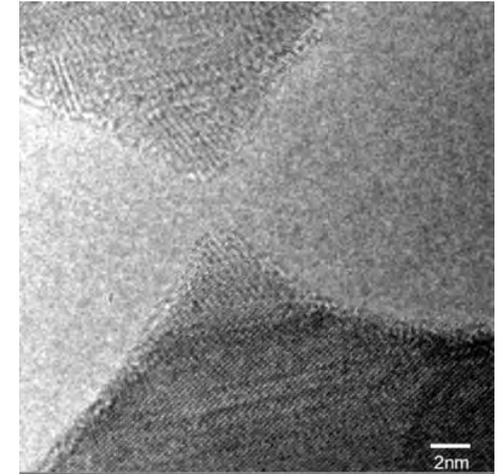
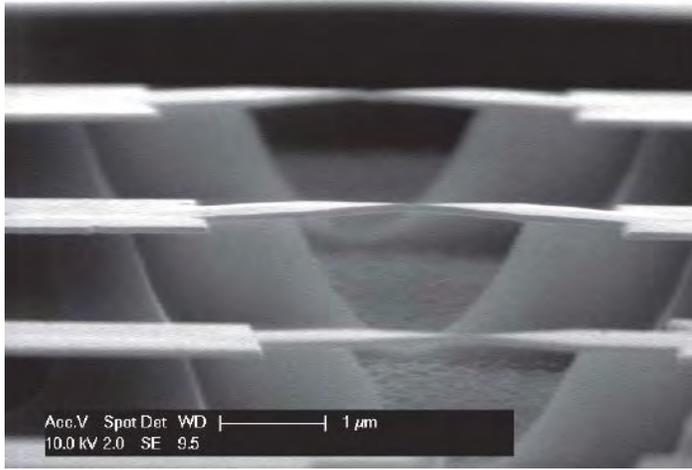


transport through (magnetic) nanoscale objects

Herre van der Zant



Single Molecule

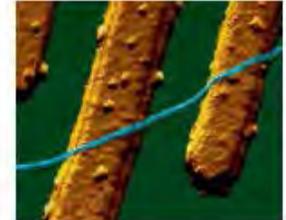
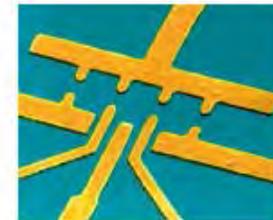
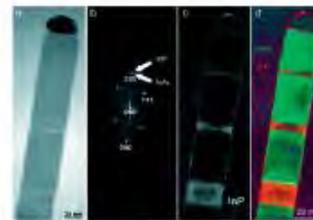
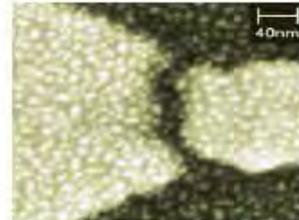
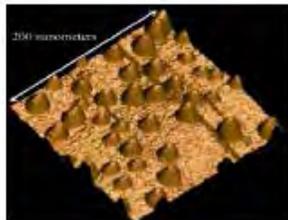
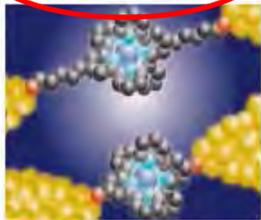
Self-assembled QD

Metallic island

InAs/InP nanowire

Semi-conducting QD

Carbon nanotube



1 nm

10 nm

10 nm

100 nm

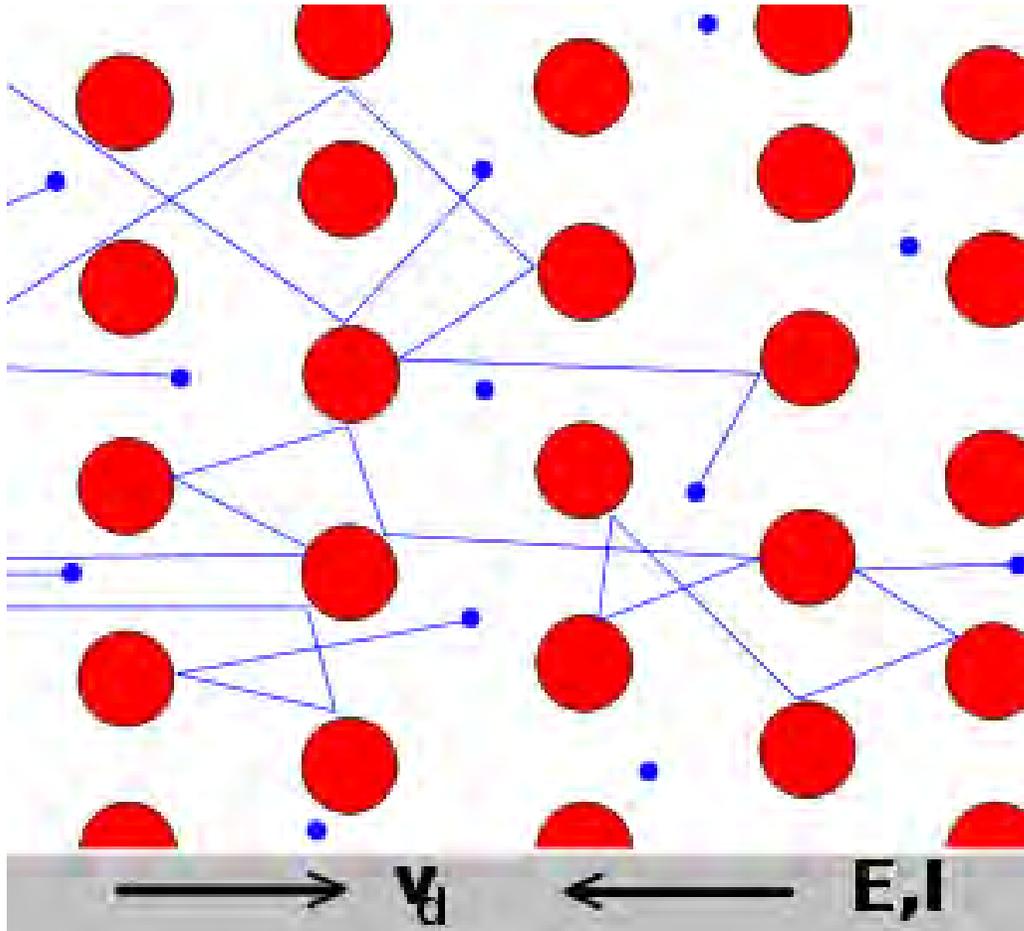
> 100 nm

1 μm

Molecular Electronics and Devices group

transport mechanisms: Ohms law $J = \sigma E$

electrons are viewed as particles in a pinball machine, bouncing around
resistance results from (back) scattering and can be characterized by the mobility (a material dependent property).



How fast does an electron move in an electric field?

$$\vec{v}_d \equiv \langle \vec{v}(t) \rangle = -\frac{e\vec{E}\tau}{m^*} \equiv -\mu\vec{E}$$

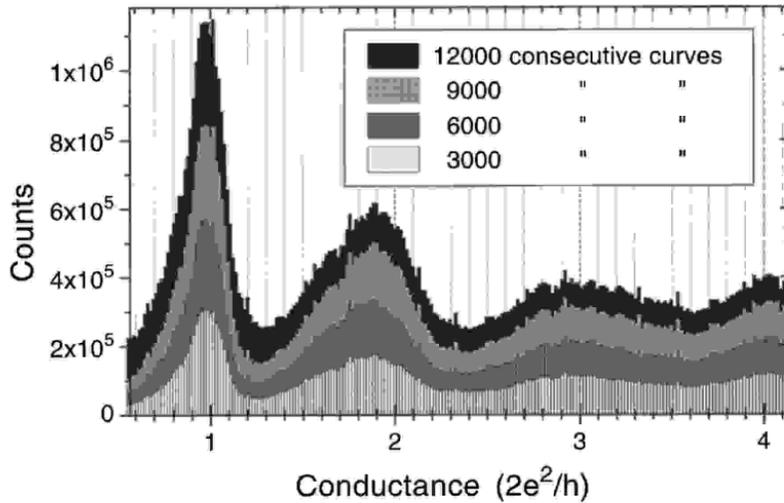
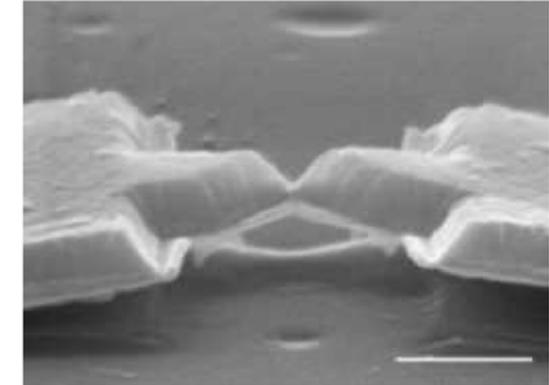
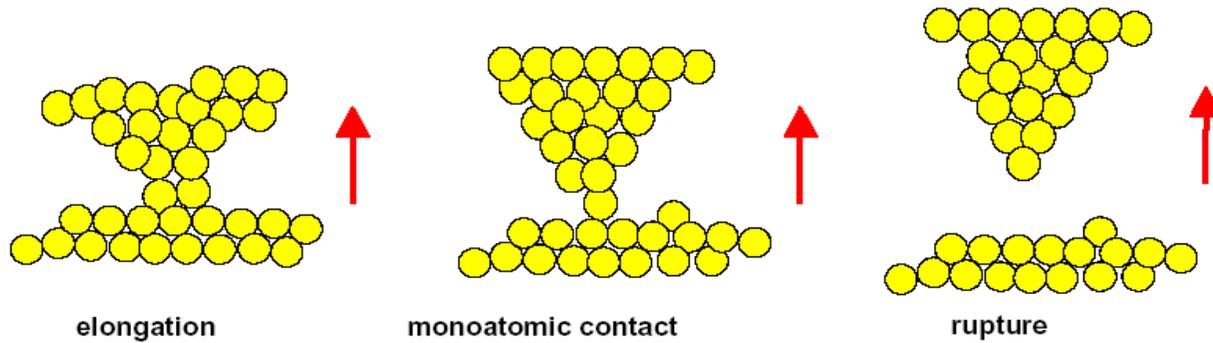
$$\text{mobility } \mu \equiv \frac{e\tau}{m^*}$$

Drude conductivity

$$\sigma = \frac{\vec{j}}{\vec{E}} = \frac{-en\langle \vec{v} \rangle}{\vec{E}} = ne\mu = \frac{e^2 n \tau}{m^*}$$

ballistic transport: 1D channel or a single atom

electrons are viewed as waves that are transmitted in channels; the transmission determines the conductance which is quantized with a value independent on the material



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

T_i : transmission of channel i

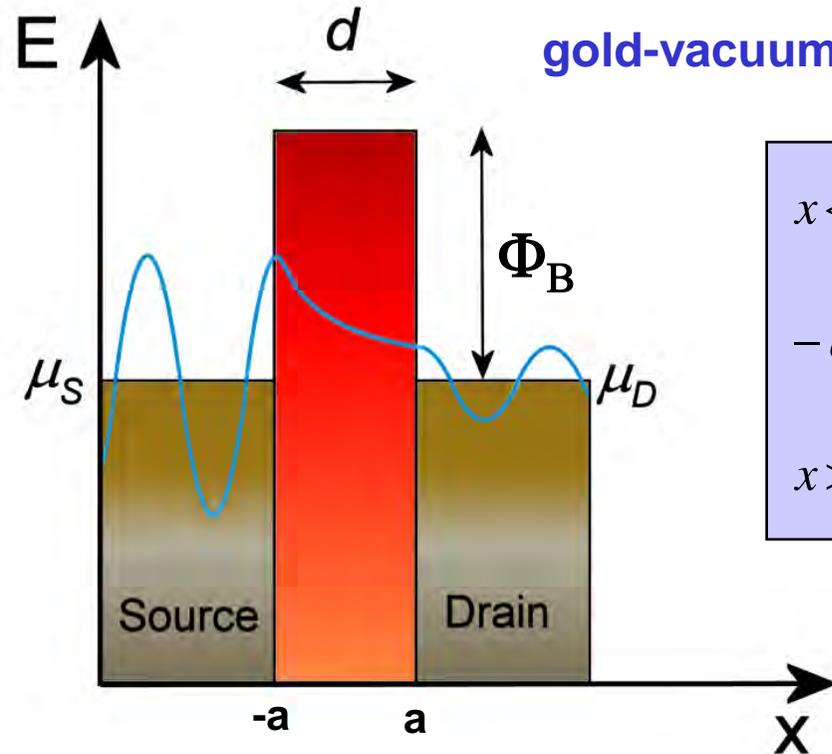
For one channel and perfect transmission

$$G = \frac{2e^2}{h} = (12.9 \text{ k}\Omega)^{-1}$$

Which physical quantity determines the number of channels? How fast do the electrons go?

tunneling in one dimension: single-barrier case

gold-vacuum-gold junction: direct, through space tunneling



$$x < -a \quad : \quad u(x) = e^{ikx} + R e^{-ikx}$$

$$k^2 = \frac{2mE}{\hbar^2}$$

$$-a < x < a \quad : \quad u(x) = A e^{-\gamma x} + B e^{\gamma x}$$

$$\gamma^2 = \frac{2m(V_0 - E)}{\hbar^2}, \quad E < V_0$$

$$x > a \quad : \quad u(x) = T e^{ikx}$$

$$k^2 = \frac{2mE}{\hbar^2}$$

Φ_B = work function
= 5.3 eV
(= Fermi-energy gold)

