Berry-Phase Induced Kondo Effect in Single-Molecule Magnets

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Overview

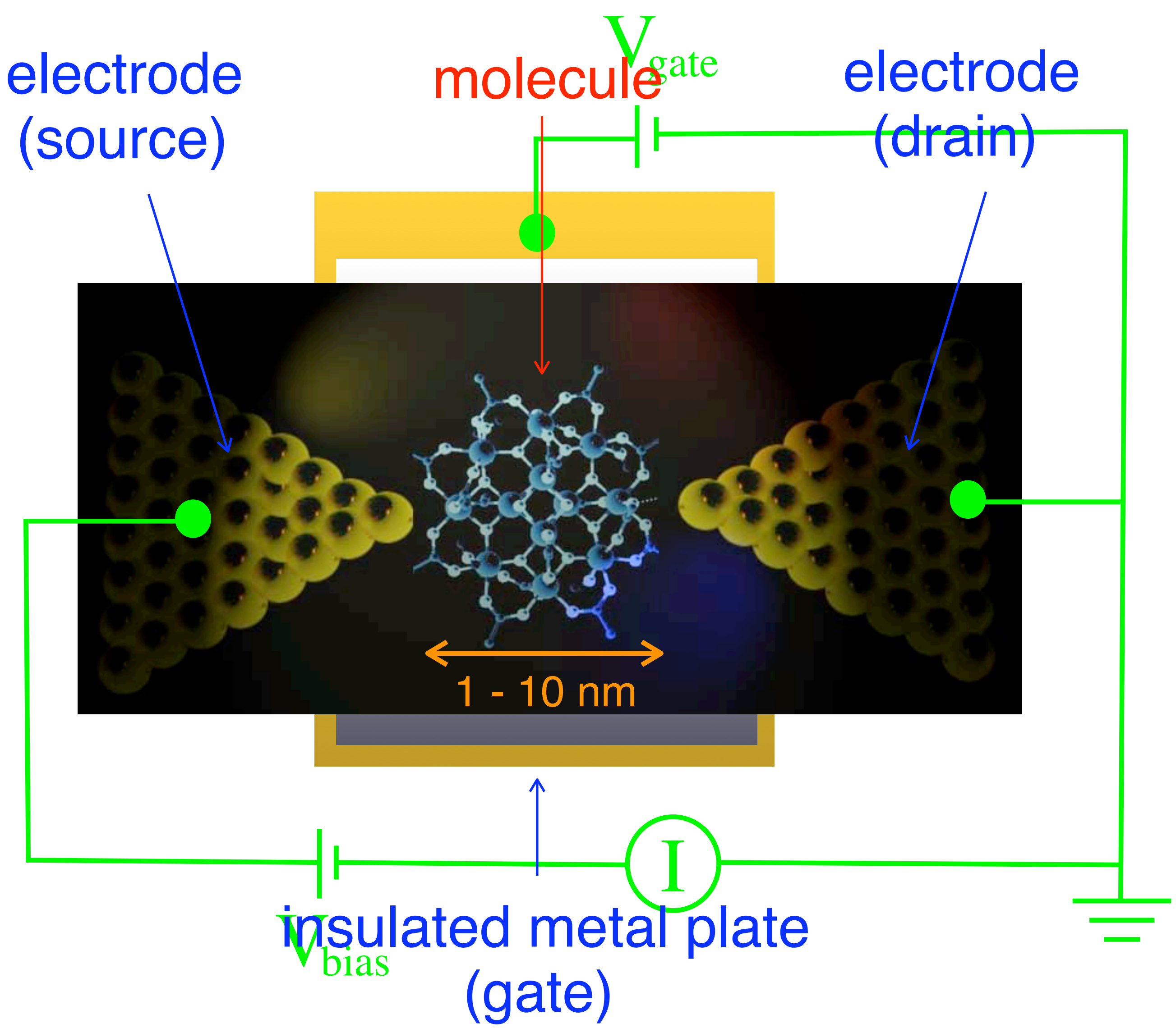
- Single-molecule electronics

- Single-molecule magnets:

    - Berry-phase blockade in single molecules

    - Kondo effect in SMMs

Single-molecule electronics: *molecular transistor*

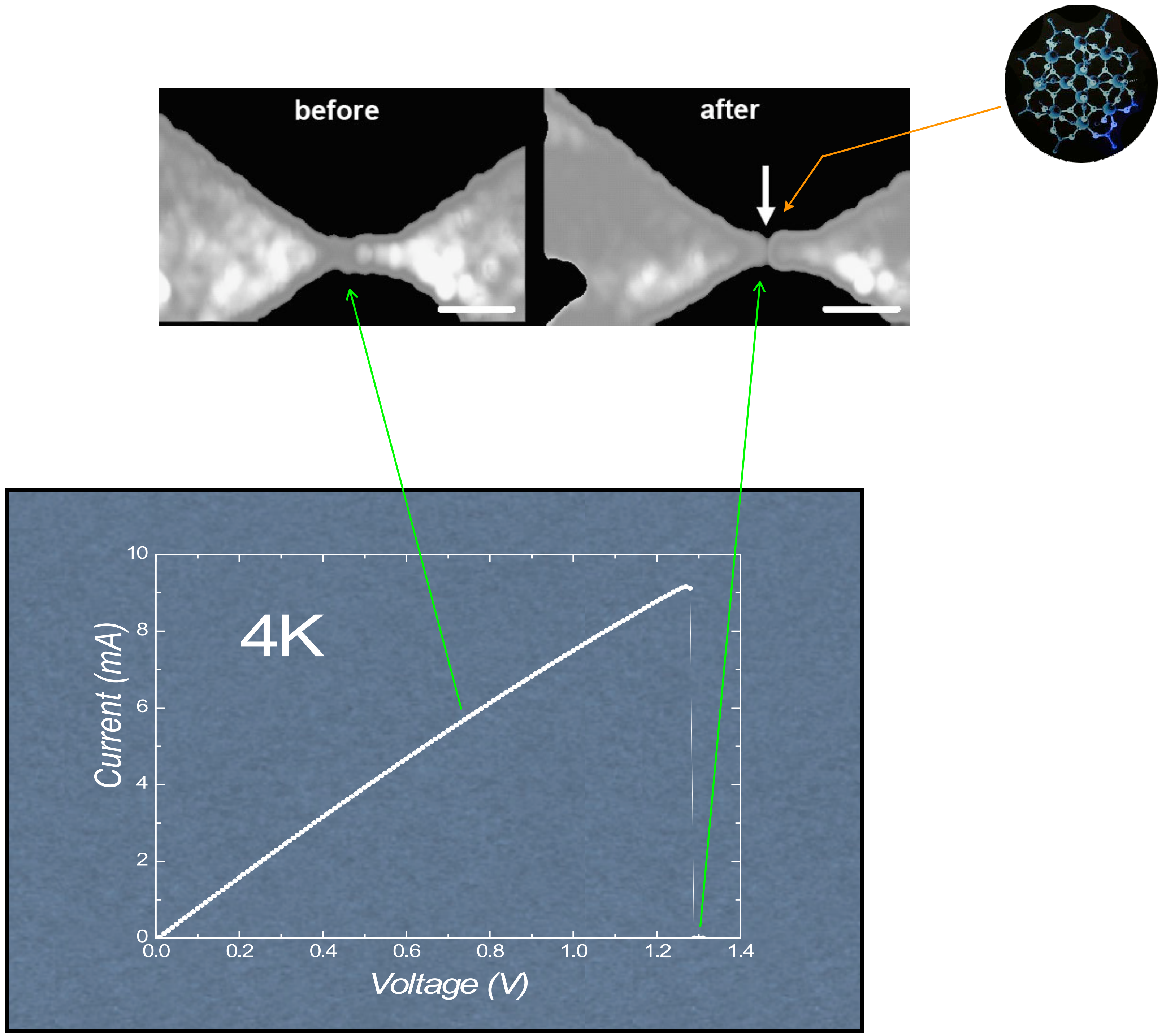


Potential advantages:

