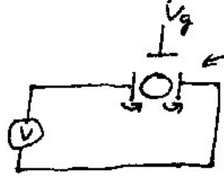
Coulomb Blockade and Tunneling in Small Magnets

Theme today - how do energy levels in a small magnet evolve as a function of applied magnetic field.

With increasingly sensitive experiments, develop a direct view into the correlated, many-body physics caused by strong electron interactions inside a magnet. Ideas of quasi-independent electron band structure will fail.

First: background on Coulomb blockade



small grain, small capacitance C to outside world

Can't ignore classical charging energy $E_c \sim \frac{e^2}{2C}$ even for one electron.

for aluminum oxide junctions $(100 \times 100)\,nm^2$ $C \sim 0.5fF$ $E_c \sim 0.2\,meV$ or $(2k)\,k_B$

for $(5 \times 5)\,nm^2$ junctions $C \sim 1aF$ $E_c \sim 80\,meV \sim (800k)\,k_B$

At kT, eV lower than E_c, Coulomb blockade can block current flow - electrons in electrodes have insufficient energy to hop onto the island and off the other side

For eV comparable to E_c, at most one excess electron at a time can occupy the island $\Rightarrow$ single electron tunneling

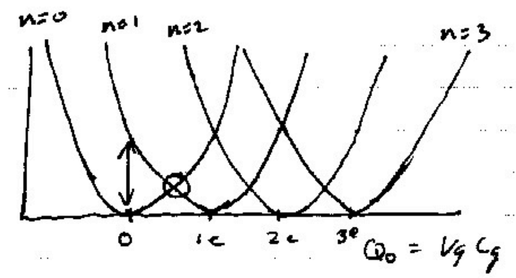
With a tunable gate voltage V_g, can make a single-electron transistor. Tunes the energy cost for adding an electron.

Energy of island = E(n electrons) (for V=0) $= \frac{(ne)^2}{2C} - neV_g\frac{C_g}{C} = \frac{1}{2C}\left[ne - V_gC_g\right]^2 - \frac{(V_gC_g)^2}{2C}$

What matters is $E(n \pm 1) - E(n)$ = energy required to change the number of electrons by one. So can ignore the last term because it is independent of n.

$\Rightarrow E(n) = \frac{1}{2C}\left[V_gC_g - ne\right]^2 \equiv \frac{1}{2C}\left[Q_0 - ne\right]^2$ where $Q_0 \equiv V_gC_g$ is called the "offset charge", but really it is due to the effects of an external potential graphically:

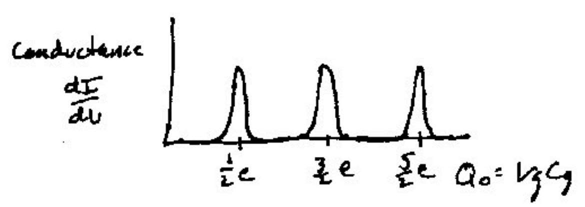
$$E(n, Q_0) = \frac{[Q_0 - ne]^2}{2C}$$



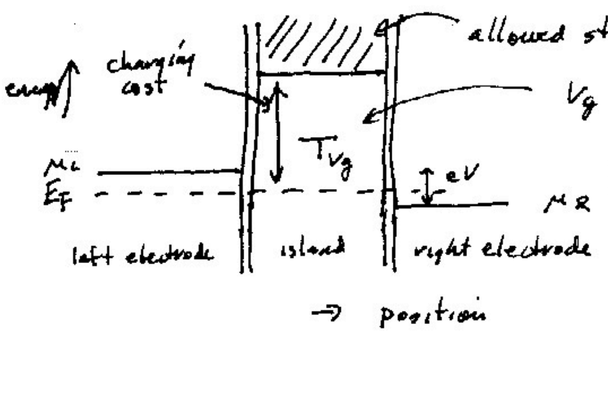
different charge states have different energies. With a gate voltage, you can change how many electrons are in the ground state of the island

For each value of Q_0, there is a minimum energy cost for the island to change charge number (vertical arrows)

At $Q_0/e = \frac{1}{2}$ + integer values, 2 charge states are degenerate ground states. At these values of gate voltage, charge can flow with zero Coulomb energy cost. Gate voltage has tuned away the Coulomb blockade



Another way to picture the same physics

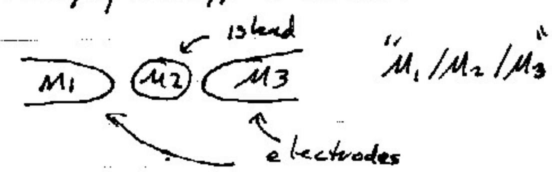


V_g shifts the energy levels on the island up or down relative to the Fermi level in the electrodes. When the levels are shifted down to E_F, there is no charging energy.

How do the energy levels change in a magnetic field?

In a non-magnetic particle / electrodes, charging energy is insensitive to magnetic fields

We will consider tunneling devices where any combination of M_1, M_2, M_3 may be magnetic.



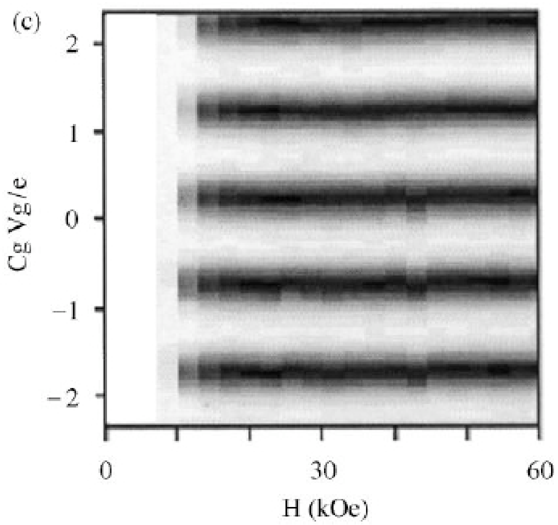
Will tell only part of the story – Will focus on what a magnetic field does to energy thresholds for tunneling. Other experiments have looked into how the tunneling rates depend on the relative orientation of magnetic moments.

We will see that in an applied magnetic field the energy levels available for tunneling on a magnetic island will shift.
This will be a cautionary tale. Magnetism can be trickier than you expect!

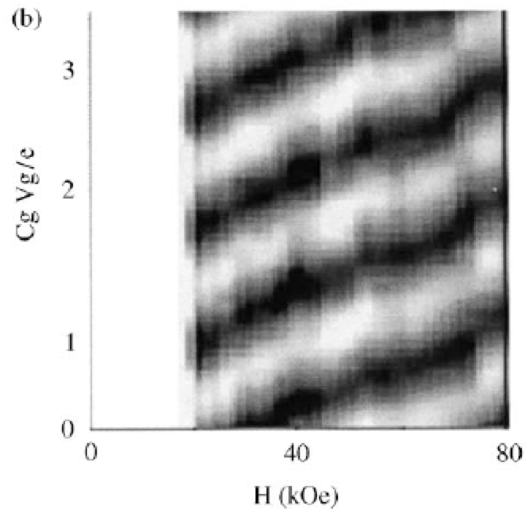
Look at Ono / Ootuka data.

As B increases, energy levels on a Co island shift to larger values of V_g ⇒ higher energies for electrons.

Al / Al / Al

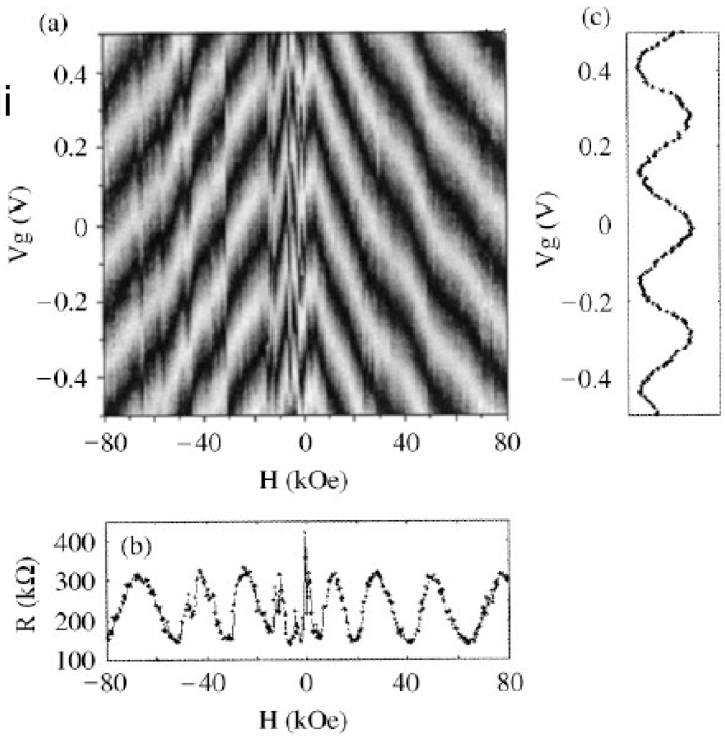


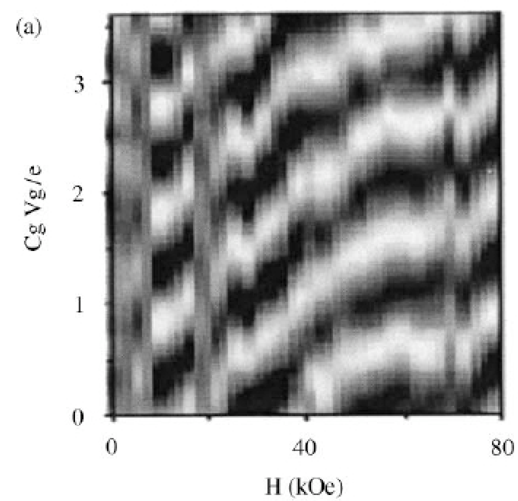
Al / Co / Al



Magneto-Coulomb oscillations in single-electron transistors made with ferromagnetic elements.