$d = 2a$

$$\text{tunnel probability: } t = TT^* = \frac{1}{1 + \left(\frac{k^2 + \gamma^2}{2k\gamma} \right)^2 \sinh^2(2\gamma a)}$$

$$\text{strong barrier } (2\gamma a \gg 1) : t \approx \left(\frac{2k\gamma}{k^2 + \gamma^2} \right)^2 e^{-4\gamma a} \Rightarrow G = G_0 e^{-4a \sqrt{\frac{2m\Phi_B}{\hbar}}}$$

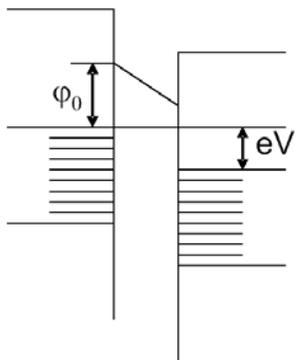
voltage dependence: Simmons' formula for tunneling

d = barrier width
 Φ_B = barrier height

$$I = \left(\frac{eA}{4\pi^2 \hbar d^2} \right) \left[\left(\Phi_B - \frac{eV}{2} \right) e^{-\frac{2d\sqrt{2m}}{\hbar} \sqrt{\Phi_B - \frac{eV}{2}}} - \left(\Phi_B + \frac{eV}{2} \right) e^{-\frac{2d\sqrt{2m}}{\hbar} \sqrt{\Phi_B + \frac{eV}{2}}} \right]$$

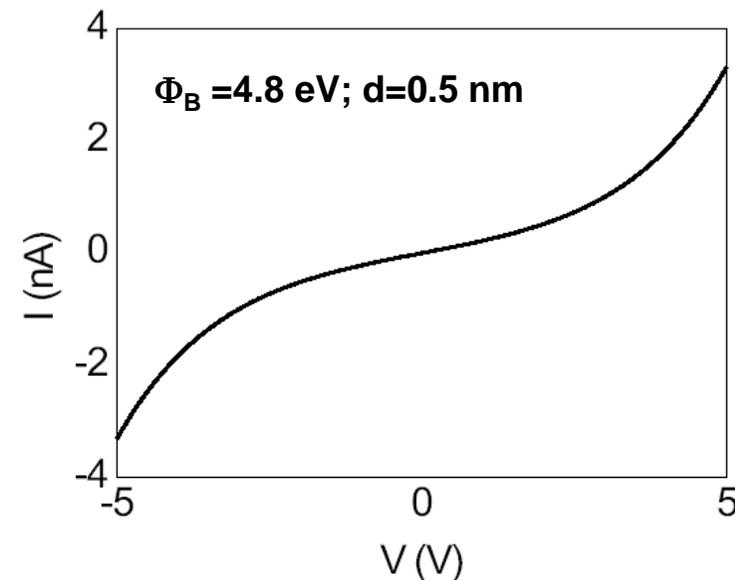
expanding the square root ($\Phi_B \gg eV$):

$$I \approx \left(\frac{eA}{2\pi^2 \hbar d^2} \right) \Phi_B e^{-\beta_0 d} \sinh(\beta_V V d)$$



$$\beta_V = \frac{e}{\hbar} \sqrt{\frac{m}{2\Phi_B}}$$

$$\beta_0 = \frac{e\sqrt{2m\Phi_B}}{\hbar}$$



linear response (zero-bias conductance)

$$\sinh(\beta_V V d) \approx \beta_V V d \Rightarrow G = G_0 e^{-\beta_0 d}$$

gold-vacuum-gold junction

$$\Phi_B = 5.3 \text{ eV}$$

$$m = m_0 = 9.1 \cdot 10^{-31} \text{ kg}$$

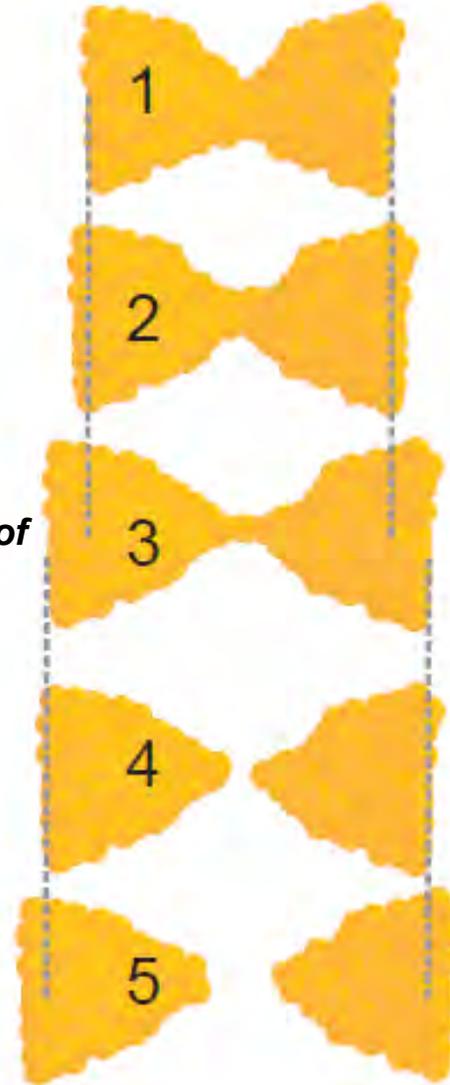
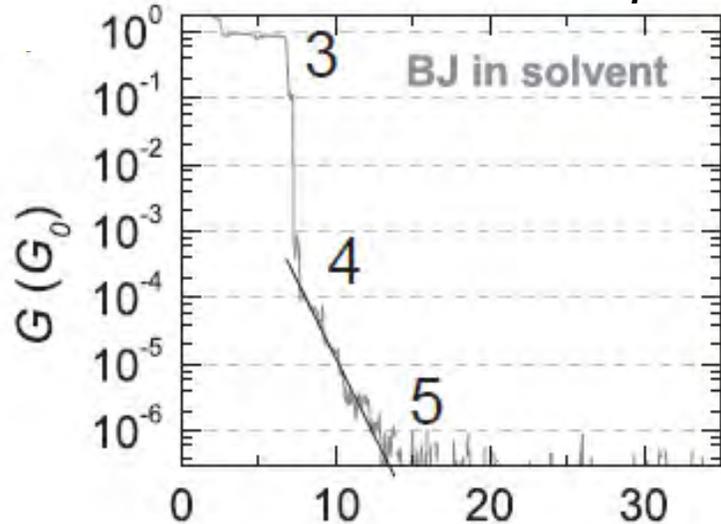
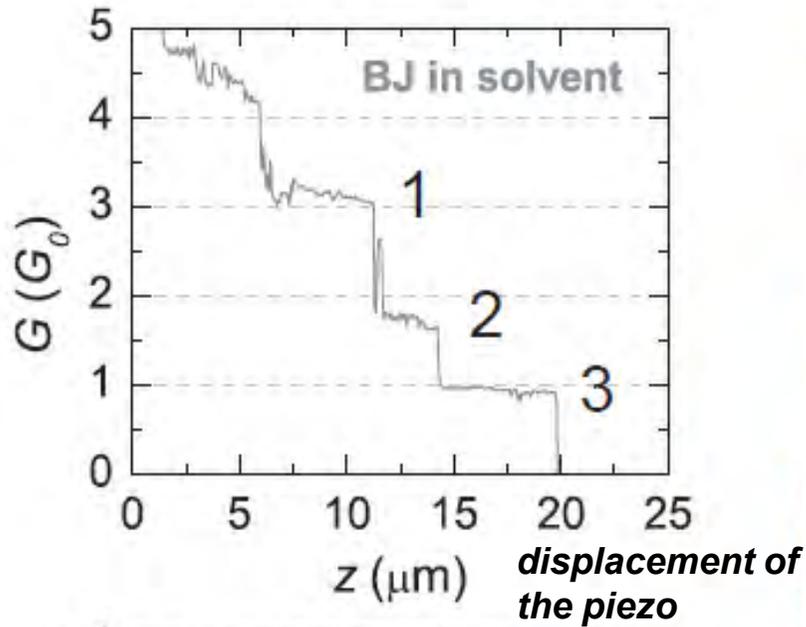
$$\beta_V = \frac{e}{\hbar} \sqrt{\frac{m}{2\Phi_B}} = 1.1 \text{ (nm)}^{-1}$$
$$\beta_0 = \frac{e\sqrt{2m\Phi_B}}{\hbar} = 2.34 \text{ (\AA)}^{-1}$$

**these are the maximum values
when working with gold: in
practice lower due to image
charges etc.**

β_0 : decay length

an example: breaking of a gold contact

PhD. Thesis Roman Huber



(1,2,3): quantized conductance (G_0) in metallic regime

Landauer formalism:

$$G = G_0 \sum T_i$$

$$G_0 = 2e^2/h \quad (12.9 \text{ K}\Omega \text{ or } 77 \text{ mS})$$

(4): relaxation of the contact

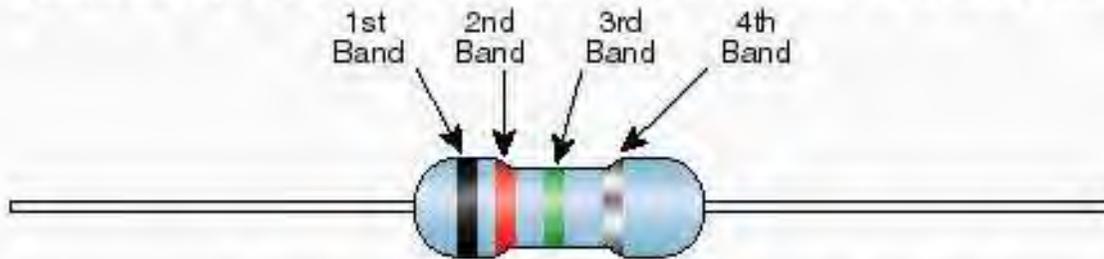
(5): tunneling

$$G(d) \propto \exp\left(-\frac{\sqrt{8m_e\Phi_m}}{\hbar}d\right)$$

Why is the second step not exactly on $2G_0$?

What is the resistance of a single-molecule?

Standard EIA Color Code Table 4 Band: $\pm 2\%$, $\pm 5\%$, and $\pm 10\%$



Color	1st Band (1st figure)	2nd Band (2nd figure)	3rd Band (multiplier)	4th Band (tolerance)
Black	0	0	10^0	
Brown	1	1	10^1	
Red	2	2	10^2	$\pm 2\%$
Orange	3	3	10^3	
Yellow	4	4	10^4	
Green	5	5	10^5	
Blue	6	6	10^6	
Violet	7	7	10^7	
Gray	8	8	10^8	
White	9	9	10^9	
Gold			10^{-1}	$\pm 5\%$
Silver			10^{-2}	$\pm 10\%$



transmolecular transport: double-barrier problem

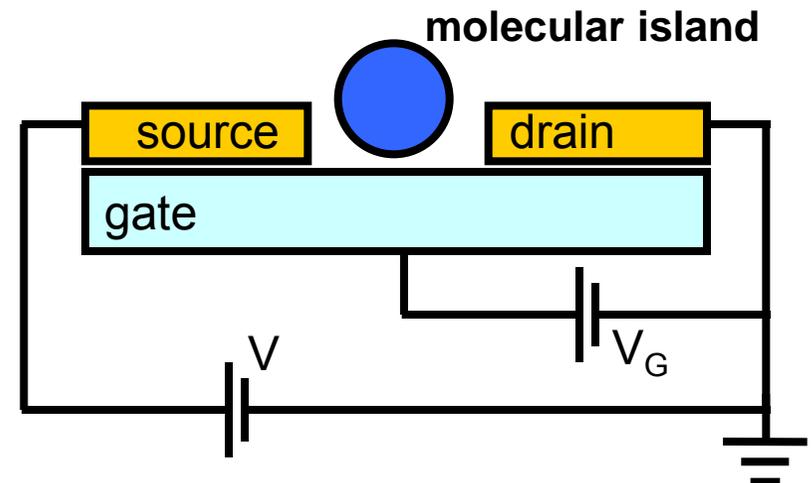
The **reservoirs (source and drain)** are bulk-like regions where the electrons are in equilibrium. These regions are kept at some temperature, and the number of electrons is variable as they are connected to the voltage source. The electrons in these reservoirs are distributed according to Fermi functions.

The **molecular island** is the part of the system, which is small in all directions— hence, this is the part where the **Coulomb interaction** (E_C) plays an important role. It is useful to take as a reference the isolated island. In that case we have a set of **quantum states** with discrete energies (levels, energy Δ).