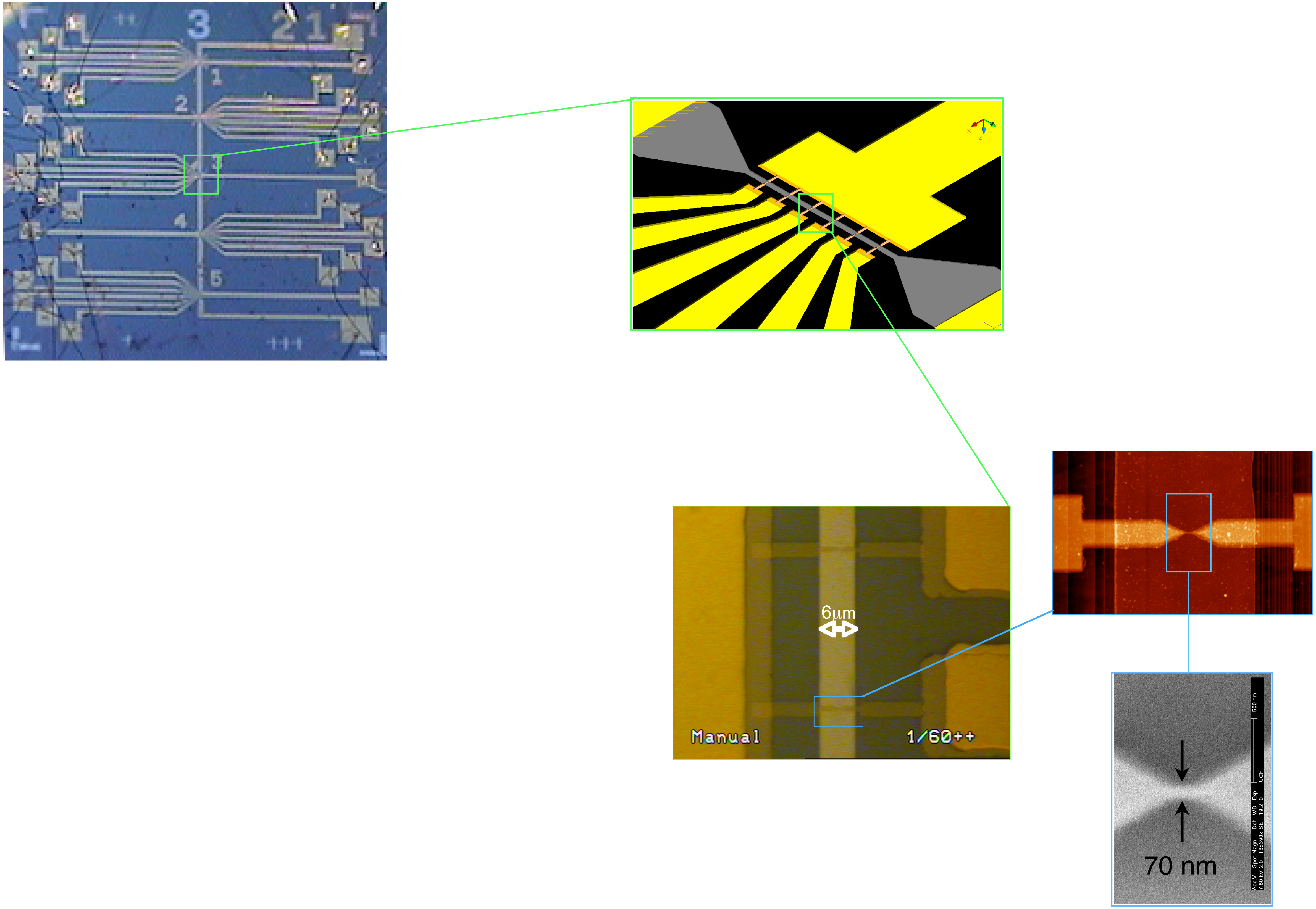
- fast operation
- large energy scales (eV)
- quantum effects at high temperatures ?!

Fabrication of the nano gaps: *Electromigration and breaking of nanowires*

(Enrique del Barco, UCF)

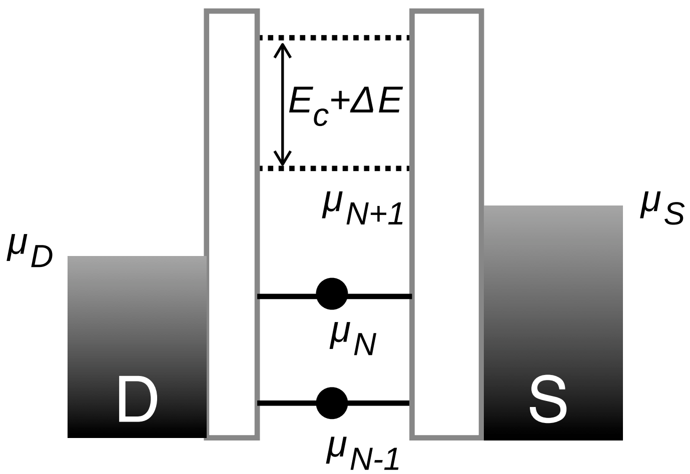


Multiwire chip: Trial and error approach



Single-electron transistors: *What is actually measured?*

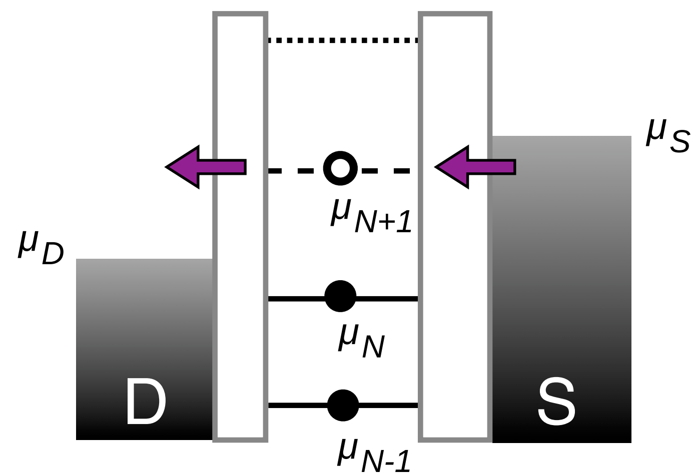
$\mu_N < \mu_S, \mu_D < \mu_{N+1}$



no current

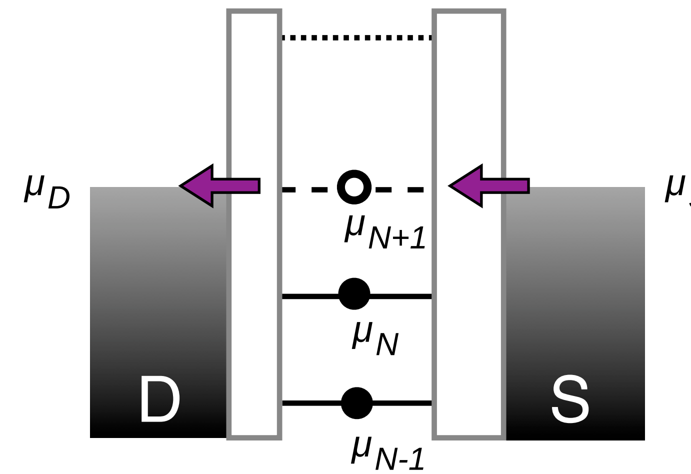
(Coulomb blockade)

$\mu_D < \mu_{N+1} < \mu_S$

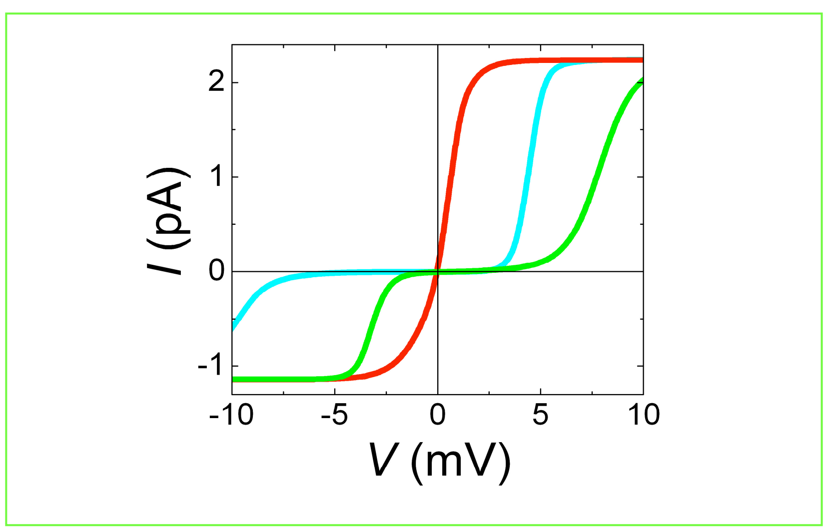


finite current
with finite bias

$\mu_S = \mu_{N+1} = \mu_D$



finite current with
(nearly) zero bias



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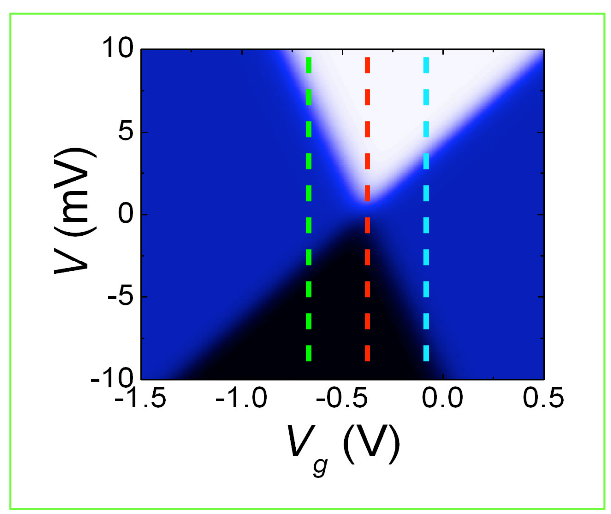
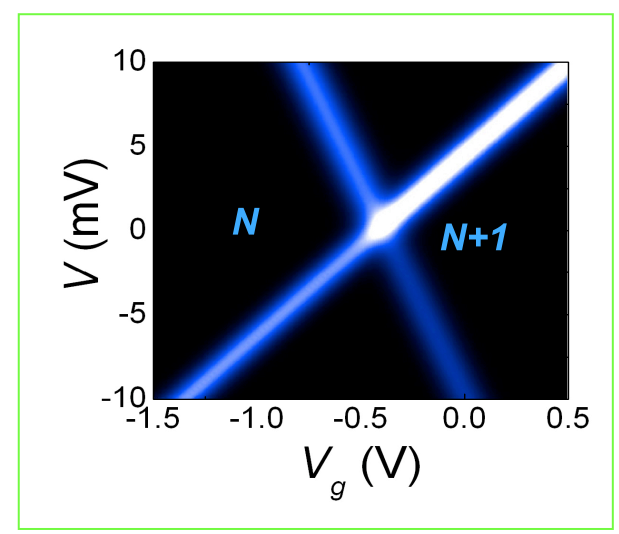