Ni / Co / Ni

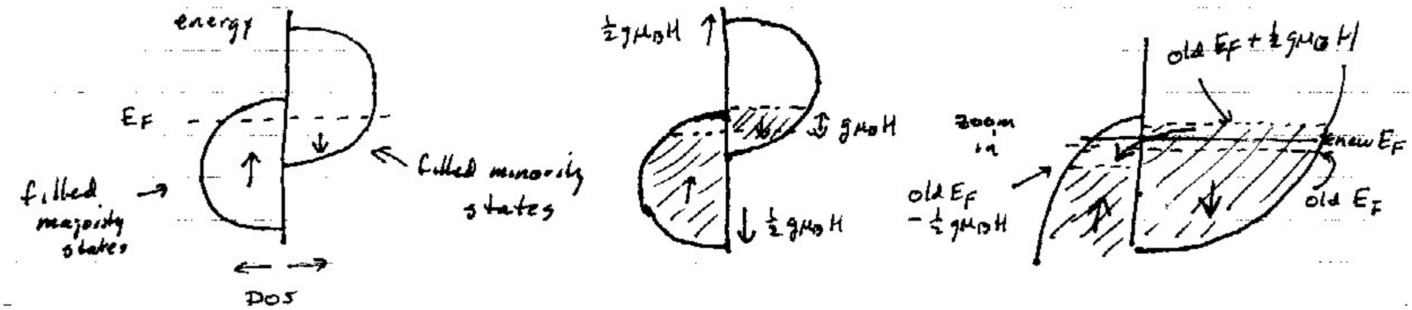




Co / Ni / Co

Y. Ootuka et al.
Physica B 280, 394 (2000)

First explanation: From the experimentalists, Stoner Model



B = 0 cartoon of density of states

apply B ≠ 0, assume electrons are momentarily frozen in their states

allow electrons to relax to lower energy states

If the densities of states at the Fermi level $D_\uparrow$ and $D_\downarrow$ are not equal, the Fermi level must shift as spin down electrons flip over to spin up.

If $D_\downarrow > D_\uparrow$, fermi level will go up.

Spin down electrons subtracted = Spin up electrons added

$$\left(\tfrac{1}{2} g \mu_B H - \Delta E_F\right) D_\downarrow = \left(\tfrac{1}{2} g \mu_B H + \Delta E_F\right) D_\uparrow$$

solve $$\Delta E_F = \tfrac{1}{2} g \mu_B H \frac{(D_\downarrow - D_\uparrow)}{D_\downarrow + D_\uparrow} = -\tfrac{1}{2} g \mu_B H \, P_{DOS}$$

where $P_{DOS} = \dfrac{D_\uparrow - D_\downarrow}{D_\downarrow + D_\uparrow}$

"thermodynamic" density of states.

What is wrong with this picture?

Electron interactions! The whole idea of the Stoner model is positive feedback. Having more spin ↑ electrons lowers the energy of spin-up states, and favours having even more spin ↑ electrons.

This is the reason that the ferromagnet exists in the first case.

Put in exchange interactions (mean field)
assume unit volume

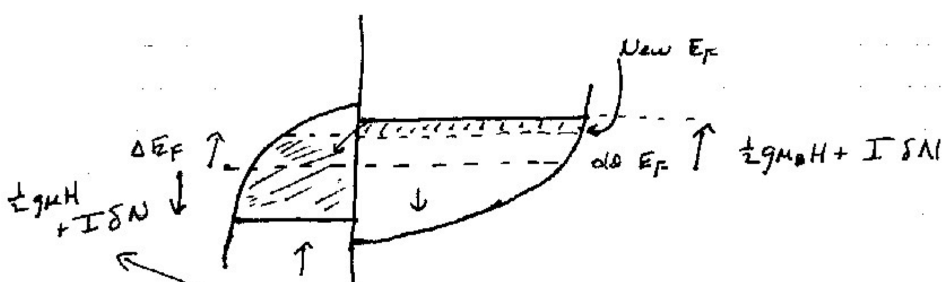
$$H_{exch} = -I \sum_{i,j} (n_{i\uparrow} n_{j\uparrow} + n_{i\downarrow} n_{j\downarrow}) \quad \text{favors alignment of spins}$$

$$= -I \sum_i n_{i\uparrow} \underbrace{\sum_j n_{j\uparrow}} - I \sum_i n_{i\downarrow} \underbrace{\sum_j n_{j\downarrow}}$$

$N_\uparrow$ density of $\uparrow$ electrons $N_\downarrow$ density of $\downarrow$ electrons.

Interpretation: Exchange lowers the energy of each state $i\uparrow$ by $I N_\uparrow$ and energy of each state $i\downarrow$ is lowered by $I N_\downarrow$.
If δN electrons flip from $\downarrow$ to $\uparrow$, the effect of exchange is to lower the energy of every spin $\uparrow$ state by $I\delta N$ and raise the energy of every spin $\downarrow$ state by $I\delta N$.

Correct Stoner Model



more spin $\uparrow$ electrons lowers the energy of all the other filled states a little bit more.

spin down electrons subtracted = spin up electrons added

$$\left(\tfrac{1}{2} g\mu_B H + I\delta N - \Delta E_F\right) D_\downarrow = \left(\tfrac{1}{2} g\mu_B H + I\delta N + \Delta E_F\right) D_\uparrow$$

$$\delta N = 2\left(\tfrac{1}{2} g\mu_B H + I\delta N - \Delta E_F\right) D_\downarrow$$

algebra: (2 eqns, 2 unknowns : δN, ΔE_F)

$$\Delta E_F = \left(\frac{D_\downarrow - D_\uparrow}{D_\downarrow + D_\uparrow}\right) \frac{\frac{1}{2} g\mu_B H}{\underbrace{\left[1 - \frac{4 D_\downarrow D_\uparrow I}{D_\downarrow + D_\uparrow}\right]}} = -\tfrac{1}{2} g\mu_B H \, P_{eff}$$

positive feedback enhances ΔE_F beyond the naive value from the polarization

experimentally, P_{eff} for Co ≈ -0.37
Ni ≈ -0.66 or more negative

band structure predictions Co ≈ -0.59
Ni ≈ -0.79

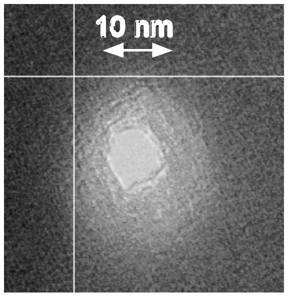
Sign is negative (good) - opposite tunneling DOS.
Would expect P_{eff} more negative than band structure because of interactions.
We will see this is not the whole story.

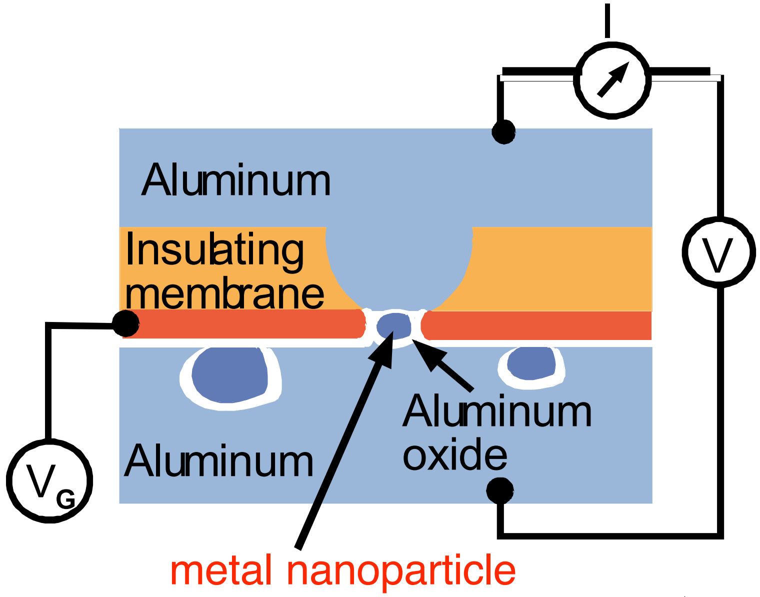
Next: Make devices with much smaller islands.
Small enough that the available states cannot be thought of as a continuum, but are individually resolvable.

(Need particles with diameter $\approx$ 10 nm in order that ΔE, particle-in-a-box level spacing, is greater than kT at 1 K.)

Introduction to tunneling spectroscopy

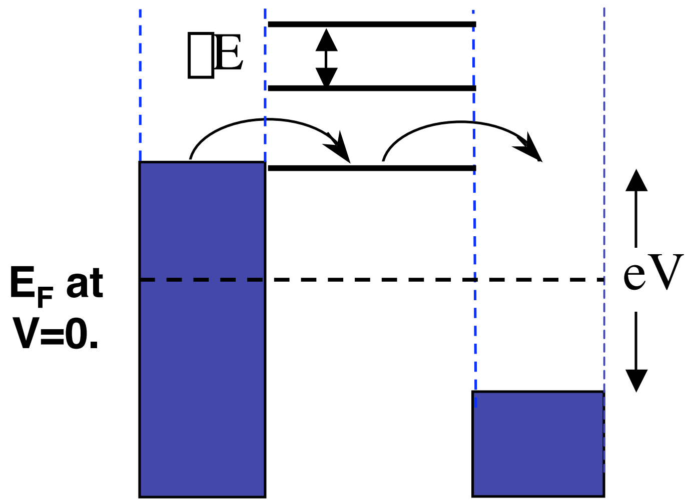
Measuring "electrons-in-a-box" levels in a metal nanoparticle

