Chapter 8: Coulomb blockade and Kondo physics

REFERENCES

1) Chapter 15 of Cuevas& Scheer.

2) *"Charge transport and single-electron effects in nanoscale systems"*, J.M. Thijssen and H.S.J. Van der Zant, Phys. Stat. Sol. (b) **245**, 1455 (2008).

3) "*Coulomb blockade oscillations in semiconductor nanostructures*", H. van Houten, C.W.J. Beenakker, and A.A.M. Staring in *Single Charge Tunneling*, edited by H. Grabert and M.H. Devoret, NATO ASI Series B294 (Plenum, New York, 1992).

4) *"The revival of the Kondo effect"*, L.P. Kouwenhoven and L. Glazman, Physics World, pag. 33, January 2001.

8.1 Introduction

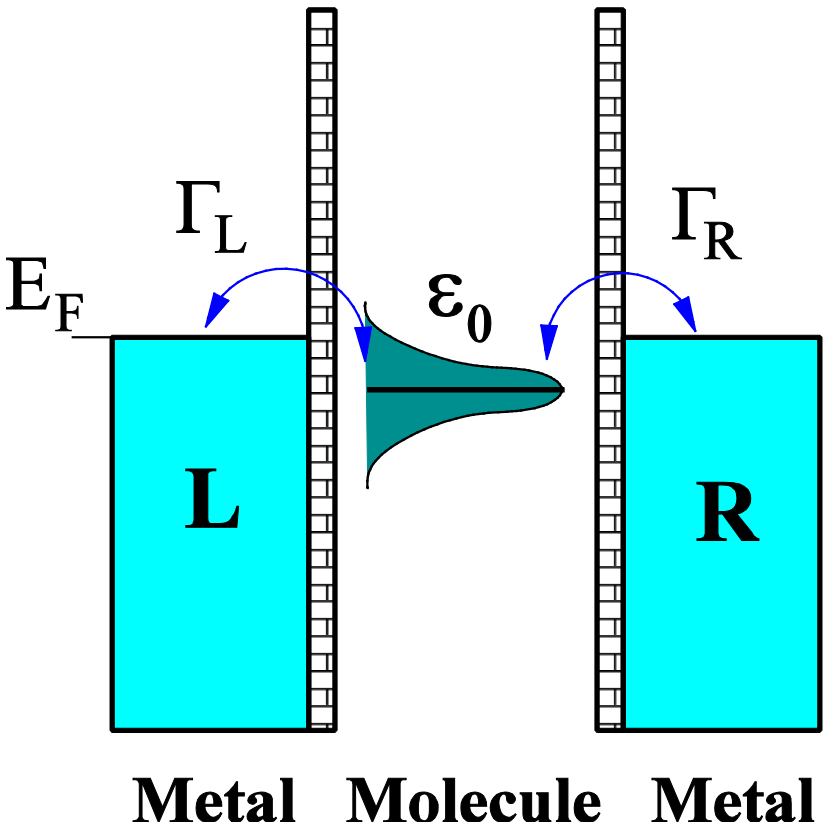
$\Delta E = |\varepsilon_0 - E_F| =$ injection energy

$\Gamma = \Gamma_L + \Gamma_R =$ level width

- **Traversal time:**

$$\tau = \hbar / \sqrt{\Delta E^2 + \Gamma^2}$$

- **Energy scale of the Coulomb interaction:** U



In this chapter we focus on situations in which

$$\tau \gg \frac{\hbar}{U}$$

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

This situation is realized when the metal-molecule coupling is relatively weak.

8.2 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?

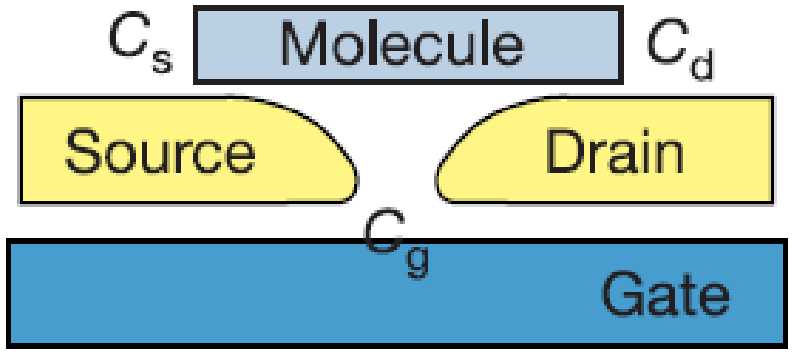
1. The capacitance C of the island (or dot) has to be such that the *charging energy* (e^2/C) is larger than the thermal energy ($k_B T$):

$$e^2/_C \gg k_B T$$

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

$$\Delta E \Delta T = \left(e^2/_C\right)(R_t C) > H \implies R_t \gg h/e^2$$

In molecular transistors these two requirements can be met.



8.2 Charging effects in transport through nanoscale devices

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

- The level spacing at the Fermi energy for a box of size *L* depends on the dimensionality:

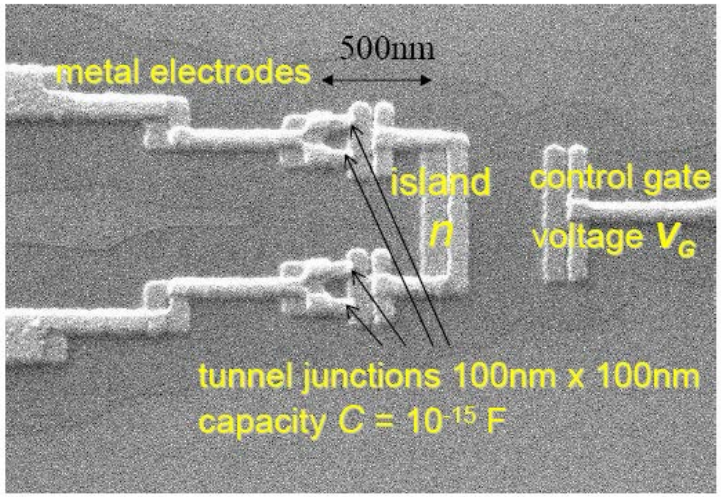
$$\Delta E = \frac{\hbar^2 \pi^2}{mL^2} \times \begin{cases} N/4 & (1\mathrm{D}) \\ 1/\pi & (2\mathrm{D}) \\ (3\pi^2 N)^{-1/3} & (3\mathrm{D}) \end{cases}$$

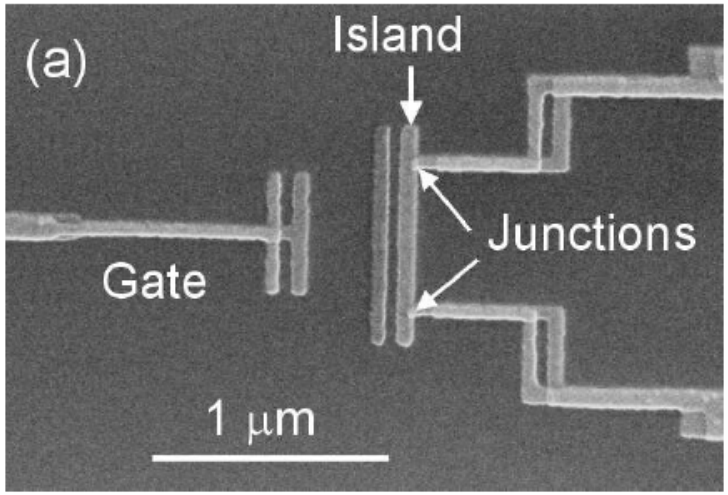
- The level spacing of a 100 nm 2D dot is around 0.03 meV, which is large enough to be observable at dilution refrigerator temperatures (100 mK → 0.0086 meV).

- Using 3D metals to form a dot, one needs to choose a radius of around 5 nm in order to see atom-like properties.

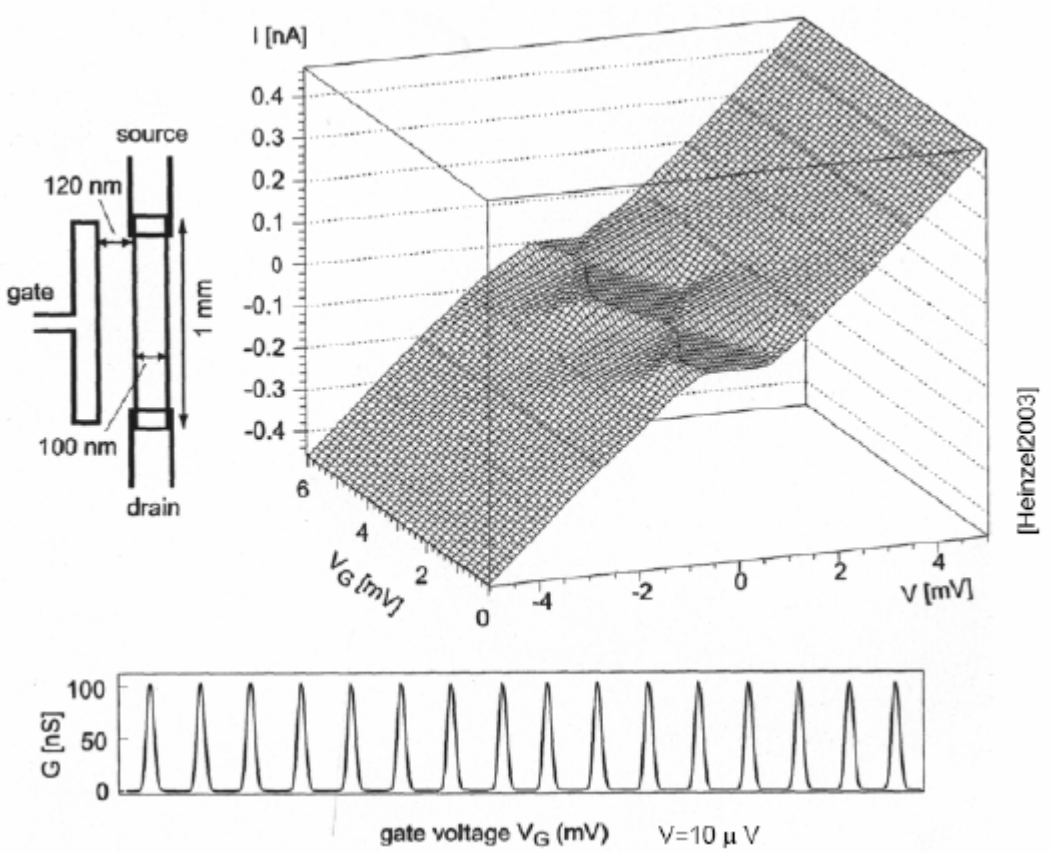
- In the case of molecular junctions, the level spacing is essentially the HOMO-LUMO gap and it is typically several electronvolts. Therefore, the level quantization is easily observable in molecular transistor even at room temperature.

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





Metallic islands



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

Nanoparticles

VOLUME 74, NUMBER 16 PHYSICAL REVIEW LETTERS 17 APRIL 1995

Spectroscopic Measurements of Discrete Electronic States in Single Metal Particles

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

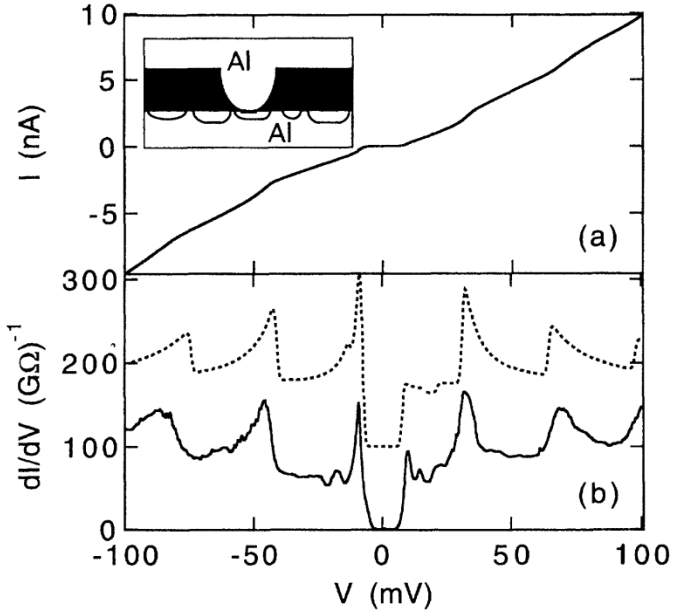


FIG. 1. (a) I vs V and (b) (solid curve) dI/dV vs V for tunneling via a single particle at 4.2 K and $H = 0$. (b) Dashed curve: Theoretical fit discussed in the text, offset 100 $G\Omega^{-1}$. Inset: Schematic diagram of device.

