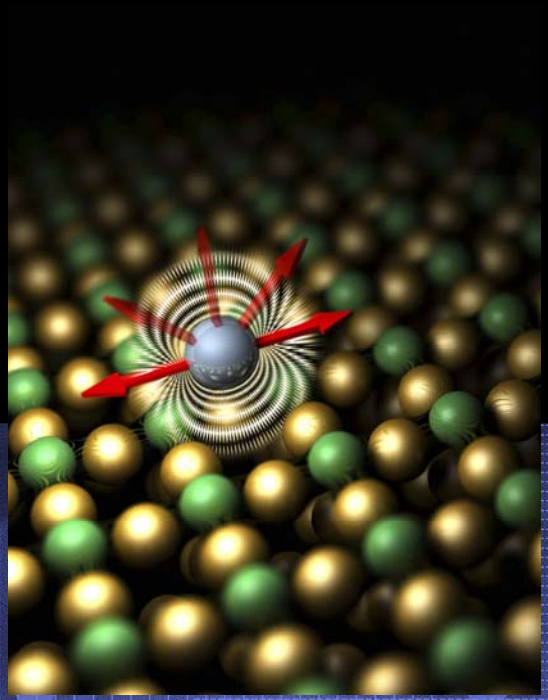
Studying magnetic molecules one atom at a time



Andreas Heinrich
IBM Research

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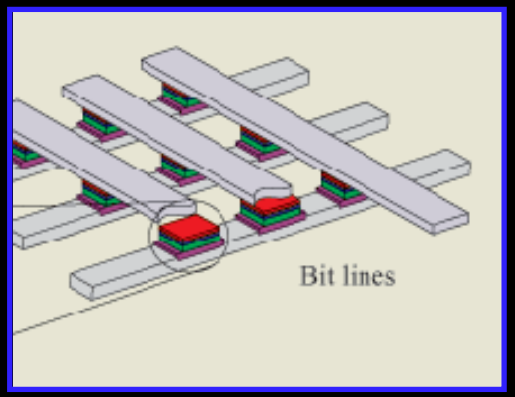
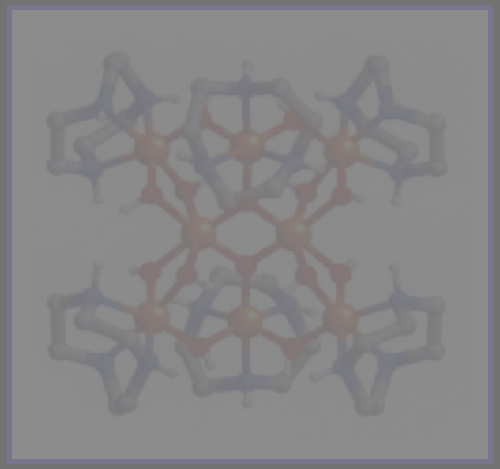
Nanomagnets in science and technology

	Top-down	Bottom-up
		
Address individual structure	✓	✗
Magnetic Manipulations	✓	✗ ✓
Atomic-scale control	✗	✓

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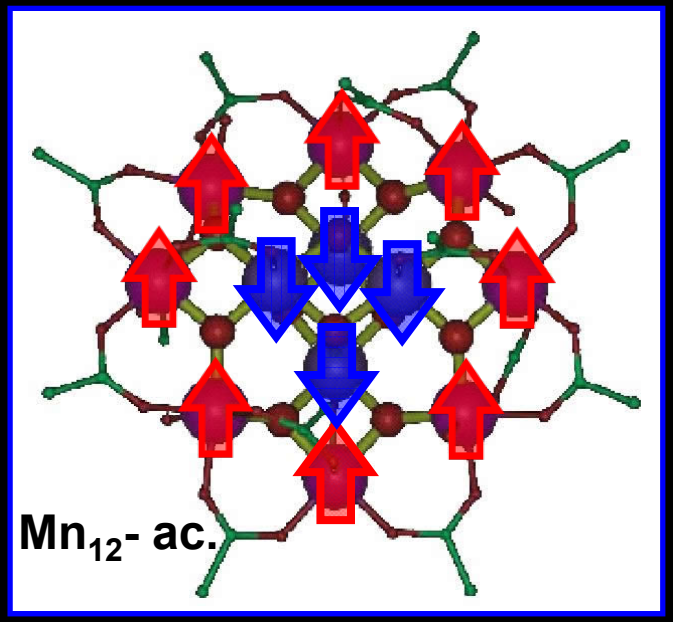
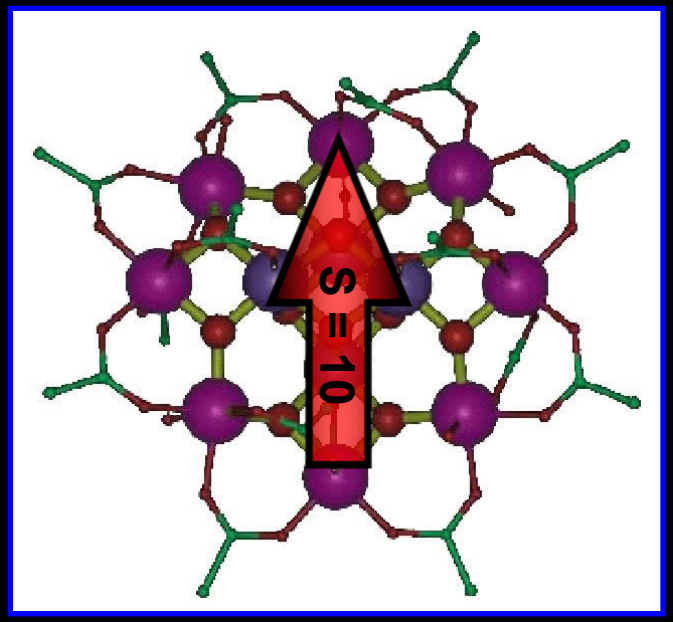
The giant-spin model of molecular magnets





- **Spin coupling: Quantum Heisenberg**
  - 8 Mn atoms with S = 2 $\rightarrow$ S = 16
  - 4 Mn atoms with S = 3/2 $\rightarrow$ S = 6
  - Total S = 10
- **Magnetic anisotropy: Spin Hamiltonian**

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Electrical measurements of molecular magnets

- Very difficult to control the junctions
- Environmental impact on magnetic and electrical properties

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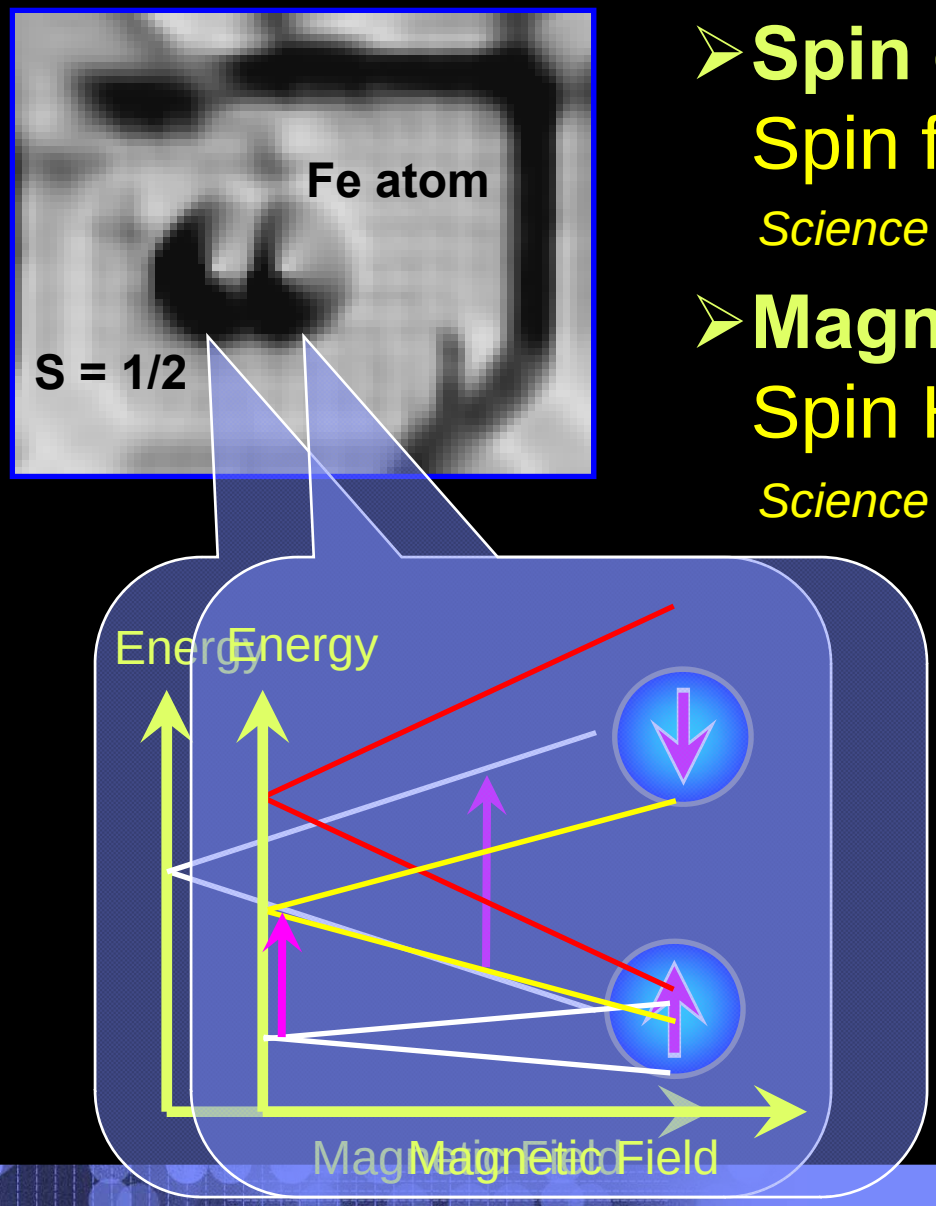
Studying magnetic molecules one atom at a time



- **Spin excitation spectroscopy:**
  Spin flips of single atoms
  Science **306**, 466 (2004)
- **Magnetic anisotropy:**
  Spin Hamiltonian, Selection rules
  Science **317**, 1199 *(2007)*

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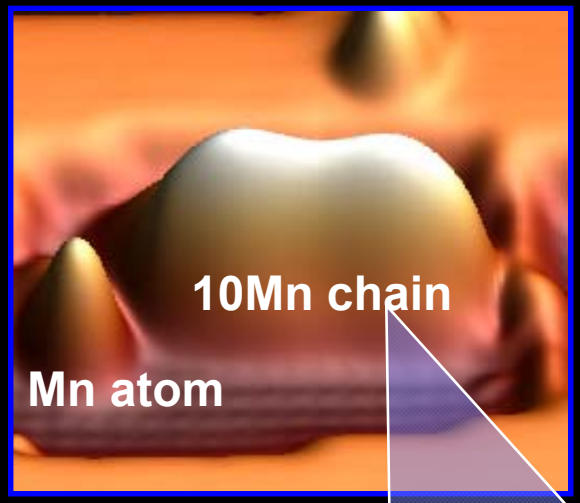
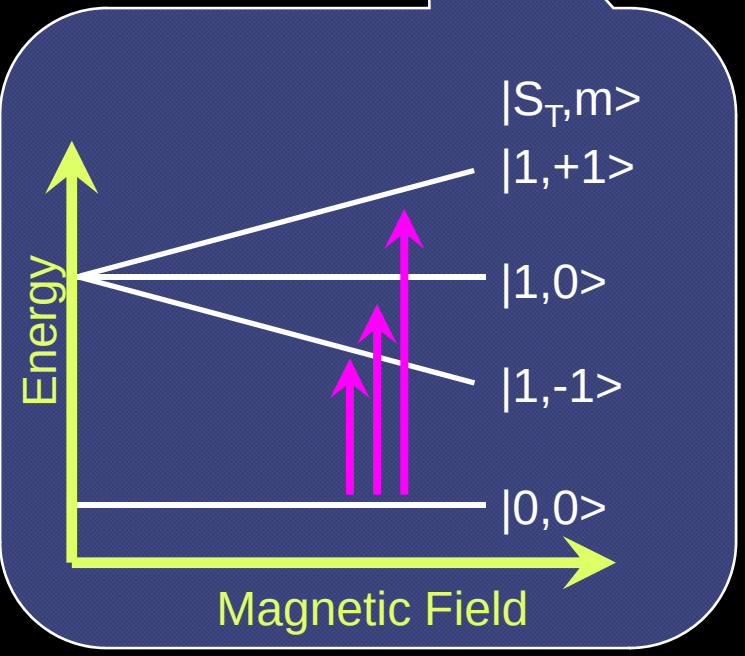
Studying magnetic molecules one atom at a time





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- **Spin-spin interactions:**
  Heisenberg exchange coupling
  Unpublished and Science ***312****, 1021 (2006)*

