Transport through single molecules

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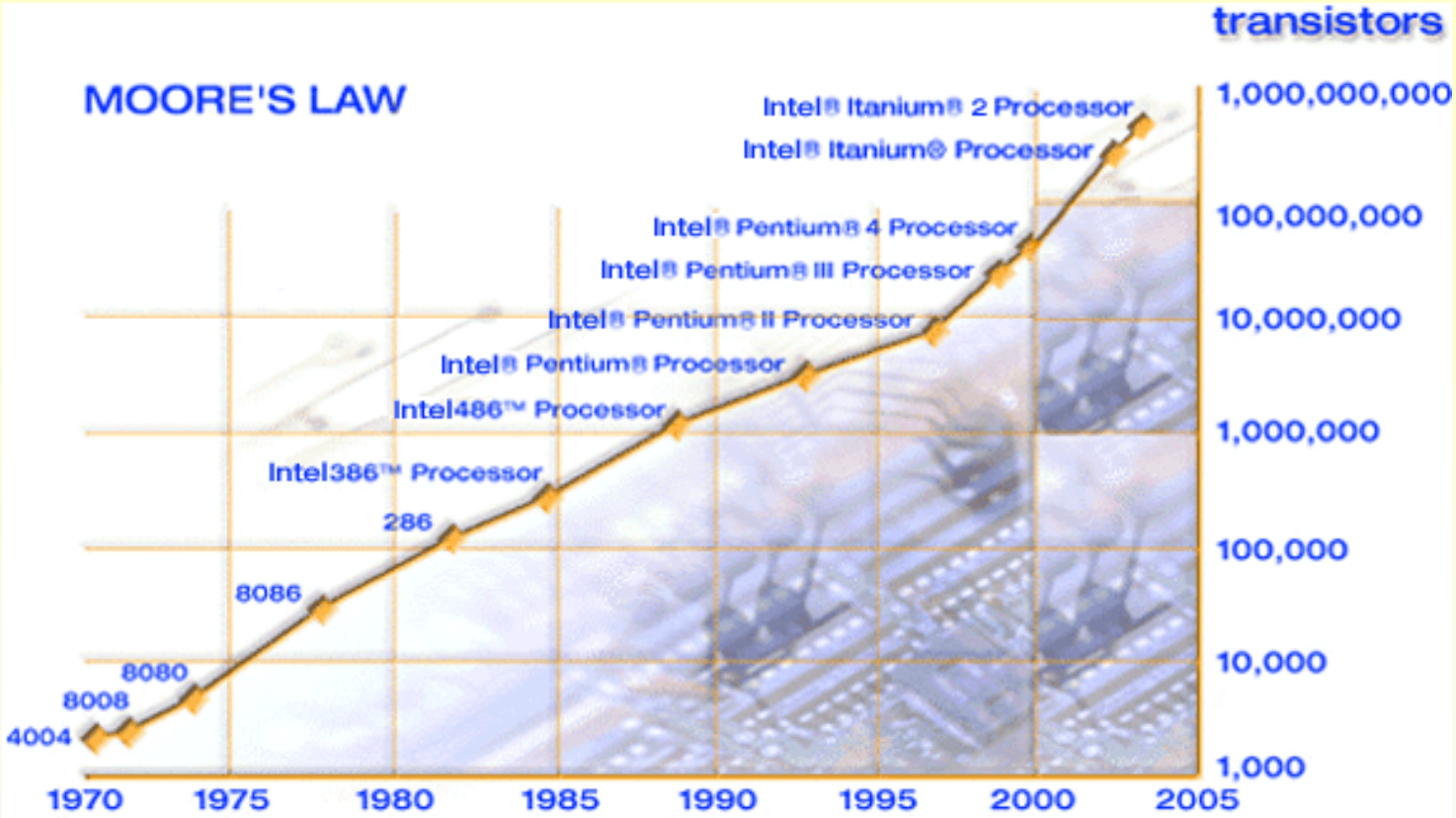
KITP June 19, 2006

- Molecular electronics
- Transport theory
- Recent experiments
- Theory: Tunneling through magnetic molecules

Molecular electronics



source: intel

➡ **extrapolation:** single molecules as transistors?

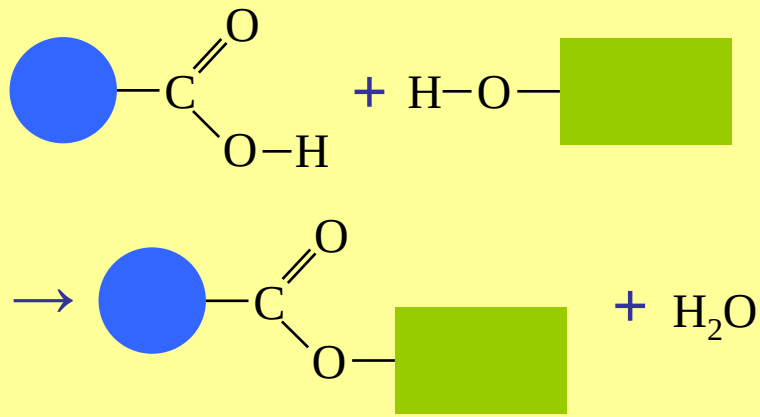
Also: possible self-assembly of components

using chemical or biochemical processes

(bottom-up approach)

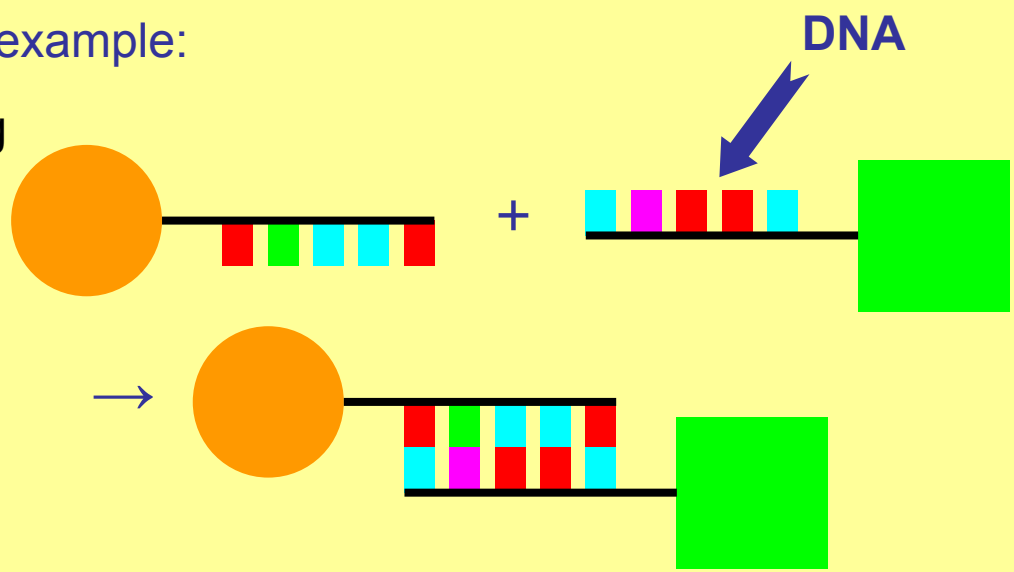
simple example:

ester synthesis



not so simple example:

DNA encoding



scalability

E. Braun *et al.*, Nature **391**, 775 (1998)

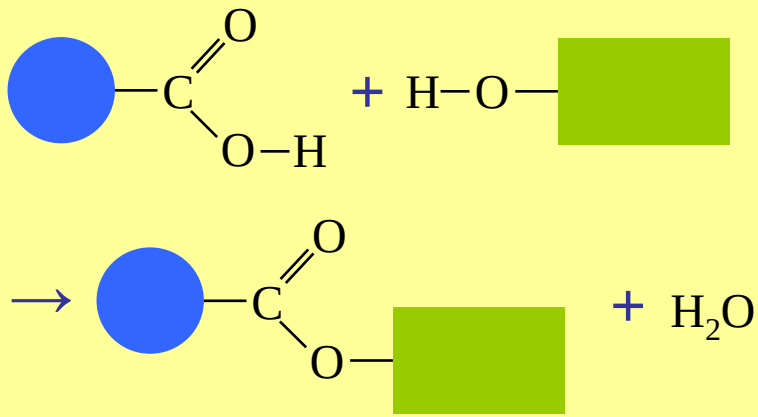
Also: possible self-assembly of components

using chemical or biochemical processes

(bottom-up approach)

simple example:

ester synthesis



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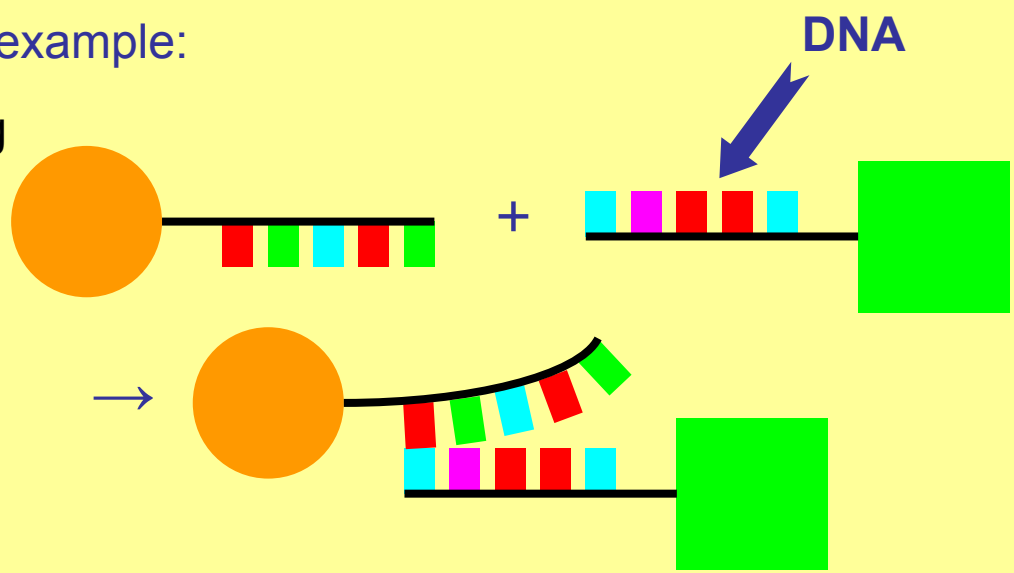

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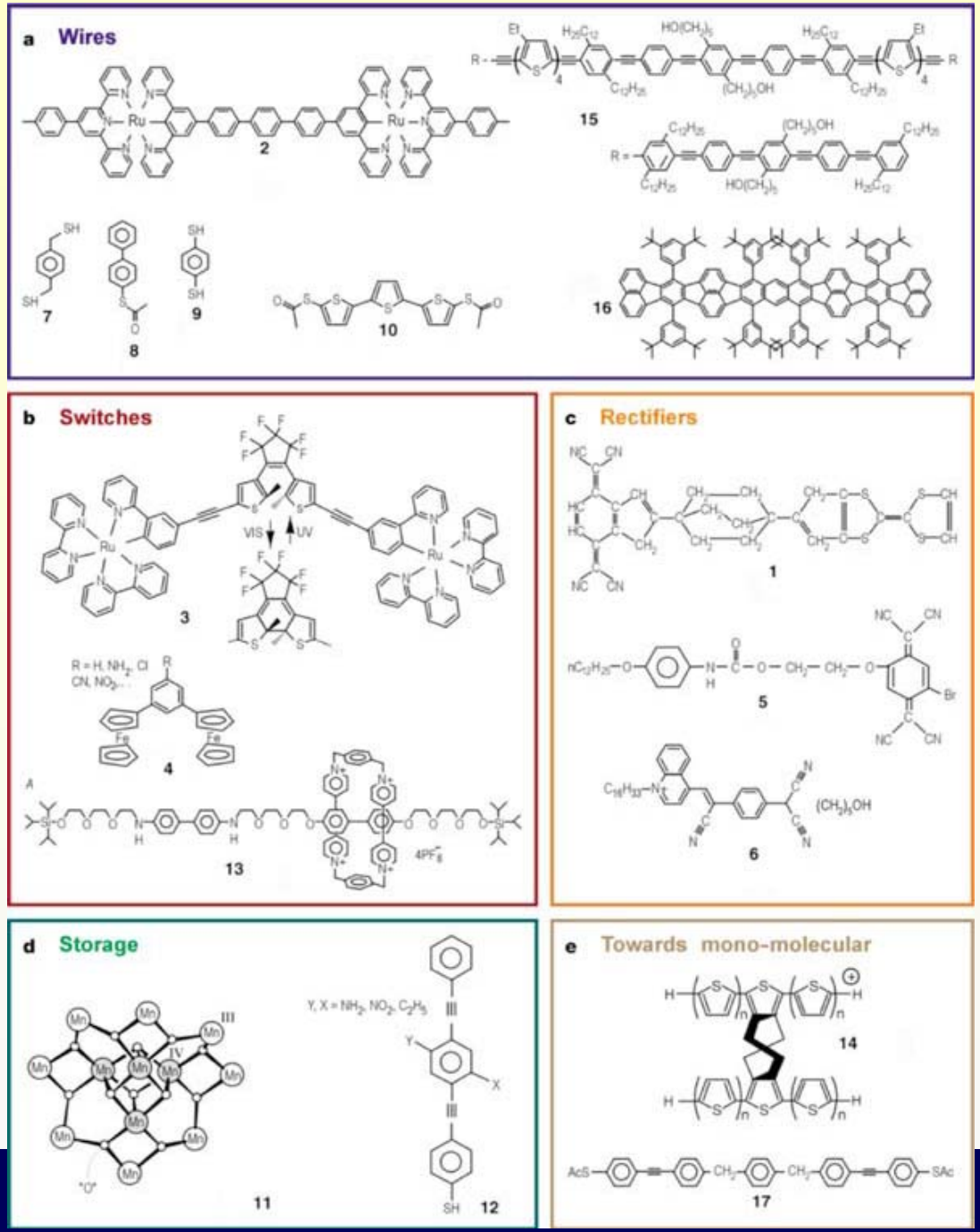