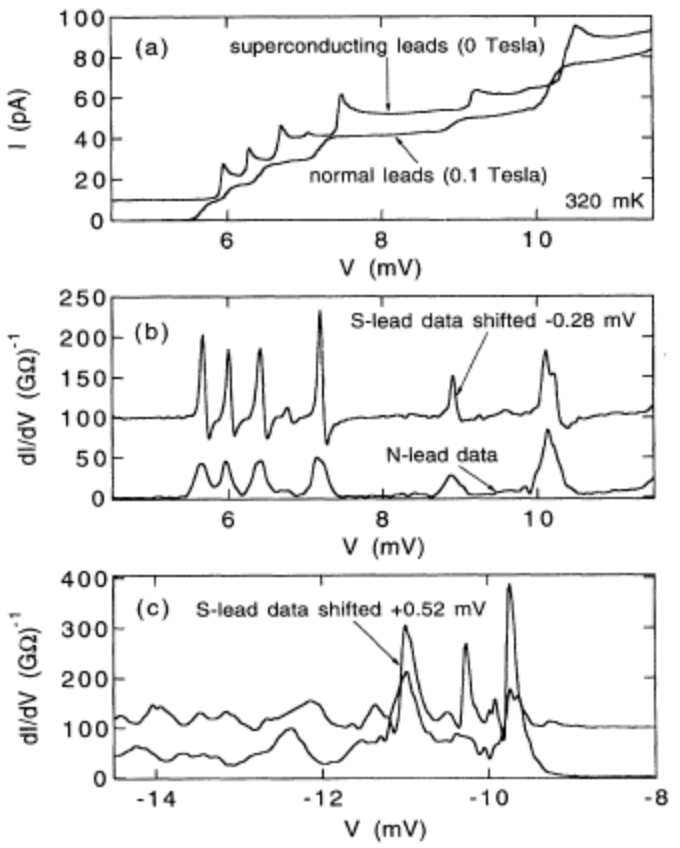
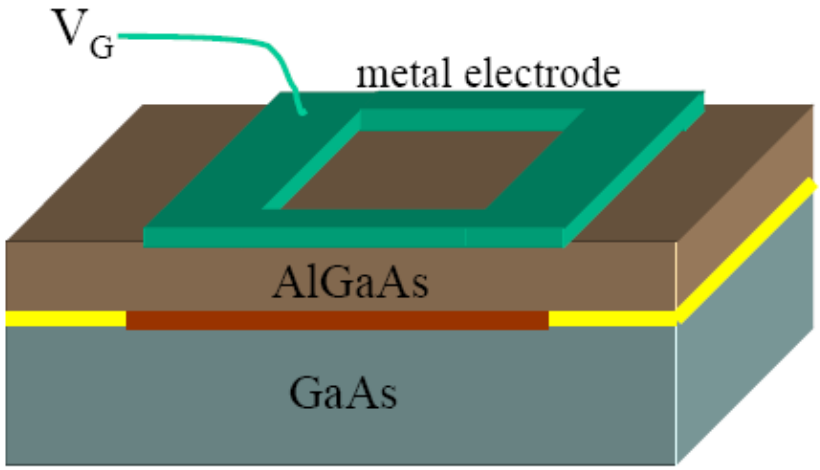


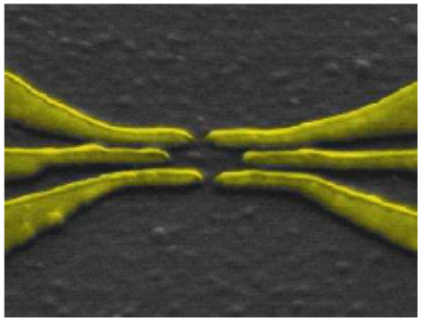
FIG. 2. Signals due to the same device as Fig. 1, at 320 mK. (a) I vs V for superconducting and normal leads. The S-lead curve has been displaced 10 pA in I. (b) and (c) dI/dV vs V for positive and negative bias, with the S-lead data shifted in V, as labeled, so as to align the maxima of dI/dV with the 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).

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

Semiconductor quantum dots

2DEG + lateral patterning





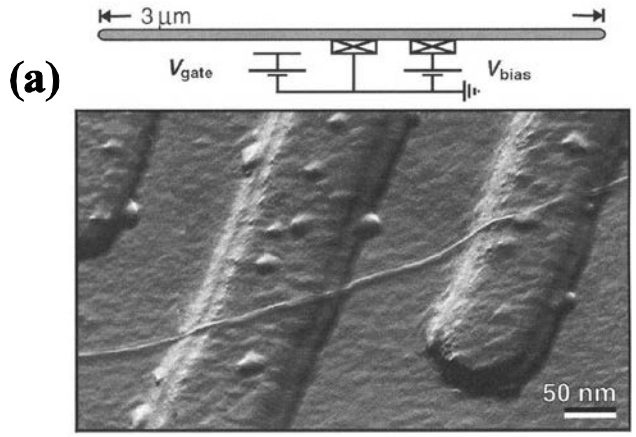
Resonant tunneling dot
Weis (MPI, Stuttgart)

2 quantum dots
Kouwenhoven (TU Delft)

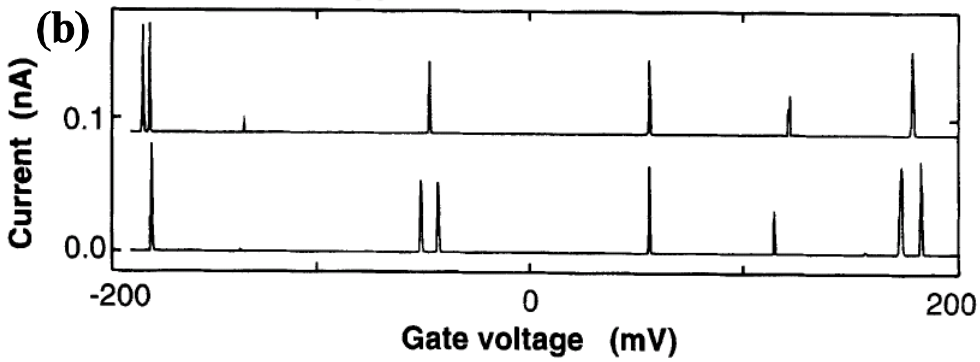
- confinement $\Rightarrow$ discrete energy levels ε_i
  some quantum number i
- $C < 10^{-15}$ F $\Rightarrow$ single-electron effects

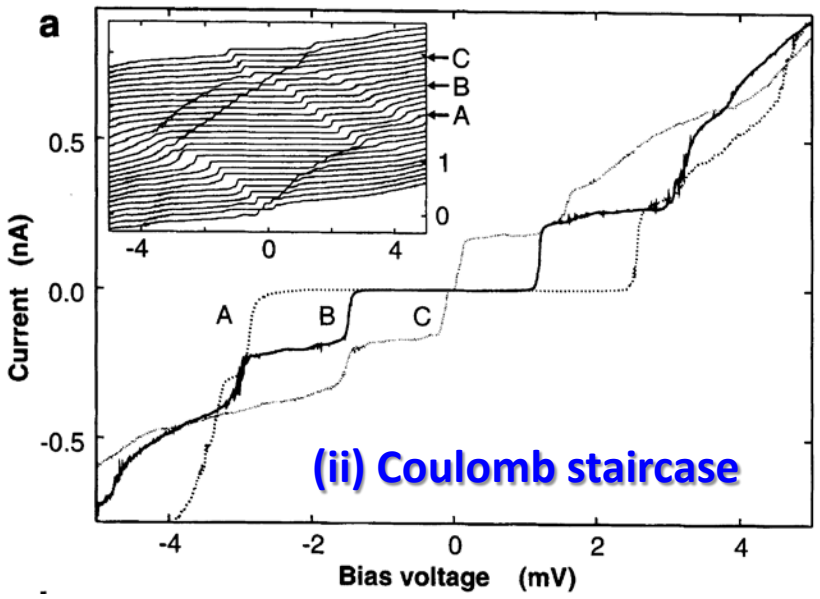
8.2 Coulomb blockade phenomenology in carbon nanotubes

