Decoherence in molecular magnets: Fe_8 and Mn_{12}

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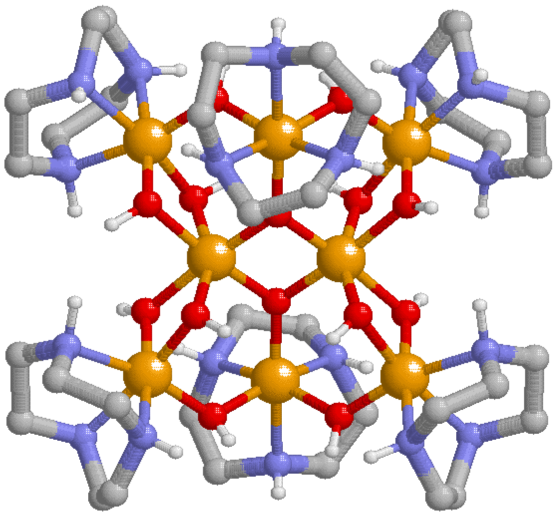
Early 70-s: Fast magnetic relaxation in rare-earth systems (Dy_3Al_2, $SmCo_{3.5}Cu_{1.5}$)
Quantum Tunneling Phenomenon

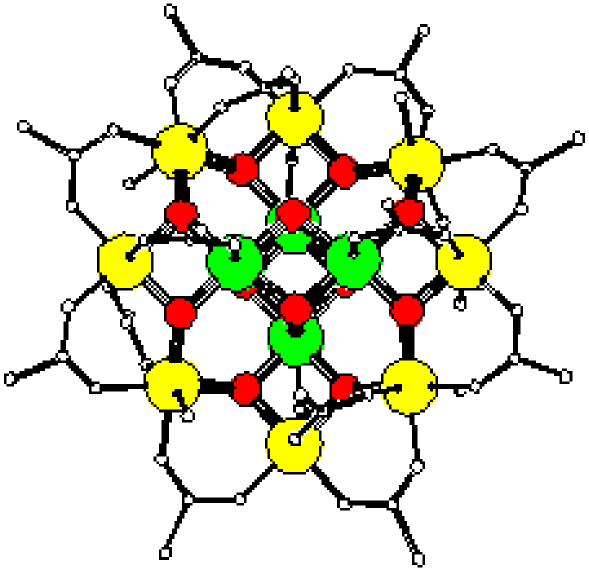
Early 90-e: Single-molecule magnets (SMM)



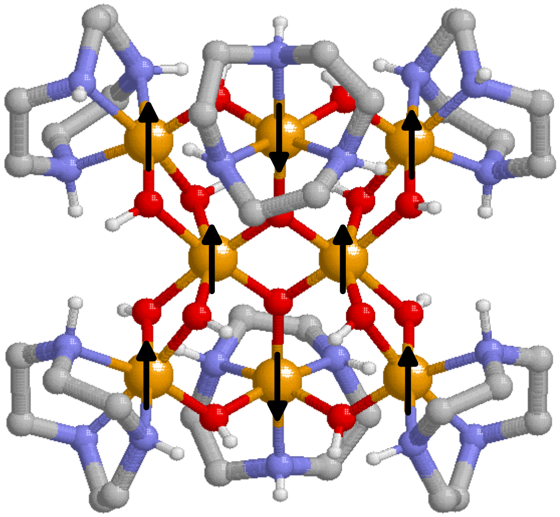
Quantum Relaxation in crystals of SMM

Fe_8: S = 10 **Mn_{12}: S = 10**

Present days:
Quantum Coherent Oscillations?

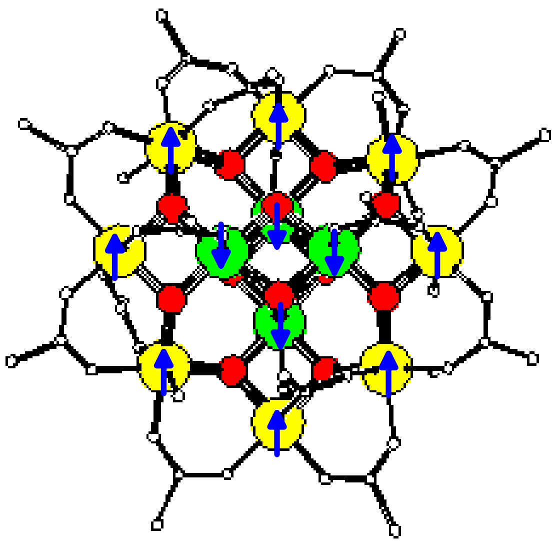


More than 100 systems are synthesized these days; **S = 0, 1/2, 1, 3/2, …, 51/2, …?**



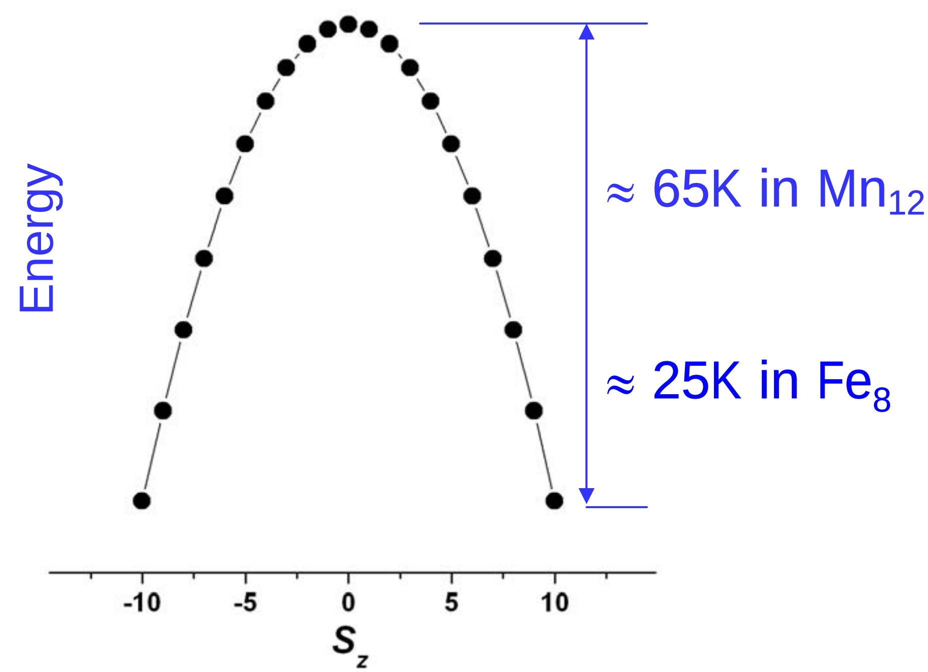
Fe_8, **T < 10 K, S=10**

Each molecule contains a core of magnetic ions, characterized by nonzero electronic spins $\boldsymbol{s}_i$ *(5/2 in* Fe_8 *, 3/2 and 2 in* Mn_{12}*)*, surrounded by various atoms with nonzero, or zero nuclear spins. At low-T all $\boldsymbol{s}_i$ are strongly coupled together forming the so called Central, or Giant Spin $\boldsymbol{S}$.



Mn_{12}, **T < 40 K, S=10**

The states with positive and negative S_Z are separated by the potential barrier



The Central Spin Hamiltonian

Low-T – all electronic spins are strongly coupled together

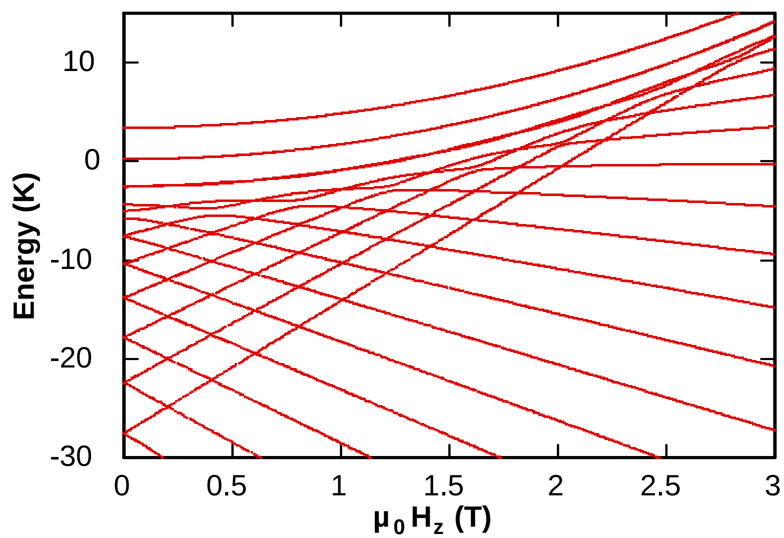
Fe_8: **T < 10 K** (S=10)

$$H_S^{(Fe)} = -DS_z^2 + ES_x^2 + K_4^{\perp}(S_+^4 + S_-^4) - g_e \mu_B \vec{H}\vec{S}$$

Mn_{12}: **T < 40 K** (S=10)