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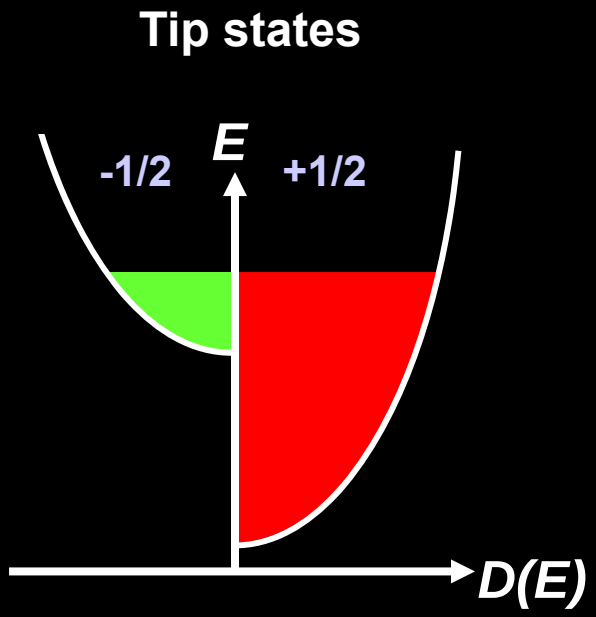
Studying magnetic molecules one atom at a time



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- **Spin-spin interactions:**
  Heisenberg exchange coupling
  *Unpublished and Science **312**, 1021 (2006)*
- **Spin-polarized excitations:**
  A probe for magnetic bits
  Unpublished

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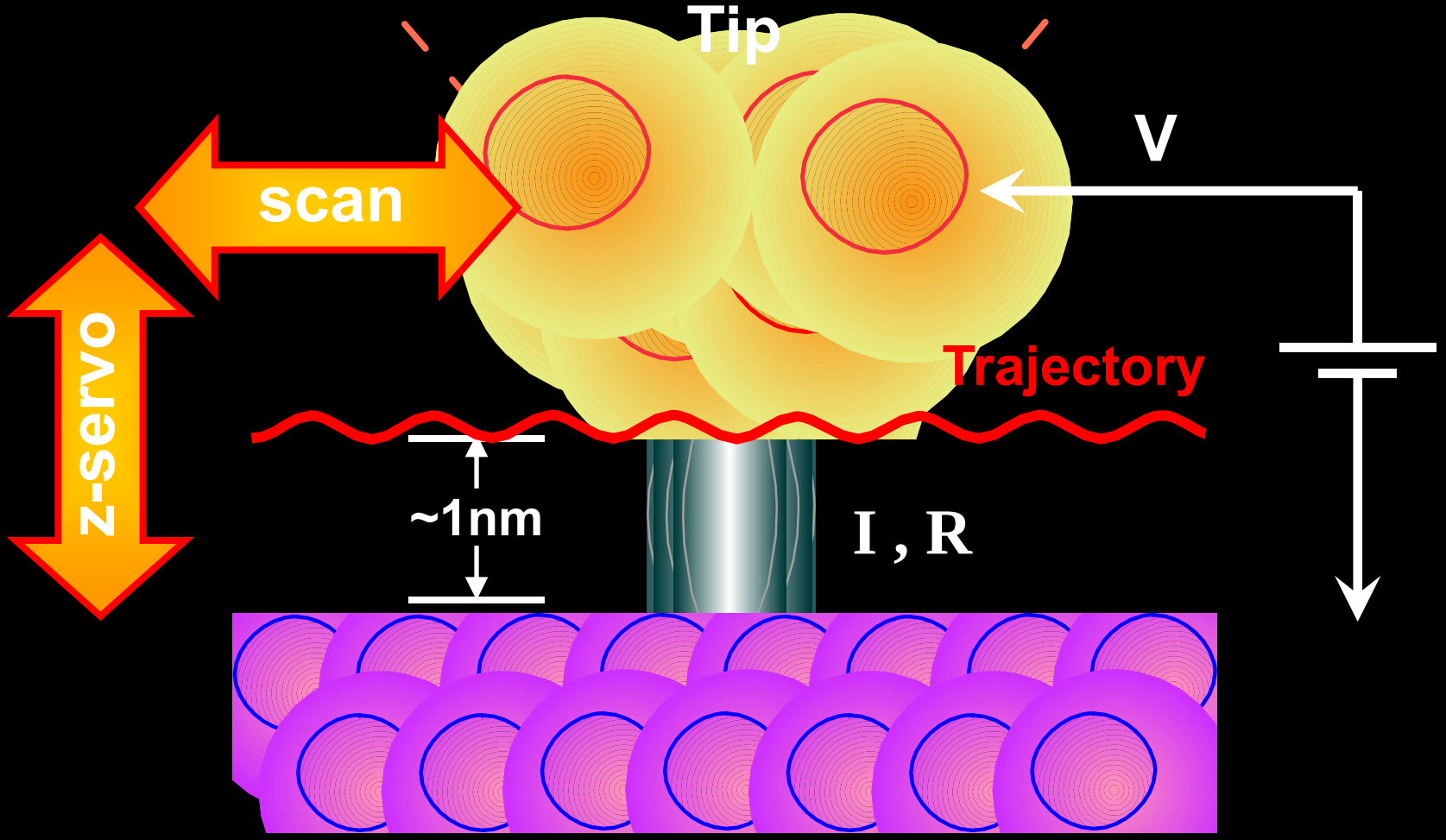
How does an STM image a surface?



➢ Keep I constant

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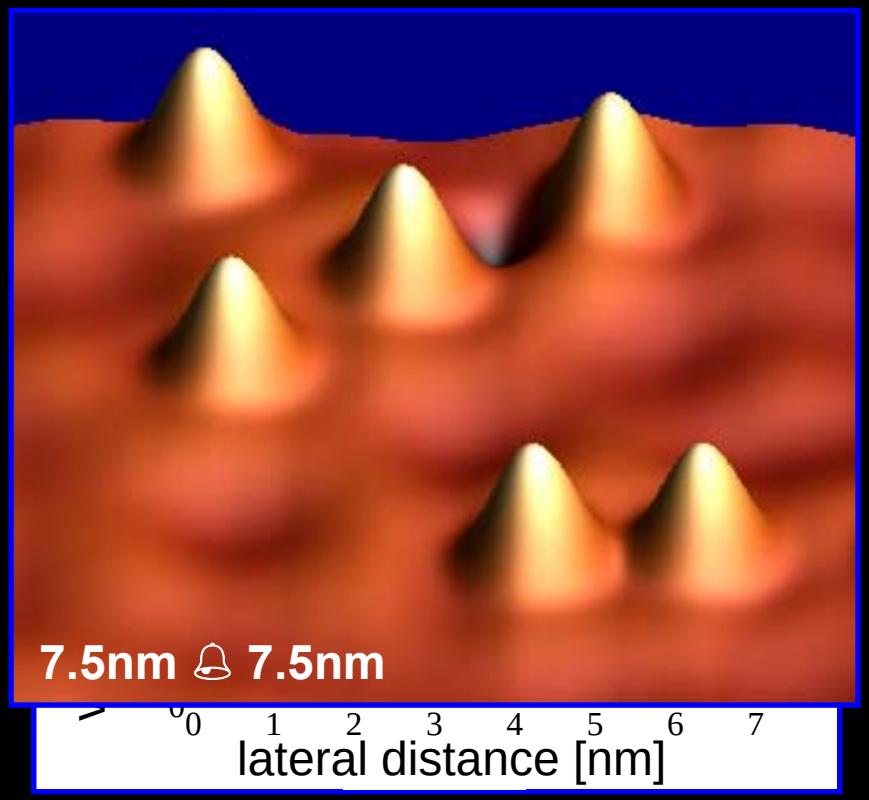
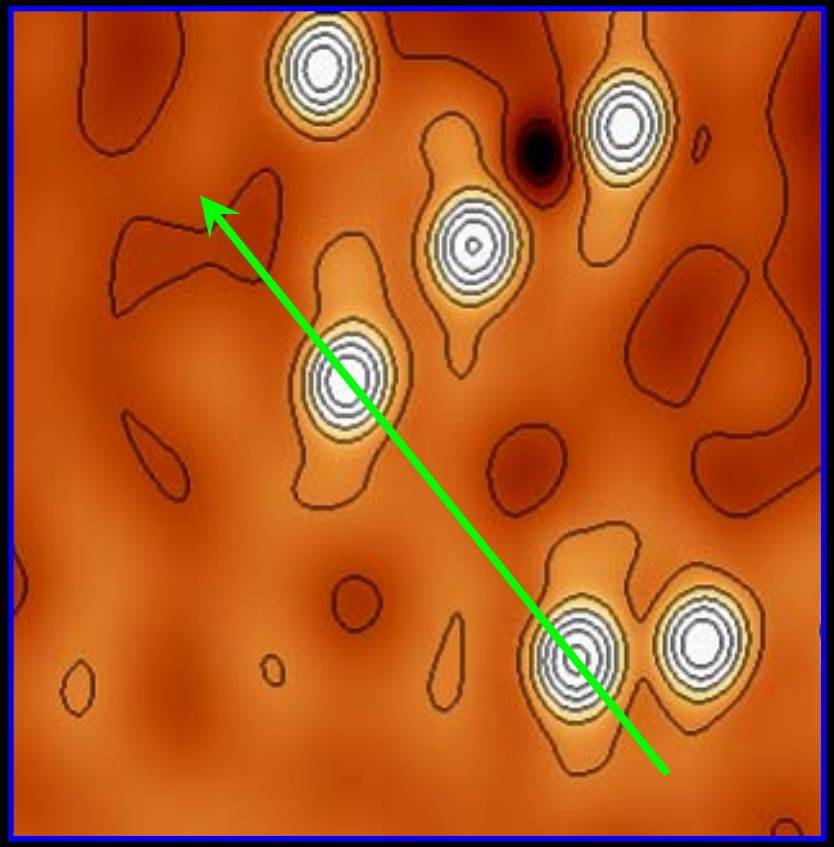
Atomic resolution?





- Co atoms on clean Cu (111)
- Co atoms appear as 1Å high “bumps” about 10Å wide

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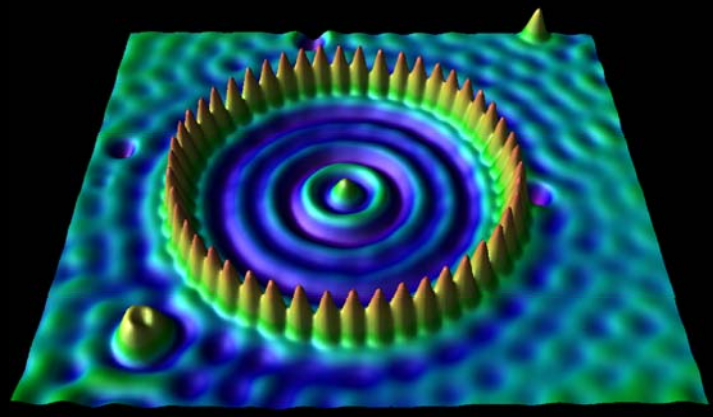
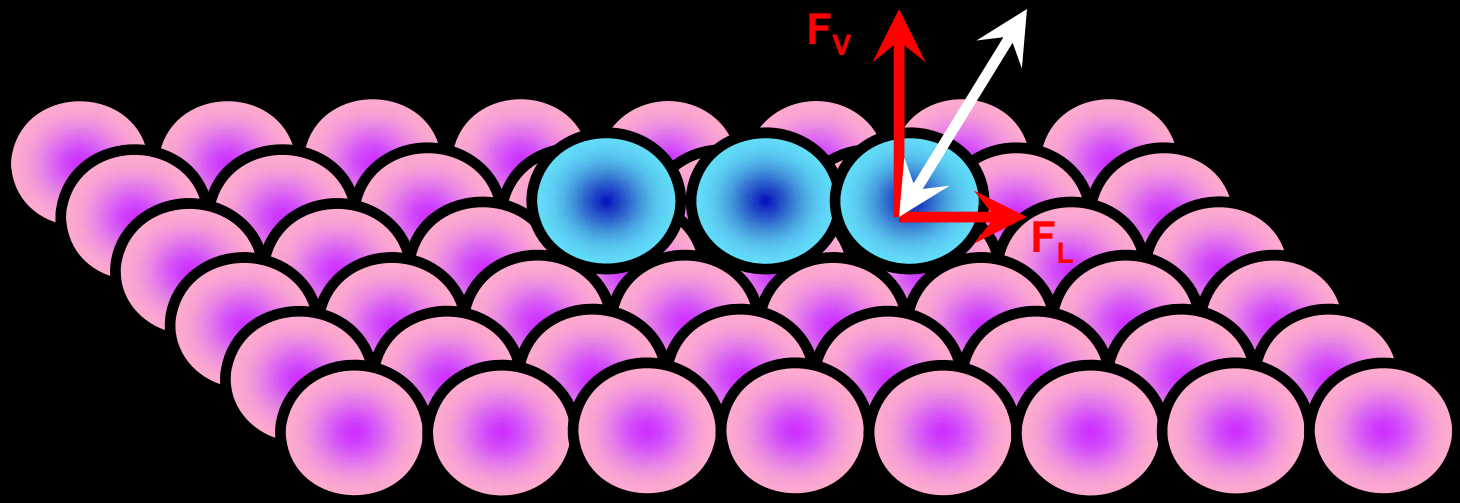
How to move atoms with STM?

What forces are involved?