*S.J. Tans et al., Nature **386**, 474 (1997)*

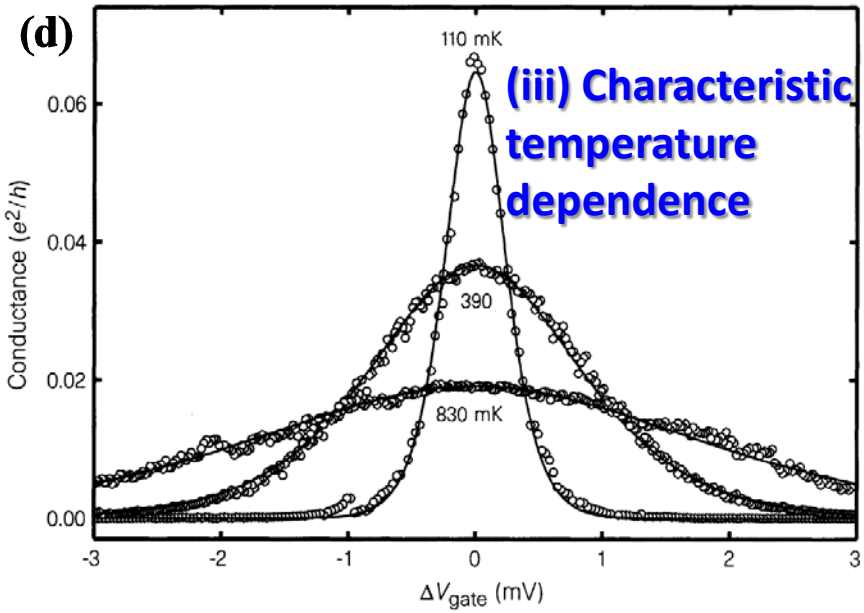


(i) Coulomb oscillations



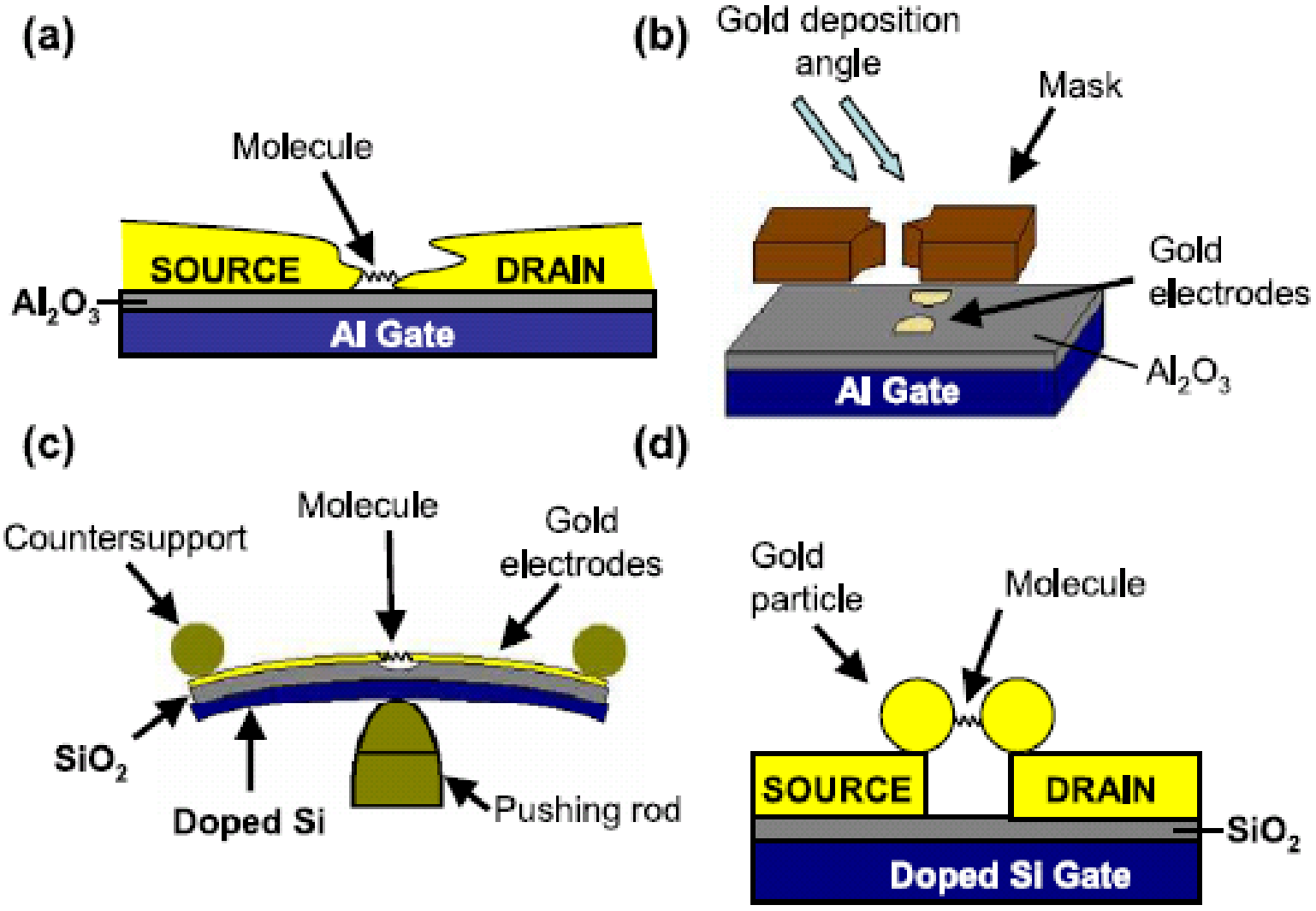


(ii) Coulomb staircase

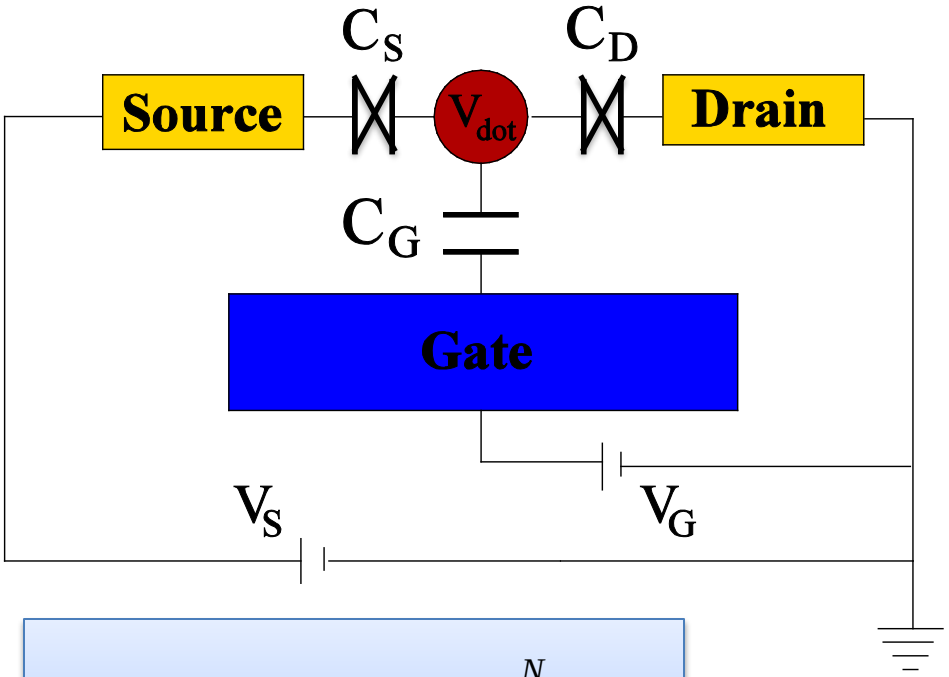


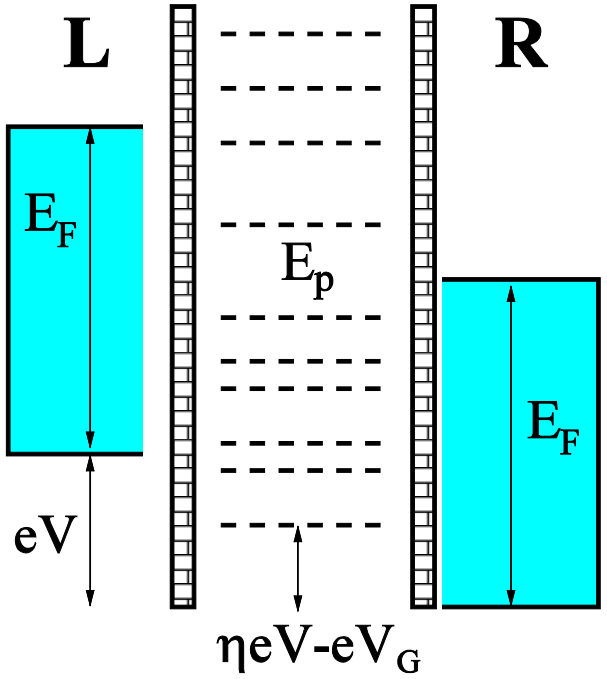
(iii) Characteristic temperature dependence

8.3 Single-molecule three-terminal devices



8.4 Coulomb blockade theory: constant interaction model





$$E_{Dot}(N) = U(N) + \sum_{p=1}^{N} E_p$$

$E_p \ (p = 1,2,\ldots) =$ single-electron energy levels

$$U(N) = (Ne)^2/2C - NeV_{ext}$$

$$C = C_S + C_D + C_G$$

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

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

$$k_B T, \Delta E \gg h(\Gamma_L{}^{(p)} + \Gamma_R{}^{(p)})$$

(weak coupling)

8.4 Coulomb blockade theory

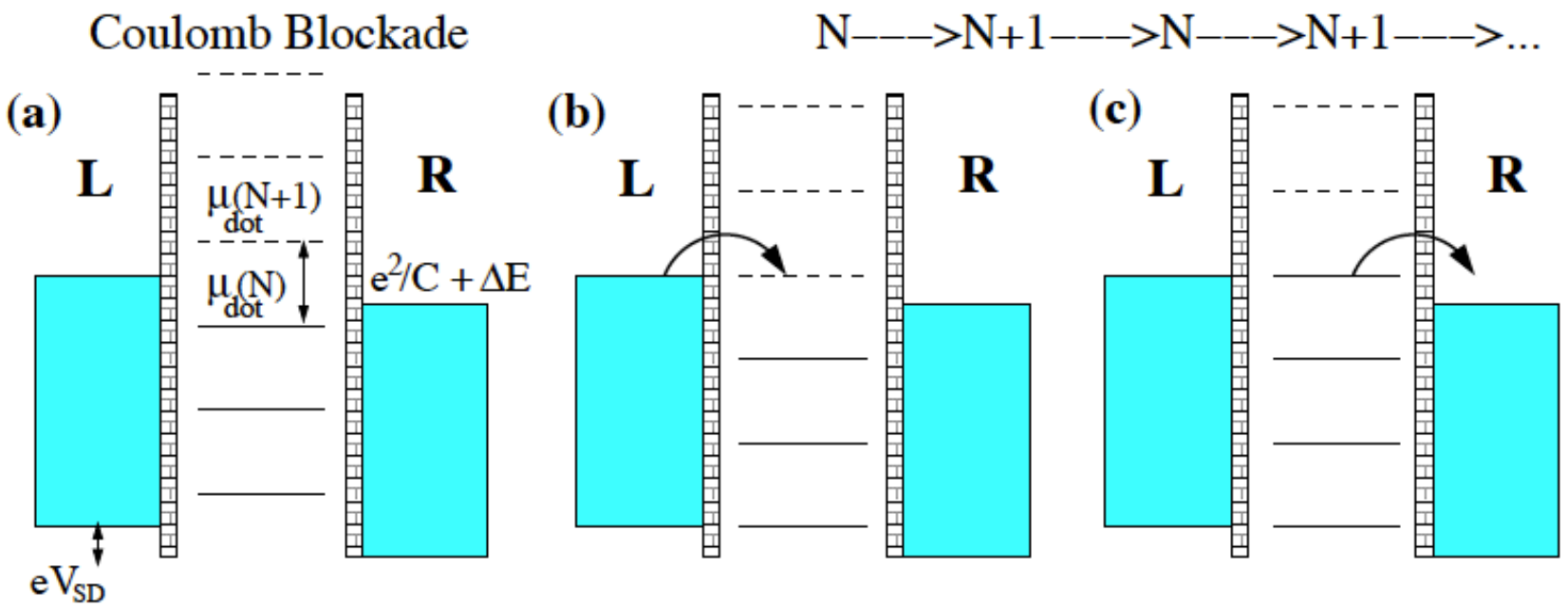
Periodicity of the oscillations

- 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:

$$\mu_L > \mu_{Dot} > \mu_R$$



8.4 Coulomb blockade theory

- For small bias voltages, $V_{SD} \approx 0$:

$$\mu_{Dot}(N) = \left(N - \frac{1}{2}\right)\frac{e^2}{C} - e\alpha V_G + E_N; \qquad (\alpha = C_G / C = \text{ gate coupling})$$

- 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 ΔE of the single-electron levels. The charging energy e^2/C, in contrast, leads to a regular spacing. 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.

8.4 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):

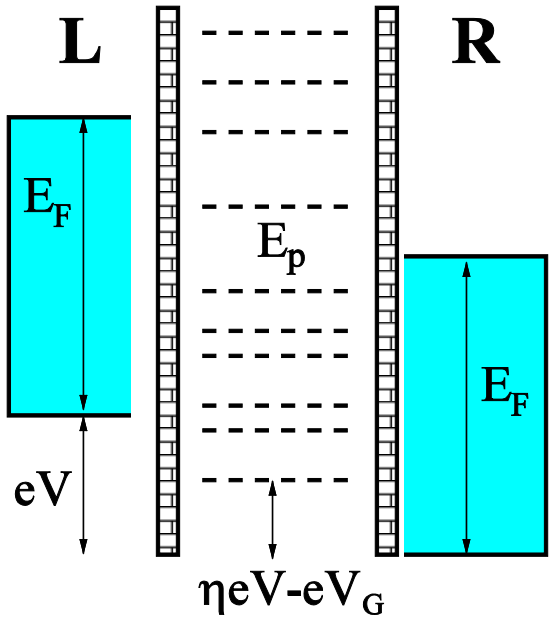
$$E_p^{i,l}(N) = E_p + U(N+1) - U(N) - (1-\eta)eV$$

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

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

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

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



η: fraction of voltage dropping at the right barrier

- **Stationary current through the left barrier:**

$$I = e\sum_{p=1}^{\infty}\sum_{\{n_i\}}\Gamma_L^{(p)}P(\{n_i\})\left(\delta_{n_p,0}\,f(E_p^{i,l}(N)-E_F) - \delta_{n_p,1}[1-f(E_p^{f,l}(N)-E_F)]\right)$$

8.4 Coulomb blockade theory

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:

$$\frac{\partial}{\partial t}P(\{n_i\}) = 0$$

$$= -\sum_p P(\{n_i\})\delta_{n_p,0}[\Gamma_L^{(p)} f(E^{i,l}(N) - E_F) + \Gamma_R^{(p)} f(E^{i,r}(N) - E_F)]$$

