\) layer on top. We use the silicon substrate as a back gate. To be able to measure the transition temperature \(T_C\) and the critical field \(B_C\) of the trilayer films at low temperatures we furthermore define a four probe device of the superconducting trilayer. For the device below, we find
Figure 7.1: Current and linear conductance versus gate voltage at $T = 300 \text{ mK}$. The device exhibits a semiconducting behavior, and four period Coulomb blockade structure as well as Fabry-Perot resonances are seen.

$T_C = 750 \text{ mK}$, $B_C = 75 \text{ mT}$ and from BCS theory a superconducting energy gap of $2\Delta = 3.5k_BT_C = 230 \mu \text{eV}$ is calculated. However, the actual effective value of $\Delta$ for the SWCNT weak link might differ from this measured value due to interface effects and, indeed, we found from the fit of the excess current measurements (see below) that the effective gap is reduced by about a factor of $\sim 0.7$. All measurements are performed at $300 \text{ mK}$ in a sorption pumped $^3\text{He}$ cryostat (Oxford Instruments Heliox). The measurements are made with standard DAQ cards, lock-in amplifiers (excitation $5 \mu \text{V}$), and opto-couplers to reduce noise.

Figure 7.1 shows a gate sweep from $-10 \text{ V}$ to $0 \text{ V}$ with $V_{sd} = 1 \text{ mV}$ ($> 2\Delta/e$). It displays strong gate dependence, i.e., high linear conductance at high negative gate voltages and low linear conductance at small gate voltages. This indicates that the SWCNT is semiconducting and the measurements are of hole transport through the valence band. The device can thus be tuned from a closed quantum dot (QD) with large Schottky barriers to an open quantum dot (Fabry-Perot regime) with negligible Schottky barriers due to gate dependent Schottky barriers at the electrode-SWCNT interfaces.

From $V_{gate} \sim -4 \text{ V}$ to $V_{gate} \sim -2 \text{ V}$ the device is in the closed QD regime, where Coulomb blockade peaks are clearly visible. Some of them are spaced into periods of four due to spin and orbital degeneracy of the SWCNT confirmed by bias spectroscopy plots (not shown). Such regular characteristic is
Figure 7.2: (a) Bias spectroscopy plot in the high transparency gate region with a small magnetic field ($B = 100$ mT) to suppress the superconducting state of the electrodes. The black lines indicate the Fabry-Perot interference pattern. (b) Analog to (a) but without magnetic field, i.e., with superconducting electrodes. (c) A zoom-in around small source drain voltages where the excess current is observed. Arrows are pointing to the gate voltages where the graphs in Fig. 7.3a-c are measured.
a sign of a high quality SWCNT.

The superconducting effects in more closed QD regime have been discussed in the previous chapters. Now we instead turn our attention to the regime of high conductance from $V_{\text{gate}} = -10 \text{ V}$ to $V_{\text{gate}} = -6.5 \text{ V}$. Figure 7.2a shows a bias spectroscopy plot of this gate region with a small magnetic field applied ($B = 100 \text{ mT}$) to suppress the superconducting state of the electrodes. The average differential conductance is around $\sim 2.5e^2/h$ with maxima of about $\sim 3e^2/h$, approaching the theoretical limit of $4e^2/h = (6.5 \text{ k}\Omega)^{-1}$. Compared to the closed QD-regime described above, holes are now transported (coherently) through the SWCNT with only little reflection at the electrode-SWCNT interfaces. As the gate voltage and the bias are changed the dips in conductance evolve into straight lines, forming a mesh of crossing dark lines (indicated with black lines in Fig. 7.2a). These pronounced oscillations in differential conductance versus $V_{\text{gate}}$ and bias are clear signs of Fabry-Perot interference [9] as explained in chapter 3.3.

The maxima (peaks) versus gate voltage at zero bias can also be viewed as being in resonance with a level in the SWCNT. The level spacing (or characteristic voltage [9]) can be extracted as the distance from off-resonance to a resonance peak increasing the bias at constant gate voltage (see Fig. 3.10c). From Fig. 7.2a we deduce a level spacing of $\Delta E \sim 4$ to $7 \text{ meV}$, the lowest value corresponding to more positive gate voltage. The gate dependence of the level spacing might be due to the SWCNT being semiconducting, i.e., the level spacing increases for more negative gate voltages due to a non-linear dispersion (see Fig. 1.7).

Figure 7.2b shows a bias spectroscopy plot of the same gate region, when the electrodes are in the superconducting state, i.e., zero magnetic field. An overall increase in differential conductance between $V_{sd} \sim \pm 2\Delta/e$ is observed which is more clearly revealed in Fig. 7.2c. Detailed measurements with lock-in amplifier of the differential conductance versus $V_{sd}$ at the gate voltages indicated in Fig. 7.2c are shown in Fig. 7.3a-c. (a) and (b) are at two different gate voltages off resonance in the Fabry-Perot pattern with a large difference in normal state conductance ($G_N$) while (c) is at resonance.

A characteristic conductance variation between $V_{sd} \sim \pm 2\Delta/e$ is seen for all gate voltages. Close to $|V_{sd}| \sim 2\Delta/e$ the conductance starts to increase while at smaller bias voltages a dip centered around zero bias also develops. In Fig. 7.3b this dip can be seen between $V_{sd} \sim \pm 80 \mu\text{V}$ and more strongly in Fig. 7.3a, where the dip evolves down below the normal state conductance. Similar strong dips are also observed at $V_{\text{gate}} = -6.5 \text{ V}$ and $V_{\text{gate}} = -8.7 \text{ V}$. The change in conductance between $V_{sd} \sim \pm 2\Delta/e$ to typically higher, but also lower values than $G_N$, is because superconductivity induced transport mechanisms occur.
Figure 7.3: Differential conductance versus bias measured with lock-in amplifier (5 µV excitation) at different gate voltages as indicated in Fig. 7.2c. Black and red points correspond to the leads being in the superconducting and normal state, respectively. Superconductivity in the leads is suppressed by a magnetic field of 100 mT. (a-b) Two different antiresonances of the Fabry-Perot interference pattern. (c) At resonance with increasing magnetic fields applied. Development from tunnel-like to Andreev-like characteristic from (a) to (c) is seen consistent with the increasing normal state conductance.
Between $V_{sd} \sim \pm 2\Delta/e$ transport is governed by Andreev reflections (ARs) [87] and normal reflections. No single particle tunneling is allowed, since no single particle states exist below the superconducting gap. An electron with energy $|\epsilon| < \Delta$ relative to the Fermi energy in the normal region has a probability depending on the interface barrier for being AR on the superconductor as a hole effectively transferring two electrons (one Cooper pair) through the NS interface [88, 105]. For $|\epsilon| > \Delta$ ARs are still possible but falls off rapidly. Multiple Andreev reflections (MARs) between the two superconducting electrodes give rise to a sub-gap structure (SGS) at finite bias [106, 107, 86], while a dissipationless supercurrent can flow at zero bias providing that the interfaces are sufficiently transparent (see chapter 4). The off resonance bias cuts in Fig. 7.3a-b both show SGS, while it is less clear on resonance as shown in Fig. 7.3c. We also note that a narrow zero bias peak with a width of only $V_{sd} \sim 25 \mu V$ is present on all three bias cuts and also clearly visible for all gate voltages in Fig. 7.2c. A quantitative comparison between theory and experiment of the SGS would be interesting and might be subject for further studies.