The **molecule-lead coupling** is characterized in terms of the rate, Γ , at which electrons cross the tunnel barriers separating the island from the leads. The transport through the barriers is a tunneling process. Γ also sets the life-time of a charge on a molecular state and hence determines **the broadening of the level**; at present the molecule-lead coupling can still not be controlled and even predicted.

essential for understanding transport:

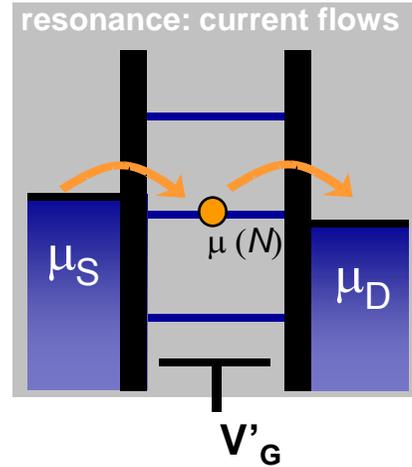
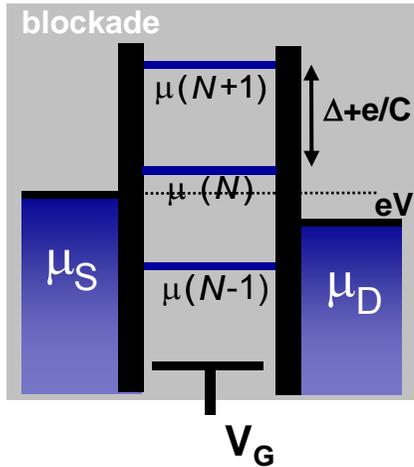
- location of the levels with respect to the Fermi energy of the electrodes
- the molecule-lead coupling (Γ)



resonant and off-resonant transport

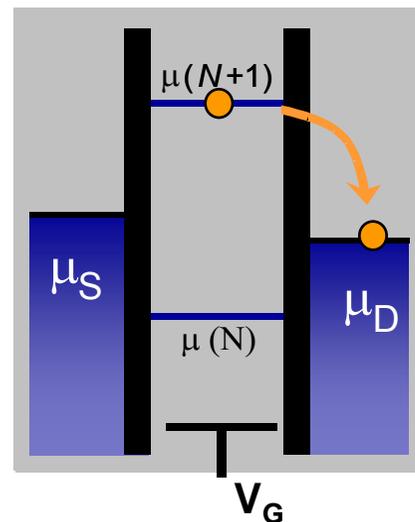
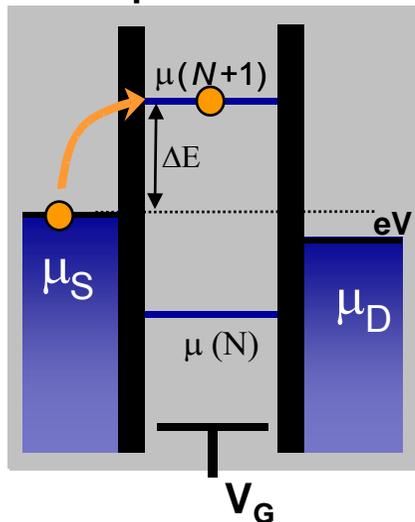
Schematics of the electrochemical potentials of an island connected to two reservoirs, across which a small (negative) bias voltage V is applied. A gate voltage is used to shift the electrostatic potential of the energy level.

first order processes



Resonant transport (first-order transport): resonant transport becomes possible when the gate voltage pushes one of the levels within the bias window eV . The $\mu(N)$ level is aligned with μ_S and the number of electrons on the dot alternates between N and $N-1$ (sequential tunneling).

second order processes



Off-resonant transport: the levels are not aligned. Coulomb blockade fixes the number of electrons on the dot to N . Transport, however, is possible through a virtual co-tunnel process in which a unoccupied level is briefly occupied. A similar process exists for the occupied level, $\mu(N)$, which can be briefly unoccupied. In contrast to resonant transport the level is empty (full) most of the time.

off-resonant tunneling through molecular junctions

same exponential distance decay as the single-barrier case but

- $\Phi_B \Rightarrow E_F - E_{\text{LUMO}}$ or $E_F - E_{\text{HOMO}}$
- $m \Rightarrow m^*$
- $\beta_0 \Rightarrow \alpha\beta_0$ (α takes into account non-rectangular barriers)

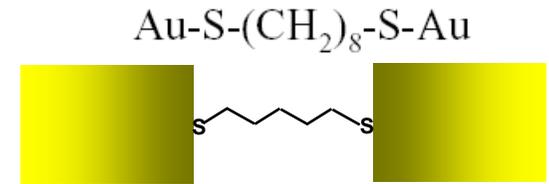
β_0 characterizes electron transfer molecules

alkanes: $\beta_0 \approx 0.9 \text{ \AA}^{-1}$

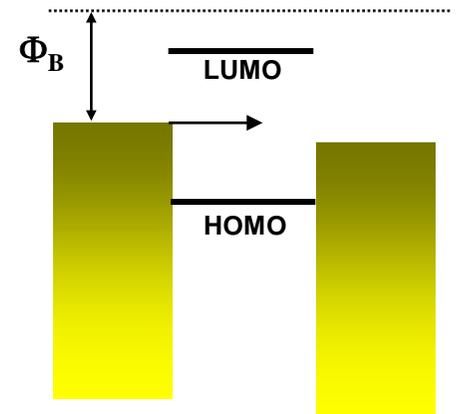
polyenes: $\beta_0 \approx 0.19 \text{ \AA}^{-1}$

oligophenyls: $\beta_0 \approx 0.28 \text{ \AA}^{-1}$

conjugated molecules: $\beta_0 \approx 0.1-0.3 \text{ \AA}^{-1}$



“co-tunneling”

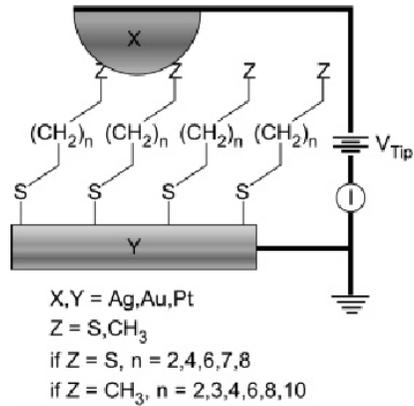


$$G = G_0 e^{-\beta_0 d}$$

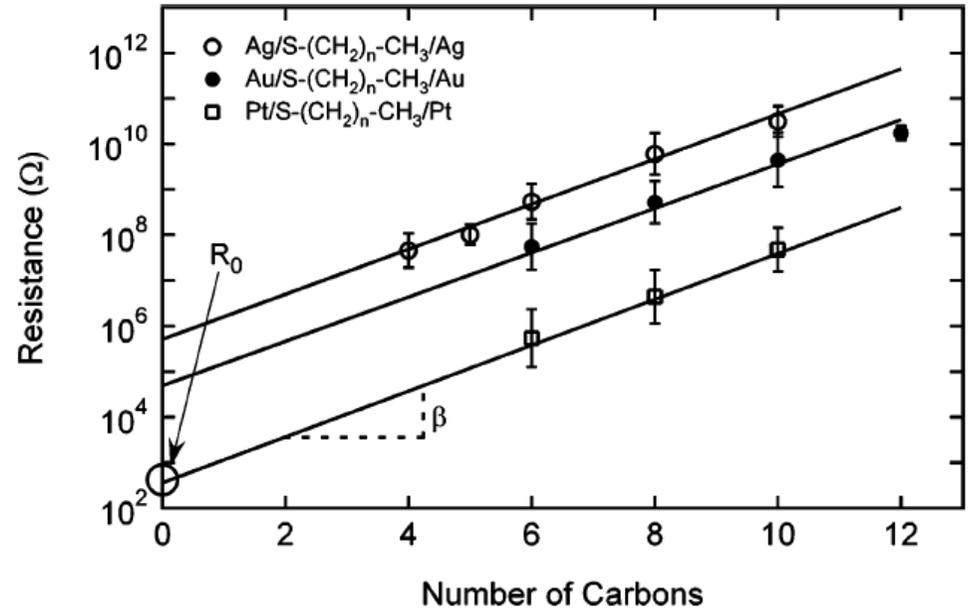
the further the molecular level (either the HOMO or the LUMO) is away from Fermi energy of the electrodes (ΔE), the larger the zero-bias resistance

off-resonant tunneling through dithiol-alkanes

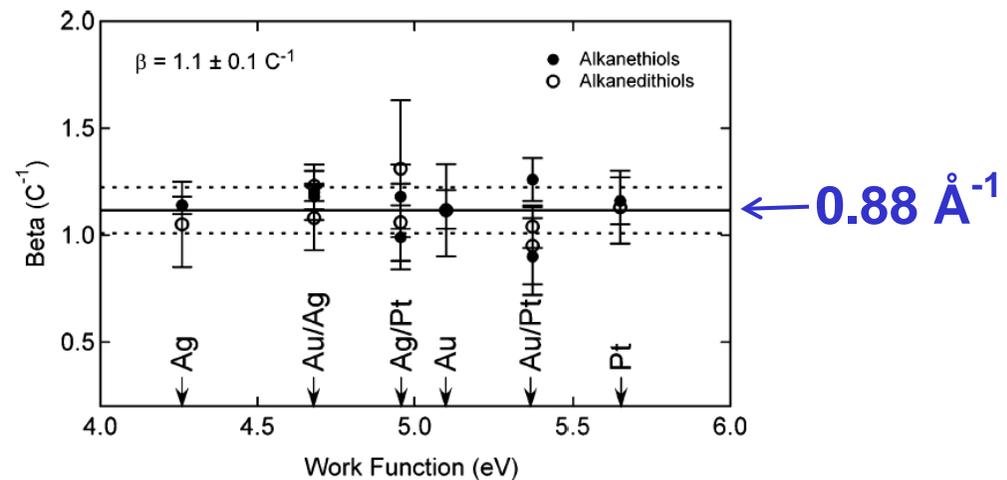
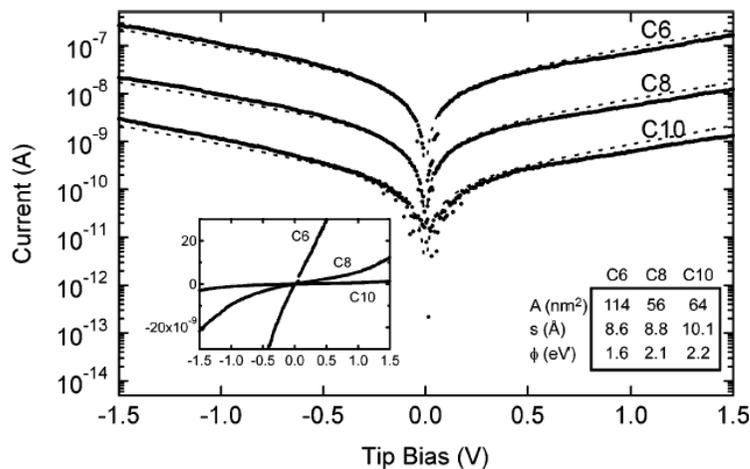
conducting AFM



exponential length dependence zero-bias resistance

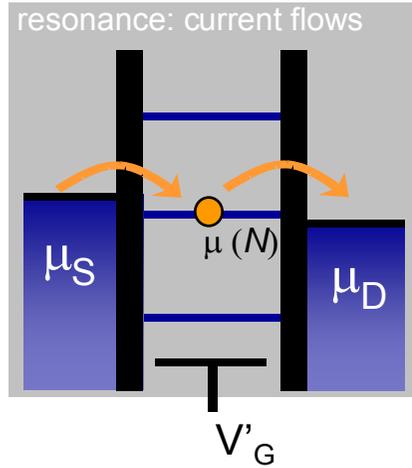
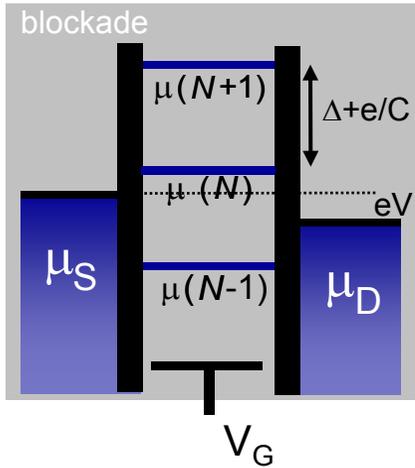


IV characteristics



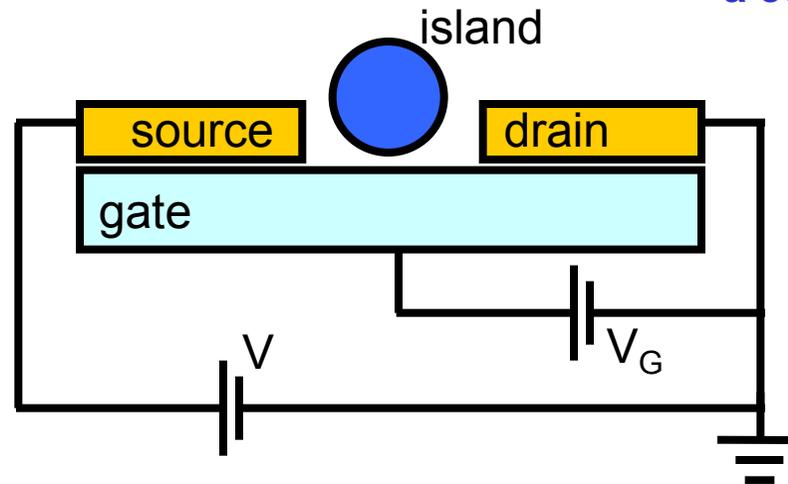
resonant transport: three-terminal devices

first order processes: sequential tunneling (incoherent)



three-terminal devices:

- levels can be brought in resonance with the leads (if the gate coupling is large enough)!
- molecule can be oxidized or reduced (change its charge state) and the properties of the charged molecules can be studied in detail: this makes it a completely different story !!

