## Introduction to Molecular Magnetism

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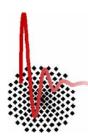
### Aims and contents

- What is a single molecule magnet?
- What is so interesting about single molecule magnets?
- What is the origin of the slow relaxation?
- What is Quantum Tunneling of the Magnetization?
- What is Mesoscopic Quantum Coherence?
- What is the Berry Phase and how can you observe it in single molecule magnets?

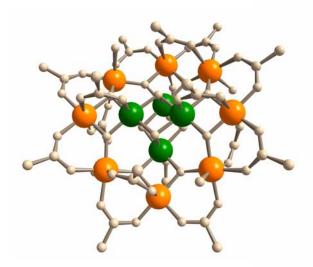
### What is a Single Molecule Magnet

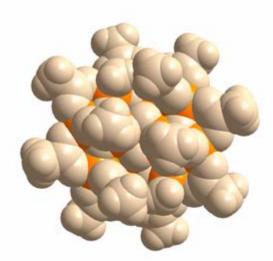


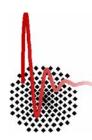
- A single molecule magnet is a molecule that shows slow relaxation of the magnetization of purely molecular origin.
- It is a molecule that can be magnetized in a magnetic field, and that will remain magnetized even after switching off the magnetic field.
- This is a property of the molecule itself. No interaction between the molecules is necessary for this phenomenon to occur.
- This makes single molecule magnets fundamentally different from traditional bulk magnets.
- You can dissolve a single molecule magnet in a solvent or put it in some other matrix, like a polymer, and it will still show this property.



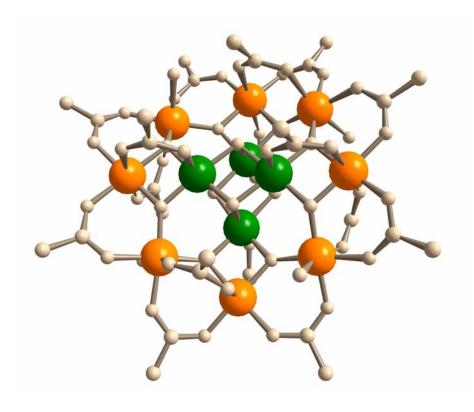
- Single molecule magnets belong to the more general class of compounds called exchange coupled clusters.
- A small number (~4 to 30) of paramagnetic transition metal ions are linked together by simple bridges such as O<sup>2-</sup>, OH<sup>-</sup>, OCH<sub>3</sub><sup>-</sup>, F<sup>-</sup>, Cl<sup>-</sup>, RCOO<sup>-</sup>.
- This bridge creates a superexchange pathway giving rise to an isotropic exchange coupling in the order of 1 to 100 cm<sup>-1</sup>.
- The organic ligands on the outside shield the exchange coupled cluster from the environment, esp. with respect to exchange interactions.
- Often single molecule magnets are portions of a mineral lattice encapsulated by organic ligands







The most famous examples are Mn<sub>12</sub>Ac, Fe<sub>8</sub>, [Mn<sub>4</sub>]<sub>2</sub>



### Mn<sub>12</sub>Ac

 $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$ 

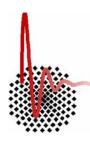
 $4 \text{ Mn}^{4+} \text{ ions } (S = 3/2): S = 6$  $8 \text{ Mn}^{3+} \text{ ions } (S = 2)$ : S = 16

Total **S** = **10** 

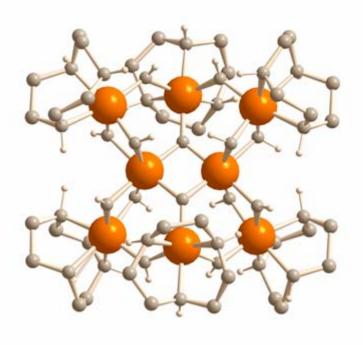
Mn ions are linked by O<sup>2-</sup> bridges.

Acetate ligands are bound on the outside of the molecule.

These acetates can be chemically replaced, tuning properties or for linking of molecules to surfaces.



•The most famous examples are Mn<sub>12</sub>ac, Fe<sub>8</sub>, [Mn<sub>4</sub>]<sub>2</sub>



### Fe8 $[(tacn)_6Fe_8(O)_2(OH)_{12}(H_2O)]$

8 Fe<sup>3+</sup> ions (S = 5/2)

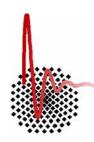
2 ions with spin down: S = 56 ions with spin up: S = 15

Total **S** = **10** 

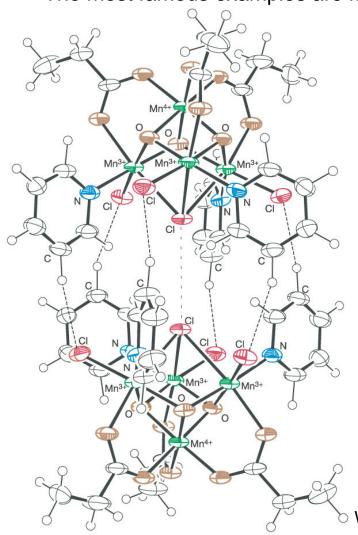
Fe ions are linked by O<sup>2-</sup> and OH<sup>-</sup> bridges.

tach ligands are bound on the outside of the molecule.