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

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

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

8.4 Coulomb blockade theory

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

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

$$P_{eq}(N, n_p = 1) = \sum_{\{n_i\}} P_{eq}(\{n_i\})\delta_{N,\sum_i n_i}\delta_{n_p,1}$$

In terms of this probability the conductance is given by:

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

- **Limit:**

$k_B T \gg e^2/C, \Delta E$

$$\begin{cases} G(V_G, T)/G_{\max} = \cosh^{-2}\left(\dfrac{e\alpha(V_G - V_0)}{2k_B T}\right) \\ G_{\max} = \left(\dfrac{e^2}{h}\right)\dfrac{\pi}{2k_B T}\dfrac{\Gamma_L^{(N_0)}\Gamma_R^{(N_0)}}{\Gamma_L^{(N_0)} + \Gamma_R^{(N_0)}} \end{cases}$$

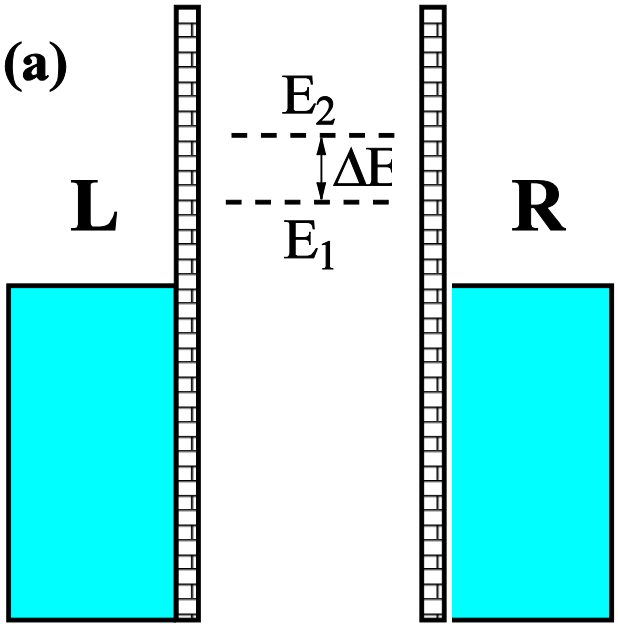
V_0: gate voltage at N_0th resonance (maximum of the CB oscillation)

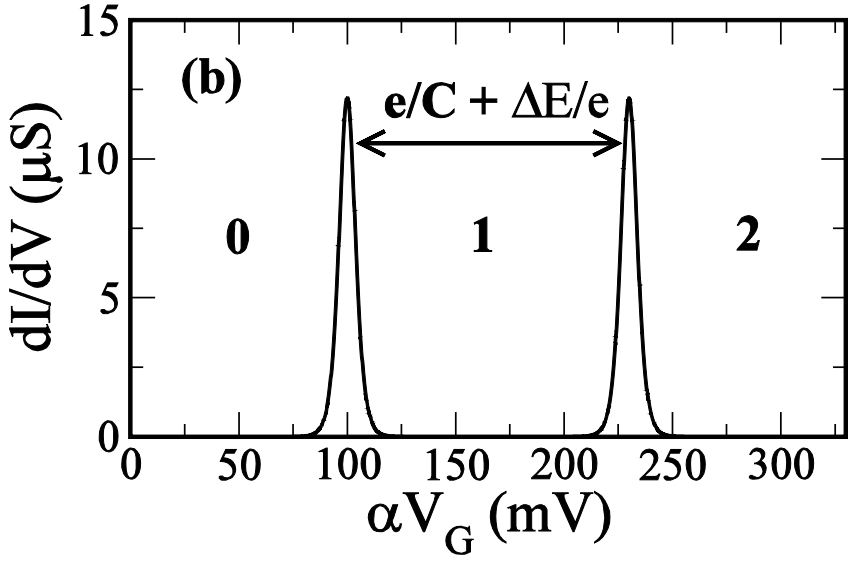
8.4 An example: Coulomb oscillations and staircase

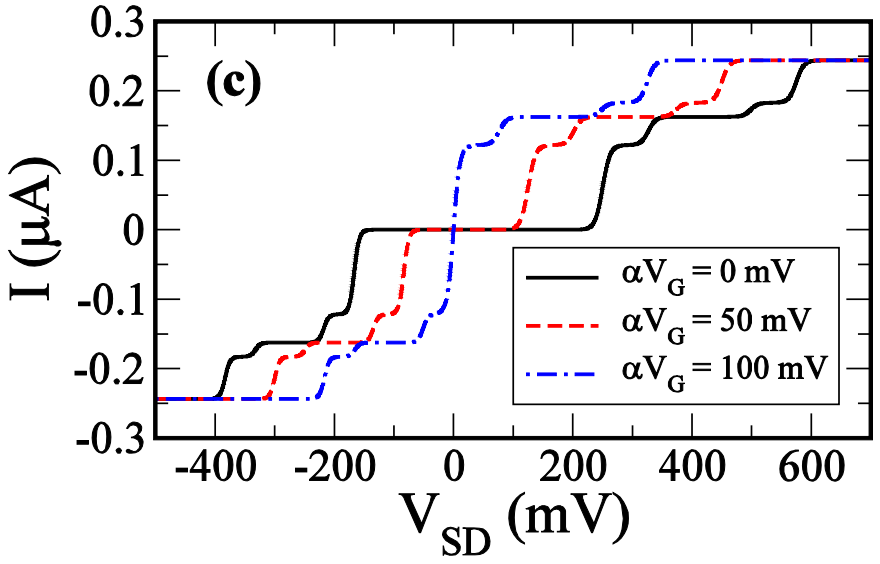
$E_1 - E_F = 50$ meV; $E_2 - E_F = 80$ meV

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

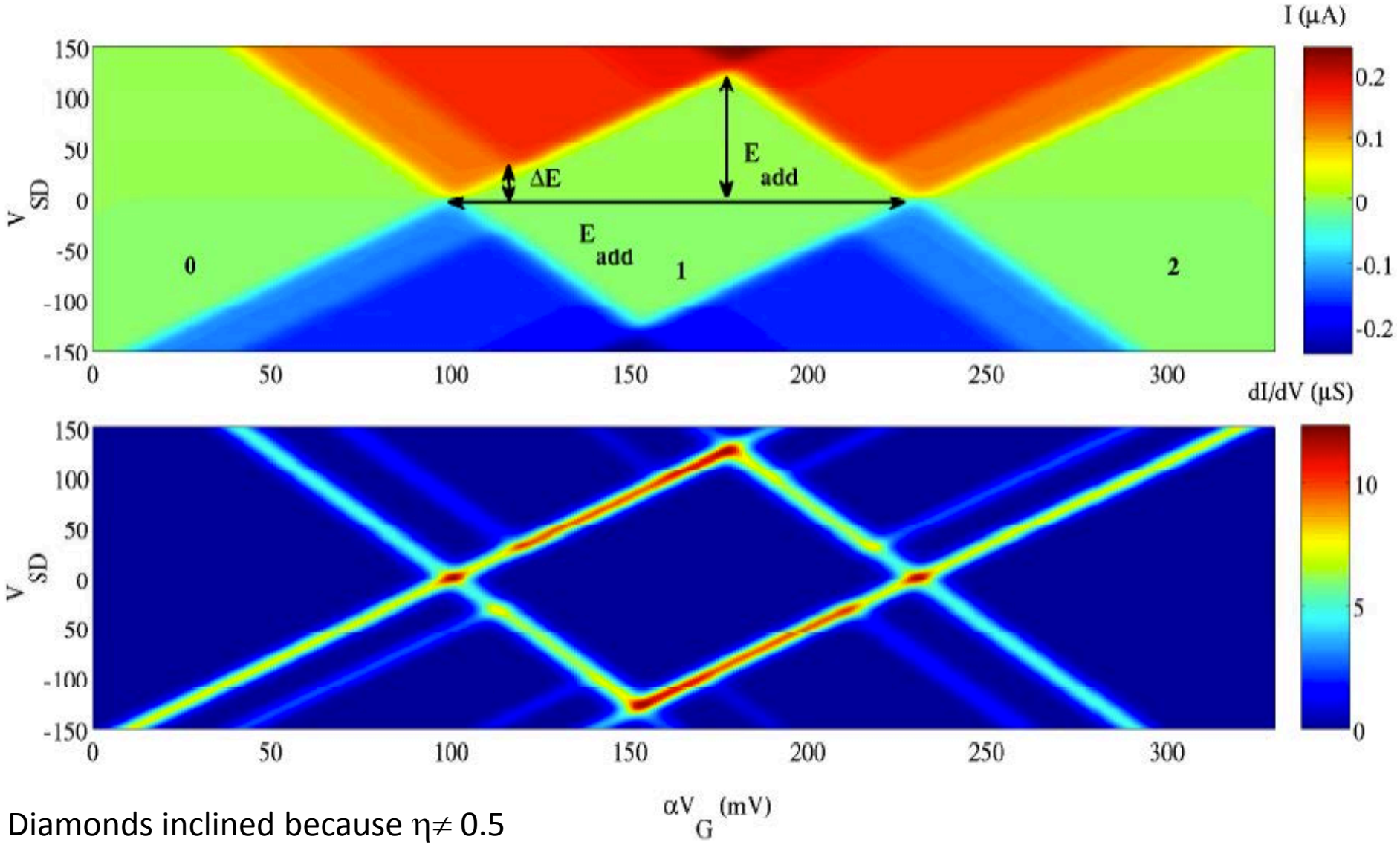
$T = 30$ K; $\Gamma_L^{(p)} = \Gamma_R^{(p)} = 1$ meV; $\eta = 0.6$







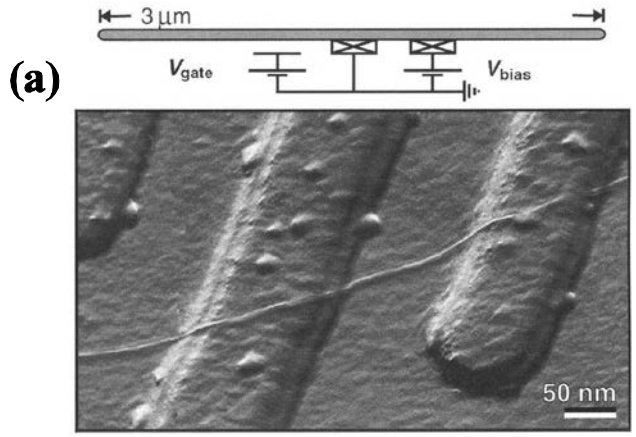
8.4 An example: Stability diagrams and Coulomb diamonds



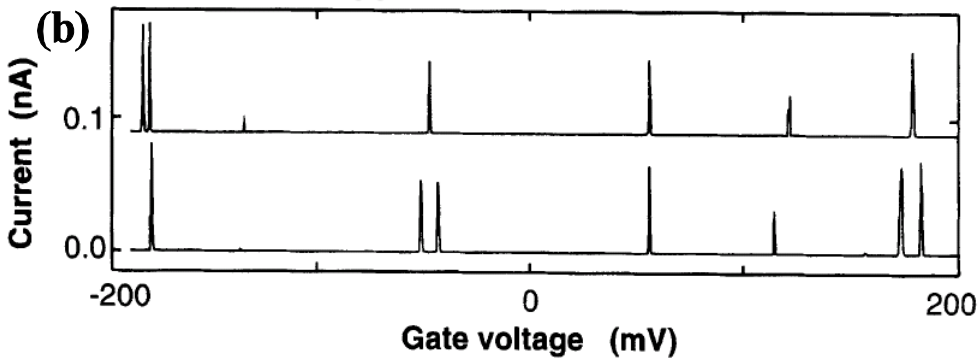
Diamonds inclined because $\eta \neq 0.5$

