

Interacting Electrons in Metal Nanoparticles

Expectation from theory: the "Universal Hamiltonian"

ref: Glazman lectures; I.L. Kurland et al. PRB 62, 14886 (2000);
I.L. Aleiner et al. Physics Reports 358, 309 (2002)

$$H_{\text{int}} = E_c \hat{N}^2 - J (\hat{S})^2 - \lambda_{\text{pbc}} \hat{T}^\dagger \hat{T} \quad (\text{for small magnetic fields})$$

charging exchange pairing

where \hat{N} is the electron number operator $= \sum_{n,s} d_{ns}^\dagger d_{ns}$
 \hat{S} is the total spin operator $\frac{1}{2} \sum_{n,s,s'} d_{ns}^\dagger \vec{\sigma}_{ss'} d_{ns'}$
 \hat{T} is the pair annihilation operator $\sum_n d_{n\uparrow}^\dagger d_{n\downarrow}^\dagger$

The next-order terms in the Hamiltonian all give corrections of order $\frac{1}{g} = \frac{\delta}{E_{\text{th}}}$, where E_{th} is the Thouless energy and δ is the mean level spacing. These corrections are expected to be negligible in metal particles that are not too small on the scale of the Fermi wavelength ($g \approx 50$ for my particles)

Important point: E_c , J , and λ_{pbc} have no state index. They should not vary among the delocalized orbital states in a given quantum dot.

This is a great simplification.

For states with a fixed number of electrons, don't worry about E_c .

For repulsive e-e interactions, $J > 0$. λ_{pbc} renormalizes to something small.

For attractive effective e-e interactions, $\lambda_{\text{pbc}} > 0$

Interesting physical regimes:

1) $J > 0$, $J < \delta$. no magnetism in the macroscopic limit, but a possibility of non-zero spin states in quantum dots

3) $J > 0$, $J > \delta$. Ferromagnetism

2) $\lambda_{\text{pbc}} > 0$ ($J < 0$). Pair-correlated ground state.

will discuss this one last

Note: The "Universal Hamiltonian" is not completely universal. For instance, it is not straightforward to incorporate spin-orbit interactions together with electron-electron interactions

1) Weak exchange interactions and non-zero spin states.

When will a quantum dot become magnetic?

$S \neq 0$ for an even number of electrons, $S \neq \frac{1}{2}$ for odd.

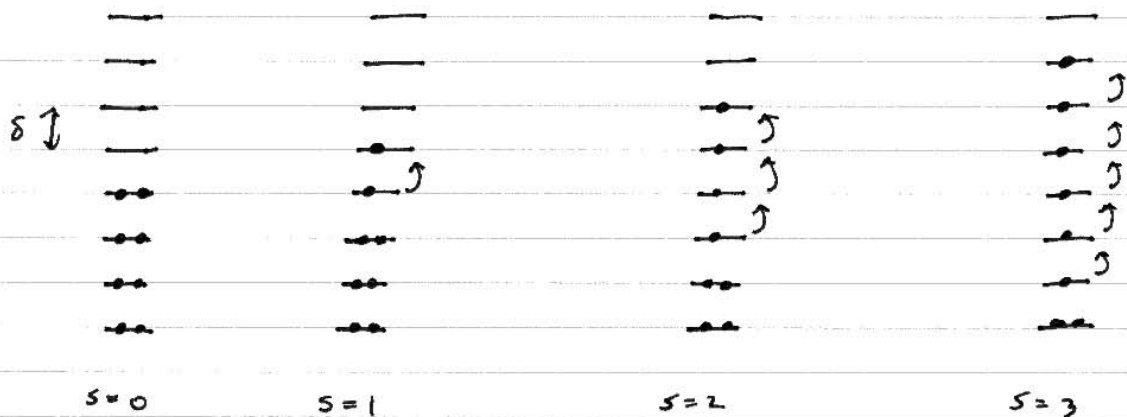
$$H = \sum_{\alpha, \sigma} \epsilon_{\alpha} d_{\alpha\sigma}^{\dagger} d_{\alpha\sigma} - J (\hat{S})^2$$

The answer to this question lies in competition between kinetic energy and exchange energy.

For Bulk Systems: Stoner Model

Assume for simplicity equal level spacings, even # of electrons

How do the kinetic and exchange energies for non-zero spin states compare to $S=0$?



extra KE = δ

exchange = $-J (\hat{S}=1)^2$

extra KE = $\delta + 3\delta = 4\delta$

exchange = $-J (\hat{S}=2)^2$

extra KE = $4\delta + 5\delta = 9\delta$

exchange = $-J (\hat{S}=3)^2$

In the bulk limit, the energy of the state with spin S ($\gg 1$) is

$$E(S) = \delta S^2 - J S^2 = (\delta - J) S^2$$

so if $J < \delta$ by this argument expect $S=0$ state

if $J > \delta$ expect the maximal spin state

(this is the Stoner instability)

For quantum dots, it is necessary to consider the possibility of small spin states, $S=1, 2, \dots$, and not only $S=0$ and large extensive values of the spin, because small non-zero spin states have experimental consequences.

The standard Stoner Model result is changed for at least 2 reasons

(a) I cheated on the calculation on the previous page

If $E(S) = \delta S^2 - J(\vec{S})^2$, then actually,

$$E(S) = \delta S^2 - JS(S+1)$$

$E(1)$ will be less than $E(0)$ when $\delta - 2J < 0$, or $J > \frac{\delta}{2}$, not δ

→ magnetic states of small spin can be stabilized for weaker interactions than the Stoner criterion $J = \delta$.

(If S were continuous, the minimum energy would be achieved by $S = \frac{J}{2(\delta - J)}$. At the Stoner limit, the ground state spin goes to infinity in the model, but it can assume non-zero values already for $J > \delta/2$.)

(b) In real nanoparticles, the level spacing is non-uniform. The levels are not completely random - there is some level repulsion as predicted by random matrix theories. But some levels will be closer together than others.

If the first excited state is less than the average level spacing δ above the ground state, then there is less kinetic energy cost to make a non-zero spin state.

references:

P. W. Brown et al., Phys Rev B 60, R13977 (1999)

H. U. Baranger et al., Phys Rev B 61, R2425 (2000)

G. Usaj and H. U. Baranger, Phys Rev B 67, 121308 (2003)

In GaAs lateral quantum dots, there is evidence for non-minimal spin states from several different experiments.

(from thesis of Josh Folk, Stanford)

