
References

Chapter 15
Molecular Electronics: An Introduction to Theory and Experiment,

See also:


2.1 Introduction

\[ \Delta E = |\varepsilon_0 - E_F| = \text{injection energy} \]

\[ \Gamma = \Gamma_L + \Gamma_R = \text{level width} \]

- **Traversal time:**
  \[ \tau = \frac{\hbar}{\sqrt{\Delta E^2 + \Gamma^2}} \]

- **Energy scale of the Coulomb interaction:** \( U \)

In this lecture we focus on situations in which:

\[ \tau >> \frac{\hbar}{U} \]

and therefore, the transport is dominated by the Coulomb repulsion of the electrons inside the molecule.

Specially, this situation is realized in resonant situations when the metal-molecule coupling is relatively weak.
2.1 Charging effects in transport through nanoscale devices

How small and how cold should a conductor be so that adding or subtracting a single electron has a measurable effect?

1) The capacitance $C$ of the island (or dot) has to be such that the charging energy ($e^2/C$) be smaller than the thermal energy ($k_B T$):

$$ \frac{e^2}{C} \gg k_B T $$

2) The barriers have to be sufficiently opaque such that the electrons are located in the dot:

$$ \Delta E \Delta t = (\frac{e^2}{C})(R_tC) > h \Rightarrow R_t \gg \frac{h}{e^2} $$

In molecular transistors these two requirements can be easily met!!!
2.1 Charging effects in transport through nanoscale devices

- To resolve the discrete levels of a quantum dot: $\Delta E >> k_B T$

- The level spacing at the Fermi energy for a box of size $L$ depends on the dimensionality:
  
  $\Delta E = \frac{\hbar^2 \pi^2}{mL^2} \times \begin{cases} 
  N/4 & (1D) \\
  1/\pi & (2D) \\
  (1/3\pi^2 N)^{1/3} & (3D)
  \end{cases}$

- The level spacing of a 100 nm 2D dot is around 0.03 meV, which is large enough to be observable at dilution refrigerator temperatures (100 mK $\rightarrow$ 0.0086 meV).

- Using 3D metals to form a dot one needs to make dots as small as 5 nm in order to see atom-like properties.

- In the case of molecular junctions, the level space is essentially the HOMO-LUMO gap and it is typically several electronvolts. Therefore, the level quantization is easily observable in molecular transistor even at room temperature.
2.1 Coulomb blockade phenomenology

2.1 Coulomb blockade: a well-known phenomenon in mesoscopic physics

Metallic islands

[Images and diagrams related to the text]
2.1 Coulomb blockade: a well-known phenomenon in mesoscopic physics

Nanoparticles

Spectroscopic Measurements of Discrete Electronic States in Single Metal Particles

D. C. Ralph, C. T. Black, and M. Tinkham

FIG. 1. (a) $I$ vs $V$ and (b) (solid curve) $dI/dV$ vs $V$ for tunneling via a single particle at 4.2 K and $H = 0$. (b) Dashed curve: Theoretical fit discussed in the text, offset 100 GΩ⁻¹. Inset: Schematic diagram of device.

FIG. 2. Signals due to the same device as Fig. 1, at 320 mK. (a) $I$ vs $V$ for superconducting and normal leads. The $S$-lead curve has been displaced 10 pA in $I$. (b) and (c) $dI/dV$ vs $V$ for positive and negative bias, with the $S$-lead data shifted in $V$, as labeled, so as to align the maxima of $dI/dV$ with the $N$-lead data. For ease of comparison, the amplitude of the $S$-lead data is reduced by a factor of 2 and offset on the $dI/dV$ axis in (b) and (c).
2.1 Coulomb blockade: a well-known phenomenon in mesoscopic physics

*Semiconductor quantum dots*

2DEG + lateral patterning

$V_G$ metal electrode

![Diagram of a semiconductor quantum dot system with AlGaAs and GaAs layers, a 2DEG region, and a quantum dot.]