Joachim *et al.*, Nature **408**, 541 (2000)

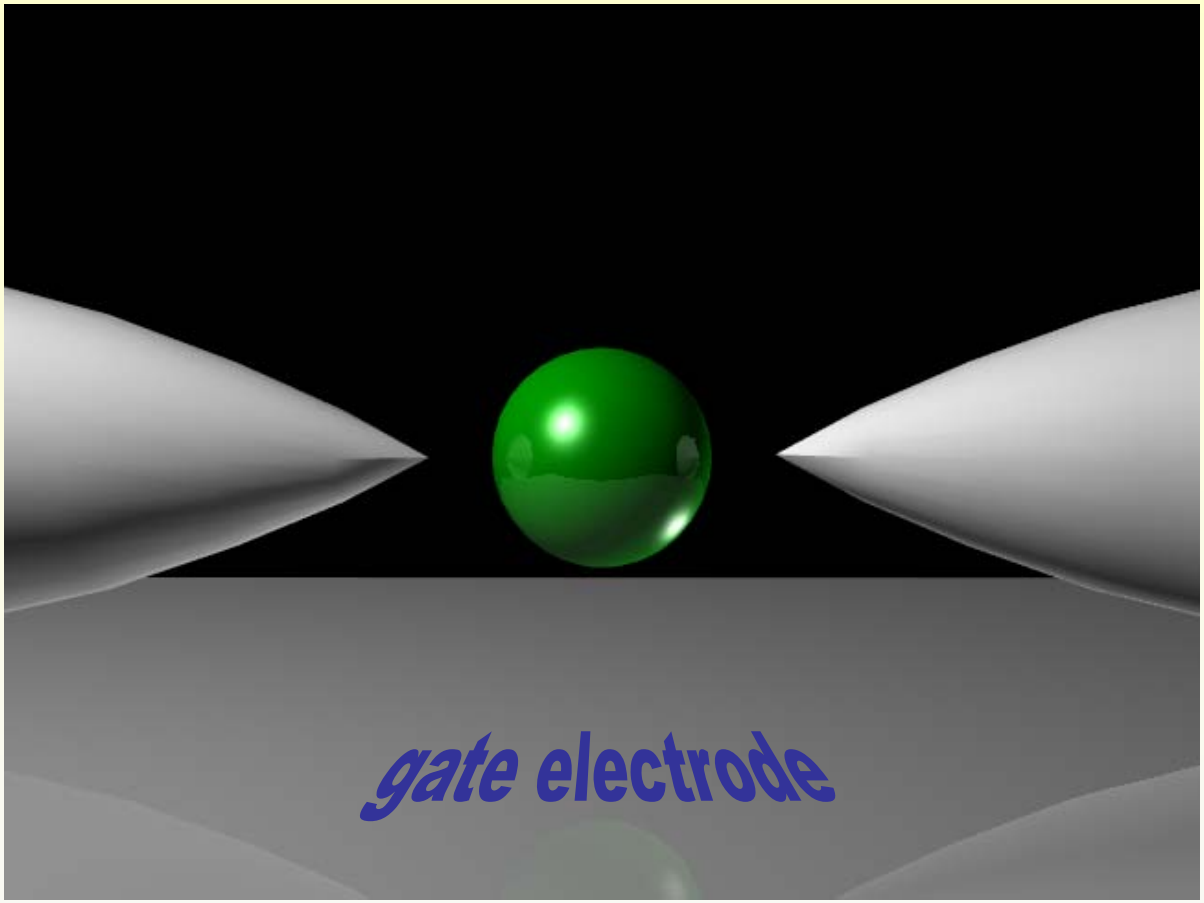
Switches and memory

- deformations, change of conformation
- local magnetic moments

Readout (and writing)

require electronic tunneling through molecules

Mechanical break junction / electromigration



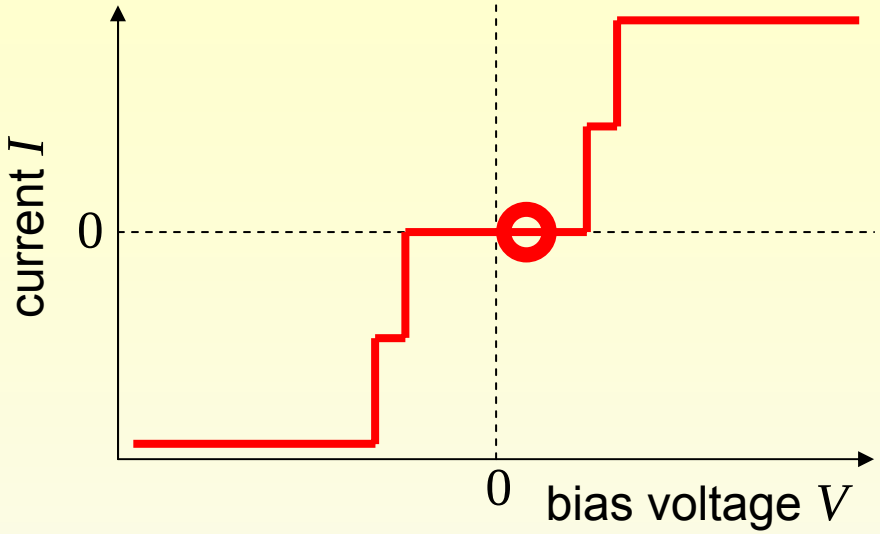
- break junctions:
  bending of substrate

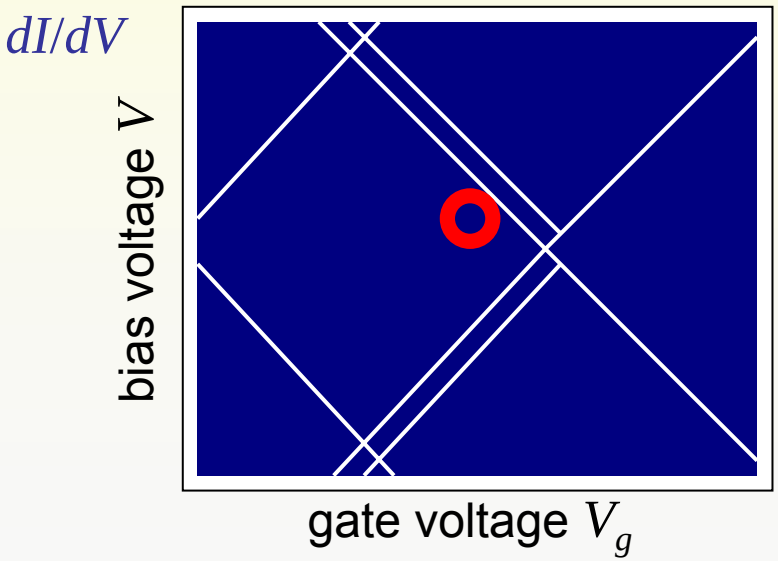
  advantage: “reversible”

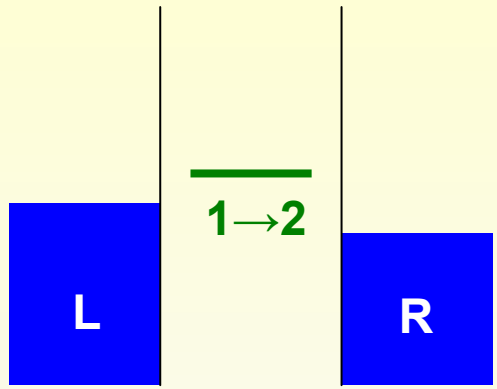
- electromigration:
  strong current, “fuse”

e.g., Reed *et al.*, Science **278**, 252 (1997)

Weak coupling, sequential tunneling regime





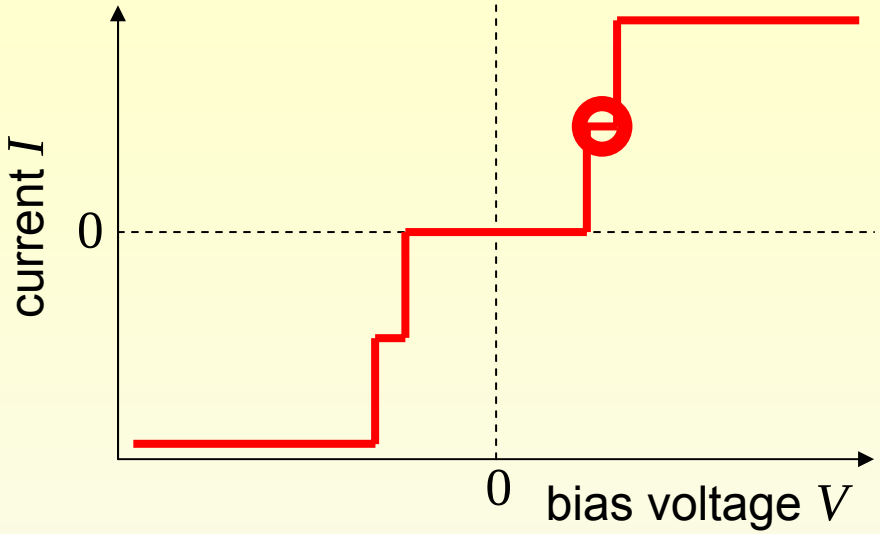


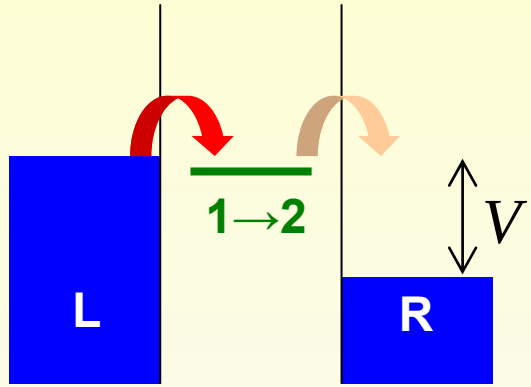
no current:

Coulomb blockade

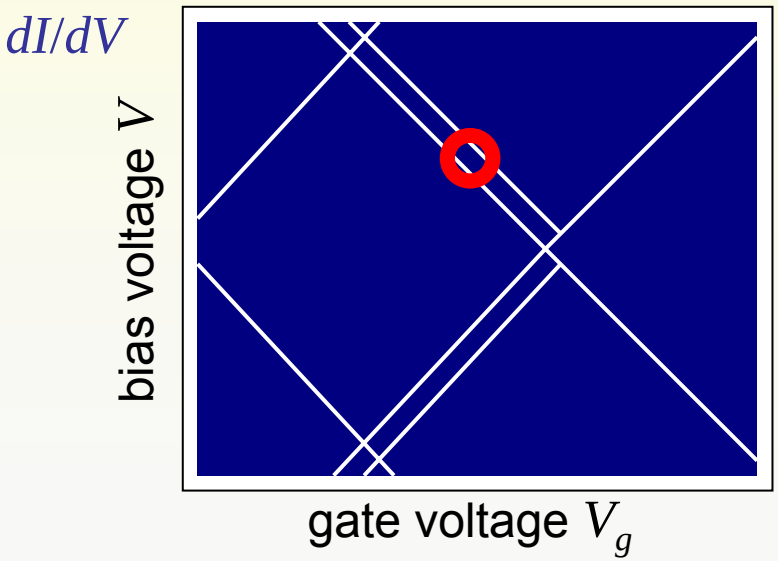
(like in quantum dots)