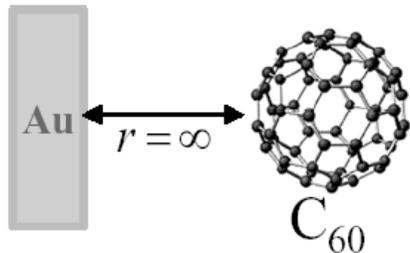
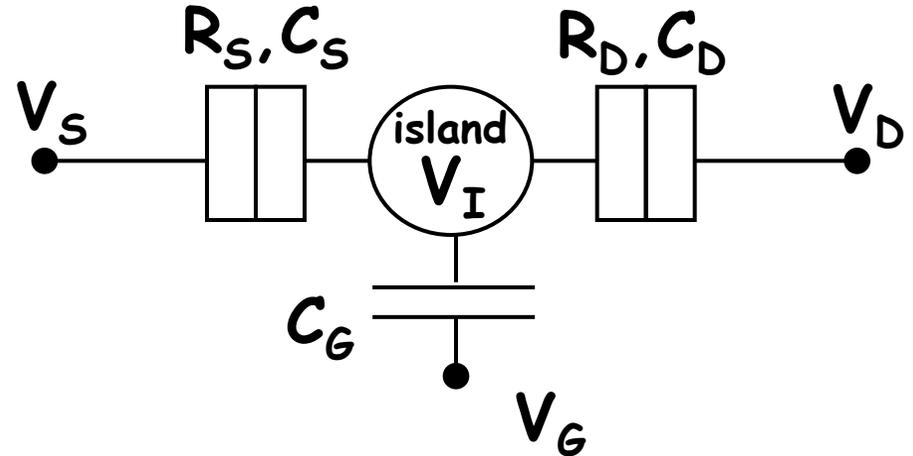


chemical potential and addition energy

From non-equilibrium thermodynamics, we know that a current is driven by a chemical potential difference – hence we should compare the **chemical potential** on the device,

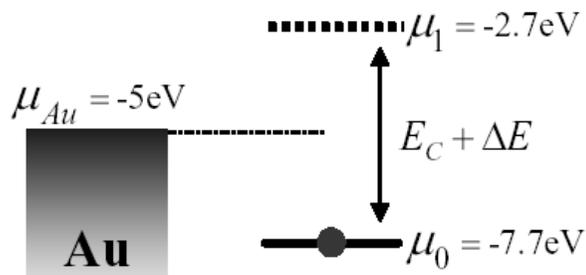
$$\mu(N) = U(N) - U(N-1) = (N-1/2) \frac{e^2}{C} - eV_{ext} + E_N$$

with that of the source and drain in order to see whether a current is flowing through the device. In experiments, we ground the drain electrode ($\mu_D = 0$).



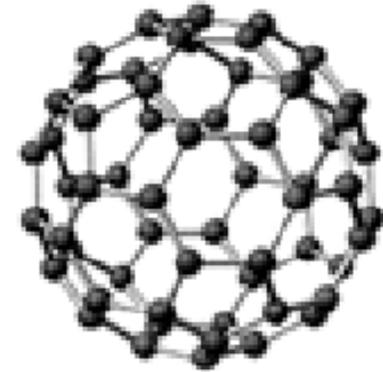
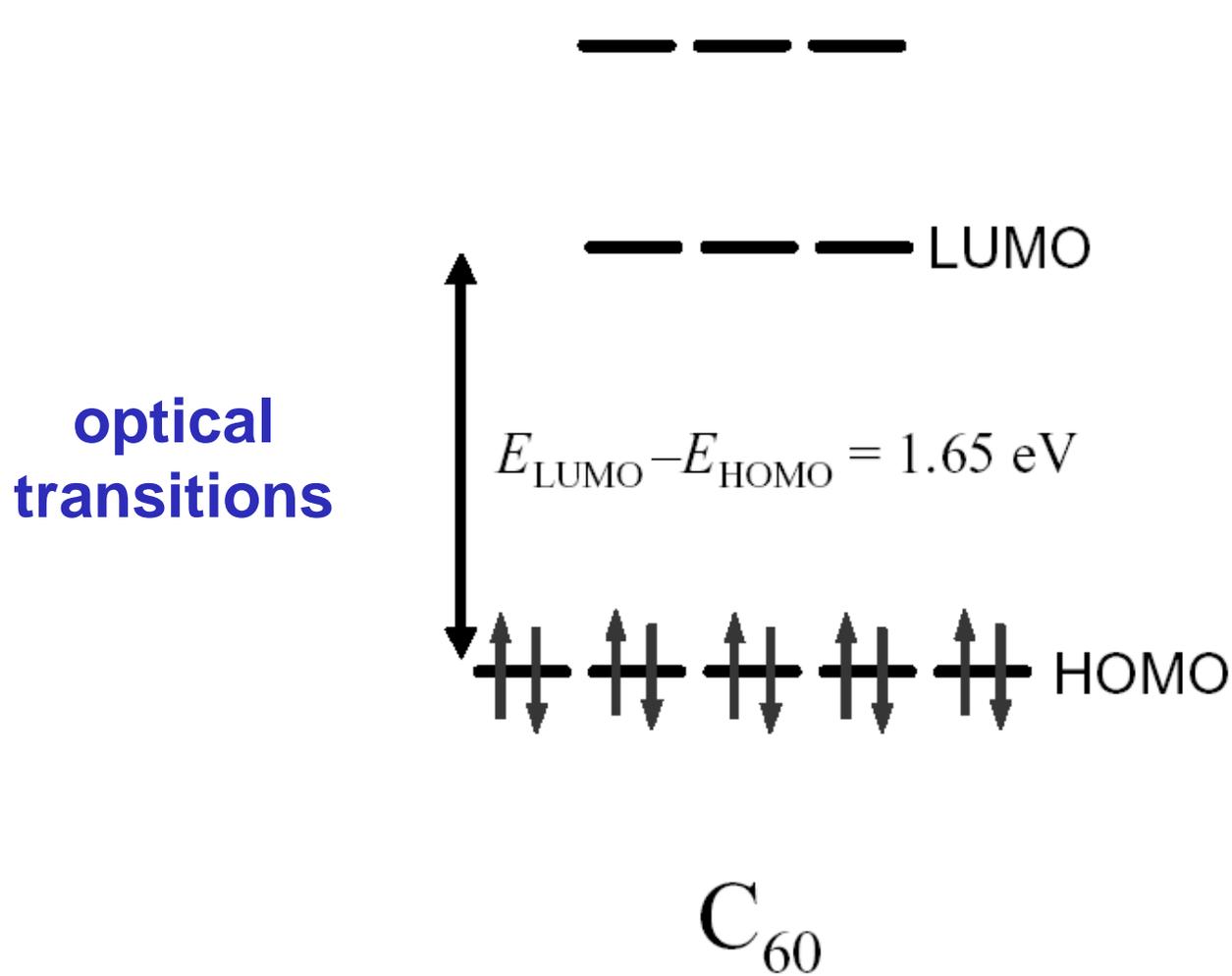
The distance between the two subsequent chemical potential levels, **the addition energy** (= the energy it costs to put an additional charge on the island) is given by

$$\mu(N+1) - \mu(N) = \frac{e^2}{C} + E_{N+1} - E_N$$



Note that the difference in energy levels occurring in this expression ($E_{N+1} - E_N$) is nothing but the level splitting.

electronic level structure isolated C_{60}

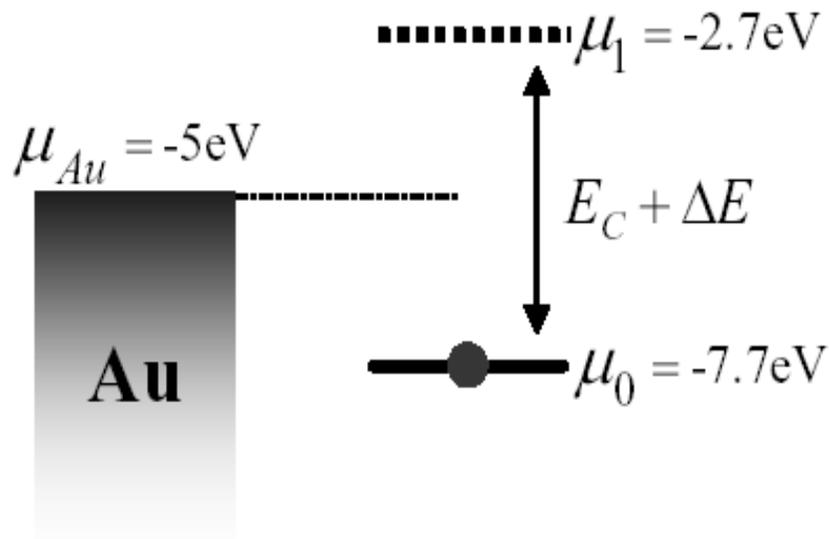


electronic energies and electrochemical potentials

$$\mu_N \equiv U(N) - U(N-1) \quad U = \text{total energy}$$

$$\mu_0 = U(C_{60}) - U(C_{60}^{1+}) \approx -7.7 \text{ eV (ionization energy)}$$

$$\mu_1 = U(C_{60}^{1-}) - U(C_{60}) \approx -2.7 \text{ eV (electron affinity)}$$



$$\mu_1 - \mu_0 = \Delta E + E_c$$

$$\Delta E = 1.65 \text{ eV}$$

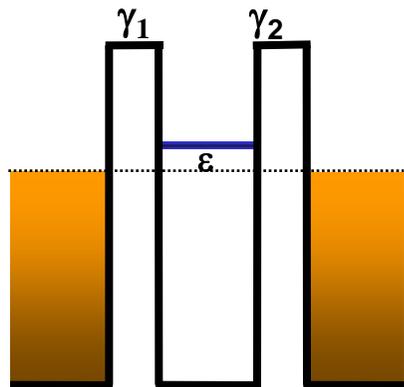
E_c : charging energy (e^2/C)

estimate E_c

metal sphere: $C = 4\pi\epsilon_0 R$

$R = 0.4 \text{ nm} \Rightarrow E_c = 3.6 \text{ eV}$

analytical solution IV characteristic single-level model



$T = 0$: $f_1 - f_2 = 1$ for $0 < E < eV$ and zero otherwise

including spin and for symmetric barriers:

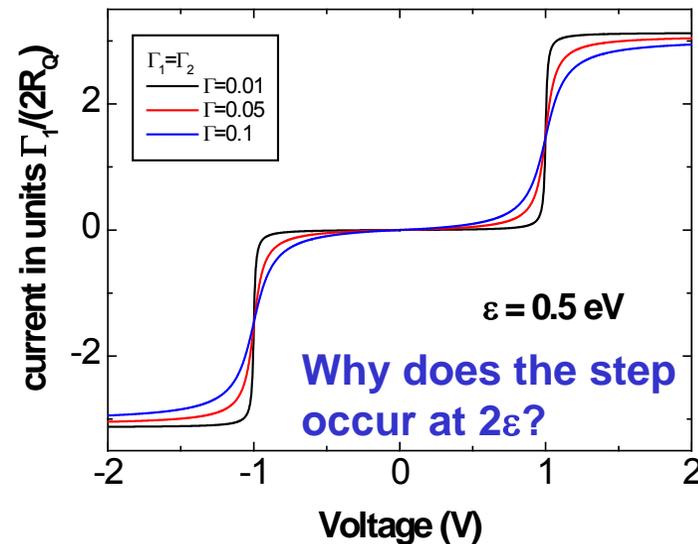
$$I = \frac{2e}{h} \int_{-eV/2}^{eV/2} \frac{\gamma_1 \gamma_2}{(E - \epsilon)^2 + (\gamma/2)^2} dE$$

$$I = \frac{2e\gamma_1\gamma_2}{h} \int_{-eV/2-\epsilon}^{eV/2-\epsilon} \frac{1}{(E - \epsilon)^2 + (\gamma/2)^2} d(E - \epsilon)$$

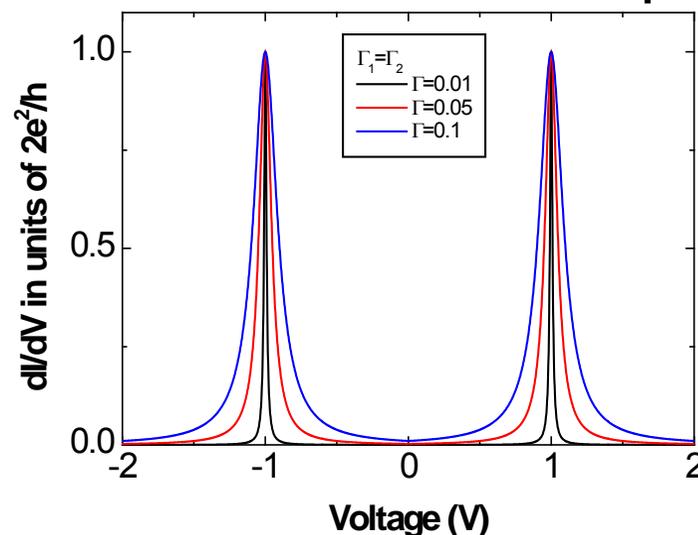
$$I = \frac{4e}{h} \frac{\gamma_1\gamma_2}{\gamma_1 + \gamma_2} \left[\arctan\left(2 \frac{eV - \epsilon}{\gamma}\right) - \arctan\left(2 \frac{-eV - \epsilon}{\gamma}\right) \right]$$

current proportional to the broadening γ

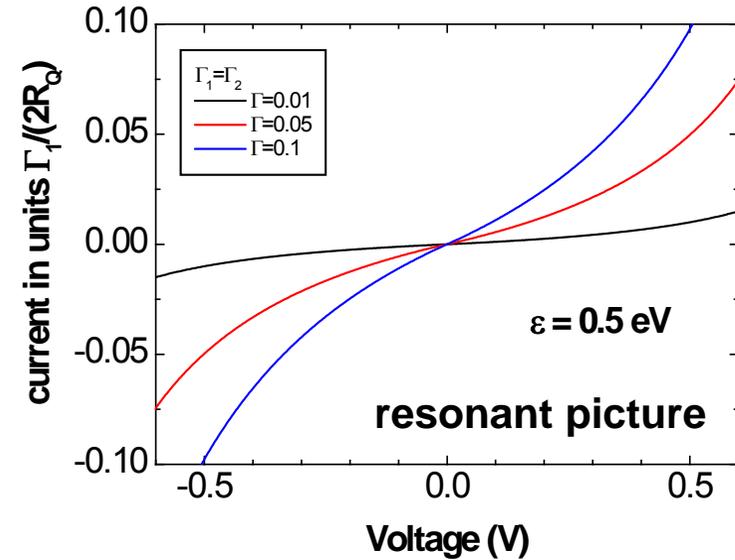
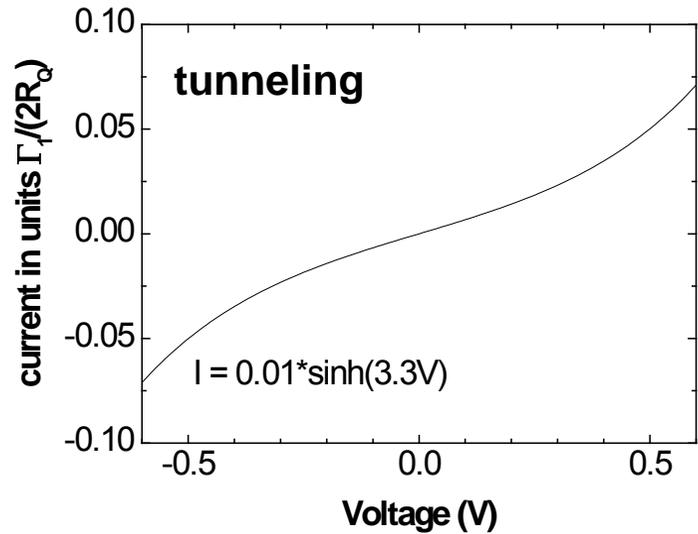
current shows **steps** as resonance crosses bias window