However, instead of studying the SGS in more detail we turn to another effect observed in several of our high transparency S-SWCNT-S junctions. It is seen that ARs give rise to a positive excess current which depends on $G_N$. We now analyze the excess current in the device reported here. Excess current $I_{exc}$ is defined as the difference in current between having the electrodes in the superconducting state and in the normal state at $V_{sd} \gg \Delta/e$. It can therefore be found as half of the difference in area between the curves for $dI/dV$ versus bias with the leads in the superconducting and the normal state, e.g., black and red curves in Fig. 7.3a-c. Figure 7.4a shows the extracted excess current versus normal state (linear) conductance obtained at different gate voltages in Fig. 7.2c. The life time broadening of the levels in this device is much bigger than the superconducting energy gap $\Gamma \gg \Delta$, i.e., the SWCNT weak link is in the short regime. We can thus use the expression for a superconducting quantum point contact [108, 109] and fit the excess current with the function\(^2\)

\[ I_{exc}(g) = \frac{e^2}{h} \frac{g^2}{(4-g)} \left[ 1 - \frac{g^2}{4(4-g)(8-g)} \log \frac{2 + \sqrt{4-g}}{2 - \sqrt{4-g}} \right] \]  

(7.1)

where $g$ is the measured conductance in units of $e^2/h$ and $\tilde{\Delta}$ is the superconducting gap of the leads at the SWCNT-interface. The blue curve in Fig. 7.4a

\(^2\)The formula is obtained from Ref. [108], Eq. (7.10) with $D = 1 - R$, $\lambda = D/(4R)$ and $h = 1$, where $D$ and $R$ are the transmission and reflection probability, respectively. The transmission is $D = g/4$ with $g$ being the conductance of the SWCNT in $e^2/h$. A factor of two is due to the two spin degenerate channels in the case of the SWCNT.
Figure 7.4: (a) Excess current versus normal state conductance. Red dots are extracted from the measurements in Fig. 7.2c while the blue curve is the best fit using $\Delta$ as fitting parameter in Eq. (7.1). (b) Zero bias peak area versus normal state conductance. Red dots are the zero bias peak areas extracted from measurements in Fig. 7.2c. The solid and dashed blue lines are the best scaled fits according to Eq. (7.2) for $aI_c$ and $aI_c^{3/2}$, respectively. (c) Linear conductance versus gate voltage for the three above analyzed Fabry-Perot oscillation. (d) Measured (red dots) and calculated excess current (blue crosses). (e) Measured zero bias peak area (red dots) and calculated $aI_c^{3/2}$ (blue crosses).
shows the best fit (least square) to the measured data (red dots). Allowing for a renormalization of the gap $\Delta \sim 0.7\Delta$ a good agreement between theory and experiment is obtained.

We now turn to the zero bias peak observed for all gate voltages. Such feature has previously been seen in experiments on S-MWCNT-S junctions [73, 72] and was attributed to quasiparticle current [101]. Here, we instead analyze the peak in terms of a supercurrent. We estimate the magnitude of the critical current by (strictly speaking half) the area of the peak (not the whole area under the peak). This yields a critical current in the order of 0.2 nA at resonance. The expected critical current at resonance is $I_c \sim e\Delta/\hbar \sim 35$ nA in the short regime [89] and much larger than the experimental value (see chapter 4). Similar discrepancy in the magnitude between the experimental and theoretical supercurrent has also been observed by Jarillo-Herrero et al. for a very similar SWCNT weak link [75]. The supercurrent they report was observed directly in the IV characteristics and 15 times lower than expected. This suppression of the supercurrent is explained by the dynamics of the phase of the resistively and capacitively shunted Josephson junction (RCSJ) with its environment\(^3\). The supercurrent obeys $I_m = aI_c^{3/2}$, where $I_c$ is the theoretical value stated above and $I_m$ is the measured value. Good agreement with measurements were shown [75] and the same approach is adopted for this junction.

Figure 7.4b shows the extracted peak area versus normal state (linear) conductance (red dots). The supercurrent is determined as\(^4\) [86, 95]

$$I_c(g) = \frac{e\Delta g \sin \varphi_{\text{max}}}{4\hbar \sqrt{1 - \frac{g}{4} \sin^2(\varphi_{\text{max}}/2)}} \tanh \frac{\Delta \sqrt{1 - \frac{g}{4} \sin^2(\varphi_{\text{max}}/2)}}{2k_B T}$$

(7.2)

where $\varphi_{\text{max}}$ is the phase for which the critical current is maximum. The dashed and solid blue lines in Fig. 7.4b are the best fit obtained by $aI_c(g)$ and $aI_c^{3/2}(g)$, respectively, using the renormalized gap obtained from the fit of the excess current. Very good agreement between theory and experiment for $aI_c^{3/2}(g)$ is obtained (solid blue line) consistent with Ref. [75]. It is also clear that $I_c(g)$ does not capture the behavior of the supercurrent. Figure 7.4e shows the same data points (red dots) and the theoretically expected

\(^3\)Since our S-SWCNT-S device is almost identical to the one in Ref. [75] we obtain a similar Q-factor, $Q \sim 2 > 1$, where the Q-factor is defined in Ref. [75].

\(^4\)In the equation for the supercurrent in Ref. [86], $\alpha = T = g/4$ is the transmission, where we assumed that each channel in the SWCNT is equally coupled to the leads. A factor of two is due to the two spin-degenerate channels of the SWCNT. Note, that this is identical to the supercurrent in the short regime Eq. (4.4) in the zero temperature limit and $T_{BW} = g/4$ [89].
supercurrent $aI_c^{3/2}(g)$ (blue crosses) versus gate voltage. An interpretation of the zero bias peak as being a supercurrent is thus fully consistent with theory and similar experiments.

In this chapter we have analyzed S-SWCNT-S Josephson junctions with high transparency contacts in the Fabry-Perot/open quantum dot regime. We observe quasiparticle tunneling at $|V_{sd}| = 2\Delta/e$, enhanced conductance below $|V_{sd}| < 2\Delta/e$ and a conductance peak around zero bias. We interpret the zero bias conductance peak present at all gate voltages as a noise smeared supercurrent. Its dependence on the normal state conductance supports this interpretation and is well captured by the dynamics of the RCSJ model taking into account the interaction with the environment. The excess current, which has not been analyzed before for such junctions, fits well to a coherent theory for a superconducting quantum point contact.
Chapter 8

Single wall carbon nanotubes and quantum information

A quantum computer is based on bits called quantum bits (qubits) that obey quantum mechanics instead of classical physics as in a conventional computer. The qubit can therefore be in a superposition of its two states, zero and one in contrast to its classical counterpart.

The concept of quantum computing has led to new algorithms by which some problems can be solved faster (until now) on a quantum computer than on a conventional computer [110, 111]. For example the problem of factorizing a large number being a product of two prime numbers can by Shor’s quantum algorithm [110] be solved exponentially more efficient with the input than by any known classical algorithm. Quantum computers can also be thought to simulate quantum systems and thus give more insight into the world of quantum mechanics.

The quest to make a quantum computer is very difficult and whether a (many qubit) quantum computer will ever be built is still a very open question. However, this effort brings rich and interesting physics as well as improved technologies along.

The qubit is basically a two-level quantum mechanical system. Such systems are encountered in many branches of physics and many candidates exist. The field of quantum computing has thus brought physicists from different areas of physics together. Some of the two-level systems now being used are ion traps [112], implanted nuclear spins (P) in silicon [113], superconducting charge, phase and flux qubits [114], charge qubits in double quantum dots (QD) and spin qubits in single QDs [115]. While the trapped ion systems are more developed than solid state implementations in the number of working qubits, these systems are believed to be difficult to scale up. On the contrary, the solid state solution is thought to be more easily scalable and might in
Single wall carbon nanotubes (SWCNTs) are also relevant for the field of quantum computation. One proposal for an architecture of a quantum computer based on SWCNTs is to use the so-called peapod nanotubes. A peapod nanotube is a SWCNT used as a hollow cylindrical container for doped $C_{60}$ molecules, which are forced to line up one by one along the tube axis inside the tube. The quantum bit consists of one magnetic impurity inside each $C_{60}$.

More closely related to the work presented in this thesis is the use of the two-level system related to the spin of the electron in SWCNT QDs as a qubit [115]. A central issue in quantum computing is the two timescales called $T_1$ and $T_2$. The first is in this case the spin relaxation time $T_1$, which determines how long time the spin stays in the spin-up/down (excited) state before it is relaxed (spin flipped). $T_2$ is the phase decoherence time that gives the time in which the superposition between the two (spin) states is not disturbed. Both timescales tell something about how well isolated the quantum system is from the environment. For lateral GaAs one electron QDs the spin relaxation time has been found to be in the order of tens of $\mu$s [116].