Sc… 2008





- **The adsorbate hops from one site to an adjacent site**

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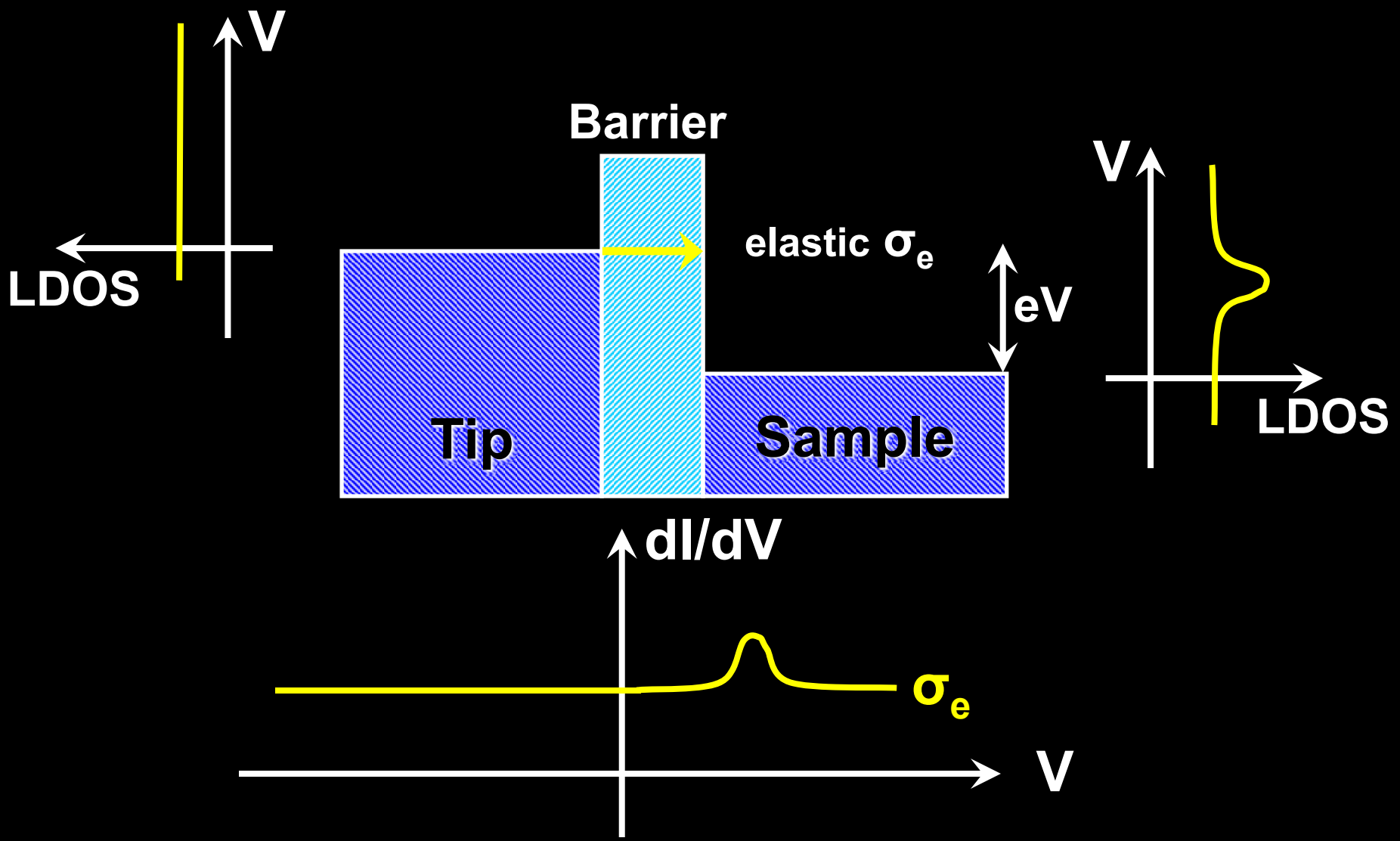
Elastic spectroscopy with STM



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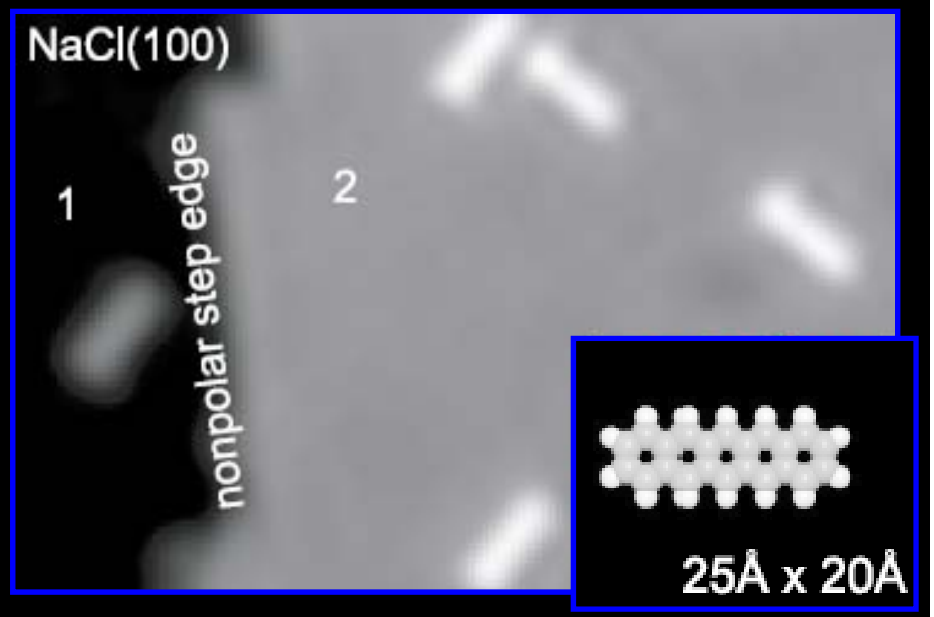
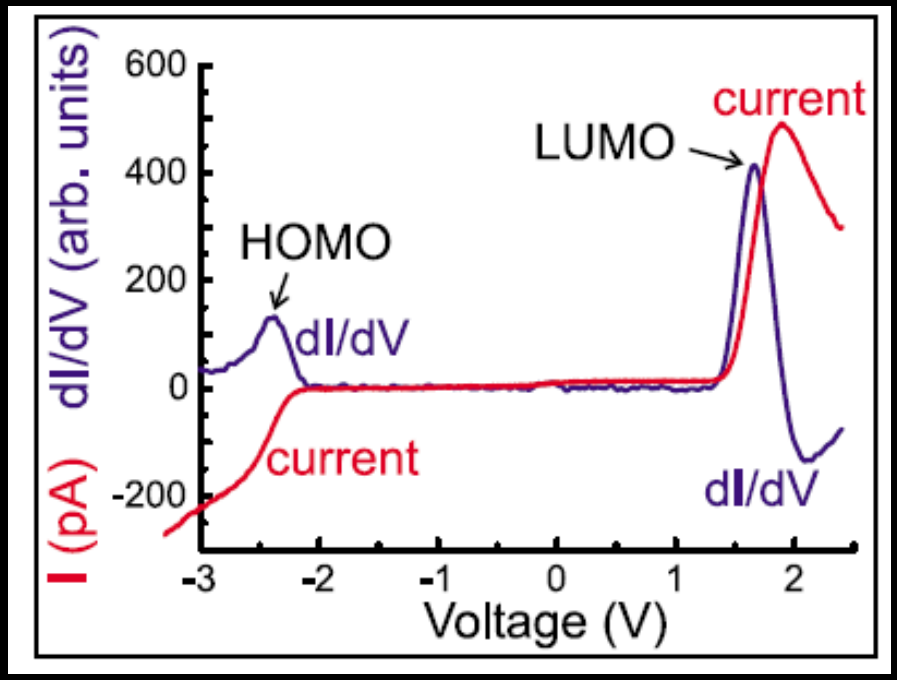
Pentacene on table salt





- J. Repp et al., *Phys. Rev. Lett.* 94, 026803 (2005).
- Pentacene on 1 and 2 layers of NaCl on Cu (100).
- About 4eV gap between HOMO and LUMO.

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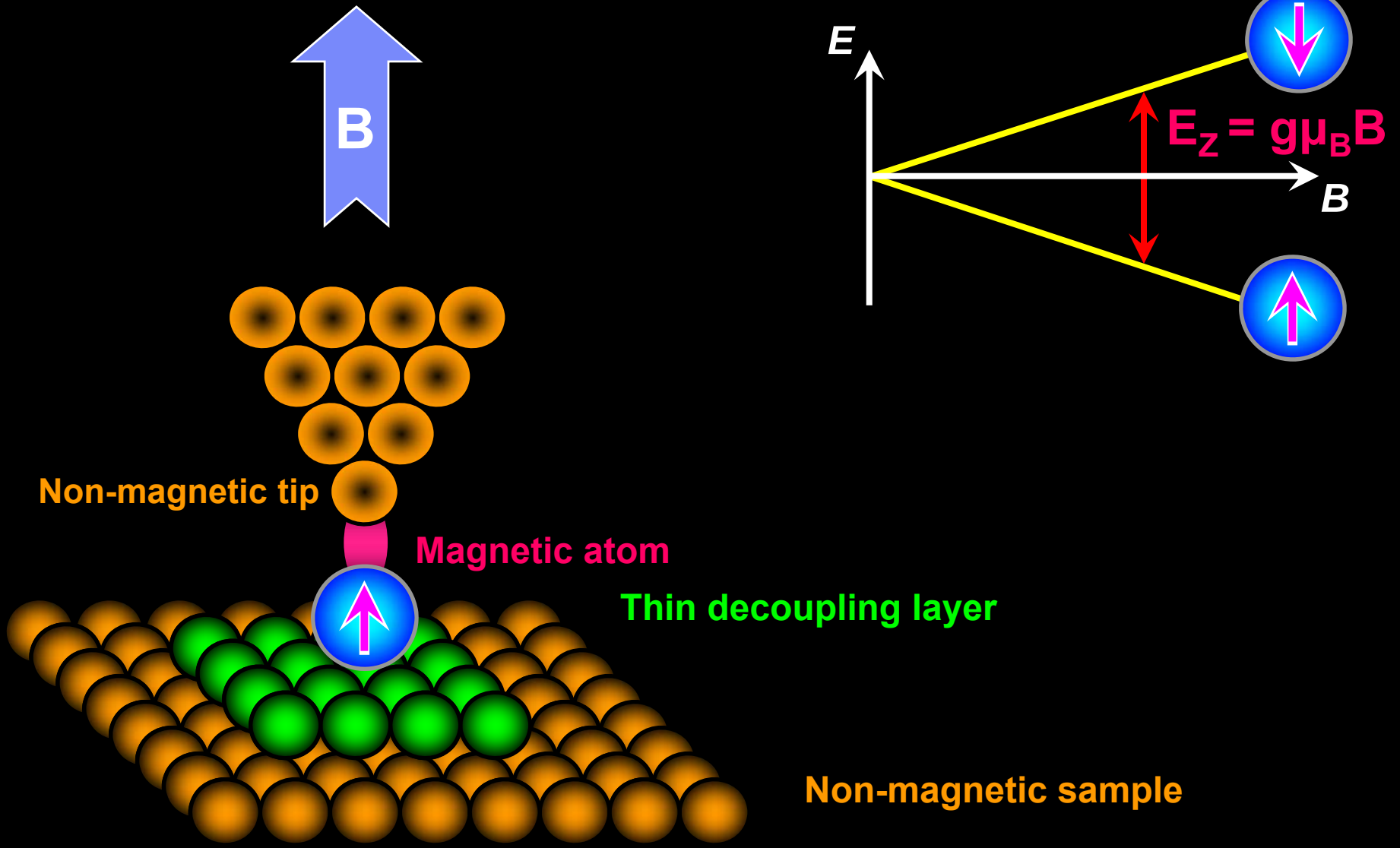
Spin excitation spectroscopy