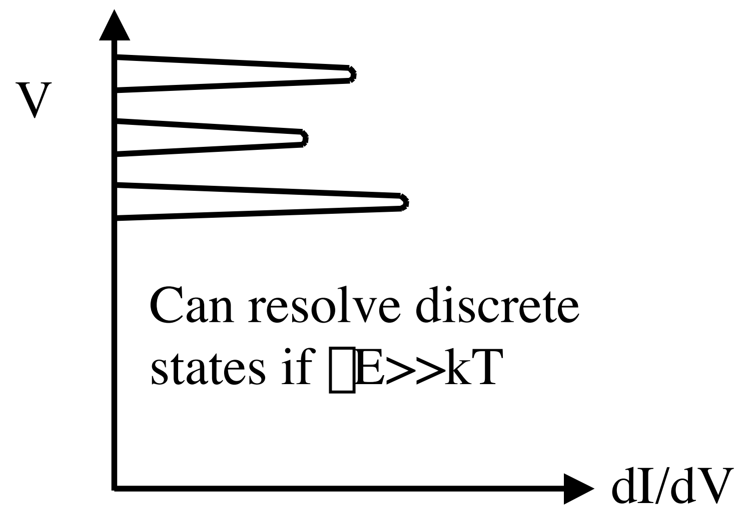




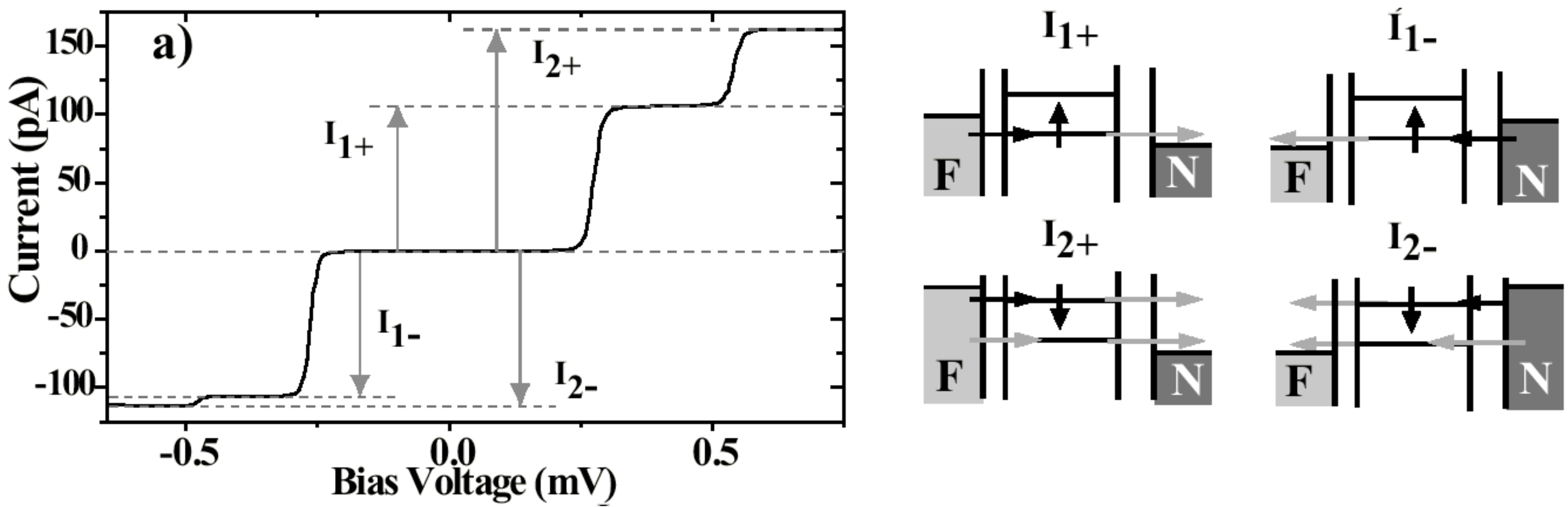
Particles 3-10 nm.