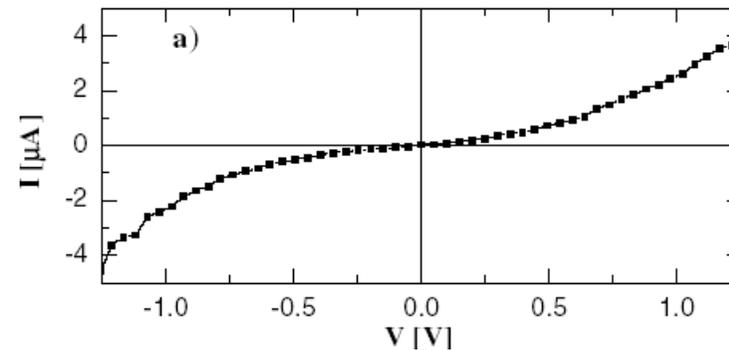
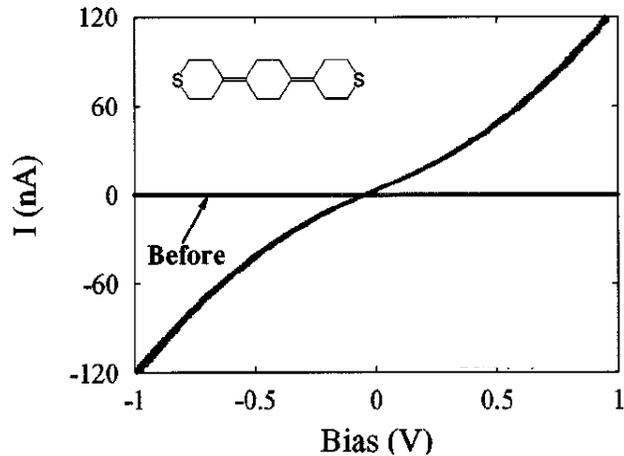
dI/dV shows Lorentzian shape



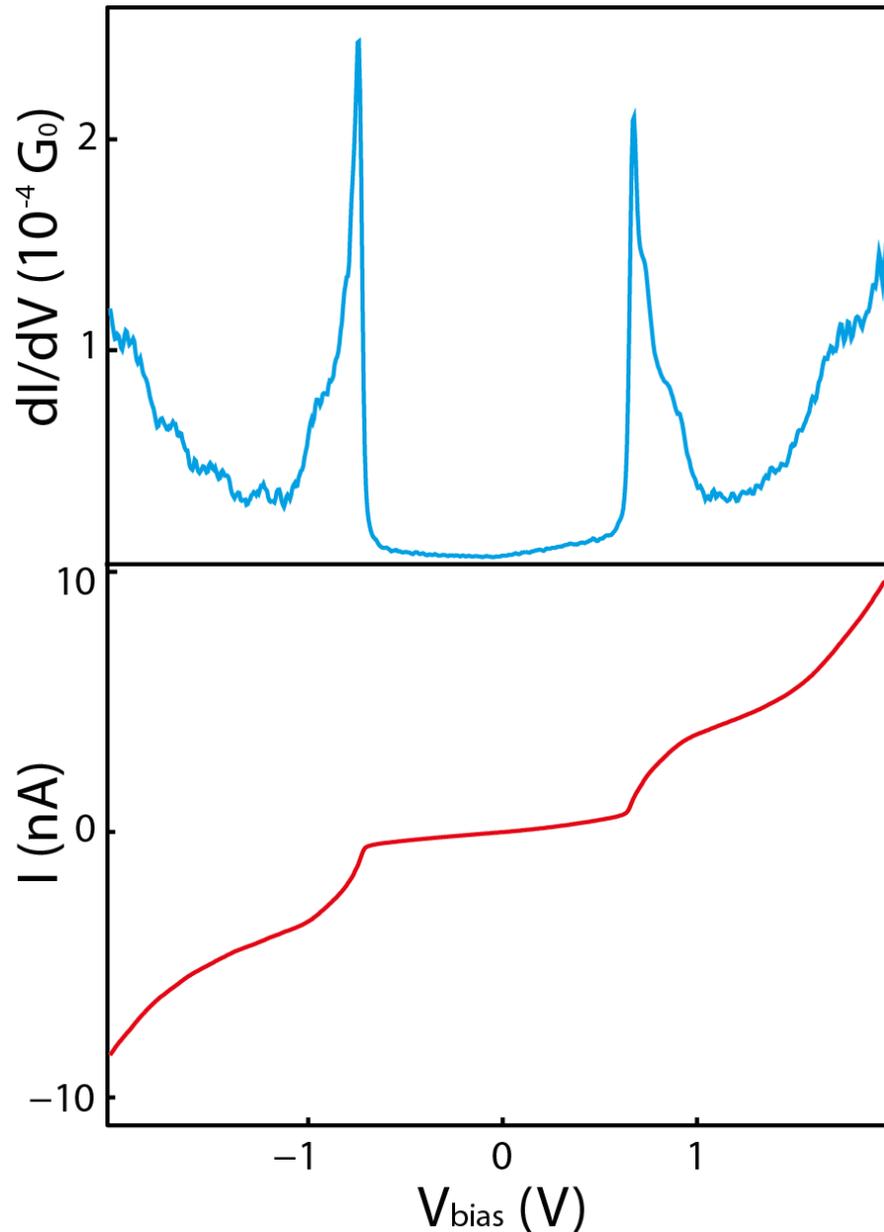
complication: at low bias the model predicts the same dependence as single-barrier tunneling



This can therefore not be used as a proof for molecular transport:



an example: a spin-crossover molecule



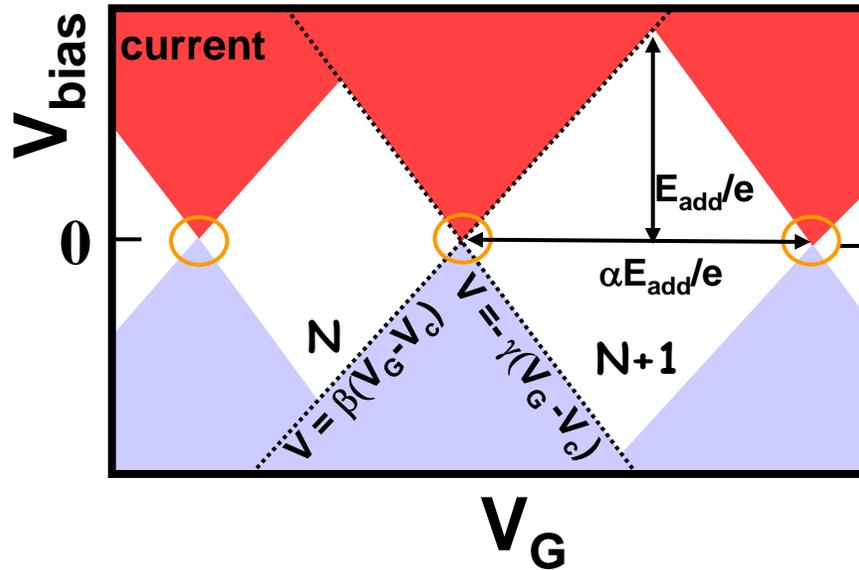
T = 6 K

mechanically controlled break junction technique

Why is the zero-bias conductance not zero?

Why do the steps not flatten out at high bias voltages?

stability diagram: vary bias and gate voltages



The current is suppressed when all chemical potential levels lie outside of the bias window. As we can tune the location of these levels using the gate voltage. We can calculate the line in the plane which separates a region of suppressed current from a region with finite current. This line is determined by the condition that the chemical potential of the source (or drain) is aligned with that of a level on the island.

$$V_C = (N - 1/2) \frac{e}{C} + \frac{E_N}{e}$$

$$\beta = C_G / (C_G + C_D)$$

$$\gamma = C_G / C_S$$

For the chemical potential to be aligned to the source ($\mu(N) = \mu_S = -eV$) and with keeping the dot's charge constant):

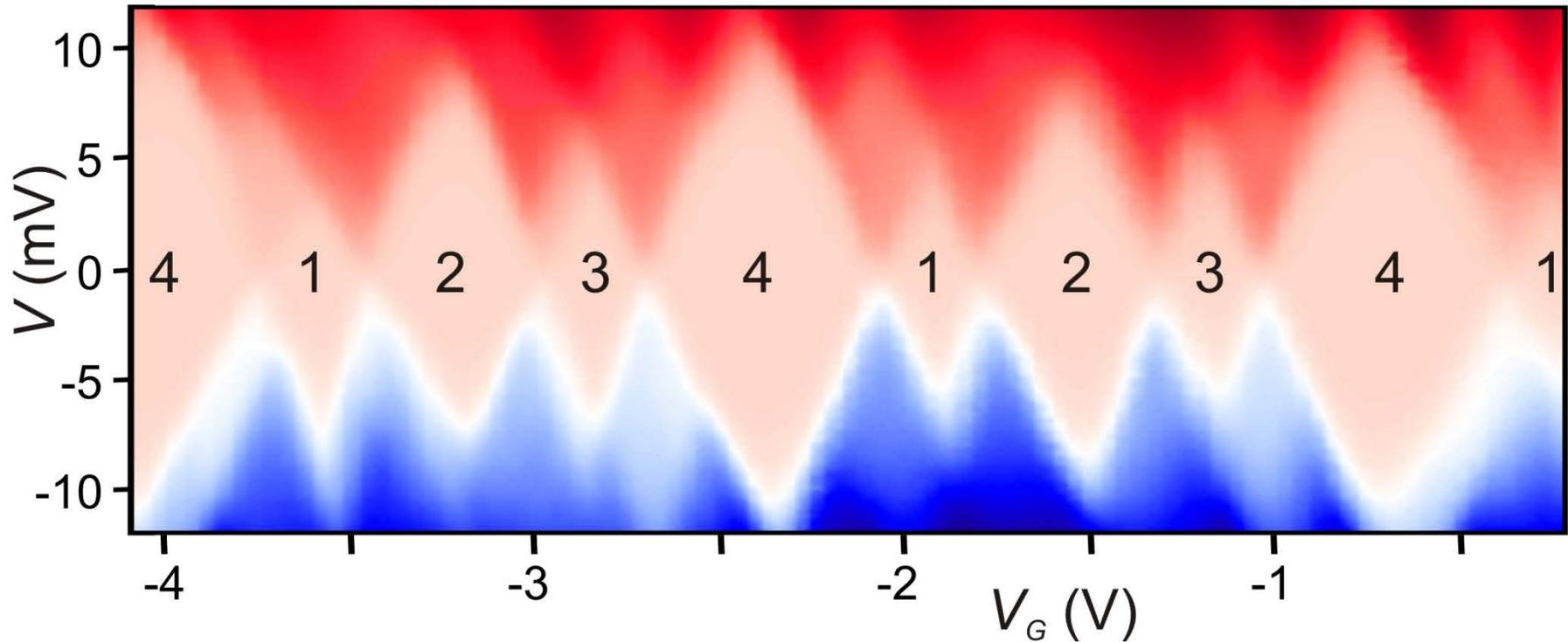
$$V = \beta(V_G - CV_C / C_G)$$

If the chemical potential is aligned with the drain ($\mu(N) = \mu_D = 0$), we have the linear relation:

$$V = \gamma(CV_C / C_G - V_G)$$

measured stability diagram carbon nanotubes

level splitting and charging energies can be determined



$$\Delta V = \frac{|\mu(N) - \mu(N+1)|}{e} = \frac{E_{add}}{e}$$

- 1: $E_C \approx 4$ meV**
- 2: $E_C + \Delta_1 \approx 8$ meV**
- 3: $E_C \approx 4$ meV**
- 4: $E_C + \Delta_2 \approx 13$ meV**

Draw the corresponding chemical potential of the levels and of the energies of the orbitals ...

most experiments thus far: off-resonant transport molecular wires behave as “semiconductors”

Only if clear steps in the current-voltage curves are observed, can we exclude that direct tunneling determines transport.