Resonant tunneling dot
Weis (MPI, Stuttgart)

2 quantum dots
Kouwenhoven (TU Delft)

- confinement $\Rightarrow$ discrete energy levels $\varepsilon_i$
- some quantum number $i$
- $C < 10^{-15} \text{F} \Rightarrow$ single-electron effects
2.1 Single-molecule three-terminal devices
2.2 Coulomb blockade theory: constant interaction model

\[ E_{\text{dot}}(N) = U(N) + \sum_{p=1}^{N} E_p \]

\[ U(N) = (Ne)^2 / 2C - NeV_{\text{ext}} \]

\[ C = C_S + C_D + C_G \]

\[ V_{\text{ext}} = \left( C_S V_S + C_G V_G + C_D V_D \right) / C \]

\[ E_p (p = 1, 2, \ldots) = \text{single-electron energy levels} \]

\[ \Gamma_L^{(p)}, \Gamma_R^{(p)} \Rightarrow \text{tunneling rates} \]

\[ k_B T, \Delta E >> h(\Gamma_L^{(p)} + \Gamma_R^{(p)}) \]

(weak coupling)
2.2 Coulomb blockade theory

Periodicity of the oscillations:

- Dot chemical potential:

\[ \mu_{dot}(N) = E_{dot}(N) - E_{dot}(N-1) = \left( N - \frac{1}{2} \right) \frac{e^2}{C} - eV_{ext} + E_N \]

- Electrons can flow from left to right when:

\[ \mu_L \geq \mu_{dot} \geq \mu_R \]
2.2 Coulomb blockade theory

- For small bias voltages, \( V_{sd} \sim 0 \):

\[
\mu_{dot}(N) = \left( N - \frac{1}{2} \right) \frac{e^2}{C} - e\alpha V_G + E_N; \quad (\alpha = C_G / C = \text{gate coupling})
\]

- Thus, the addition energy is given by:

\[
\Delta \mu(N) = \mu_{dot}(N+1) - \mu_{dot}(N) = \frac{e^2}{C} + E_{N+1} - E_N = \frac{e^2}{C} + \Delta E
\]

- In the absence of charging effects, the addition energy is determined by the irregular spacing \( \Delta E \) of the single-electron levels. The charging energy \( e^2/C \) regulates the spacing and when it is much larger than the level spacing (as in metallic islands), it determines the periodicity of the Coulomb oscillations.

- From an experimental point of view, the Coulomb oscillations are measured as a function of the gate voltage and the peak spacing is given by:

\[
\Delta V_G = \Delta \mu(N) / e\alpha = (e^2 / C + \Delta E) / e\alpha
\]

while the condition \( e\alpha V_G^N = (N - 1/2)e^2 / C + E_N \) gives the gate voltage of the \( N \)-th Coulomb peak.
2.2 Coulomb blockade theory

Amplitude and line-shape of the oscillations:

Different tunneling processes (energy conservation):

state p in the dot (N electrons) $\rightarrow$ left lead at energy $E_{p}^{f,l}(N)$:

$$E_{p}^{f,l}(N) = E_{p} + U(N) - U(N - 1) - (1 - \eta)eV$$

left lead at energy $E_{p}^{i,l}(N)$ $\rightarrow$ state p in the dot (N electrons):

$$E_{p}^{i,l}(N) = E_{p} + U(N + 1) - U(N) - (1 - \eta)eV$$

state p in the dot (N electrons) $\rightarrow$ right lead at energy $E_{p}^{f,r}(N)$:

$$E_{p}^{f,r}(N) = E_{p} + U(N) - U(N - 1) + \eta eV$$

right lead at energy $E_{p}^{i,r}(N)$ $\rightarrow$ state p in the dot (N electrons):

$$E_{p}^{i,r}(N) = E_{p} + U(N + 1) - U(N) + \eta eV$$

Stationary current through the left barrier:

$$I = \frac{e}{\hbar} \sum_{p=1}^{\infty} \sum_{\{n_i\}} \Gamma_{L}^{(p)}(\{n_i\}) \left( \delta_{n_p,0} f(E_{p}^{i,l}(N) - E_{F}) - \delta_{n_p,1} [1 - f(E_{p}^{f,l}(N) - E_{F})] \right)$$
In equilibrium the probability distribution $P\{\{n_i\}\}$ is given by the Gibbs distribution in the grand canonical ensemble:

$$P_{eq} (\{n_i\}) = \frac{1}{Z} \exp \left[- \frac{1}{k_B T} \left( \sum_{i=1}^{\infty} E_i n_i + U(N) - NE_F \right) \right]; \quad Z = \text{partition function}$$