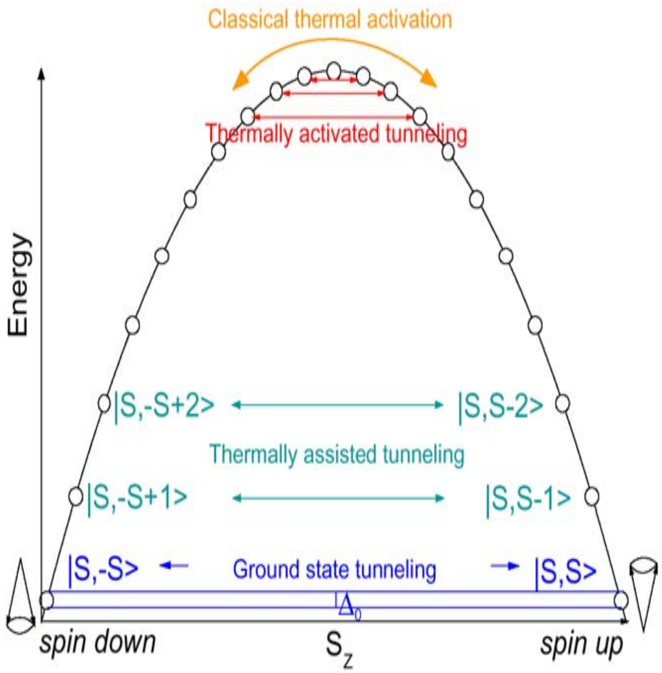
$$H_S^{(Mn)} = -DS_z^2 - K_4^{||} S_z^4 + K_4^{\perp}(S_+^4 + S_-^4) - g_e \mu_B \vec{H}\vec{S}$$

Fe_8 (*2S+1* states)

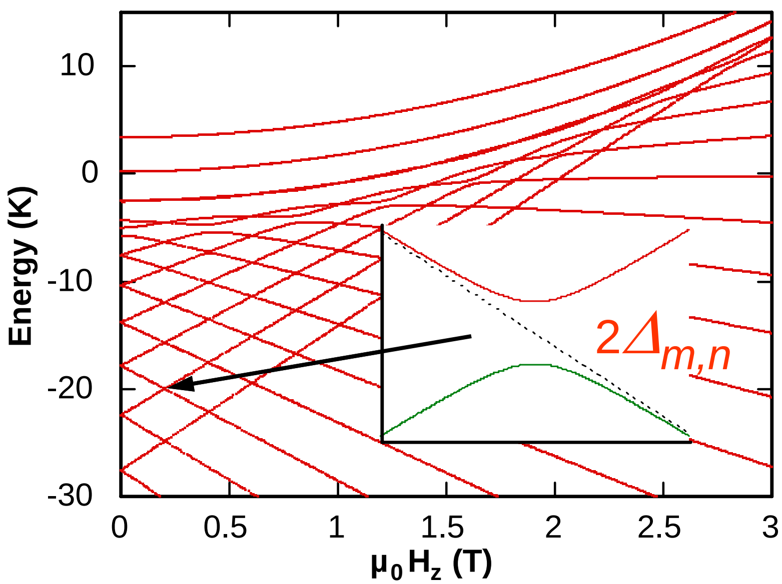


Quantum Tunneling

Classically, to go from one potential minimum to another, system can only activate over the top of the barrier. Quantum-mechanically, however, system can pass through the classically forbidden region - Quantum Tunneling.



"Anticrossing" of levels in Fe_8



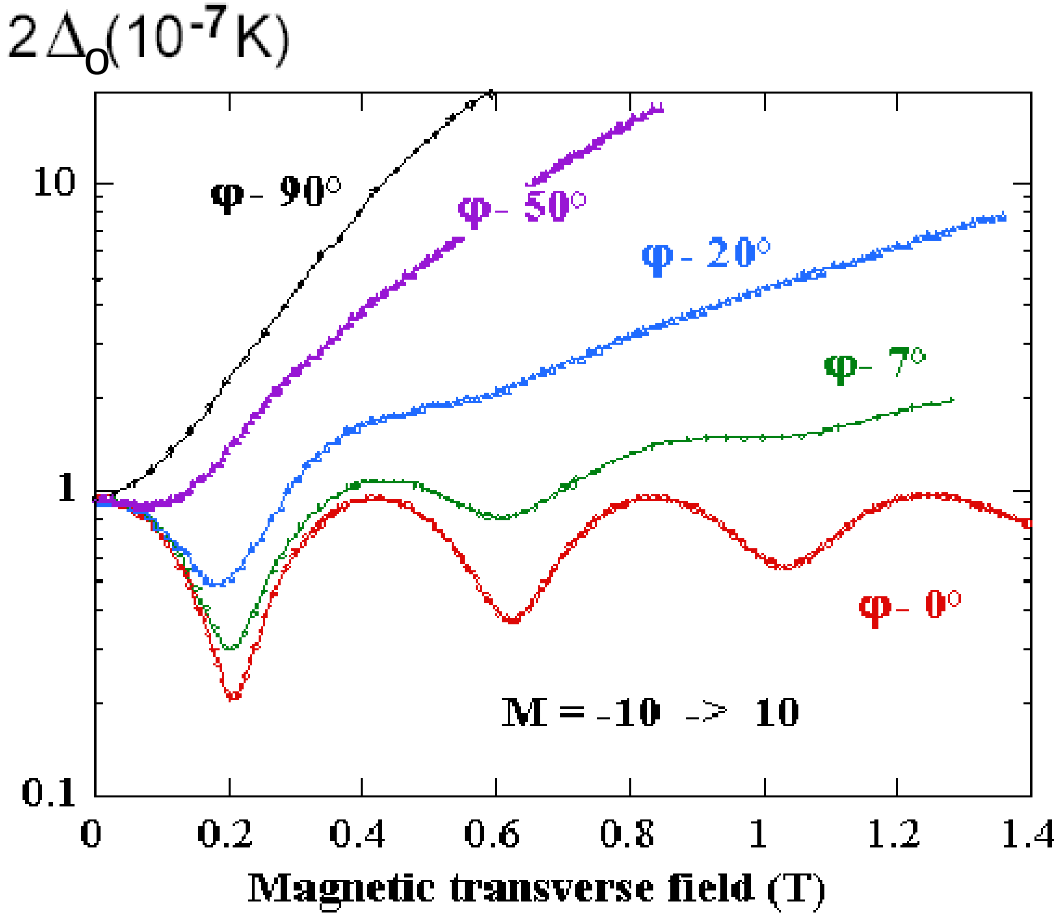
It is characterized by the tunneling matrix element $\Delta_{m,n}$ between the initial and the final states $\Delta_0 =< f \,|\, \widehat{V} \,|\, i >$, where $\widehat{V}$ is non-diagonal, like $S^{\alpha}_{\pm}$.

The tunneling splitting is then $2\Delta_{m,n}$. The higher the barrier, the smaller $\Delta_{m,n}$. Its value can be changed by applying the transverse field $H_{\perp}$.

Can the tunneling splitting be measured?

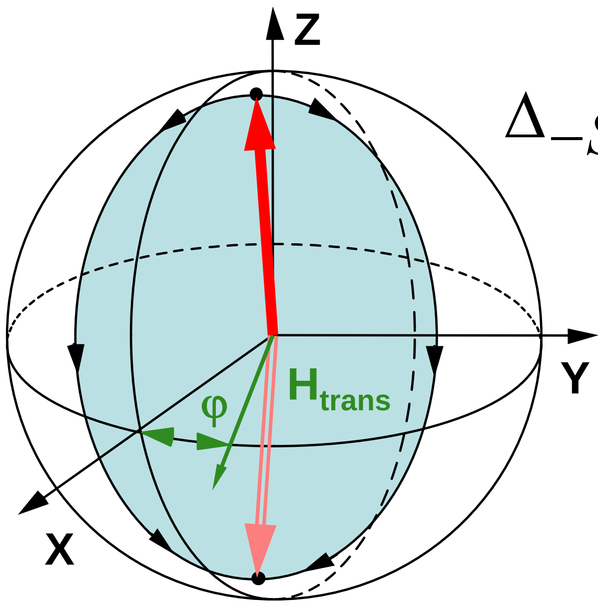
Yes, if it is not too small…

Experiment: Tunneling splitting $2\Delta_o$ between two lowest states in Fe_8 as a function of transverse magnetic field.



