Electrical Single Molecule Investigations by means of Mechanical Break Junctions

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1. INTRODUCTION

As the semiconductor industry scales down the electronic components to nanometer dimensions, molecules become potential candidates to extend the functions of silicon-based electronic components, creating new research fields: molecular electronics and bioelectronics. Some organic molecules were investigated to function as rectifier,[1] memory, amplifier[2] and single electron transistor.[3] Some biomolecules were operated as rectifier[4] and logical gates[5] or biosensors owing to their highly-specific recognition capabilities which are not accessible by silicon-based components.[6]

In molecular electronics, it is a fundamental issue to investigate electron transport through functionalized molecules.[7] Furthermore, electron transfer reactions between proteins are widely involved in many biological processes ranging from photosynthesis to aerobic respiration[30,31]. To measure molecules or other functional components individually, a source and a drain electrode separated by a nanoscale gap are required to contact a single molecule, forming a metal/molecule/metal junction, Figure 1-1.

Various nanogaps have been implemented. Some have used fabrication techniques which result in a fixed gap size, like shadow evaporation[8] on a pair of facing electrodes, and electromigration on a thin nanowire.[9] Some have a tunable gap size, such as the tip of a scanning tunneling microscope combined with an appropriate substrate,[10,11] mechanical controlled break junction,[12,13] and a pair of nanoelectrodes fabricated by electrodeposition/dissolution technique.[14-16] Tunable nanogaps are the most versatile methods to investigate the molecule properties since one can adjust the nanogap to the size of the species or objects of interest. The ability of adjusting the nanogap size increases the yields during the formation of the metal/molecule/metal junctions and allows one to investigate the influence of the gap size on the electric response of the junctions. By this means, the size of engineered devices has approached the dimensions of few or even single molecules and the charge transport within these systems can be investigated. For instance mechanical break junctions are well established tools, where individual molecules can be incorporated between two nanoelectrodes, forming metal/molecule/metal junctions[17,18]. Such molecular junctions can be reproducibly formed or broken by mechanical control and the conductance of single molecular junction can be retrieved[19]. The conductance of the molecular junctions depends on the intrinsic electrical properties of the molecule and their molecule/metal interface. Model molecules like single ring aromatic compounds or alkanes with terminal dithiol[20], diamines[21], diisothiocyanate[22], and dicarboxylic-acid groups[23] were systematically studied by several research groups and the contribution of metal/molecule bond to the electron transport pathway was discussed. More complex single molecules like fullerene[24], aniline oligomer[25], transition metal complexes[26] and DNA molecules[27] have also been investigated and the observed electron transport was related to size of the molecule, electrode coupling, their electronic structure and environment. If intermolecular electron transport is investigated, also the interface between the involved molecules needs to be considered. Wu et al. investigated electron transport through an aromatic interface by comparing the electron transport of a single molecule with two π-π coupled aromatic molecules bridging a nanoelectrode junction[28]. Electron transport properties across nucleoside interconnected by hydrogen bonds were studied by Chang et al. and a relation between nucleoside sequence and electrical properties was revealed[29].

In this script, we summarize fundamental aspects of the charge transport through three different types of junctions which all occur in the course of breaking a metal wire modified by organic molecules. This involves transport of electrons through a few Ångström wide metal constriction, tunneling through a bare metal junction, and tunneling through a molecule.

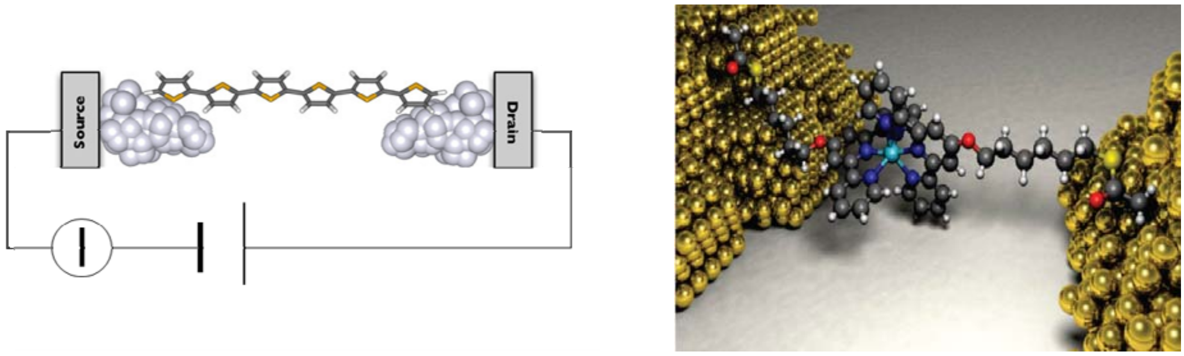


Fig. 1-1. Schematic presentation and illustration of a metal-molecule-metal junction (E. A. Osorio Nano Lett. 2010)