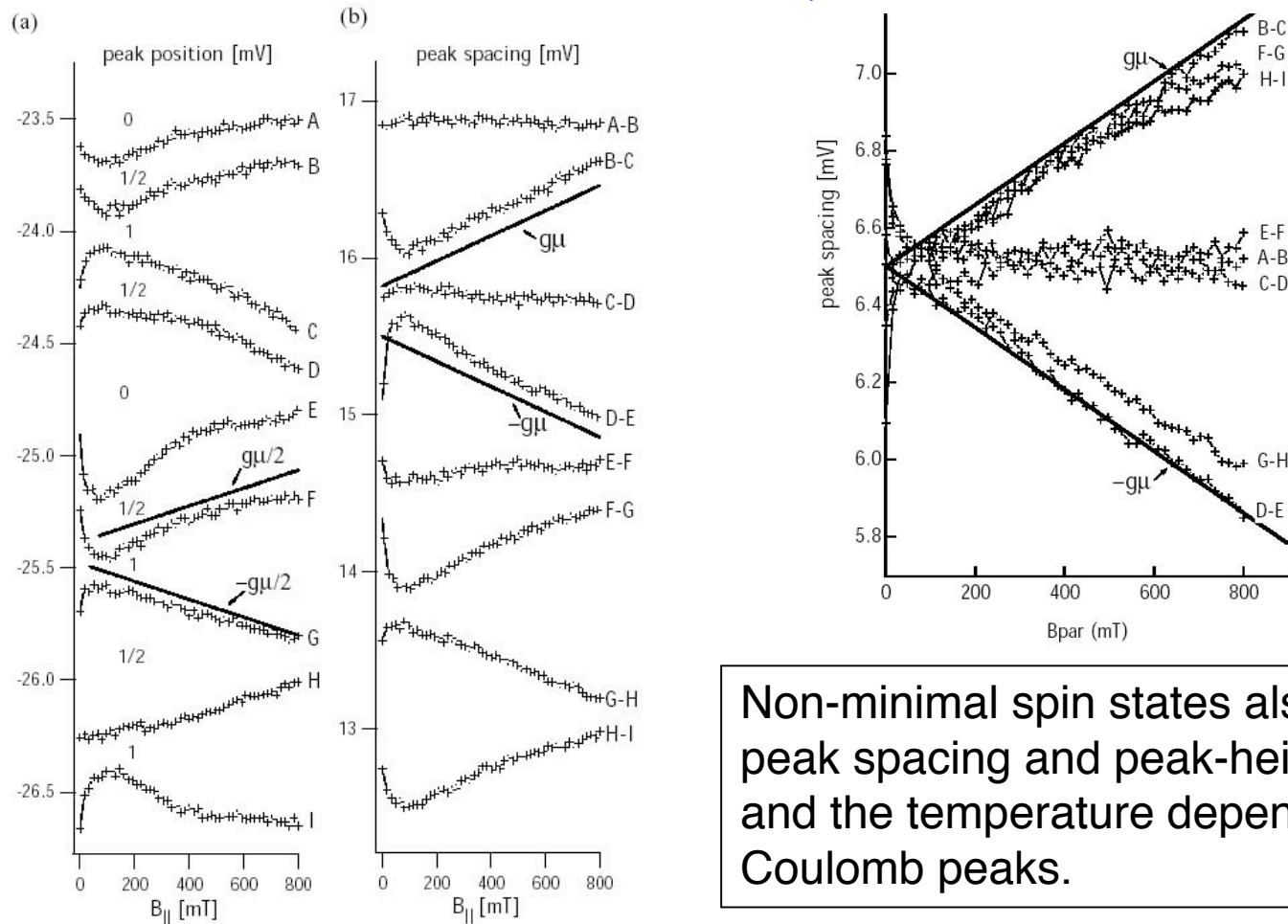
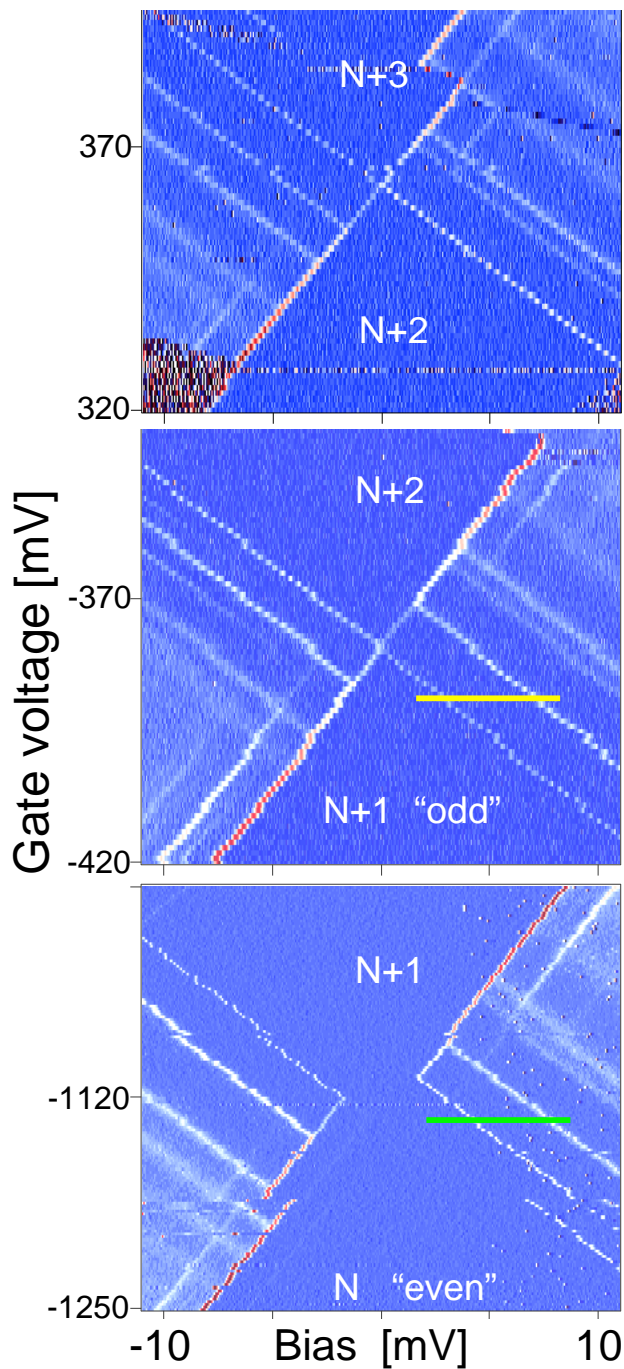
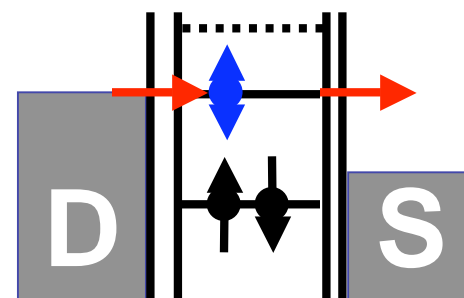
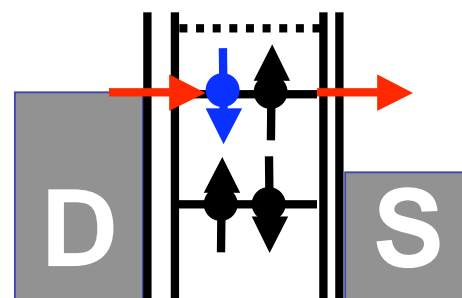
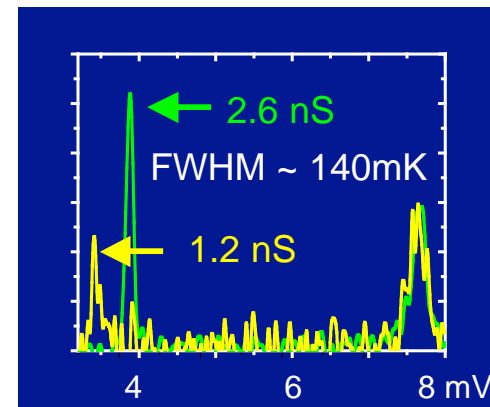
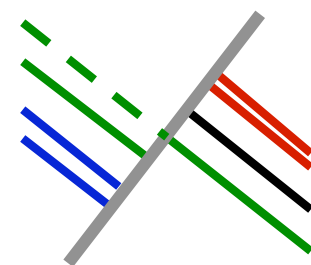
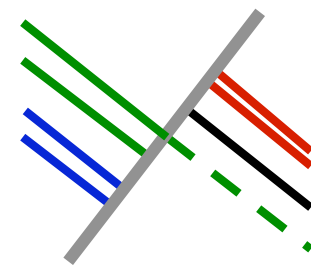
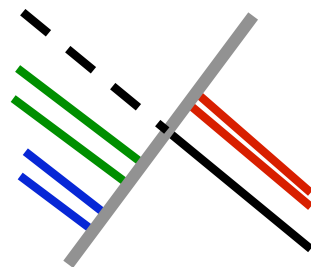


Figure 4.2: Peak positions (a) and spacings (b) extracted from the low in-plane field data shown in Fig. 4.1. Motions are consistent with $E_S = \pm \frac{1}{2}g\mu_B B$ for the peak positions and $E_S = 0, \pm g\mu_B B$ for the spacings as expected. The diamagnetic shift extracted in Fig. 4.1(b) is removed from all data shown here.



Au nanoparticle
(F. Kuemmeth and K. Bolotin, Cornell)



Spin-degenerate levels are filled as in non-interacting system

Probable explanation: For GaAs, $J/\hbar \sim 0.3$, large enough to produce a significant fraction of ground states with non-minimal spins.
 For Al and Au, $J/\hbar < 0.1$, too small.