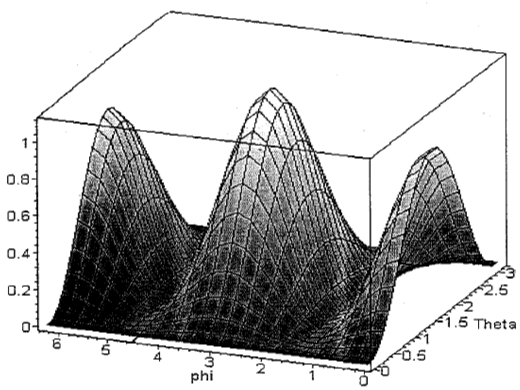
W. Wernsdorfer and R. Sessoli, 1999

Tunneling splitting: Theory

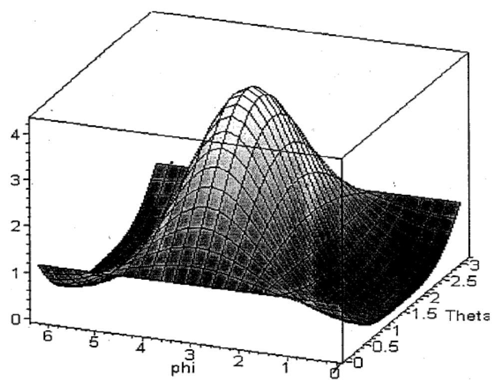


$H_\perp=0$

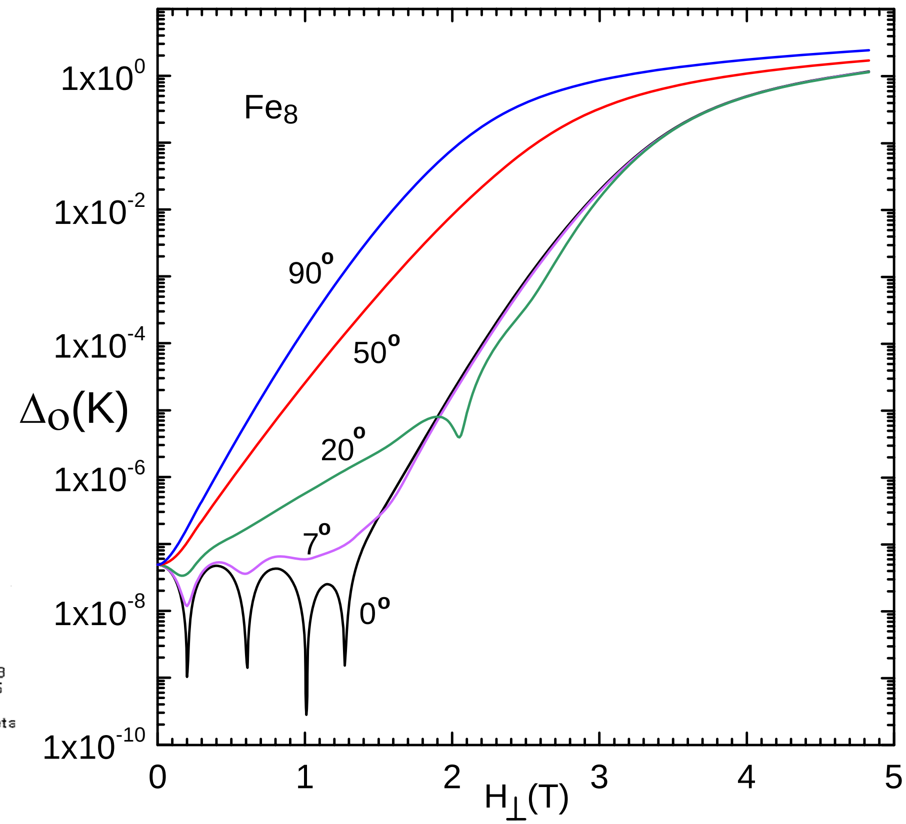
$$\Delta_{-S,S} = \Delta_o \,| e^{i\pi S} + e^{-i\pi S} | = 2\Delta_o \,| \cos(\pi S) |$$



$H_\perp < H_C$ (two ways)



$H_\perp > H_C$ (one way)



$H_\perp \neq 0$

$$\Delta_{-S,S} = 2\Delta_o \,| \cos(\pi S + i\pi H_X / T_X + \pi H_Y / T_Y) |$$

Very low-T limit – only two lowest states in both systems are occupied

Each molecule can be modeled as a Two Level System. This model works, however, only if $\Delta_o << \Omega_o$ (Ω_o is the gap to the first excited state).

Single TLS, no environment

$$H_{TLS} = -\Delta_o \hat{\tau}^x - \xi \hat{\tau}^z$$

Two solutions:

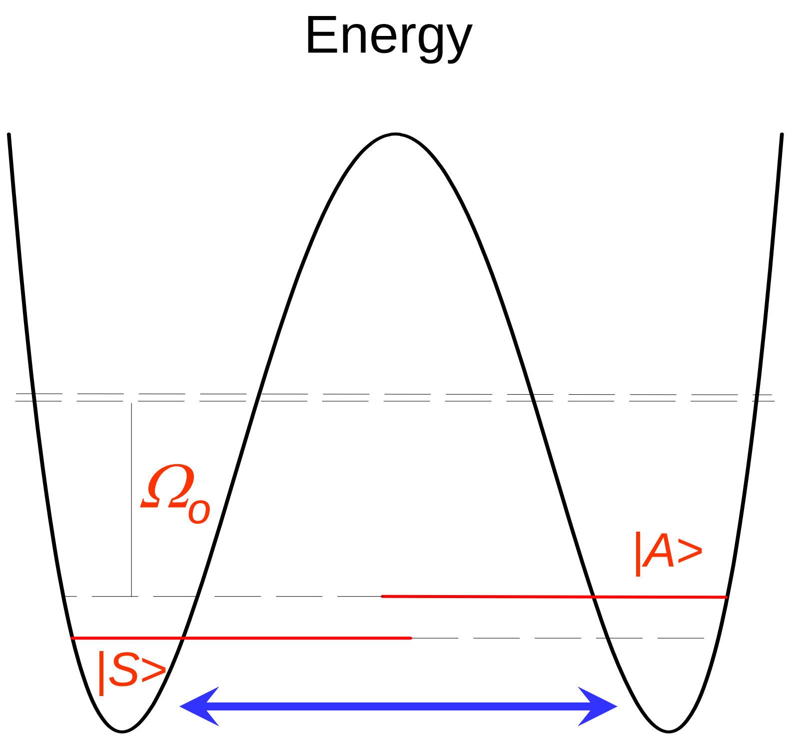
Symmetric: $|S\rangle = u|\uparrow\rangle + v|\downarrow\rangle$

Antisymmetric: $|A\rangle = -v|\uparrow\rangle + u|\downarrow\rangle$

$$E_{S,A} = 2\varepsilon;\ \varepsilon = (\Delta_o^2 + \xi^2)^{1/2}$$

Time-evolution: $\langle\uparrow| e^{-iHt/\hbar} |\downarrow\rangle$

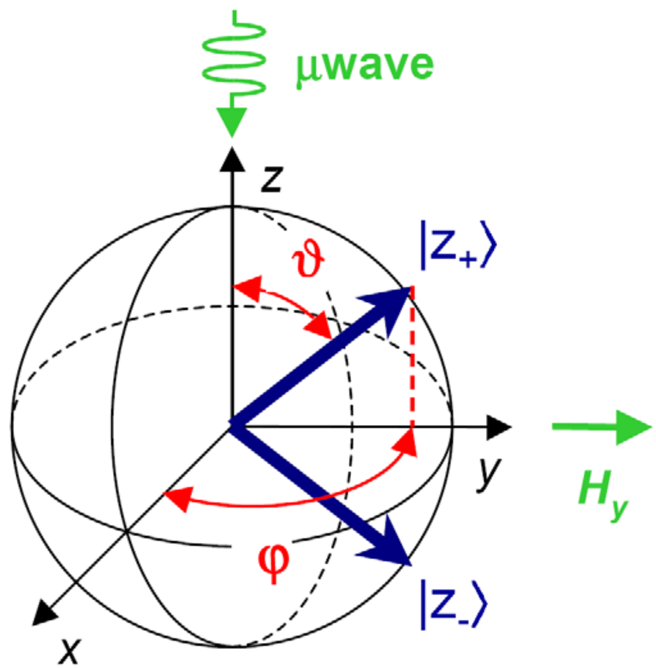
$$P_{\downarrow\uparrow} = \frac{\Delta_o^2}{\varepsilon^2} \sin^2(\varepsilon t/\hbar),$$



oscillations do not decay

Very low-T limit – real SMMs

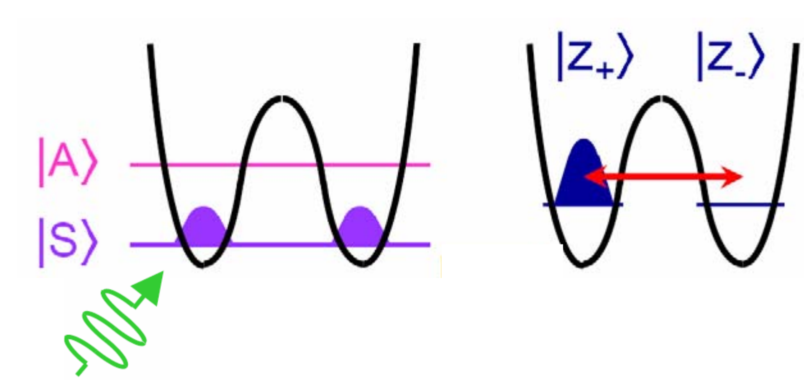
By applying transverse magnetic field one can create symmetric |S> and antisymmetric |A> states separated by the gap $2\Delta_o(H_\perp)$. By applying then micro-wave pulse one can mix up |S> and |A> states and create the one-well states $|Z_\pm>$ = $(|S> \pm |A>)/2^{1/2}$, initiating oscillations between them. Can these oscillations be coherent in a real SMM? If yes, for how long coherence can last?



$|Z_\pm>$ are not eigenstates of H_S

⇓

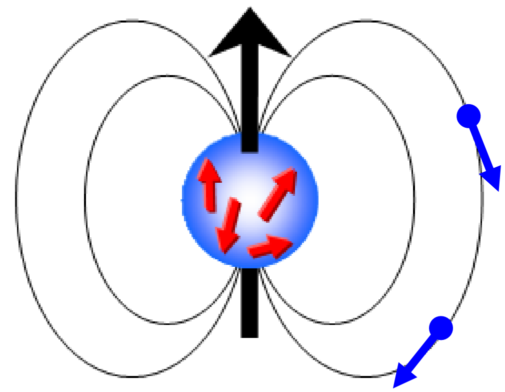
oscillations



DECAY - INTRINSIC DECOHERENCE

What in the environment in SMMs, i.e., what are the sources of DECOHERENCE?