2. Fundamentals

2.1 Quantum transport at nanoscale

Many properties of solid become different if their size decreases to the nanometer scale. The electron transport is one of them, which is greatly altered in nanoscale objects since that the quantum mechanics play an essential role in the nanoscale and ballistic transport become a distinct feature. One of the interesting phenomena is that the conductance of metal wire doesn't obey Ohm's law if the width of the metal wire decreases to a few nanometers. In such systems quantized conductance can be observed. Another example is that the electrons can tunnel through a potential barrier and that a tunneling current between a nanoscale gap formed by two facing conducting electrodes can be observed. This tunneling current is the bases of modern electron tunneling microscopy which is one of the most important inventions of the 20th century.

With the continuing decreasing size of silicon based electronic components, understanding the electron transport behavior in nanoscale materials have become increasingly important and new organic/inorganic hybrid materials and junctions have been attracting notice recently for the realization of electronic devices with better performance, lower cost or new functionality. Such knowledge will pave the way to develop even better functional materials as substitute to common silicon-based electric components or to integrate new functions such as various kinds of (bio)-sensors.

In this first chapter, the general theory of electron transport properties in the nanoscale is described. Firstly, free electron gas model and Landauer theory was introduced that can successfully explain quantized conductance. Secondly, general quantum mechanical description of electrons tunneling through a potential barrier is discussed, which is the basis to understanding the tunneling of electrons through nanoscale gap. Finally, a description of electron transport characteristics through nanoscale objects including single molecules will be given.

2.2 Conductance quantization

If an electric field E is applied on a bulk metal, the electrons move under the force $F=-eE$. e represents the elementary charge of an electron. The moving electrons collide with the impurities, lattice imperfection, and the phonons, the energy of the electrons are maintained in a steady state and the electric current density j is given by Ohm's law

$$j = ne^2 \tau E / m$$

with τ the collision time and m the mass of an electron. The electrical conductivity σ can be derived from $j=\sigma E$, and one obtains

$$\sigma = \frac{ne^2 \tau}{m}$$

The conductance for a bulk conductor with cylinder shape is given for instance as

$$G = \frac{l}{s} \sigma$$

However, this equation is not applicable when the size of the conductor is in the nanoscale. An one dimensional nanowire has a finite current-carring capacity for a given voltage. It therefore has a finite conductance even if there is no scattering in the nanowire. The fundamental difference between the nanoscale conductor and the bulk conductor is that the movement of the electrons in nanoscale conductor is confined and can not exceed the boundary of the objects. The electrons in conductor can be considered as free electron gas. In this model, the valence electrons of the constituent atoms become conduction electrons and can move about freely through the volume of the metal.

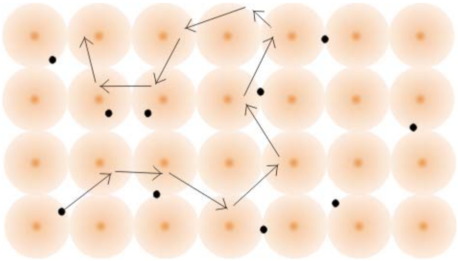


Fig. 2-1 The free electron gas model. Electrons move around in the bulk metal conductor.

The confined system can be mathematically described as electrons in potential well by the Schrödinger equations. The boundary of the well can be seen as a potential step and the height of potential step is the energy difference between the Fermi level of the metal and the energy level in vacuum. This energy difference is referred as the work function and can be determined for instance by photoelectron spectroscopy. Consider a free electron of mass m is confined to in potential well with length L. The Schrodinger equation is given by:

$$H\psi_n = \varepsilon\psi_n$$

with H as Hamilton operator and $\psi_n(x)$ as wavefunctions. The solution of Schrödinger equation of such system is a set of plane waves with discrete energy levels, which are referred as modes or channels. One mode corresponds one plane wave with specific wave number, so the modes can be noted by this wave number. The wavefunctions of the confined electrons $\psi_n(x)$ are in the form of

$$\psi_n(x) = A\sin\left(\frac{2\pi}{\lambda_n}x\right)$$

$$\frac{1}{2}n\lambda_n = L$$

The energy of the electrons can be obtained by solving the Schrodinger equation:

$$E = \frac{\hbar^2 k^2}{2m}$$

E is the electron energy and k is the wave number $k = \frac{n\pi}{L}$.