Weak coupling, sequential tunneling regime

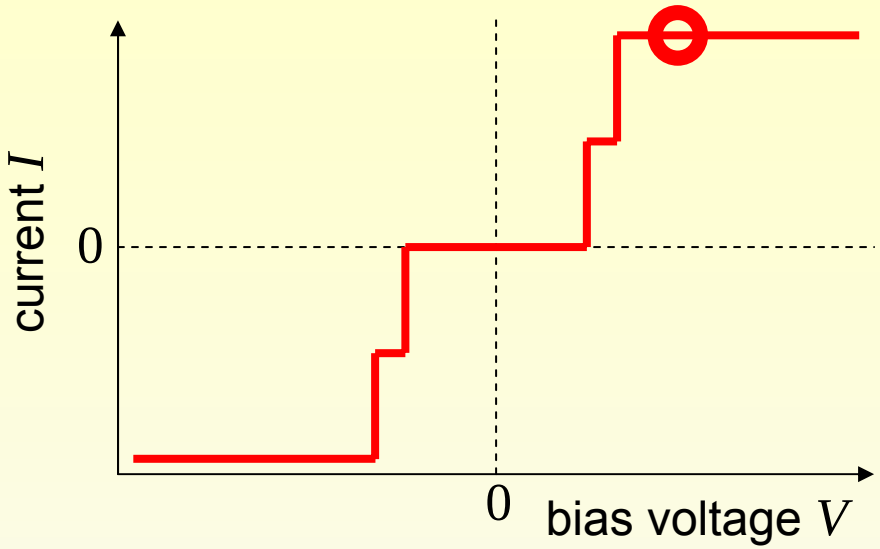


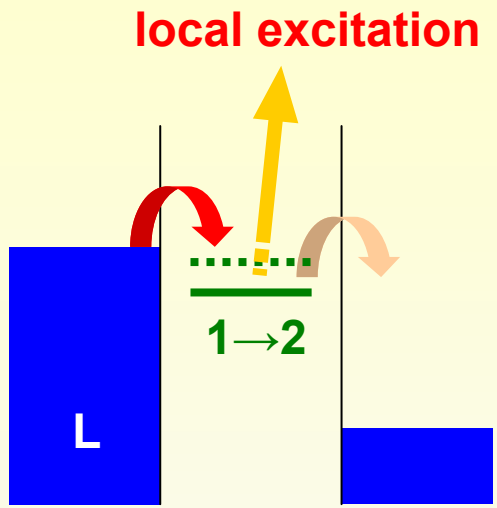


tunneling

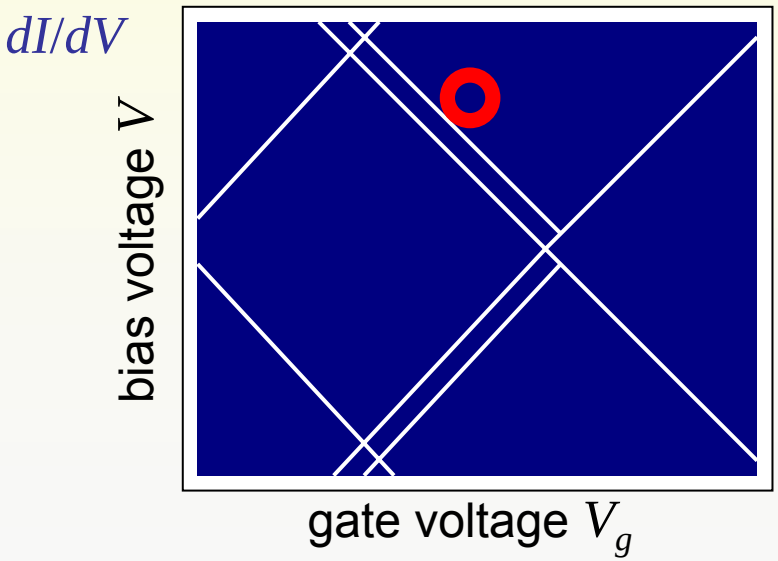


Weak coupling, sequential tunneling regime

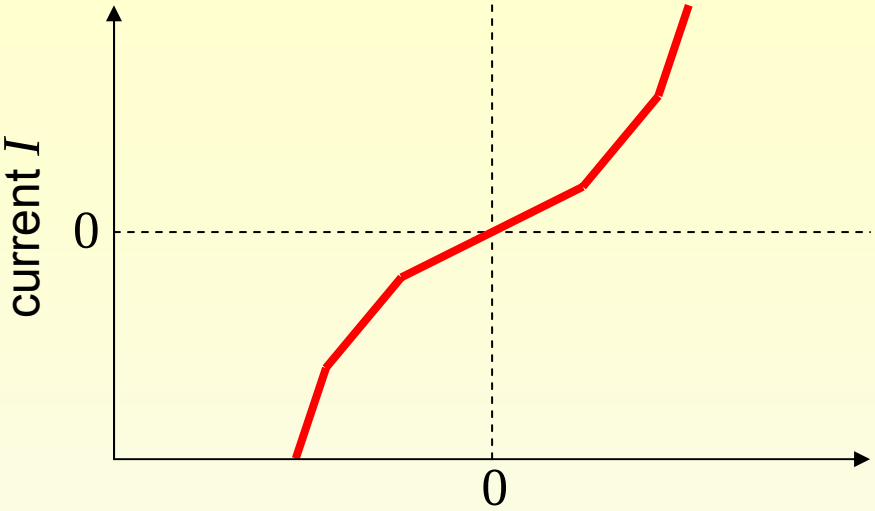


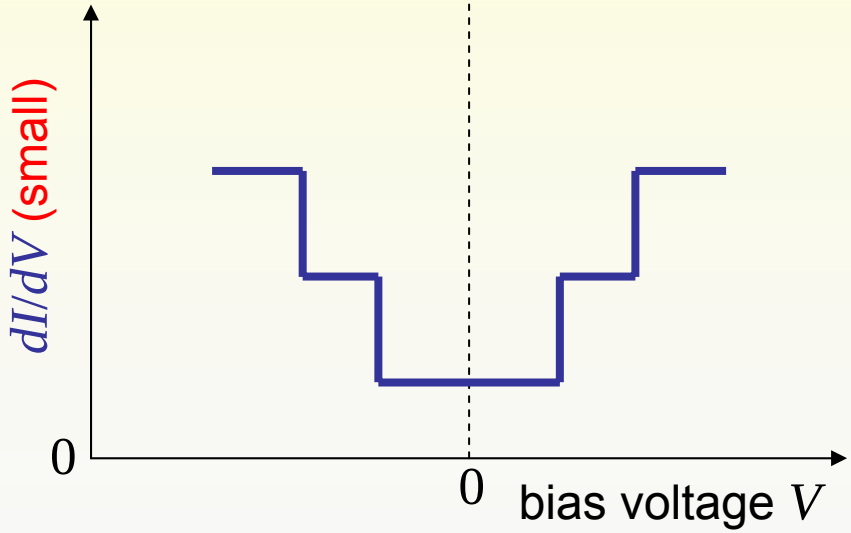


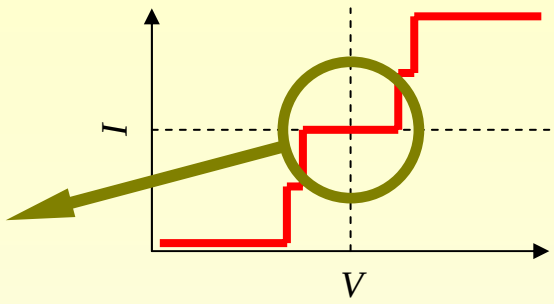
inelastic tunneling



Weak coupling, cotunneling regime

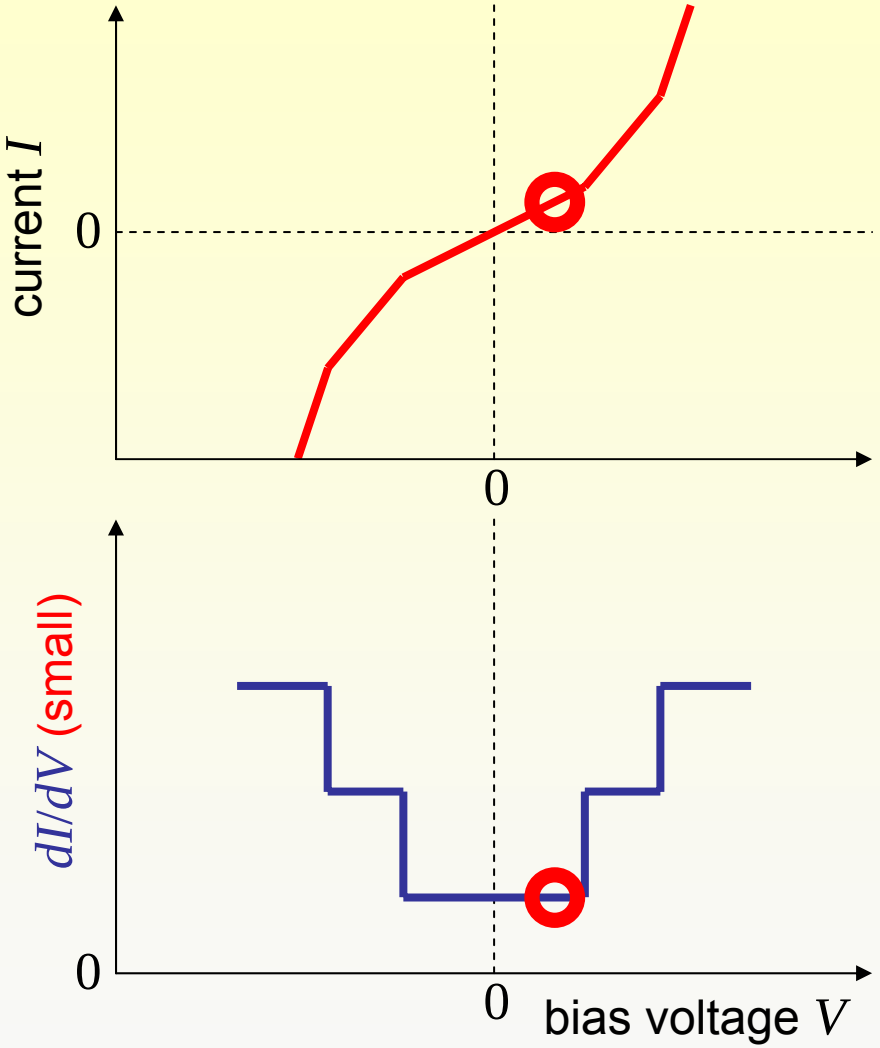


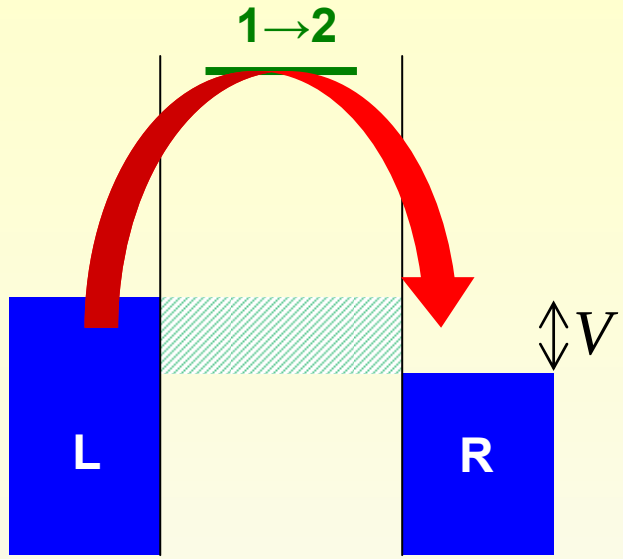




Coulomb blockade

Weak coupling, cotunneling regime



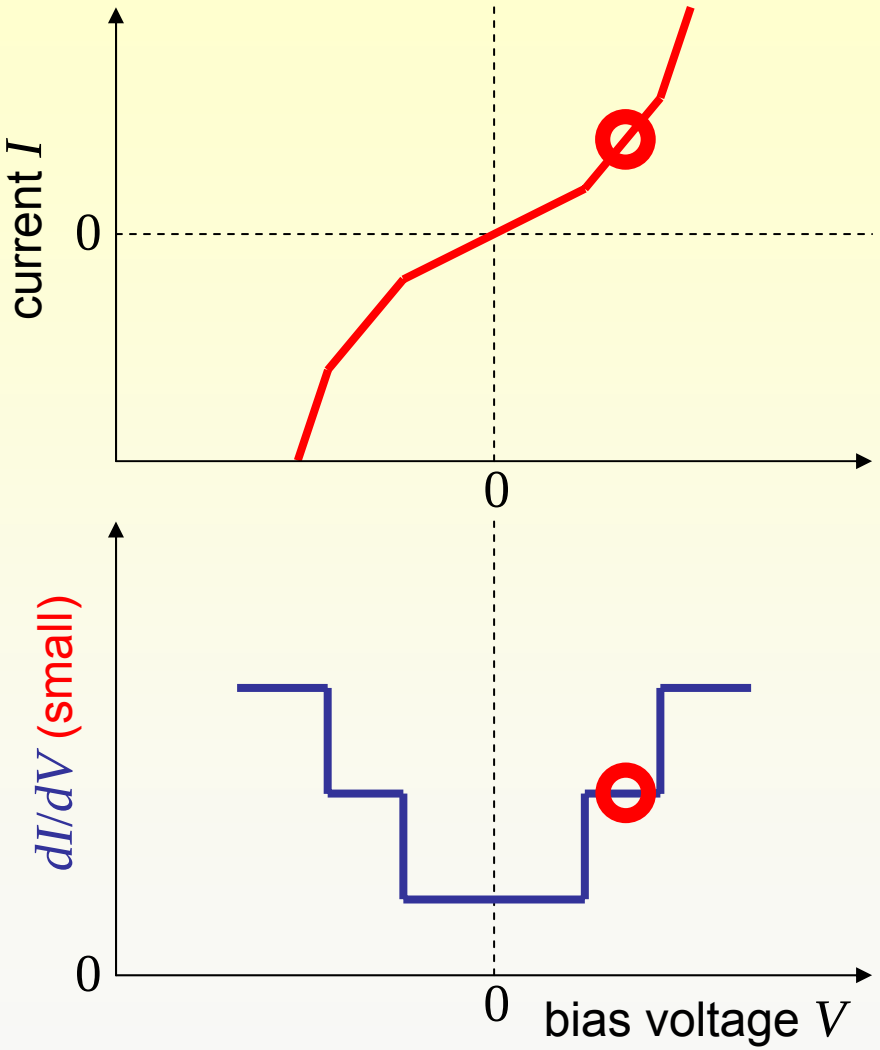


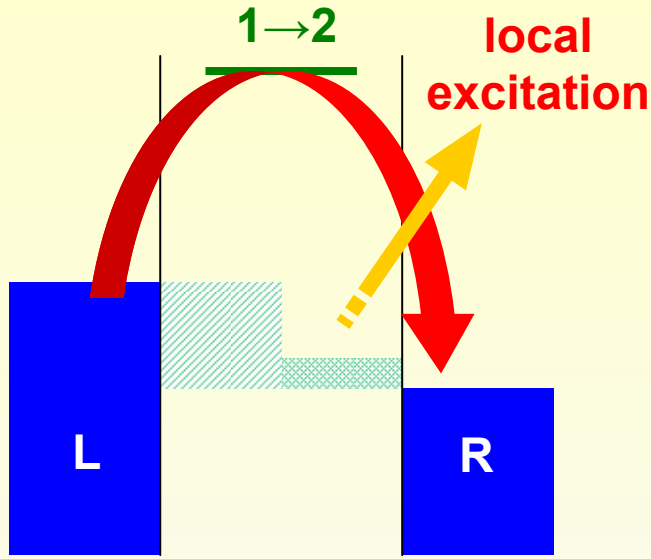
- excitation far from chemical potentials (typical if no gate)
- virtual excitation