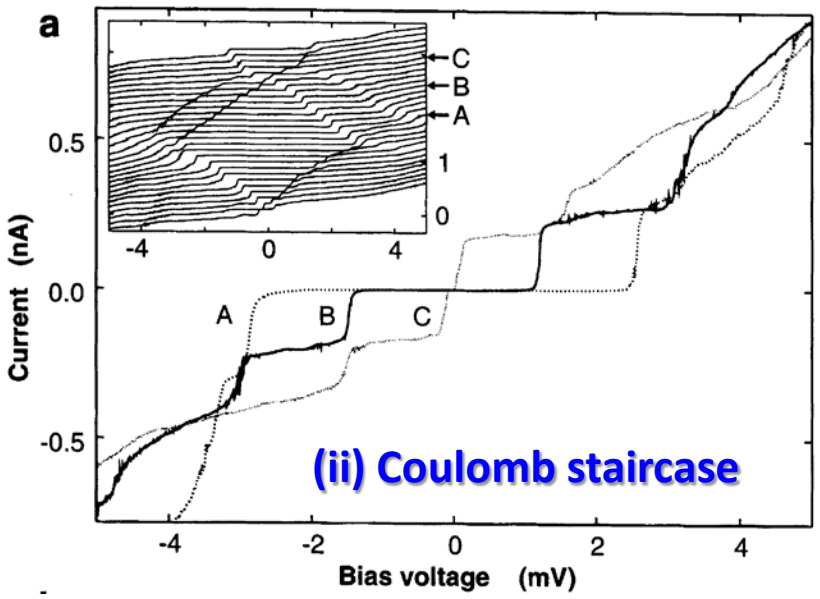
8.4 Coulomb blockade phenomenology in carbon nanotubes

*S.J. Tans et al., Nature **386**, 474 (1997)*

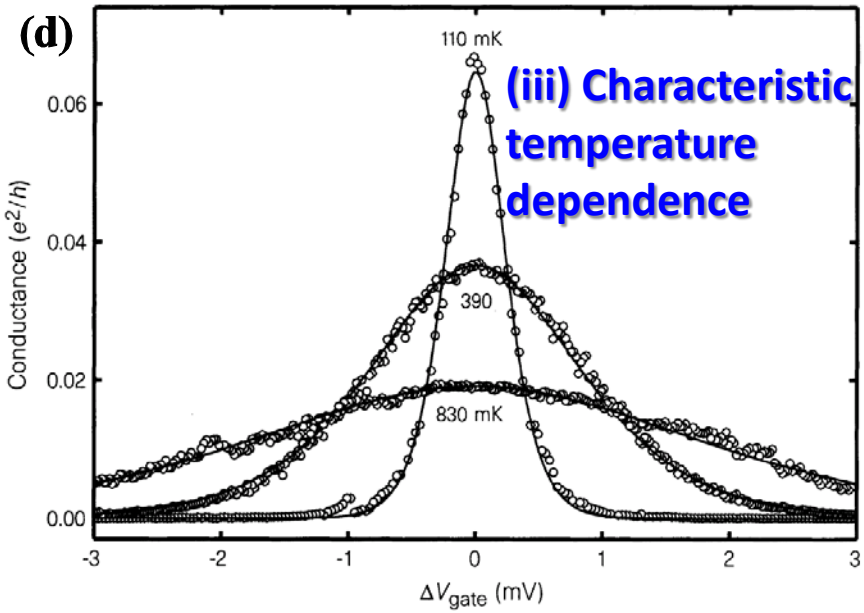


(i) Coulomb oscillations





(ii) Coulomb staircase

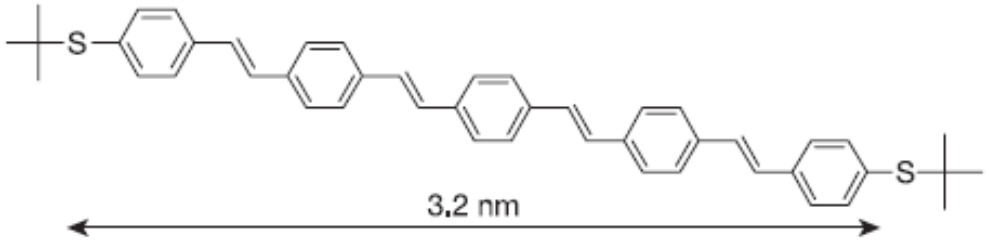


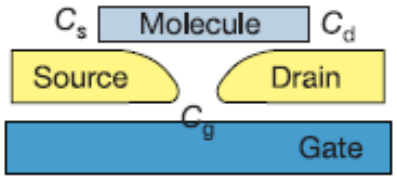
(iii) Characteristic temperature dependence

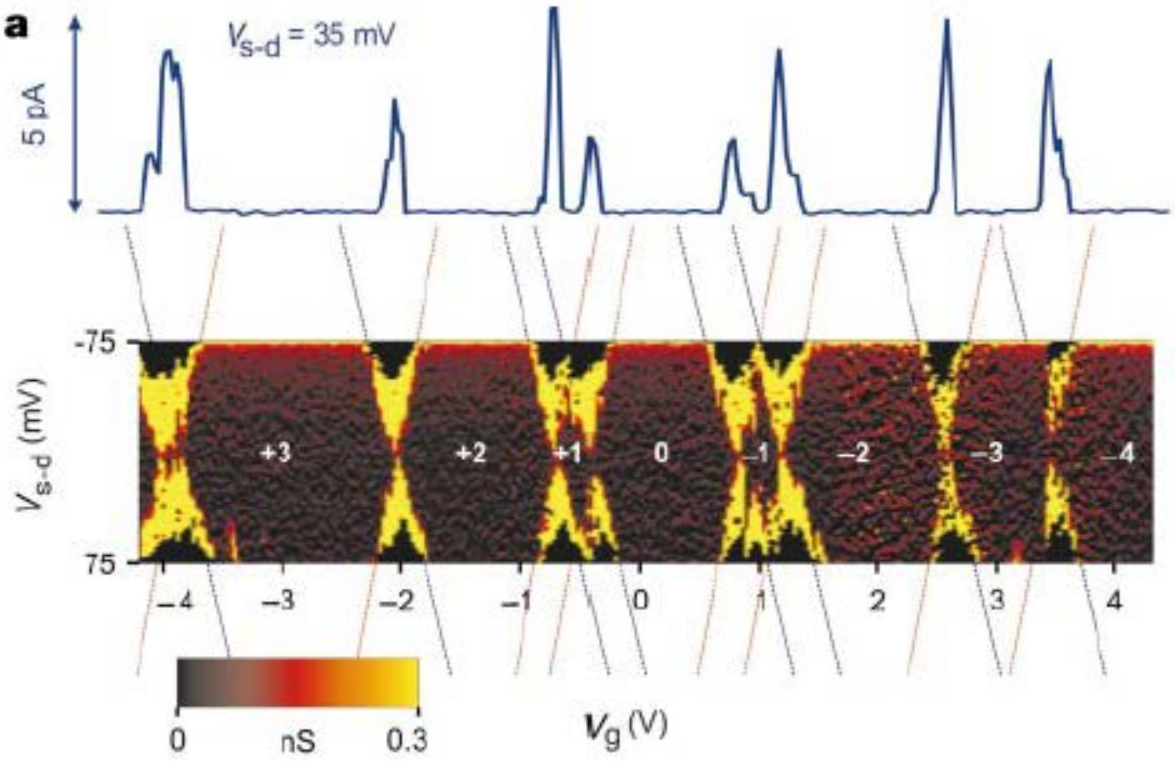
8.4 Single-molecule transistors: Observation of Coulomb blockade

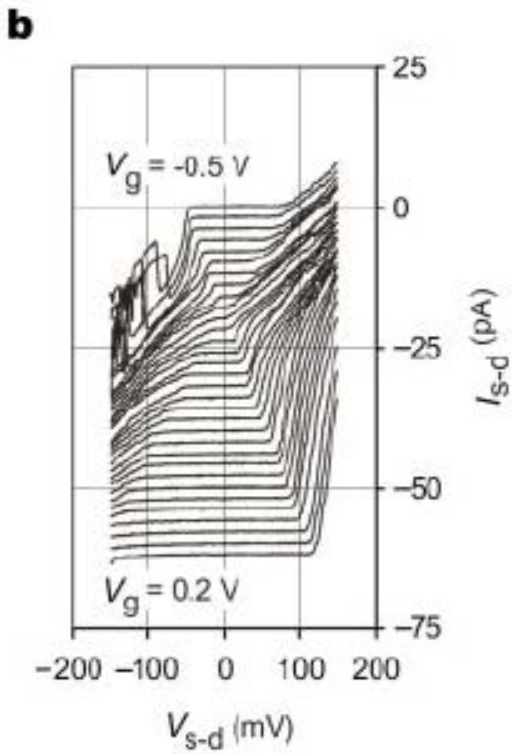
*S. Kubatkin et al., Nature **425**, 698 (2003).*

(OPV5)