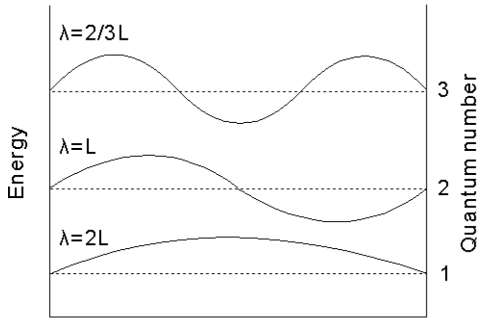


Fig. 2-2 Energy states of electrons confined in potential well

The number of quantum modes is decided by the geometry of the constriction. Briefly, as the size of the restriction is increased, more modes with increasing energy can be accommodated in the constriction. In the case of nanowire, its dimensions along x and y are in nanoscale, but it is continuous in z. Thus the energies are given by

$$E = E_{i,j} + \frac{\hbar^2 k^2}{2m}$$

Where i and j are the quantum numbers labeling the eigenstates in the $x\ y$ plane and k is the wavevector in the z direction. Note that this ground energy is the energy at absolute zero. If the temperature is increased, Fermi-Dirac distribution need to be considered which describes the probability of an orbital occupied by an ideal electron gas in thermal equilibrium.

The discrete energy state of electrons in confined systems affect the electron transport strongly since the electrons can move just via this limited number of modes. The available modes are limited by the size of the constriction, therefore, a nanoscale conductor has a finite current-carrying capability for a given voltage applied across its termini. At the same time, if the size of the conductor is decreased to the order of the electron wave length, the electrons directly transport through the conductor without collision with the phonons. In this situation, the measured conductance will be quantized due to the discrete properties the ballistic transport. To observe the quantized conductance, the size of the conductor needs to be comparable to the Fermi wavelength of the electrons. For gold, the wavelength is 0.52 nm. This order of confinement can be realized in atomic point contact configurations where one or few gold atoms are bridging a pair of nanoelectrodes. The nanoeelctrodes are considered as electron reservoirs. The leads connecting the contact to the reservoirs are confined to several nanometers, thus the electron wave function in this leads were a set of discrete states. The lowest energy level of the allowed mode can be calculated as $\frac{\hbar^2}{2m}(\frac{\pi}{w})^2$, where w is the width of the smallest constriction (3 Å in this case). This lowest energy is lower than the Fermi energy of the electron in gold electrodes. Thus, it is reasonable to assume the electrons in the gold electrode can be transmitted through this mode.

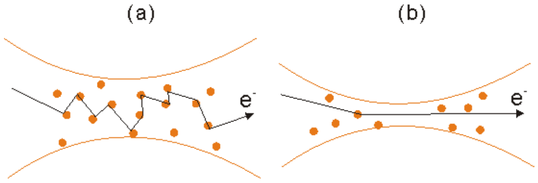


Fig. 2-3 Ballistic transport occurs if the the size of conductor is decreased to the order of Fermi wavelengh of electrons

Let's suppose there are N and M modes for the left and right leads, respectively. If one electron transport from the i mode on one side to the j mode of the other side under a small bias applied on the atomic point contact, the conductance for transporting through one channel is:

$$G_0 = 2\frac{e^2}{h}$$

G_0 is the universal quantum of conductance with the value $G_o^{-1} = 12.9$ kΩ and a perfectly transmitting one-dimensional channel which is given only by the ratio of fundamental constants. The prefactor 2 in the equation comes from the degeneracy of spin up and down and is absent for magnetic material. If the scattering of electrons at the boundary is considered, the transmission amplitude $T(E_F)$ has to be introduced.

$$G = 2\frac{e^2}{h}T(E_F)$$

If more than one channel are involved in the ballistic transport, the conductance is in the form of:

$$G = 2\frac{e^2}{h}\sum_{i,j} T_{i,j}(E_F)$$

This equation is known as Landauer Formula for the conductance and the $T_{i,j}(E_F)$ is the probability that an electron coming from the source electrode in transmission mode i is transmitted to the drain electrode into a different mode j. Note that only elastic scattering by the walls forming the boundary of the system is considered. The scattering of electrons mainly change the spin and phase of the electron wave function, while the contribution of the scattering to the condutance can be neglected, that means $|T(E_F) \leq 1|$. Since the effect of scattering is negligible, only diagonal terms remain and therefore the conductance through a channel of n modes is given by:

$$G = nG_o$$

This means that in this approximation the conductance of atomic point contact is the integer multiple of the universal quantum conductance. The number of modes involved in the transmitting increases with the transverse size of the constriction, therefore the quantized conductance can not be observed if the size of constriction is not in the atomic point contact scale.

Another requirement for observing the quantized conductance is that the difference in in energy between the ground state and the next available state should be large enough. For gold, this value is about 1 eV at room temperature, so that the quantized conductance in gold atomic point contact configuration can be observed at room temperature. For semiconducting material, the electron wavelength is in the order of a few tens of nanometer at room temperature and energy difference between the transverse modes is very small, thus the quantized conductance can be only observed at low temperature. The first experimental observation of quantized conductance was realized on a short quasi one dimensional channel formed between a 2D electron gas in a GaAS/AlGaAs heterostructure.