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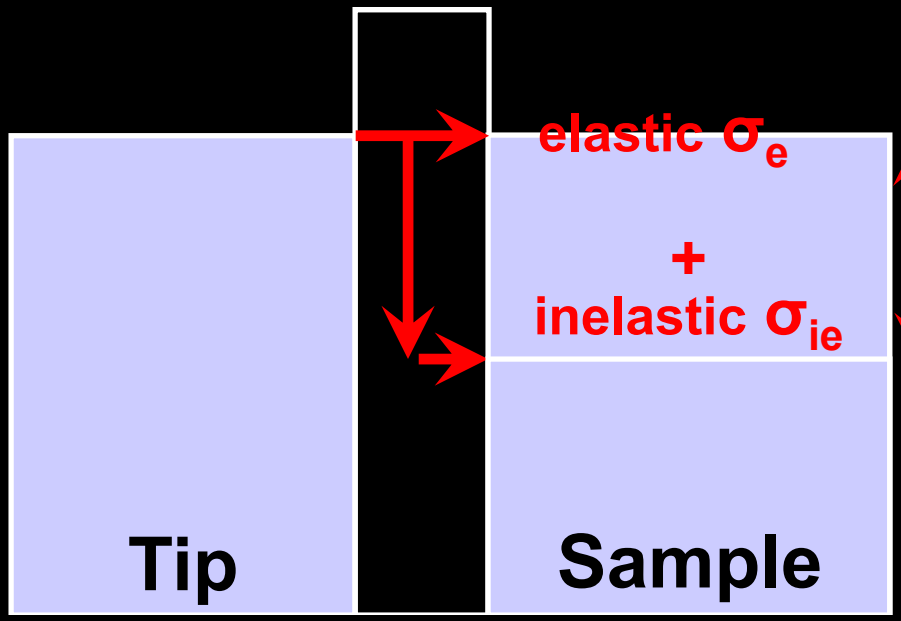
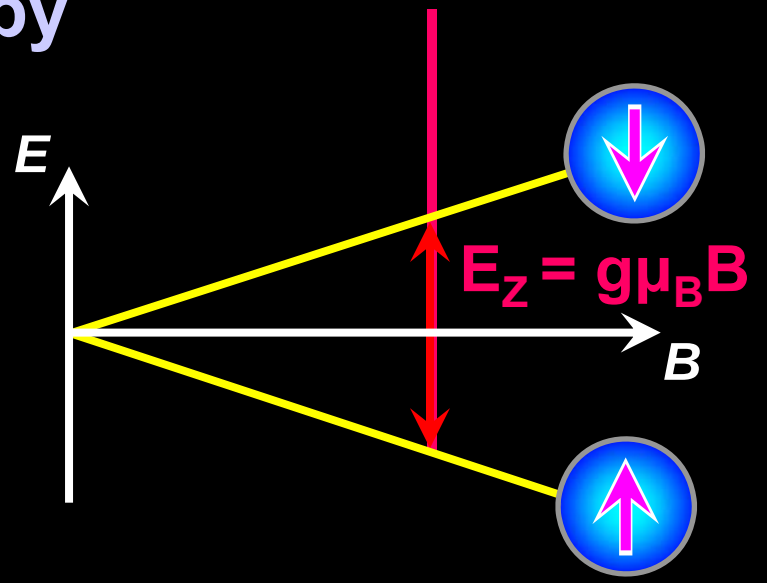
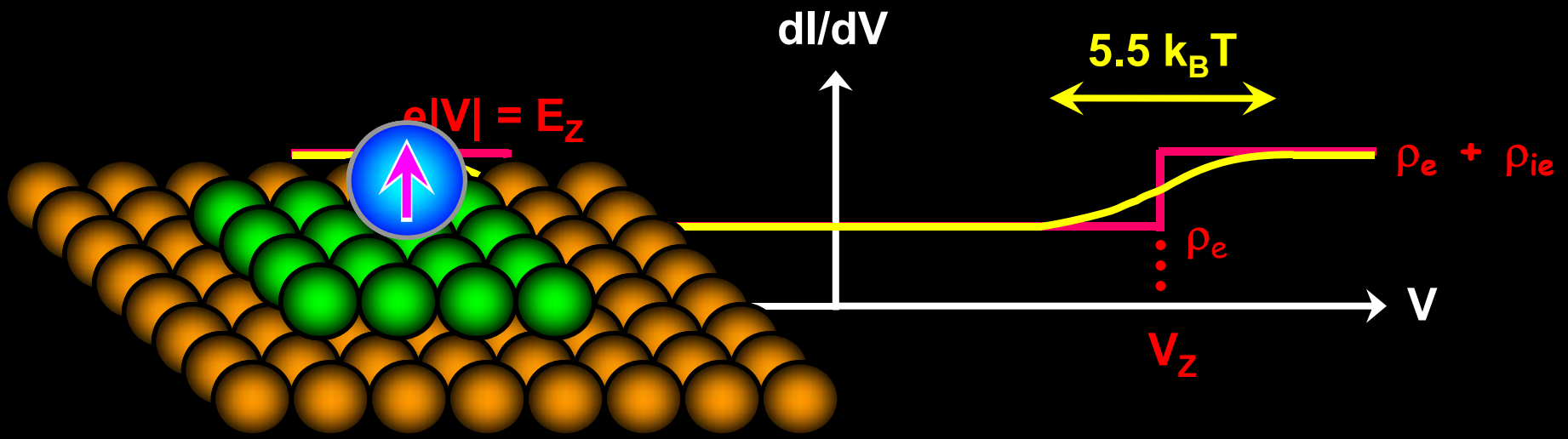
Spin excitation spectroscopy







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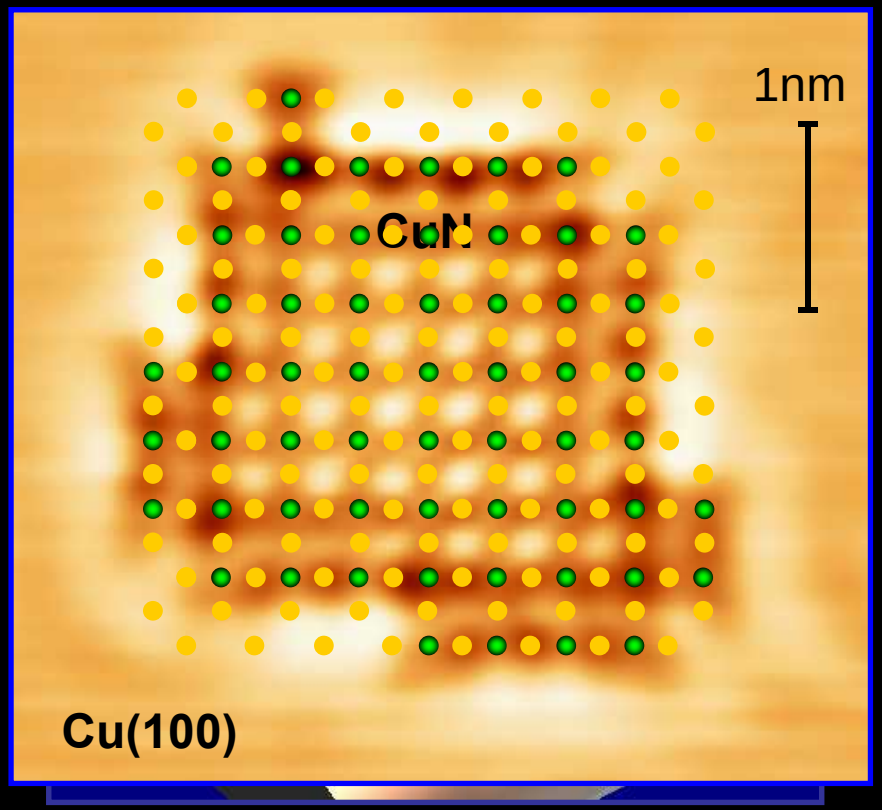
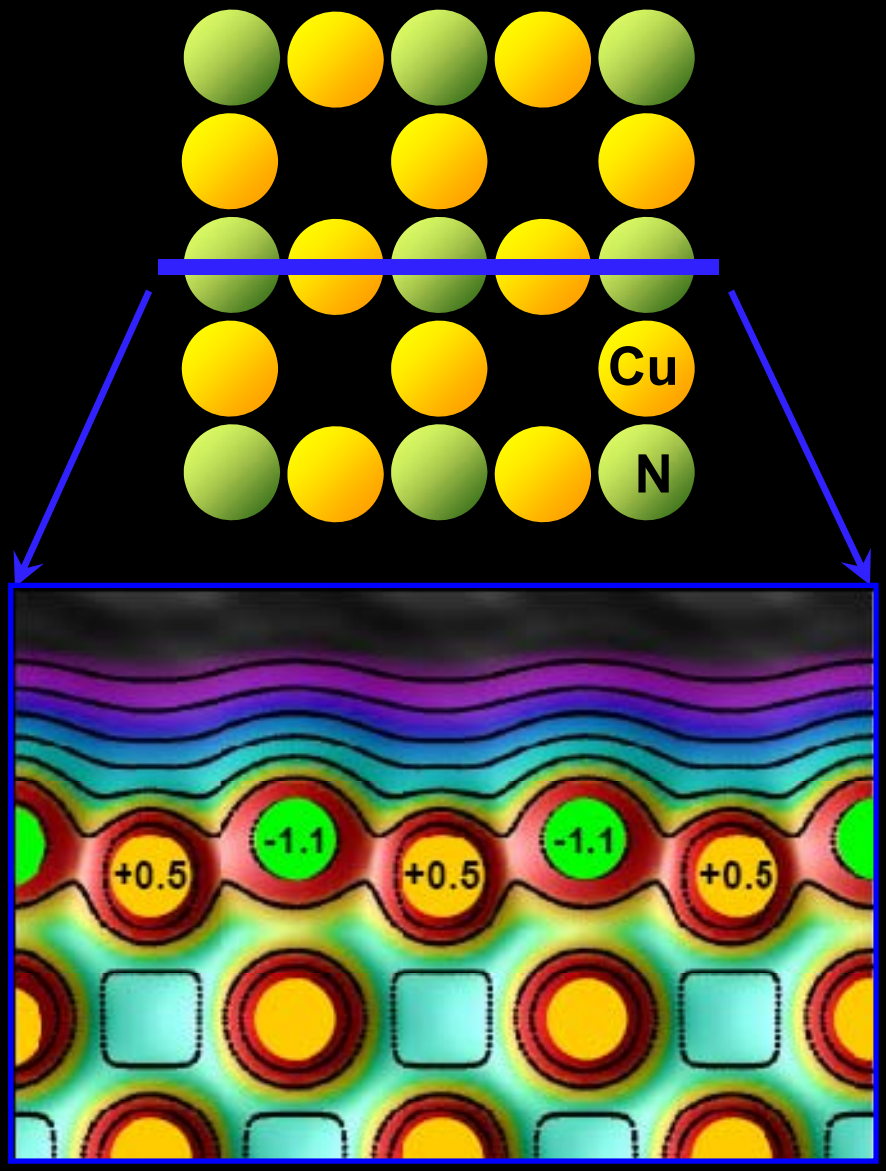
Copper-nitride islands grown on Cu





- Cu(100) + CuN
- Insulator next to metal
- Atomic resolution on CuN
- N atoms coplanar with Cu

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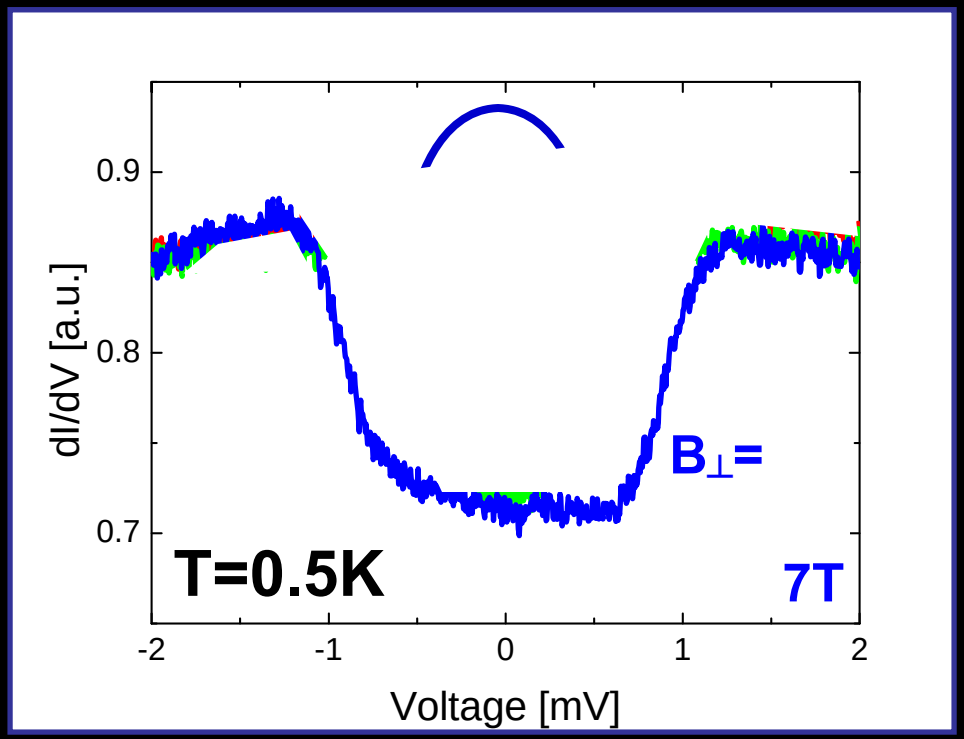
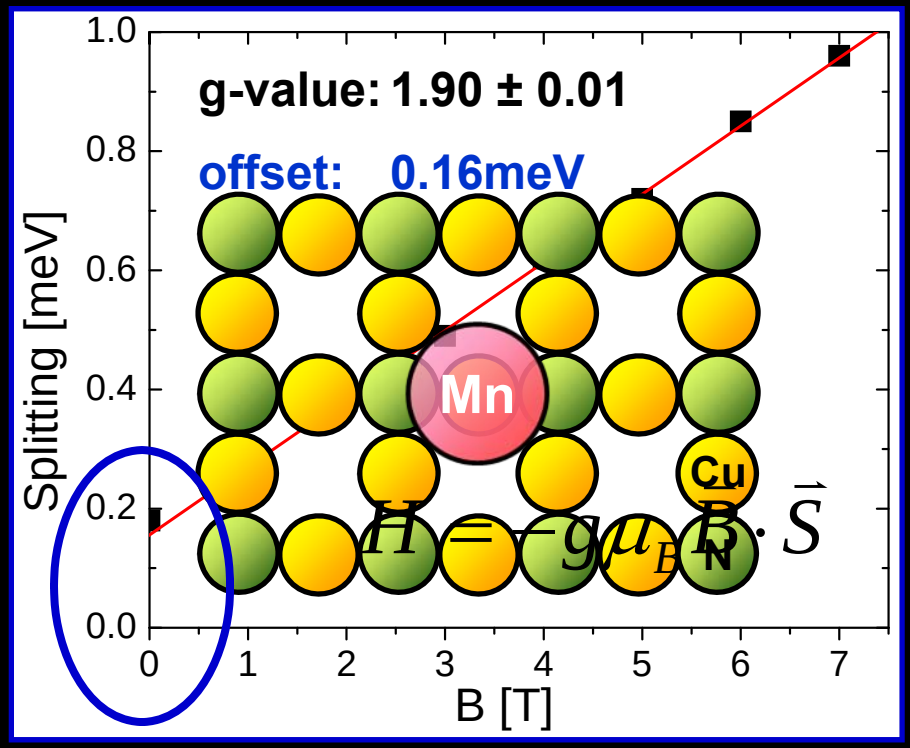
Mn on CuN: An almost pure spin