dI/dV

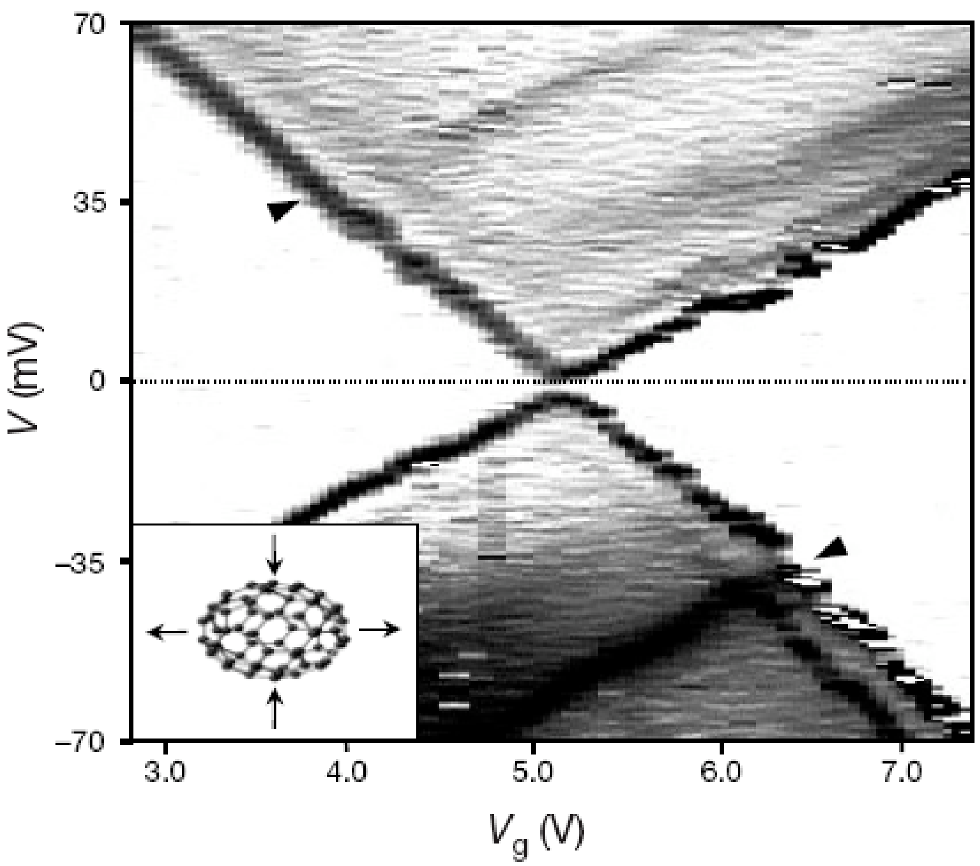


Early experiments: *Non magnetic molecules*

NATURE | VOL 407 | 7 SEPTEMBER 2000 | www.nature.com

Nanomechanical oscillations in a single-C_{60} transistor

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

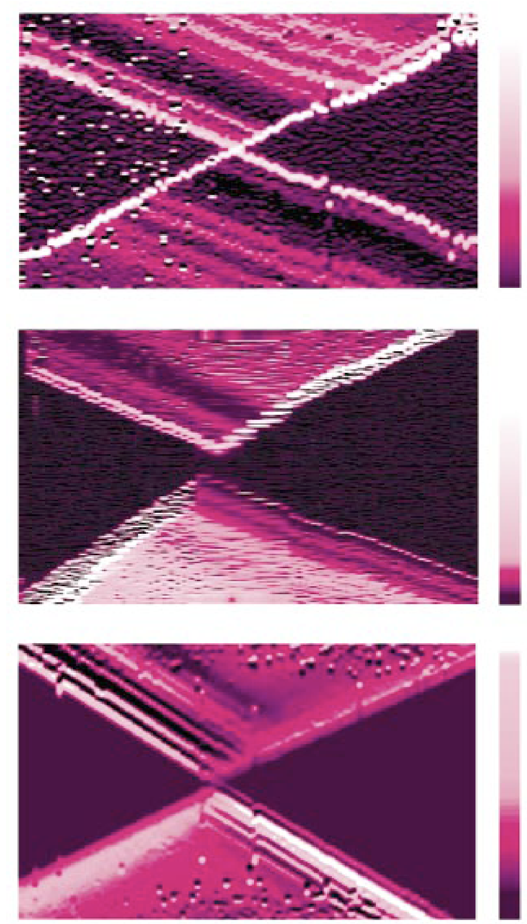


NATURE | VOL 417 | 13 JUNE 2002 |www.nature.com/nature

Coulomb blockade and the Kondo effect in single-atom transistors

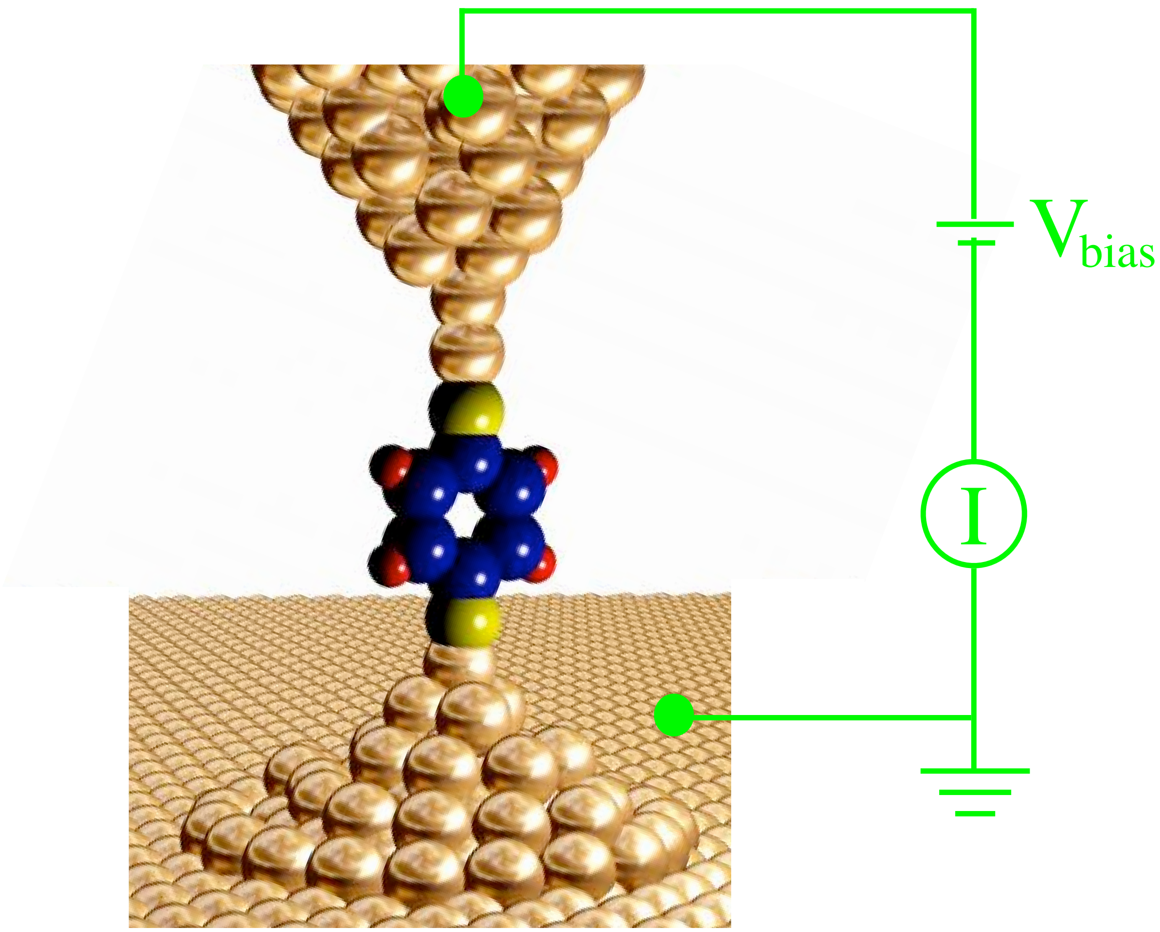
Jiwoong Park*†‡, Abhay N. Pasupathy*‡, Jonas I. Goldsmith§, Connie Chang*, Yuval Yaish*, Jason R. Petta*, Marie Rinkoski*, James P. Sethna*, He´ctor D. Abrun˜a§, Paul L. McEuen* & Daniel C. Ralph*

* Laboratory of Atomic and Solid State Physics; and § Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853, USA
† Department of Physics, University of California, Berkeley, California 94720, USA



Several other groups around the world have also observed similar effects in molecular transistors

Alternative route to molecular transistors: STM of molecules



(Photo credit: Ben Utley)

Advantages: fabrication, control

Drawbacks: no gating

A recent but extensive literature on this technique already exists.

Our Motivation:

How to increase the functionality of a molecular transistor ?

Combine electronics with magnetism:

(i) Use magnetic molecules

(ii) Use magnetic contacts

How do QTM and Berry phase interference

manifest themselves in electronic transport

through a single SMM?