I / number of channels / V

but small: I/V ¿ e^2/h

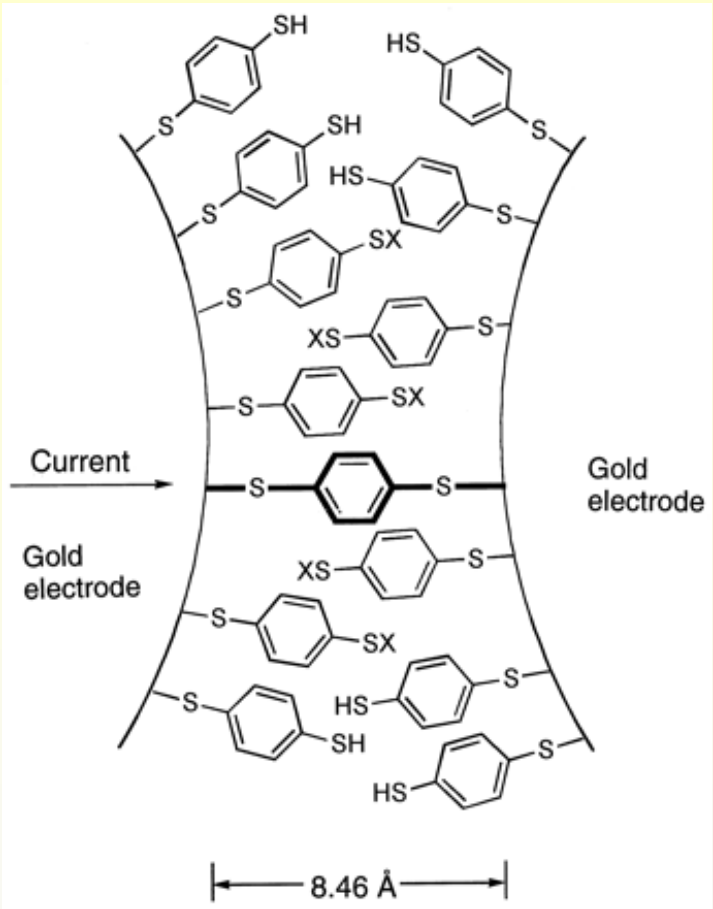
Weak coupling, cotunneling regime



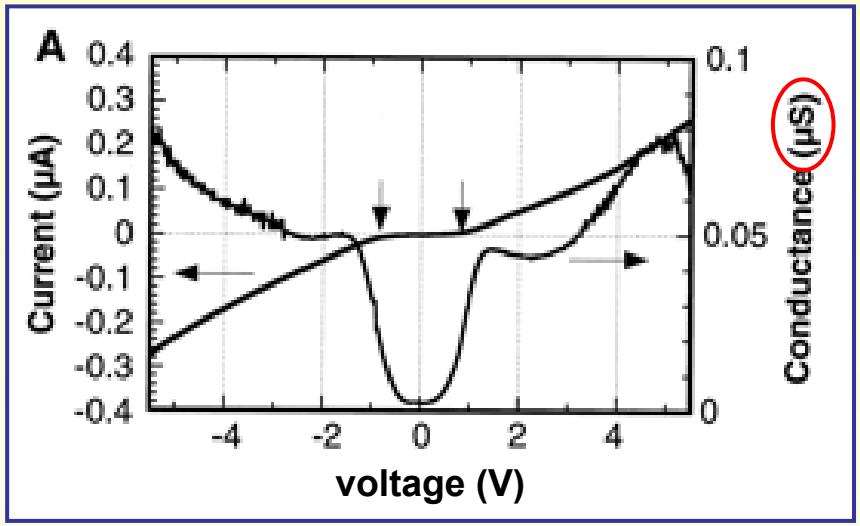


inelastic tunneling opens
new set of channels

Tunneling through single molecules: Mechanical break junction



M.A. Reed, C. Zhou, C.J. Muller, T.P. Burgin, and J.M. Tour, Science **278**, 252 (1997)



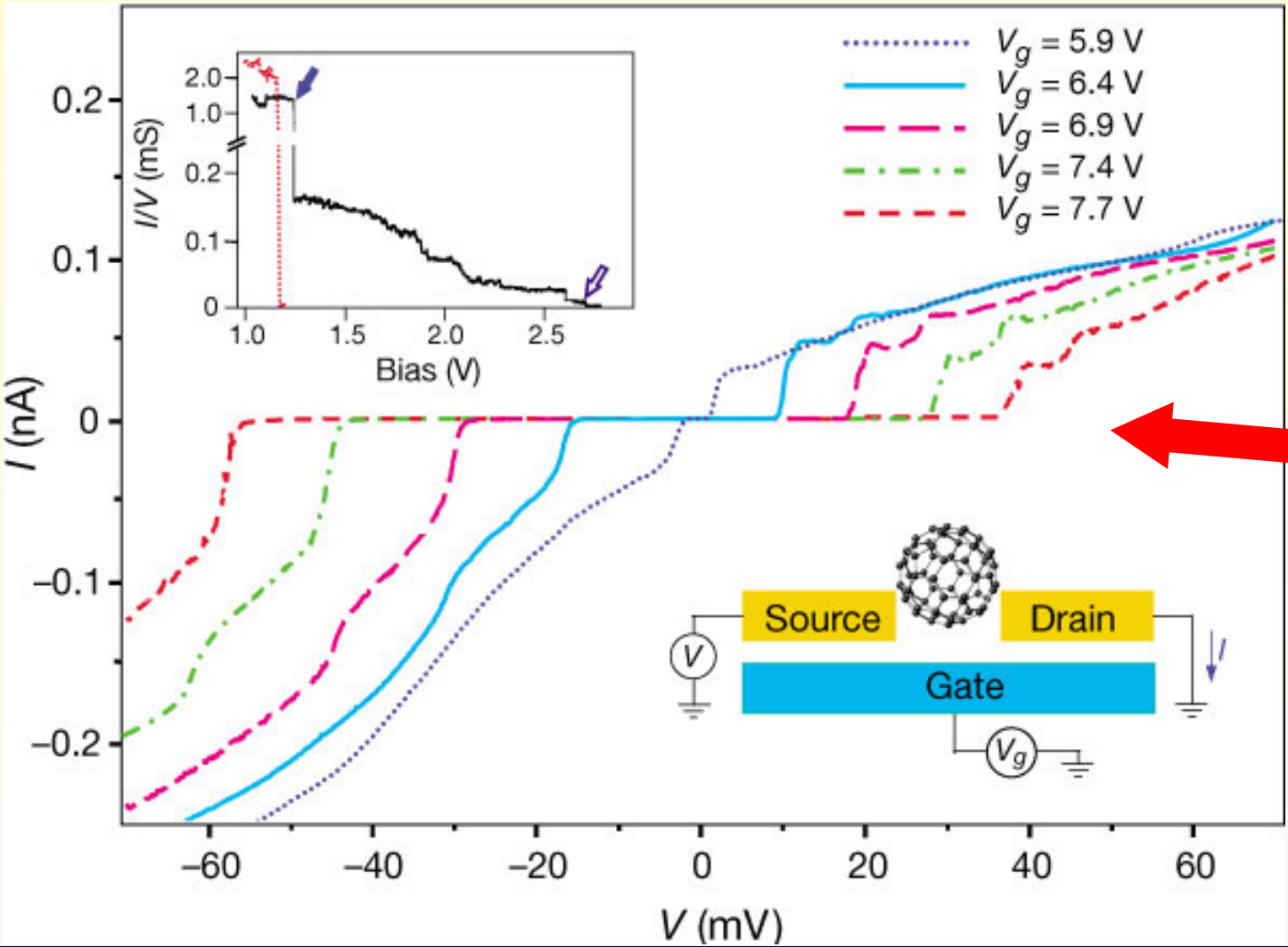
- steps in conductance
- symmetric & small $(\ll e^2/h)$ conductance

$\longrightarrow$ cotunneling, no molecular excitations close to chemical potentials