Mn atom on CuN exhibits magnetic behavior:

- **spin-flip excitation**
- **small amount of zero-field splitting**

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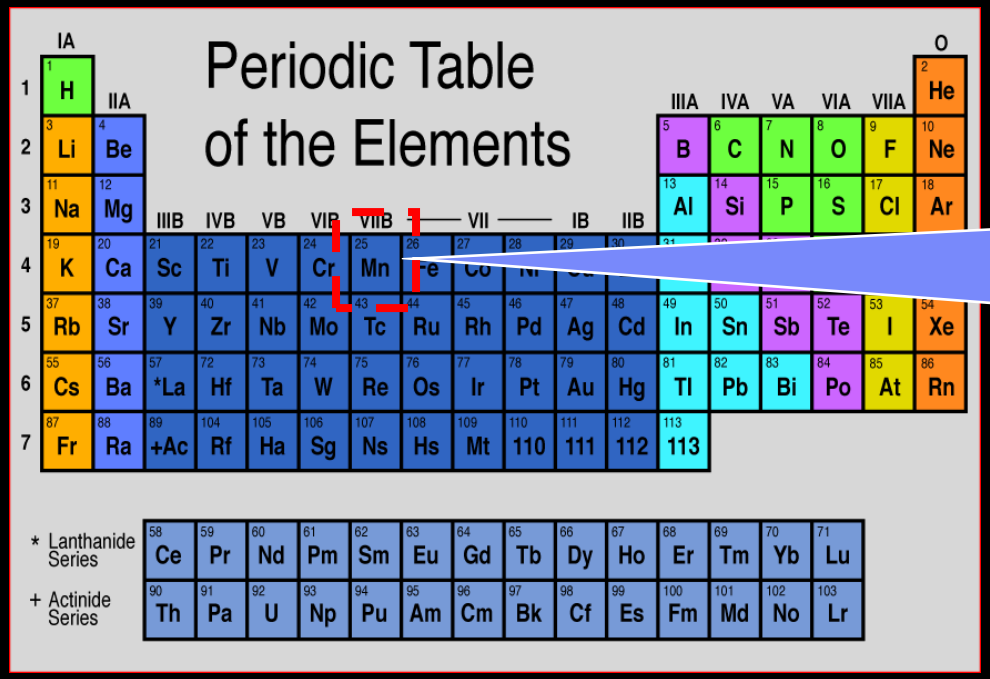
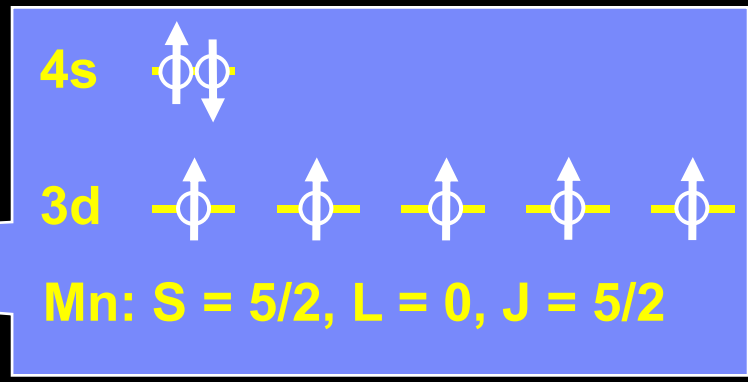
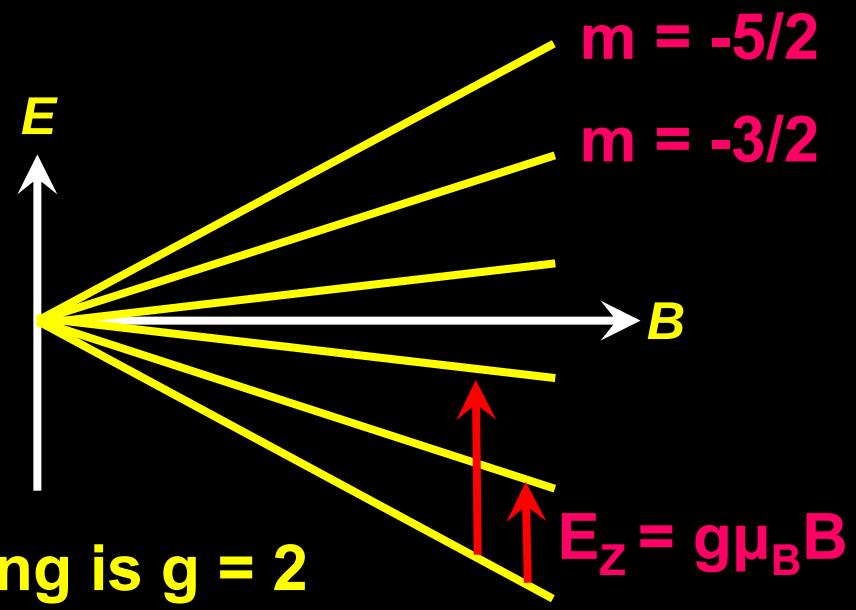
For comparison: free Mn atom







- Half filled d-shell
- Weak spin-orbit interactions
- g-value of the magnetic splitting is g = 2
- Why only one step? Selection rule?

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Atom-Resolved Spin Excitation Spectroscopy

- **Spin excitation spectroscopy:**
  Spin flips of single atoms
  Science **306**, 466 (2004)
- **Magnetic anisotropy:**
  Spin Hamiltonian, Selection rules
  Science **317**, 1199 *(2007)*
- **Spin-spin interactions:**
  Heisenberg exchange coupling
  Unpublished and Science ***312****, 1021 (2006)*
- **Spin-polarized excitations:**
  A probe for magnetic bits
  Unpublished

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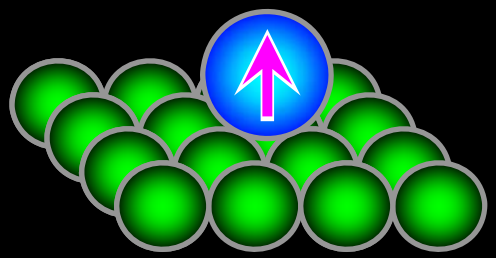
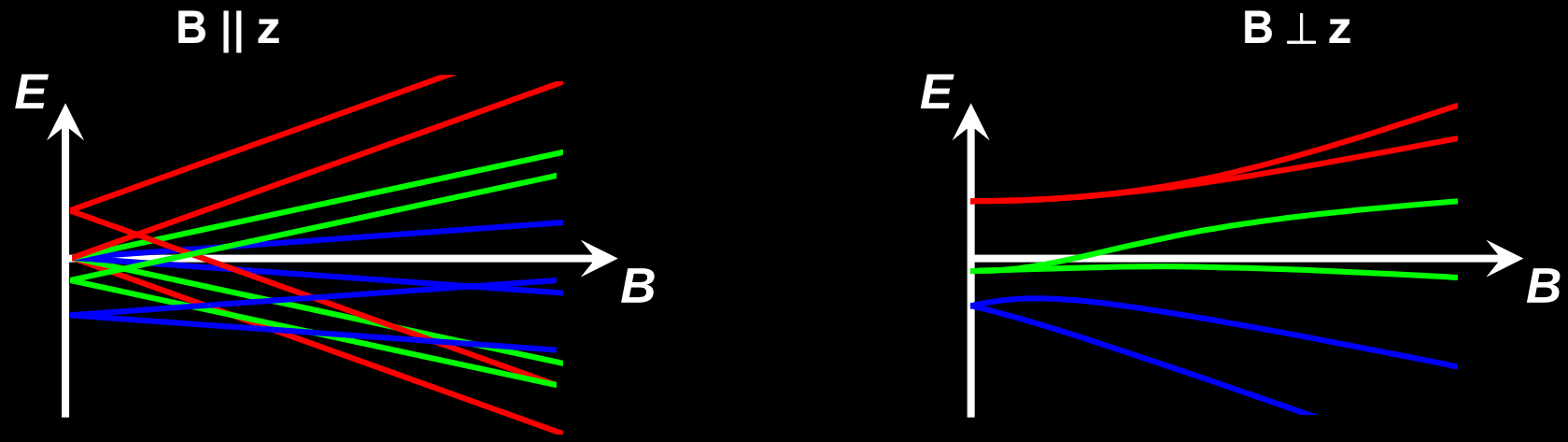
Anisotropy at a surface



- Free atomic spin is rotationally invariant: all spin orientations are degenerate.
- Loss of rotational symmetry breaks degeneracy of spin orientations.

$$H = -g\mu_B \vec{B} \cdot \vec{S} + DS_z^2$$



Magnetic field dependence varies with angle of magnetic field.

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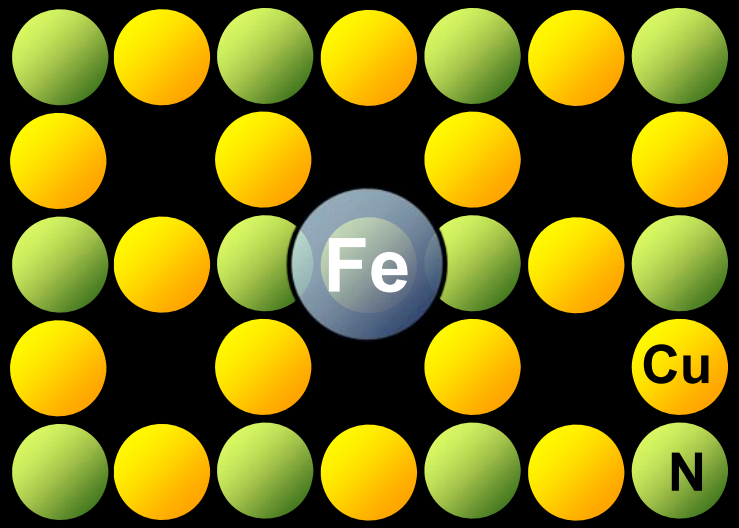
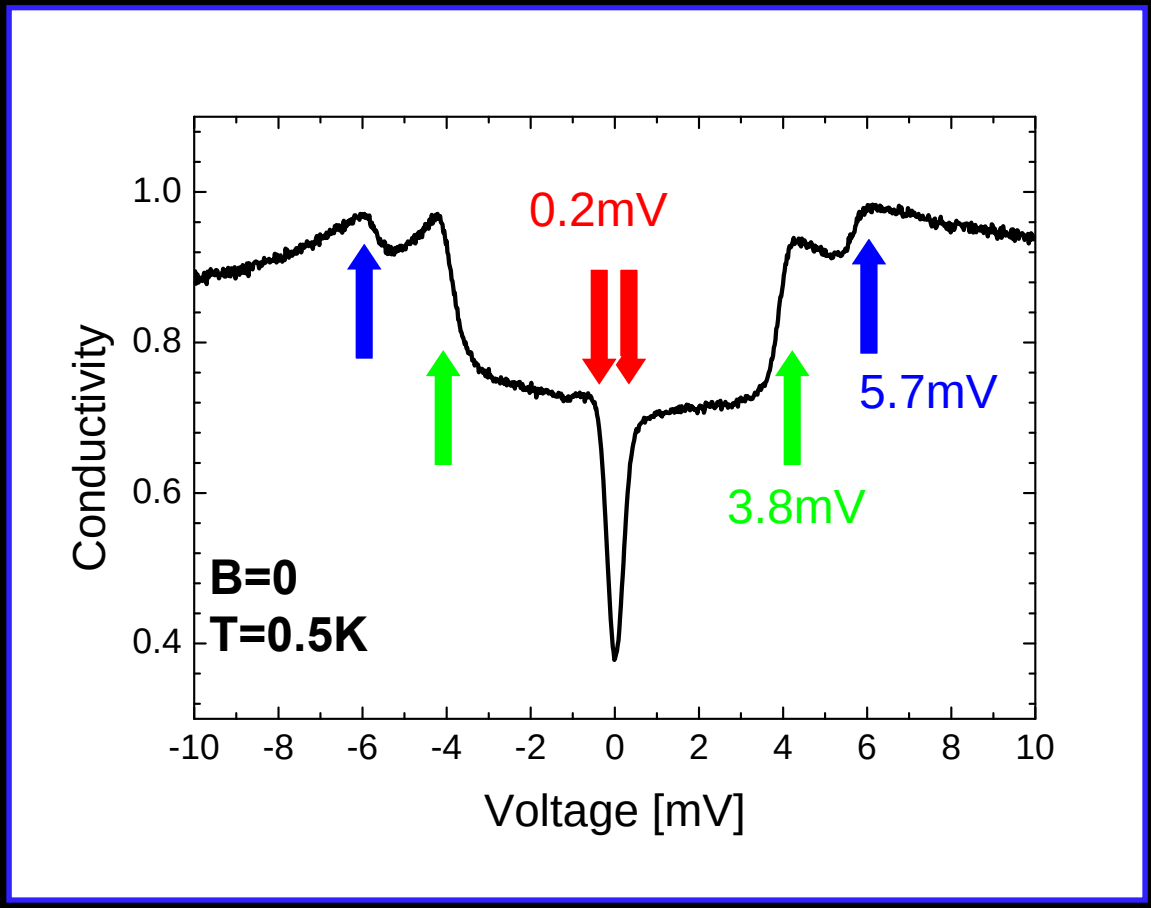
Fe on Cu-site on CuN





- 3 excitations with large cross section
- Same binding site as Mn yet quite different spectrum.