Environment

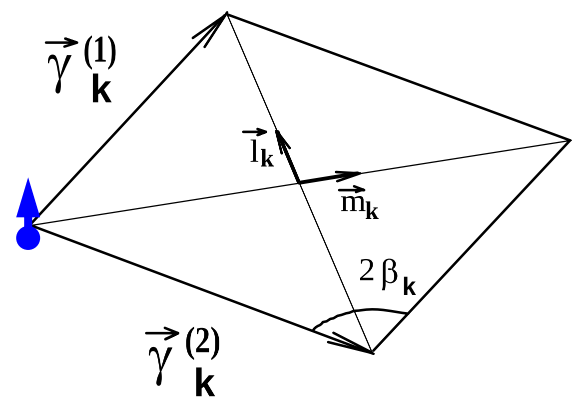


(1) Interaction with the nuclear spin bath:

$$H_{\rm nuc} = \sum_{k=1}^{N} \vec{\gamma}_k \cdot \mathbf{I}_k$$

$$H_{\rm nuc} = \frac{1}{2}\sum_{k=1}^{N}[(1+\hat{\tau}_z)\vec{\gamma}_k^{(1)} + (1-\hat{\tau}_z)\vec{\gamma}_k^{(2)}] \cdot \mathbf{I}_k$$

$$H_{nuc}^{host} = \sum_{i}^{\text{magnetic ions}} J_i \mathbf{s}_i \mathbf{I}_i$$



(2) Spin-phonon interaction:

$$H_{\rm sp-ph} = \sum_t \eta_t \hat{O}_t^P \hat{O}_t^S$$

where the sum is performed over all the terms allowed by symmetry.

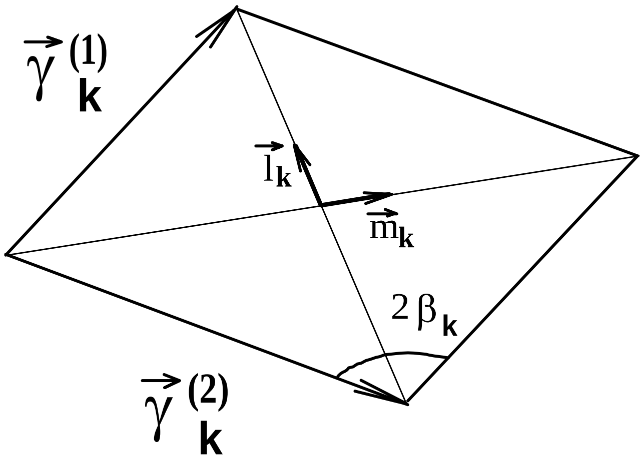
Example: $(\eta_1 \epsilon_{yz} + \eta_2 \omega_{yz})(S^y S^z + S^z S^y), \quad \mathbf{H}_\perp = \mathbf{H}_y$

(3) Pair-wise interaction with another molecules: exchange and dipolar interactions

Nuclear spin bath

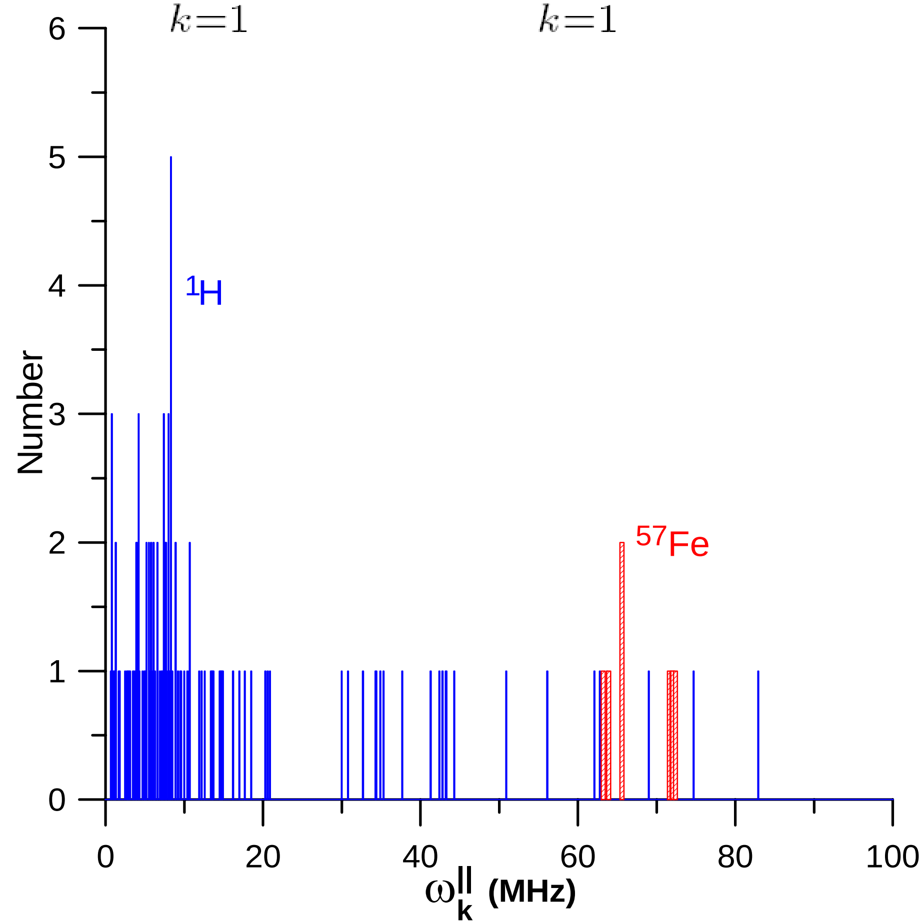
$$H_{\rm nuc} = \frac{1}{2}\sum_{k=1}^{N}[(1+\hat{\tau}_z)\vec{\gamma}_k^{(1)} + (1-\hat{\tau}_z)\vec{\gamma}_k^{(2)}]\cdot \mathbf{I}_k$$

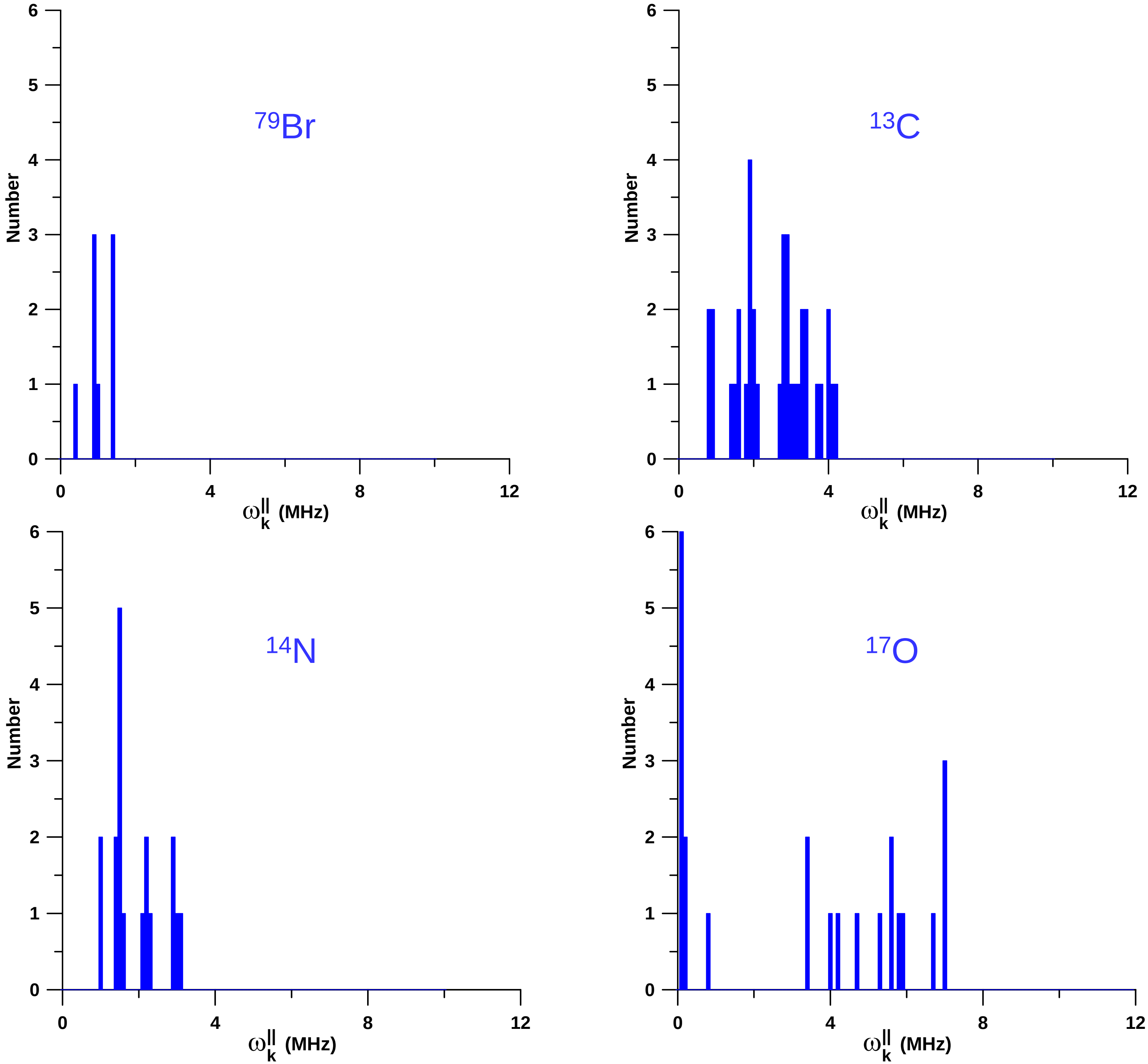
$$\equiv \hat{\tau}_z \sum_{k=1}^{N_n} \omega_k^{||}\mathbf{l}_k\cdot\mathbf{I}_k + \sum_{k=1}^{N}\omega_k^{\perp}\mathbf{m}_k\cdot\mathbf{I}_k,$$