1 H																		2 He
3 Li 0.23	4 Be 0.06- 0.08											5 B	6 C	7 N	8 O	9 F	10 Ne	
11 Na 0.22	12 Mg 0.27- 0.32																	
numbers are J/\hbar .																		
19 K 0.29- 0.30	20 Ca 0.16	21 Sc 0.59- 0.84	22 Ti 0.26- 0.30	23 V 0.57- 0.63	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu -0.03- 0.09	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	
37 Rb 0.30	38 Sr 0.00- 0.15	39 Y 0.53	40 Zr 0.16- 0.20	41 Nb 0.39- 0.42	42 Mo 0.13- 0.19	43 Tc 0.24	44 Ru 0.25	45 Rh 0.41- 0.44	46 Pd 0.84- 0.89	47 Ag 0.02- 0.07	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	
55 Cs 0.18- 0.36	56 Ba 0.22	57 La 0.52	72 Hf 0.18- 0.20	73 Ta 0.36	74 W 0.10	75 Re 0.15	76 Os 0.17	77 Ir 0.29	78 Pt 0.59- 0.72	79 Au 0.06	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	
87 Fr	88 Ra	89 Ac	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	

Other metals span a wide range of different exchange strengths, and remain to be explored.

Gorokhov and Brouwer, PRB **69**, 155417 (2004).

2) Superconducting Pairing in Quantum Dots

references:

M Tinkham, *Intro to Superconductivity*, 2nd Ed.
Ch. 7

J. von Delft & D.C. Ralph *Phys. Rep.* 345, 61 (2001).

Outline:

- What does "superconductivity" mean if the sample contains a fixed number of electrons?
- μm -sized samples
- nm -sized samples

Superconductivity with a fixed number of electrons

In BCS theory - the ground state is written as a superposition of states with different numbers of electrons:

$$| \Psi_0 \rangle = \prod_i (u_i + v_i d_{i\uparrow}^\dagger d_{i\downarrow}^\dagger) | \text{vac} \rangle$$

order parameter $\Delta_{\text{BCS}} = \lambda(\delta) \sum_i \langle d_{i\downarrow} d_{i\uparrow} \rangle = 0$ for fixed # electrons

The superconducting phase is conjugate to the electron number. If the electron number is fixed, the phase is completely uncertain

Problem? In reality, no. BCS theory assumes a grand canonical ensemble for calculational convenience. But the BCS pairing Hamiltonian can also be solved exactly using a canonical ensemble (fixed number of electrons). - R. W Richardson 1960's-70's

Attractive e-e interactions still lead to a pair-correlated ground state, with a gap to excitations, just like ordinary BCS theory.
(important for many years in nuclear physics)

Can still define an order parameter

$\Delta_{\text{can}}^2 = (\lambda\delta)^2 \sum_i (\langle d_{i\uparrow}^\dagger d_{i\downarrow}^\dagger d_{j\downarrow} d_{j\uparrow} \rangle - \langle d_{i\uparrow}^\dagger d_{j\uparrow} \rangle \langle d_{i\downarrow}^\dagger d_{j\downarrow} \rangle)$
related to the probability that pair states are occupied, beyond the probability expected randomly. (reduces to Δ_{BCS} in bulk limit)

Cartoon Picture of Superconducting Ground state

$$H = \sum_{\alpha, \sigma} \epsilon_{\alpha} d_{\alpha\sigma}^{\dagger} d_{\alpha\sigma} - \underbrace{|\lambda_{\alpha\beta}| \sum_{\alpha\beta} d_{\alpha\uparrow}^{\dagger} d_{\alpha\downarrow}^{\dagger} d_{\beta\downarrow} d_{\beta\uparrow}}_{V_{\text{pairing}}}$$

V_{pairing} - a pair of electrons is scattered from orbital state β to α , summed over all states

The minus sign assumes attractive e-e interactions.

We ignore the E_c term for fixed n , assume exchange term renormalizes to zero.

Diagonal terms $\alpha = \beta$ will sum to a constant as long as we don't break pairs, so consider only $\alpha \neq \beta$ terms in computing V_{pairing}

Suppose you have just the non-interacting electron ground state - compute the energy contribution from V_{pairing}

$$\left(\begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \uparrow\downarrow \\ \uparrow\downarrow \\ \uparrow\downarrow \end{array} \right) \left(-|\lambda_{\alpha\beta}| \sum_{\alpha \neq \beta} d_{\alpha\uparrow}^{\dagger} d_{\alpha\downarrow}^{\dagger} d_{\beta\downarrow} d_{\beta\uparrow} \right) \left(\begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \\ \\ \end{array} \right) = 0$$

If the interaction term scatters a pair from a filled state to an empty state, the result is orthogonal to the ground state

\Rightarrow each matrix element in the sum is zero

$\Rightarrow V_{\text{pairing}}$ provides no energy benefit to the non-interacting ground state (the expectation value of this energy is zero).

V_{pairing} could lower the energy of a quantum state if the orbital levels near the Fermi energy were partially occupied by pairs. Then if V_{pairing} shifted one pair, the result would not be orthogonal to the initial state. This partial occupancy would cost kinetic energy, but if the energy gain from V_{pairing} were bigger, then this is favorable.

This balance of energies will favor partial occupation of pair states within Δ of E_f .

The superconducting ground state can be viewed as a linear superposition of Slater determinant states

$$|\Psi_G\rangle = c_1 \begin{array}{c} \text{---} \\ \text{---} \\ \uparrow\downarrow \\ \uparrow\downarrow \\ \uparrow\downarrow \end{array} + c_2 \begin{array}{c} \text{---} \\ \text{---} \\ \uparrow\downarrow \\ \uparrow\downarrow \\ \uparrow\downarrow \end{array} + c_3 \begin{array}{c} \text{---} \\ \text{---} \\ \uparrow\downarrow \\ \text{---} \\ \uparrow\downarrow \end{array} + c_4 \begin{array}{c} \text{---} \\ \text{---} \\ \uparrow\downarrow \\ \uparrow\downarrow \\ \uparrow\downarrow \end{array} + c_5 \begin{array}{c} \text{---} \\ \text{---} \\ \uparrow\downarrow \\ \text{---} \\ \uparrow\downarrow \end{array} + \dots$$

Now $\langle \Psi_G | V_{\text{pairing}} | \Psi_G \rangle \neq 0$, have opened up "phase space" for pairing

typical range of pairing correlations is shown in figure.

How to detect this pair-correlated state?

- No Meissner effect for nanoscale particle - smaller than the penetration depth
- No measurable zero resistance state - we're using large- R tunnel junctions.

But there is still a superconducting gap - extra energy to add an electron to the system. If you try to put a single electron in an orbital state near E_F , this blocks pair scattering to that state and costs the entire system a minimum amount of extra energy $\sim \Delta$.