Coupling to vibrations: C_{60}

contacts: electromigration

H. Park, J. Park, A.K.L. Lim, E.H. Anderson, A.P. Alivisatos, P.L. McEuen, Nature **407**, 57 (2000)

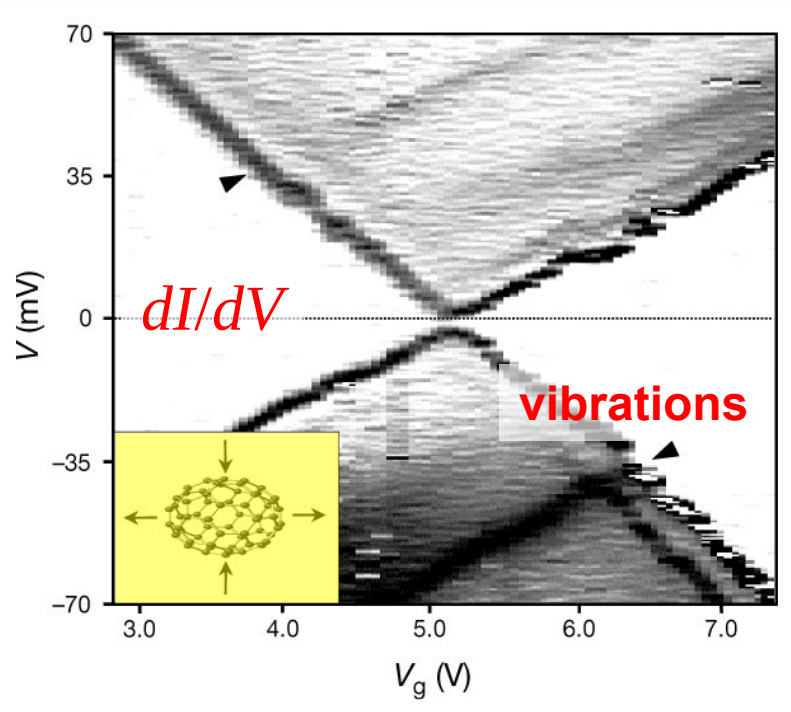


Coulomb blockade

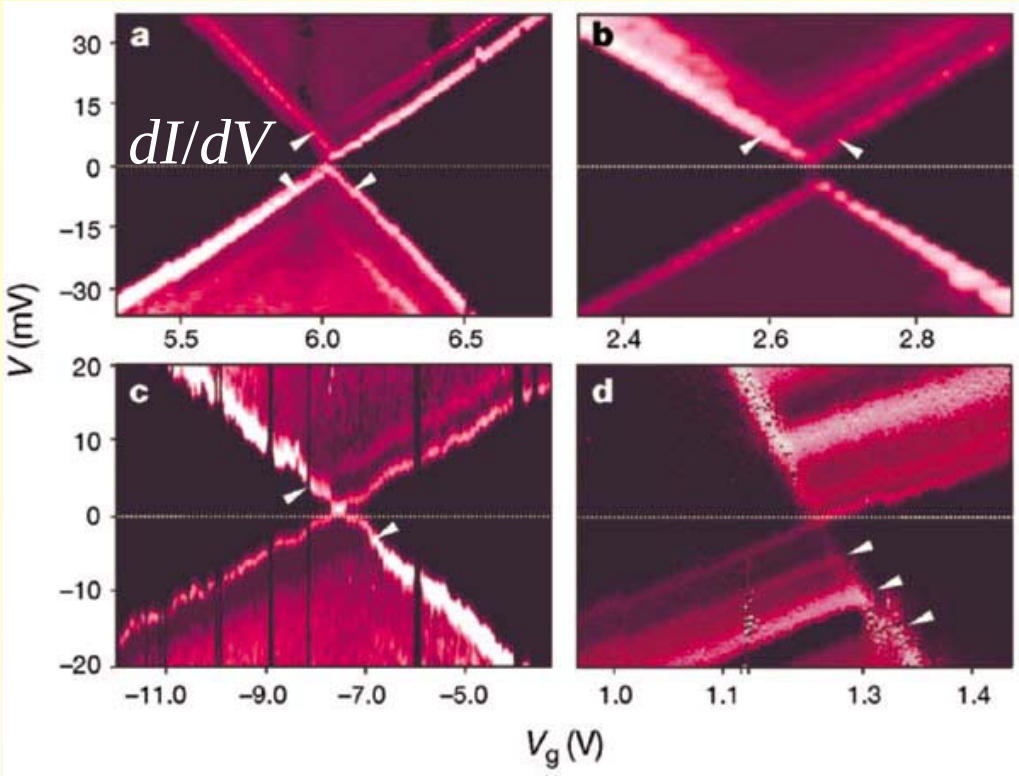
note shift with V_g

sequential tunneling

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



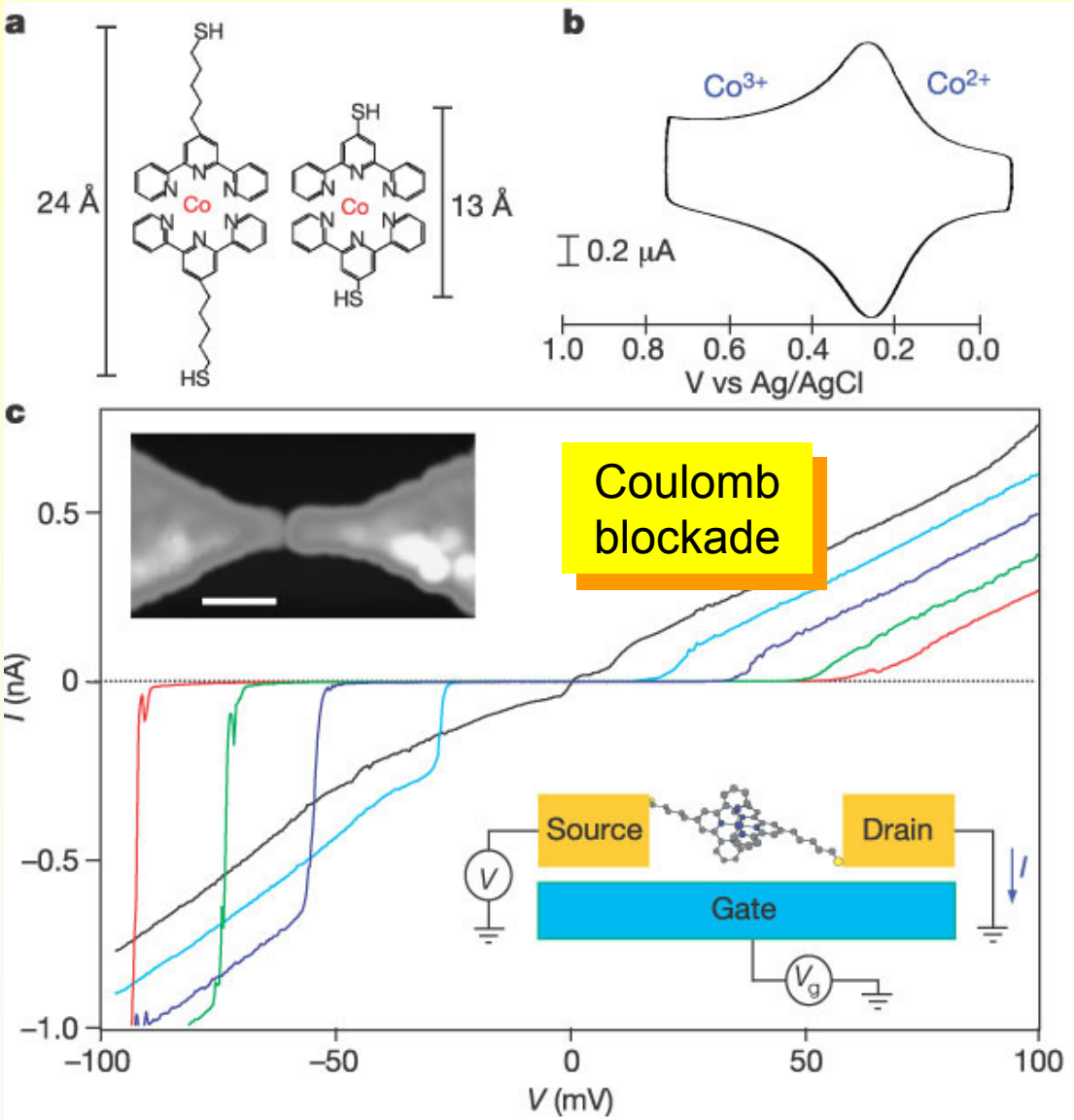
~ω ¼ 35 meV



~ω ¼ 5 meV

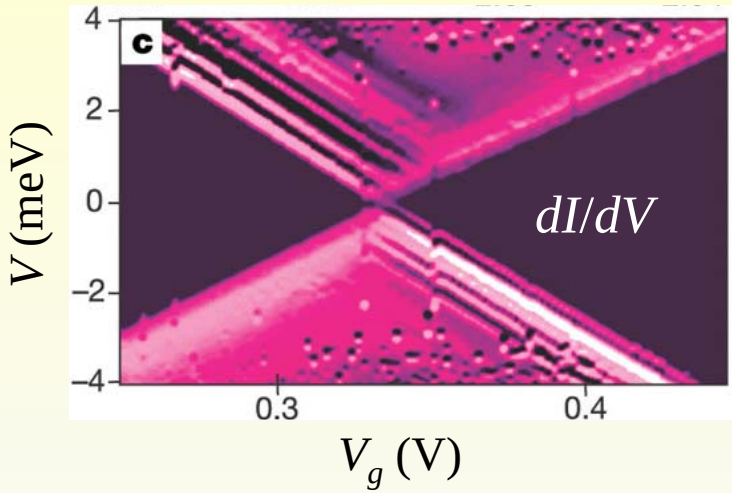
Experiments

Coupling to magnetic moment, Kondo effect

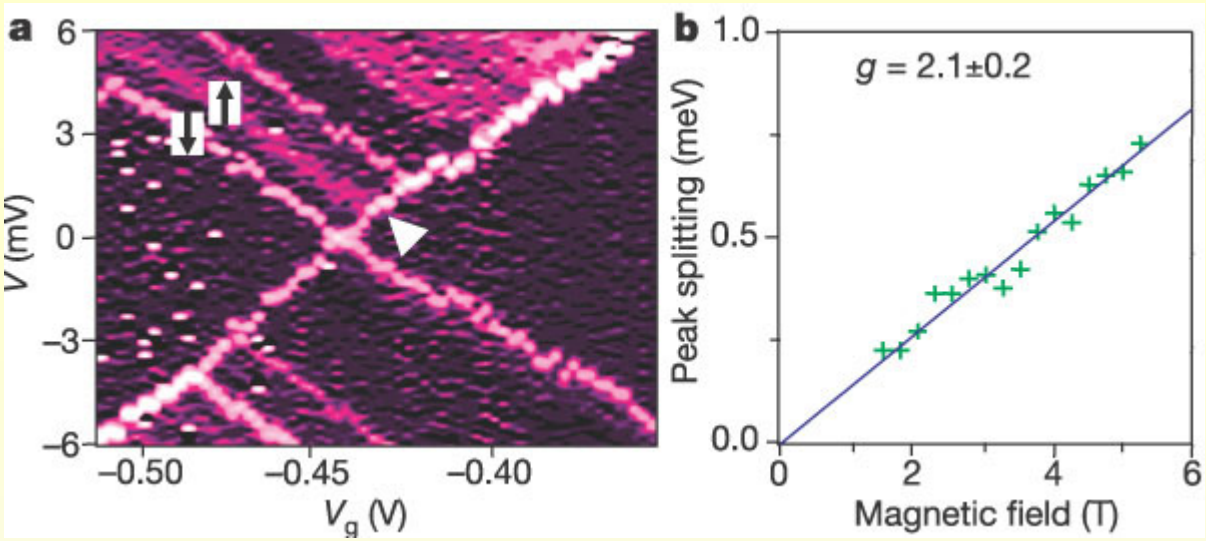


J. Park *et al.*, Nature **417**, 722 (2002)

electromigration



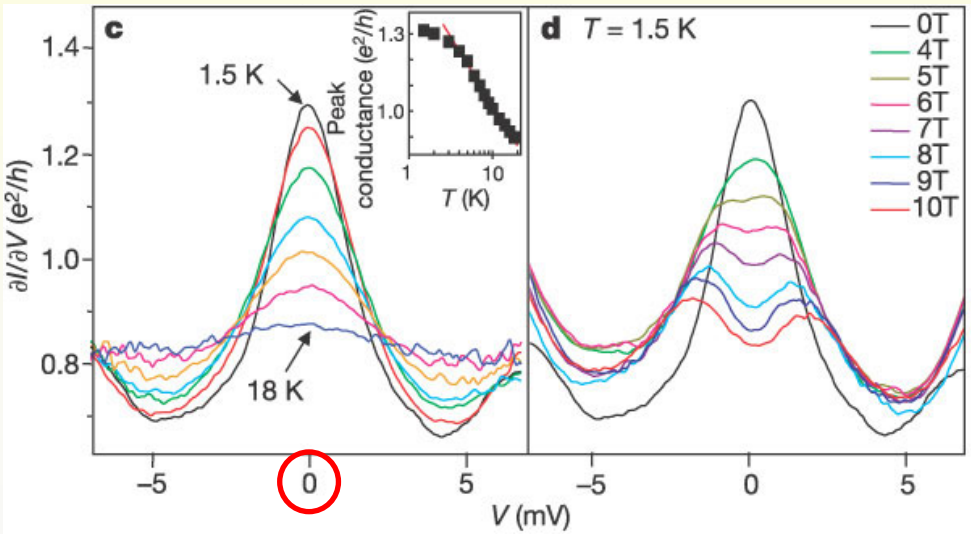
vibrations



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

weak coupling to leads

magnetic mode



vanishes for high T

splits in B field

strong coupling to leads

peak pinned at zero bias
(no shift with V_g)

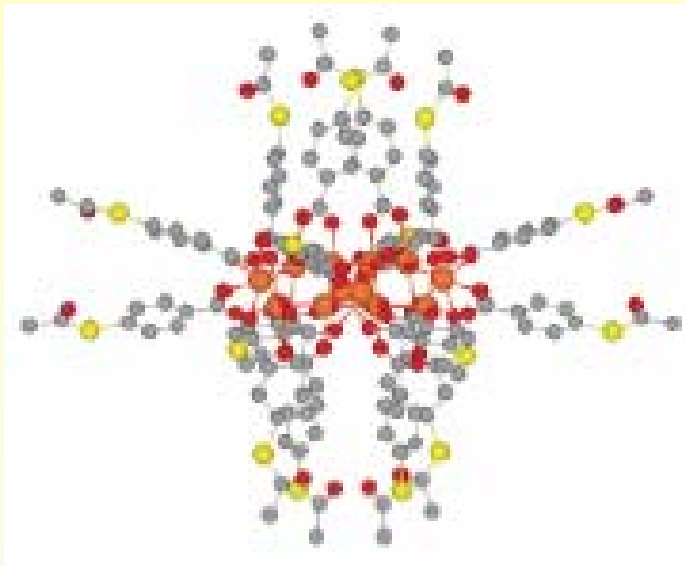
Kondo effect

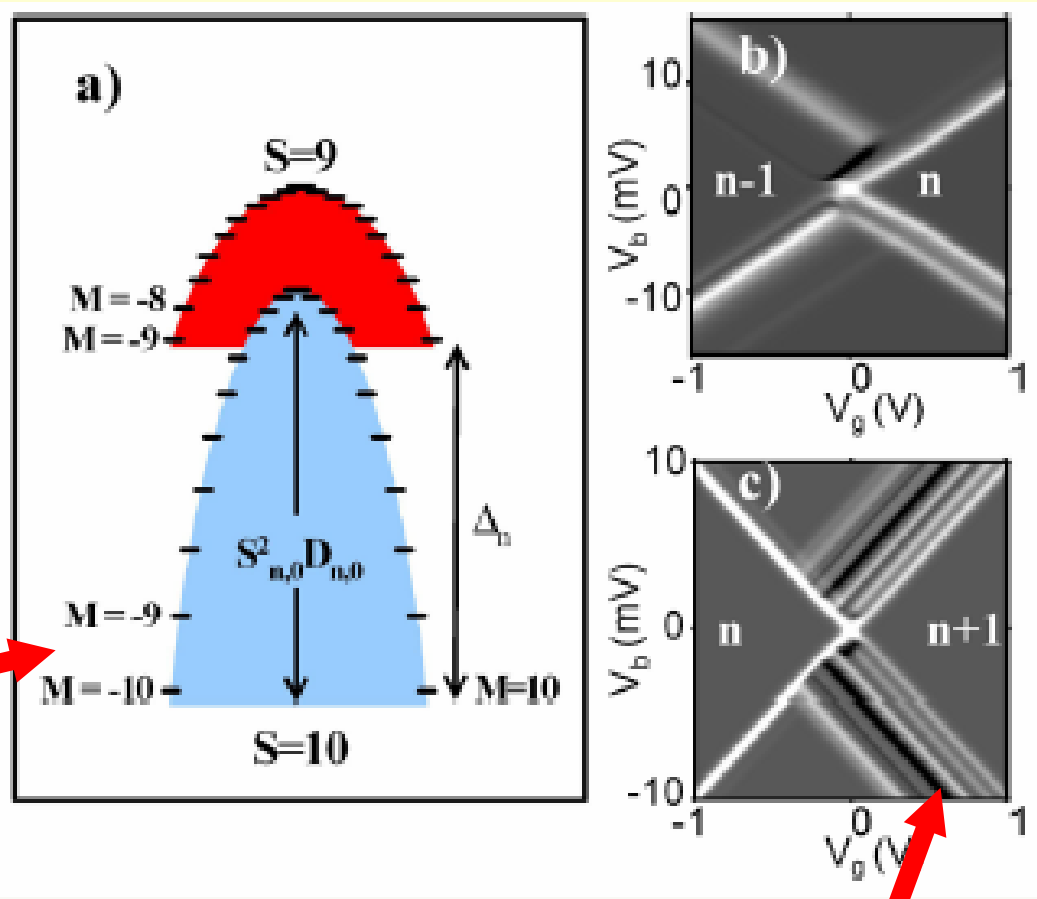
Experiments

Anisotropic magnetic molecules: Mn_{12} acetate

contacts: electromigration

H. B. Heersche *et al.*, PRL **96**, 206801 (2006)





anisotropy energy barrier

also: M.-H. Jo *et al.*, cond-mat/0603276

black: negative differential conductance $dI/dV < 0$

Theory

Molecular electronics

electronic manipulation of molecular charge, spin, conformation…:

Inelastic transport through single molecules

- coupling to internal degrees of freedom, here: spin
- using magnetic molecules as memory devices:
  - write spin information electronically
  - store spin information
  - read spin information electronically

Inelastic tunneling due to coupling to molecular spin

system: endohedral $N@C_{60}$

nitrogen retains its spin $S_N=3/2$ (Hund's 1st rule)

C_{60} has 3-fold degenerate LUMO

$$H_{\mathrm{mol}} = (\epsilon_{\mathrm{LUMO}} - eV_g)\,\hat{n} + \frac{U}{2}\,\hat{n}(\hat{n}-1) - J\,\mathbf{S}_{\mathrm{C_{60}}} \cdot \mathbf{S}_{\mathrm{N}}$$

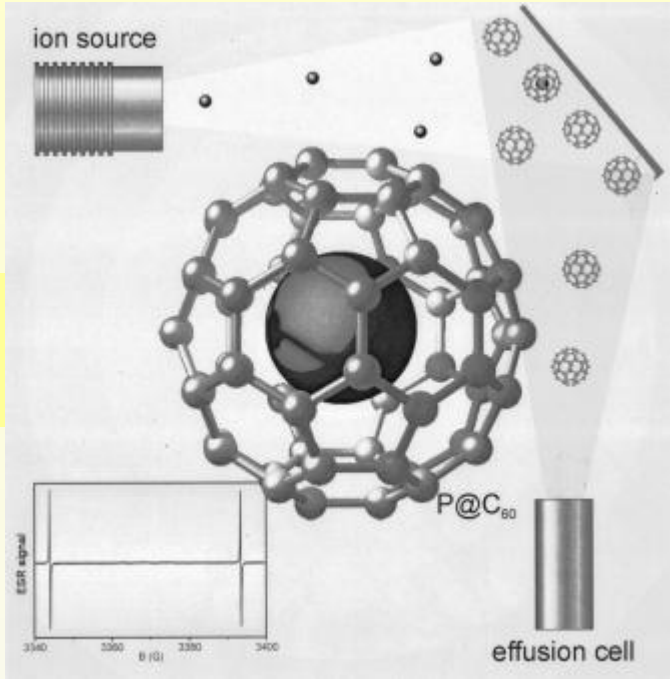
U: Hubbard repulsion on C_{60}

J: ferromagnetic exchange

$$H_{\mathrm{leads}} = \sum_{\alpha=\mathrm{L,R}} \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}\sigma} a^{\dagger}_{\alpha\mathbf{k}\sigma} a_{\alpha\mathbf{k}\sigma}$$

$$H_{\mathrm{t}} = \sum_{\alpha=\mathrm{L,R}} \sum_{n\mathbf{k}\sigma} (t_{\alpha} a^{\dagger}_{\alpha\mathbf{k}\sigma} c_{n\sigma} + t^{*}_{\alpha} c^{\dagger}_{n\sigma} a_{\alpha\mathbf{k}\sigma})$$

$$H = H_{\mathrm{mol}} + H_{\mathrm{leads}} + H_{\mathrm{t}}$$



Larson *et al.*, J. Chem. Phys. **116**, 7849 (2002)

production by ion implantation:

Almeida Murphy *et al.*, PRL **77**, 1075 (1996)

Density matrix formalism

von Neumann equation for density matrix:

$$d\rho_I(t)/dt = -i[H_{\mathrm{t}I}(t), \rho_I(t)]$$

interaction rep.

$$\rho_I(t) = \rho_I(0) - i\int_0^t dt' \, [H_{\mathrm{t}I}(t'), \rho_I(t')]$$

iteration:

$$d\rho_I(t)/dt = -i[H_{\mathrm{t}I}(t), \rho_I(0)] - \int_0^t dt' \, [H_{\mathrm{t}I}(t), [H_{\mathrm{t}I}(t'), \rho_I(t')]]$$

reduced density matrix of molecule:

$$\rho_{\mathrm{mol}I}(t) \equiv \mathrm{Tr}_{\mathrm{leads}}\, \rho_I(t)$$

Born approximation:

$$\rho_I(t) \approx \rho_{\mathrm{mol}I}(t) \otimes \rho^0_{\mathrm{leads}}$$

Markov approximation

$$\rho_{\mathrm{mol}I}(t') \approx \rho_{\mathrm{mol}I}(t)$$

at this stage leads to perturbation theory of second order in tunneling

$$d\rho_{\mathrm{mol}I}(t)/dt \approx -\int_0^t dt' \, \mathrm{Tr}_{\mathrm{leads}}[H_{\mathrm{t}I}(t), [H_{\mathrm{t}I}(t'), \rho_{\mathrm{mol}I}(t) \otimes \rho^0_{\mathrm{leads}}]]$$

(sequential tunneling)

Back in Schrödinger picture:

$$d\rho_{\rm mol}(t)/dt \approx -i\,[H_{\rm mol},\rho_{\rm mol}] - {\rm Tr}_{\rm leads}\int_0^\infty dt'\,[H_{\rm t},$$
$$[e^{-i(H_{\rm mol}+H_{\rm leads})t'}\,H_{\rm t}\,e^{i(H_{\rm mol}+H_{\rm leads})t'},\rho_{\rm mol}(t)\otimes\rho^0_{\rm leads}]]$$

cf. Mitra, Alleiner, and Millis, PRB **69**, 245302 (2004).

Can evaluate this now. Alternative derivations:

- diagrammatics on Keldysh time contour [König *et al.*, PRB **54**, 16820 (1996)]
- time-convolutionless master equation [Tokuyama and Mori, Prog. Theor. Phys. **54**, 918 (1975)]

Assuming fast dephasing = rapid decay of off-diagonal components of $\rho_{\rm mol}$ obtain rate equations for probabilities P_n of molecular many-body states

$$\dot{P}_n = \sum_{m\neq n} P_m R_{m\to n} - P_n \sum_{m\neq n} R_{n\to m} \equiv \sum_m A_{nm}P_m$$

Stationary state: $0 = \sum_m A_{nm}P_m$

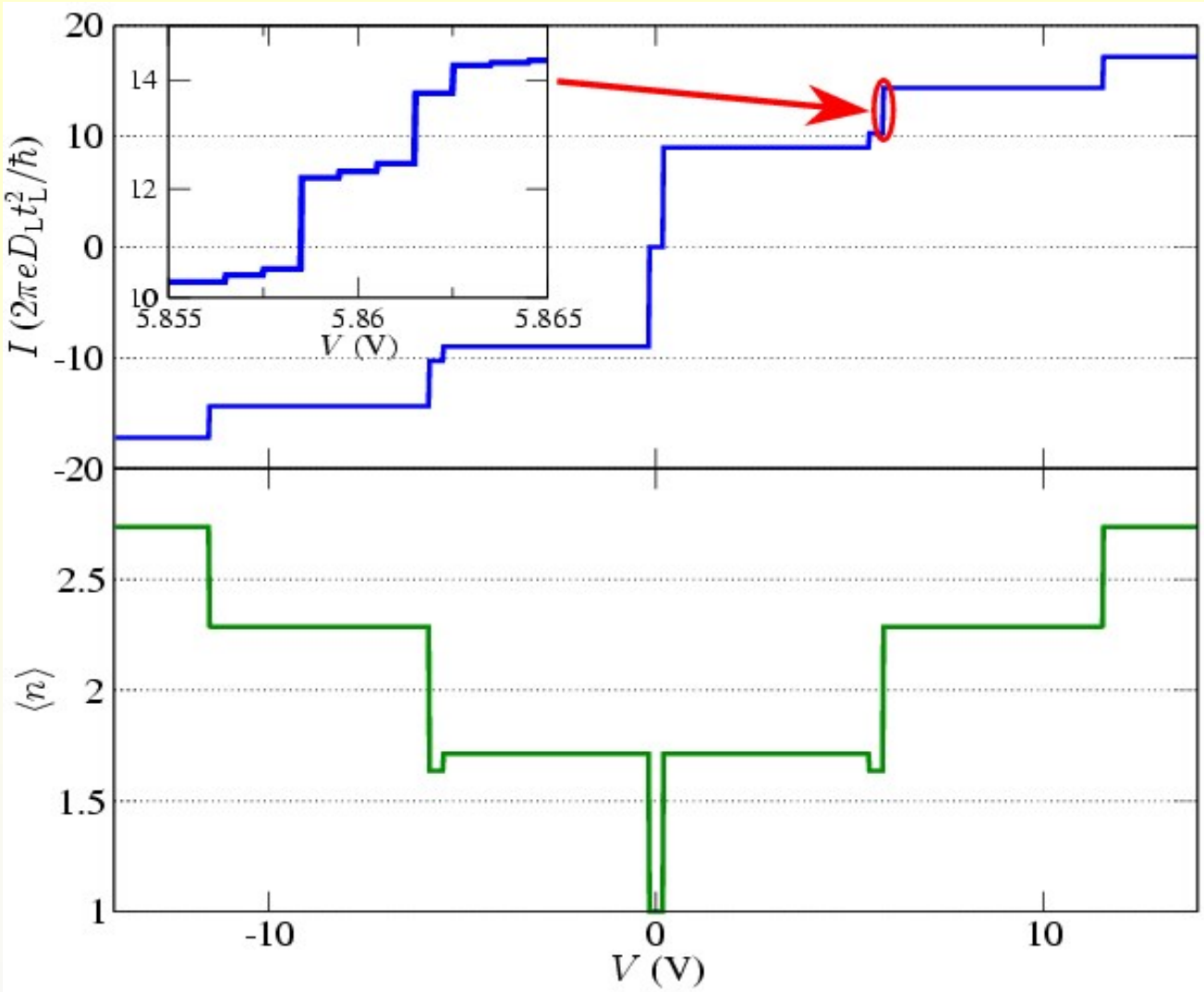
Results for stationary state

gate voltage

$V_g = 0$ V

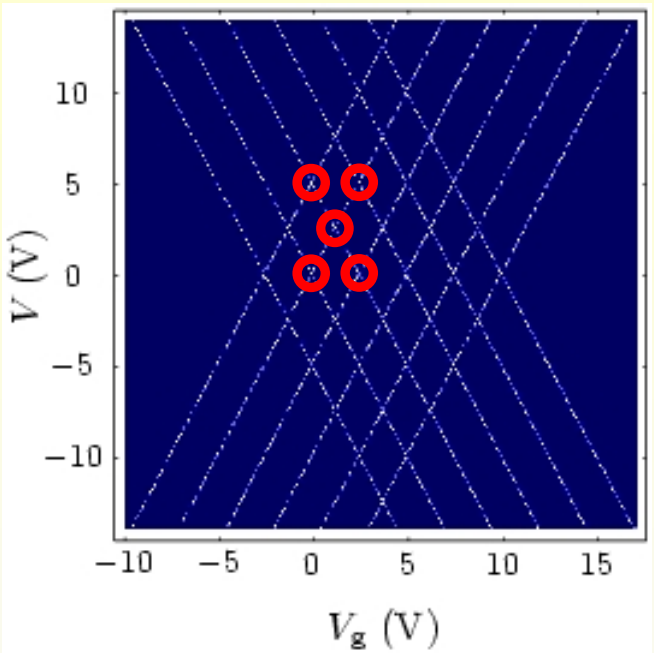
temperature

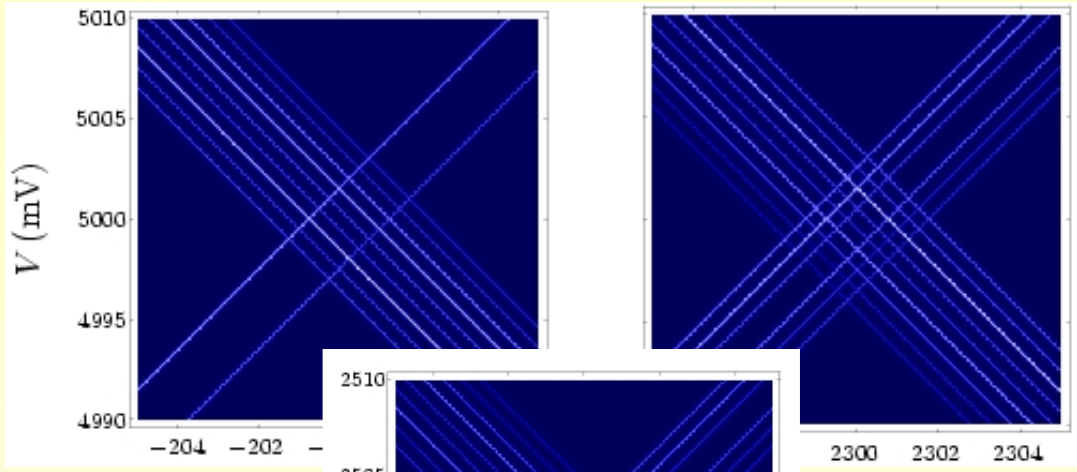
$T = 0.01$ K

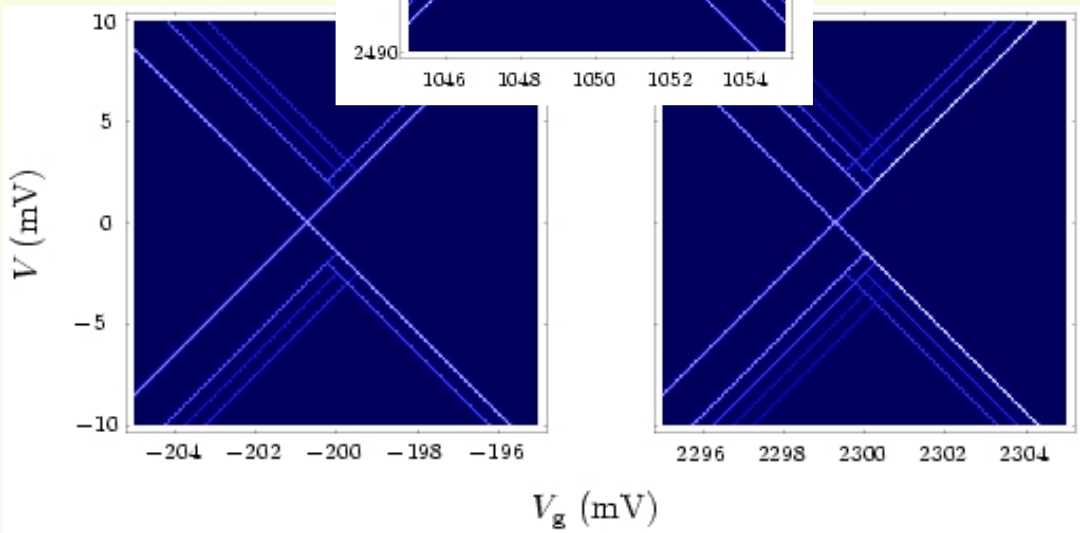


F. Elste and C.T., PRB **71**, 155403 (2005)

Differential conductance







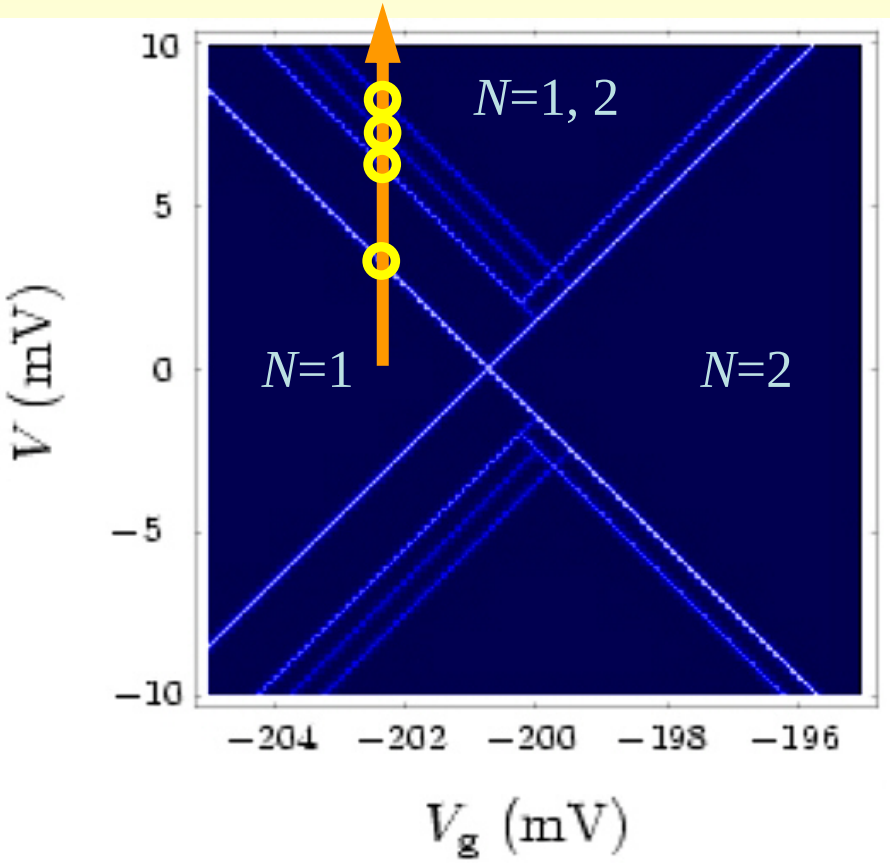
fine structure at temperature $T = 0.1$ K:

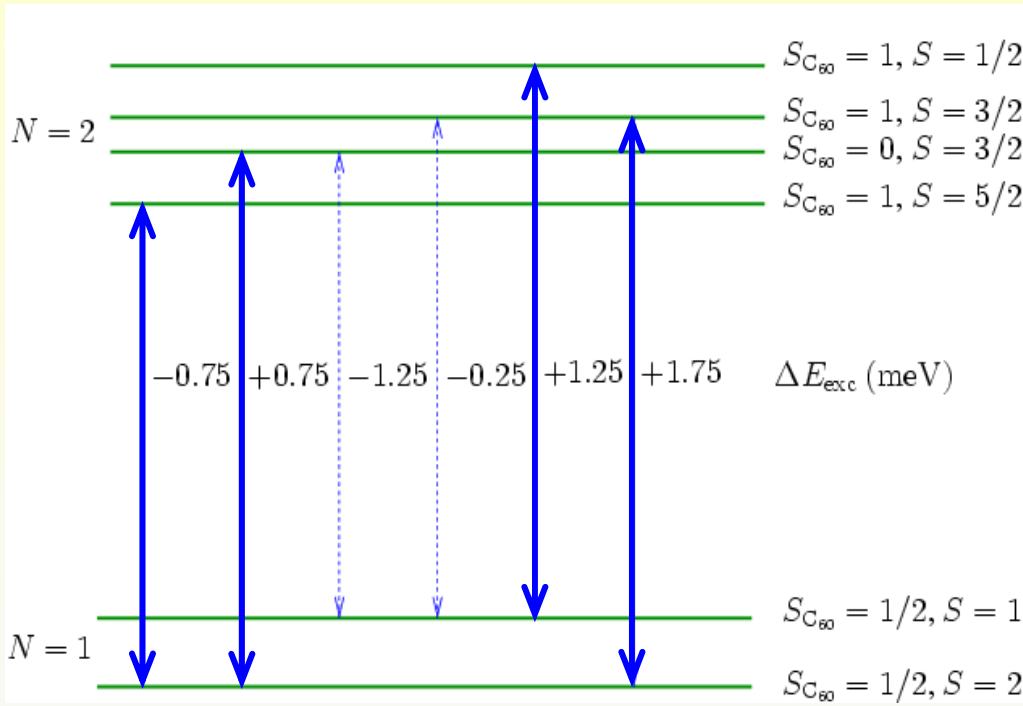
map of crossover points

Tunneling through magnetic molecules

Origin of fine structure:

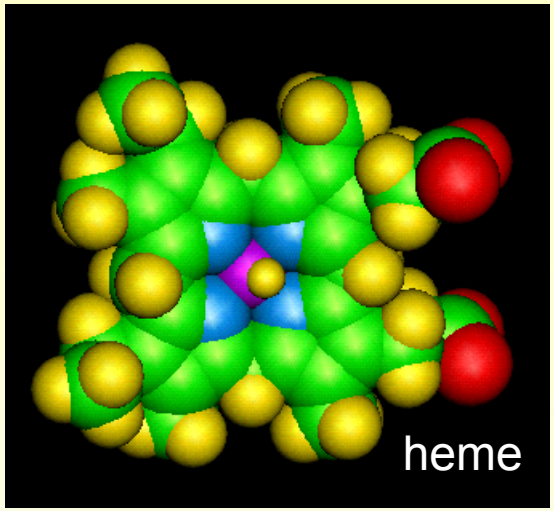
- selection rules for single-electron tunneling
- occupation of initial state

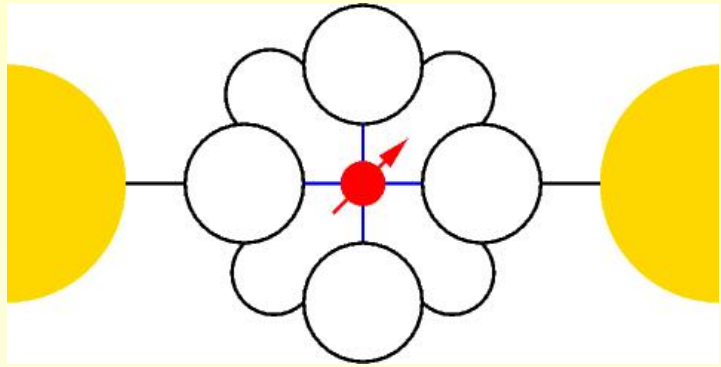




allowed transitions

Tunneling through molecule with magnetic anisotropy





$$H_{\rm mol} = (\epsilon - eV_g)\,\hat{n} + \frac{U}{2}\,\hat{n}(\hat{n}-1) - J\,\mathbf{s}\cdot\mathbf{S} - K_2\,(S^z)^2$$

easy-axis anisotropy

anisotropy → energy barrier for spin reversal

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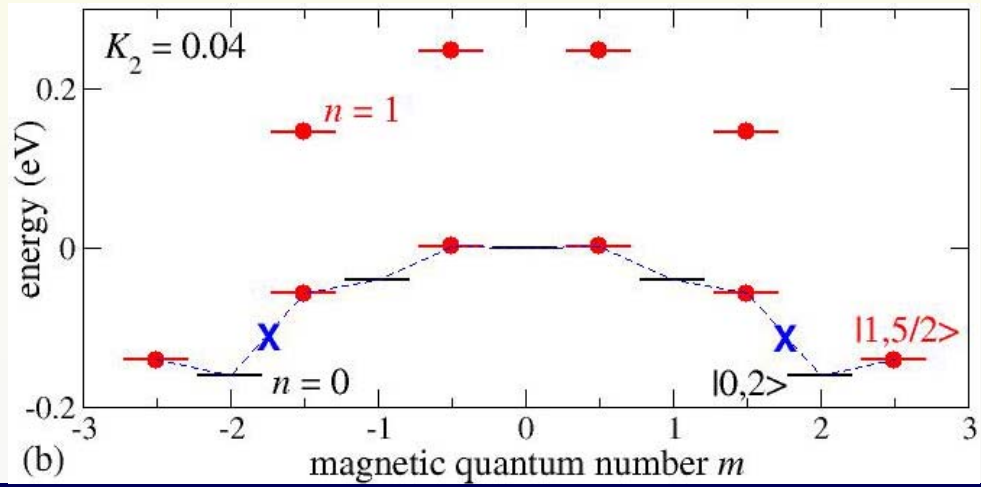
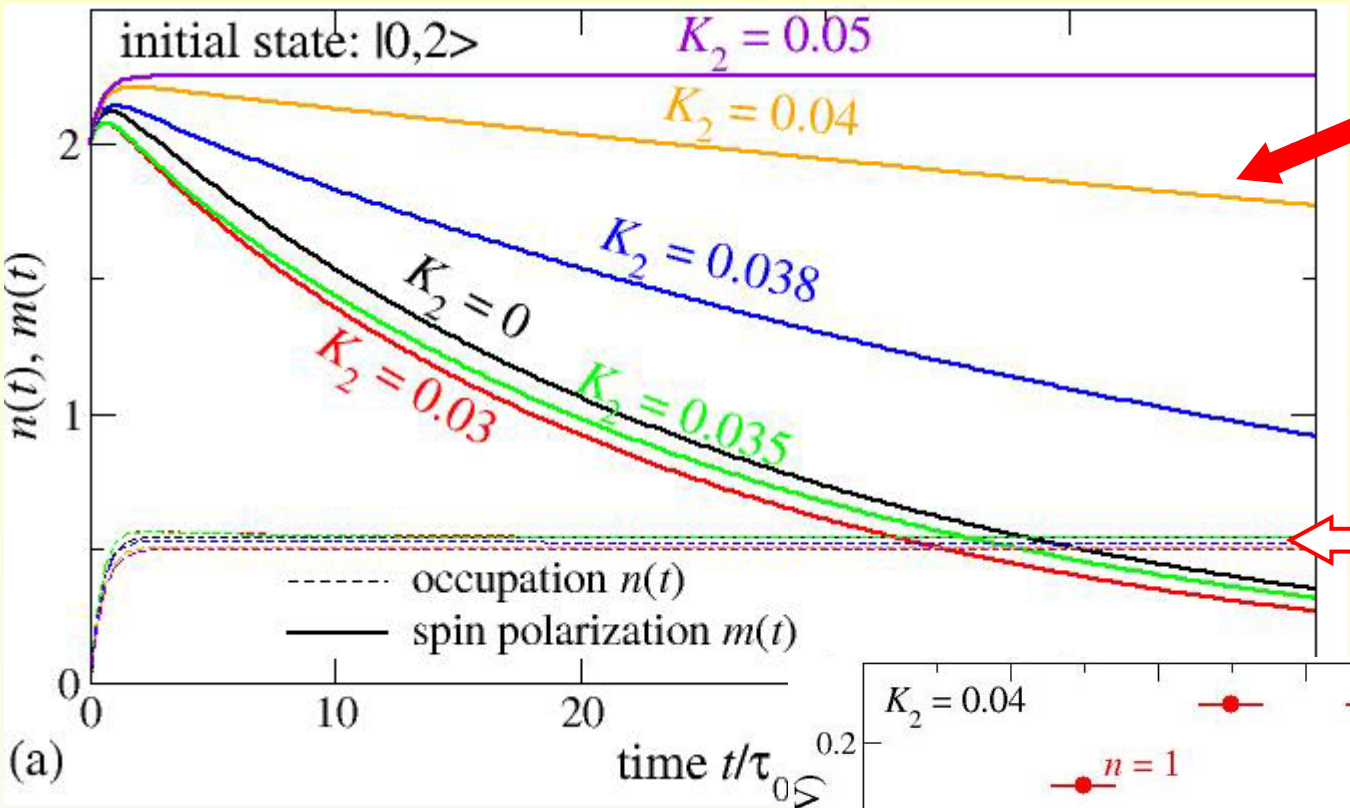
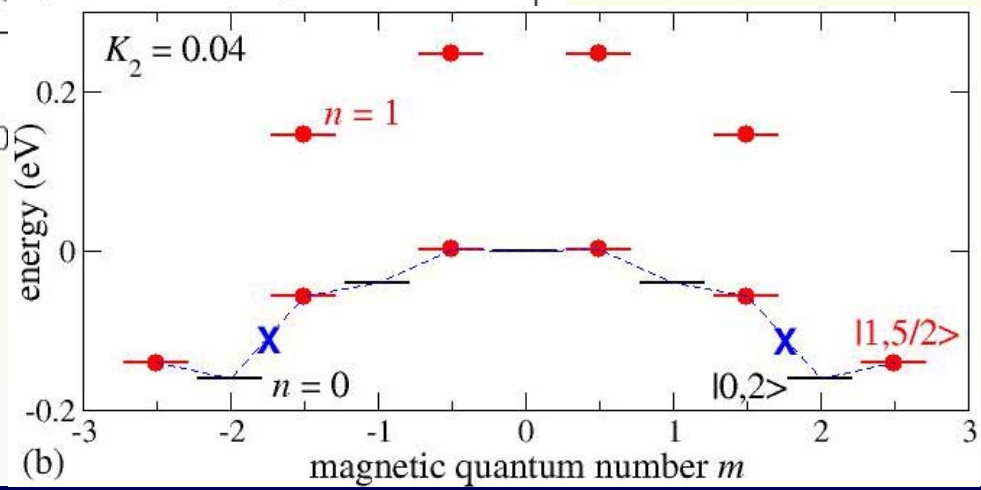