In this molecule possible synthetic variations are the counter ions (symmetry) and the isotopes (study of hyperfine influences).



•The most famous examples are Mn<sub>12</sub>ac, Fe<sub>8</sub>, [Mn<sub>4</sub>]<sub>2</sub>



### [Mn<sub>4</sub>]<sub>2</sub>[Mn<sub>4</sub>O<sub>3</sub>CI<sub>4</sub>(CH<sub>3</sub>CH<sub>2</sub>COO)<sub>3</sub>(py)<sub>3</sub>]<sub>2</sub>

1 Mn<sup>4+</sup> ion (S = 3/2): S = 3/2 3 Mn<sup>3+</sup> ions (S = 2): S = 6

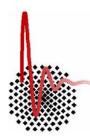
Total S = 9/2.

Mn ions are bridged by O<sup>2-</sup>, Cl<sup>-</sup>, and proprionate.

Pyridine and more Cl<sup>-</sup> ligands are bound on the outside of the molecule.

There is a weak superexchange interaction between the two molecules of the dimer.

# What is so interesting about Single Molecule Magnets?



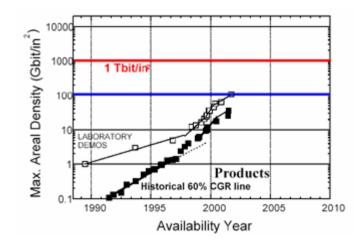
### What is so interesting about single molecule magnets?

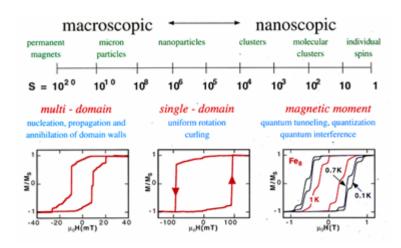
### **Materials science:**

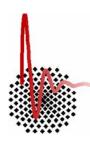
- One molecule can be seen as one bit.
- This leads to unprecedented data densities.
- Conventional materials are reaching the superparamagnetic limit.

### **Physics:**

- These systems are in between classical and quantum magnetic systems.
- They show distinct quantum properties.



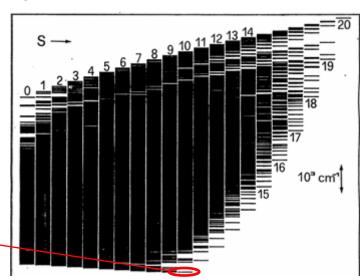


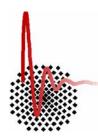


- The properties of a molecular magnet are usually described in the spin Hamiltonian model.
- Usually the strong exchange approximation is applied, meaning that the isotropic Heisenberg exchange interaction is much stronger than all other terms in the spin Hamiltonian.  $\hat{\mathbf{H}}_{\mathrm{ex}} = J\hat{\mathbf{S}}_{1}\cdot\hat{\mathbf{S}}_{2}$
- The dimensions of the Hilbert space, (2S+1)<sup>N</sup>, for large exchange coupled clusters are huge.
- Exact diagonalisation is still possible for systems like Fe<sub>8</sub>, when grouping together the states with the same total spin, and using irreducible tensor methods.

 $Mn_{12}Ac$ : 1.0 x 10<sup>8</sup>  $Fe_8$ : 1.7 x 10<sup>6</sup>  $[Mn_4]_2$ : 2.5 x 10<sup>5</sup>

spin ground state





- The large S ground state has 2S+1 spin microstates, which correspond to the M<sub>S</sub> states in the absence of transverse anisotropy.
- These can be split up in zero field by spin-orbit coupling or magnetodipolar interactions if S>½. This is called **zero-field splitting**.
- **Magnetodipolar interactions** are usually small (10<sup>-1</sup> cm<sup>-1</sup>) but the only source of ZFS for organic radicals.
- The orbital angular momentum of the electronic ground state is usually quenched by spin-orbit coupling and/or (Jahn-Teller) distortion.
- Spin-orbit coupling can mix orbital angular momentum of the electronically excited state into the ground state.



- The zero-field splitting can be described by a term in the spin Hamiltonian:
- Here **D** is a 3 x 3 matrix:

$$\mathbf{D} = \begin{pmatrix} D_{xx} & 0 & 0 \\ 0 & D_{yy} & 0 \\ 0 & 0 & D_{zz} \end{pmatrix}$$

$$\hat{\mathbf{H}}_{ZFS} = \hat{\mathbf{S}} \cdot \mathbf{D} \cdot \hat{\mathbf{S}}$$

We can rewrite the spin Hamiltonian term as:

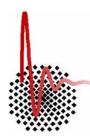
$$\hat{\mathbf{H}}_{ZFS} = D[\hat{\mathbf{S}}_{z}^{2} - S(S+1)/3] + E(\hat{\mathbf{S}}_{x}^{2} - \hat{\mathbf{S}}_{y}^{2})$$

where:

$$D = 3D_{zz} / 2$$

$$E = |D_{xx} - D_{yy}| / 2$$

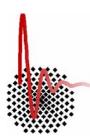
- The D term changes the energies of the M<sub>S</sub> states.
- The *E* terms **mixes the M<sub>S</sub> states** (with  $\Delta$ M<sub>S</sub>=2), i.e. the pure M<sub>S</sub> states are no longer the energy eigenstates of the system.