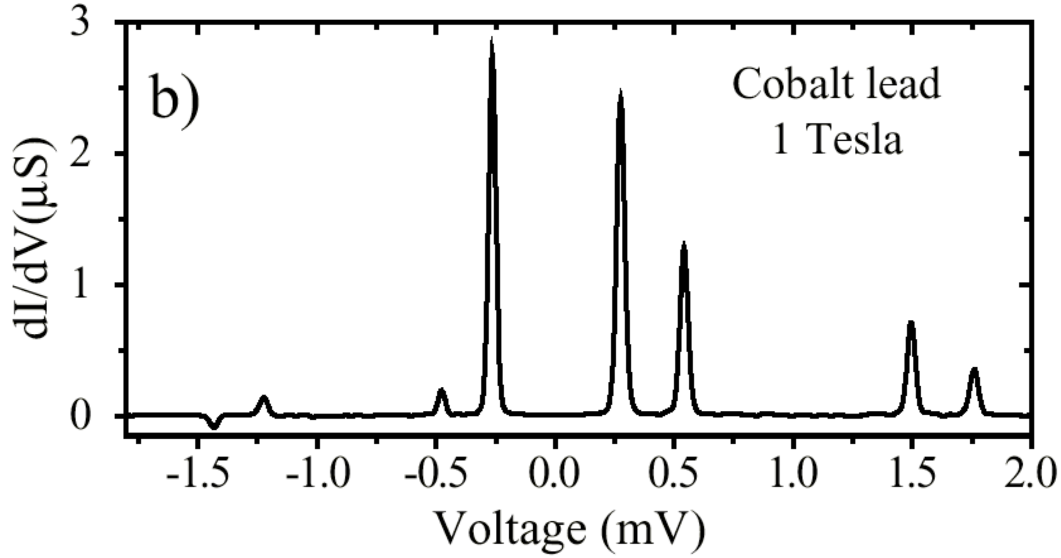
$\Gamma \ll kT \ll \Delta E \ll E_c$



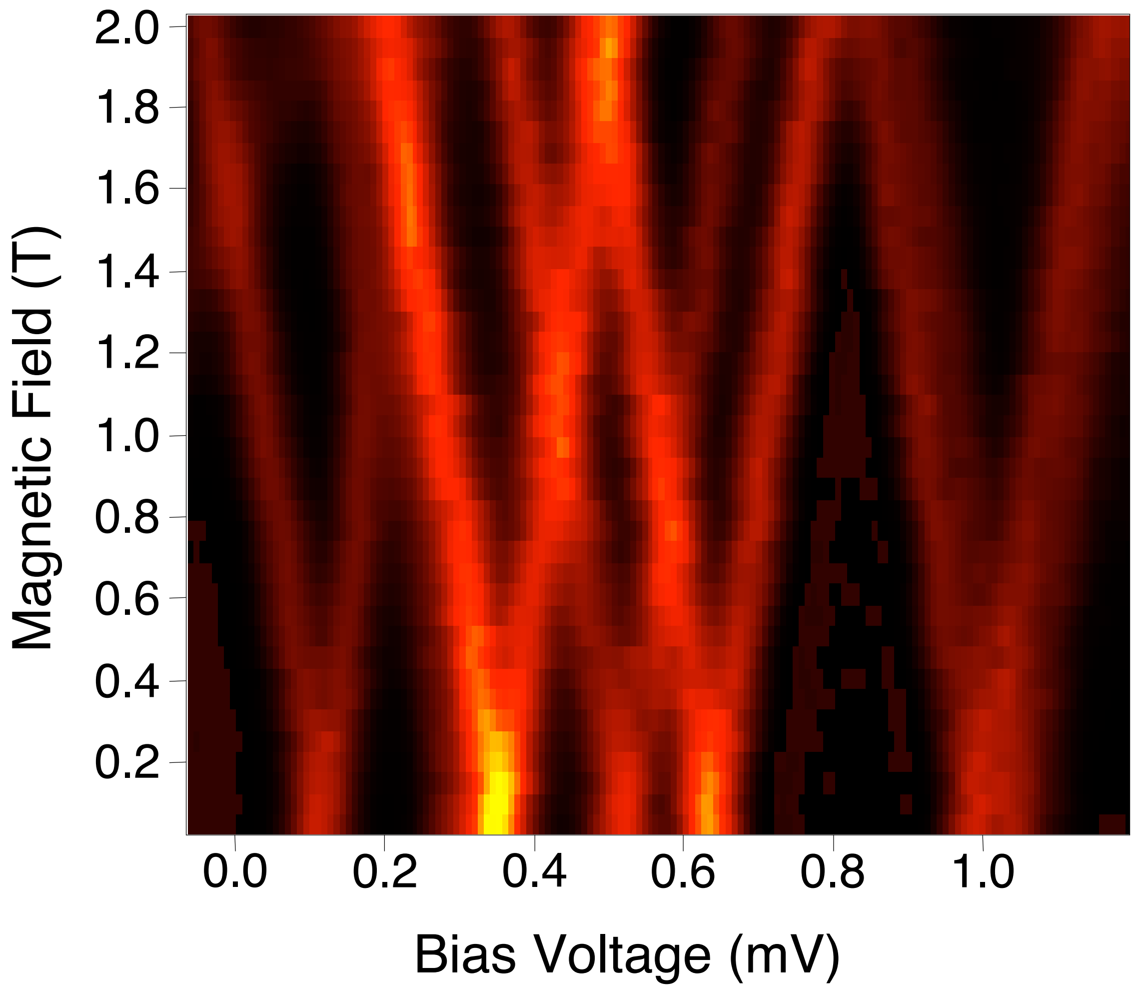


□ << kT


a)
Current (pA)
Bias Voltage (mV)
I1+
I2+
I1-
I2-
F
N

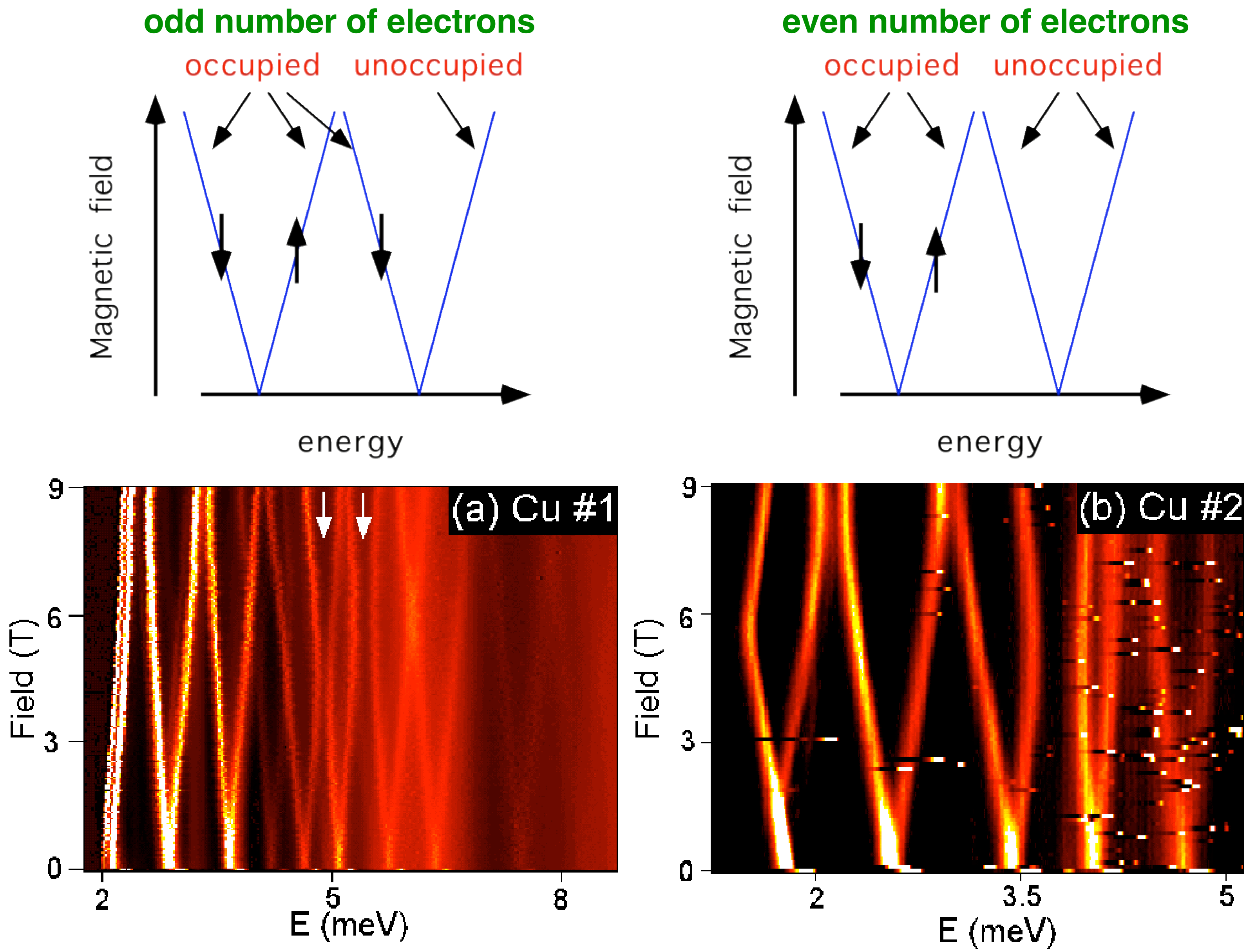

b)
Cobalt lead
1 Tesla
dI/dV(μS)
Voltage (mV)

Magnetic-Field Dependence of Aluminum Levels

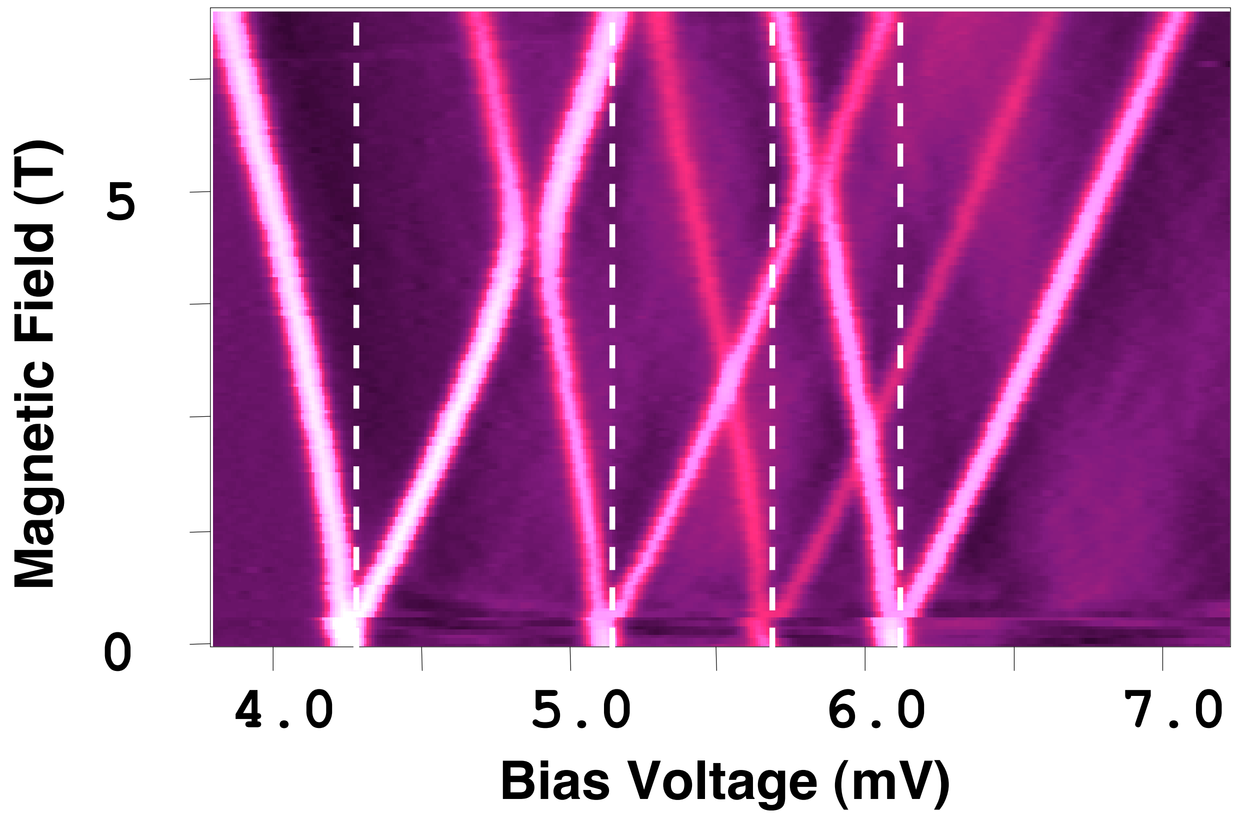


g = 2.0 ± 0.1 for Al.

Even vs. Odd Numbers of Electrons:



one Ni electrode / Al particle / Al electrode



Effective Polarizations from Energy Shifts:

Co: P_{eff} ~ -0.1 ± 0.1, -0.37 ± 0.05, -0.7 ± 0.1 in different samples

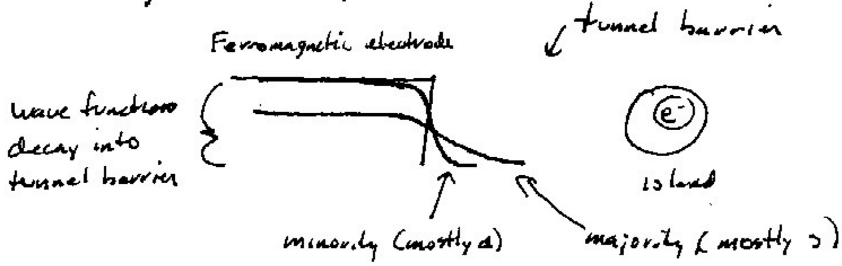
Ni: P_{eff} ~ -0.15 ± 0.1, -0.2 ± 0.1, -0.45 ± 0.05 in different samples

Band structure: Co, P < -0.59. Ni, P < -0.79.

What have we missed?

Assumed that when electrons flipped from ↓ to ↑ that the overall charge density stayed in the same place → the magnetic field did not cause charges to move and change the electric fields inside the device.

If you think about the real wavefunctions, this may not be a good assumption



When we apply a magnetic field, will move electrons from ↓ → ↑, d → s.

This will shift charge density a little farther into the tunnel junction

The charge motion will do work on an electron in the island - will increase its energy.

This will decrease the size of the energy shift in the ferromagnet relative to the island, and will make it look as if the effective polarization has a smaller magnitude

If the barrier quality varies from device to device in nanojunctions, the wavefunction tails might change and numbers will fluctuate.

If σ is the flipped charge density per unit area in one monolayer at the interface

$$\sigma = e a D_\downarrow \left(\tfrac{1}{2} g \mu_B H - \Delta E_F\right) \quad \text{(ignoring interactions)}$$
$$= e a g \mu_B H \frac{D_\uparrow D_\downarrow}{D_\downarrow + D_\uparrow}$$

relative shift of island energy due to work from the moving charge density

$$W \approx e \underbrace{4\pi\sigma}_{\text{change in E-field}} \Delta x$$

← movement of the center of mass of the charge toward the island.

$$\Rightarrow W \approx 4\pi e^2 a \,\Delta x \left(\frac{D_\uparrow D_\downarrow}{D_\uparrow + D_\downarrow}\right) g \mu_B H$$

putting in numbers, shift of interface charge density by only 0.01 Å can alter the measurements of P_{eff} by 20%.