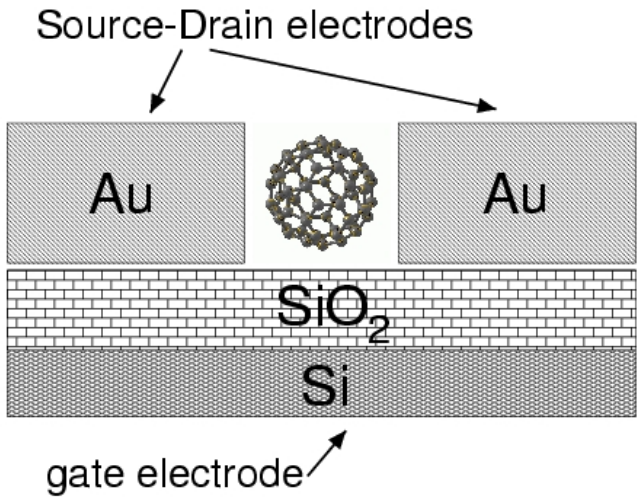


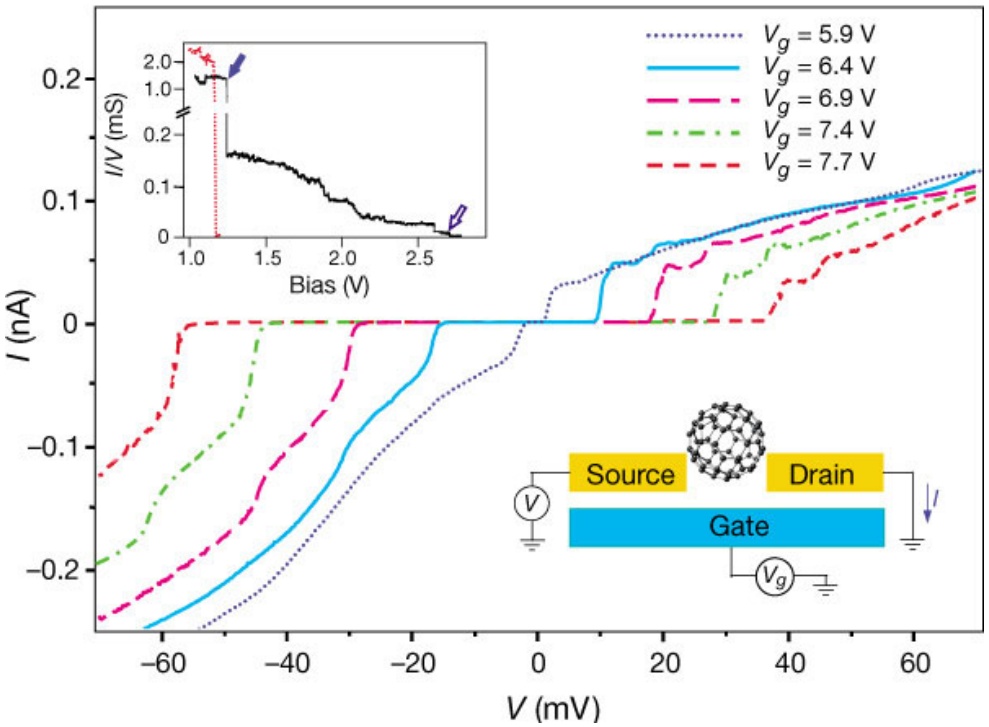


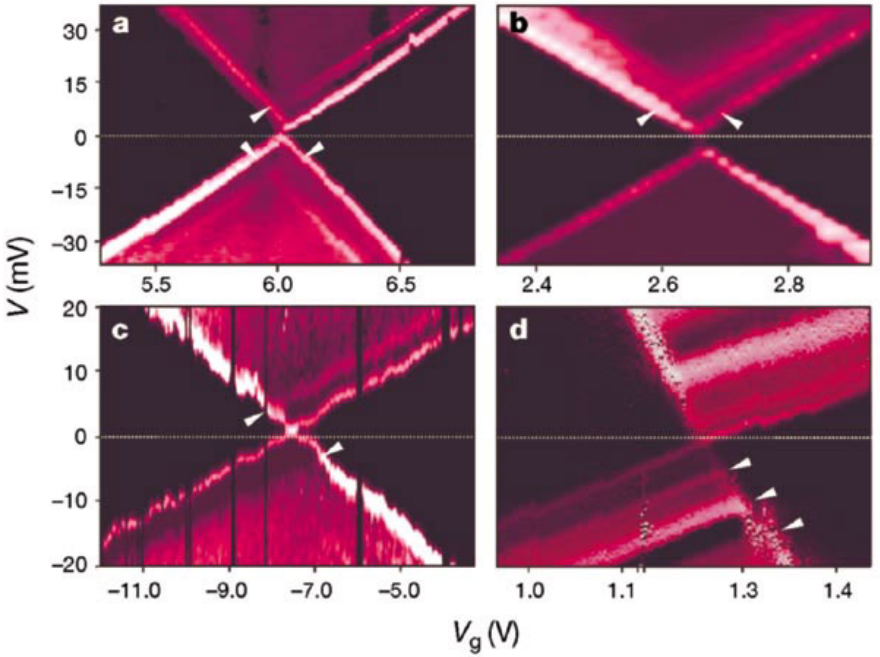
8.4 Single-molecule transistors: Observation of Coulomb blockade

Nanomechanical oscillations in a single-C_{60} transistor

Park et al., Nature **407**, 57 (2000)

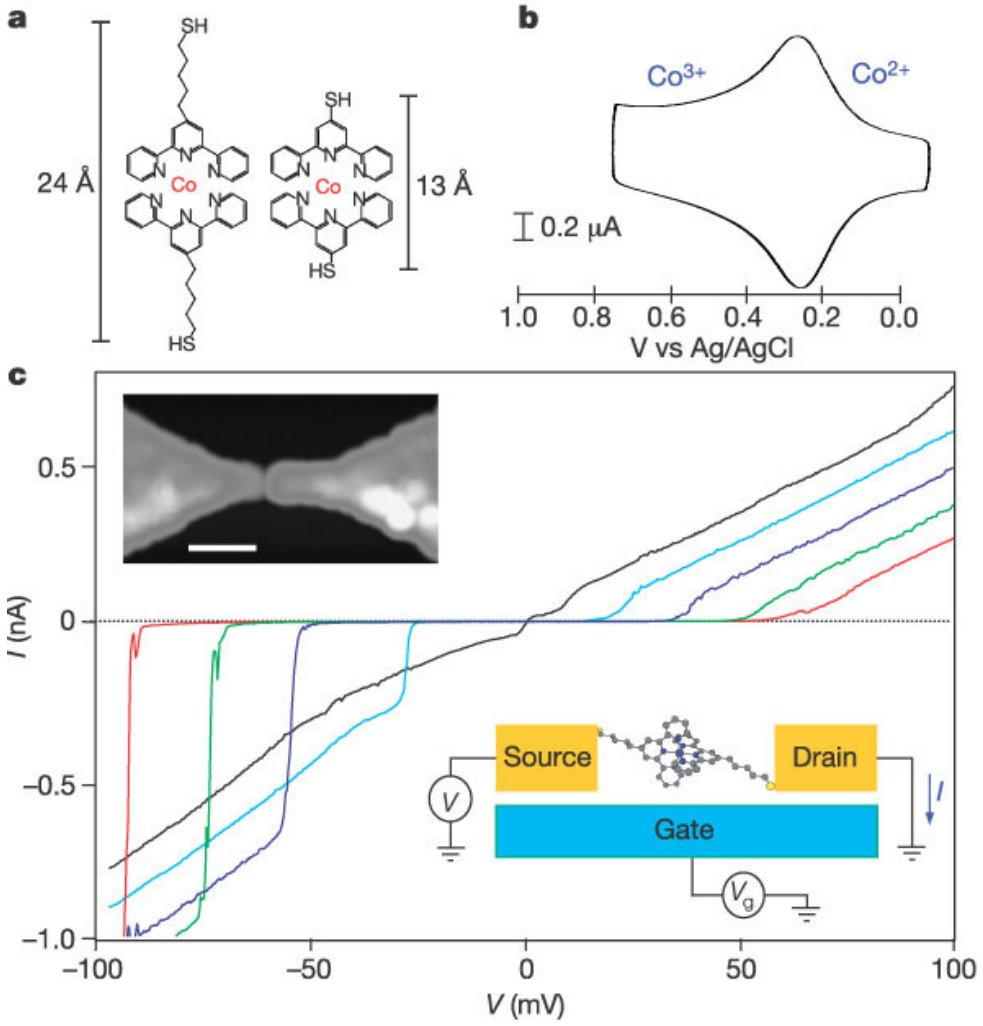


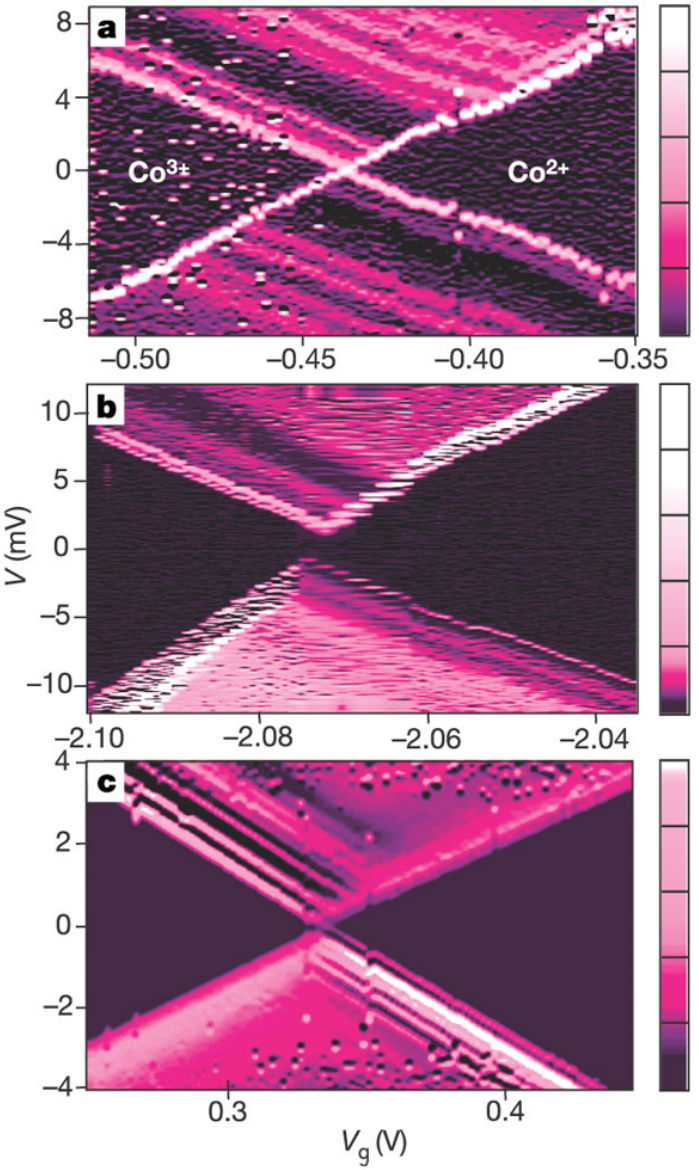




8.4 Single-molecule transistors: Observation of Coulomb blockade

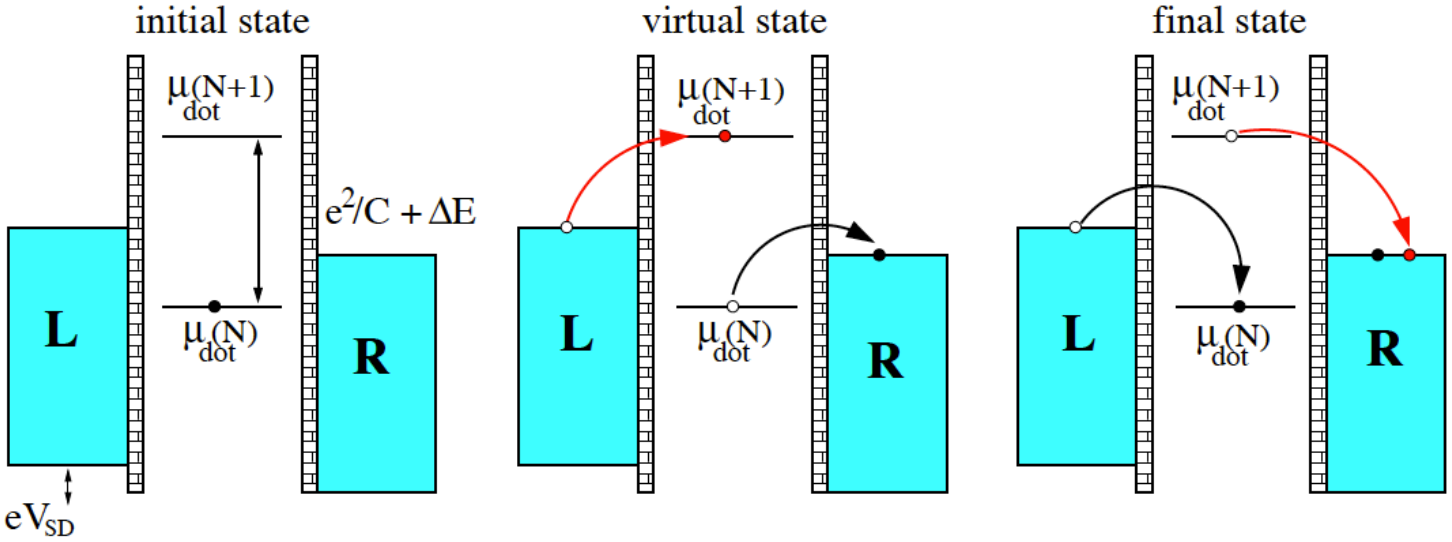
Park et al., Nature **417**, 722 (2002)