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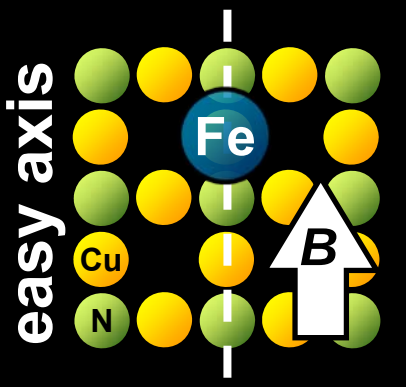
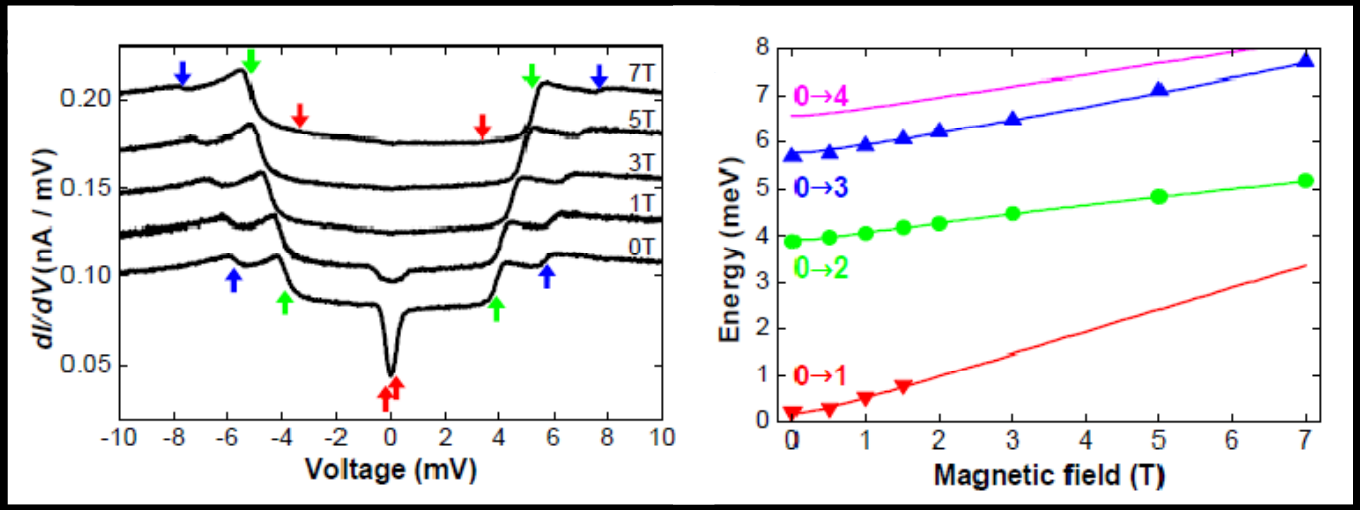
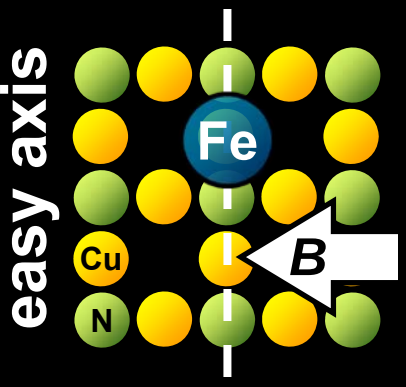
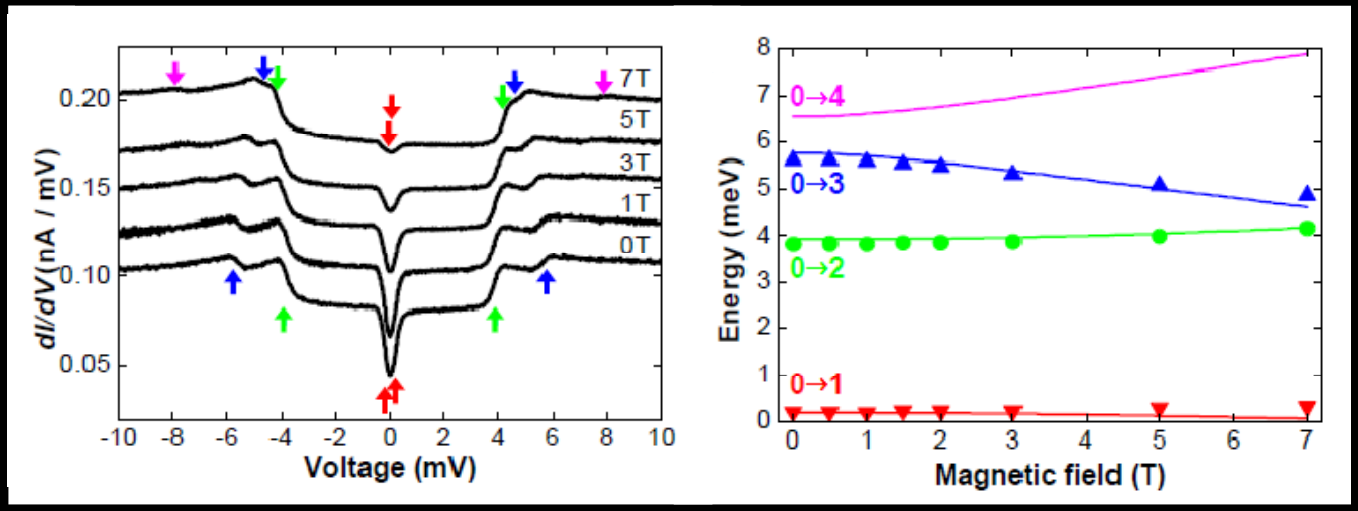
Field dependence of Fe spin excitations









➢ ***Out-of-plane*** **dependence is different yet !**

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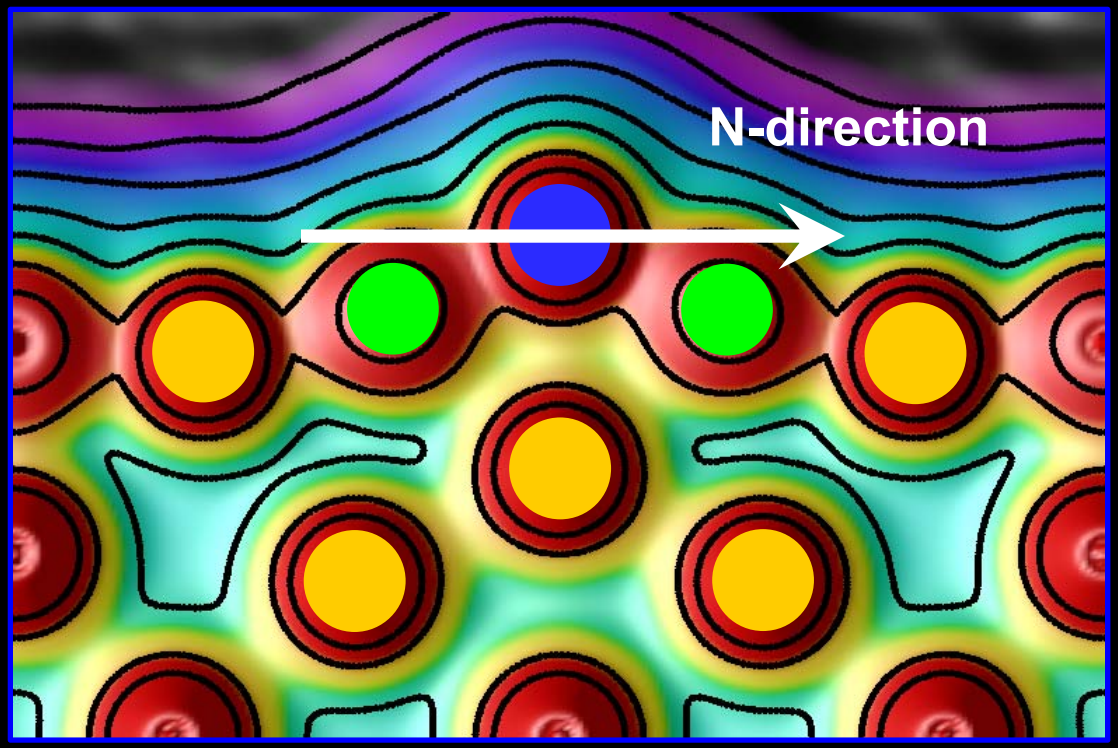
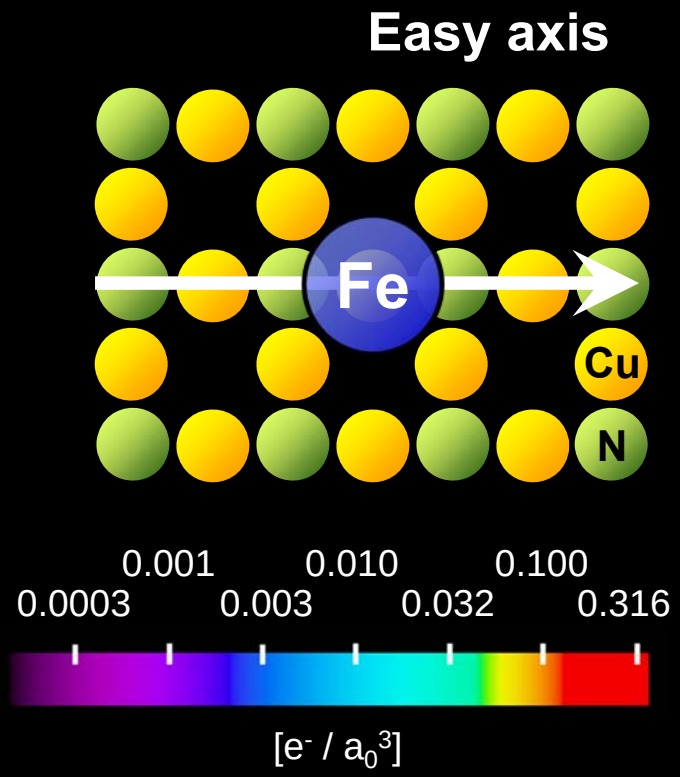
Origin of *in-plane* easy axis





- DFT to model structure and spin properties.
- Strong one-dimensional bonding.
- Spin of Fe complex is S = 2.