Relaxation of spin becomes slow



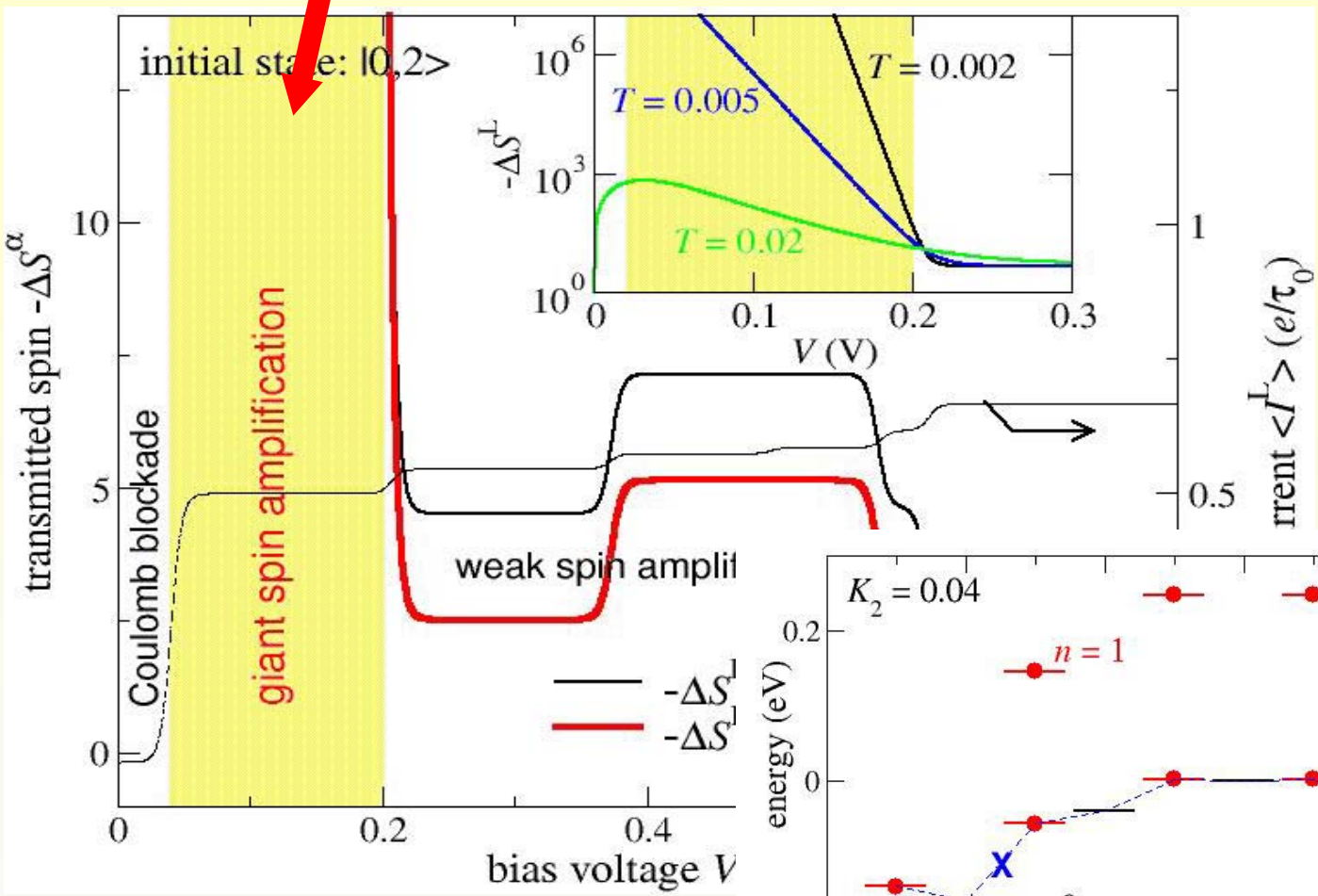
magnetization

occupation

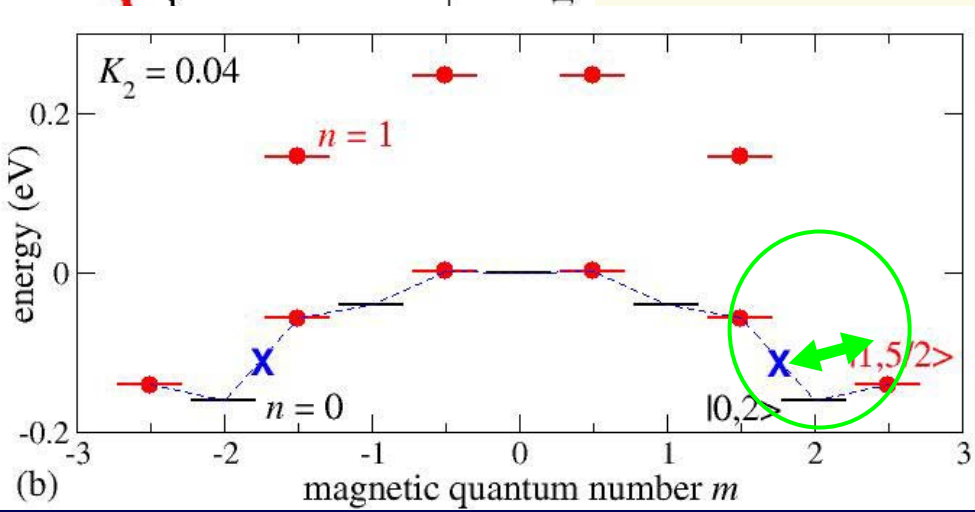


The transitions **X** become thermally suppressed around $K_2 = 0.04$

The only energetically allowed transitions from $n = 0$, $m = 2$ is to $n = 1$, $m = 5/2$ → spin-down electron tunnels in (from right) then tunnels out (to left)



Spin-polarized current



Tunneling through magnetic molecules

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A spin-polarized current is flowing until the molecular spin relaxes (very slowly)

→ A macroscopic magnetic moment is transferred through the molecule

Here: relaxation due to thermal activation. Also possible due to spin tunneling from “up” to “down”, see C. Romeike *et al.*, cond-mat/0511391

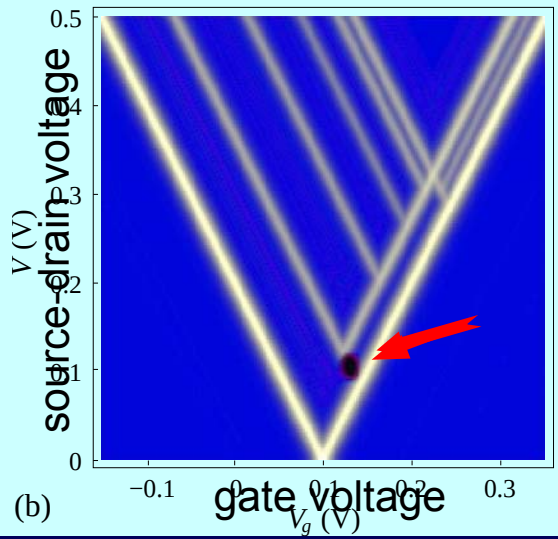
Macroscopic spin transfer is due to the small quantum spin **S** of the molecule

→ Giant spin amplification

Possible read-out mechanism for molecular electronics

Anisotropy also leads to negative differential conductance (NDC)

$$dI/dV < 0$$



Tunneling through magnetic molecules

Tunneling with one ferromagnetic and one nonmagnetic lead

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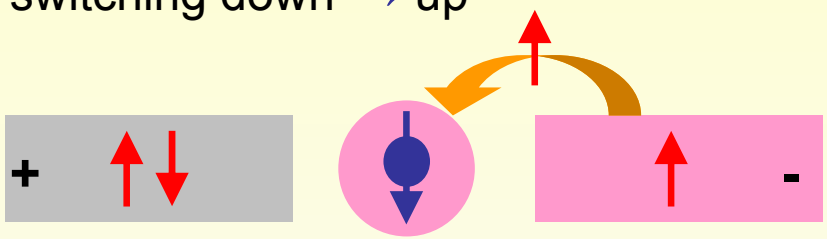
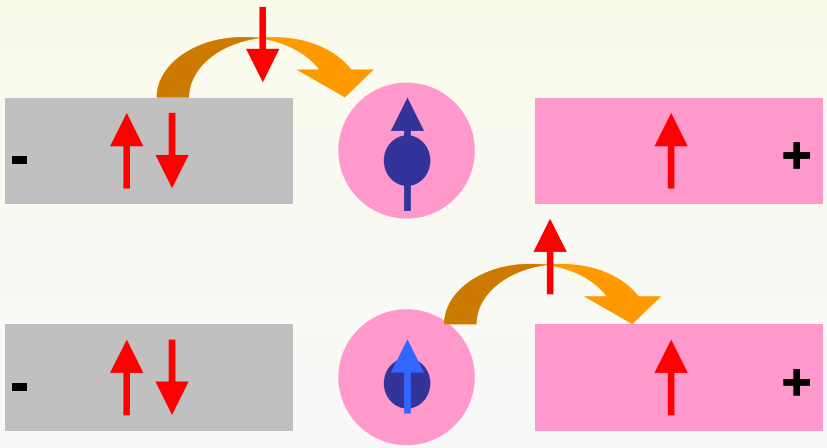
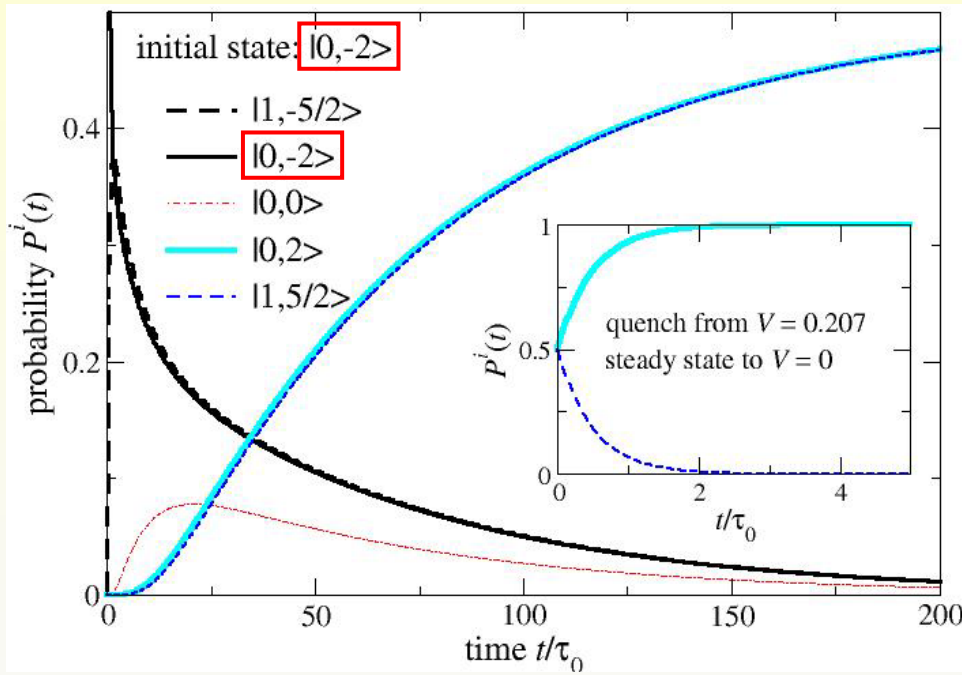
can write the spin by applying a bias voltage (no magnetic field):

switching down → up

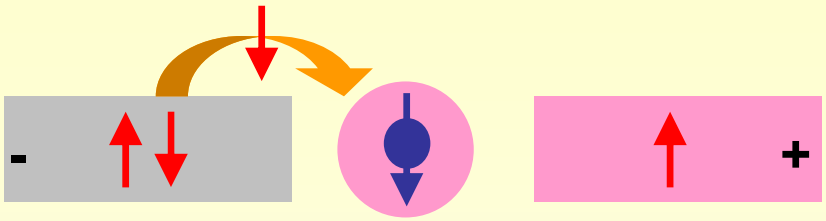


switching up → down

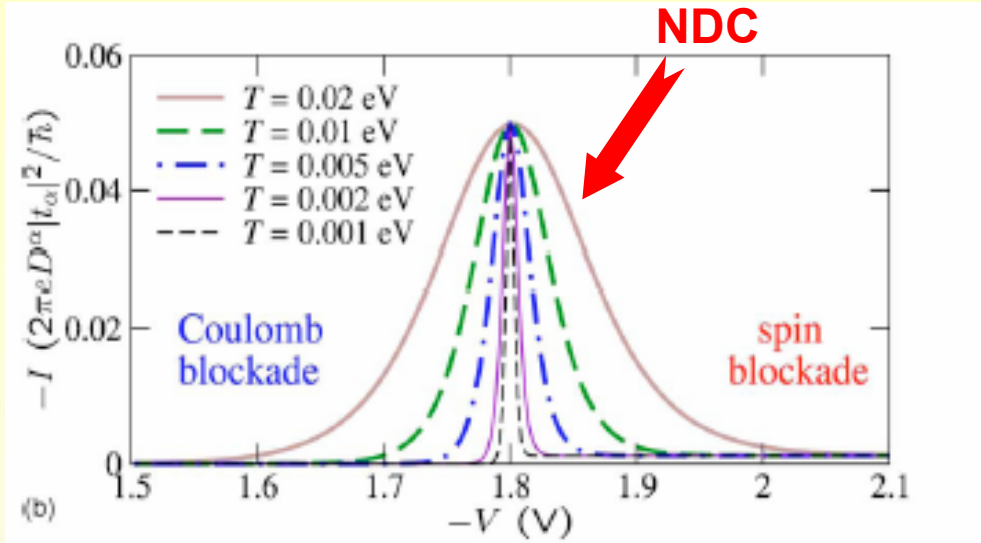


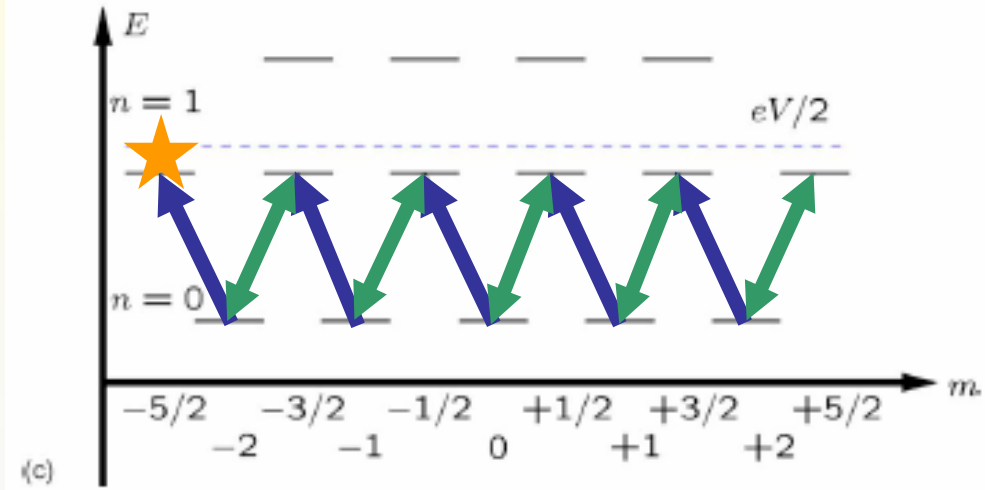


Ferromagnetic/nonmagnetic leads: Spin blockade



vanishing anisotropy, $K_2 = 0$





transition $n = 1 \rightarrow 0$, $m \rightarrow m+1/2$ (spin-down electron out) is suppressed by DOS in ferromagnetic lead

molecule trapped in low-spin state: spin blockade

Conclusions

Molecular electronics

Inelastic transport through single molecules

Theory for magnetic molecules:

- coupling to spin: fine structure
- anisotropy: slow relaxation
- anisotropy: giant spin amplification
- one ferromagnetic lead: spin writing
- one ferromagnetic lead: spin blockade

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