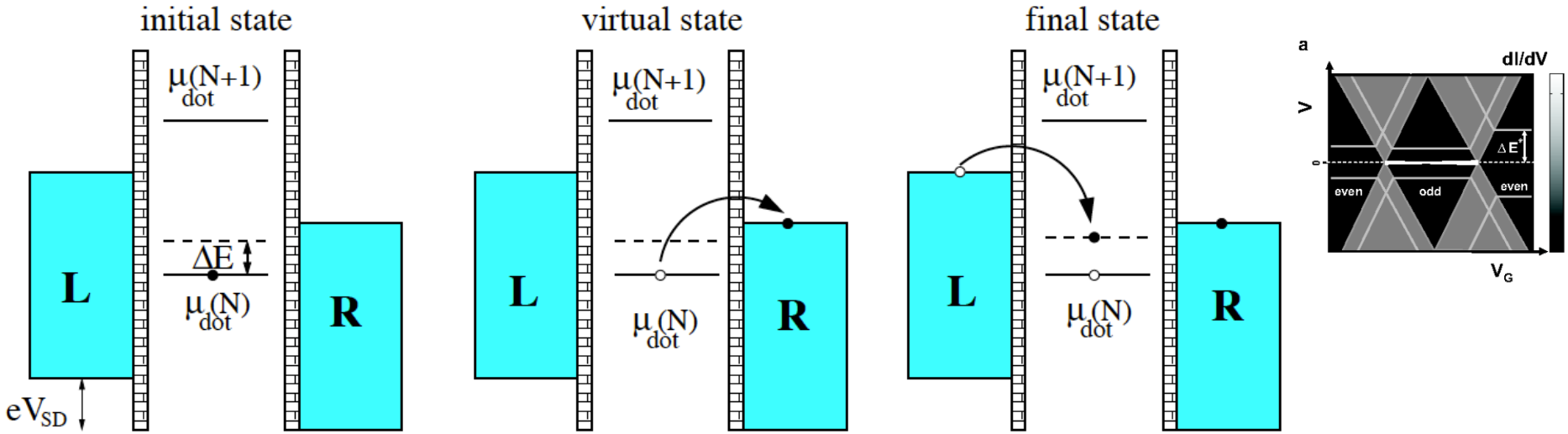


8.5 Elastic and inelastic cotunneling

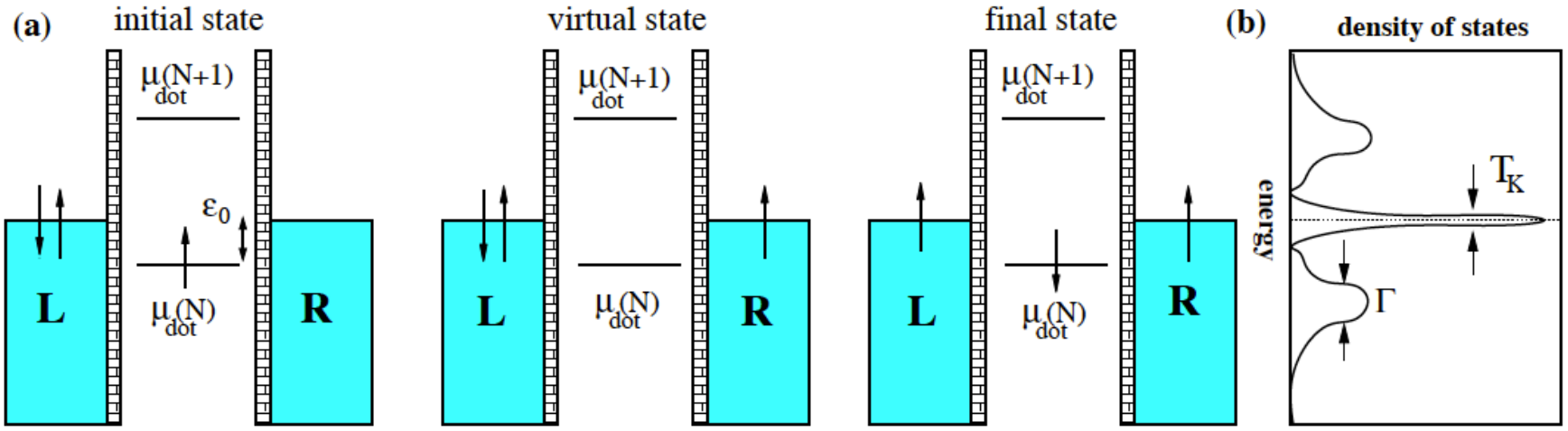
- **Elastic cotunneling process:** Non-zero background conductance within diamonds



- **Inelastic cotunneling process:** Horizontal line in diamonds at $eV_{SD} = \Delta E$



8.6 Kondo effect

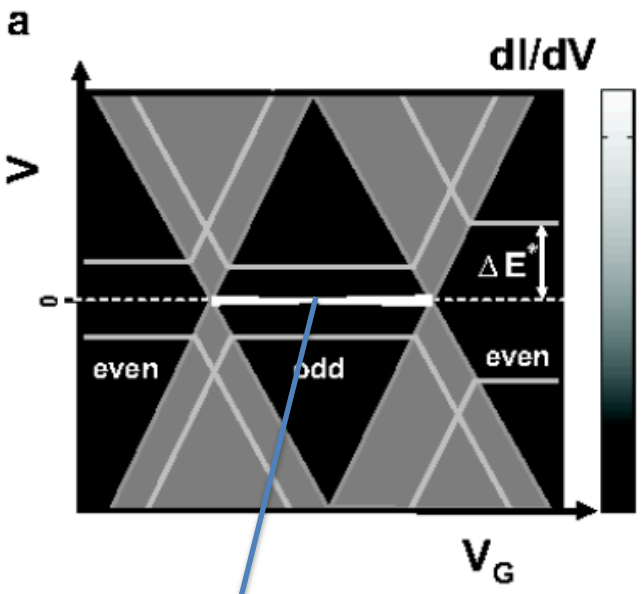


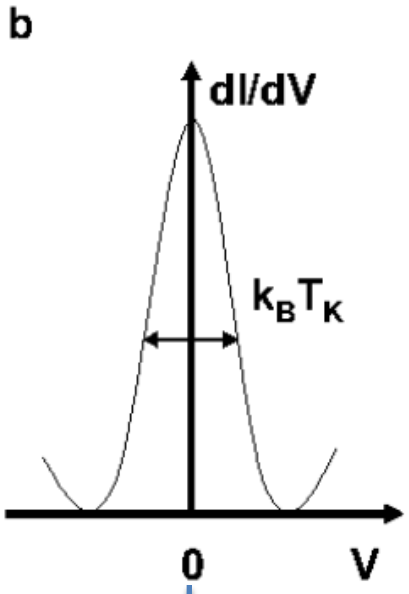
- Spin-flip cotunneling processes can change the spectrum of the dot leading to the screening of the localized spin and to the appearance of the so-called Kondo resonance.
- The Kondo resonance lies exactly at the Fermi energy, independent of the position of the original level. For this reason, the Kondo 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. For a single-level model it reads:

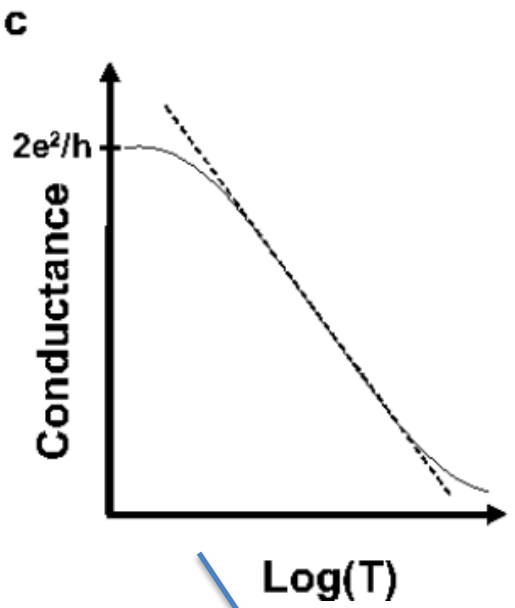
$$k_B T_K = \frac{\sqrt{\Gamma U}}{2} \exp\left(\frac{\pi \varepsilon_0 (\varepsilon_0 + U)}{\Gamma U} \right)$$

8.6 Kondo effect

Transport signatures of the Kondo effect







Zero-bias line in the stability diagram for an odd number of electrons in the dot.

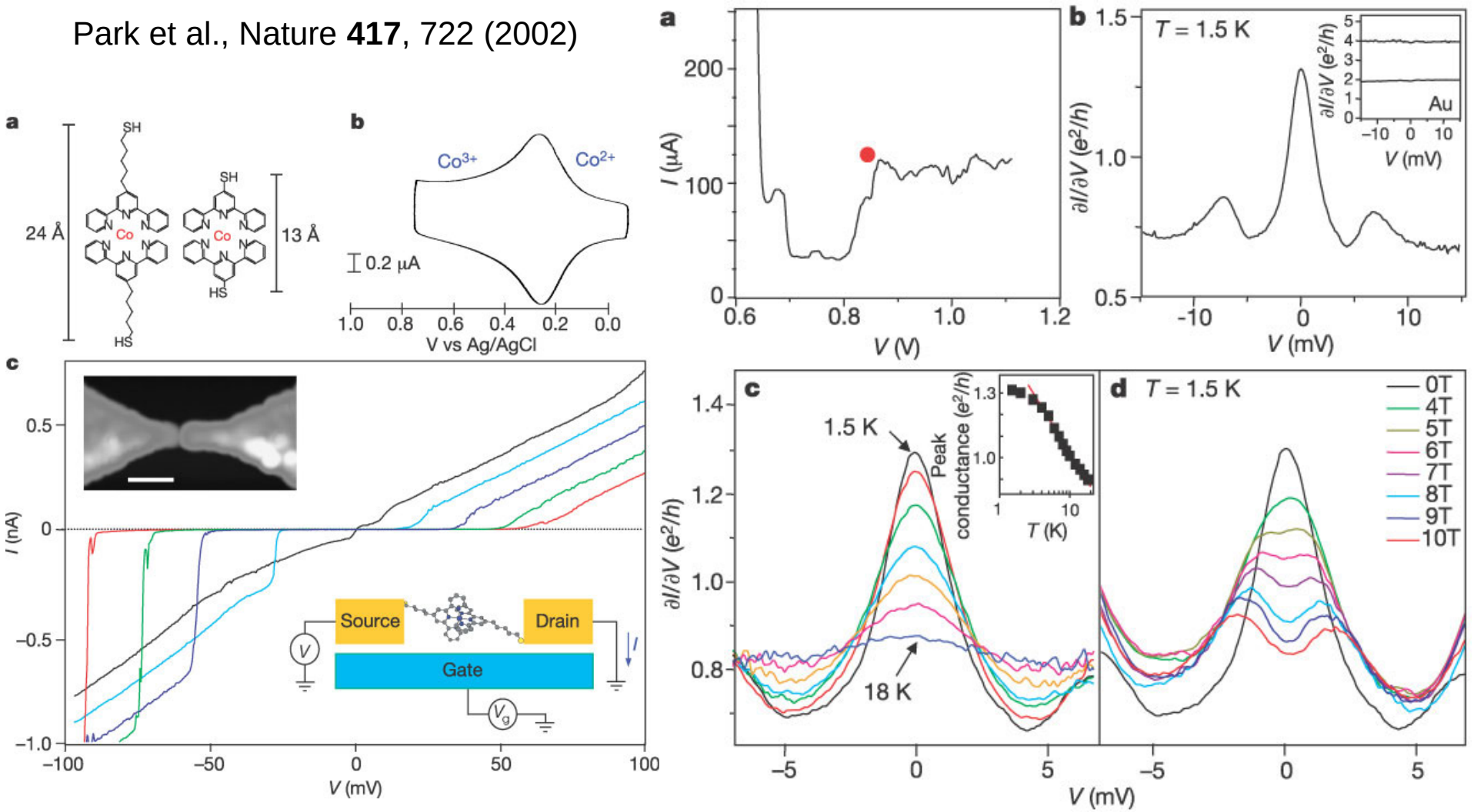
Peak in the low-bias conductance at low temperatures with a width equal to the Kondo temperature.

"Kondo ridge"

Characteristic temperature dependence of the linear conductance.