- The zero-field splitting can be expanded in a series of magnetic multipoles, where we just saw the first term.
- In principle terms up to the order of 2S can be included.
- For terms higher than the second power of the spin operators, usually Stevens operator equivalents are used.
- The fourth order term in the spin Hamiltonian is:

$$\hat{\mathbf{H}}_{\mathrm{ZFS}} = \sum_{k} B_4^k \mathbf{O}_4^k$$

- The Stevens operators  $O_4^k$  are linear combinations of the spin operators to the fourth power.
- The sum runs over k = 0 to k = 4.
- For tetragonal symmetry only terms with k = 0 and k = 4 are nonzero.
- For trigonal symmetry only terms with k = 0 and k = 3 are nonzero.
- For orthorhombic symmetry, only terms with k = 0, k = 2, and k = 4 are nonzero.
- These terms correspond to higher order mixing of excited states into the ground state.

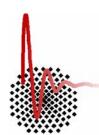


The full spin Hamiltonian is then:

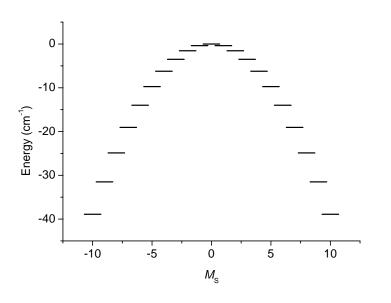
$$\hat{\mathbf{H}} = D[\hat{\mathbf{S}}_{z}^{2} - S(S+1)/3] + B_{4}^{0}\hat{\mathbf{O}}_{4}^{0} + g\mu_{B}\hat{\mathbf{S}}_{z}\mathbf{H}_{z} + E(\hat{\mathbf{S}}_{x}^{2} - \hat{\mathbf{S}}_{y}^{2}) + B_{4}^{2}\hat{\mathbf{O}}_{4}^{2} + B_{4}^{4}\hat{\mathbf{O}}_{4}^{4} + g\mu_{B}\hat{\mathbf{S}}_{x,y}\mathbf{H}_{x,y}$$

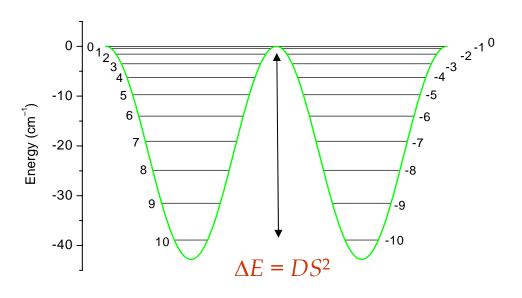
Axial terms change the energies of the spin microstates but not the characters.

Transverse terms change the characters of the spin microstates.

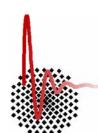


One can plot the energies of the microstates against  $M_{\rm S}$  ....or against the angle of the magnetic moment with the quantisation axis.



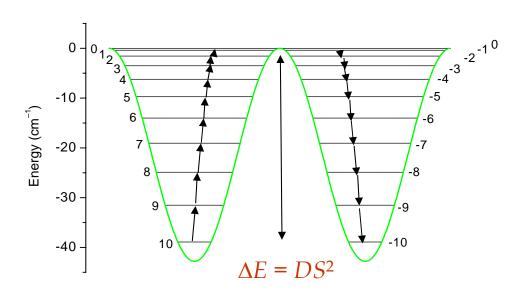


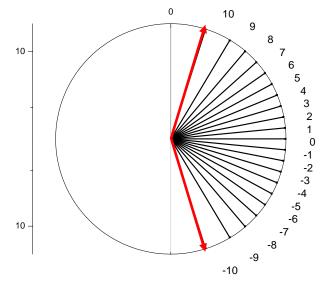
 $< B c \longrightarrow$ 

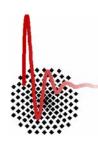


Phonon induced transitions between spin microstates are only allowed with  $\Delta M_S = 1$  or  $\Delta M_S = 2$ .

This creates an energy barrier towards thermal inversion of the magnetic moment.





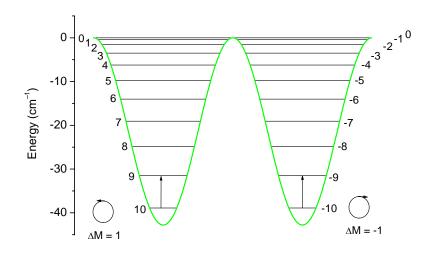


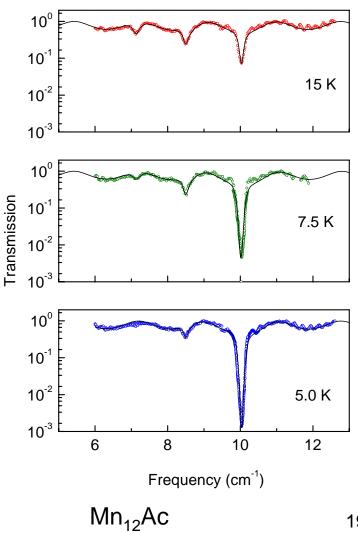
Experimental determination of the zero field splitting:

**High Field Electron Paramagnetic Resonance (HFEPR)** 

**Inelastic Neutron Scattering (INS)** 

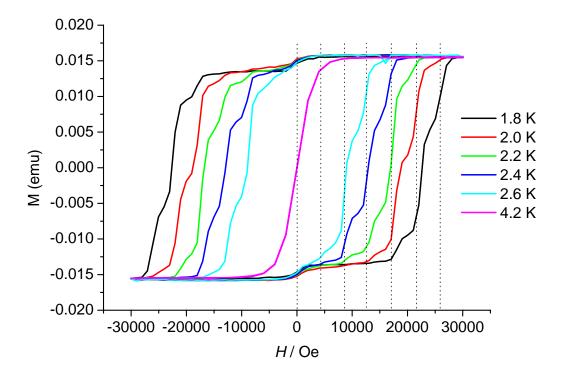
**Frequency Domain Magnetic Resonance (FDMRS)** 

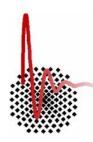




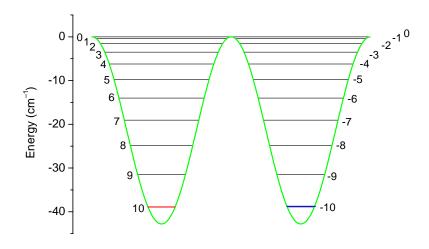


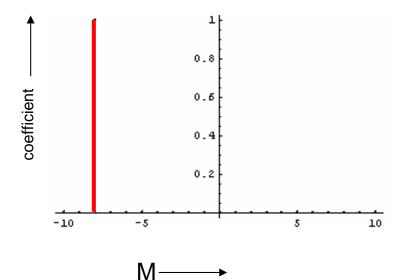
- In 1995 it was discovered that there are steps at regular field intervals in the magnetic hysteresis curve of Mn<sub>12</sub>Ac.
- Apparently at certain fields, the magnetisation relaxes faster.
- This phenomenon became later known as Quantum Tunneling of the Magnetisation.

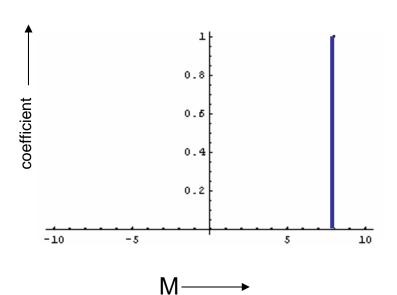




- In zero field, the levels on the left and right sides of the potential energy double well are degenerate.
- In the absence of transverse anisotropy, the energy eigenstates of the systems are the pure M<sub>S</sub> states.

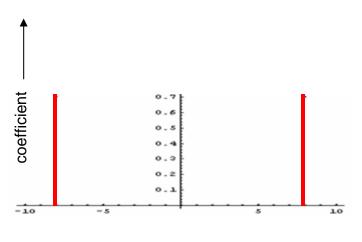




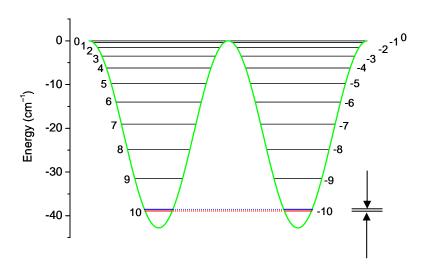


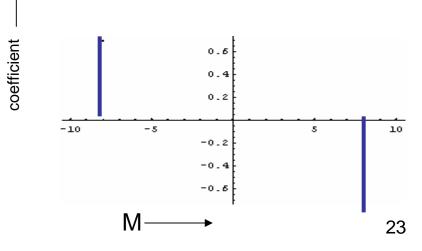


- As soon as there is a transverse anisotropy, the M<sub>S</sub> states are no longer the energy eigenstates.
- Near the bottom, the eigenstates are then the superpositions of the M<sub>S</sub> states on the left and right of the potential energy double well.
- At higher energy the second order transverse anisotropy mixes  $M_S$  levels with  $\Delta M_S$ =2, and the fourth order transverse anisotropy those with  $\Delta M_S$ =4.



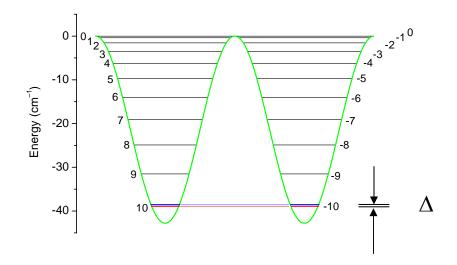


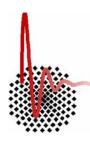






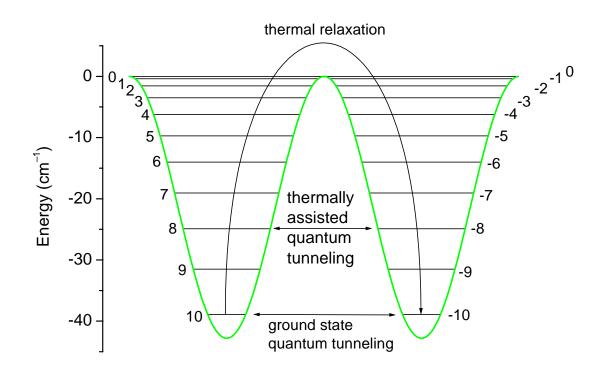
- The eigenstates are now  $|M_S>+|-M_S>$  and  $|M_S>-|M_S>$ .
- The splitting between them is called tunnel splitting ( $\Delta$ ).
- In a static picture one can say that the system is located both on the left and right of the energy barrier.
- In a dynamic picture one can say that the system oscillates coherently between the two sides at a frequency which is equal to the tunnel splitting, until coupling to the environment destroys coherence.
- The tunnel splitting in SMM is very small.
- The magnetisation can tunnel but only incoherently.