$$\omega_k^{||} = \frac{1}{2}|\vec{\gamma}_k^{(1)} - \vec{\gamma}_k^{(2)}|$$

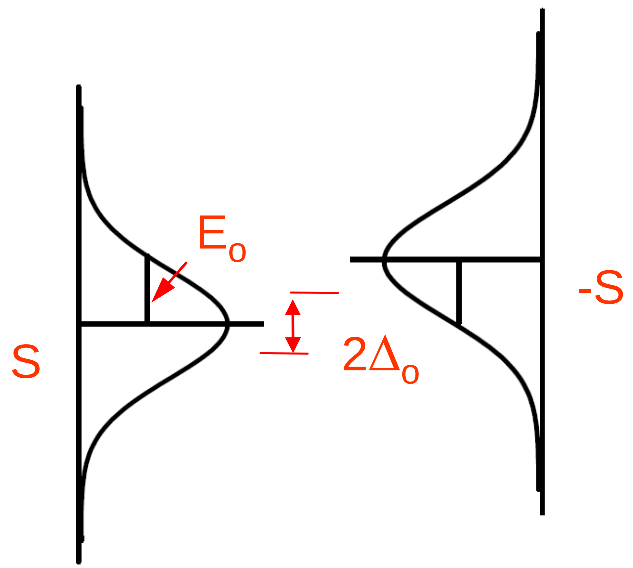
$$\omega_k^{\perp} = \frac{1}{2}|\vec{\gamma}_k^{(1)} + \vec{\gamma}_k^{(2)}|$$





^{79}Br
^{13}C
^{14}N
^{17}O
Number
$\omega_k^{||}$ (MHz)
0
1
2
3
4
5
6
0
4
8
12

Nuclear spin bath



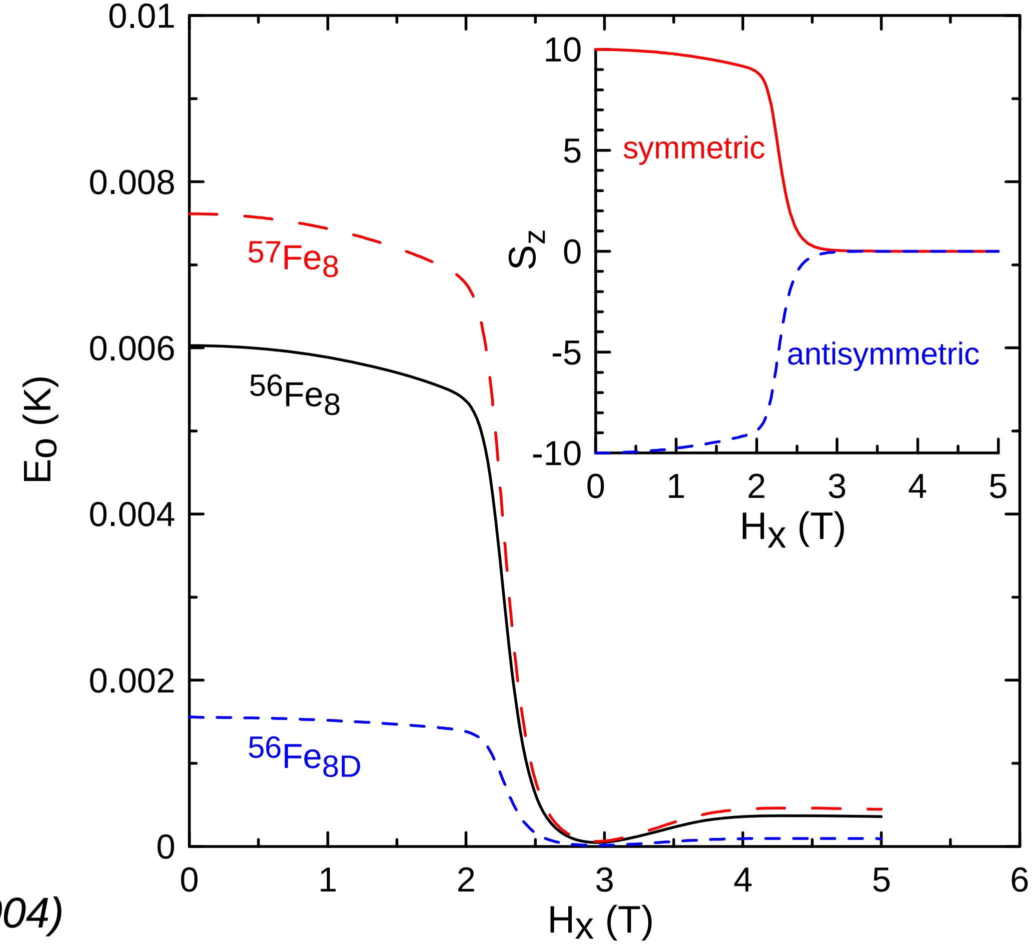
Interaction with the nuclear spin bath leads to the spread of each electronic energy level and the half-width of the distribution of states, E_o, describes the static properties of the nuclear spin bath. Knowing positions of all the ions in the molecule, it is easy to calculate E_o.

$$E_o^2 = \sum_k \frac{(I_k+1)I_k}{3}(\omega_k^{\parallel})^2$$

P.C.E. Stamp and I.S. Tupitsyn, PRB 69 (2004)

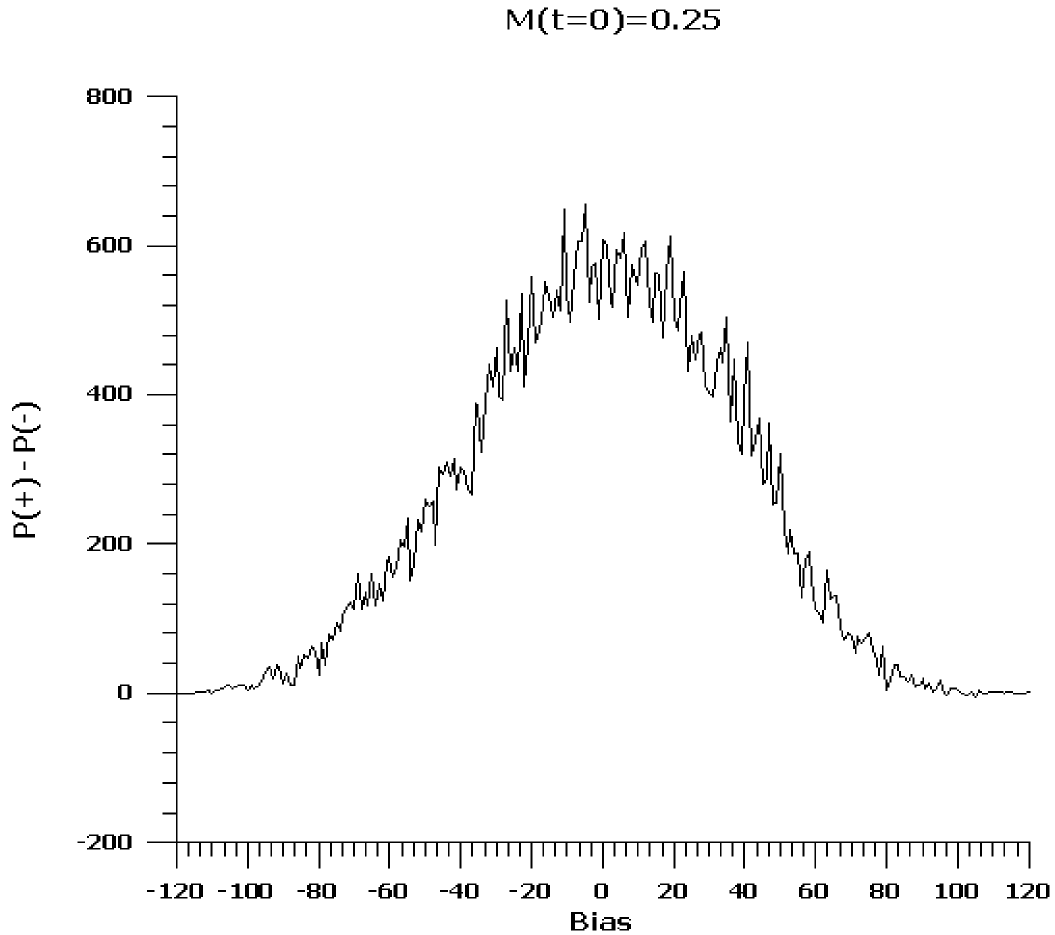
Fe_8, $H_Z=0$

8 irons, 120 hydrogens, 8 bromines, 18 nitrogens, 36 carbons and 23 oxygens

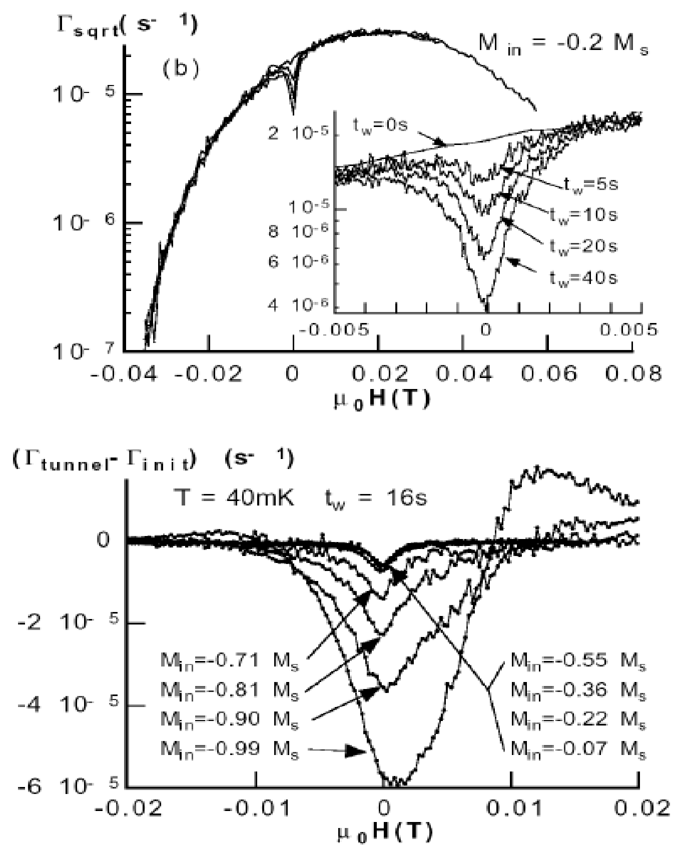


Nuclear spin bath

How E_o can be measured? As it has been shown (*Prokof'ev and P.C.E. Stamp, PRL 80 (1998)*), due to interactions with the nuclear spin bath the short-time low-T relaxation in crystals of magnetic molecules follows the square-root law and during the relaxation the hole in the dipolar fields distribution is growing. The shape of this hole is Lorentzian and its short-time half-width is E_o *(I.S. Tupitsyn, P.C.E. Stamp and N.V. Prokof'ev, PRB 69 (2004)).*



