Quantized Electrical Conductance of Carbon nanotubes (CNTs)

By

Boxiao Chen

PH 464: Applied Optics

Instructor: Andres LaRosa
Abstract

One of the main factors that impacts the efficiency of solar cells is due to the scattering of electrons inside the cells. Carbon nanotubes (CNTs) have proposed to use in solar cells due to their ballistic transport properties: electrons travel through CNTs without experiencing scattering or experiencing negligible scattering. The conductance of CNTs is shown to be quantized and has a multiple amounts of $G_0$ which has the conductance $2e^2/h = \frac{1}{12.9 \text{ k} \Omega}$. This paper mainly focuses on the quantized electrical conductance of CNTs through the analysis of the theory and the experimental results.

What are Carbon nanotubes?

Carbon nanotubes (CNTs) can be thought as rolled up graphene sheets in to cylindrical shapes. The diameter of a CNT is about a few nanometers, and the ratio between its diameter and its length can reach as high as 1: 132,000,000 [1]. CNTs include two types: single-walled nanotubes (SWNT) and multiple-walled nanotubes (MWNT). The couple integer indices $(n,m)$ represents the numbers of unit vectors $(a_1, a_2)$ along two direction of a crystal lattices of a graphite sheet [1]. The circumference of the nano-tubes is represented by the magnitudes of the chiral vector, $c_{mn} = n\vec{a}_1 + m\vec{a}_2$, and the nanotube diameter $d = a\sqrt{(n^2 + nm + m^2)}/\pi$ (where $a=0.246 \text{ nm}$); the chiral angle is $\theta = \tan^{-1} \sqrt{3m/(2n + 7)}$ and is measured from the chiral vector and the zigzag axis (See Figure 1) [2].

![Image](image.png)

Figure 1. Left: A tube has a couple of integer indices $(n,0)$ and is called zigzag tube, while a tube with indices $(n,n)$ is called a armchair tube. Right: A single-walled armchair nanotube which has a couple integer indices $(n,n)$ is shown above.
The electrical properties of a CNT changes with its geometrical structures, depending on the ways a graphene sheet is rolled up. CNTs have the electrical properties of metal when \((n - m) = 3z\); CNTs become semiconducting tubes when \((n - m) = 3z \pm 1\) (where \(z\) is integer) [2]. The electrical properties of a material are determined by its energy bands that can be below or above the Fermi level. Fermi level describes the top collection of electrons energy level at absolute zero temperature (See Figure 2) [3]. For semiconductors, the Fermi level is between the band gap of conduction band and the valences band. For metallic conductors, the band gap is zero and the Fermi level is in the overlapped area of conduction band and the valences band. Then, a portion of valence electrons can travel across the material.

![Energy of electrons](image)

Figure 2. Schematic diagram of conduction band and valance band of insulator, semiconductor, and conductor are shown above. The energy gap between the conduction and valence band determines the conductivity of a material. The energy of electrons is along the vertical direction.

By the same token, the band structures of a CNT determine its conductivity. The conductivity of a CNT depends on how a graphene sheet is rolled up. When a nanotube is made by rolling up a graphene sheets around the y-axis, the nanotube behaves like metal with a Fermi velocity that is similar to metals due to the Fermi level is in the overlapped region of the two bands of the tube (See Figure 3) [4]. When a graphene sheet is rolled up around the x-axis, the semiconducting nanotube is constructed because the Fermi level is between the two bands.
Figure 3. For a metallic nanotube, the Fermi level is in the overlapped region between the conduction and valence band. For a semiconducting nanotube, the two bands do not across the Fermi level.

**The theory of quantized electrical conductance of CNTs**

When the transport of electrons in a medium experiences negligible or no scattering due to atoms or impurities, this phenomenon is called ballistic transport [4]. When the electronic mean free path of a wire is larger than the length of the wire, the electron transport in the wire is ballistic [5]. More surprisingly, the conductance in the wire is quantized. The wire acts like an electron waveguide and each conduction channel (or transverse waveguide mode) has an amount conductance of \( G_0 = \frac{2e^2}{h} \), where \( G_0 \) is called “conductance quantum” and has the value of \( \frac{1}{12.9 \, \text{k}\Omega} \), given \( e \) is the electron charge and \( h \) is the Planck’s constant [5].

The following derivation from reference [5] shows how \( G_0 \) is obtained.

Consider a one dimensional wire that connects “adiabatically” (no heat is being lost from the system) to two electrochemical potential reservoirs \( \mu_1 \) and \( \mu_2 \) (See Figure 4). Two assumptions also need to be taken into account: \{1\} there are no reflections of electrons between the reservoirs; \{2\} the wire is very narrow in order for the lowest transverse modes (corresponding to the lowest level of energy) in the wire to be below the Fermi energy. Fermi energy is the energy of highest occupied quantum state in a system of fermions (including electrons) at absolute zero temperature.

![Figure 4](image)

Figure 4. A one dimensional wire is connected to two reservoir adiabatically with electrochemical potential \( \mu_1 \) and \( \mu_2 \).

The current \( I \) is the same as the current density in one dimension. Hence, the current density is

\[
\vec{J} = e \ast v (\mu_1 - \mu_2) \frac{dn}{d\varepsilon} \tag{1}
\]

where \( \frac{dn}{d\varepsilon} \) is the density of states and \( v \) is the electron velocity.