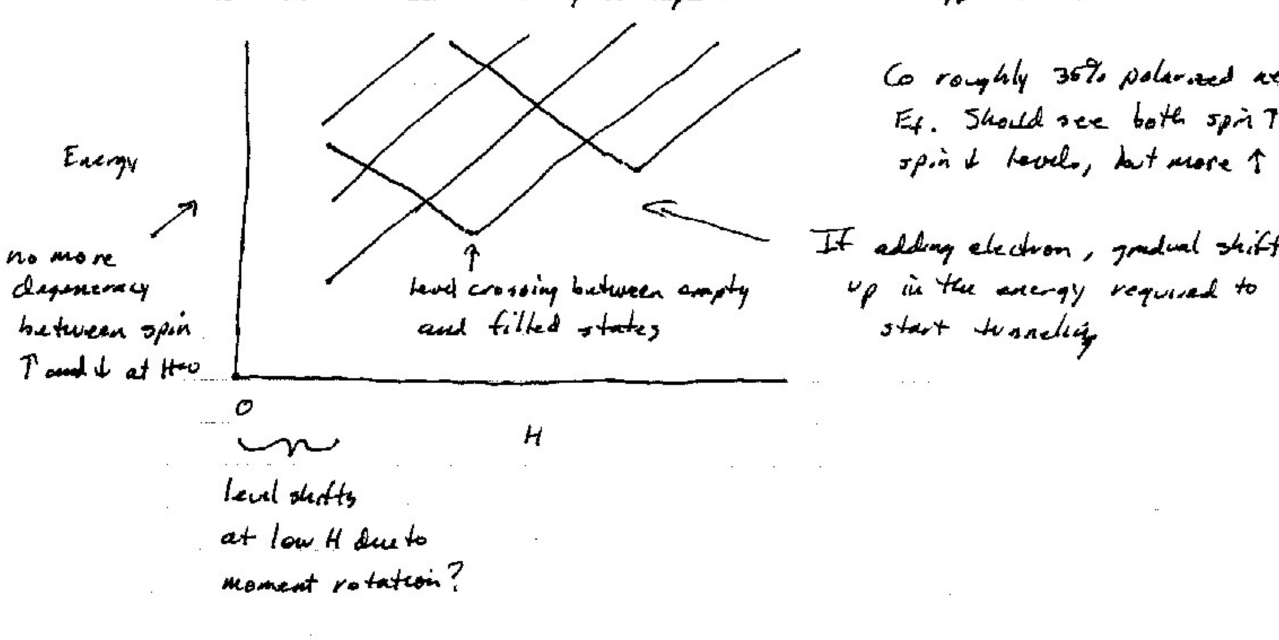
Very sensitive! The real wavefunctions often matter in magnetism!

Last topic: What are the real energy levels in a magnetic system small enough to resolve individual energy levels?

Ferromagnetic nanoparticles → eventually, single magnetic molecules

Band structure not appropriate anymore – will turn out that we really have to deal with true many-electron quantum states. Challenging, unsolved. But making some progress.

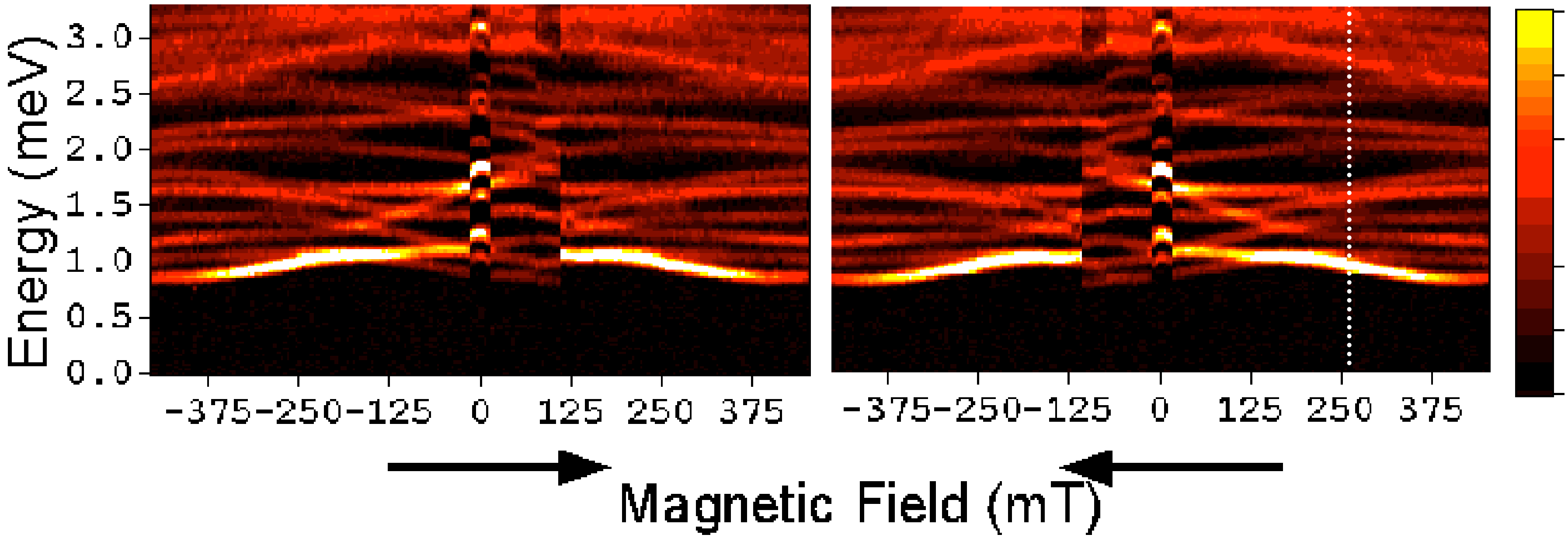
Straw man: What would you expect in Stoner-type model?



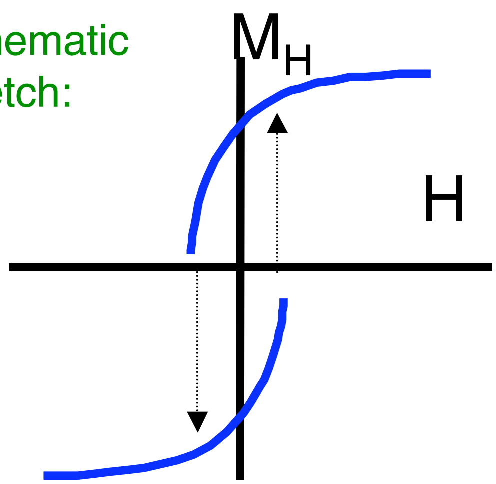
Co roughly 35% polarized near E_f. Should see both spin ↑ and spin ↓ levels, but more ↑

Ferromagnetic nanoparticles

Low field behavior

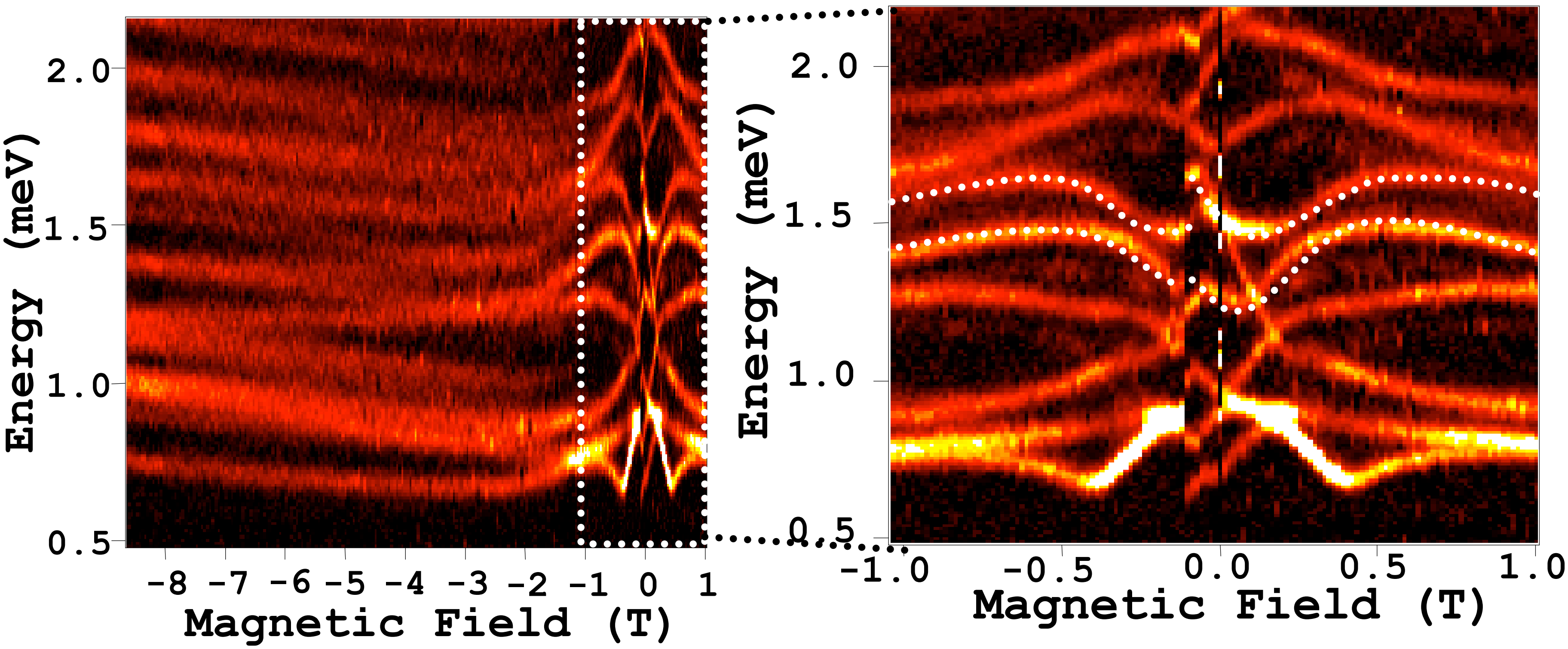


schematic sketch:



- No more simple Zeeman splitting -- internal magnetic field.
- Strong coupling between energy levels and magnetic moment.
- More levels than expected for particle in a box, due to the effects of spin waves.
- Detailed microscopic picture of the effects of exchange interactions and magnetic anisotropy.