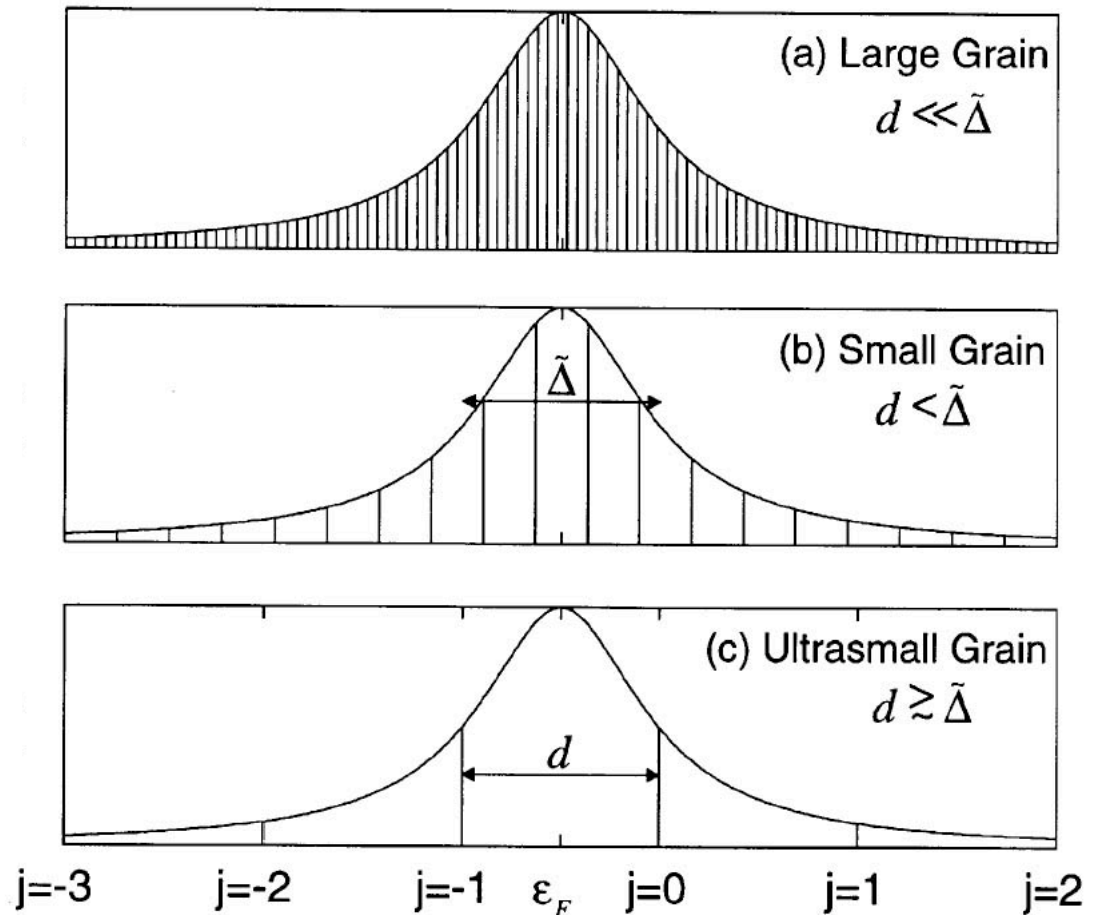
This extra energy for having an unpaired electron is measurable even in micron-sized superconducting islands.

Enhancement of pair correlations about the Fermi level.

Probability of partial pair occupancy in the superconducting ground state

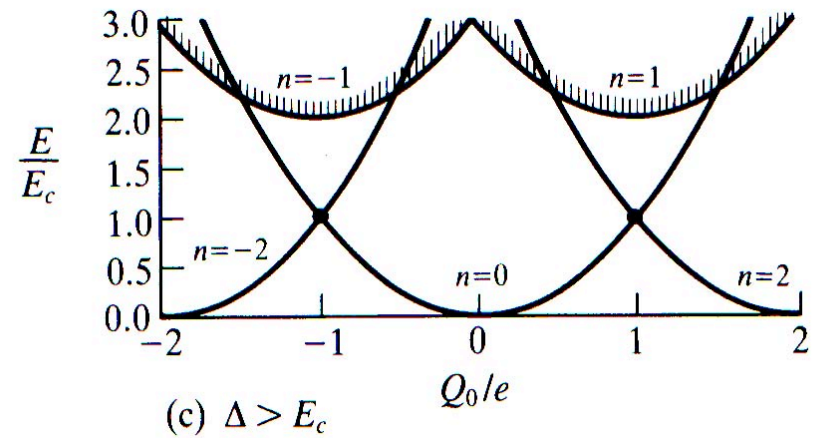
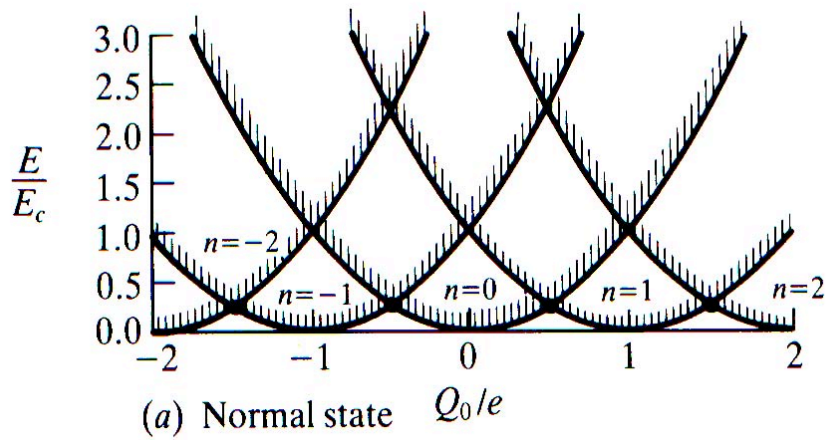
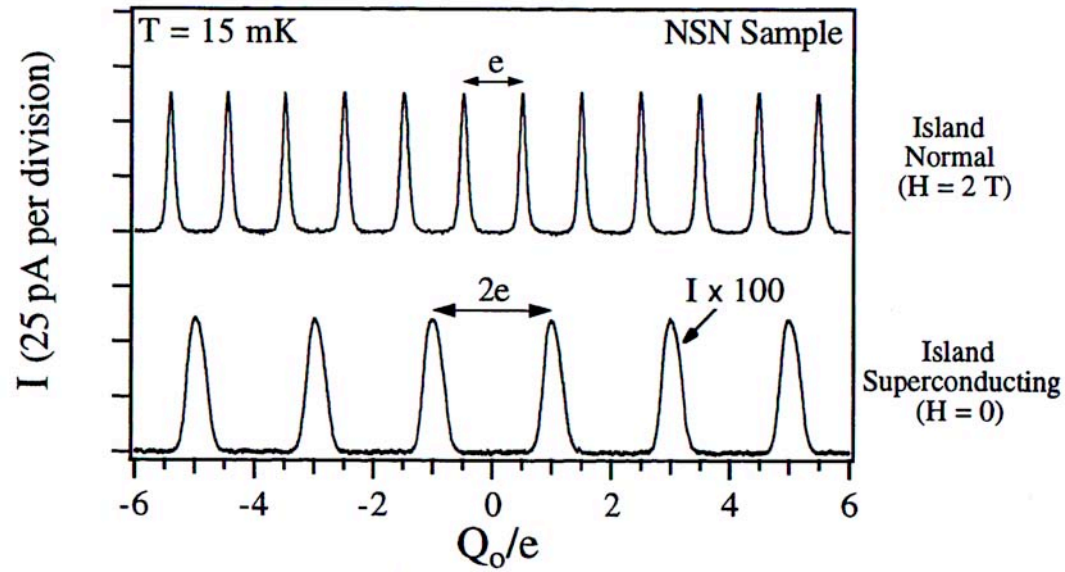
$$\left\langle a_{i\uparrow}^\dagger a_{i\downarrow}^\dagger a_{i\downarrow} a_{i\uparrow} \right\rangle \left\langle a_{i\downarrow} a_{i\uparrow} a_{i\uparrow}^\dagger a_{i\downarrow}^\dagger \right\rangle$$

(prob. full)x(prob. empty)