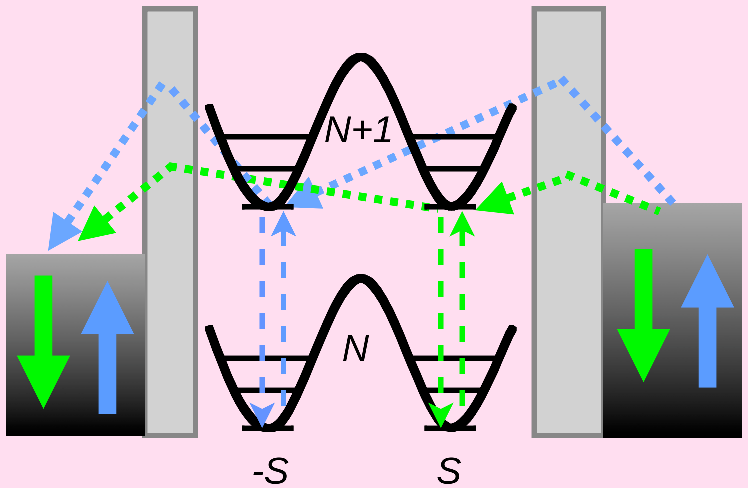
- Spin-current blockade

- Kondo effect

Berry-phase blockade:

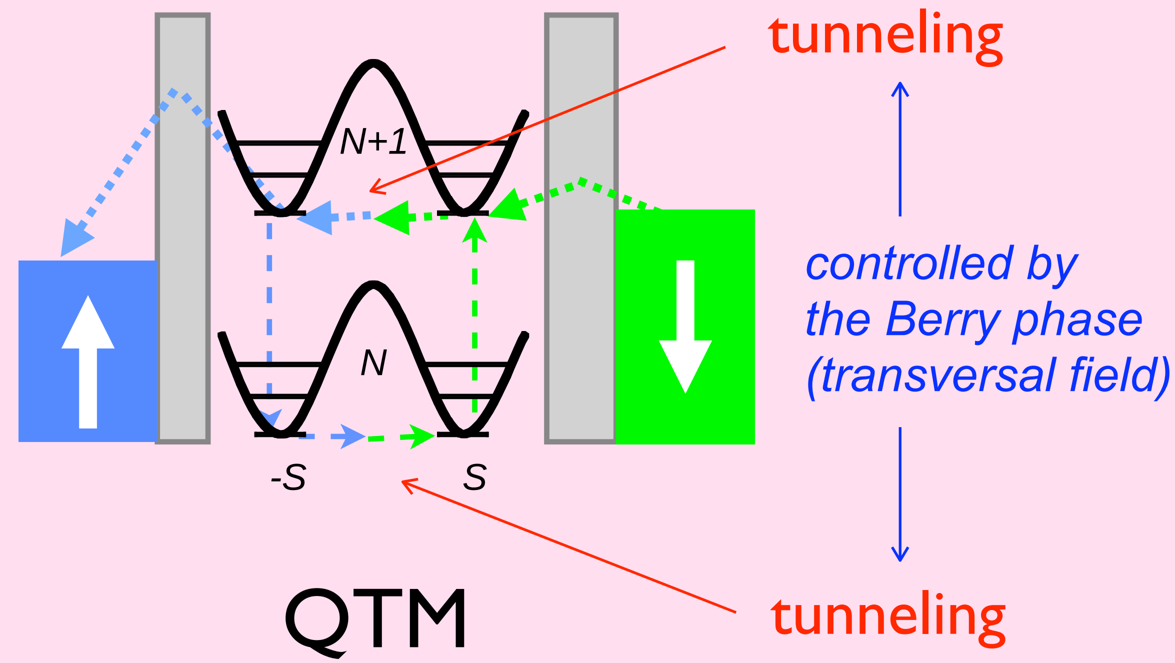
G. Gonzalez and M. Leuenberger [PRL 98, 256804 (2007)]
G. Gonzalez, M. Leuenberger, ERM [PRB 78, 054445(2008)]

unpolarized leads



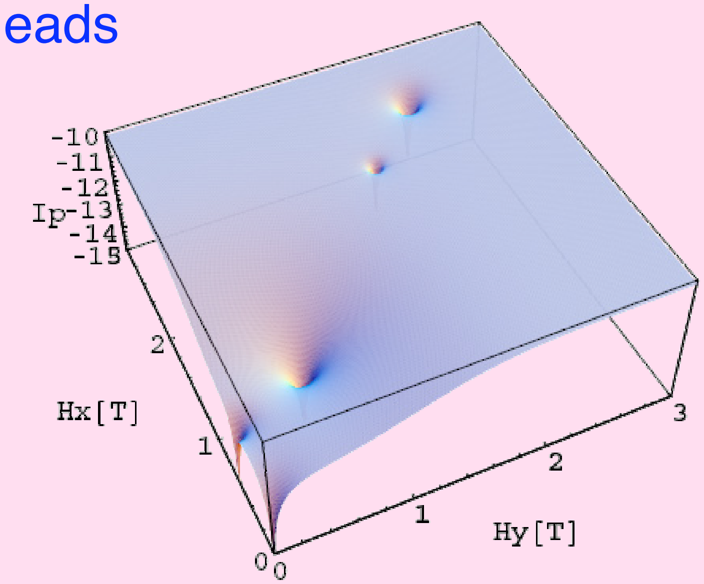
no QTM

polarized leads

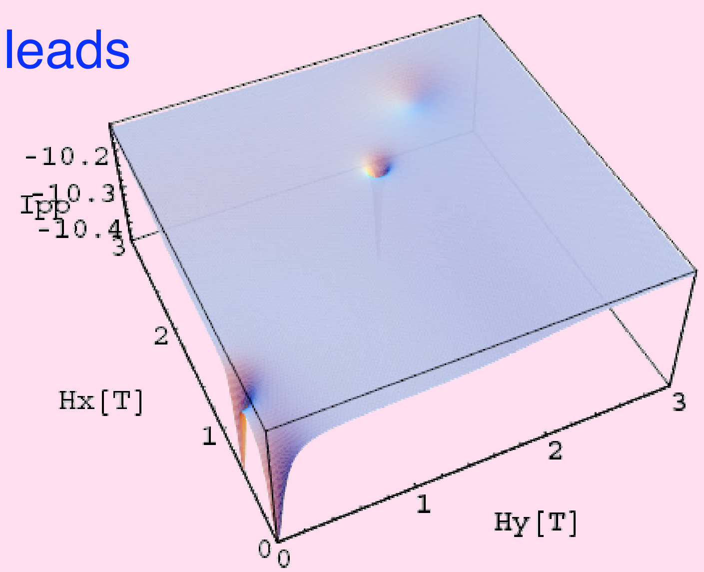


QTM

fully polarized leads

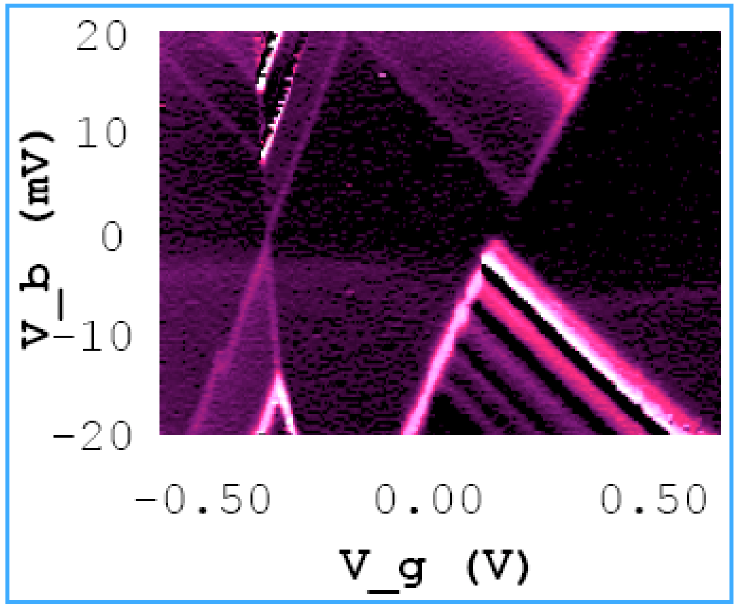


partially polarized leads

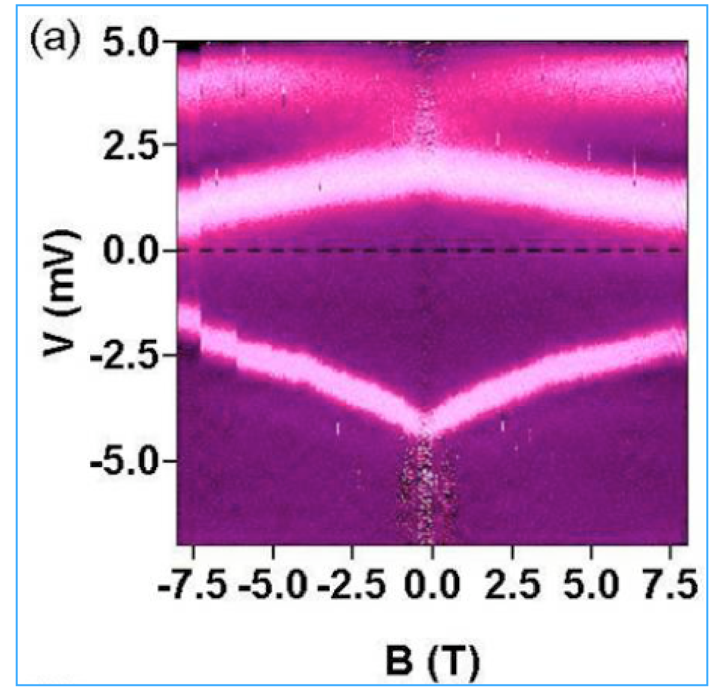


Recent experiments (Mn_{12}): Still not very conclusive...