Several experimental setups have been realized to investigate conductance quantization. Scanning tunneling microscope (STM) and mechanically controllable break junction (MCBJ) experiment are two of them. Both methods can create atomic point contact: the STM creates the atomic point contact by crashing the gold tip into a gold surface and retracting the gold tip; the MCBJ setup establishes the atomic point contact by breaking a thin metal nanowire fixed on a flexible material like steel. By analyzing the histogram of the conductance when breaking and closing the point contact, quantized conductance can be observed (Fig. 2-4).

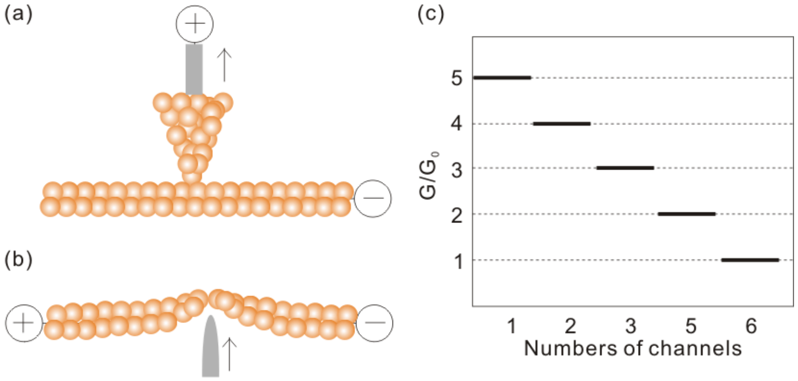


Fig. 2-4 Shematic of atomic point contacts formed by STM (a) and MCBJ (b)

2.3 Electron tunneling through nanogap

If the atomic point contact breaks, then the two facing electrodes are separated and a nanoscale gap can be formed. The gap size can be adjusted by a mechanical controlled peizo system from atomic point contact to serveral nanometers. The gap between two metallic electrodes can be modeled by a square potential barrier of height χ. If a voltage bias is applied across the gap, this square potential will have a saw tooth shape due to the shifted Fermi energy of the leads. The electrons have small but not zero probability to be transported across this gap. This electron transfer from the occupied electronic states of the source to the unoccupied states of the drain is referred as 'tunneling'.

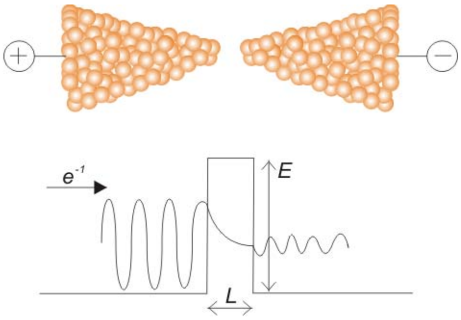


Fig. 2-5 Electron tunneling through a nanogap represented by a potential barrier

Sommerfeld and Bethe derived a model for tunneling current at very low voltage and at high voltages under the WBK approximation (Wentzel–Kramers–Brillouin). The basic idea is to calculate the transparency of the electrons from one end to the other which is determined by the wavefunction of the electrons at eiher end of the nanogap. The wavefunction has the form

$$\psi(x,t) = \psi(0)e^{\pm ikx}$$

where

$$k = \sqrt{2m(E_x - U)}\big/\hbar$$

E_x is the electron kinetic energy in x direction and U is the potential barrier. The stationary solution of the Schrödinger equation has the form:

$$\psi(x,t) = \frac{A}{\left(E_x - U\right)^{1/4}}\exp\left(\pm\frac{i}{\hbar}\int_0^x \sqrt{2m\left[E_x - U(x^{'})\right]}dx^{'} - \frac{iE_x t}{\hbar}\right)$$

Thus, the barrier transparency coefficient $T(E_x)$ (or transmission coefficient) calculated from the outgoing and incoming wave function is equal to

$$T(E_x) = \left|\frac{\psi(x_1)}{\psi(x_2)}\right|^2 = \exp(-\frac{2}{\hbar}\int_{x_0}^{x_1}\sqrt{2m\left[U(x) - E_x\right]}dx^{'})$$

Simmons derived a generalized formula for the electron tunneling between similar electrodes separated by a nanogap which permits more accurate expressions for both high and low voltages. The Simmons model expresses the tunneling current density through a barrier as

$$J = \frac{e}{4\pi^2 \hbar d^2} \left\{ (\phi_B - \frac{eV}{2}) * \exp\left[-\frac{2(2m)^{\frac{1}{2}}}{\hbar} \alpha (\phi_B - \frac{eV}{2})^{\frac{1}{2}} d \right] - (\phi_B + \frac{eV}{2}) * \exp\left[-\frac{-2(2m)^{\frac{1}{2}}}{\hbar} \alpha (\phi_B + \frac{eV}{2})^{\frac{1}{2}} d \right] \right\}$$

where m is the electron mass, d the barrier width, ϕ_B the barrier height and V is the applied bias.