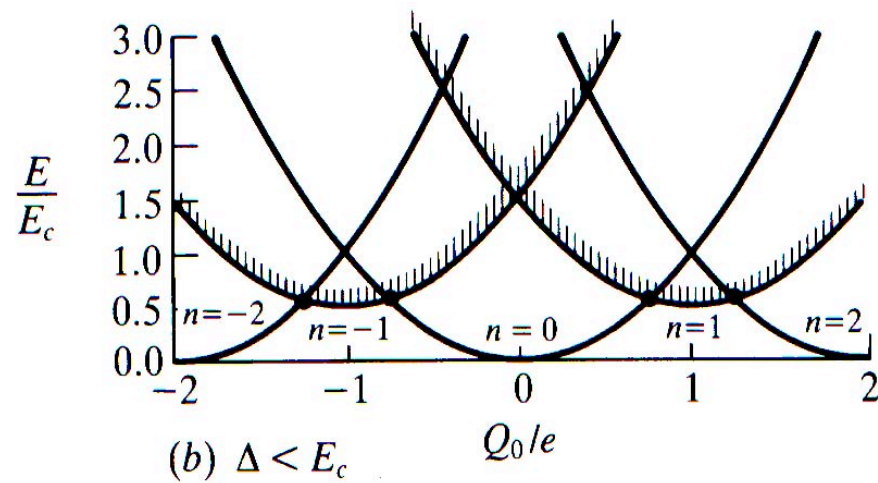
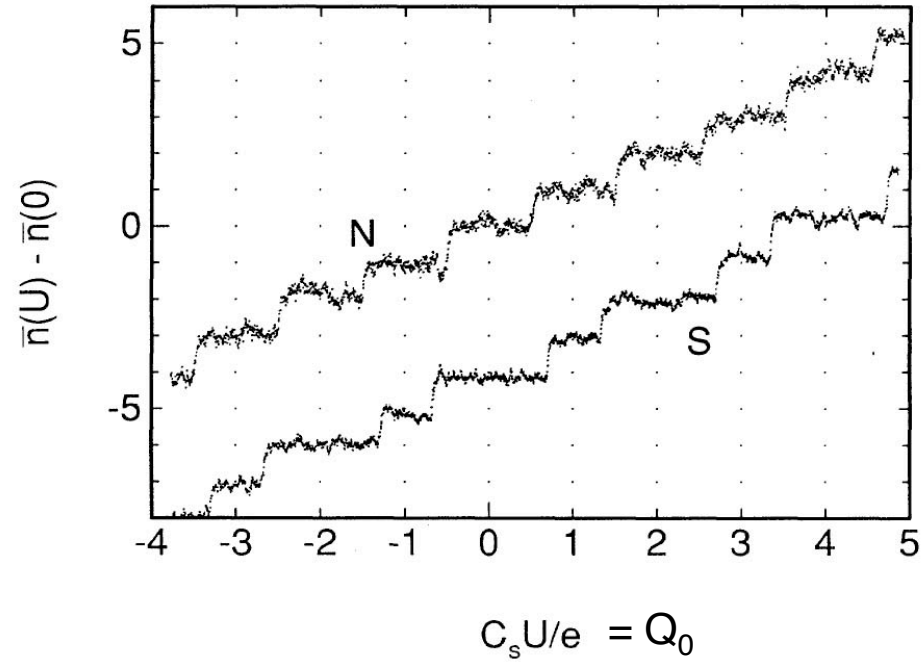
Micron-scale aluminum island

J. Hergenrother



Direct measurements of average charge on an aluminum island

P. Lafarge et al.
PRL **70**, 994 (1993)



How small can you make a metal particle and still have it retain these pair correlations? (Anderson, 1959)

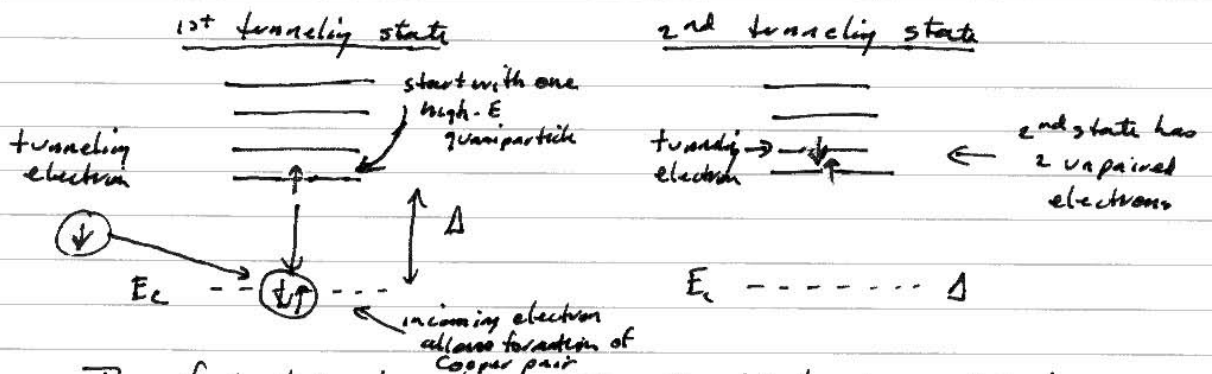
? superconducting coherence length $\xi_0 = \frac{\hbar v_F}{2\Delta} \sim 2000 \text{ nm}$ in Al

Is superconductivity possible on the nanometer scale, and how would you tell?

→ on nanoscale $E_c \sim 50 \text{ meV} \gg \Delta \sim 0.2 \text{ meV}$, so hard to see effects of Δ on the charge states

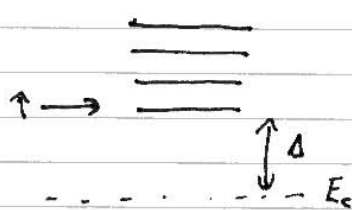
But, can still see effects of the pairing correlations in the excited states for tunneling:

The odd-to-even case is most dramatic:



The first two tunneling states should be separated in energy by $\sim 2\Delta$

Even-to-odd case:

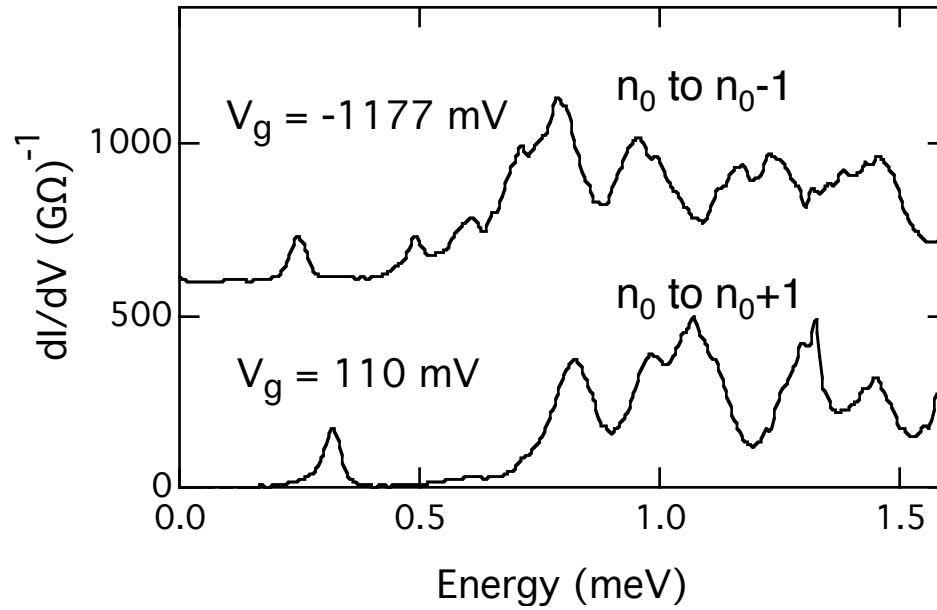


The incoming electron must enter as an unpaired quasiparticle. No gaps with the measured spectrum, but should expect the tunneling threshold to go down if Δ is reduced by applying a magnetic field.

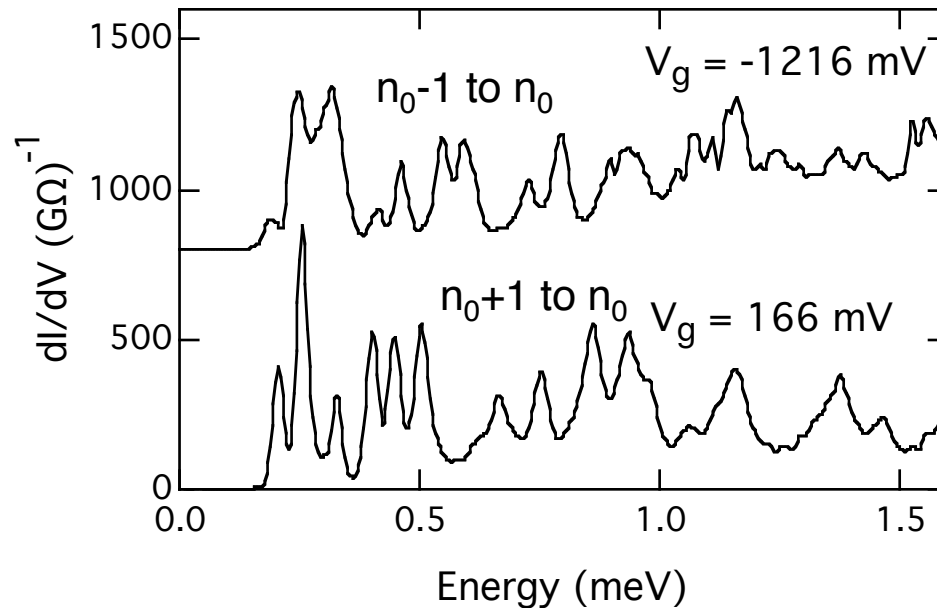
If you destroy pairing correlations with B, in the odd-to-even case the tunneling threshold will go up, because pairing assists tunneling in this case.