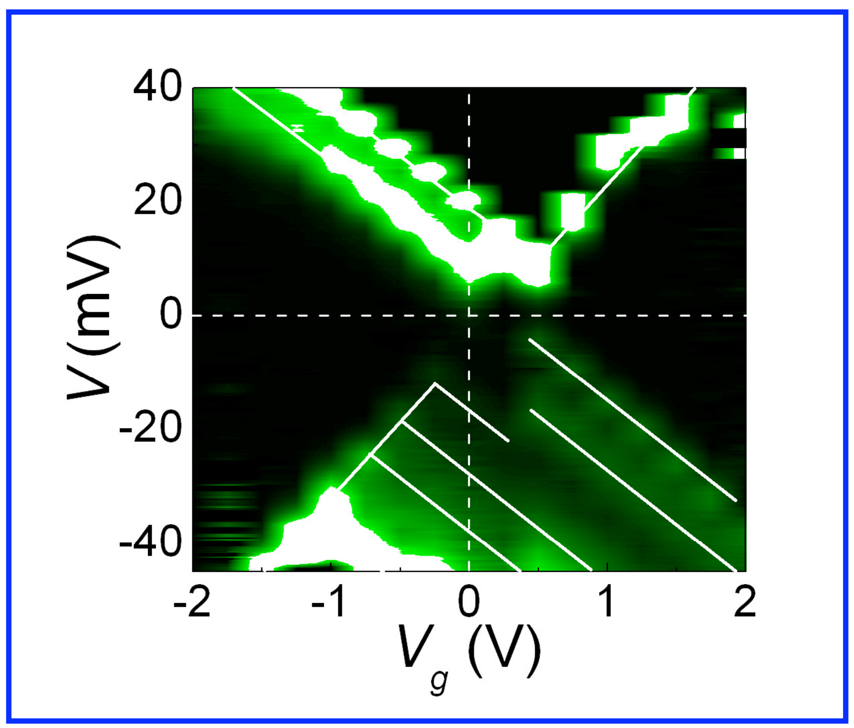
Herre van der Zant (Delft)



Dan Ralph (Cornell)



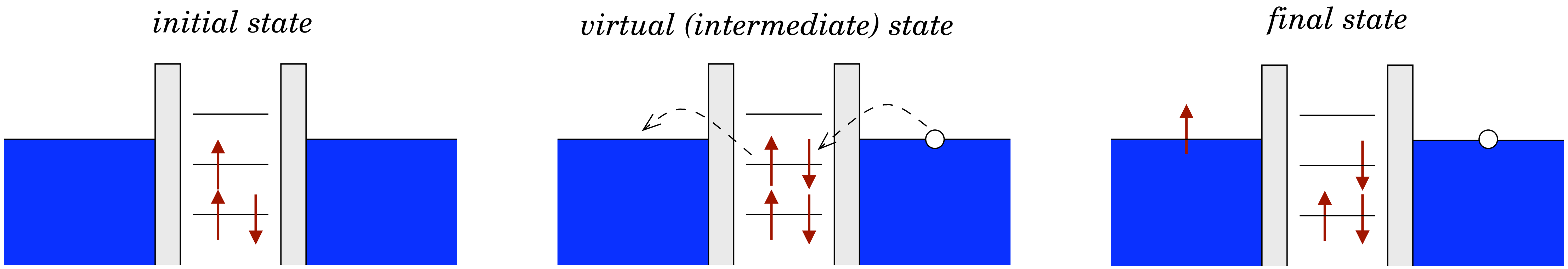
Enrique del Barco (UCF)



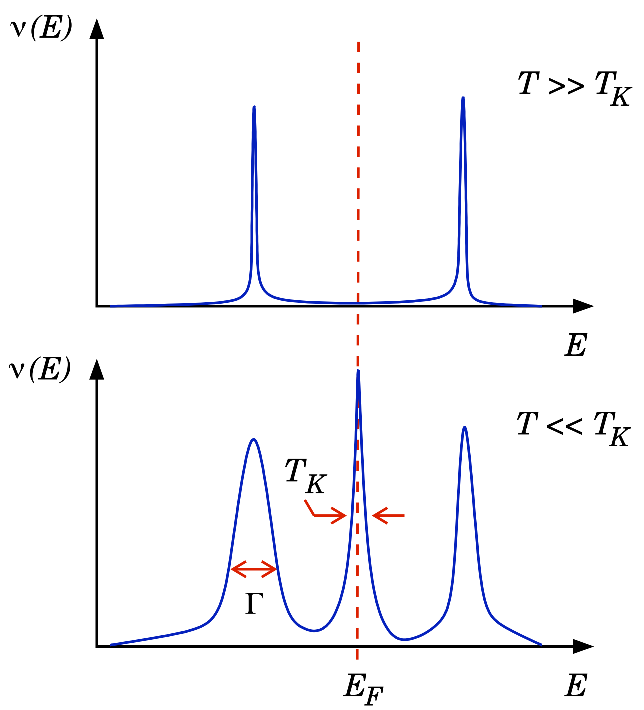
No experiment has yet seen a unambiguous manifestation of QTM, much less Berry phase interference...

Kondo effect: *The case of quantum dots and molecules attached to leads*

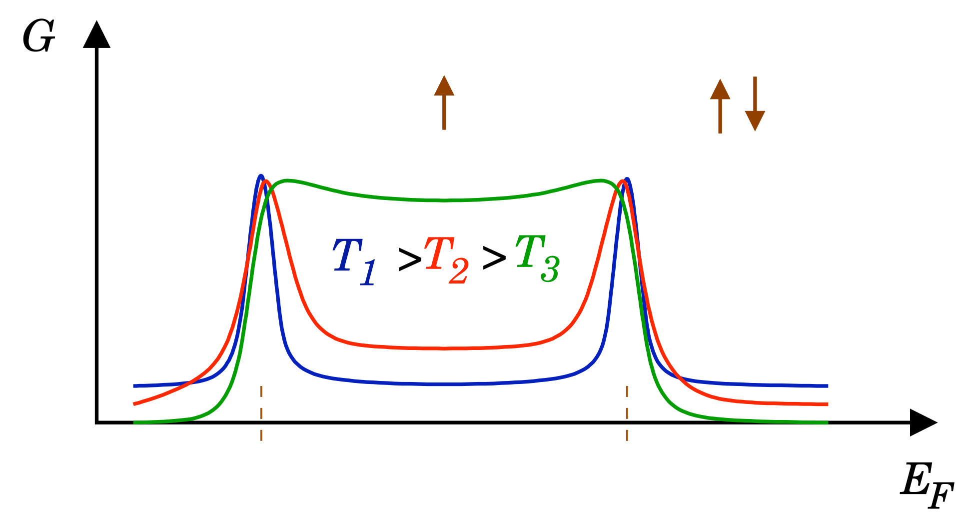
At low temperatures, spin flip processes strongly renormalize the conductance



Sharp resonance at the Fermi level appears at $T<T_K$



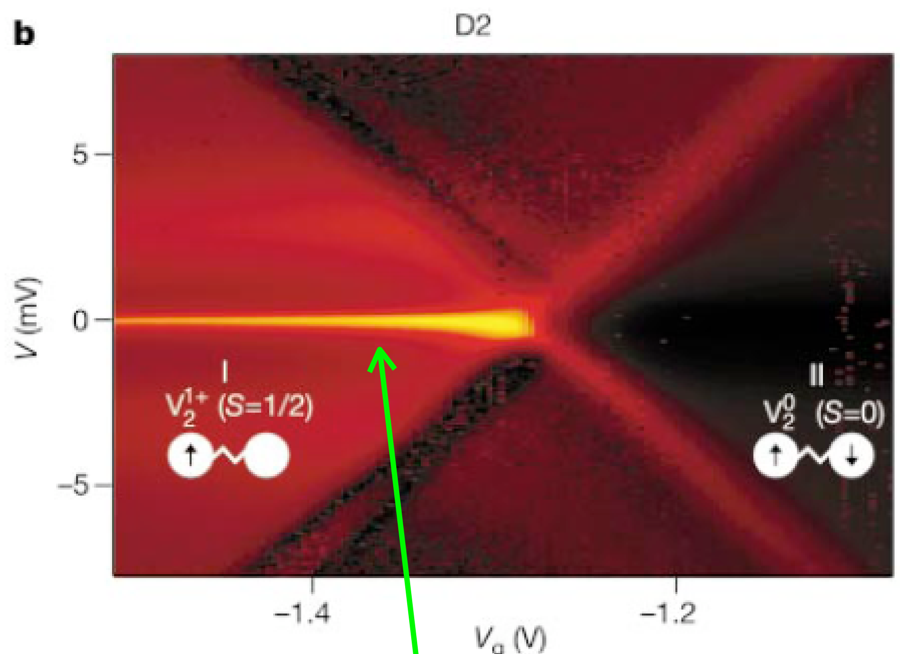
Tunneling conductance *increases* as the temperature goes down!



Another way of probing QTM: *Kondo effect*

NATURE | VOL 417 | 13 JUNE 2002 | www.nature.com/nature

Wenjie Liang*, Matthew P. Shores†, Marc Bockrath*, Jeffrey R. Long† & Hongkun Park*



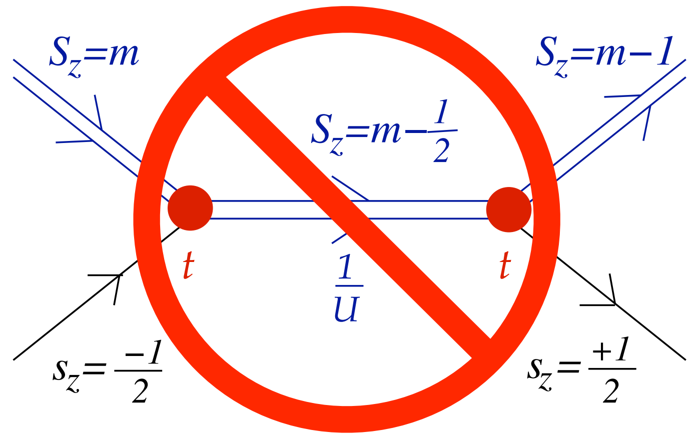
no Coulomb blockade!