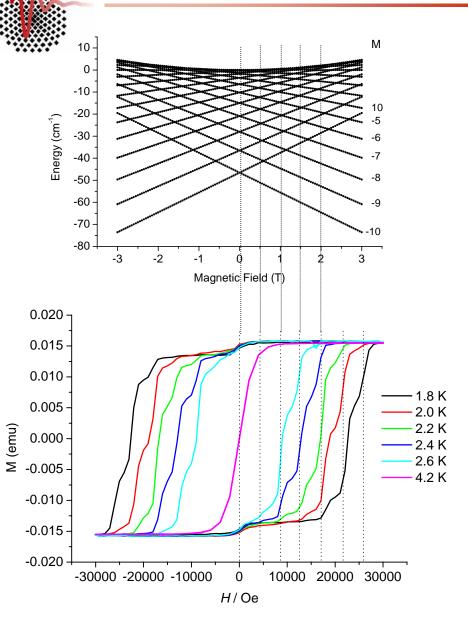




There are three ways that the magnetisation can invert.

- Thermal relaxation
- 2. Thermally- (phonon-) assisted tunneling
- 3. Ground state tunneling.

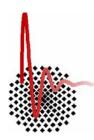


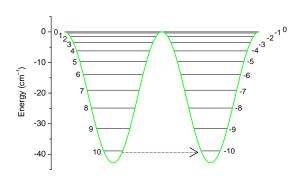


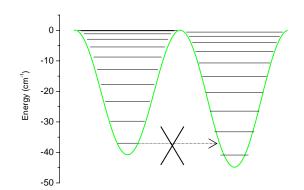
When a longitudinal field is applied, the spin microstates change energy according to the Zeeman interaction.

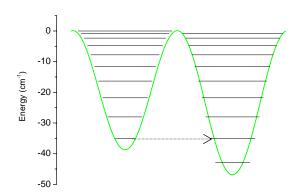
At certain levels the microstates cross.

The transverse anisotropy mixes the MS levels at those fields making tunneling of the magnetisation possible



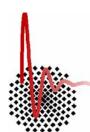


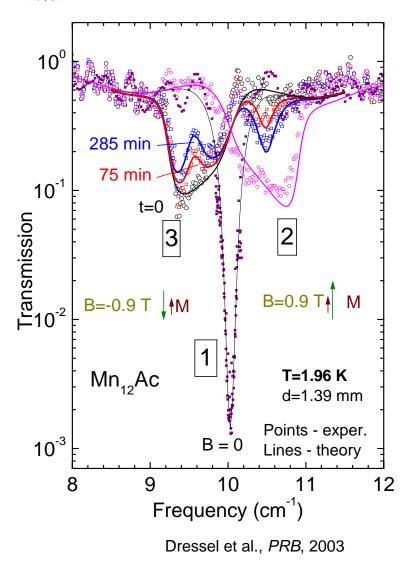




### In the double well picture:

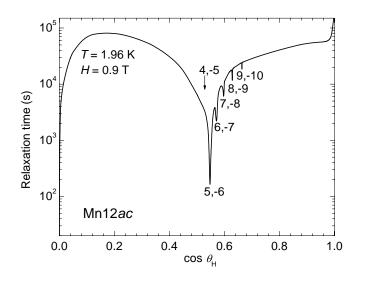
- At zero field, the M levels on the left and right are in resonance.
- Application of a magnetic field lifts this degeneracy.
- At a certain field levels on the left and right come into resonance again.





We were able to see QTM also spectroscopically:

- At zero field, the magnetic resonance line of a powder sample of Mn<sub>12</sub>Ac lies at ~10 cm<sup>-1</sup> [1].
- In a field cooled sample, the line broadens and shifts to higher frequency [2].
- On reversing the field, the system ends up in a metastable state [3].
- Some molecules experience a longitudinal field such that QTM occurs and a tunnel dip forms in the spectra.



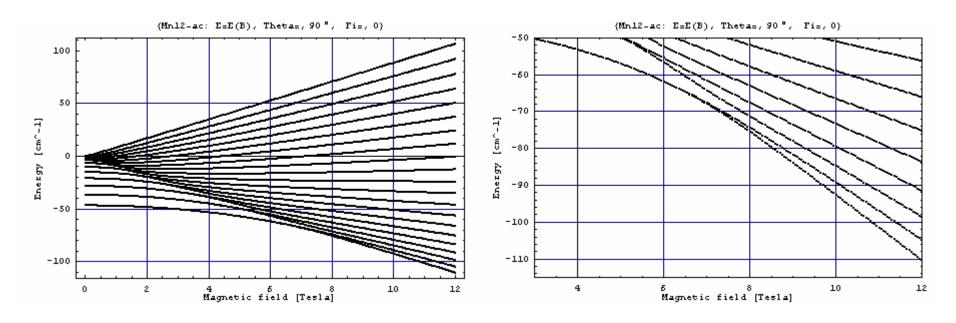


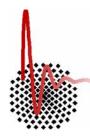
- Macroscopic Quantum Coherence is realised when quantum tunneling between energetically degenerate and macroscopically different states occurs at a rate which is large compared to the decoherence rate
- Another view is that the energy eigenstates are coherent superpositions of states which are macroscopically different.
- Mesoscopic is used here to indicate the scale between microscopic and true macroscopic phenomena.