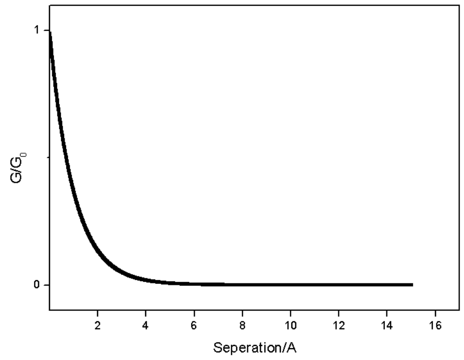


Fig. 2-6 Tunneling through a gap between two electrodes: the conductance decrease exponentially with the the gap size.

2.4 Charge transport through molecules

The major difference between molecules and metal/silicon based devices is their electronic structures. Metals are characterized by the existence of a quasi-continuum of states near the Fermi level, on the contrary, the energy states of molecules are discrete. However, if the metal and semiconductor have nanoscale dimensions, the degeneracy of energy states is lifted and the levels become discrete as well. Ultimately, if the object is composed of only a few tens of atoms, similar electronic structures like molecules are found and the difference between metal and molecule is not so distinctive.

As an approximation to reduce the complexity of the investigated system, most models are considering mainly the occupied and unoccupied states near the Fermi level of molecules or quantum dot. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are especially of interest since they are related to measurable quantities and are involved in many electronic transport processes. The energy of HOMO and LUMO can be estimated by ab initio calculation and measured by optical techniques. The energy gap between HOMO-LUMO can be also investigated experimentally by recording $I-V$ characteristics of molecules or quantum dot junctions since the tunneling current is suppressed within the gap and rises at HOMO and LUMO level. The size of the HOMO-LUMO gap depends for metal nanoparticle on material properties and on their size, for example, a gold nanoparticle of 20 atoms has a gap of 1 eV while it is 2 eV for a cluster of 10 atoms.

For molecules, the HOMO-LUMO gap depends not only on their size and the kind of atoms involved, but also on their hydridisation and arrangement in the molecule. Even small distortions of the molecular structure can alter their electronic properties significantly. Furthermore, the position of the molecular orbitals and thus the electron transport through the molecules are determined not only the molecules themselves but also the contact configuration to the metal leads and the micro environment of the molecules. It was observed in the photoemission spectroscopy and single molecule $I-V$ characteristics that the effective HOMO-LUMO gap of metal-molecule-metal junctions can be significantly smaller than for the corresponding isolated molecule. The interface between the molecule and the electrodes affect the electron transport mechanism greatly. If the coupling between the molecules and the electrode is strong, the electrons in either molecules or the electrodes will be delocalized and the electron tunneling occurs in a one step process and the interaction between the tunneling electrons and the electrons occupying lower lying states is also decreased. The electron transport from the source electrode to the drain electrode via the molecule occurs in a single step. This type of transport is called coherent tunneling. In coherent tunneling, the tunneling time throught the molecules is much smaller than the time needed in noncoherent tunneling, since the the molecules are not charged or discharged during the electron transport process.

To describe the degree of coupling between electrode and molecule, the tunneling current can be modeled by the following relation:

$$I=\frac{e^2}{\pi\hbar}\int_{-\infty}^{+\infty}T\left(E,V\right)\left[f\left(E-\mu_1\right)-f(E-\mu_2)\right]dE$$

$T\left(E,V\right)$ is the effective transparency, $\mu_{1,2}$ is the chemical potential of the electrode and $f(\varepsilon)$ is the Fermi function at the temperature of the experiment.

$$\mu_2 = E_F + (1-\eta)eV$$

$$\mu_1 = E_F - \eta eV$$

η is a parameter used to describe the strength of coupling between the molecule and the electrodes. From this equation, it can be concluded that the current depends on three factors: the overlap between the obitals of the metal electrode and the molecules, the localization of the molecular orbitals and the symmetry between the two metal-molecule contacts.

If the coupling between molecules and metal electrodes is weak, the coupling can be treated as perturbation to molecules and leads.

$$H = H_0 + V$$

H_0 represents the Hamiltonian of uncoupled electrodes and molecules and V is the coupling between them. Then the transparency coefficient across the molecular junctions is:

$$\left|T(E)\right|^2 = \left|\left\langle i\middle|H\middle|f\right\rangle\right|^2$$

where i, f are the states of electrodes and molecule responsible for conduction, and where H is the Hamiltonian of the total system. For the weak coupling approximation one can assume that the molecular orbitals in the system are localized and very close to those of the isolated molecules. As a consequence, the electron transport through the weakly coupled molecular junctions can become a sequentially two-step process if an HOMO or LUMO of the molecule aligns with the energy of the Fermi level of one electrode (adjusted by the applied bias). Firstly, the electrons pass to the molecules and reside on the molecule (the molecule is now charged), secondly, the electrons tunneled from the molecule to the second electrode (the molecule is successively discharged). This type of transport with two consecutive steps is called noncoherent tunneling.