The density of state for an electron including spin degeneracy (spins up and spins down) is

\[
\frac{dn}{d\varepsilon} = \frac{2}{h \ast v} \tag{2}
\]
The chemical potential difference between the reservoirs is an electron charge multiplies the voltage $V$ across the reservoirs:

$$ (\mu_1 - \mu_2) = -e * V \quad (3) $$

From equation (1), (2), and (3), the total conductance is given by

$$ G = \frac{I}{V} = \frac{2e^2}{h} \quad (4) $$

In fact, the general formula for the conductance is given by the Landauer formula:

$$ G = \frac{2e^2}{h} * T*M (\mu) \quad (5) $$

, where $T$ is the transmission probability for a conducting channel and $M (\mu)$ is the number of conduction channels and is a function of energy ($\mu$) [6]. In this case, a conduction channel is characterized by the $T*M (\mu)$ and contributes to the total conductance $G$ by $G_0 * T*M (\mu)$ [7].

For an ideal case (100% of transmission), a “wire” with one conduction channel ($M=1$) has conductance of $G_0=\frac{2e^2}{h}$ which is equation (4). One should notice that $G_0$ is independent of the material properties of a conductor and its dimensions. Hence, when the length of a wire is smaller than its electronic mean free path, its conductance changes only in unit of $G_0$ as conduction channels varies.

Since the diameter of CNTs can be made very small due to the ratio between its diameter and its length can reach as high as 1: 132,000,000, electrons travel only along the tube’s axis. CNTs can be considered to be one-dimensional. Thus, electron transport in CNTs is believed to be ballistic, if the tube’s length is smaller than the electronic mean free path.
Experimental results of Conductance Quantization for CNTs

Many experiments show that CNTs are ballistic conductors. The following experiment is chose from Stephan Frank’s group [8]. Stephan Frank et al is one of the first groups to report evidences for ballistic transport in MWNT. MWNT with diameters from 5 to 25 nm was mounted on the fiber that was attached to a gold wire. The upper part of fiber was installed in the tip of a scanning probe microscopy (SPM) so that nanotubes contact could be raised and be lowered by the SPM into a mercury (Hg) bath under a heater (See Figure 5).

![Figure 5](image_url)

Figure 5. Schematic diagram of a MWNT is immersed a mercury bath and hence a circuit is established (Left). The conductance of the nanotube was a function of the z-potion that is the displacement of the z-Piezo. The conductance of the nanotube was measured to be in the unit of $G_0$ (Right).

A complete circuit established when the tip of the nanotubes made contact with the Hg bath. The nanotube was cyclically (with frequency from 0.1 to 10 Hz) driven in and out of the Hg bath under piezo control. The applied voltage across the gold wire and the tip of the nanotubes was typically from 10 to 50 mV. The conductance of the MWNT was measured as a function of piezo displacement (or the depth of the nanotube dipped into the Hg bath).

When the longest nanotube first made contact with the bath, the conductance of the tube jumped from 0 to $\sim 1 \ G_0$. That conductance remained in the value of about 1 $G_0$ until the second longest nanotubes inserted in the Hg bath. During that time, the z-position of the longest tube was measured to be about 2 μm along the tube. When the second longest dipped into the Hg bath, the conductance increased from $G_0$ to 2 $G_0$ (See Figure 5: Right). The conductance continued to increase in units of about $G_0$ as the nanotube further lowered into the bath. Stephan Frank et al believed that conductance of MWNT was quantized due to the unit increment of the $G_0$.

Although conductance of 0.5 $G_0$ was also observed for the first 25 nm dipped depth, this was due to the tapered tips (twice as long as the tubes’ diameter) of nanotubes (See Figure 6). The “tip-to-shift” interface could elastically scatter electrons and could reduce the transmission
coefficient. After the 25 nm immersion length passed, electron scattering was considerably absent inside the tube.

Figure 6 A conductance of 0.5 $G_0$ was observed for the first immersion length (Left). This was due to the tapered tips (Right), which elastically scattered electrons and lowered the conductance.

Moreover, Stephan Frank et al discovered that the nanotubes were not damaged even in the relatively high applied voltage such as 6 V that should correspond to a current density of more than $10^7 \frac{A}{cm^2}$. Typically, such current would heat a 1 µm long nanotube with 20 nm in diameter to a temperature $T_{max} = 20,000 K$. This is impossible since the nanotube would start to burn at 700 °C. Such difference in temperature indicated that most of the heat dissipated elsewhere. Stephan Frank et al concluded that the nanotube was ballistic conductor because, in ballistic transport, heat is dissipated in the electrical leads (such as the connection between the gold wire) not in the conductor itself.

However, Stephan Frank et al found a discrepancy in this data corresponding to the theory. Since a SWNT has two conduction channels (M=2 from equation (5) and assuming perfect transmission), thus the increment should be in a unit of 2$G_0$ instead of $G_0$. For a nanotube with 5 to 30 layers, the expected conductance should be in the range of 10$G_0 < G < 60G_0$. The conductance of 2$G_0$ is from the fact that there are two are two bands (conduction and valence) near the Fermi level for an ideal SWNT [9]. Each band contributes $G_0$ to the total conductance. This discrepancy was later explained by Sanvito’s group. By using a scattering technique, they discovered that some of the conduction channels were blocked nearby the Fermi energy. This was due to the interwall interactions that redistribute the current nonuniformly over each tube [10].
Conclusion

Much theoretical work has been shown that the conductance of CNTs in one dimensional is quantized with a discrete value of $G_0 = \frac{2e^2}{h} = \frac{1}{12.9\, \text{k}\Omega}$. The theory was confirmed by the Stephan Frank's group and many others'. The experimental data from Stephan's group indicated that the conductance of MWNTs increased in the unit step of $G_0$. Although the expected conductance should be in unit step of $2G_0$, this discrepancy was later explained by Sanvito's group. They pointed out that the interwall interaction between each nanotube caused the drop of conductance from $2G_0$ to $G_0$. CNTs are demonstrated for improved photovoltaic device such as solar cells due to their ability of ballistic transport of electrons [2]. Such application could increase the efficiency of energy conversion in solar cells.
Reference