The Kondo effect in a non-magnetic single-electron transistor has already been observed by several groups...

... but not yet for SMMs.

Unconventional Kondo effect in SMMs: *How it happens*

M. Leuenberger and ERM [PRL 97, 126601 (2006)]

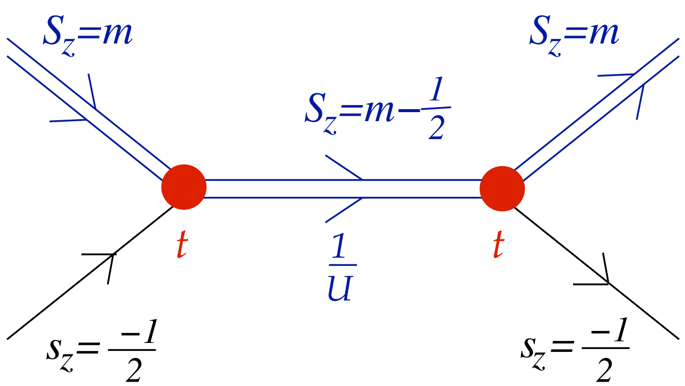


$(\Delta S_z=-1,\ \Delta s_z=+1)$

$\sim \frac{t^2}{U}$

inelastic (suppressed at zero bias)

$(E_m \neq E_{m-1})$



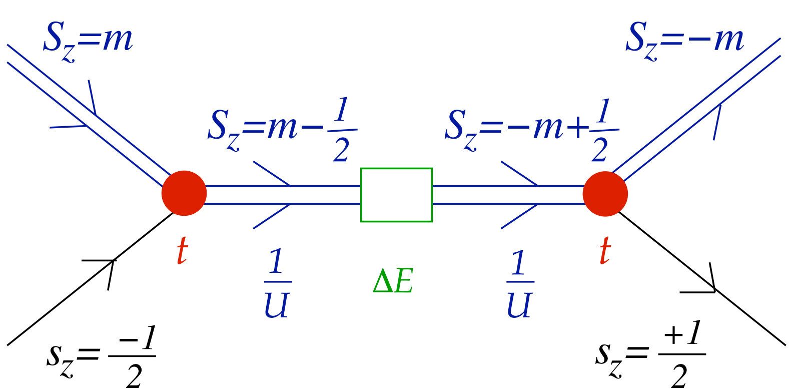
$(\Delta S_z=0,\ \ \Delta s_z=0)$

$\sim \frac{t^2}{U}$

elastic

J_z

no spin flipping



$(\Delta S_z=-2m,\ \ \Delta s_z=+1)$

$\sim \frac{t^2}{U^2}\Delta E$

elastic

$(E_m = E_{-m})$

$J_\perp$

spin flipping

Kondo effect in SMMs: *detailed theory*

effective Hamiltonian $\mathcal{H} = \mathcal{H}_{\rm SMM} + \mathcal{H}_{\rm Kondo}$

$$\mathcal{H}_{\rm SMM} = \sum_{m^*} E_{m^*} |m^*\rangle\langle m^*|, \qquad E_{m^*} = E_{-m^*} \quad [\Delta_{m^*,-m^*}(H_x^*) = 0]$$

local exchange term

$$\mathcal{H}_{\rm Kondo} = \sum_{k,\alpha} \left(\xi_k + \frac{g\mu_B H_x^* s_x}{2}\right) \psi^\dagger_{k\alpha}\psi_{k\alpha} + \mathcal{H}_{\rm ex}$$

project it onto the {|m⟩} subspace

$$\mathcal{H}_{\rm ex} = \frac{1}{2}\sum_m \sum_{k,k'} \left[j_+^{(m)}\Sigma_+^{(m)}\psi^\dagger_{k\downarrow}\psi_{k'\uparrow} + j_-^{(m)}\Sigma_-^{(m)}\psi^\dagger_{k\uparrow}\psi_{k'\downarrow} + j_z^{(m)}\Sigma_z^{(m)}\left(\psi^\dagger_{k\uparrow}\psi_{k'\uparrow} - \psi^\dagger_{k\downarrow}\psi_{k'\downarrow}\right)\right]$$

pseudo-spin flipping terms

pseudo-spin operators

$$\Sigma_z^{(m)} = \frac{1}{2}\left(|m\rangle\langle m| - |-m\rangle\langle -m|\right)$$

$$\Sigma_\pm^{(m)} = |\pm m\rangle\langle \mp m|$$

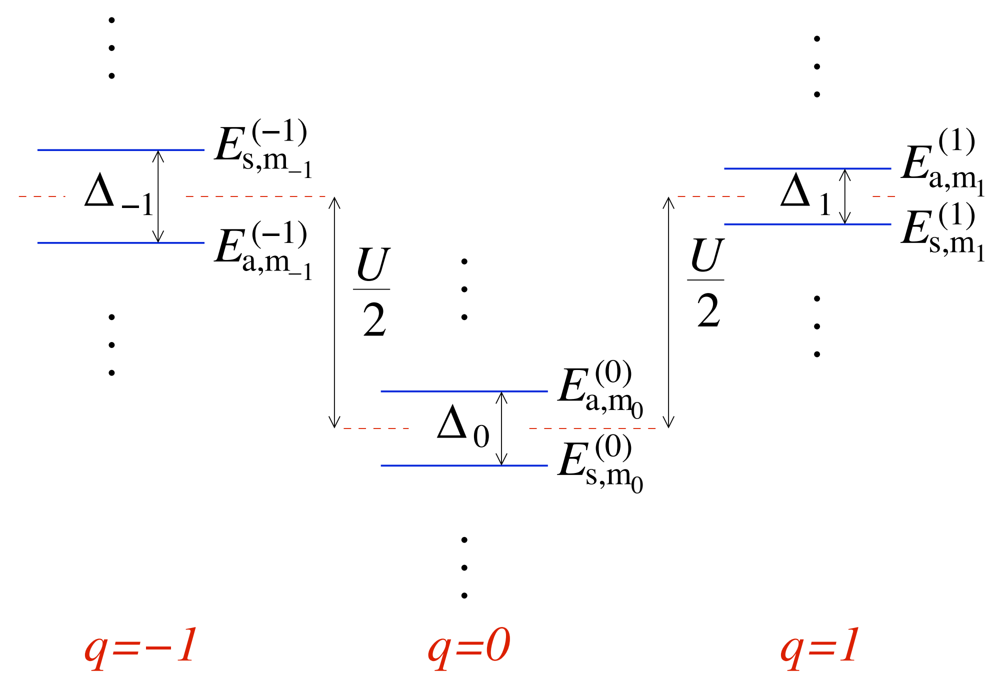
anisotropic coupling constants

$$j_z^{(m)} = 2J_z\langle m|S_z|m\rangle$$

$$j_\pm^{(m)} = J_\pm\langle \pm m|S_\pm|\mp m\rangle$$

Kondo effect in SMMs: *microscopic derivation of coupling constants*

energy levels relevant to the Kondo effect



$$j_z = \pm 2t^2 \left[\frac{U+\Delta_0}{(U+\Delta_0)^2 - \Delta_1^2} + \frac{U+\Delta_0}{(U-\Delta_0)^2 - \Delta_1^2} \right] \approx \pm \frac{4t^2}{U}$$

→ The sign depends on the intermediate spin state of the molecule!

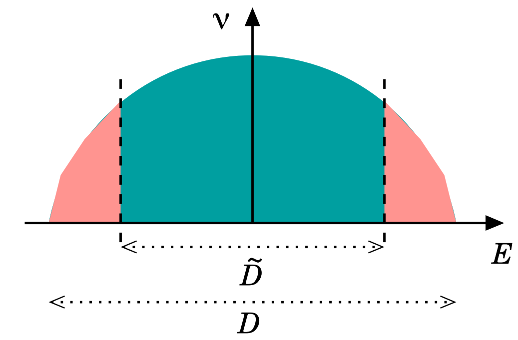
$$j_\perp = 4t^2 \left[\frac{\Delta_1}{(U+\Delta_0)^2 - \Delta_1^2} + \frac{\Delta_1}{(U-\Delta_0)^2 - \Delta_1^2} \right] \approx \frac{8t^2\,\Delta_1}{U}$$