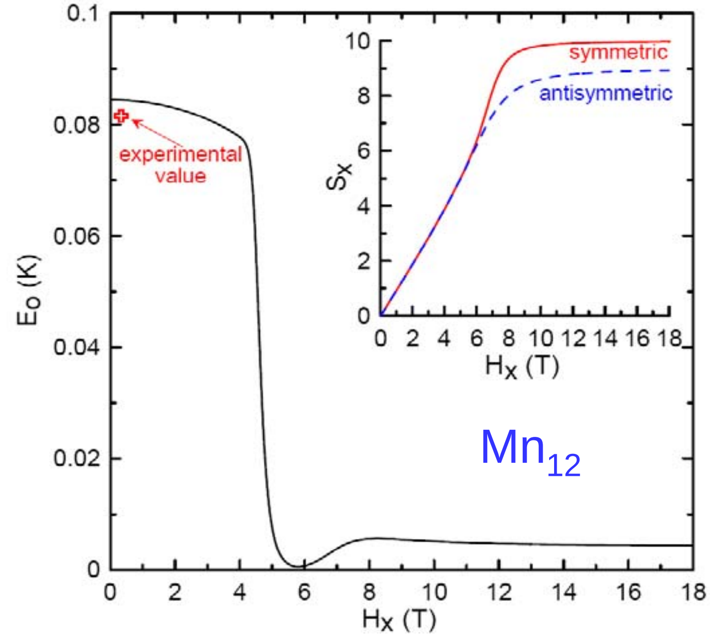
W. Wernsdorfer *et al., PRL 82 (1999)*

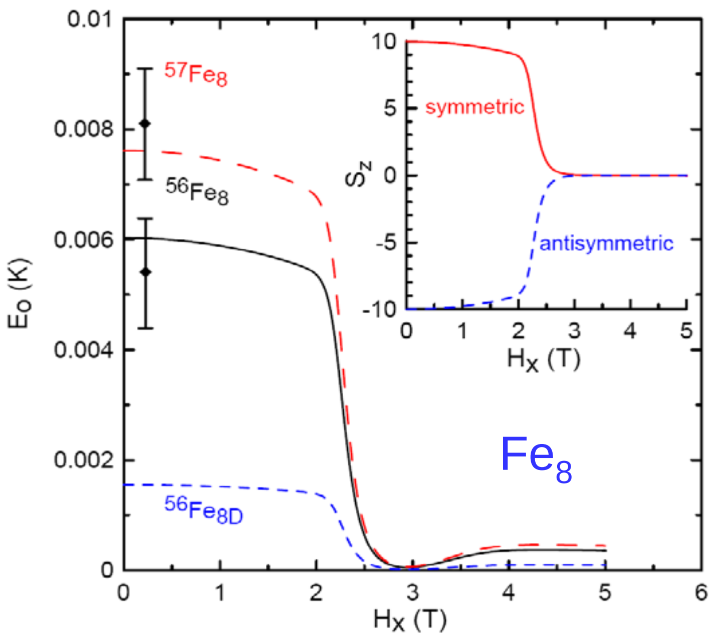


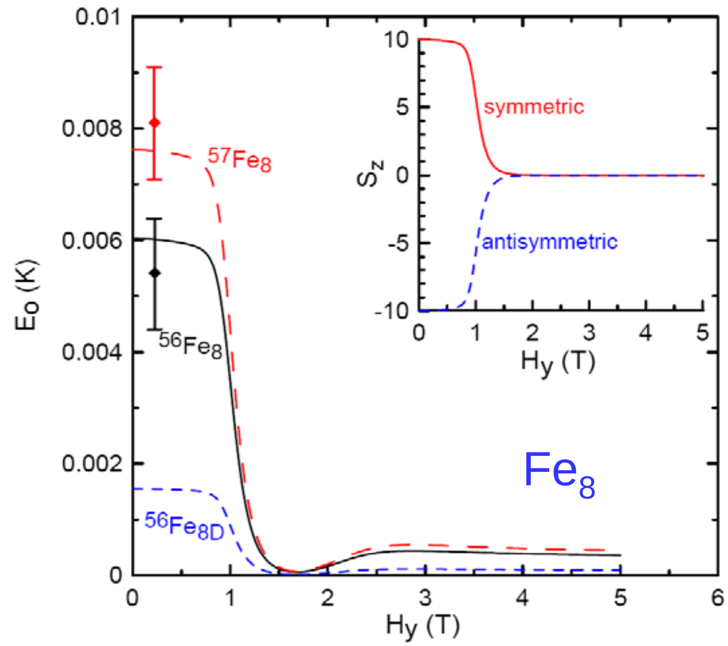
Nuclear spin bath

E_o in Fe_8 and Mn_{12}

comparison with experimental results of Wernsdorfer et. al. PRL 82 (1999); PRL 84 (2000); and Europhys Lett. 47 (1999).







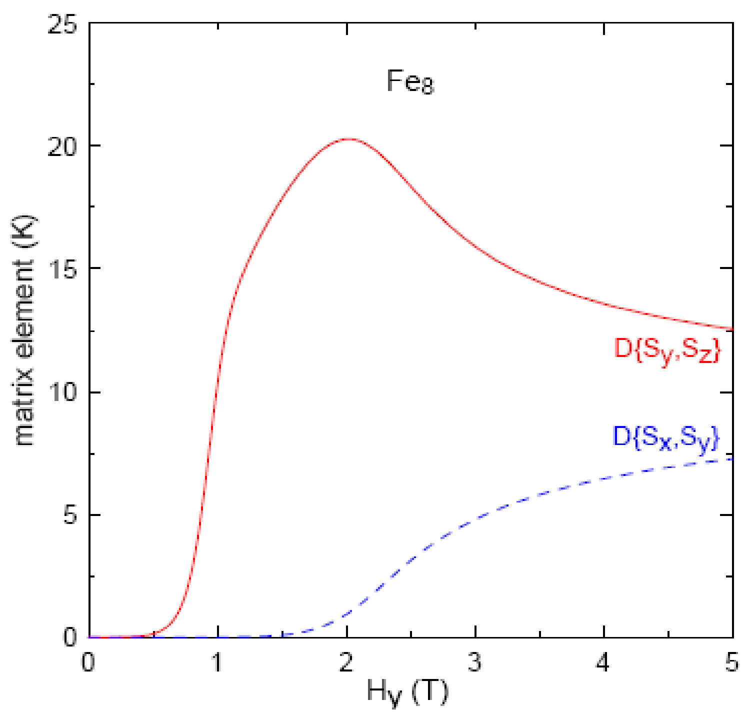
Phonon bath

$$H_{\mathrm{sp-ph}} = \sum_t \eta_t \hat{O}_t^P \hat{O}_t^S$$

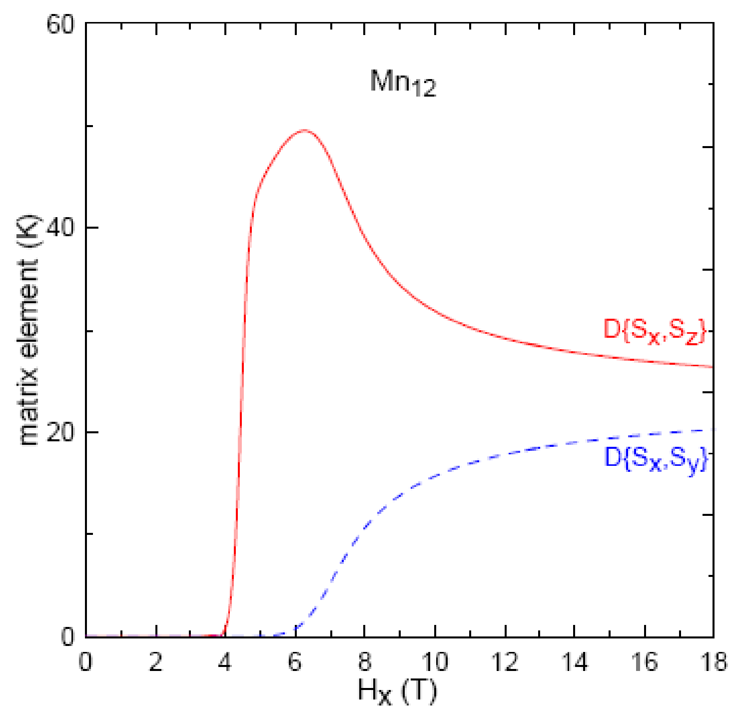
Considering all the terms allowed by symmetry of problem, we can keep only the dominant ones. These can be filtered by studying the field dependence of the spin part of $H_{sp\text{-}ph}$. For $H_{\perp}=H_Y$ in Fe_8 and for $H_{\perp}=H_X$ in Mn_{12} these are:

$$(\eta_1^{Fe}\epsilon_{yz} + \eta_2^{Fe}\omega_{yz})(S^yS^z + S^zS^y)$$

$$(\eta_1^{Mn}\epsilon_{xz} + \eta_2^{Mn}\omega_{xz})(S^xS^z + S^zS^x)$$



η_i=D



Coherence Window

Decoherence in many solid-state systems is anomalously high. At the same time, it has been shown *(P.C.E. Stamp and I.S. Tupitsyn, PRB 69 (2004))*, that in magnetic insulators there is a transverse field region, where the phonon and nuclear spin mediated decoherence is drastically reduced. Such a "coherence window" opens up around some critical field, where the total nuclear spin bath and phonon dimensionless decoherence rate $\gamma_\phi = \hbar/(\Delta_o \tau_\phi)$ reaches its minimum.