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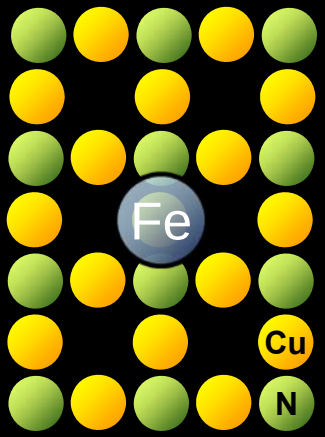
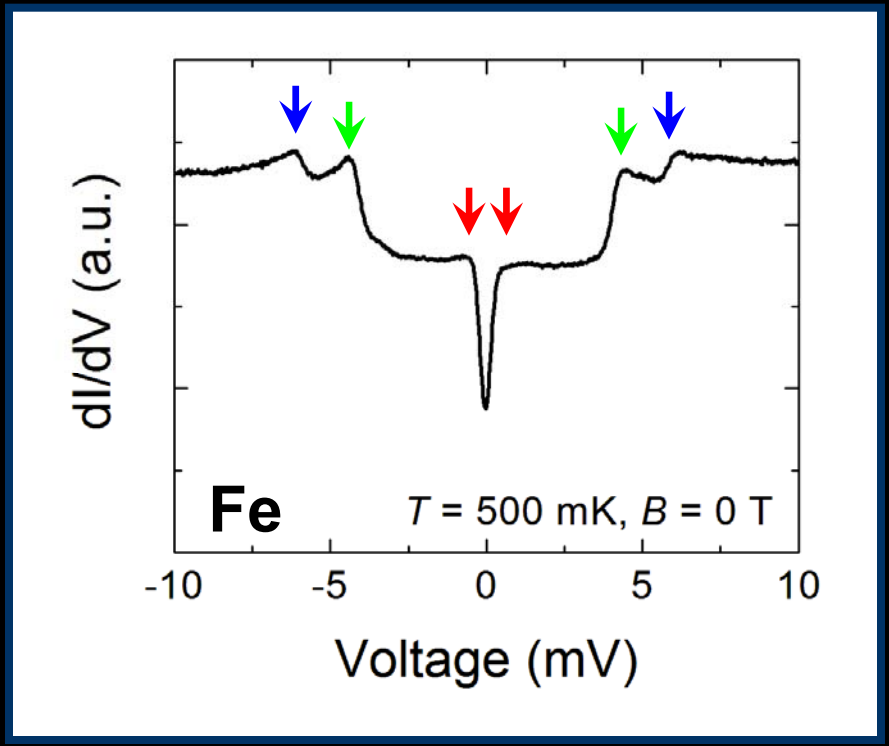
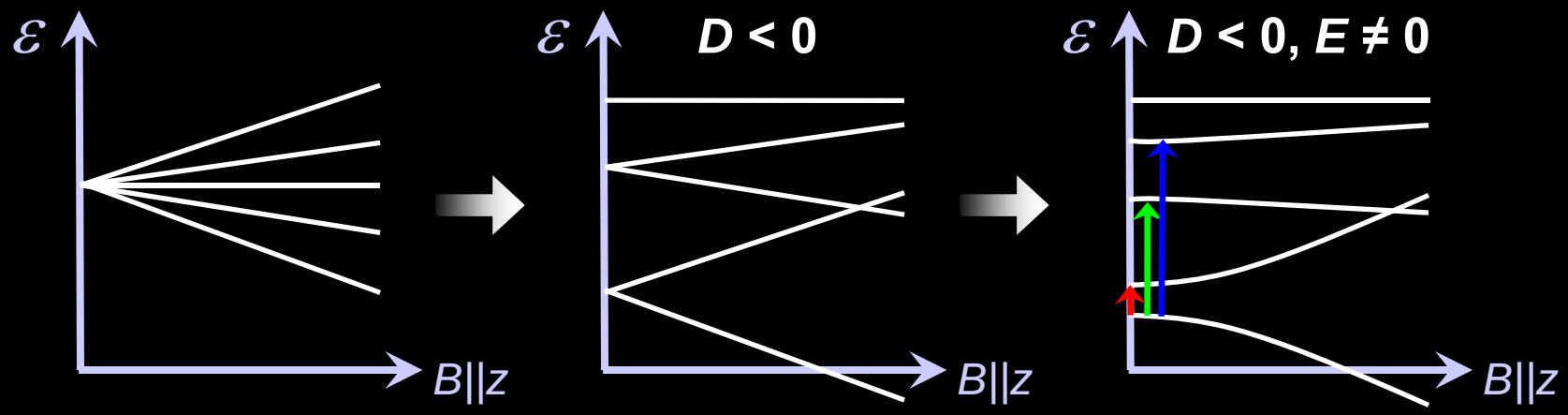
Anisotropy in Fe



$$H = -g\mu_B \vec{B} \cdot \vec{S}$$





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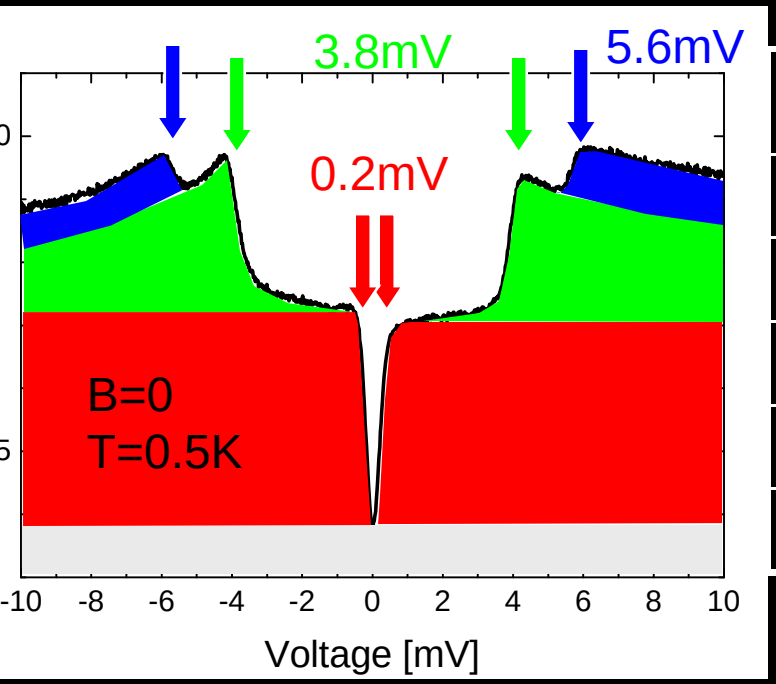
Mixed eigenstates are great for science

$$H = DS_z^2 + E(S_x^2 - S_y^2) \quad D = -1.5meV,\ E = 0.3meV$$



Eigenvalue	|+2>	|+1>	|0>	|-1>	|-2>
0	0.70		-0.17		0.70
0.17	0.71				-0.71
3.77		0.71		-0.71	
5.57		0.71		0.71	
6.34	0.12		0.99		0.12

- Mixed m_z eigenstates have more transitions with Δm_z=0, ±1.
- Anisotropy allows the observation of several spin excitations.

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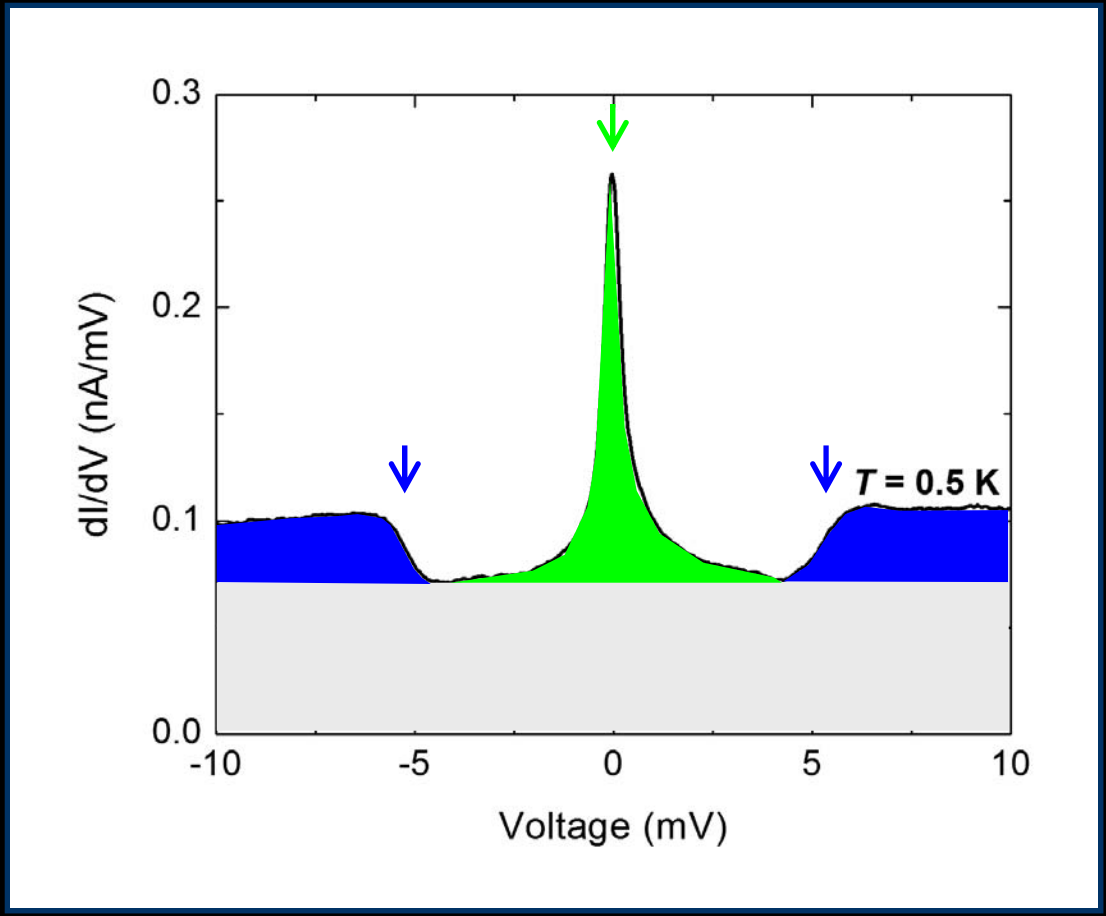
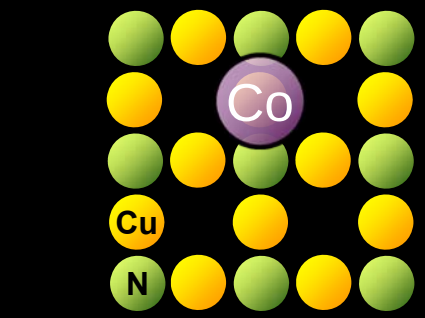
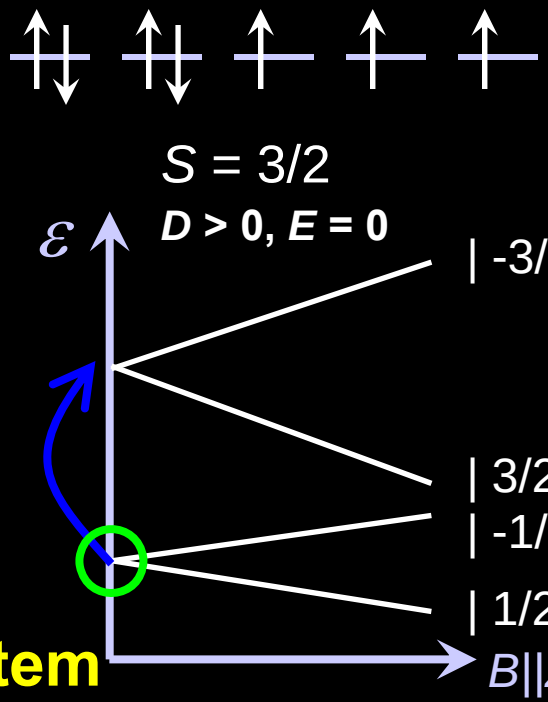
Brief comment: Kondo interactions







- S = 3/2 spin system with anisotropy
- Anisotropy creates pseudo S = ½ system
- Two-state system is Kondo screened

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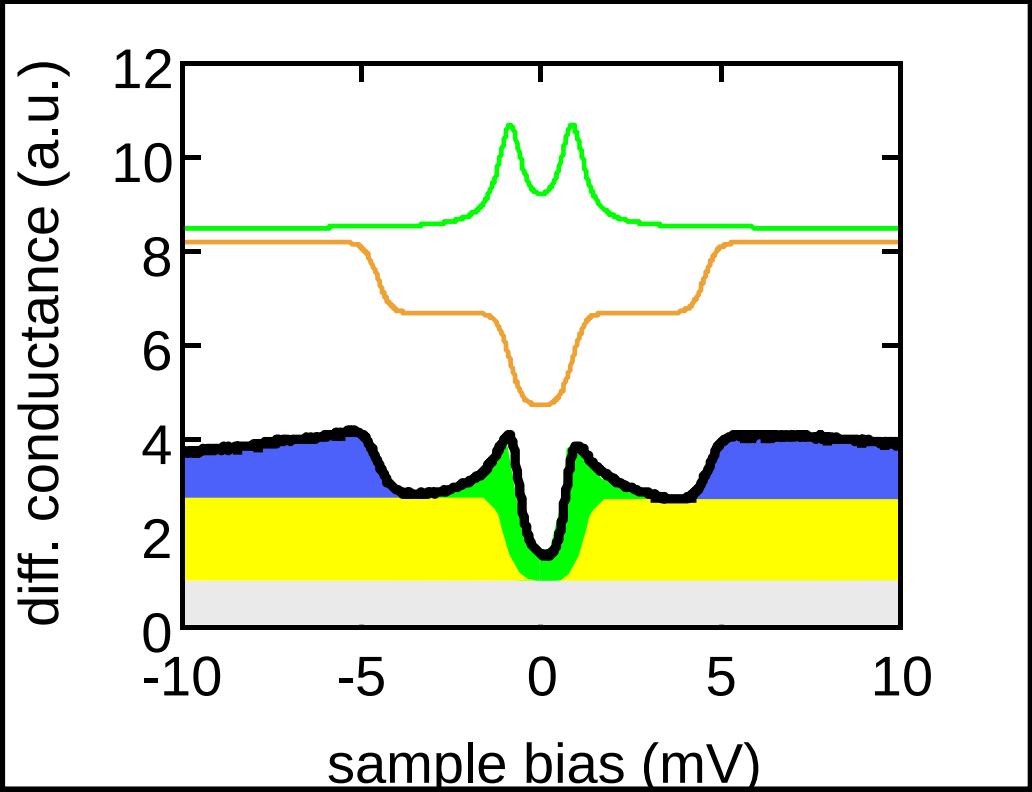
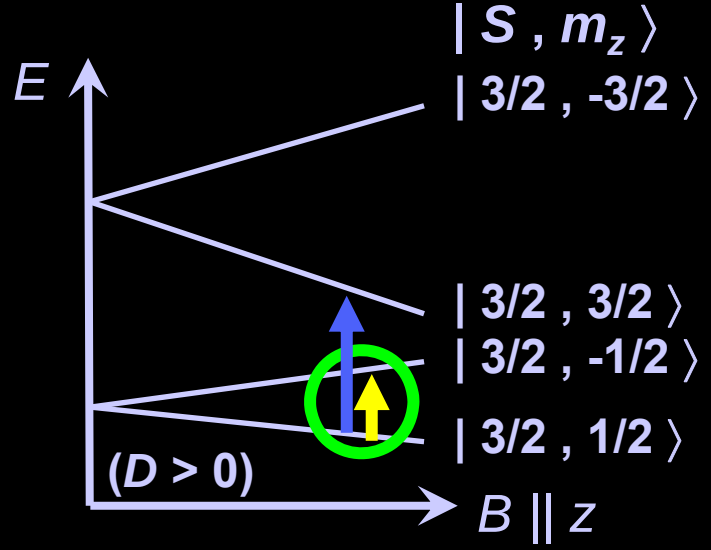
What transitions do we see at field?