$|j_z| \gg j_\perp$ ⟶ anisotropic exchange interaction

$S_1 = S_0 - \frac{1}{2} \Longrightarrow$ AF

$S_1 = S_0 + \frac{1}{2} \Longrightarrow$ FM

Kondo effect in SMMs: *poor man's Renormalization Group*



total Hamiltonian in projected subspace

$$\mathcal{H} = \sum_m \left[E_m \left(\Sigma_z^{(m)}\right)^2 + \eta^{(m)} H_x^* \Sigma_x^{(m)} \right] + \sum_{k,\alpha} \xi_k \psi_{k\alpha}^\dagger \psi_{k,\alpha} + \mathcal{H}_{\rm ex}$$

$$\eta^{(m)} = 1 - \frac{\nu j_\perp^{(m)}}{2}$$

Knight shift → *molecule's pseudo-spin couples to transversal field*

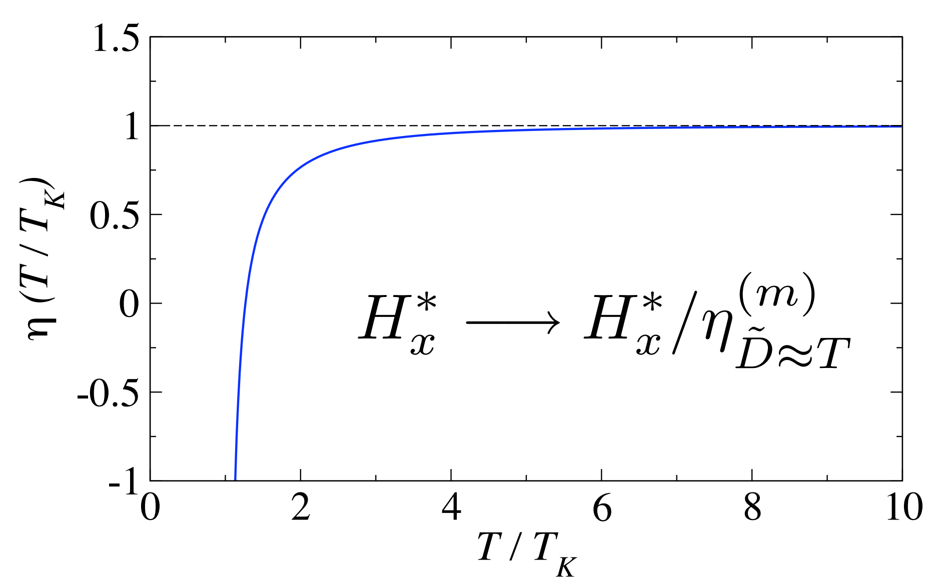
Renormalization Group flow equations... $\zeta = \ln(\tilde{D}/D)$

$$\frac{dj_z}{d\zeta} = -2\nu\, j_+ j_- \qquad \frac{dj_\pm}{d\zeta} = -2\nu\, j_\pm j_z \qquad \frac{d\eta}{d\zeta} = \frac{\nu^2}{2}\left(j_+ + j_-\right) j_z$$

... and solutions

$$j_z^2 - j_\perp^2 = C > 0$$

$$\frac{1}{2\nu\sqrt{C}} \operatorname{arctanh}\left(\frac{\sqrt{C}}{j_z}\right) = \ln\left(\frac{\tilde{D}}{T_K}\right)$$



Kondo effect in SMMs: *Conductance*

Linear conductance (T dependence)

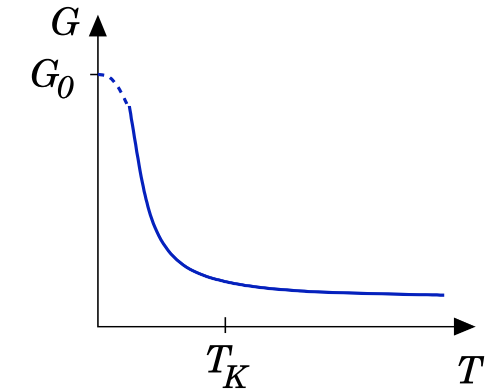
scattering amplitude

$$G(T) = G_0 \int d\omega \left(-\frac{df}{d\omega}\right) \frac{\pi^2\nu^2}{16} \frac{\sum_m e^{-E_m/k_BT} |A^{(m)}(\omega)|^2}{\sum_m e^{-E_m/k_BT}}$$

$$A^{(m)}_{\omega\approx\tilde{D}} \approx j^{(m)}_{\perp,\omega\approx\tilde{D}} = \sqrt{C}\left[\frac{(\omega/T_K)^{2\nu\sqrt{C}}}{(\omega/T_K)^{4\nu\sqrt{C}} - 1}\right]$$

1st order perturbation theory

singularity for $T \ll T_K$



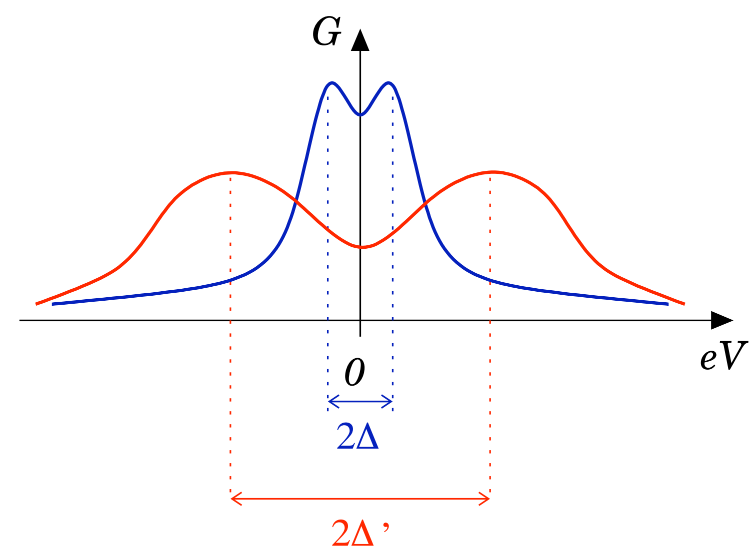
Non-linear conductance (T=0) away from the degeneracy points

$$A^{(m)}_{\omega\approx\tilde{D}} \approx j^{(m)}_{\perp,\omega\approx\tilde{D}} + \nu j^{(m)}_{\perp,\omega\approx\tilde{D}}\, j^{(m)}_{z,\omega\approx\tilde{D}} \ln\left|\frac{\omega+\tilde{D}-eV/2}{\omega-\tilde{D}+eV/2}\right|$$

2nd order perturbation theory

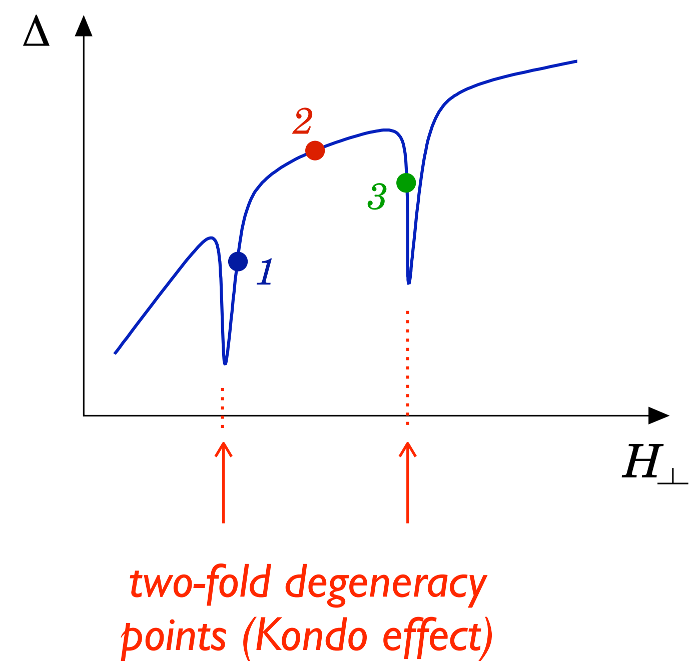
($T_K \ll |eV|$)

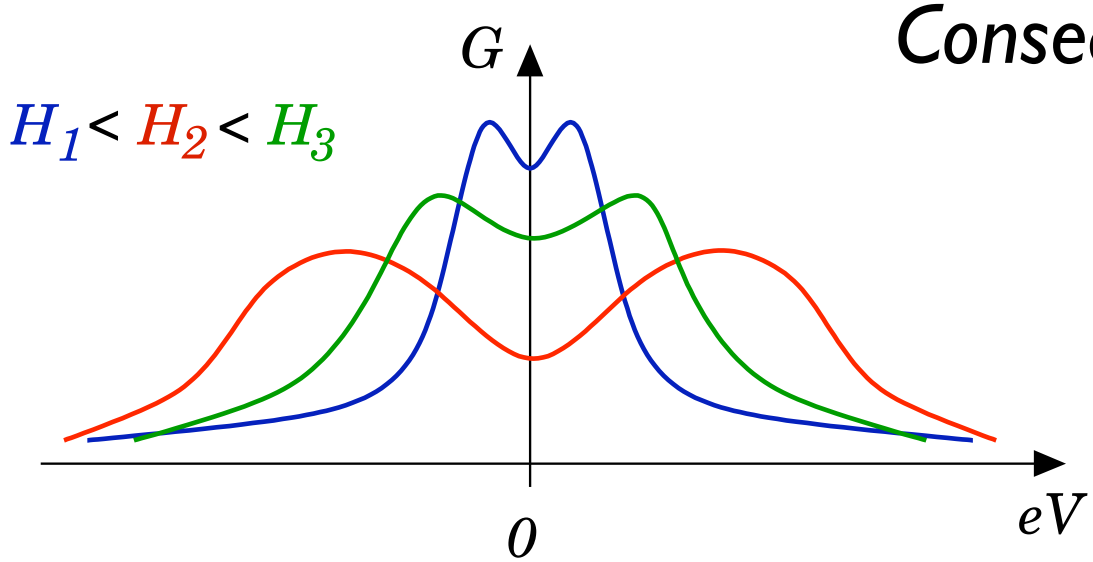
$$G(V) = G_0 \frac{\pi^2\nu^2}{16} j^2_{\perp,\tilde{D}} \left[\delta_{eV,0} + \nu j_{z,\tilde{D}} \ln\left(\frac{\Delta_{m,-m}}{||eV| - \Delta_{m,-m}|}\right)\right]$$



Kondo effect in SMMs: *Berry phase oscillations*

The tunnel splitting is an oscillating function of the transverse magnetic field due to the Berry phase interference.