Carbon nanotube quantum dots are predicted to have long decoherence times and are thus promising candidates for quantum information devices. This is due to superior material related properties compared to GaAs quantum dot [117]. Spin-orbit interactions, which are limiting the spin relaxation time $T_1$ in GaAs QDs is smaller in SWCNT QDs due to the lower mass of the carbon atoms. Furthermore, the decoherence time $T_2$ is also expected to be longer in SWCNT QDs than in GaAs QDs due to the vanishing hyperfine interaction in SWCNT. The most abundant carbon isotope\(^1\) (98%) has zero nuclear spin and thus no hyperfine interaction between the electron spin and the nuclei exists. On the contrary, GaAs has a finite nuclear spin and the hyperfine interaction limits the decoherence time [118, 119].

The first experiment presented below is aimed at measuring the relaxation time from an excited state (ES) to the ground state (GS) in a SWCNT QD. If the SWCNT QD is in a static magnetic field these two states would be the spin-up and spin-down state, i.e., relaxation governed by $T_1$. However, the attempt is just to measure the relaxation time from an ES to the GS. This transition is probably shorter than the time to relax from a spin-up to a spin-down state depending on whether the relaxation process involves a spin flip as well. Unfortunately, as shown below no estimation of the relaxation time could be made.

\(^1\)The SWCNT should be composed only of the isotope $^{12}$C and not $^{13}$C, which has nuclear spin $S = 1/2$. 
8.1. RELAXATION TIME MEASUREMENTS IN SWCNT QDs

The second experiment (electron spin resonance) will just be outlined since no samples were sufficiently well behaved. This involves measuring a pumping current through a SWCNT QD due to induced coherent oscillation of the spin between its two eigenstates. Such measurements would allow an extraction of $T_2$ \[120\].

Finally, in the light of the previous chapters on SWCNT weak links we also mention the theoretical ideas to use nanotubes and superconductors as an electron entangler. Two nanotubes close to each other (within the radius of a Cooper pair) in contact with a superconducting electrode and two individual normal contacts in the other ends can be used as an entangler between the two electrons constituting a Cooper pair if the two electrons tunnel into different SWCNTs \[121\].

8.1 Relaxation time measurements in carbon nanotube quantum dots

We want to study the relaxation from the first excited state (ES) to the ground state in a SWCNT QD with $N$ electrons. Relaxation has been studied extensively in both lateral and vertical quantum dots in GaAs/AlGaAs structures \[122, 123, 116\]. The conventional approach is to apply a voltage pulse to the gate which modifies the configuration of the levels in the QD. In the simplest case the pulse has two voltage levels, a high pulse and a low pulse as shown in Fig. 8.1a. The pulse can be varied in amplitude, length of repetition cycle and duty ratio, \textit{i.e.}, the ratio between the length of the low and the high pulse.

The scheme to extract a relaxation rate (or time) for relaxation events from the first ES to the GS is sketched in Figs. 8.1b-c. First of all the QD is assumed to have different coupling to the two leads shown by the arrows, \textit{i.e.}, asymmetric coupling $^2\Gamma_L \gg \Gamma_R$. Figure 8.1b shows the energy diagram in the low pulse condition where the QD is initialized by emptying the ground and the excited state(s). The length of the low pulse has to be longer than the time related to empty the QD $\tau_{\text{low}} \gg \Gamma^{-1} = (\Gamma_L + \Gamma_R)^{-1} \sim \Gamma_L^{-1}$. The latter equation is due to the higher tunnel rate of the left barrier (asymmetry). The pulse is now changed to the high pulse during a rise time $\tau_{\text{rise}}$. Figure 8.1c shows the configuration of the QD in the high pulse, where the ES lies in the bias window. Note, that the rise time has to be shorter than the times it takes to tunnel into the ground state ($\tau_{\text{rise}} \ll \Gamma_L^{-1,\text{GS}}$) or the GS will

\[2\] The coupling parameter is in this chapter given as a rate instead of in energy as in the rest of the thesis.
CHAPTER 8. SWCNTs AND QUANTUM INFORMATION

Figure 8.1: (a) Pulse with two voltage levels, high pulse and low pulse applied to the gate in energy diagrams (b-c). The pulse shown has duty ratio of 0.5. (b) Initialization of the quantum dot, i.e., both the ground state (GS) and the excited state (ES) are made empty. The charging energy is much larger than the level spacing and an asymmetric tunnel coupling to the leads is assumed. (c) High pulse: The ES state is placed in the bias window and current runs through the dot. The current becomes blocked due to Coulomb blockade when an electron relaxes to the ground state. By varying the pulse length a relaxation rate can be estimated.

be occupied during the pulse shift. An electron is now likely to tunnel into either the ES or the GS from the left and less likely to tunnel into the GS from the right. In the case of the ES being occupied the electron can either tunnel out of the QD or relax to the GS provided that the relaxation time \( \tau \) is faster than \( \Gamma_{R,ES}^{-1} \). When the GS becomes occupied transport through the QD is blocked due to Coulomb blockade \( (E_c \gg \Delta E) \). The current through the QD depends on the relaxation time and can be extracted by varying the length of the pulse. We summarize the conditions for using the two-level pulse measurement scheme [123].

- \( \Gamma_L \gg \Gamma_R \)
- \( \tau_{rise} \ll \Gamma_{L,GS}^{-1} \)
- \( \Gamma_L^{-1} \ll \tau \ll \Gamma_R^{-1} \)

In the case where the relaxation time is very long \( \tau \gg \Gamma_R^{-1} \) a three level pulse scheme is used to extract the relaxation time. This will however not be explained here and the reader is instead referred to Ref. [123].

Initially the SWCNT QDs were to be pulsed as explained above by a nearby side gate. Unfortunately, the side gate did only couple very weakly to the potential on the QD, while the back gate is too slow to use for pulse techniques.
8.1. RELAXATION TIME MEASUREMENTS IN SWCNT QDs

Figure 8.2: (a) Initialization: The GS and the ES are likely to be empty due to the fast tunneling rate out of the QD. Note, that current flows through the QD in contrast to the case when the gate is pulsed (Fig. 8.1b). (b) An electron can tunnel into either the GS or ES. In the latter case a current runs through the ES until an electron relaxes to the GS. Transport is then blocked (c) due to Coulomb blockade. (d) Schematic diagram of $dI/dV$ versus bias and gate voltage. The two points 1 and 2 corresponds to the condition of (a) and (b-c), respectively.

Instead, the pulse is now applied to one of the electrodes. This complicates the experiment in the sense that the signal for current through the ES is superposed on a much larger background signal from the initialization process (see below) and thus more difficult to detect.

Figure 8.2 shows the analog diagrams now with the pulse on one of the electrodes (drain) instead of the side gate. The back gate is still used to change the potential of the QD by a DC-voltage. In Fig. 8.2a the QD is initialized and the ground and excited states are likely to be empty due to the asymmetric configuration of the tunnel barriers. There will thus be a current running through the dot during this process. When the voltage is changed (Fig. 8.2b) electrons are allowed to tunnel one by one through the ES of the QD provided that no relaxation event to the ground state happens nor that the ground state was initially occupied. Note, that the current now is opposite the current in the initialization step. This sign change of the difference in the chemical potential of the leads (polarity) between (a) and (b) is important. Imagine that the polarity is the same in both steps (i.e., same as Fig. 8.2a) and the dot is empty after initialization. In this case an electron in the right lead having the fastest rate immediately tunnels into the GS and blocks further transport due to Coulomb blockade. No current through the ES will be measured and the relaxation time can not be extracted. Figure 8.2c shows exactly the blocked transport condition with an electron in the ground state either from a relaxation event or an electron tunneling from the leads. Similar to the back gated case, the relaxation time can be estimated.
Figure 8.3: A schematic figure of the measurement setup and sample holder for pulse measurement at 30 mK of a back gated sample. The pulse is applied to one of the electrodes connected to the nanotube. An attenuator ensures the inner wire of the coax is thermally anchored at 4K (room temperature attenuators are not shown). DC-voltages are applied to the drain and back gate.

by varying the pulse length and measuring the current. This pulse scheme leads to a superposition of two Coulomb blockade bias spectroscopy plots shifted in the bias direction by the amplitude of the pulse. The duty ratio determines the relative magnitude of the two contributions.