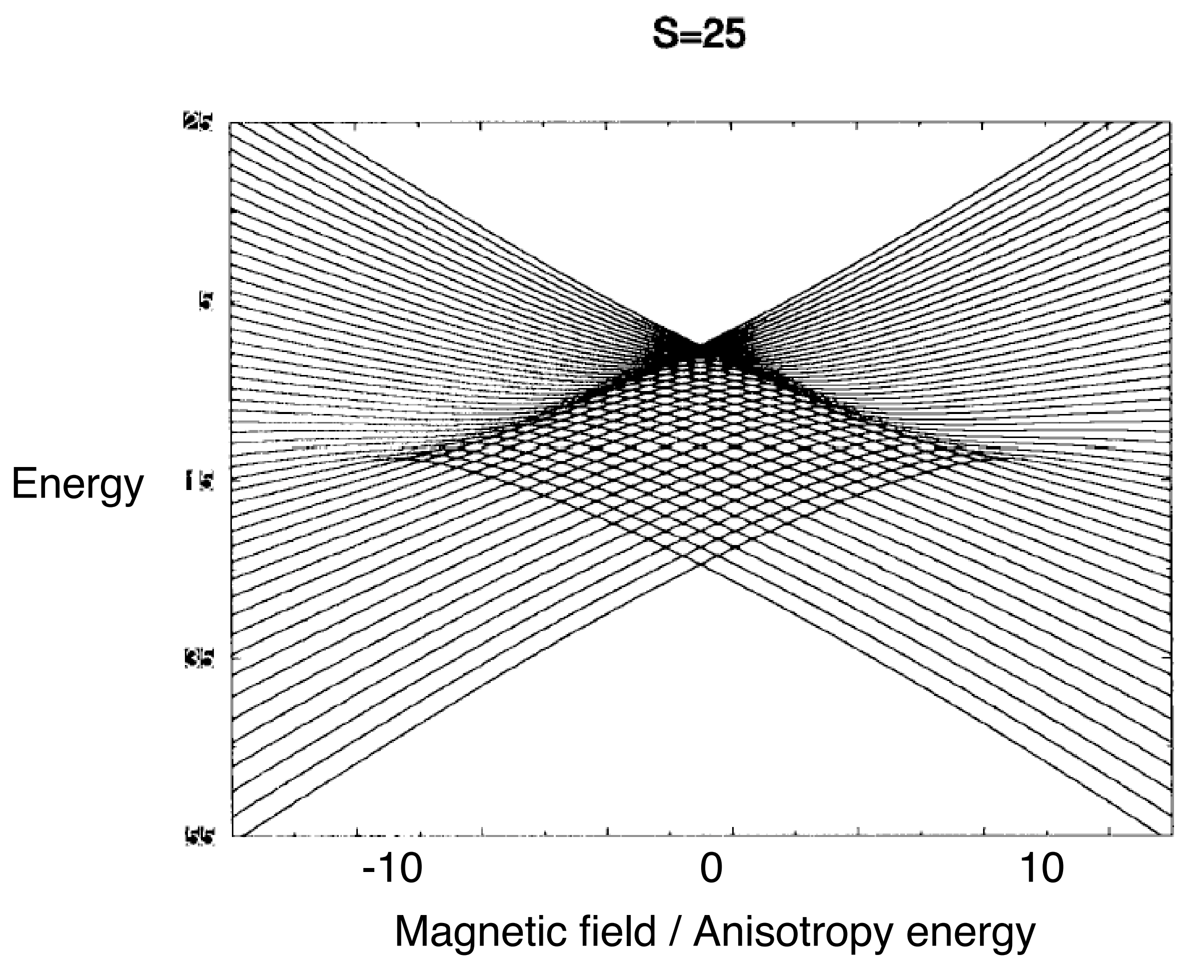
High field behavior



•Non-monotonic shifts of energy levels w

•One sign of slope at high field.

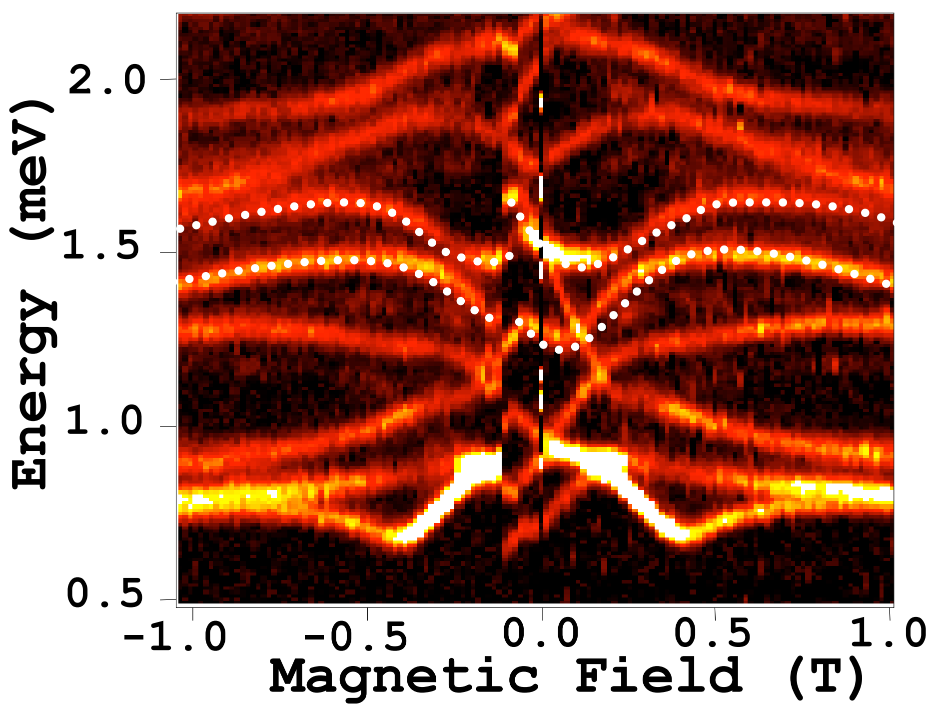
•Typical level spacing is ~0.2 meV -- much smaller than estimates based on independent-electron model.

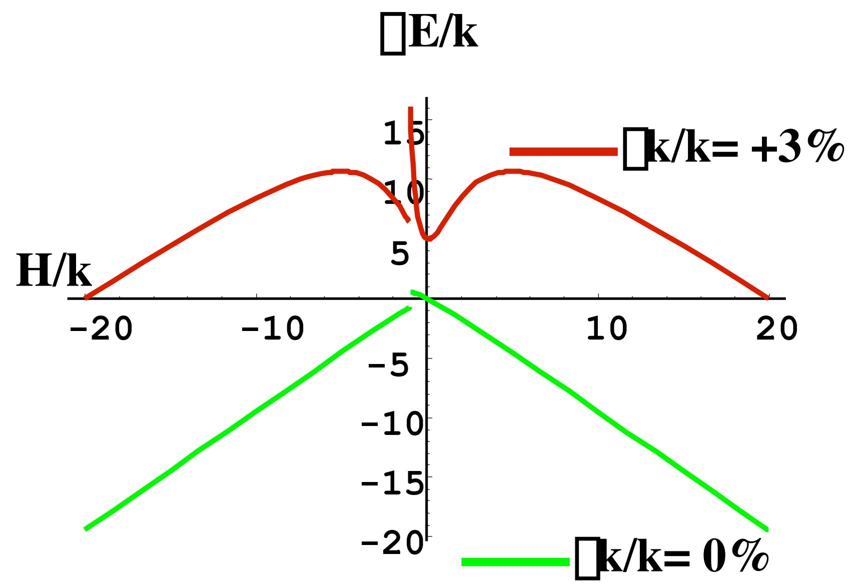

S=25
Energy
25
5
35
55
-10
0
10
Magnetic field / Anisotropy energy

Anisotropy varies from state to state

Explains:

- The different energy shifts for each tunneling resonance.
- The form of the non-monotonic dependence at low field.





□E =Energy required to add/ remove one ***e***

k = anisotropy constant

□**k/k** relative variation

Aspects of the measurements that we have not been able to explain within simple Stoner Models:

- Every state has a different field dependence at low field.
- Jumps both up and down in energy when magnet switches
- Very strong energy shifts as the moment rotates (stronger than can be explained by the changing demag field in the particle)
- Non-monotonic field dependence – lots of wiggles
- Too many levels – at high field they all shift one way

The true quantum-mechanical energy levels are correlated states of many electrons. Can we make progress thinking in a many-body framework?

Yes: 2 Strategies

(I) Big computer simulations: see Cehovin, Canali, MacDonald, PRB <u>66</u>, 094430 (2002)
cond-mat/0304427

(II) Effective Spin Hamiltonians: Canali & MacDonald PRL <u>85</u>, 5623 (2000); Solid State Comm. <u>119</u>, 253 (2001).
Kleff et al., PRB <u>64</u>, 220401 (2001).

In the limit of strong exchange interactions it takes a lot of energy to change the total spin for a fixed number of electrons. As a beginning model, can think of total S as a good quantum number (states with a given S are many-body states), and diagonalize Hamiltonian just within the $2S+1$ states of one spin multiplet.

Analogous to models of spin states in single-molecule magnets. (Wernsdorfer will tell you about them.)