8.6 Single-molecule transistors: Observation of the Kondo effect

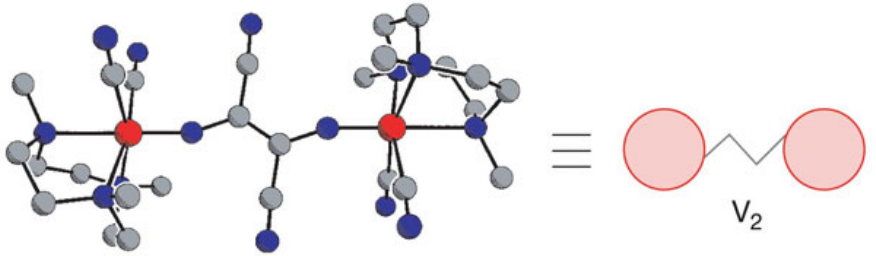
Park et al., Nature **417**, 722 (2002)

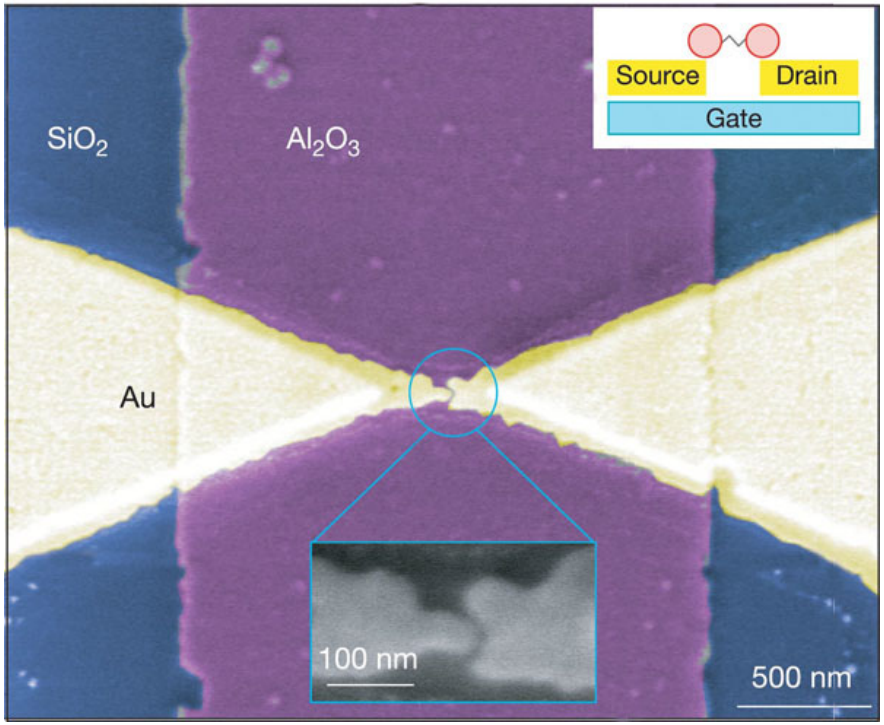


Molecules: Co-ion compounds; T_K = 10-25 K.

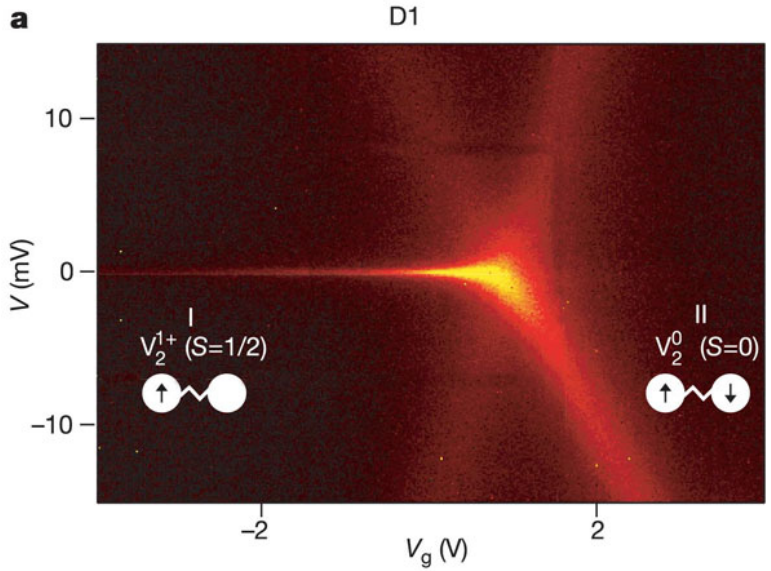
13.6 Single-molecule transistors: Observation of the Kondo effect

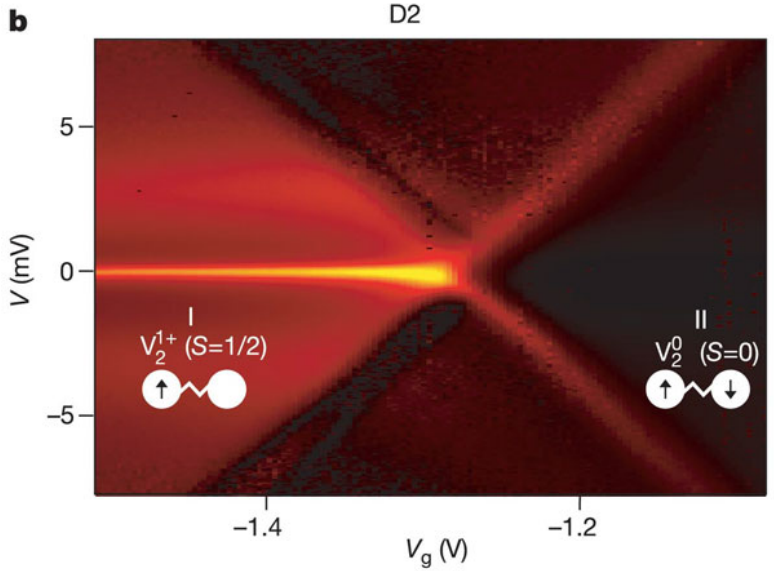
Liang et al., Nature **417**, 725 (2002)





Molecules: Divanadium compounds.





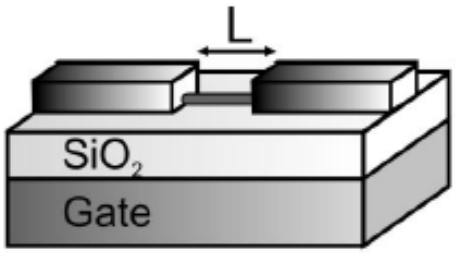
Summary: Chapter 8: Coulomb blockade and Kondo physics

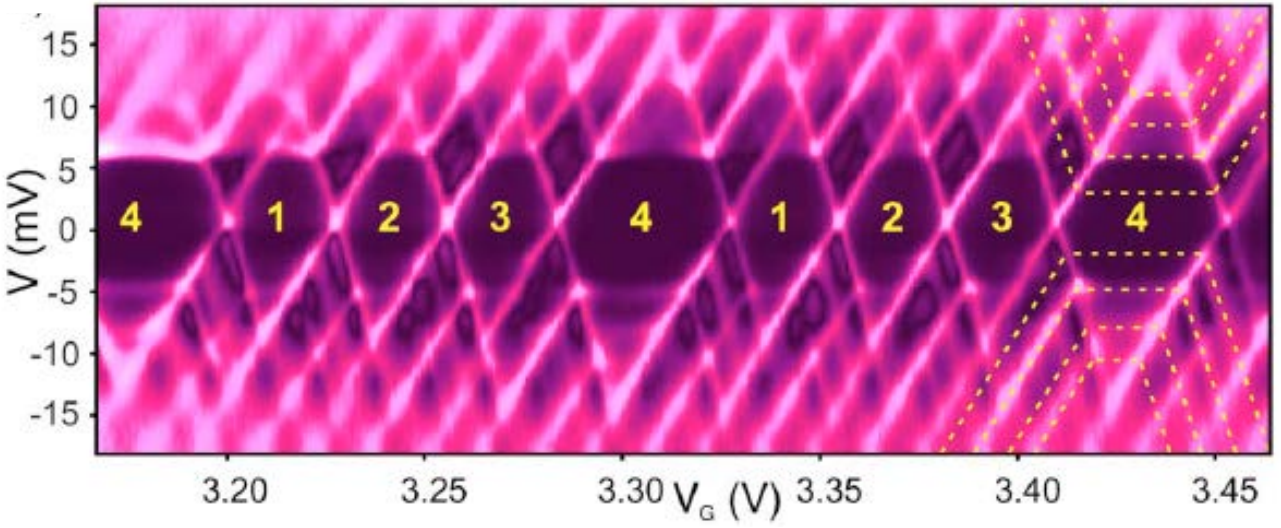
Different transport regimes

Open QD regime: $\Gamma \gg E_C = e^2/C$
$\rightarrow$ Quantum interference is important (classical analogon: Fabry-Perot)

Intermediate QD regime: $\Gamma \leq E_C$
$\rightarrow$ Interference, charging effects, higher order processes in the coupling

Closed QD regime: $\Gamma \ll E_C$
$\rightarrow$ Charging effects dominate (Coulomb blockade for: $\Gamma \ll k_B T \ll E_C$)





S. Sapmaz et al., Phys. Rev. B 71, 153402 (2005)

Summary Chapter 8: Coulomb blockade and Kondo physics

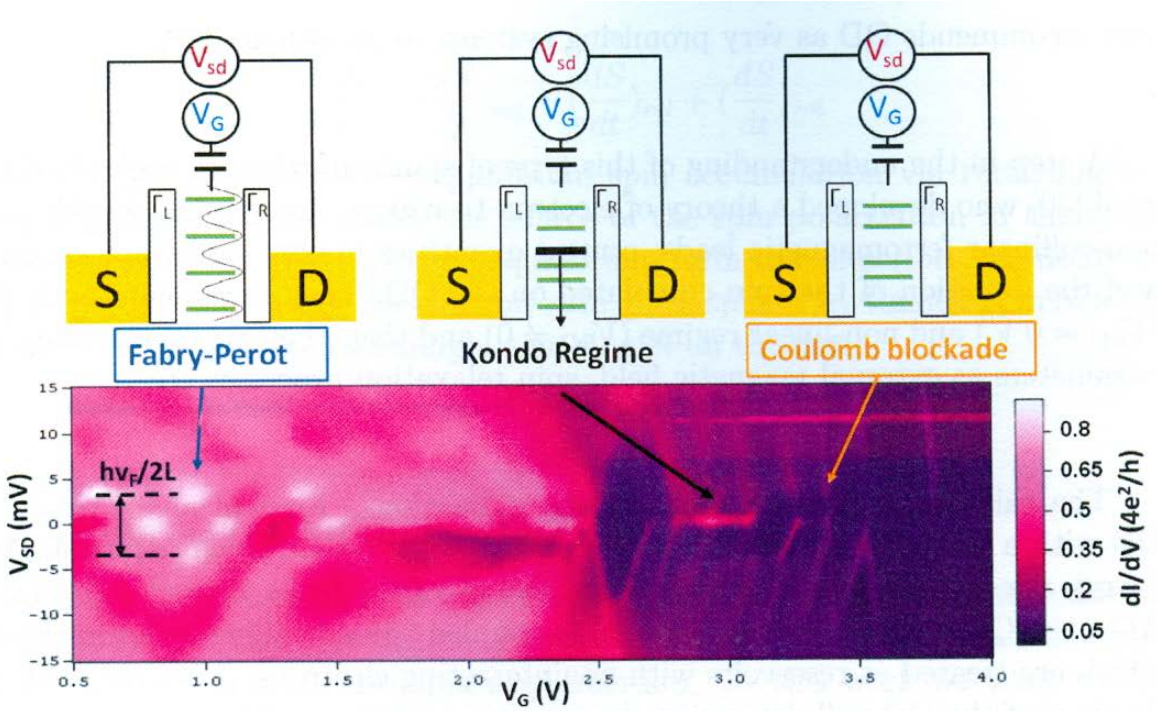


Figure 2.15: *Spectroscopy showing different types of transport regimes [27]. For highly transparent barriers between the QD and the metallic leads one gets the rhombic structure specific to the Fabry Perot transport regime with broaden spacing between the energy levels inside the nanotube. The distance between the centers of the adjacent rhombus is equal to the double of the spacing between the energy levels of the quantum dot and depends on the length of the nanotube. For low transparent barriers one gets a Coulomb blockade regime with narrow spacing between the energy levels. Fabry-Perot regime is observed at smaller gate voltages while the Coulomb blockade is in the higher gate voltage area. Between the two regimes we have also the Kondo ridge.*

Quantum dot made of a carbon nanotube

$E(k)=\hbar v_F k$

$\Delta E=\hbar v_F \Delta k=hv_F/(2L)$
with $\Delta k=\pi/L$

T. Delattre, *Current quantum fluctuations in carbon nanotubes*, PhD Thesis, University Paris VI (2009)