Before presenting the measurements a discussion of the high frequency setup will be given. Figure 8.3 shows a schematic of the sample holder used for relaxation time measurements\(^3\). The sample used has a back gate, which should be kept at a constant potential while the pulse is applied to the drain. The capacitance from the drain to the back gate can be estimated by a plate capacitor with the area of the electrode. The area is roughly the size of the bonding pad \(A = (200 \mu m)^2\), which gives a capacitance of \(C_D = \frac{\epsilon r \epsilon_0 A}{d} \sim 5 \text{ pF}\). Here \(\epsilon_0 = 8.85 \times 10^{-12} \text{ F/m}\) is the vacuum permittivity, \(\epsilon_r \sim 4.5\) is the dielectric constant of SiO\(_2\) and \(d = 367 \text{ nm}\) is the thickness of the oxide layer. A metal coated aluminum oxide capacitor (blue/yellow slab) with a bigger capacitance than the capacitance between the bonding pad and the back gate \(C_D\) is placed between the back gate and ground. This prevents the back gate from being influenced by the pulse. The pulse is applied through a coaxial cable due to the high frequency signal and the coax inner wire (launcher) is placed as close as possible to the relevant bonding pad. This makes the bonding wire short and diminishes the distortion of the sharp pulse signal.

\(^3\)The cryostat and the sample holder have not been described under methods, because they are only relevant for this chapter.
For longer bonding wire the rise time of the reflected signal was observed to increase from 400 ps to 800 ps. The bonding pads for DC voltages are connected normally through wire bonding.

A good way to determine the quality of the rf-line in the cryostat is to examine the reflected signal in an oscilloscope. Figure 8.4 shows the shape of a ~6 ns pulse and its reflected signal. The reflected signal has much lower amplitude due to attenuators between the pulse generator and the sample. The time delay between the two signals is ~14 ns corresponding to the round trip to the sample and back \( c \times 14 \text{ ns} \sim 4 \text{ m} \). Here we used the speed of light \( c = 3 \times 10^8 \text{ m/s} \) as the velocity of the signal. The quality of the reflected signal is quite good. The rise time can be deduced from the left inset as ~400 ps. Some ringing is sometimes superposed on the signal, which is clearly revealed on another signal shown in the right inset.

The cryostat is equipped with copper powder and RC-filter at low temperature to reduce noise for DC-signals. The coax line for the high frequency signal is made of stainless steel to reduce heat conduction and the inner wire is thermally anchored at 4 K through a 20 dB attenuator. The pulse is generated by an Anritsu Pulse Pattern Generator MP1775A with a minimum rise time of 80 ps (maximum frequency of 12.5 GHz).

Now we return to the measurements on a metallic SWCNT QD. Figure 8.5a shows dI/dV versus bias and gate voltage around a charge degeneracy point (Coulomb conductance peak) for having \( N - 1 \) and \( N \) electrons on the QD. Several excited states are seen. We now want to apply a pulse...
Figure 8.5: (a) Bias spectroscopy plot of two Coulomb blockade diamonds showing ground state and excited state lines. Blue: Low dI/dV, brown: High dI/dV. (b) Pulse configuration for measurements. The red arrow corresponds to the pulse being in the high state, which gives a positive current contribution shown as a function of gate voltage below the arrow. The initialization state 1 is marked by the green dot. The low pulse state corresponds to the blue arrow at slightly negative voltage and gives a negative current contribution. When pulsed an additional negative current is expected in the otherwise Coulomb blockaded region due to current through the ES state. (c) The two current contributions are added, where the duty ratio between the two pulses determines the weight.

to the drain electrode. The two pulse configurations (Fig. 8.2a and Fig. 8.2b-c) are marked by the green dots in Fig. 8.5b showing a schematic bias spectroscopy plot (similar to Fig. 8.2d). Experimentally the gate voltage is swept while keeping the bias and the pulse parameters constant. A small negative bias gives a current contribution along the horizontal blue line. Without a pulse a small negative current arises from the region between the N-1 and N electron CB regions marked by the solid blue profile along the blue arrow. When the pulse is applied, an additional negative contribution from electrons tunneling through the ES is expected in the region marked by the dotted blue current profile. This current is the relaxation dependent signal we are looking for. As explained above these two negative current contributions have to be superposed on a contribution from the high pulse given along the red horizontal arrow. The high pulse current profile is shown in the simple case considering only the GS and the first ES for N electrons on the QD.

Figure 8.5c shows the expected combined current profile as a function of gate voltage. The current profile depends on several parameters. First,
the bias voltage, \textit{i.e.}, the exact position of the blue line. Next, the pulse amplitude can be varied. It is important that the amplitude is sufficiently large that the QD is being emptied during the initialization step. However, a too large amplitude might lead to a large positive current, that hides the small negative signal. Furthermore, the time the pulse is in the high state and the low state can be controlled. It will thus be an advantage to stay only as long as is necessary to empty the dot $\sim \frac{1}{\Gamma_L}$ in the high pulse and long time in the low state to increase the signal. However, note that the transport is blocked if the GS becomes occupied either by a relaxation event or an electron from the leads tunneling to the GS instead of the ES. The signal would therefore also be enhanced by increasing the rate of the repetition cycles of the pulse. The shortest cycle is determined by the measurement equipment and especially the connection from the rf-launcher (assuming good equipment) to the sample. Preliminary tests on this sample showed that the pulse amplitude stays constant down to 1 ns, while it afterwards decreases (measured until 400 ps) due to non perfect pulse signal shape (ringing). This parameter space was explored but no negative current signal was unfortunately detected.

An improvement of the sensitivity can be obtained by modulating the pulse by a slowly varying step pulse ($< 200$ Hz) and subtract the two signals by lock-in techniques (Fig. 8.6a). Figure 8.6b shows the bias configuration preferable to eliminate the large high pulse background signal. The modulating step pulse should make the low pulse alternate between slightly negative bias and zero. The two current profiles are shown in Fig. 8.6b, where the solid line profile corresponds to the condition explained above at slightly negative bias (Fig. 8.5c). The dotted profile corresponds to zero bias, \textit{i.e.}, only a current contribution from the high pulse. These two current profiles are subtracted to eliminate the high pulse signal.

The expected profile is shown in Fig. 8.6c, where the red GS and ES signals are from the high pulse state, while the blue GS stems from the current for the low pulse. The arrow points to the signal we are looking for, \textit{i.e.}, pumped current through the first ES.

Figure 8.6d shows the current difference\footnote{Basically the difference in current is measured with a 200 \mu V modulating voltage.} as a function of bias and gate voltage with constant parameters for the pulse. The duty ratio is 0.1 and the amplitude is $V_{\text{ampl}} = 2.6$ mV. The most clear features are obtained during the high pulse marked by dashed blue lines and labels, while the dashed red lines are the signal during the low pulse. The bias axis is defined so the crossing of the CB diamond for the low pulse is shifted to $V_{sd} = -2.6$ mV due to the amplitude of the pulse. The desired signal is expected to appear as an extension of the high pulse ES into the N electron CB region marked...
Figure 8.6: (a) The sensitivity of the measurement is improved by applying an additional slowly varying step pulse (< 200 Hz) using lock-in techniques. (b) A sketch of the preferred bias configuration for observing the desired signal. The solid current profile is for a small negative bias (Fig. 8.5c), while the dotted profile is at zero bias (corresponding to high bias of the modulation pulse). (c) The two current profiles are subtracted by lock-in technique giving well defined peaks corresponding to ES and GS for the high pulse (red) and the low pulse (blue). The arrow marks the current signal from which the relaxation time can be determined. This pattern is expected to be seen at slightly negative biases $V_{sd} \sim -200 \mu V$. (d) The current difference is measured as a function of bias and gate voltage with the pulse applied. Blue: Low, black: High. $V_{ampl} = 2.6 \text{ mV}$, duty ratio 0.1 with $t_{high} = 10 \text{ ns}$ and $t_{low} = 90 \text{ ns}$. The ES and GS from the two voltage levels of the pulse are seen, but no relaxation signal is observed, i.e., an extension of the blue ES into white ellipse).