What about molecular signatures? (additional energies will not work because

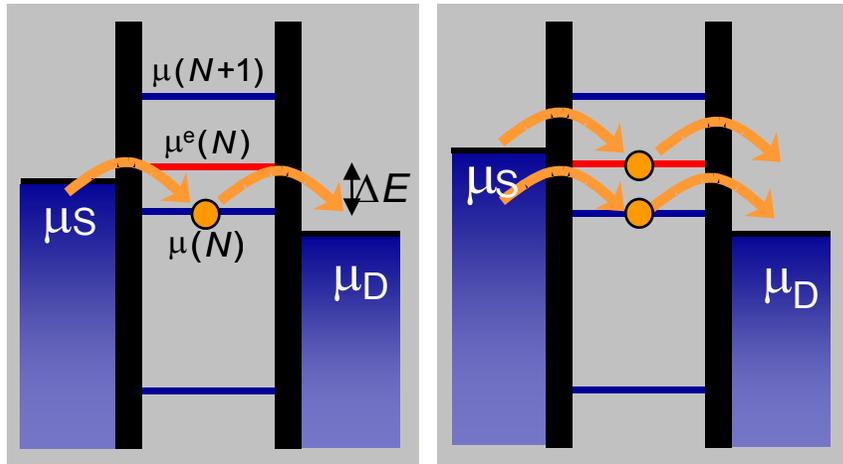
Where to look for molecular signatures:

- Choose for molecules whose (internal) orbital structure does not allow a description in terms of a single tunnel barrier (e.g. quantum interference molecules)
- Perform detailed spectroscopy on the molecules looking for molecule-specific properties (vibrations, spin-related excitations,

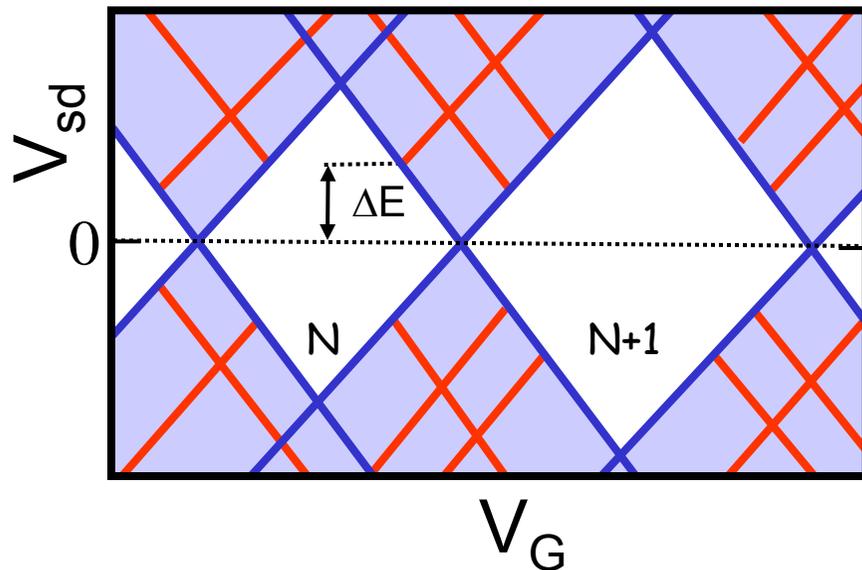
Why do you want to perform the spectroscopy at low temperatures?

level spectroscopy: excited states ($\Gamma \ll U$)

incoherent, resonant transport: non-linear regime

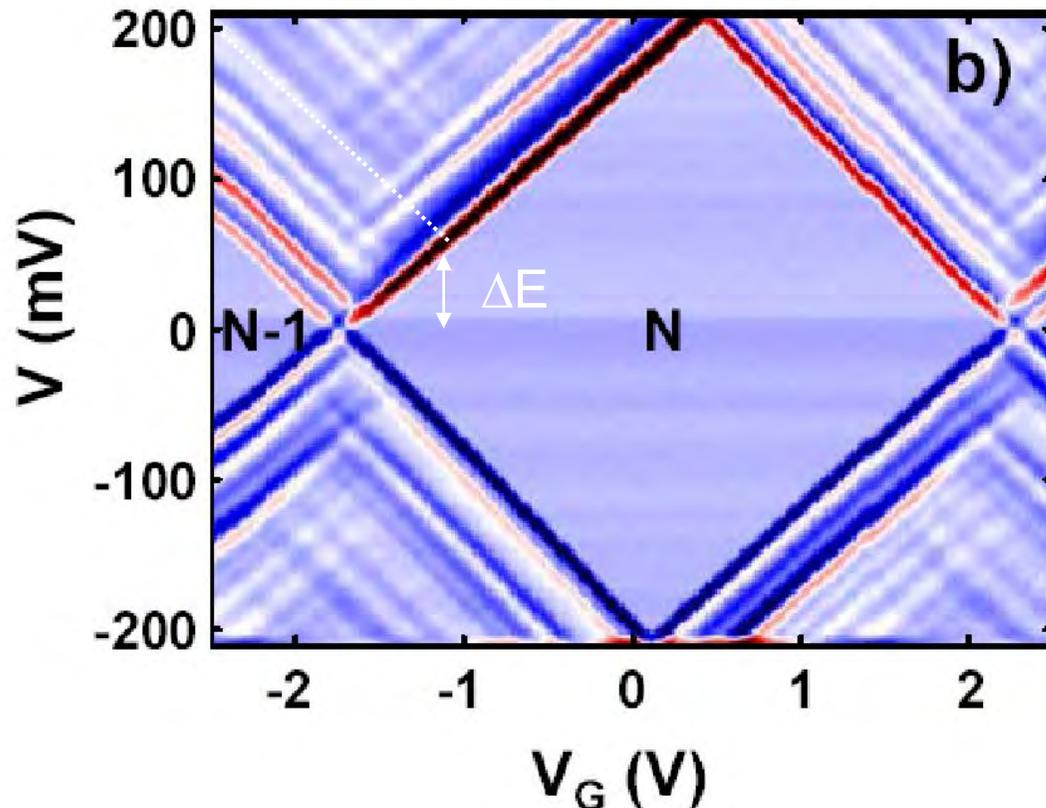
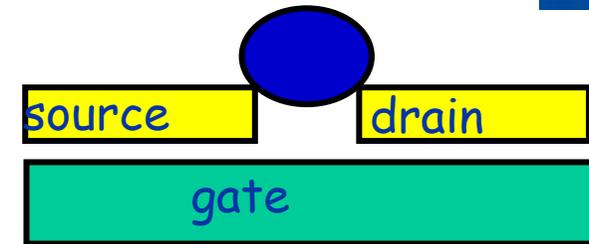
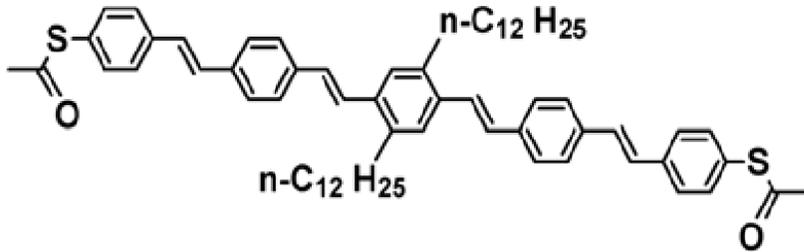


- two 'knobs': V_{SD} and V_{gate}
- state contributes to transport if $\mu_s > \mu(N) > \mu_d$



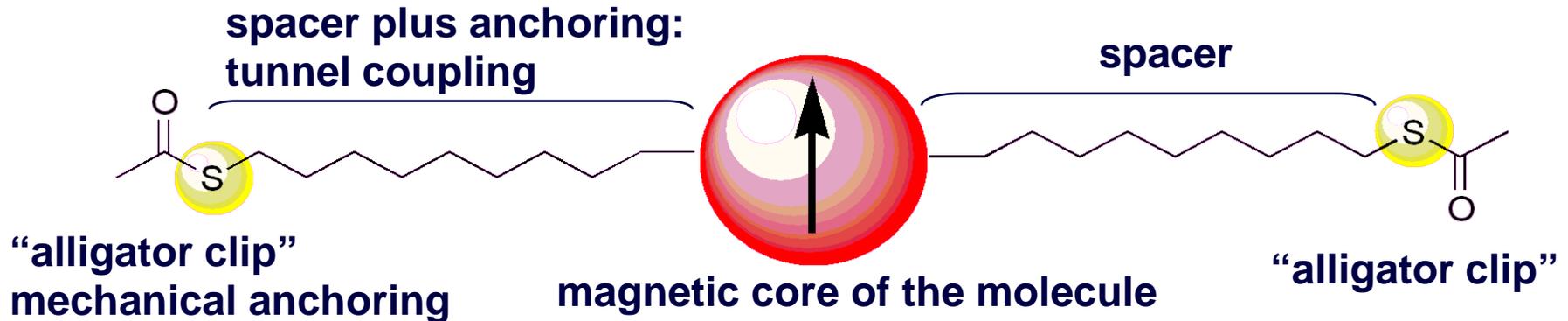
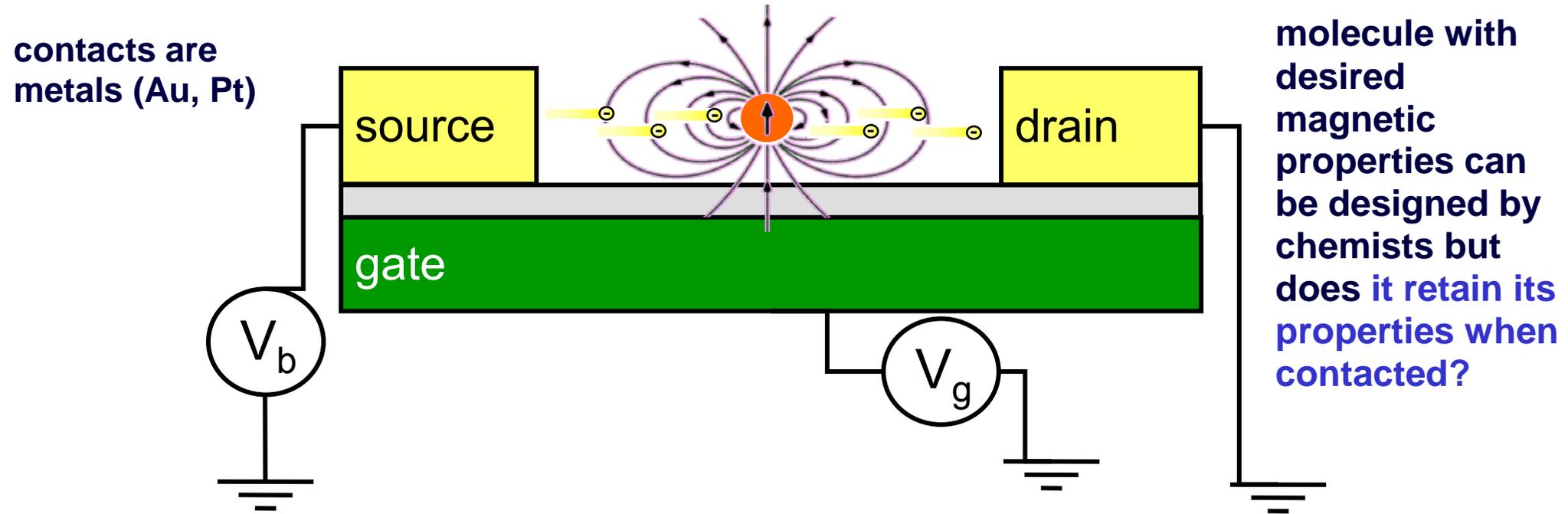
- excited states result in extra lines in stability diagram (red)
- excitations can probe electronic spectrum, spin or vibrational states

excitation lines: electronic fingerprints of molecular vibrations ($\Gamma \ll U$)



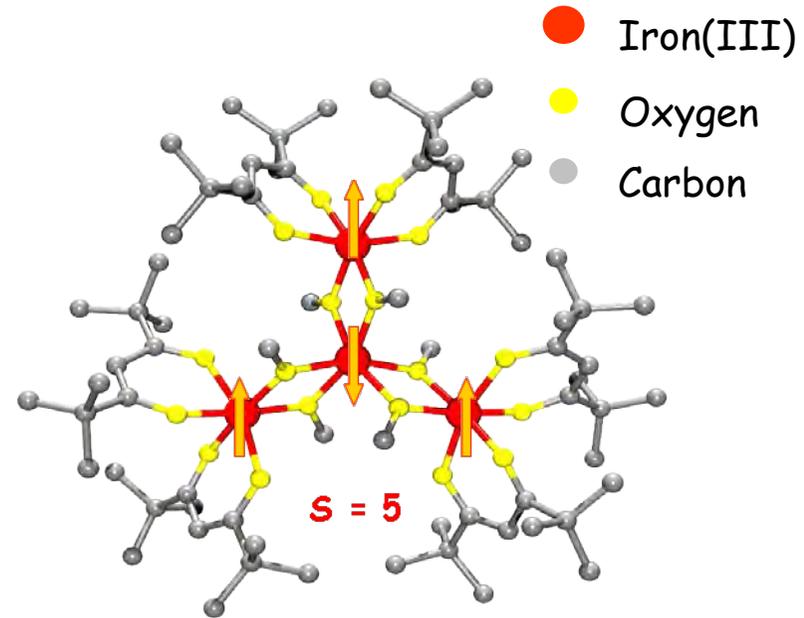
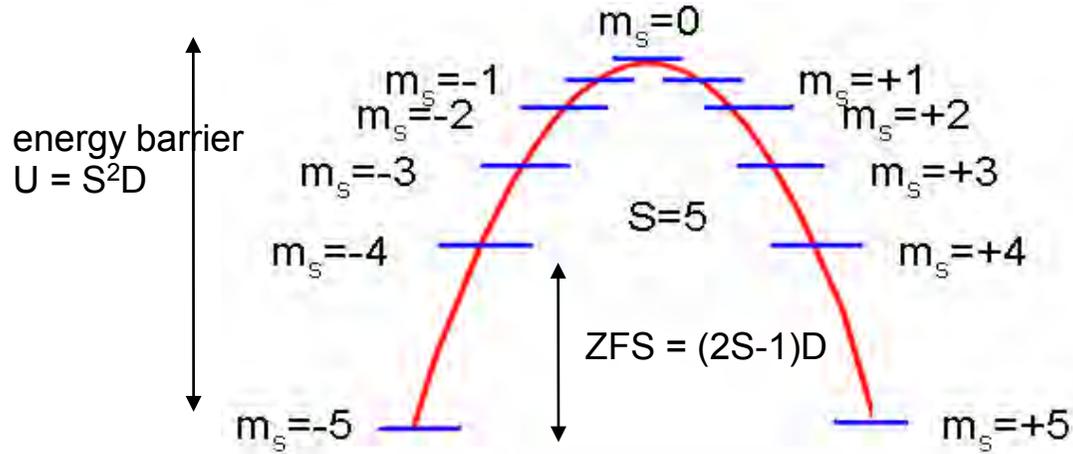
- symmetric with respect to the bias voltage
- excitations the same for different charge states
- more than 15 lines separated by a few meV: unlikely electronic excitations in such a small molecule