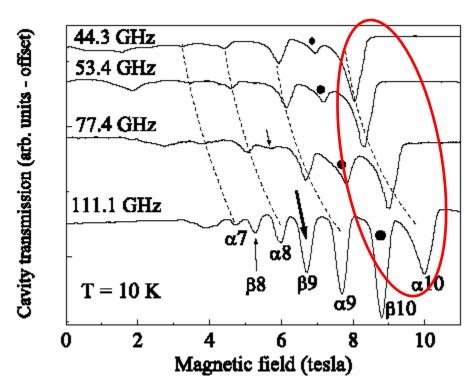
The zero field tunnel splittings in high spin clusters are generated by transverse crystal field splitting.

- They are small:
  - Ground state tunnel splitting ( $\Delta$ ) in Mn<sub>12</sub>Ac:  $\Delta/k_{\rm B} \sim 10^{-10}$   $10^{-11}$  K.
  - Tunnel splitting is larger for higher M states:  $M = \pm 4$ ,  $\Delta/k_B = 10^{-2}$  K;  $M = \pm 2$ ,  $\Delta/k_B = 0.7$ K.
  - In Fe<sub>8</sub>, ground state tunnel splitting perhaps 10<sup>-7</sup> K.
- The main sources of decoherence are intermolecular dipolar interactions (0.1 K) and hyperfine interactions (0.01 0.1 K).
- Application of a transverse magnetic field leads to an increase in the tunnel splitting.

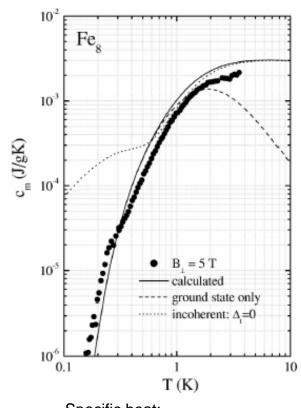




- On application of a transverse magnetic field the tunnel splitting can be made larger than sources of decoherence,.
- If the field is large enough it may be observed in experiment.
- This is sometimes taken as proof for the occurrence of MQC.



HFEPR: Hill et al., cond-mat/0302052

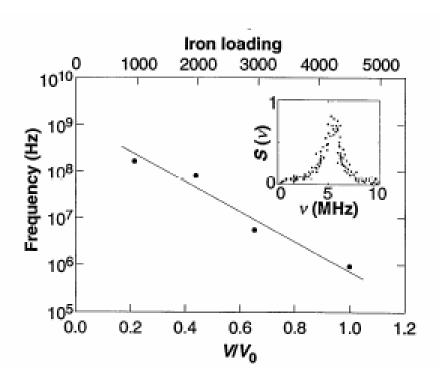


Specific heat: Mettes et al., *PRB*, 2001 Luis et al., *PRL*, 2000

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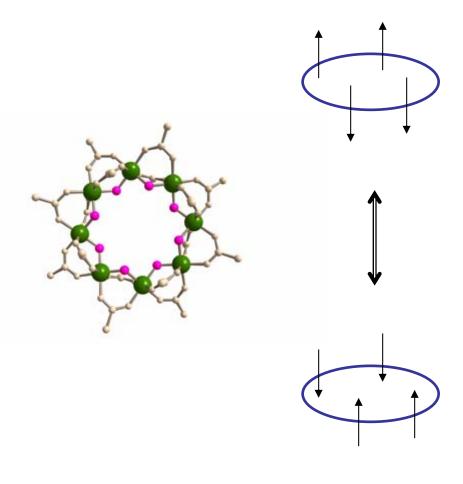
- In antiferromagnetic systems the spin dynamics are governed by the exchange interaction.
- In these cases tunnel splittings can easily be made larger than the sources of decoherence.
- Furthermore because of the small net magnetic moment, coupling to the environment is small.
- The first experimental claims of MQC were made on ferritin, a naturally occurring antiferromagnetic system.
- MQC is observed as coherent tunneling of the Neel vector.



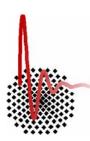
Gider et al., Science, 1995



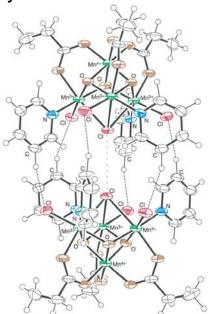
- In antiferromagnetic rings with an even number of paramagnetic ions the total spin is S = 0.
- The ground state is the superposition of the two Neel states.
- On tunneling of the Neel vector, the net magnetic moment does not change
- Therefore a local probe is needed which couples to the oscillations of the Neel vector (NMR).
- Another solution is to replace one of the spins by different one, to create a net magnetic moment.
- In that case EPR can be used to observe the tunneling of the Neel vector.