The parameter space for the pulse has been examined to optimize the signal as well as looking at other CB diamonds. The gate region in Fig. 8.6d is chosen in such way that GS from the nearby CB peaks are not seen. Furthermore, the polarity was reversed to test whether the QD had opposite polarity.

The reason for the signal not to be observed is probably because the most transparent barrier is too open and the ground state thus becomes occupied
during the shift between the two voltage levels of the pulse. Another reason could be a very fast relaxation rate, so that no electron actually tunnels through the ES before it is relaxed to the GS. Such scenario would also block all transport through the ES and no signal would be observed. However, the first reason is more likely due to the relative high transparency of the device (broad features in the bias spectroscopy plot). Experimental problems with sample reproducibility and thermal cycling did not allow to do the same measurement on a sample with lower transparency.

A new generation of sample is now being made on sapphire (insulating) and with side gate. As shown in the previous chapters better quality and thus yield of SWCNT QDs have been achieved. This and the quest for tunable barriers in SWCNT QDs [124, 117, 125] seem promising for future experiments on extracting the relaxation time in a SWCNT QD.
8.2 Electron spin resonance

A much more difficult experiment is electron spin resonance (ESR) on a single spin in a single wall carbon nanotube QD [120]. The aim of the experiment is to manipulate a single spin qubit, which is necessary for using spin qubit as the building blocks in a quantum computer [115]. Furthermore, a determination of $T_2$ for a SWCNT QD system would be possible, which is still to be reported. For poor contacts to the electrodes the nanotube behaves as a QD with narrow discrete spin-degenerate energy levels at low temperatures. In a static magnetic field these spin-degenerate energy levels are split (Zeeman splitting) and by an appropriate configuration of the SWCNT QD, transport for a spin-up electron through the dot is blocked (Coulomb blockade), while spin-down electrons are allowed to tunnel out of the dot. By applying an oscillating magnetic field perpendicular to the static field the electron spin is coherently turned from spin-up to spin-down. An originally spin-up blockaded electron is thus allowed to tunnel out of the dot. A new spin-up electron can now enter the dot and the process restarts, which gives rise to a pumping current. The experiment was not carried out due to experimental difficulties, but samples were made and a short outline of the experiment will thus be given below.

Figure 8.7 shows the sample geometry for an ESR experiment. Two independent SWCNT QD are defined (just to increase the yield) between the two side electrodes and a center electrode. The potential of the QD is varied by the side gates. The substrate consists of a layer of SiO$_2$ on a moderately doped back gate, which freezes out at low temperature ($T < 1$ K).

An energy level is split by a constant magnetic field perpendicular to the SWCNT giving rise to a Zeeman splitting of $E_Z = g\mu_B B \sim 115 \mu eV$ for a magnetic field of $B = 1$ T. Here $g = 2$ is the g-factor for SWCNT [5] and $\mu_B = 5.8 \times 10^{-5} eV/T$ is the Bohr magneton. A small oscillating magnetic field perpendicular to the static field is obtained by applying a high frequency AC-current through the microwave-line shown in the Fig. 8.7. When the frequency of the oscillating magnetic field is equal to the Zeeman splitting, the spin will perform Rabi-oscillations [21], i.e., the electron performs coherent oscillations between its two eigenstates, spin-up and spin-down. The resonance condition yields a frequency $\nu = E_Z/h \sim 28$ GHz, which is achievable in today’s high frequency laboratories. The small Zeeman splitting requires low temperature $k_B T \ll E_Z$ and small lifetime broadening of the level(s) $\Gamma_\uparrow, \Gamma_\downarrow \ll E_Z$ (sufficiently closed QD). Here $\Gamma_\uparrow$ and $\Gamma_\downarrow$ are the line width of the spin-up and spin-down level, respectively.

Figure 8.8 shows the configuration of the SWCNT QD to measure a pumping current due to Rabi-oscillation of the spin. In Fig. 8.8a the spin-up elec-
Figure 8.7: Sample geometry for electron spin resonance measurements. Two SWCNT quantum dots are defined in the two gaps, where the potential of each SWCNT QD can be modified by a side gate. A static magnetic field $B_z$ is applied to split the spin-degenerate states. An AC-current is applied to the microwave wire to create an oscillating magnetic field around the wire (blue lines). The electron spin on the quantum dot now feels one static magnetic field modulated by a smaller perpendicular magnetic field. At resonance (frequency corresponding to the Zeeman splitting) the spin on the quantum dot will do Rabi-oscillation between the spin-up and down states.

tron is trapped on the QD below the chemical potential of the leads, while the ES spin-down state (Zeeman split) is in the bias window. No single electron transport occurs through the ES due to Coulomb blockade ($E_c \gg \Delta E$) and cotunneling is suppressed due to the assumption of a very closed QD ($\Gamma$ small). A resonant magnetic field turns the spin-up into a spin-down electron, which tunnels out of the QD. The process can now be started again and the large tunnel rate to/from the left lead compared to the right lead ($\Gamma_L \gg \Gamma_R$) ensures that an electron enters from the left and exits to the right. This gives rise to a pumping current provided that the frequency of the AC-current in the microwave line is resonant with the Zeeman splitting. The relaxation time $T_2$ can be extracted from the pumping current by varying the frequency. The above takes only into consideration one spin-degenerate level.

The experiment turned out to be too difficult and an appropriate starting point would be to first succeed with the relaxation experiment, which is less challenging.

An improvement of both experiments would be to have tunable barriers to the SWCNT as shown by several groups [124, 117, 125]. The tunneling rates to the SWCNT QD are then controlled and could easily fulfill the
Figure 8.8: Energy diagrams of the mechanism behind an electron spin resonance pumping current. (a) Consider an electron in the spin-up ground state. The excited state is a spin-down state separated from the ground state by the Zeeman energy due to a static magnetic field. The quantum dot is configured so the spin-up electron is trapped due to Coulomb blockade. A resonant AC-magnetic field perpendicular to the static magnetic field makes the electron perform Rabi-oscillations. During a half Rabi-period the electron is turned coherently into the spin-down state. (b) A spin-down electron can now tunnel out through the right barrier and a new electron from the left side is likely to enter the quantum dot due to the (assumed) asymmetric barriers. This repetitive process gives rise to a pumping current related to the frequency of the Rabi-oscillation.

requirement of asymmetric very opaque barriers. We experienced instabilities in the transport characteristic, that might be due to the frozen out back gate. However, further experiments are needed to verify the cause of these instabilities. Samples are at the moment being processed on an insulating substrate as sapphire to avoid these problems.
Chapter 9

Summary

9.1 Conclusion and achievement

We have succeeded in producing high quality single wall carbon nanotubes (SWCNTs) confirmed by two terminal low temperature electronic transport measurements. Devices range from open to closed quantum dots ideal for the studying of size quantization, Coulomb blockade and Kondo physics. The observation of these phenomena in our devices constitutes the basis for more interesting and complex experiments.

SWCNT have thus been successfully fabricated with superconducting electrodes of different materials. The superconducting property of the contacts manifests itself by a sub gap structure (SGS) or tunnel characteristics in the transport measurements. New results on this SGS in the closed quantum dot regime are presented and analyzed, where the SGS shows strong dependence on the electron filling. However, additional experiments and theoretical understanding are needed and pursued at the moment.