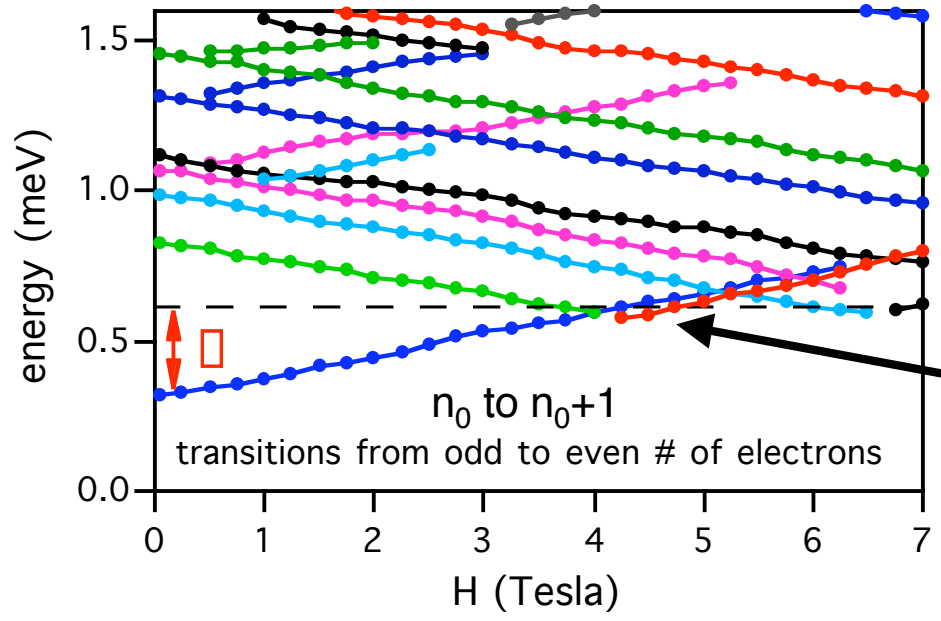
Same Al nanoparticle.
Charge state changed
using a gate electrode.

Odd to even transitions

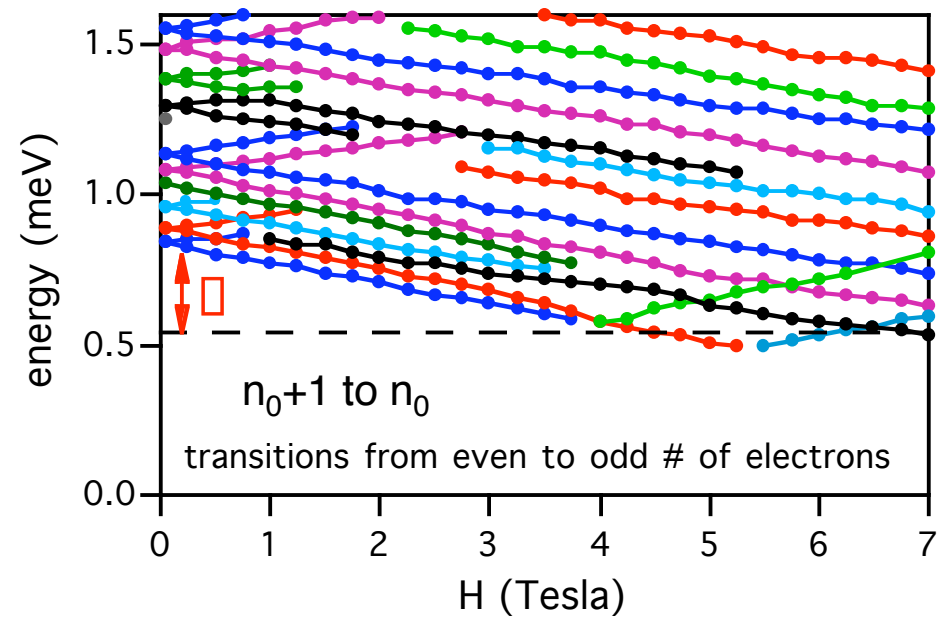


Even to odd transitions





Note that transitions are continuous kinks, not discontinuities.

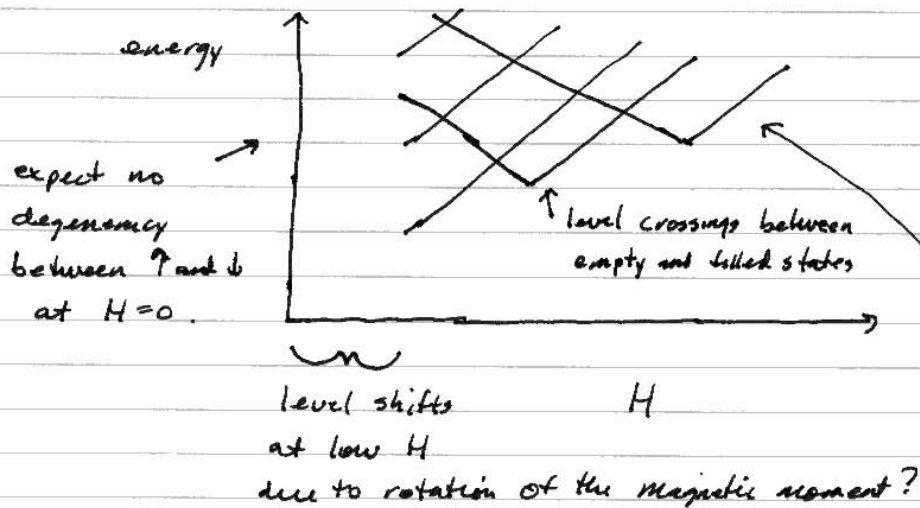


3) Strong Exchange ($J > \delta$, Ferromagnetism) and Magnetic Anisotropy Forces

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

This will turn out to be a hard problem, harder than the other examples. It looks like the usual pictures of band structure are not appropriate anymore - and we really have to deal with the complications of the full many-electron quantum states. Certainly exchange and spin-orbit interactions are intertwined in a non-trivial way. Unsolved, but making some progress.

Begin with a "straw man" argument. If the Stoner Model were an accurate description of a magnetic nanoparticle, what would the tunneling spectrum look like?



Co roughly 75% polarized near E_f . Should see both minority and majority levels, but more minority. (moving up for electron addition)

If adding electrons, a gradual shift up in the energy required to start tunneling. (This is the analog of the effect from the last page.)

(go to data)

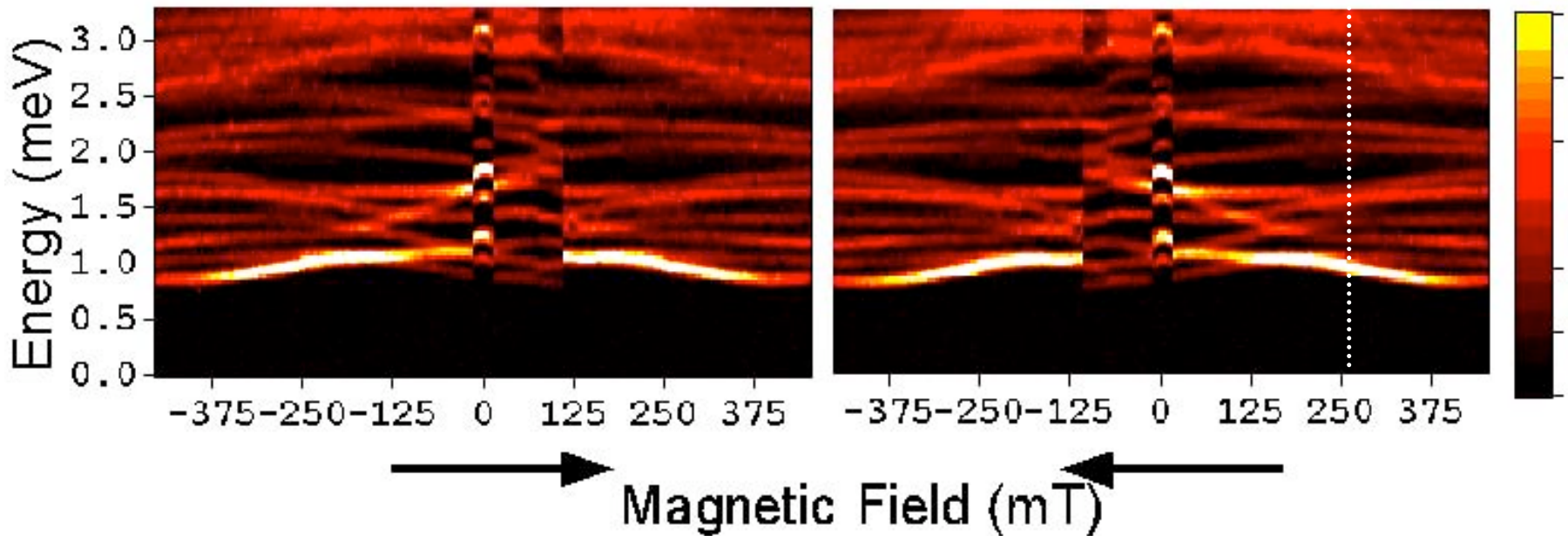
references:

S Guéron et al. Phys Rev. Lett. **83**, 4148 (1999).

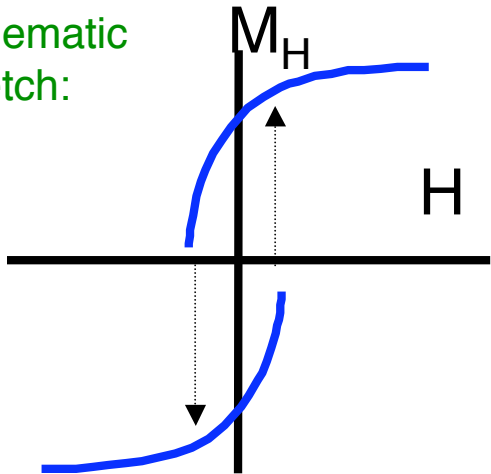
M. Deshmukh et al. Phys Rev. Lett. **87**, 226801 (2001).

Ferromagnetic nanoparticles

Low field behavior

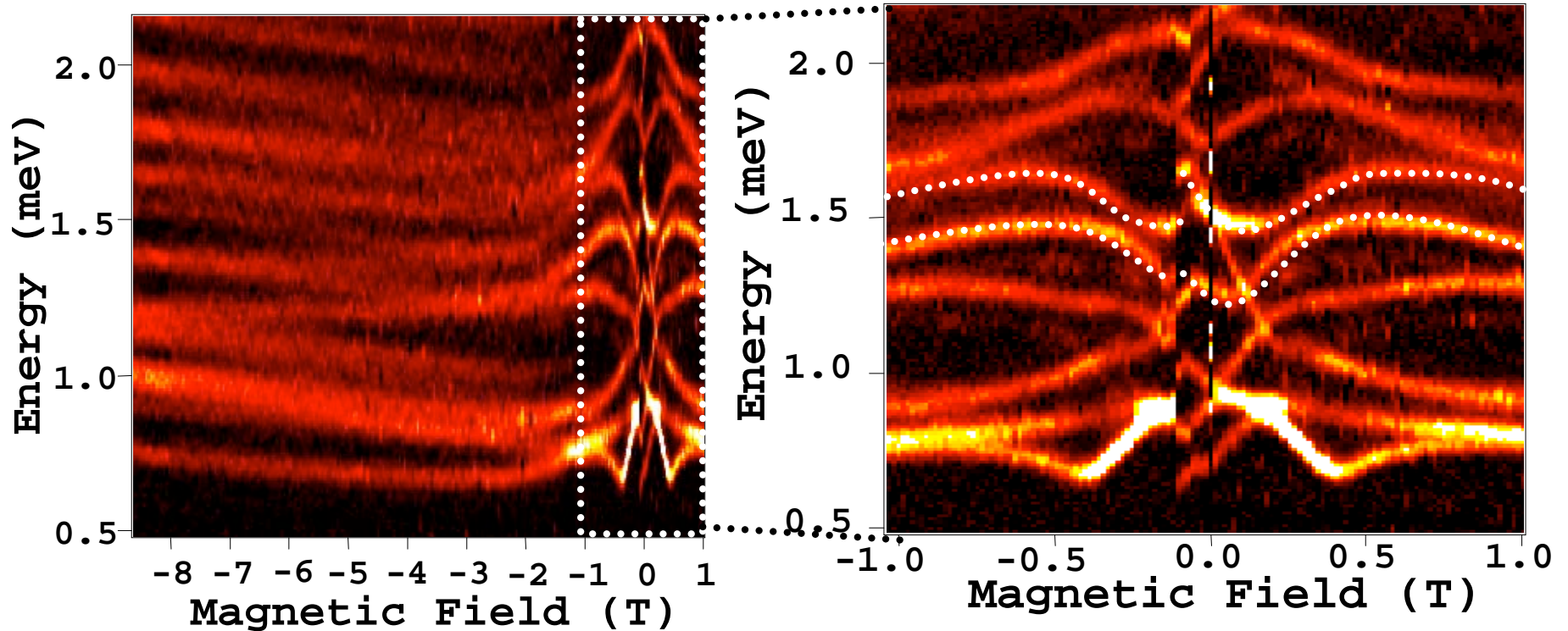


schematic sketch:



- 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
- One sign of slope at high field.
- Typical level spacing is ~ 0.2 meV -- much smaller than estimates based on independent-electron model.

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 magnet 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

① Big computer simulations: see Cahoon, Canali, MacDonald, PRB 66, 094430 (2002), PRB 68, 014423 (2003) PRB 69, 045411 (2004)

② Effective Spin Hamiltonians: Canali + MacDonald PRL 85, 5623 (2000); Solid State Comm. 119, 253 (2001).

Kleff et al., PRB 64, 220401 (2001); G Usuj and Baranger cond-mat/040777

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.

also see Gordon
↓ cond-mat/0412488

Many-body Hamiltonian

$$H = H_0 + H_{\text{exch}} + H_{\text{Zeeman}} + H_{\text{anis}}$$

$$H_0 = \text{single-electron state energies} \quad \sum \epsilon_j a_j^\dagger a_j$$

$$H_{\text{exch}} = \text{exchange energy} = -\frac{U}{2} \vec{S} \cdot \vec{S} \quad (\text{constant in one spin multiplet})$$

$$H_{\text{Zeeman}} = -\frac{1}{2} g \mu_B \vec{H} \cdot \vec{S} = -\frac{1}{2} g \mu_B H S_z \text{ or } -\frac{1}{2} g \mu_B |\Omega| \vec{H} \cdot \hat{\Omega}$$

$$H_{\text{anis}} = ? = \text{try simplest uniaxial example} = -k_B |\Omega| \hat{S} \cdot \hat{d}$$

$\hat{d} = \text{easy axis direction}$

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 $\approx E(n+1) - E_g(n)$ ← ground state

Problem: If effective Hamiltonian is $H_{\text{Zeeman}} + H_{\text{anis}} = -\frac{1}{2} g \mu_B |\Omega| \vec{H} \cdot \vec{S} - k_B |\Omega| \vec{S} \cdot \hat{d}$ then this just scales with $|\Omega|$.