- **IETS inner step at known energy and known intensity**
- **IETS spectrum WITHOUT Kondo effect**
- **Kondo contribution fitted as two Lorentzians**
- ***Nature Physics*, November 2008**

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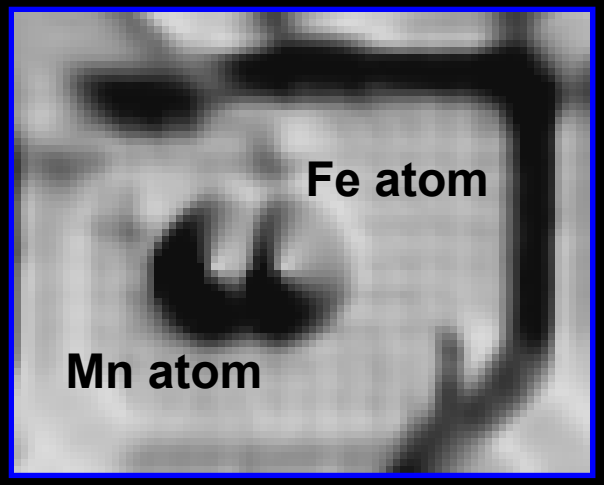
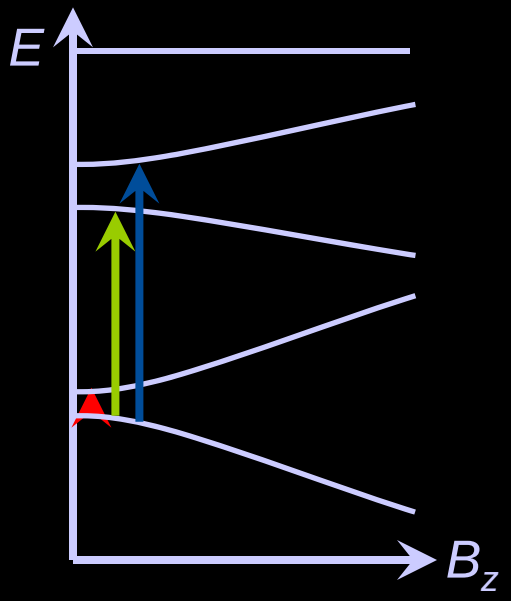
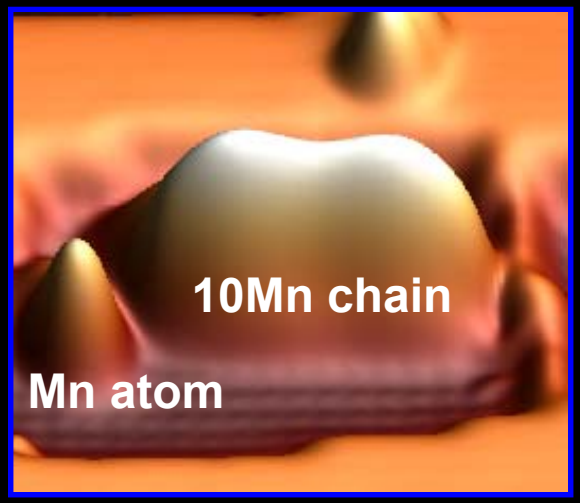
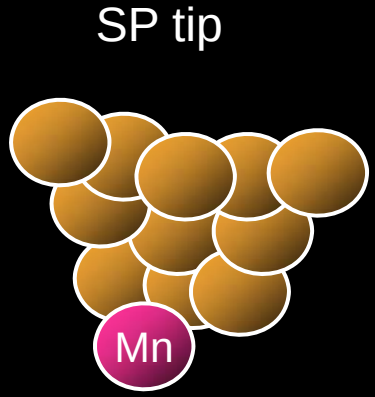


Summary

- Spin excitation spectroscopy probes individual spin systems
- STM allows precise assembly
- Magnetic anisotropy
- Spin coupling: Heisenberg exchange
- Spin-polarized spectroscopy







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The STM and theory team

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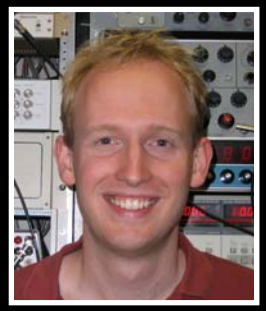

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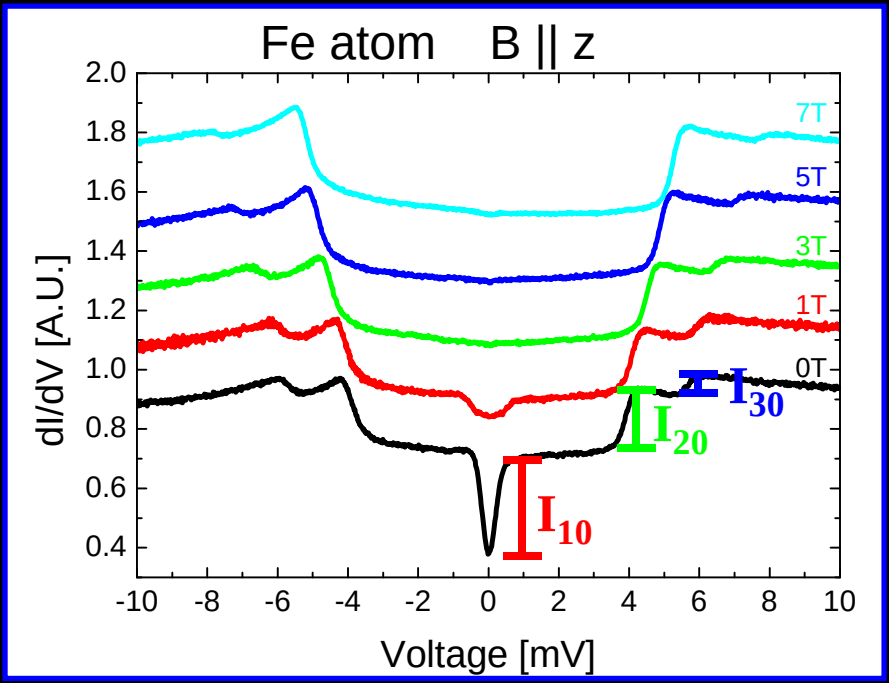
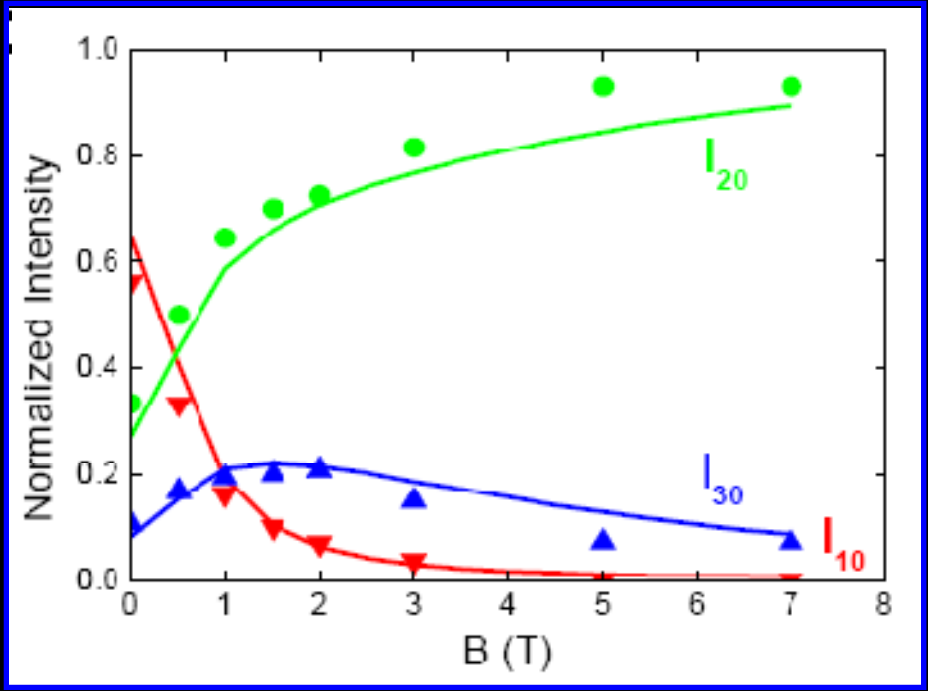
Why are some spin transitions strong?





- **Empirical selection rule: $\Delta m_z = 0, \pm 1$**

$$I_{fi} \propto \left|\langle \psi_f | S_+ | \psi_i \rangle\right|^2 + \left|\langle \psi_f | S_- | \psi_i \rangle\right|^2 + 2\left|\langle \psi_f | S_z | \psi_i \rangle\right|^2$$

- **Transition Hamiltonian equals inelastic neutron scattering!**

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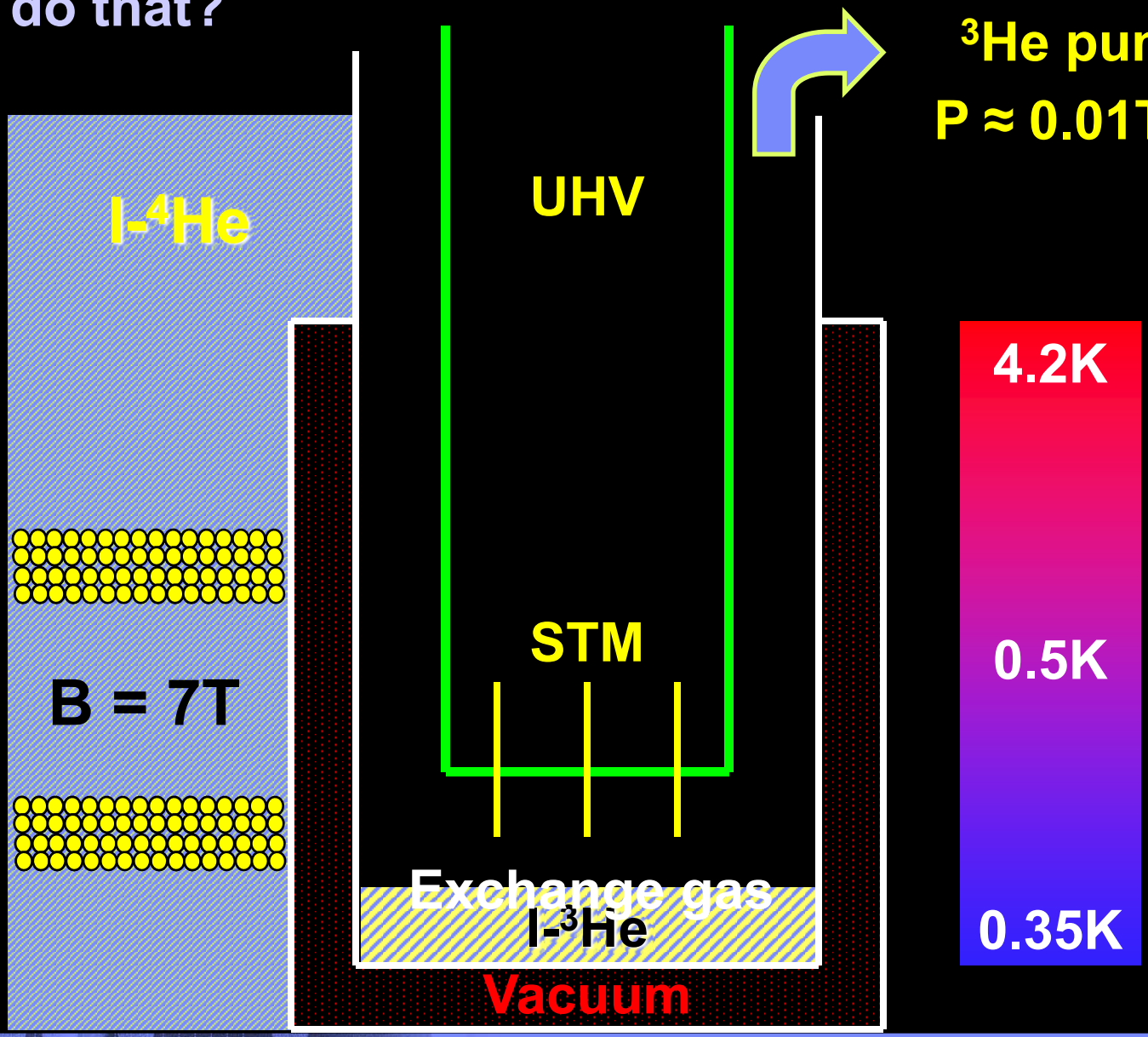
How to do that?



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