The non-equilibrium probability distribution $P$ is a stationary solution of the kinetic equation:

$$\frac{\partial}{\partial t} P(\{n_i\}) = 0 = \sum_{p} P(\{n_i\}) \delta_{n_p,0} \left[ \Gamma_L^{(p)} f (E_i^l (N) - E_F) + \Gamma_R^{(p)} f (E_i^r (N) - E_F) \right]$$

$$- \sum_{p} P(\{n_i\}) \delta_{n_p,1} \left[ \Gamma_L^{(p)} (1 - f (E_i^l (N) - E_F)) + \Gamma_R^{(p)} (1 - f (E_i^r (N) - E_F)) \right]$$

$$+ \sum_{p} P(n_1,\ldots,n_{p-1},1,n_{p+1},\ldots) \delta_{n_p,0} \left[ \Gamma_L^{(p)} (1 - f (E_i^l (N + 1) - E_F)) + \Gamma_R^{(p)} (1 - f (E_i^r (N + 1) - E_F)) \right]$$

$$+ \sum_{p} P(n_1,\ldots,n_{p-1},0,n_{p+1},\ldots) \delta_{n_p,1} \left[ \Gamma_L^{(p)} f (E_i^l (N - 1) - E_F) + \Gamma_R^{(p)} f (E_i^r (N - 1) - E_F) \right]$$
2.2 Coulomb blockade theory

+ Linear response theory: \[ P(\{n_i\}) = P_{eq}(\{n_i\}) \left( 1 + \frac{eV}{k_B T} \Psi(\{n_i\}) \right) \]

The joint probability that the quantum dot contains \(N\) electrons and that the level is occupied is:

\[ P_{eq}(N,n_p = 1) = \sum_{\{n_i\}} P_{eq}(\{n_i\}) \delta_{N,\sum n_i} \delta_{n_p,1} \]

In terms of this probability the conductance is given by:

\[ G = \frac{e^2}{k_B T} \sum_{p=1}^{\infty} \sum_{N=1}^{\infty} \frac{\Gamma_R^{(p)} \Gamma_R^{(p)}}{\Gamma_L^{(p)} + \Gamma_R^{(p)}} P_{eq}(N,n_p = 1) \left[ 1 - f(E_p + U(N) - U(N - 1) - E_F) \right] \]

- Limit:

\[ k_B T \ll e^2 / C, \Delta E \]

\[ G(V_G,T)/G_{max} = \cosh^{-2} \left( \frac{e \alpha(V_G - V_0)}{2k_B T} \right) \]

\[ G_{max} = \left( \frac{e^2}{\pi} \frac{\Gamma_L^{(N_0)} \Gamma_R^{(N_0)}}{2k_B T \Gamma_L^{(N_0)} + \Gamma_R^{(N_0)}} \right) \]
2.2 An example: Coulomb oscillations and staircase

$E_1 - E_F = 50 \text{ meV}; \ E_2 - E_F = 80 \text{ meV}$

$\Delta E = 30 \text{ meV}; \ e^2/C = 100 \text{ meV}$

$T = 30 \text{ K}; \ \Gamma_L^{(p)} = \Gamma_R^{(p)} = 1 \text{ meV}; \ \eta = 0.6$
2.2 An example: Stability diagrams and Coulomb diamonds
2.3 Elastic and inelastic cotunneling

- **Elastic cotunneling process:**

- **Inelastic cotunneling process:**
2.3 Kondo effect

- Spin-flip cotunneling processes can change the spectrum of the dot leading to the screening of the localized spin and to the appearance of the so-called Kondo resonance.

- The Kondo resonance lies exactly at the Fermi energy, no matter the position of the original level. For this reason, the Kondo effect leads to an enhancement of the conductance. The only requirement for this effect to occur is that the temperature is below the Kondo temperature (see below).

- The width of the Kondo resonance is proportional to the characteristic energy scale for Kondo physics, the so-called Kondo temperature:

\[
k_B T_K = \frac{\sqrt{\Gamma U}}{2} \exp\left(\frac{\pi \varepsilon_0 (\varepsilon_0 + U)}{\Gamma U}\right)
\]
2.3 Kondo effect

Transport signatures of the Kondo effect:

- Zero-bias line in the stability diagram for odd number of electrons in the dot.
- Peak in the low-bias conductance at low temperatures with width equal to the Kondo temperature.
- Characteristic temperature dependence of the linear conductance.
2.4 Single-molecule transistors: Observation of Coulomb blockade

Nano-mechanical oscillations in a single-C₆₀ transistor

Hongkun Park*, Jiwoong Park†, Andrew K. L. Lim*, Erik H. Anderson*, A. Paul Alivisatos*‡ & Paul L. McEuen†‡

2.4 Single-molecule transistors: Observation of Coulomb blockade

*Park et al., Nature 417, 722 (2002)*
2.4 Single-molecule transistors: Observation of Coulomb blockade


(OPV5)
2.4 Single-molecule transistors: Observation of the Kondo effect

Molecules: Co-ion compounds; $T_K = 10 - 25$ K.
2.4 Single-molecule transistors: Observation of the Kondo effect


Molecules: divanadium compounds.