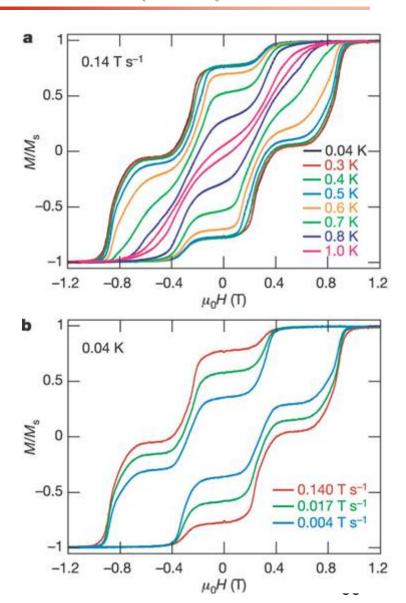
Meier, Loss, PRL 2001, PRB, 2001



- Recently, a single molecule magnet was reported that consists of two molecules that are weakly superexchange coupled in the crystal.
- The used abbreviation is [Mn<sub>4</sub>]<sub>2</sub>.
- The exchange interaction shifts the steps in the magnetic hysteresis curve.

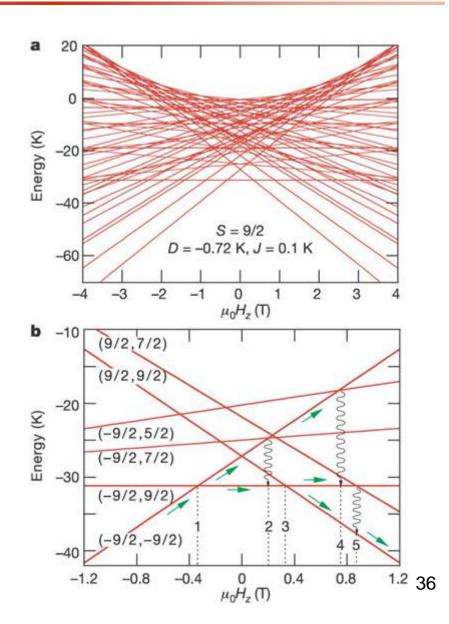


Wernsdorfer et al., Nature 2002

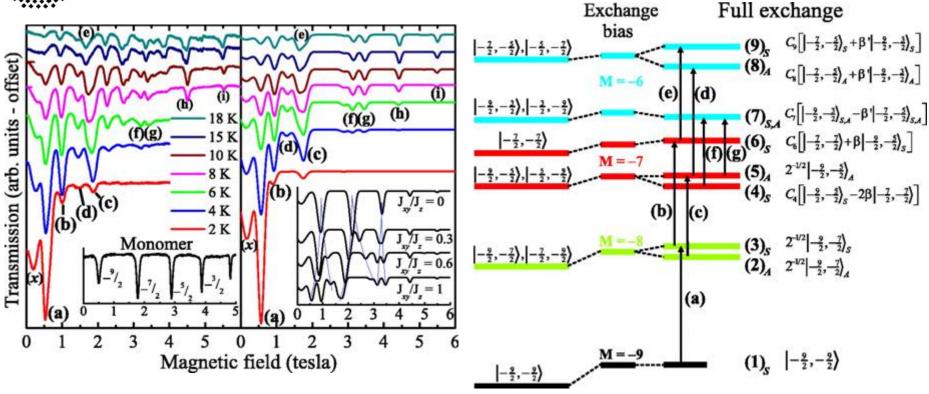




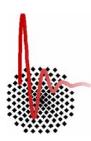
- Due to the weak exchange interaction (J ~ 0.1 cm<sup>-1</sup>), the system behaves as two exchange coupled S = 9/2 spins.
- This leads to the absence of a level crossing at zero field.







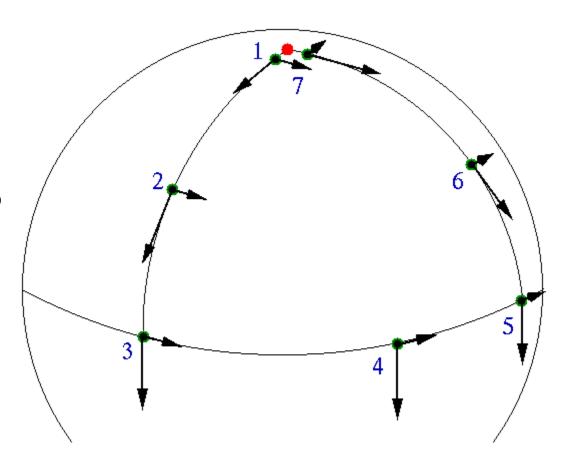
- The HFEPR spectrum shows a much more complicated pattern than monomeric derivatives of Mn₄.
- Since the energy splittings are much larger than possible sources of decoherence, this was claimed as an observation of mesoscopic quantum coherence.

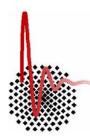


Any "vector" object which is parallel transported along a path back to the original place, may acquire an *angle* with respect to its initial direction prior to transport. This angle is a geometric property.

A phase change can occur when the surface along which the vector object is transported is not flat.

No phase change is observed when the vector object is transported along a flat surface.