Furthermore, an observation of a supercurrent as a zero bias peak is seen for relatively transparent devices (Kondo and open quantum dot regime). Such measurements in well defined regimes have only been presented very recently by one group in the open quantum dot regime. Our result is consistent with their findings. Furthermore, the excess current in the open quantum dot regime has been extracted and analyzed with a coherent theory. In the Kondo regime the supercurrent has to the best of our knowledge not previously been (experimentally) analyzed. It is shown that it depends strongly on the hole filling and the strength of the Kondo resonances compared to the superconducting gap.

An attempt to measure the relaxation time in SWCNT quantum dots encountered several difficulties due to poor device quality. However, the mea-
measurements illustrate the possibility for future studies and the techniques used in high frequency measurements are presented.

Finally, a very simple model is introduced to derive the levels for finite SWCNTs. It is shown that the orbital splitting depends on the length of the SWCNT for some tubes depending on the chirality. In armchair SWCNTs the obtained values of the orbital splitting is in good agreement with related experiments. This implies atomically sharp SWCNT-electrode interfaces and that finite SWCNT not necessarily are born with four-fold degenerate levels (depends on length and chirality). This has to the best of our knowledge not been pointed out before.

9.2 Outlook

The interesting transport measurements on SWCNTs at low temperatures have in some sense become more challenging after the initial years, where the field was completely open. However, the improved control of SWCNT quality and knowledge about contacts open up for the study of more complex physics.

The SWCNTs coupled to superconductors make it possible to study the behavior of the superconducting effects such as multiple Andreev reflections and supercurrent in quantum dots not being easily accessible by other systems. Still many interesting effects predicted by theory can be pursued as well as possibly observing new phenomena. Several theoretical predictions in the Kondo regime and interesting effects related to the filling of shells as shown in this thesis are to be explored in more detail. Furthermore, observing a supercurrent in closed SWCNT quantum dot in the Coulomb blockade region is still an open experimental issue. The combination with ferromagnetic contacts, where the spin becomes even more important is also very interesting and promising.

The single spin as the key part of the device is also the focus of a carbon nanotube quantum dots as a spin quantum bit. This quantum bit is just one of many candidates ranging from solid state physics to atomic physics implementations. The first step is to measure the spin relaxation time and obtain coherent control of one electron spin (electron spin resonance). One of the challenges in this regard is to be able to routinely achieve tunable control of the barriers to the SWCNT quantum dot as has been demonstrated by several groups. The knowledge and techniques from the quantum dots in 2DEG could then be transferred.

Despite the improvement of processing techniques and all the result obtained so far very fundamental challenges still have not been resolved. The
chirality of the tube is not controlled and even though some effort on being able to preselect a semiconducting or metallic tube is being made, most transport measurement are still performed testing each SWCNT device electrically after fabrication. Thus there is plenty of room for more interesting physics, technological achievement and application in this field.
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Appendix A

Notes for KelvinOx

The Kelvinox insert is closed by an Indium wire seal.

1. Break vacuum to IVC. Remove the outer shield by unscrewing screws. Leave two screws and let outer shield drop a couple of millimeters.

2. Clean the top surface of the KelvinOx outer shield and the Kelvinox with IPA. Watch out for wires.

3. Place the Indium wire on the outer shield having a centimeter overlap. Bend one wire outwards and let the other lie across. Press the two wires together with the end of a pair of tweezers (if the indium wire is new, the two wires should stick easily.)

4. Place the shield and tighten the screws in several rounds.

Pumping systems: Two rotary pumps are available on the right wall. There are both turned on (power switch) to the left of the computer in the middle room. Make sure that nobody else are using the pumps.

Prepumping: If the system has not been used for a long time evacuation of the still, the IVC and the condenser line is needed.

1. Transfer the system from the wall to the transport holder. Connect the IVC (yellow valve A), still and mixing chamber line to the rotary pump and evacuate the lines.

2. Evacuate first the mixing chamber through the still to prevent an overpressure relative to the IVC that might cause the bottom of the mixing chamber to be detached from the mixing chamber itself (it is sealed by vacuum grease.).

3. Evacuate then the condenser line without closing the valve to the still.

4. Close the valves to the condenser line and the still and evacuate the IVC.

5. When relative low pressure is reached open the valves to the condenser line and the still, pumping on all three chambers at the same time.

6. When pressure reaches around $5 \times 10^{-3}$ mbar, close all valves and disconnect the rotary pumping lines.
Circulating the mixture (manual 2.5 p.31):

1. First evacuate the tubes in the mixture system. Two tubes should be evacuated. The big diameter tube from the still and the smaller diameter tube to the condenser line through the cold trap. Use the horizontal pumping line going into the back of the mixture control box. The line is controlled by the black valve denoted 'vent' (valve 4) on the mixture control box.

2. Open the valve to the condenser line (valve 1), open to the still line (valve 5), open to the cold trap (valve 3) and watch for pressure rise on p1. Finally open the 3 valves (speedy valves) on the He cold trap. Let the pressure fall to \(< 6 \times 10^{-1}\) mbar. Important: Make sure not to open the valves to the rotary pump, where part of the mixture is stored.

3. Flush the system with Helium a couple of times to remove moisture, etc. from the tube. Use the recovery line and connect it to valve C. Close pumping line, open valve to He gas, close valve to He gas and then pump it down again.

4. Stop evacuation. Close the output valve (3) to the cold trap and insert the cold trap into the LN\(_2\) dewar.

5. Close the valve to the condenser line (1), the valve to the rotary pump (4) and the three valves on the condenser line tube.

6. Turn on the mixture rotary pump (contact in the middle room denoted mix. circ. pump). The pressure should be around 700 mbar rising to 800 mbar, because the pump warms up.

7. Now let the mixture circulate through the cold trap (valve 8+3), valve 5, valve 2 and the mixture circulation pump. The last valve to open should be opened only slightly and slowly to ensure slow circulation of the mixture. A too fast circulation leads to ice forming on the tubes above the cold trap and in the worst case making the o-ring leaky letting the mixture out. For instance have valves 5,2,8 open and valve 3 only slightly open. Check that the pressure after the rotary pump and before the high impedance valve 3 (G2) is high while the pressure after the cold trap (valve 3) should be low (G1+P1). Let the mixture circulate for around an hour.

8. Shutdown circulation of the mixture. Close the entrance valve to the cold trap (8) and wait for the pressure to fall (now open the valve 3 fully), i.e. all the mixture is between valve 8 and the rotary pump at the diagram. Close valve 5 and 2. Leave valve 3 open to monitor the pressure in the cold trap. Now shut down the pump (contact in middle room).

9. Take up the cold trap, and monitor the pressure, while it warms up. If a leak is present the pressure will rise dramatically.

10. Check whether there is any mixture in the dump. Now all valves are closed. Open valve 9 to dump plus the two valves on the dump itself (IN+OUT). Pressure should read 790-800 mbar corresponding to no mixture lost.

Evacuating the transfer tube: Find the valve to attach to the transfer tube and evacuate it with the rotary pump. A pressure below \(1.4 \times 10^{-2}\) mbar is okay.

Evacuating the OVC:
1. Connect the rotary pump to the OVC valve (big red valve on dewar) through yellow valve B.

2. Evacuate first the pumping line and open slowly the OVC valve, while monitoring the pressure on the pressure gauge 2 (turn on the pressure gauge electronics), whether the pressure drops or rises. If the pressure rises, use the rotary pump to obtain rough vacuum. Otherwise close valve and use diffusion pump.

3. Flush one or two times with air. Important, no He is wanted in the OVC.

4. When rough vacuum is reached start the diffusion pump. First open for the water cooling on the brown valve on the lower left wall in the middle room.

5. Pump on the backside of the diffusion pump and turn it on (green contact next to the pump). Let it warm up for 10 min. and check whether the cooling is appropriate.

6. If the rotary pumps are not to be used, vent it!!

Pumping time with the diffusion pump of 1-2 hours should be enough. Pressures < $10^{-5}$ Torr.

Preparing cryostat:

1. Transfer the system from the wall to the transport holder. Connect the IVC and the condenser line to the rotary pump and the still to the 1K pot rotary pump leaving the fine scale manometer (0-40) on the still.