Consequences:

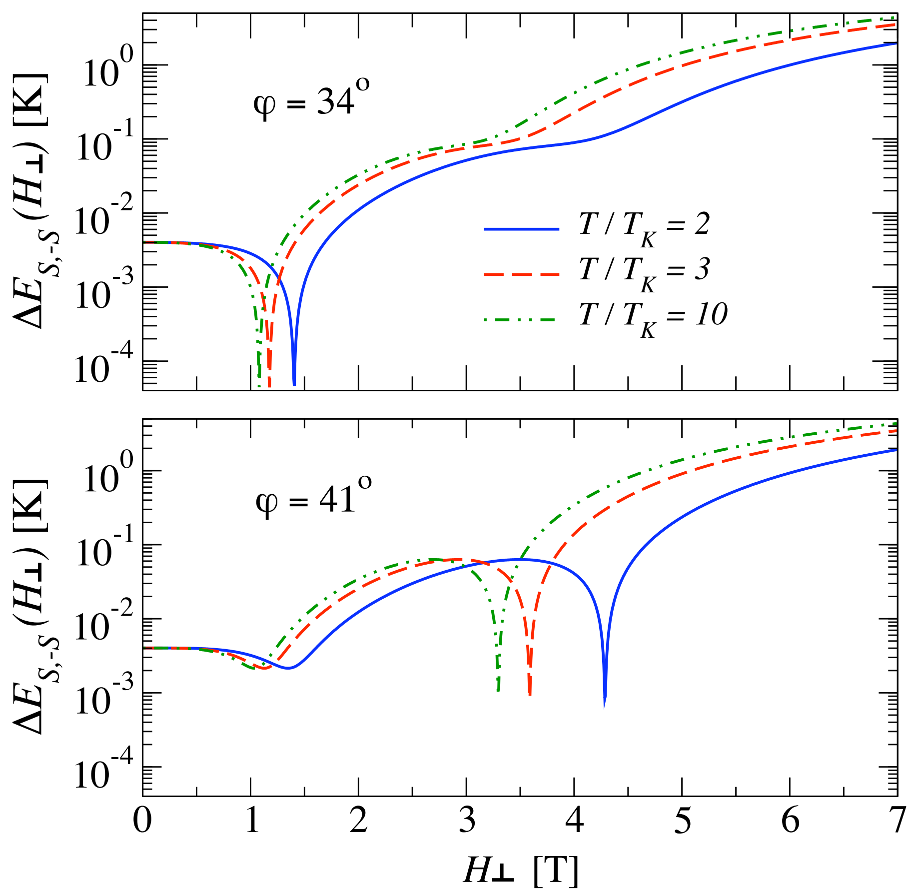
1) The Kondo peak splitting is a non-monotonic function of the transverse magnetic field.

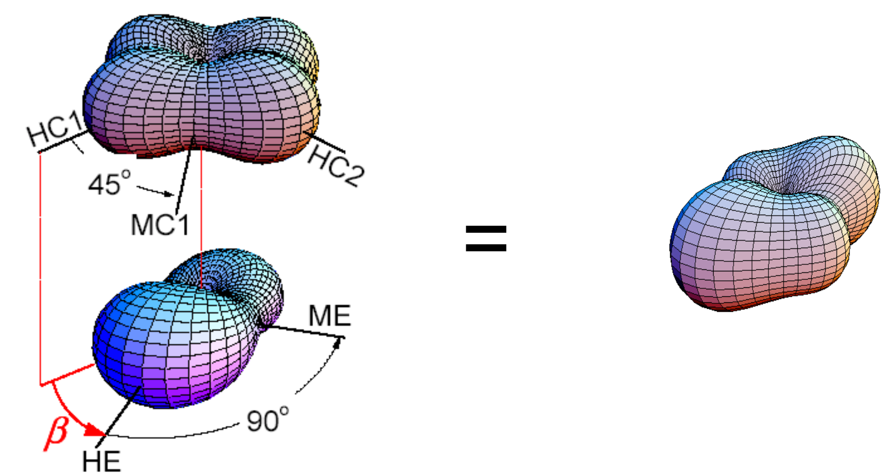
2) The period of Berry oscillations is renormalized by the Kondo effect (strongly temperature dependent, with a universal function form).

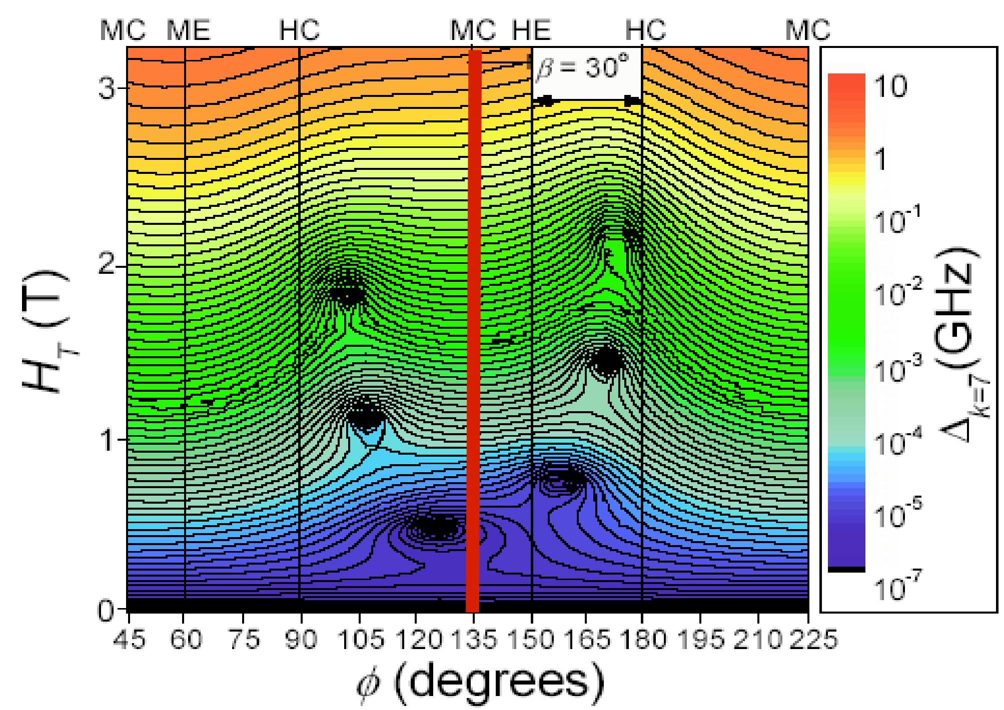
Kondo effect in SMMs: *Ni_4, the best candidate*

$[Ni_4(ROH)_4L_4O_{12}]$ (R=Me,Et) *Sieber et al. (2005)*

Spin tunneling splitting Δ (numerical simulations)







Some estimates (Ni_4):

M. Leuenberger and ERM [PRL 97, 126601 (2006)]

$$T_K \approx D \exp\left[-\text{arctanh}\left(\sqrt{C}/j_z\right)/2\nu\sqrt{C}\right]$$

$$\begin{cases} \nu(J_z - J_\pm) \approx 0.15 \\ \Delta E = D = \left|A\left[S^2 - (S-1)^2\right]\right| \approx 9.3\,\mathrm{K} \end{cases} \longrightarrow \boxed{T_K \approx 1.2\,\mathrm{K} \quad (m = \pm 4)}$$

crucial requirements:

i) large spin tunnel splitting

ii) large coupling to states in the leads

issues under investigation:

i) quantitative theory for transport (NRG, DMRG?)

ii) spin/angular momentum relaxation in isolated molecules

See also related work by the Aachen group (H. Schoeller).

Some Questions and Challenges for the STM group:

(1) How does the SMM bind to metallic surfaces?

(2) Where does the additional electron go in a SMM?

chemistry/electronic structure

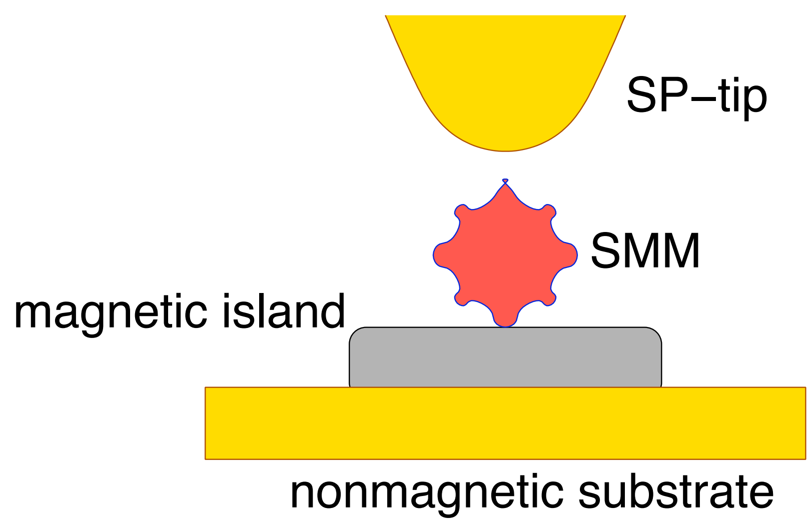
(3) Can the SMM be manipulated by the SMT tip?
(move it, flip it, and extract or modify ligands)

technical challenge

(4) Does the tip position change the electric response of the SMM?

(5) Can a SP-STM measure the magnetization curve of a SMM (quantum tunneling, coherent oscillations, decoherence)?

physics



SMMs have intrinsically large magnetization and strong anisotropy, so a magnetic island may not be necessary.

The End