<u>Many-body Hamiltonian</u>

$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{exch} + \mathcal{H}_{Zeeman} + \mathcal{H}_{anis}$

$\mathcal{H}_0$ = single-electron state energies $\sum \varepsilon_j c_{j\sigma}^{+} c_{j\sigma}$
$\mathcal{H}_{exch}$ = exchange energy $= -\frac{U}{2}\vec{S}\cdot\vec{S}$ (constant in one spin multiplet)

$\mathcal{H}_{Zeeman} = -\frac{1}{2} g\mu_B \vec{H}\cdot\vec{S} = -\frac{1}{2} g\mu_B H S_z$ or $-\frac{1}{2} g\mu_B |S|\ \vec{H}\cdot\hat{s}$

$\mathcal{H}_{anis}$ = ? = try simplest uniaxial example $= -k_a|S|\ \hat{s}\cdot\hat{d}$
$\hat{d}$ = easy axis direction

For a given spin multiplet made of a given set of single-electron states, it is easy to solve the Spin Hamiltonian

<show picture>

To compare to experimental data
(a) Solve for energies of n electrons in one spin multiplet S
(b) Solve for energies of n+1 electrons in $S\pm\frac{1}{2}$ multiplet.
(c) Measurement = $E(n+1) - E_g(n)$ ← ground state

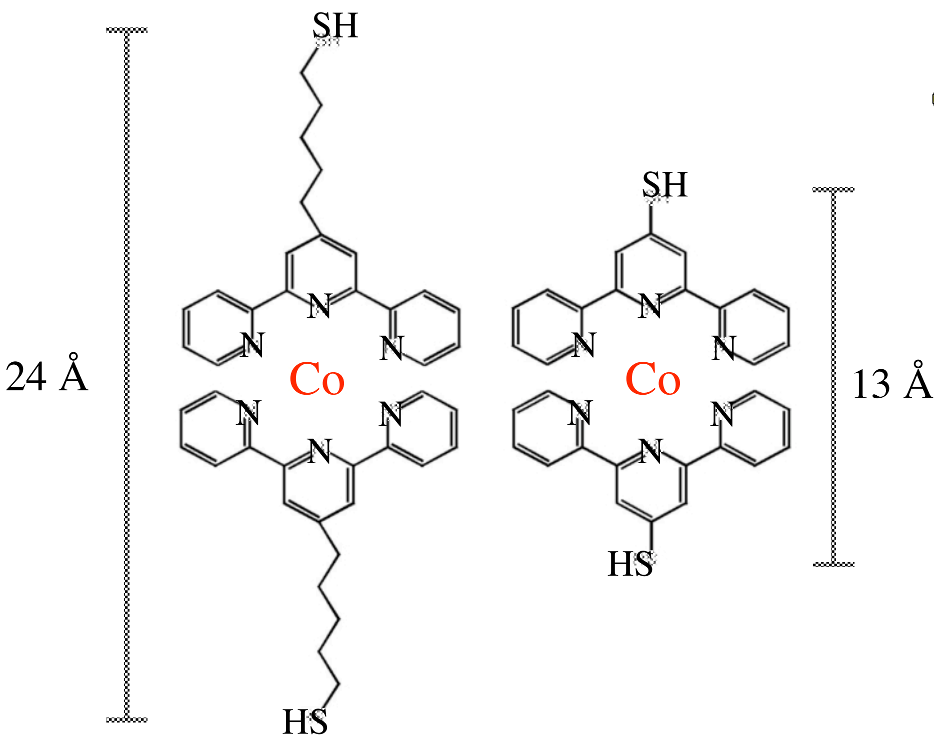
Problem: If effective Hamiltonian is $\mathcal{H}_{Zeeman} + \mathcal{H}_{anis} = -\frac{1}{2} g\mu_B |S|\vec{H}\cdot\hat{s} - k_a|S|\hat{s}\cdot\hat{d}$, then this just scales with $|S|$.
$E_g(n+1) - E_g(n) = \frac{1}{2} E_g(n)/S$ ← not what we see.

If we assume that the anisotropy term can vary between spin multiplets whenever we change electron number, single-electron occupations, etc., we can explain both the non-monotonic functional forms and the differences in the field dependence of different states.

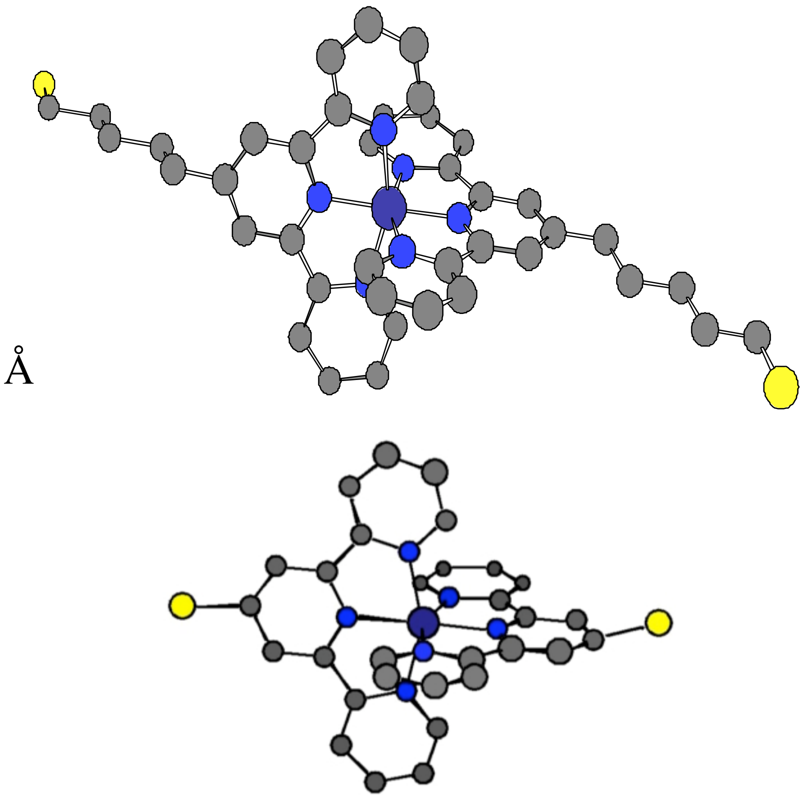
experimentally, it looks like adding 1 electron to 1000 can change the total anisotropy by 2-3%. ← unexpectedly large.

Numerical simulations provide support for this picture

Designer molecules for making transistors



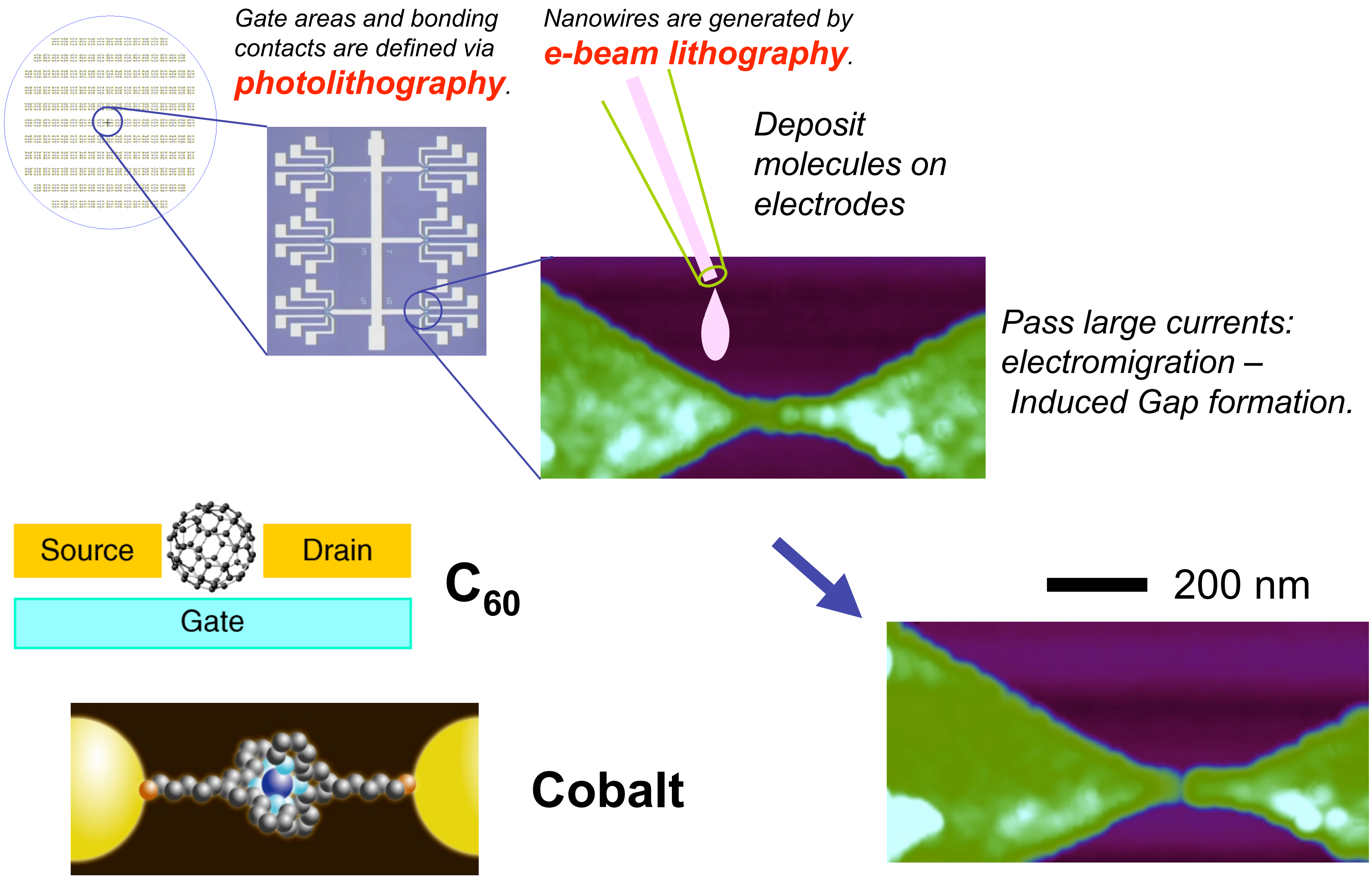
$Co^{2+}(tpy(CH_2)_5SH)_2$ $Co^{2+}(tpySH)_2$