2. Evacuate first the mixing chamber through the still line (big valve) to prevent an overpressure relative to the IVC that might cause the bottom of the mixing chamber to detached from the mixing chamber itself (it is sealed by vacuum grease.).

3. Evacuate then the condenser line without closing the valve to still.

4. Close the valves to the condenser line and the still and evacuate the IVC.

5. Open the valves to the condenser line and the still pumping on all three chambers at the same time, when the IVC is at around the same pressure as in the other two lines.

6. When pressure reaches around $5 \times 10^{-3}$ mbar, close all valve and disconnect the rotary pumping lines. Flush IVC with He several times to remove moisture, if pressure falls slowly. Change Indium seal if appropriate pressure is not reached.

7. Evacuate the 1K pot, closing the needle valve and leave 1 bar Helium pressure inside.

8. Make a flow test of the impedance between the condenser line and still. Put 1 bar on the condenser line (important that it is on condenser line, because the IVC still is evacuated) giving a 1 bar pressure difference between the still and the condenser line. Watch the pressure rise to around 18-20 torr on G5 during 12 min. for proper impedance (the still line has been pumped, but close the valve to the pump during the flow test.).
9. Fill exchange 0.1 mbar He exchange gas into the IVC monitored on pressure gauge 2. Additional corner piece and tube from bladder can be given as exchange gas. Be careful to add exchange gas when the insert is in the bath still warm since He evaporates immediately when the He sees the hot insert. Pump out the tube having the valve to the IVC closed. Close valve to pump letting He gas from the recovery system until 0.1 bar is reached on gauge 2. Close valve to recovery line. Open valve to IVC.

10. Now the KelvinOx is ready to be inserted in the dewar.

Nitrogen transfer:
Fill \( \text{N}_2 \) into the inner dewar to cover the magnet. Do it slowly with pressures on the nitrogen dewar around 0.2-0.4 bar overpressure. Use the stick to test whether the Nitrogen covers the magnet (blue pipe, 10 cm of it is not covered). Watch out for the lid of the cryostat that will be blown off at high pressure. Place something heavy on the lid! Stop the Nitrogen transfer and let magnet thermalize for one hour.

Transfer \( \text{N}_2 \) to outer Nitrogen shield:
Transfer \( \text{N}_2 \) through the Nitrogen Fill/vent bushes - use short and long metal pipe and plastic tube. Close the evaporation outlet and turn on the Nitrogen level meter. Put a small nitrogen pressure through the small Fill/vent bush to the main bath - take nitrogen gas from the nitrogen gas line in the middle room (open only slightly). Check whether the liquid is still being transferred by looking at the transparent plastic tube. When finished replace the small metal pipe by the rubber tube plus clamp. If the nitrogen level does not reach 95% transfer liquid nitrogen from a transport dewar (30 min.). The liquid Nitrogen meter might show a finite value initially and then drop to zero as the bath is cool. It starts rising when the bath becomes filled with liquid.

Now pump on the magnet dewar (main bath) through the recovery line. It is important to pump slowly, because liquid nitrogen becomes solid, if the temperature is lowered too much. Monitor the pressure on gauge G5 and G4 (on pump). Use G3 to measure the pressure in the main bath. When G3 reaches \(-600\) mbar stop pumping and monitor whether the pressure rises. At this pressure (i.e. temperature) the nitrogen is in its liquid phase. If pressure does not rise, no more liquid is left and the main bath can be completely evacuated (G5: < 0 bar, G4,G3 out of scale, below -760 mbar). Fill the bath with He gas from the recovery system. (One time only reached G5 12 torr, okay).

Helium transfer:
Connect the exhaust line to the recovery system. Use the Kelvinox transfer (siphon) tube located at the wall in the KelvinOx room to do the Helium transfer. A special top valve piece (labeled Kelvinox) is needed on the transport dewar that fits with the diameter of the transfer tube. Evacuate the transfer tube using the valve that fits to the transfer tube. Only rough vacuum is needed \( 1.4 \times 10^{-2} \) mbar, but flush the tube with air two times to be sure that no Helium is left in the vacuum shield (i.e. the air freezes out on the tube making the vacuum better during transfer). If the mixture is not circulated the transfer tube can be inserted in the transport dewar (short tube - use extension piece) and the main bath Fill/vent bush at the same time. Close the valve to the recovery line on the transport dewar to build up a pressure. Let the gas pass through the "table tennis ball gauge" to monitor whether the He evaporates at too fast rate. Open then the bypass line. Let the pressure be around 0.1-0.3 bar (normally using bladder the pressure becomes 0.1 to 0.15 mbar) in the transport dewar to ensure a sufficient rate. Use the the Helium
"trædepude" to keep this pressure. When the Helium level reaches 95-97% release pressure in transport dewar and take out the transfer tube (several hours for first transfer). Beware that cold Helium gas is coming out of the main bath when removing the transfer tube. If the mixture is circulated the He needs to be liquid before the transfer tube is inserted in the fill/vent bush on the inner chamber. Wait for the liquid to come out of the transfer tube and insert it quickly. Remember that during each transfer around 7-8 liters of Helium evaporated. Check the pressure on the high-pressure bottle in the hallway (second floor). If at 150 bar the bottles need to be changed.

Inserting the Kelvinox:
If not already done, place the connector box on the Kelvinox and ground all connectors. Furthermore place a rubber band around the 1K pot pipe to keep it close to the insert. Now the 1K pot should have 1 bar He pressure inside, the still and the condenser line is evacuated and the IVC has a pressure of 0.1 mbar measured on gauge 2. Take the sliding shield and place it in front of the Kelvinox dewar. Place the Kelvinox carefully inside the sliding shield and fasten the 3 short screws to keep the Kelvinox together with the sliding shield.

Use the heat gun to warm-up the lid to the main bath and remove it, when unfrozen (if transfer has just been made). Lift the Kelvinox with the crane and lower it slightly into the main bath connecting the sliding shield to the rubber tube recovery line. Cool the Kelvinox slowly writing down the counter number before and after. (It costs around 4 liters of He.).

Check temperature sensor:
Turn on the AC-resistance bridge and check the values of the resistor R0-R5 (i.e. channel 0-5). Approximate values of resistances at room temperature are given. Shut down the multi gauge since it interfere with the temperature sensor.

Check the heaters (2603 Power supply):
Sorb: Turn on sorb heater 20 mW and turn knob to check whether a current/voltage builds up.
Still: Turn on still heater 50 mW.
Mix: Turn on mixing chamber heater 2 µW.

When the Kelvinox is almost completely lowered make sure that the "indhak" in the sliding shield is located at the position of the exhaust tube. Now connect the still tube, the condenser tube and the 1K tube. Now pump the still tube and the condenser line through the vent valve on mixture control box (i.e. open 4,1 and 5). Watch the pressure on gauge 1. Flush with Helium and pump down again (see below). Pump on the 1K tube with the 1K pot pump. Check the 1K needle valve and whether the IVC is leak tight. Let a small amount of Helium enter the pot after which the needle valve is closed again. Now pumping on the 1K pot with the valve closed, the temperature of the 1K pot should drop to around 1.5 K (620 Ω). Run the 1K pot in continuous mode by opening the needle valve slightly (R around 600 Ω or the pressure above the 1K pot equal to 3 mbar measured on gauge G5 on the wall).

Condensing the mixture:
First step is to let the mixture run several times through the lN₂ trap to remove impurities
from the mixture. However as explained above first evacuate the condenser line, the still line and the cold trap with the 1K pump (open valve 4 to pump, 5 to still, 1 to condenser line and 3 to cold trap). Flush with Helium and pump down again. The pressure should reach 2 mbar on P1. Check if the pressure is stable during a minute. Otherwise leak in mixture circuit!!

Now close the valve to the pumping line (4) and the cold trap 3. Fill nitrogen in the cold trap (place the trap behind the mixture control box.) and put in the cold trap. Use a 60 l dewar for Helium cold trap. Close the valves for the He trap (on the condenser line) leaving the bypass valve open and insert it into the dewar. Use the special top piece for the dewar and place the o-ring on the trap before inserting it, since it often freezes, which makes it difficult to insert the He trap.