$$\gamma_\phi^{\mathrm{nuc}} = \frac{1}{2}\left(\frac{E_o}{\Delta_o}\right)^2$$

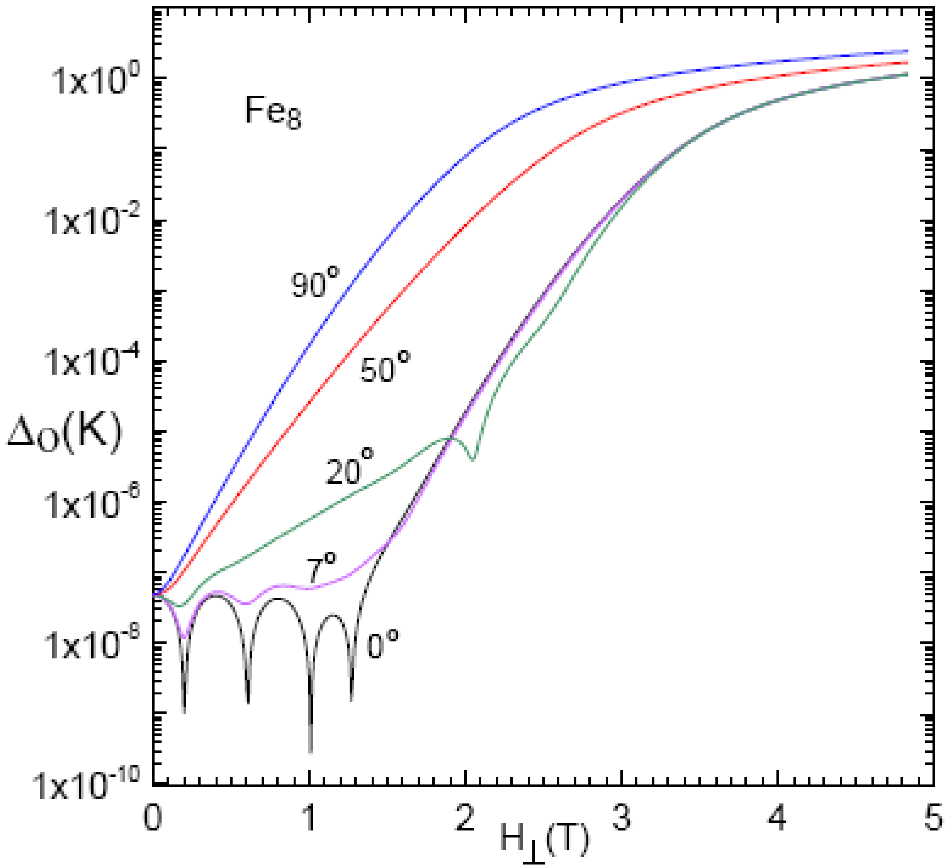
$$\gamma_\phi^{\mathrm{ph}} = \frac{\mathcal{M}_{AS}^2 \Delta_o^2}{\pi \rho c_s^5 \hbar^3} \coth(\Delta_o / k_B T)$$

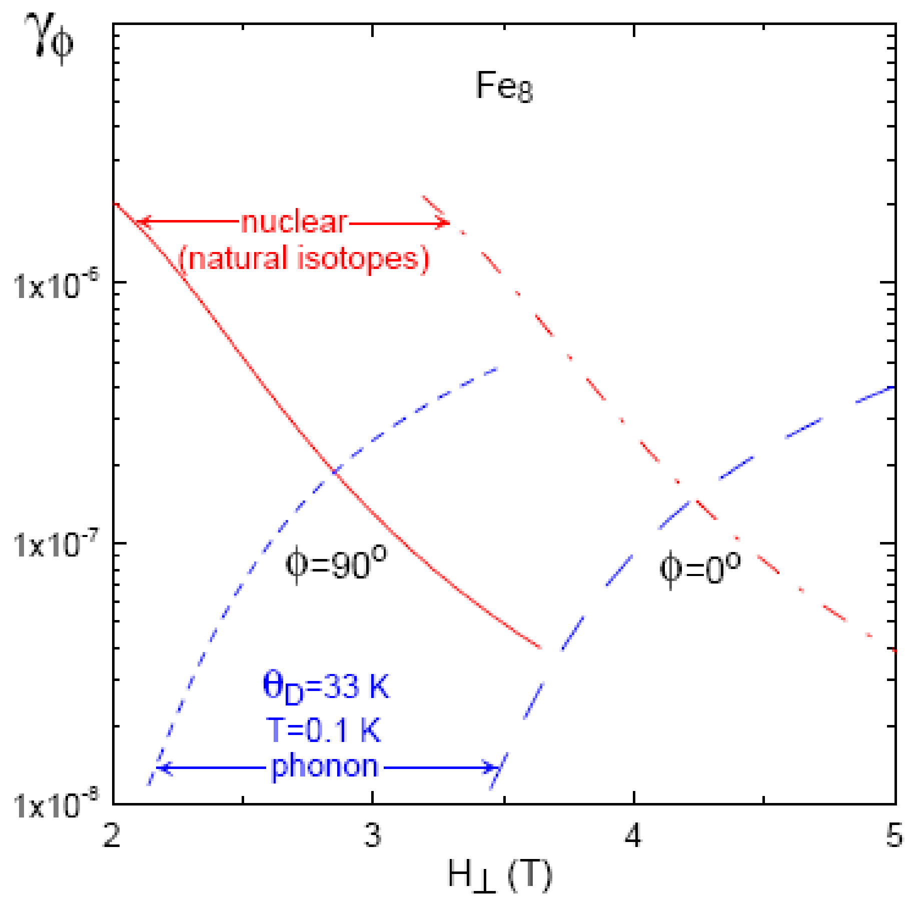
$$\mathcal{M}_{FI}^2 = \int_0^\pi d\theta \sin\theta \int_0^{2\pi} \frac{d\phi}{\pi} \Big| \sum_t \eta_t f_t(\theta,\phi) \langle F | \hat{O}_t^S | I \rangle \Big|^2$$

(N.V. Prokof'ev and P.C.E. Stamp, cond-mat/0006054; P.C.E. Stamp and I.S. Tupitsyn, PRB 69 (2004)); (A. Morello, P.C.E. Stamp, and I.S. Tupitsyn, PRL 97 (2006))