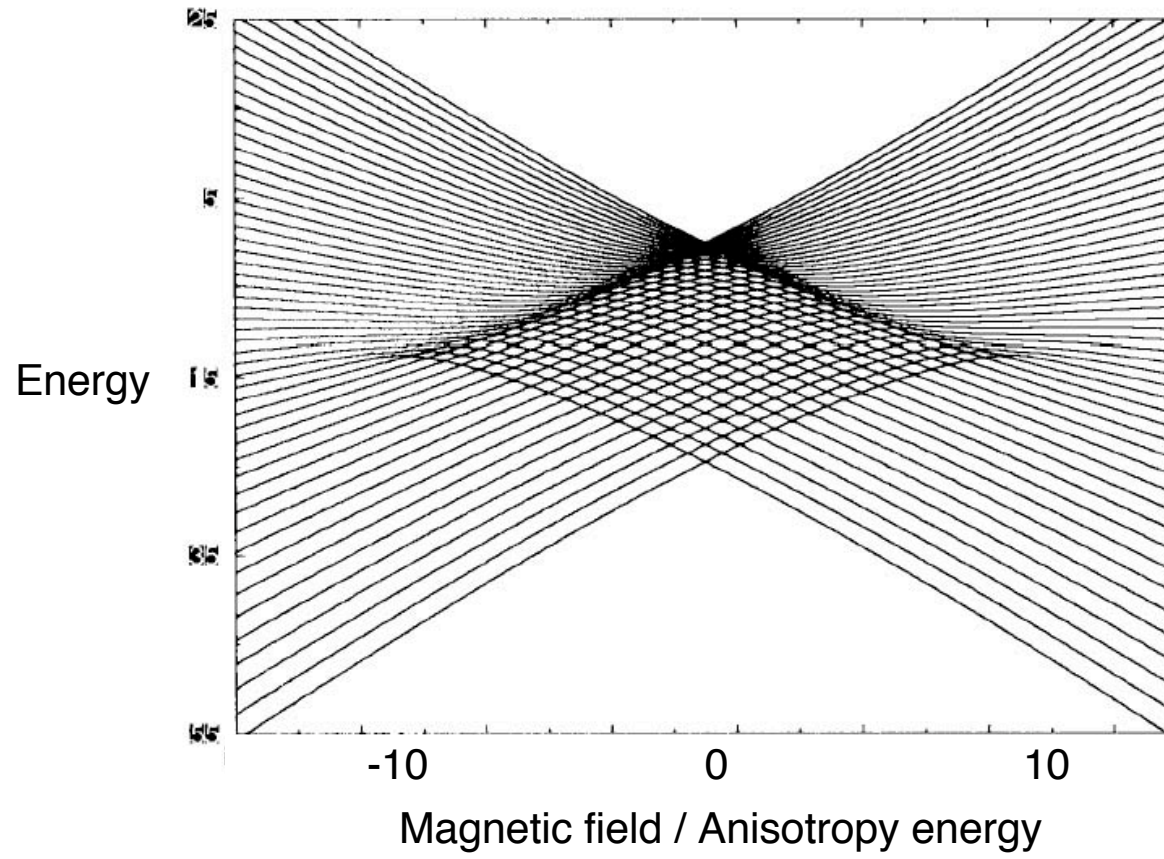
$$E_g(n+1) - E_g(n) = \frac{1}{2} E_g(n) / S \quad \leftarrow \text{not what we see.}$$

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 fractional 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

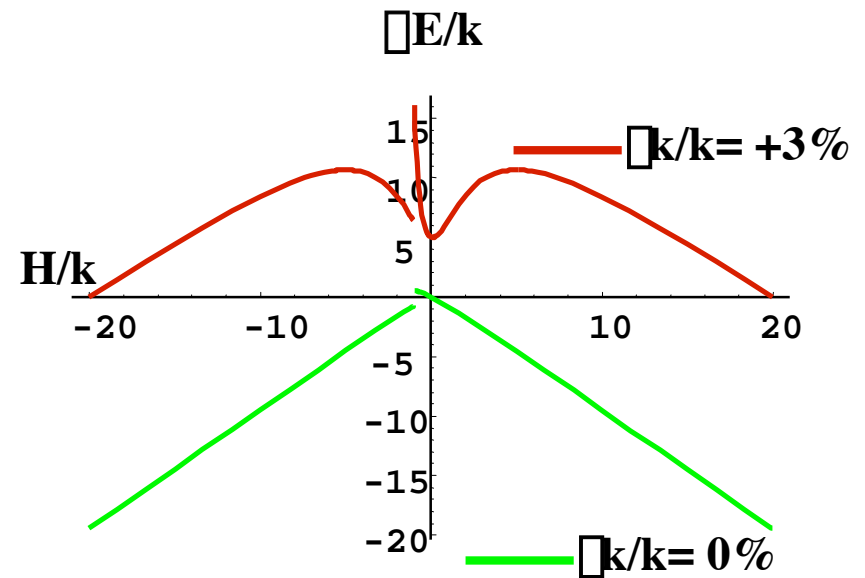
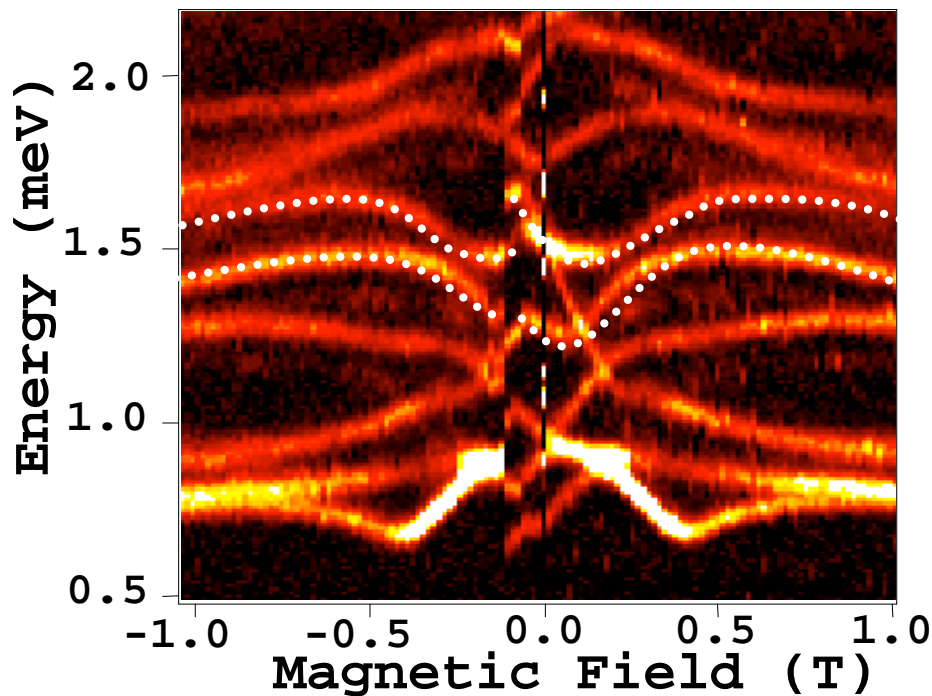
S=25



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.



ΔE = Energy required to add/ remove one e
 k = anisotropy constant
 $\Delta k/k$ relative variation

Summary

- For modelling the effects of electron-electron interactions in metallic nanoparticles \rightarrow "Universal Hamiltonian"
Exchange and pairing are the only nontrivial terms
(The Universal Hamiltonian does not include spin-orbit interactions)
- Normal-metal quantum dots can have non-minimal spin ground states ($S > \frac{1}{2}$) even when the exchange interaction strength is less than the Stoner criterion for bulk magnetism

GaAs ($J/\delta \sim 0.3$), $S > \frac{1}{2}$ sometimes seen

Al, Au ($J/\delta < 0.1$) only $S=0, \frac{1}{2}$ seen so far.

- Superconducting pairing is allowed even in samples with a fixed number of electrons
- In nm-sized samples, pairing is visible directly in the "electron-in-a-box" level spectrum
- A paired ground state persists as long as $\Delta \gtrsim \delta$.
(For smaller nanoparticles (larger δ) we can't distinguish the pairing gap from the simple finite-size level spacing, so we can't say anything experimentally in this regime.)
- Understanding ferromagnetic nanoparticles is a challenging problem. Some progress in both large-scale numerics and effective-spin Hamiltonians. The effective-spin Hamiltonians are similar to models of single-molecule magnets (but with larger spins).

References

Universal Hamiltonian

- I. L. Kurland et al., PRB 62, 14886 (2000)
- I. L. Aleiner et al., Physics Reports 358, 309 (2002)
- D. A. Gorokhov and P. W. Brouwer, PRB 69, 155417 (2004)
↖ also considers spin-orbit interaction

Non-minimal spin states for weak exchange interactions

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