Now we are ready to let the mixture go through the Nitrogen cold trap.

1. Turn on the pump on the switch marked circulation pump in the middle room.
2. Let the gas out of the dump (open 9 and the valves on the dump). The pressure on G2 should be 700 mbar when the pump is cold reaching 790 mbar for a warm pump.
3. Let the mixture slowly into the nitrogen cold trap through 8.
4. Let the mixture into still and the condenser line (open first 3, then 1 and 5).
5. Pump the mixture through the trap back to the dump. Close 8 and slowly open 2. Wait for the pressure on G2 to reach 790 mbar. Close 2 and repeat a couple of times.
6. Now let the gas pass a couple of times through the He cold trap. Open the valves on the trap and close the bypass valve. Assuming that all the mixture is in the dump and pump, open valve 8 to let the gas into the Nitrogen cold trap, the still tube, the condenser line and the helium cold trap. Repeat the procedure by closing 8 and pumping the gas back to the dump.
7. Note: The above steps should be performed if it is first cool down. Otherwise the He and the N trap step can be done simultaneously.

Starting condensation:
8. Pump all the mixture into the dump/pump (G2 = 790 mbar) and close 2. Now we are ready to condensate through the still. Close the valve out of the N2 cold trap (3) and open the valve to the cold trap (8) and the still valve on the insert.
9. Open 3 slowly until G1 shows a condensing pressure of 150 mbar (max 200 mbar). Make sure that the 1K pot temperature is $R_5 > 580 \Omega$ (keep pressure on G5 at 5-7 torr). Adjust the vapor pressure/temperature with the needle valve. When the pressure of G1 is almost equal to G2 (around 100 mbar) the circulation can be started. Around 1-2 hours.
10. Open the condenser valve on the insert. Close valve 5 connecting the still and the condenser line. Open 2 slowly monitoring that the 1K pot $R_5 > 580 \Omega$ and that $G1 <= 150$ mbar (try around 150 mbar). In the beginning the pressure and 1K pot temperature is very sensitive to small valve 2. Now the temperature of the still
should drop (R4 increases, 380 →, R0 increases 4 kΩ ⇒). After a while valve 2 can be opened completely.

11. Heat the still at P=1-2.5 mW to increase circulation (temperature of still R4 = 740 Ω ). Check that the voltage and current are reasonable (i.e. no bad connection)

12. Now wait for the KelvinOx to reach basetemperature R = 116 kΩ . If temperature stalls at 1-2 kΩ remove or add some mixture from the dump. When removing mixture the pressure in the dump can be monitored.

Tricks:

13. To add mixture. Open the valve to the dump on the front side of the pump (10) slowly until pressure on P1 rises to 0.6 mbar. Close 10 when and the condensing pressure G1 is 150 mbar.

14. To remove mixture: Close valve 8 and open 9, wait for the pressure G2 in the dump to reach 100 mbar. Now close 9 and open 8. This should be the right value for this dilution fridge. Set the still at 2 mW and the fridge should cool from 800 Ω to 24 kΩ in 45 min.

Temperature control:
Turn on the temperature control electronics. Settings: INPUT 2, CONTROL: integral 1, proportional 10,30, differential 30 ms. Monitor R0. Put the AC bridge in manual range and select the range where the temperature is to be set. Now go to adj. Ref and use the knob to set the correct temperature. When ’set ref’ is used, the heater will start to warm. Change the output power to an appropriate scale. Do not change the resistor range while heating, since it will alter the reference temperature. The range can be changed by turning the mixing chamber max heating down on the knob, so that when the range is changed the heater can not apply the maximum power.

Magnetic field measurements:
To ensure a homogenous field the insert plus sliding shield has to be lifted around 5 cm. Use the crane. For sweeping the magnetic turn on the heater and wait 20s for the superconductor leads to become normal. Then press goto set to let the magnet sweep to the desired set point. The magnet goes to 7 T corresponding to a current of 102.39 A. Even for low rate 2 A/min (140mT/min) some heating is observed. Actually just turning the magnet power supply on seems to affect the sample temperature. The resistor R0 is quite sensitive to magnetic field.

A labview program for sweeping the magnet and measuring one AD has been made.

Warming up:

1. Close valve 8 to the cold trap to have all the mixture in the pump and the dump.

2. Open to the dump valve 9 and the bypass valve 7. Now pumping on both lines to the mixing chamber.

3. If not already open, open fully to the condenser and the still.

4. Close the needle valve and top to 1K pot.
5. Heat sorb to max 18mW, heat still to 10 mW. Heat mixing chamber to 10-20mW. Beware that cables have a bad connection.

6. Let 100 mbar He gas into IVC. For instance set pressure gauge G4 to around -700 torr. Monitor the pressure of the mixture on gauge P1. When the insert is empty the pressure should drop (from $3 \times 10^{-1}$ mbar to $6 \times 10^{-3}$ mbar). Takes around 30 min. The pressure on G2 should be around 790 mbar, if no mixture is lost. Watch the temperature of the sample R0 go to 4K (22 $\Omega$).

7. Close the still and condenser valve on the insert.

8. Close the valve to the condenser line 1, to the still 2 and the bypass 7. Close also the dump 9 and the two valves physically located on the dump.

9. Set the AC bridge to zero mode, disconnect temperature leads.

10. Close He cold trap valve

11. Disconnect all tubes from the insert.

12. Shot down circulation pump. 13. Pump the still tube and condenser line tube 14. Remove the 3 screws from the sliding shield (bottom ones.). Use crane to lift the insert and sliding shield. Either take it fully up or stop at the red mark on the sliding shield. Be careful when it reaches the top of the cryostat. Close cryostat. Let it hang for a short while and transfer the insert to the wall. 15. For quick heating use the heat gun to heat up part where small metal part are not located. Be gentle.

Warming up cold traps:
The cold trap might have trapped impurities in the mixture. When the cold traps are being lifted out of the liquid monitor the pressure on P1 with the venting line 4 evacuated (open 3 for Nitrogen cold trap, open 1 and valves to the cold trap on the condenser line for cold trap). Open the venting valve 4 to the evacuated pumping line, if pressure rises (or have the valve open from the beginning).

Indium wire:
All Indium wire tools are placed in a plastic box. The Indium wire is made from used Indium wire by pressing them through a tiny hole. Talk to Carsten at the workshop for using his Indium wire device. When the Indium wire is too dirty it should be cleaned by heating up the Indium and removing the top dirty layer of the liquid.
Appendix B

Superconducting devices

A number of devices with superconducting Ti/Nb/Ti electrodes were not measured and is planned to be cooled down to 30 mK to explore the effect of superconducting leads in the Coulomb blockade regime in more detail. The layer are (10 nm/70 nm/4 nm) starting with the lowest Ti layer by thermal evaporation. The Nb is DC-sputtered prior to a 10 min. cleaning of the Nb-target.

Figure B.1: Five devices with superconducting contacts showing regular Coulomb blockade oscillations at 6 K have still not been measured.
Appendix C

Publications and preprints

Preprints based on the Ph.D. thesis:
K. Grove-Rasmussen, H. Ingerslev Jørgensen, and P.E. Lindelof
Interplay between supercurrent and Kondo effect in single wall carbon nanotube Josephson junctions
condmat/0601371, 2006.

H. Ingerslev Jørgensen, K. Grove-Rasmussen, T. Novotný, Karsten Flensberg, and P.E. Lindelof
Electron transport in single wall carbon nanotube weak links in the Fabry-Perot regime
condmat/0510200, 2005.

Publications prior to Ph.D. studies:
F. Giazotto, K. Grove-Rasmussen, R. Fazio, F. Beltram, E. H. Linfield and D. A. Ritchie
Josephson current in ballistic Nb/InAs/Nb highly transmissive junctions

A. Bachtold, M. de Jonge, K. Grove-Rasmussen, P. L. McEuen, M. Buitelaar and C. Schönemberger
Suppression of Tunneling into Multiwall Carbon Nanotubes
Bibliography