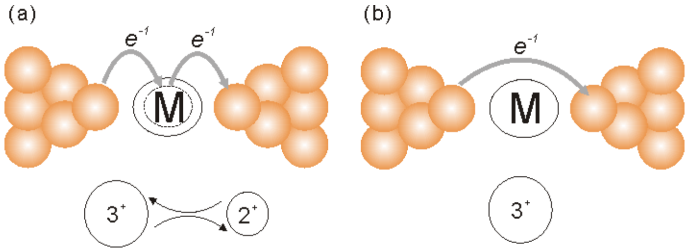


Fig. 2-7 Noncoherent tunneling with alteration of the molecule charge during the tunneling process (a) and coherent tunneling without charge alteration (b)

Models used within this course

A detailed analysis of coupling terms between molecules and electrodes requires usually quantum mechanical calculations. For the interpretation of the data recorded in the scope of this course we mainly neglect these parameters and use exclusively the Simmons model for the data interpretation. This model can be also applied to metal-molecule-metal junctions, as long as nonresonant tunneling occurs (which is the case for the employed molecules). When the Fermi level of the metal is aligned close enough to one energy level (either HOMO or LUMO), the effect of the other distant energy level on the tunnelling transport is negligible, and the Simmons model represents an appropriate approximation for the target molecules.

For molecular systems, the Simmons model has been modified with a parameter α. α is a adjustable parameter that is introduced to provide a way of applying the tunneling model of a rectangular barrier to tunneling through a nonrectangular barrier. Alternatively, the parameter can be used to adjust the effective mass (m^*) of the tunneling electrons through a rectangular barrier. If α is set to 1 a conventional rectangular barrier and bare electron mass is applied. By fitting individual $I\ (V)$ data using this equation, ϕ_B and α values can be determined. A reasonable and often used approximation is the zero-bias limit where the barrier is rectangular and the Simmons equation reduces to

$$J \approx \left(\frac{(2m\phi_B)^{1/2} e^2 \alpha}{\hbar^2 d} \right) V \exp\left(-\frac{2(2m)^{1/2}}{\hbar} \alpha d \phi_B^{1/2} \right)$$

In the following, this approximation is used to describe direct tunneling processes. Here, the barrier height ϕ_B can be approximated by the energy offset between the Fermi level of the nanoelectrode and the nearest molecular orbital. As an opposite limit one can consider the case when a high bias is applied which exceeds the barrier height. As a consequence the barrier transforms from a trapezoidal to triangular shape. For this assumption, the electron transport mechanism will change from direct tunneling to field emission. The Simmons equation becomes

$$J \approx \left(\frac{e}{4\pi^2 \hbar d^2} \right) \left(\phi_B - \frac{eV}{2} \right) \exp\left(- \frac{2(2m)^{1/2}}{\hbar} \alpha d \left(\phi_B - \frac{eV}{2} \right) \right)$$

and can be further converted to:

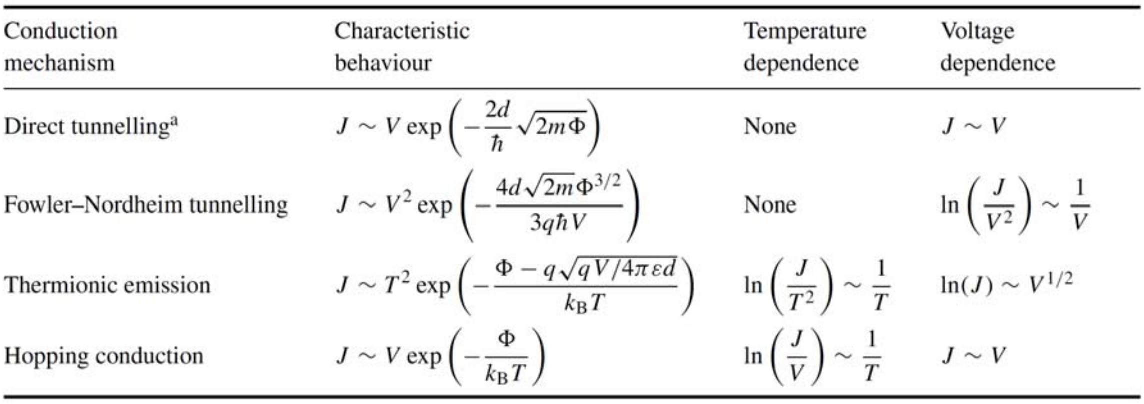
$$\ln(J/V^2) \propto - \frac{4d\sqrt{2m\phi^3}}{3\hbar q} \left(\frac{1}{V} \right) \qquad (2.5)$$

In the field emission regime, $\ln(I/V^2)$ depends linearly on $1/V$ for a fixed *d*, see equation. Applying the models to measured I-V characteristics allows to distinguish between direct tunneling and Fowler–Nordheim tunneling.