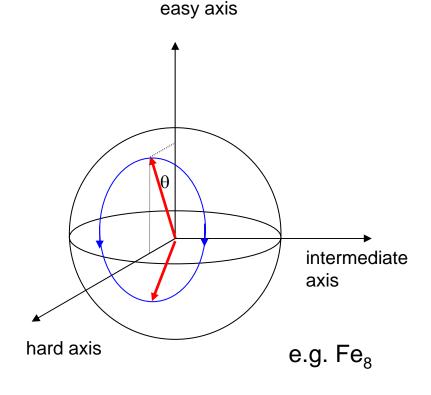
The magnetic moment is preferentially oriented along the easy axis, i.e. the z axis

In the xy plane it has a preference for the intermediate or y axis.

In order to invert, the magnetic moment can choose two pathways, clockwise and anticlockwise in a plane parallel to the yz plane.

The two paths lead to different acquired phases.

Applying a magnetic field along the hard axis tilts the magnetic moment towards the hard axis.



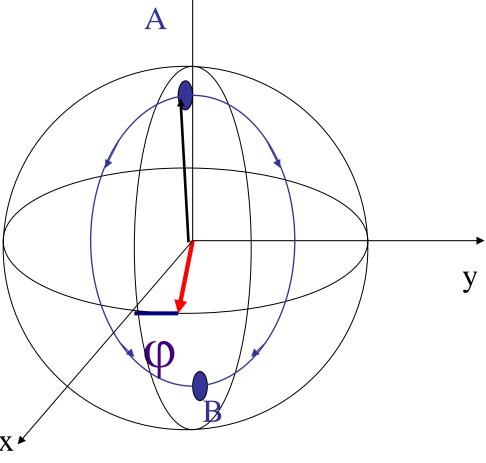
The acquired phases on reversal change with the applied field.

For some magnetic fields the acquired phases are opposite and the tunneling probability becomes zero due to their interference.

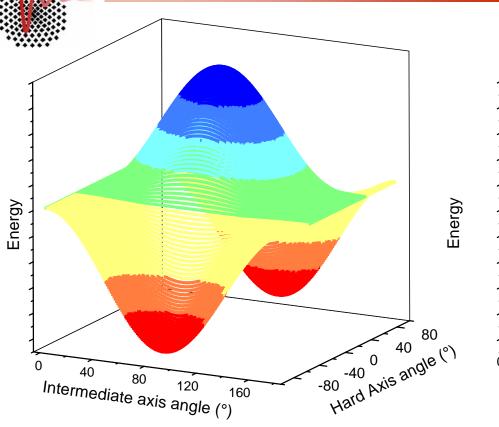


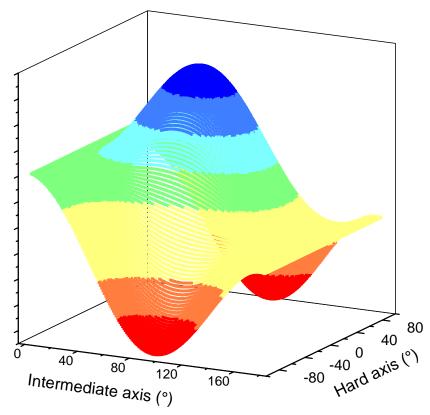
For a magnetic field component along the intermediate axis there is only one tunneling path.

Hence there is no interference.

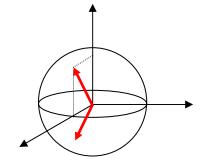


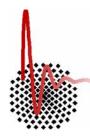
 $\uparrow Z$ 





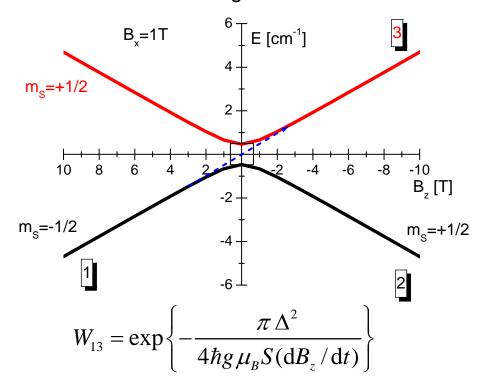
The tunneling path is that which passes the lowest barrier, i.e. it minimises the classical action

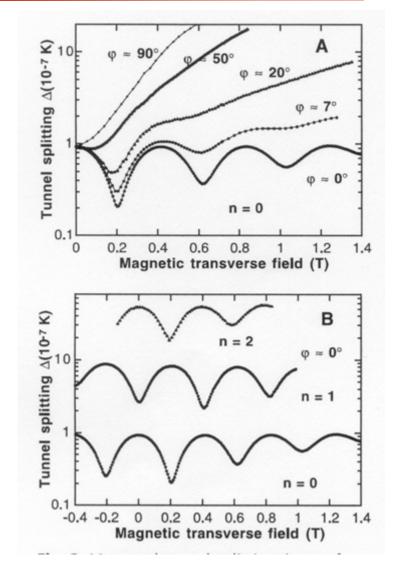




The occurence of periodic quenching of the tunnel splitting was experimentally observed in Fe<sub>8</sub> by a method known based on Landau-Zener tunneling.

For smaller sweep rates the system has more time to relax to the ground state.





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This effect can also occur in Mn<sub>12</sub>Ac.

Since the symmetry is tetragonal, the x- and y-axes are both intermediate axes.

The hard axis lies along the bisecting line.