molecular spin transistor: addressing magnetic properties on a single molecule level using electrons



the molecule: single-molecule magnet Fe₄

$$H = DS_z^2$$



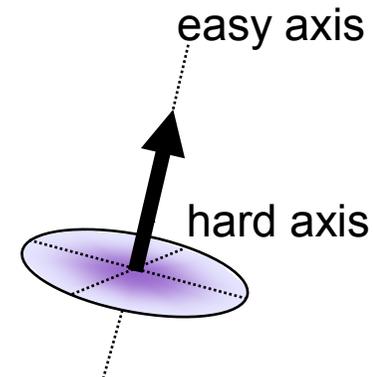
synthesis: Andrea Cornia

- high stability of Fe₄; retains its magnetic properties when dispersed on a metallic surface (Nat. Mat. 8 (2009) 194; Nature 468 (2010) 417)

- bulk zero-field splitting: ZFS = (2S-1)D = 0.6 meV; energy barrier: U = 1.4 meV

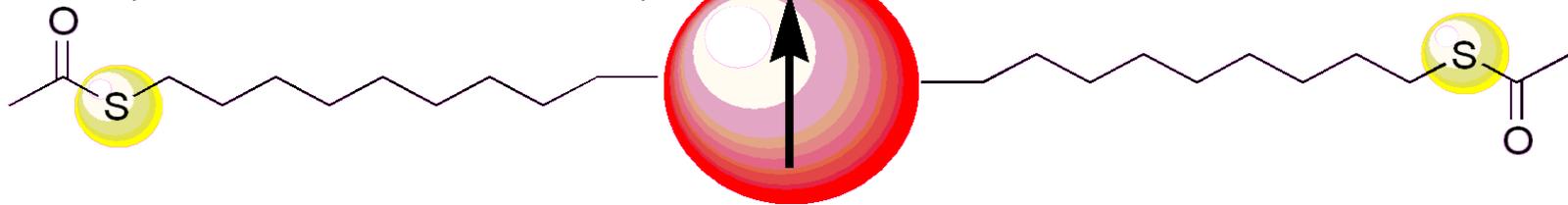
- moderate quantum tunneling ($H = DS_z^2 + E(S_+^2 + S_-^2)/2$); bulk: E = 2 meV

- How to observe anisotropy in an experiment (as Γ in general larger than ZFS)? What are the magnetic parameters for an individual molecule in a solid-state device?



role of the molecule-lead coupling

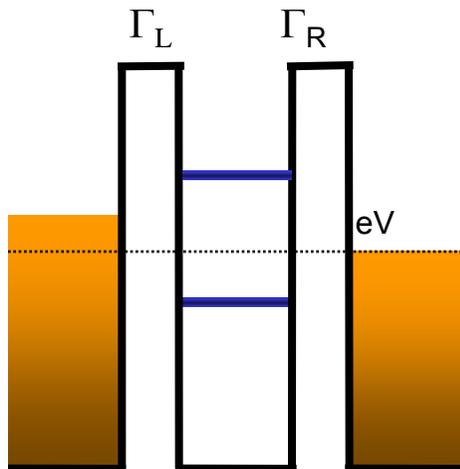
spacer plus anchoring:
tunnel coupling



experimentally, the coupling (Γ) can be controlled to some extent; full control requires fixing all atoms positions in the junction

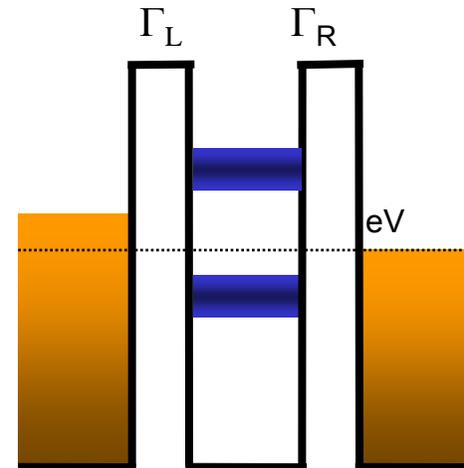
long spacer: weak coupling
Delta function DOS

current is blocked to first order
involves two **(single-particle)** charge states



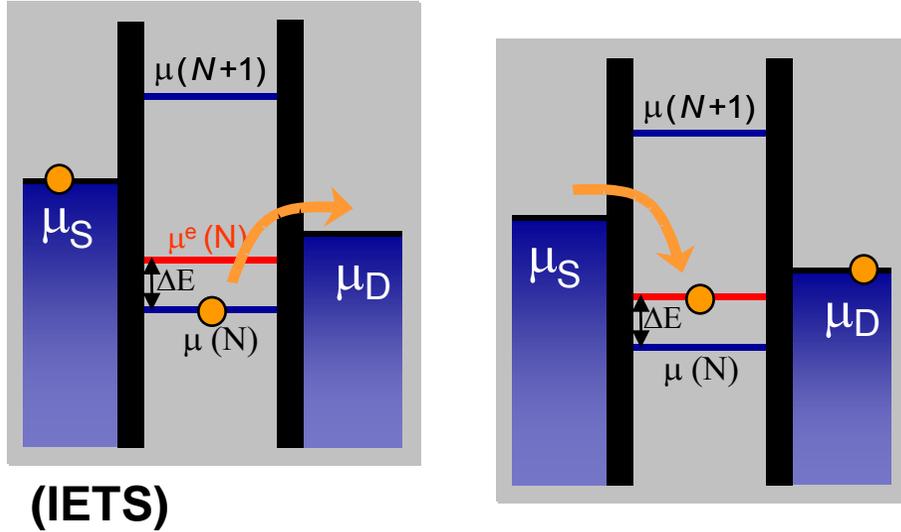
short spacer: intermediate to strong coupling
Lorentzian DOS

higher-order tunneling processes (coherent)
inelastic spin-flip, Kondo
involves only one charge state

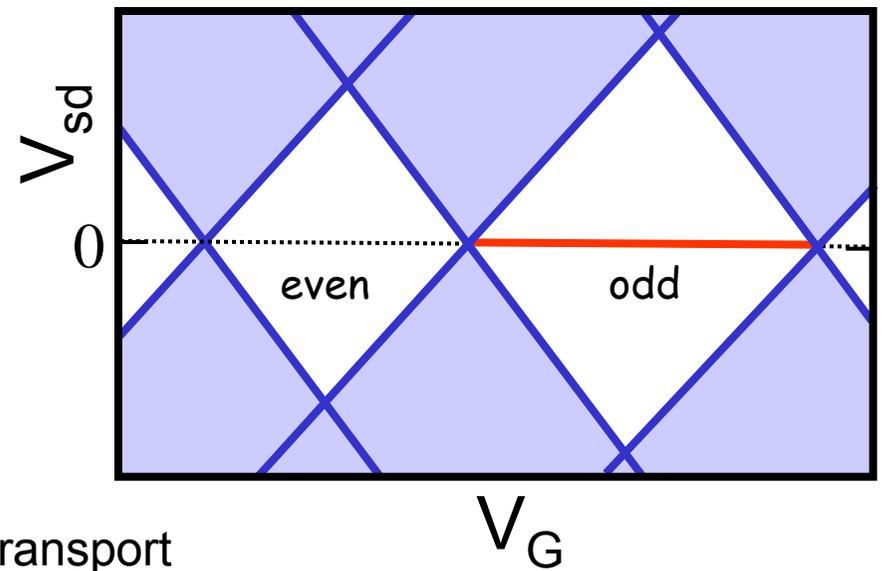
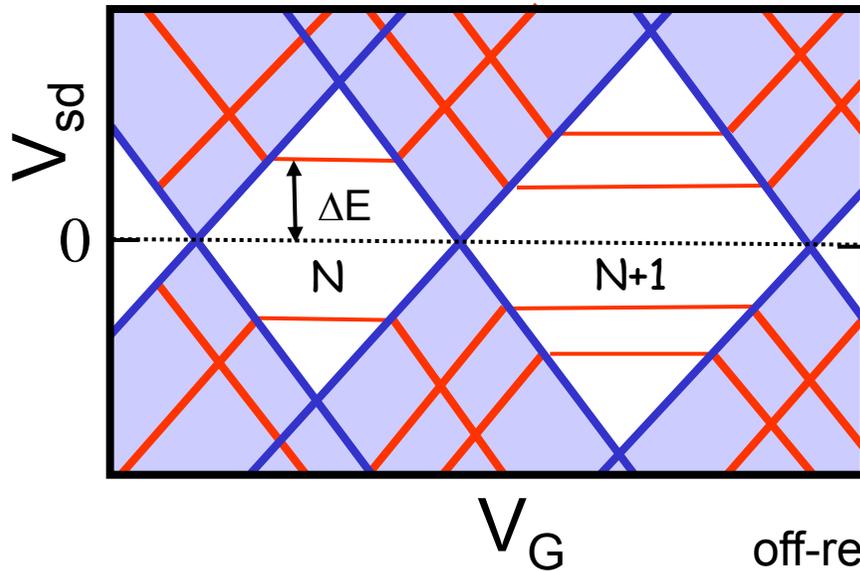
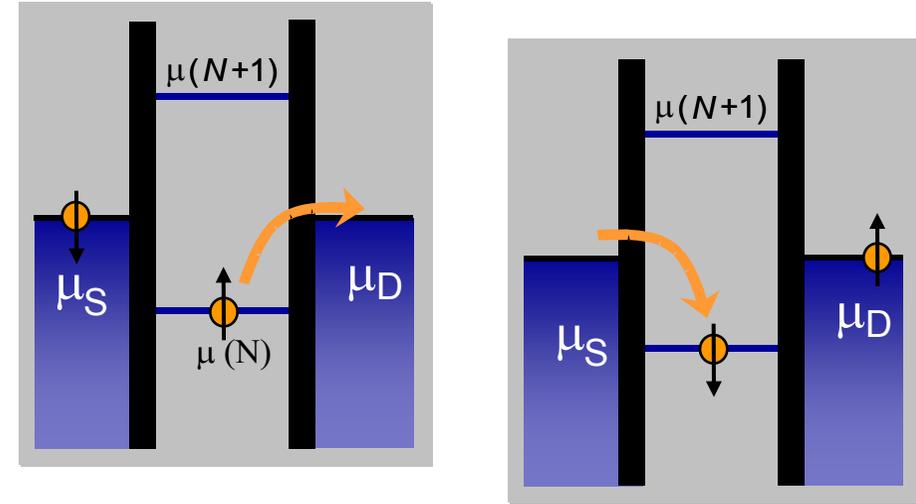


higher-order processes in Coulomb blockade

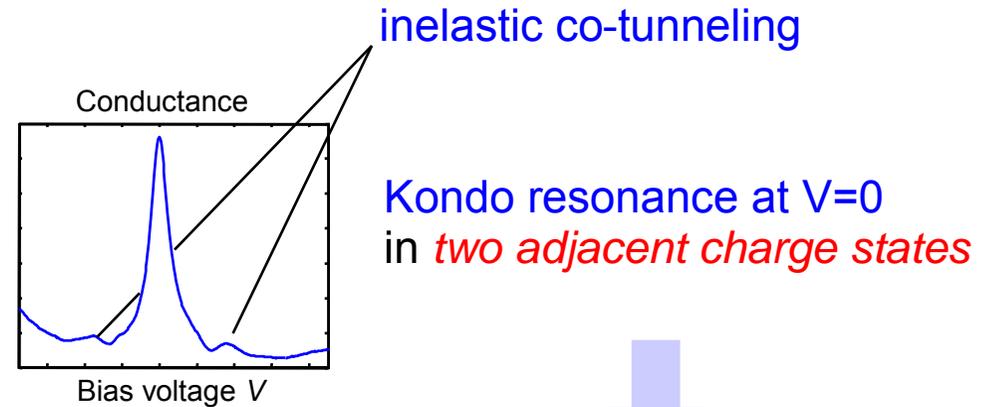
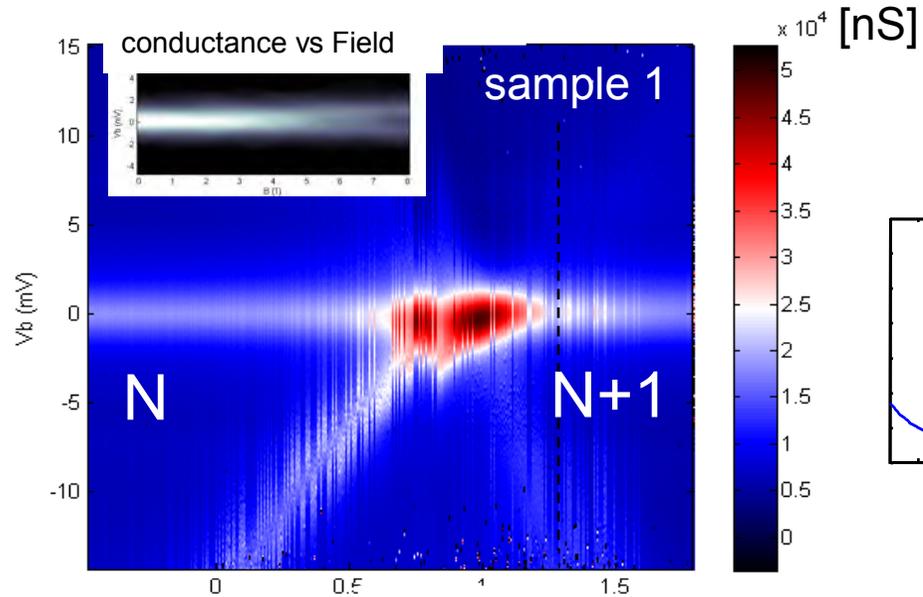
inelastic tunneling spectroscopy (IETS)