Table 1 gives a list of possible conduction mechanisms with their characteristic current, temperature and voltage-dependences[30]. In general one can distinguish two types of conduction mechanisms: (i) thermionic or hopping conduction which have temperature-dependent $I\ (V)$ behavior and (ii) direct tunneling or Fowler–Nordheim tunneling, which does not have temperature-dependent $I\ (V)$ behavior.

Thermionic and hopping conductions have been observed for long molecules as for instance 4-thioacetylbiphenyl and many biomolecules. Direct and Fowler–Nordheim tunneling are rather found when the Fermi levels of contacts lie within the large HOMO–LUMO gap for short chain molecules like alkanethiols (used here). The transport mechanism depends on the length of the molecules. Frisbie *et al* reported that they observed the theoretically predicted change in current transport from direct-tunneling to hopping when the length of the molecule was increased stepwise by adding equal molecule sequences. To distinguish between thermal activated and tunneling transport one can determine the tunneling current versus temperature relation (Arrhenius plot) or measure the dependence of the current on the molecular length (see table 1).

Table 1: Possible conduction mechanisms [30]



Conduction mechanism	Characteristic behaviour	Temperature dependence	Voltage dependence
Direct tunnelling[a]	$J \sim V \exp\left(-\frac{2d}{\hbar}\sqrt{2m\Phi}\right)$	None	$J \sim V$
Fowler–Nordheim tunnelling	$J \sim V^2 \exp\left(-\frac{4d\sqrt{2m}\Phi^{3/2}}{3q\hbar V}\right)$	None	$\ln\left(\frac{J}{V^2}\right) \sim \frac{1}{V}$
Thermionic emission	$J \sim T^2 \exp\left(-\frac{\Phi - q\sqrt{qV/4\pi\varepsilon d}}{k_B T}\right)$	$\ln\left(\frac{J}{T^2}\right) \sim \frac{1}{T}$	$\ln(J) \sim V^{1/2}$
Hopping conduction	$J \sim V \exp\left(-\frac{\Phi}{k_B T}\right)$	$\ln\left(\frac{J}{V}\right) \sim \frac{1}{T}$	$J \sim V$

Reference List

1. Aviram, A.; Ratner, M. A. Molecular Rectifiers. *Chemical Physics Letters* **1974,** *29* (2), 277-283.

2. Aviram, A. Molecules for Memory, Logic, and Amplification. *Journal of the American Chemical Society* **1988,** *110* (17), 5687-5692.

3. Kubatkin, S.; Danilov, A.; Hjort, M.; Cornil, J.; Bredas, J. L.; Stuhr-Hansen, N.; Hedegard, P.; Bjornholm, T. Single-electron transistor of a single organic molecule with access to several redox states. *Nature* **2003,** *425* (6959), 698-701.

4. Liu, Y.; Offenhaeusser, A.; Mayer, D. Electrochemical current rectification at bio-functionalized electrodes. *doi:10. 1016/j. bioelechem. 2009. 06. 015* **2009**.

5. Baron, R.; Lioubashevski, O.; Katz, E.; Niazov, T.; Willner, I. Logic gates and elementary computing by enzymes. *Journal of Physical Chemistry A* **2006,** *110* (27), 8548-8553.

6. Tamerler, C.; Sarikaya, M. Genetically Designed Peptide-Based Molecular Materials. *Acs Nano* **2009,** *3* (7), 1606-1615.

7. Tao, N. J. Electron transport in molecular junctions. *Nature Nanotechnology* **2006,** *1* (3), 173-181.

8. Philipp, G.; Weimann, T.; Hinze, P.; Burghard, M.; Weis, J. Shadow evaporation method for fabrication of sub 10 nm gaps between metal electrodes. *Microelectronic Engineering* **1999,** *46* (1-4), 157-160.

9. Park, H.; Lim, A. K. L.; Alivisatos, A. P.; Park, J.; Mceuen, P. L. Fabrication of metallic electrodes with nanometer separation by electromigration. *Applied Physics Letters* **1999,** *75* (2), 301-303.

10. Tao, N. J.; Li, C. Z.; He, H. X. Scanning tunneling microscopy applications in electrochemistry - beyond imaging. *Journal of Electroanalytical Chemistry* **2000,** *492* (2), 81-93.

11. Donhauser, Z. J.; Mantooth, B. A.; Kelly, K. F.; Bumm, L. A.; Monnell, J. D.; Stapleton, J. J.; Price, D. W.; Rawlett, A. M.; Allara, D. L.; Tour, J. M.; Weiss, P. S. Conductance switching in single molecules through conformational changes. *Science* **2001,** *292* (5525), 2303-2307.