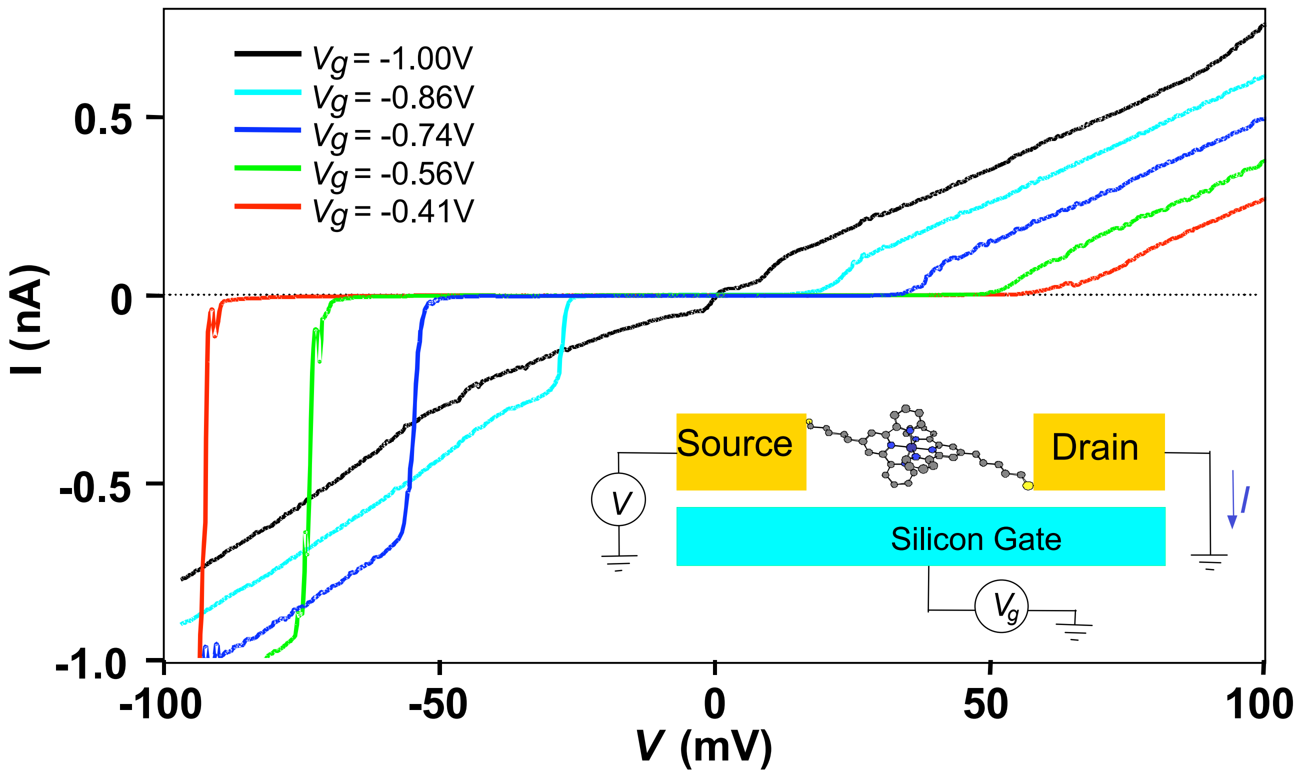
- Longer molecule: Coulomb-blockade effects.
- Shorter molecule: Kondo effect.

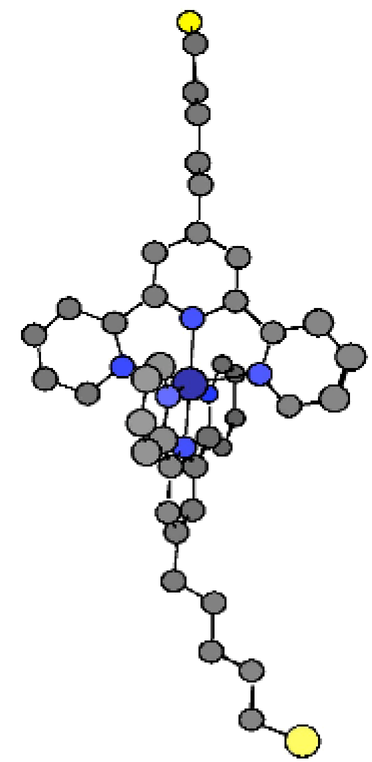
Related measurements, different molecules : H. Park (Harvard)

Creating Single Molecule Transistors



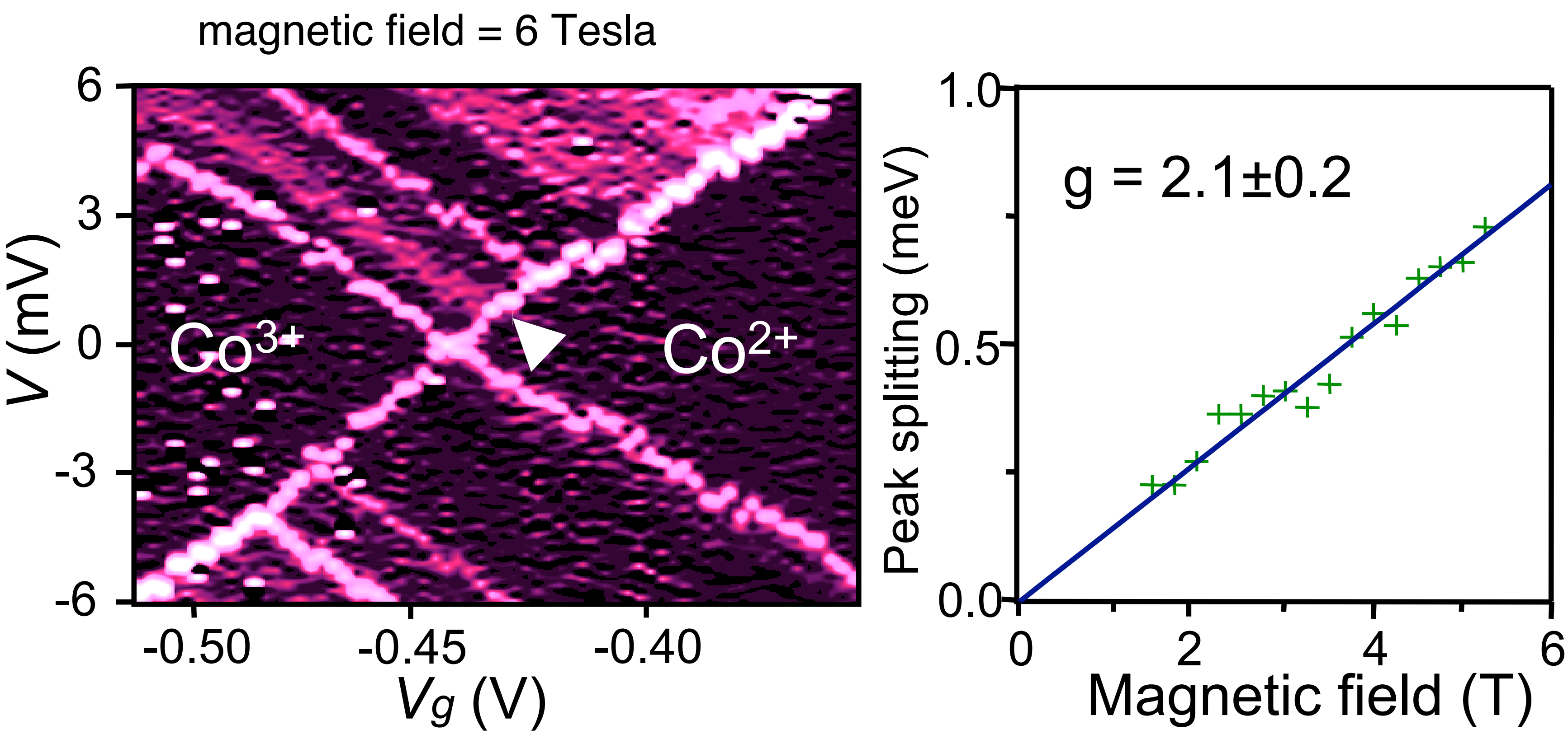
Coulomb-Blockade Effects in the Longer Molecule





- High resistance (> megaOhms) - single electron charging.
- Coulomb blockade > 150 meV (unstable beyond this).

Zeeman Splitting in a Magnetic Field



S=1/2 for Co^{2+}, S=0 for Co^{3+}.

Summary

For a fixed number of electrons on a magnetic island, applying a magnetic field can shift the Fermi energy

At first one might think that this is simply a function of different densities of states at the Fermi level for spin ↑ and ↓.
Wrong: Also affected by exchange interactions and redistribution of charge density at magnetic interfaces.

Magnetic nanoparticles: small enough to resolve individual quantum states.
Not successful in understanding these within standard Stoner Model pictures. Probably need many-body approach. Challenging problem. Effective spin Hamiltonians are very similar to models of single-molecule magnets (but with larger spins)

Measurements on individual magnetic molecules are within reach.

References: Coulomb Blockade and Tunneling in Small Magnets

General reference on Coulomb blockade: M. Tinkham, Superconductivity, 2nd Edition (McGraw-Hill, 1996) sections 7.4-7.5

K. Ono et al., Spin polarization and magneto-Coulomb oscillations in ferromagnetic single electron devices, J. Phys. Soc. Jpn. 67, 2852 (1998).

A. H. MacDonald, Spintronic Spin Accumulation and Thermodynamics, in Proceedings of the XVI Sitges Conference on Statistical Mechanics (Springer-Verlag, Berlin, 2000). p. 211

M. M. Deshmukh et al., Using single quantum states as spin filters to study spin polarization in ferromagnets, PRL 89, 266803 (2002)

M. M. Deshmukh et al., Magnetic anisotropy variations and nonequilibrium tunneling in a cobalt nanoparticle, PRL 87, 226801 (2001)

C. M. Canali and A. H. MacDonald, Theory of tunneling spectroscopy in ferromagnetic nanoparticles, PRL 85, 5623 (2000).

A. H MacDonald and C. M. Canali, Quantum description of ferromagnetic metal nanoparticles, Solid State Comm. 119, 253 (2001)

S. Kleff et al., Model for ferromagnetic nanograins with discrete electronic states PRB 64, 220401 (2001)

A Cehovin et al., Magnetization orientation dependence of the quasiparticle spectrum and hysteresis in ferromagnetic metal nanoparticles, PRB 66, 094430 (2002)

A Cehovin et al., Elementary excitations of ferromagnetic metal nanoparticles, cond-mat/0304427 (2003)