Kondo-effect (elastic): spin filling

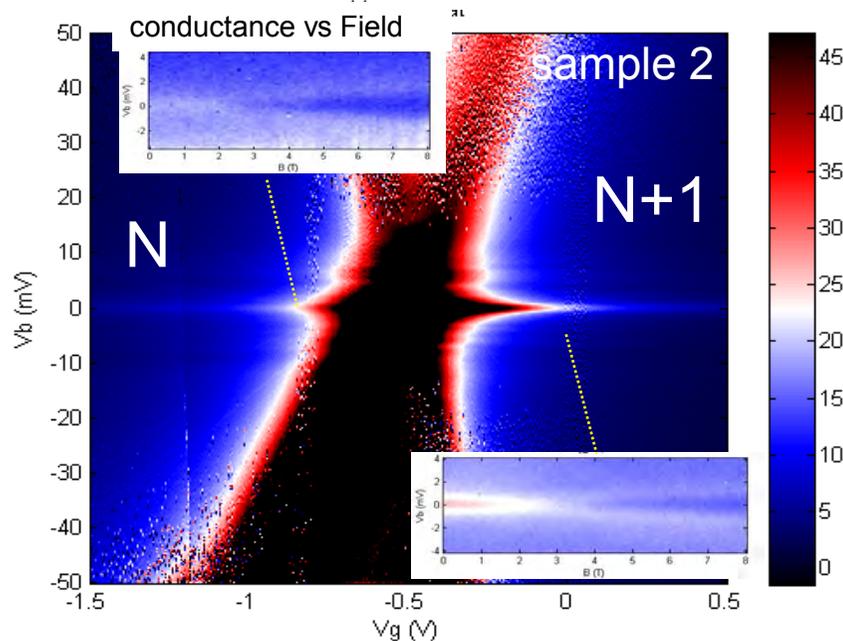


Kondo: signature of a large quantum spin



unpaired high quantum spin
at least one state has spin $> 1/2$!

$T_K \sim 10$'s of Kelvin

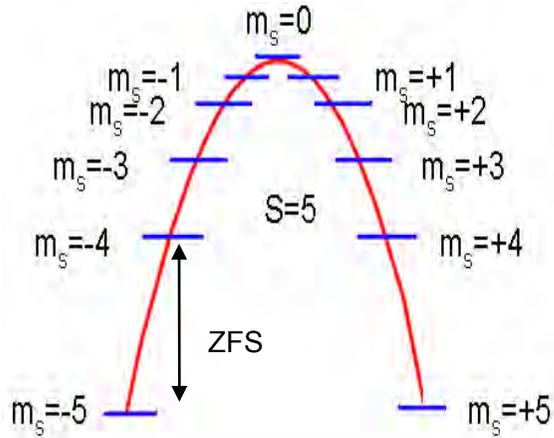


zero-field splitting
masked by
strong Kondo
($\Gamma, T_K > \text{ZFS}$)



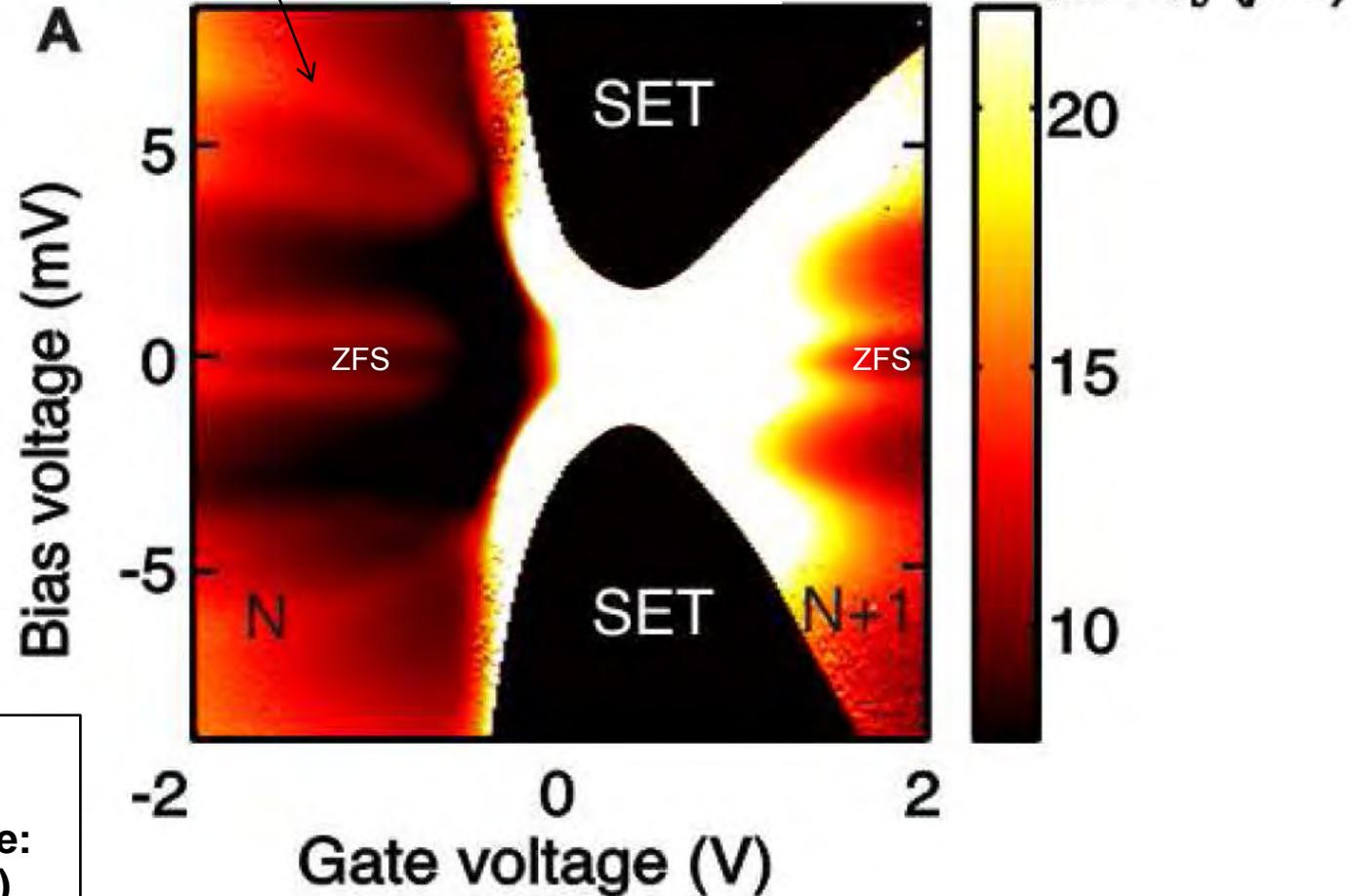
weaker coupling

inelastic cotunneling: signatures of zero-field splitting



magnetic transitions (i.e.,
from $S=5$ to $S=4$)

red: co-tunnel regime



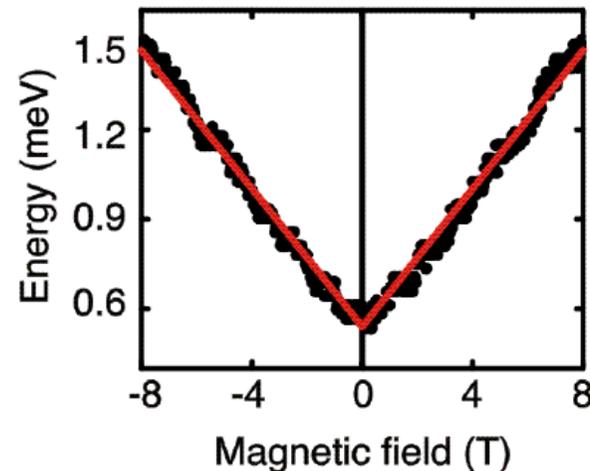
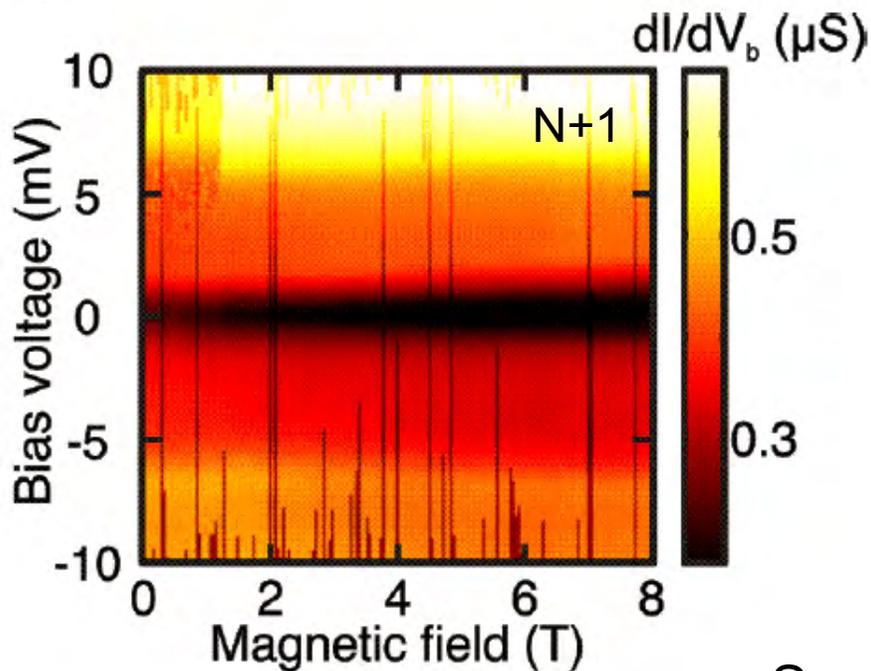
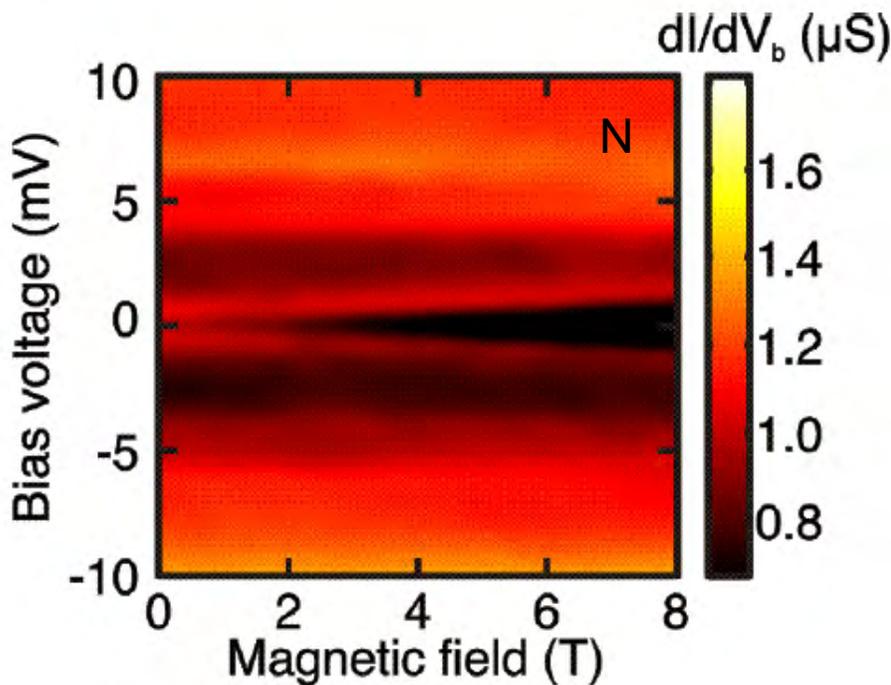
$$\text{ZFS} = (2S-1)D$$

expected value neutral molecule:
0.056 meV (bulk measurements)

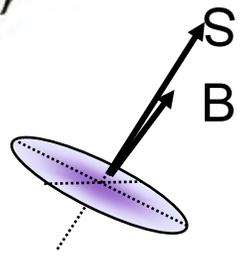
observed in adjacent charge
states

$T = 1.5 \text{ K}$

magnetic field dependence: energy splitting increases with B and is symmetric around B=0



$S = 5$
 $D = -0.056 \text{ meV}$
 $\text{theta} \sim 0^\circ g = 2.1$



measurements indicate that the angle is between 0 and 30 degrees

D-parameter in the reduced state larger than in the neutral state (50%)

consistent with expectations for ZFS !!