12. Xu, B. Q.; Tao, N. J. J. Measurement of single-molecule resistance by repeated formation of molecular junctions. *Science* **2003,** *301* (5637), 1221-1223.

13. Reichert, J.; Ochs, R.; Beckmann, D.; Weber, H. B.; Mayor, M.; von Lohneysen, H. Driving current through single organic molecules. *Physical Review Letters* **2002,** *88* (17), 176804-1-176804-4.

14. Xiang, J.; Liu, B.; Wu, S. T.; Ren, B.; Yang, F. Z.; Mao, B. W.; Chow, Y. L.; Tian, Z. Q. A controllable electrochemical fabrication of metallic electrodes with a

nanometer/angstrom-sized gap using an electric double layer as feedback. *Angewandte Chemie-International Edition* **2005,** *44* (8), 1265-1268.

15. Kervennic, Y. V.; Van der Zant, H. S. J.; Morpurgo, A. F.; Gurevich, L.; Kouwenhoven, L. P. Nanometer-spaced electrodes with calibrated separation. *Applied Physics Letters* **2002,** *80* (2), 321-323.

16. Li, C. Z.; He, H. X.; Tao, N. J. Quantized tunneling current in the metallic nanogaps formed by electrodeposition and etching. *Applied Physics Letters* **2000,** *77* (24), 3995-3997.

17. McCreery, R. L.; Bergren, A. J. Progress with Molecular Electronic Junctions: Meeting Experimental Challenges in Design and Fabrication. *Adv. Mater.* **2009,** *21* (43), 4303-4322.

18. Tao, N. J. Electron transport in molecular junctions. *Nat. Nanotechnol.* **2006,** *1* (3), 173-181.

19. Xu, B. Q.; Tao, N. J. J. Measurement of single-molecule resistance by repeated formation of molecular junctions. *Science* **2003,** *301* (5637), 1221-1223.

20. Xiao, X. Y.; Xu, B. Q.; Tao, N. J. Measurement of single molecule conductance: Benzenedithiol and benzenedimethanethiol. *Nano Lett.* **2004,** *4* (2), 267-271.

21. Widawsky, J. R.; Kamenetska, M.; Klare, J.; Nuckolls, C.; Steigerwald, M. L.; Hybertsen, M. S.; Venkataraman, L. Measurement of voltage-dependent electronic transport across amine-linked single-molecular-wire junctions. *Nanotechnology* **2009,** *20* (43), 434009.

22. Ko, C. H.; Huang, M. J.; Fu, M. D.; Chen, C. H. Superior Contact for Single-Molecule Conductance: Electronic Coupling of Thiolate and Isothiocyanate on Pt, Pd, and Au. *J. Am. Chem. Soc.* **2010,** *132* (2), 756-764.

23. Chen, F.; Li, X. L.; Hihath, J.; Huang, Z. F.; Tao, N. J. Effect of anchoring groups on single-molecule conductance: Comparative study of thiol-, amine-, and carboxylic-acid-terminated molecules. *J. Am. Chem. Soc.* **2006,** *128* (49), 15874-15881.

24. Kiguchi, M.; Murakoshi, K. Conductance of single C-60 molecule bridging metal electrodes. *J. Phys. Chem. C* **2008,** *112* (22), 8140-8143.

25. Chen, F.; He, J.; Nuckolls, C.; Roberts, T.; Klare, J. E.; Lindsay, S. A molecular switch based on potential-induced changes of oxidation state. *Nano Lett.* **2005,** *5* (3), 503-506.

26. Albrecht, T.; Guckian, A.; Ulstrup, J.; Vos, J. G. Transistor-like behavior of transition metal complexes. *Nano Lett.* **2005,** *5* (7), 1451-1455.

27. Kang, N.; Erbe, A.; Scheer, E. Observation of negative differential resistance in DNA molecular junctions. *Appl. Phys. Lett.* **2010,** *96* (2), 023701.

28. Wu, S. M.; Gonzalez, M. T.; Huber, R.; Grunder, S.; Mayor, M.; Schonenberger, C.; Calame, M. Molecular junctions based on aromatic coupling. *Nat. Nanotechnol.* **2008,** *3* (9), 569-574.

29. Chang, S. A.; He, J.; Lin, L. S.; Zhang, P. M.; Liang, F.; Young, M.; Huang, S.; Lindsay, S. Tunnel conductance of Watson-Crick nucleoside-base pairs from telegraph noise. *Nanotechnology* **2009,** *20* (18), 185102.

30. Wang, W. Y.; Lee, T.; Reed, M. A. *Reports on Progress in Physics* **2005,** *68* (3), 523-544.