Coherence Window

Fe_8 - SMM

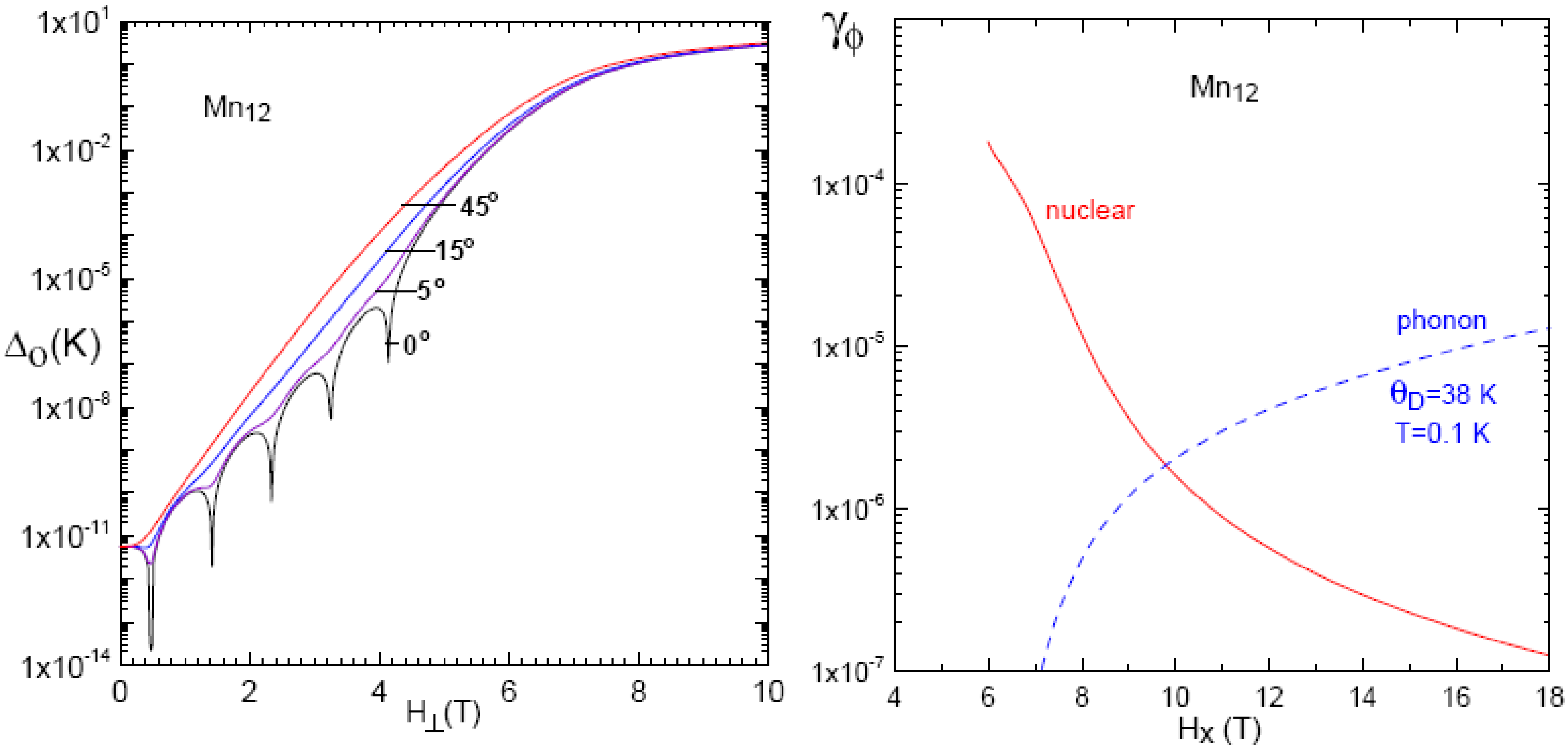




Number of coherent oscillations $Q \sim 1/\gamma_\phi$

Coherence Window

Mn_{12}- SMM

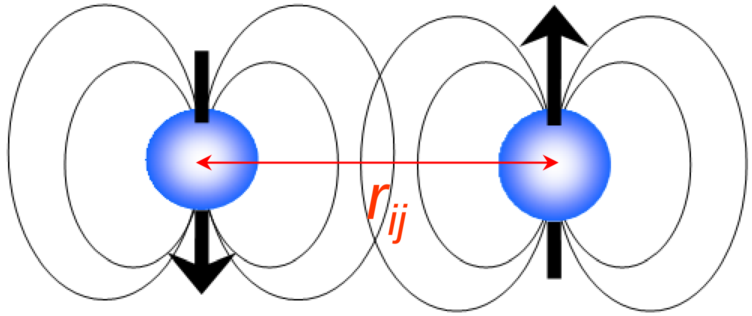


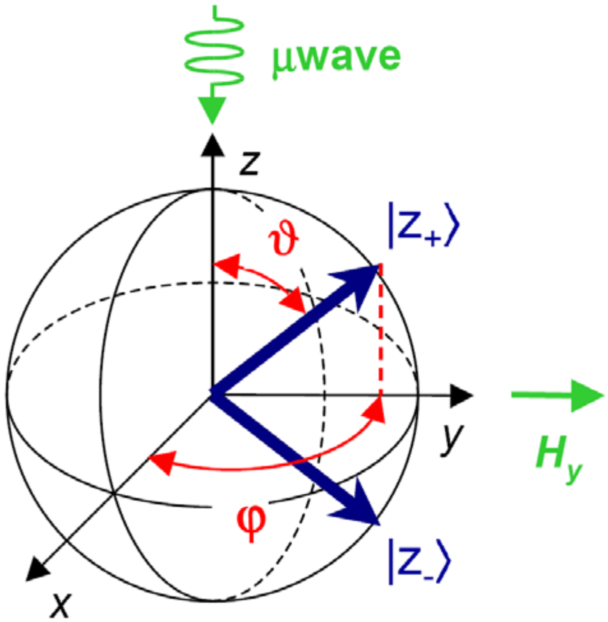
Number of coherent oscillations $Q \sim 1/\gamma_\phi$

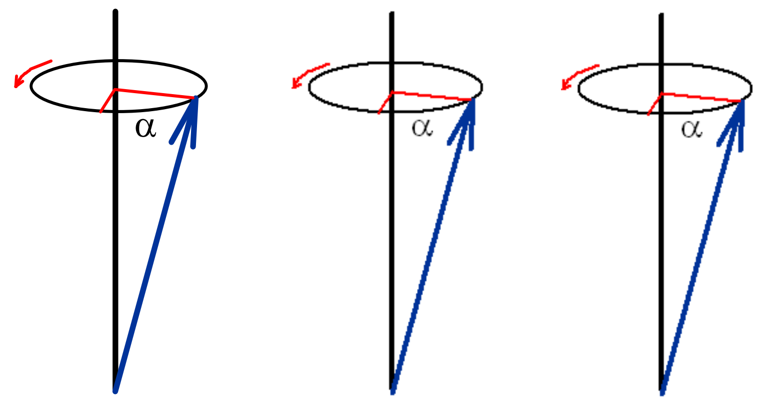
Ensembles of SMMs

3) Pair-wise interaction with another molecules:

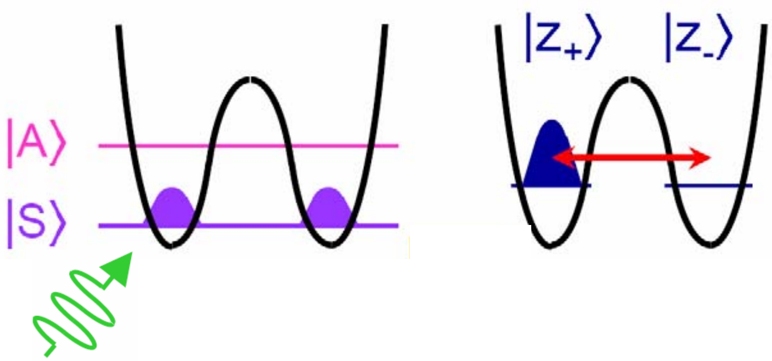
$$V_{ij}^{dd}(r) = \frac{\mu_o}{4\pi}\frac{g_e\mu_B}{r_{ij}^3}\left(\vec{S}_i\vec{S}_j - 3\frac{(\vec{S}_i\vec{r}_{ij})(\vec{S}_j\vec{r}_{ij})}{r_{ij}^2}\right)$$







Uniform precession --> q=0 magnon

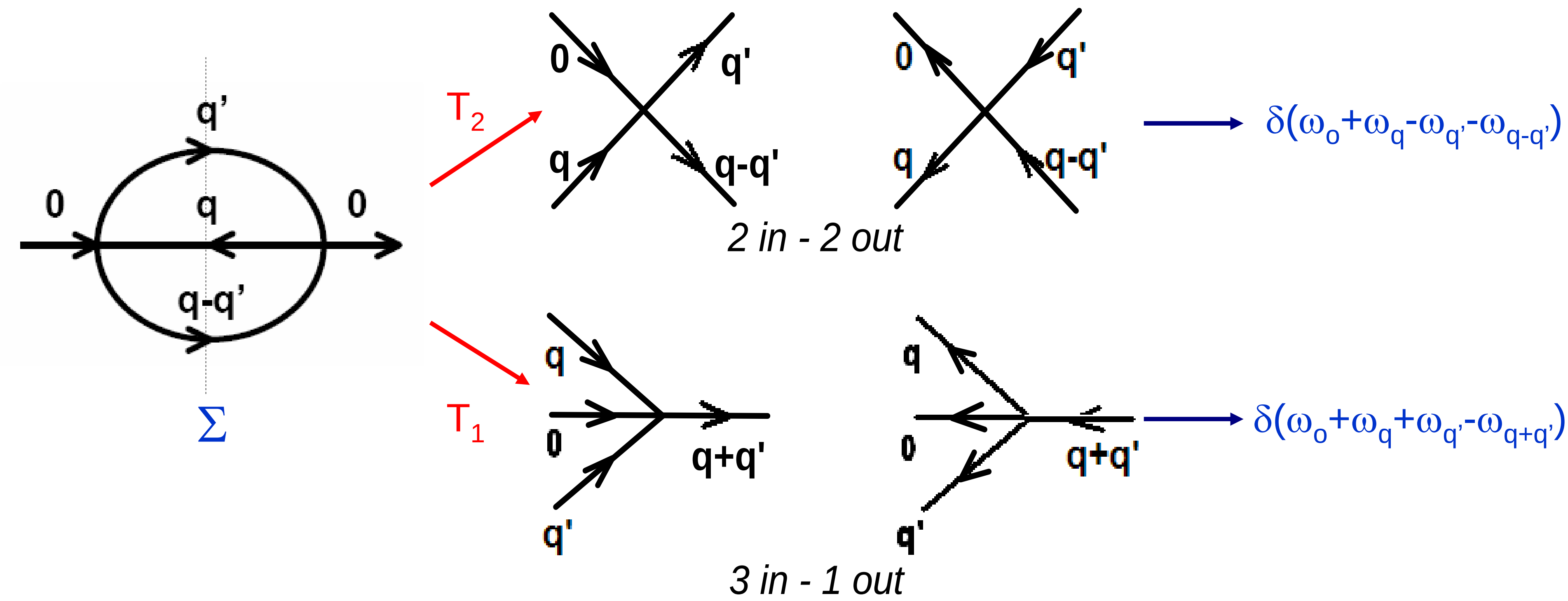


In a transverse magnetic field the oscillations are equivalent to a uniform spin precession along the field directions, i.e., to a *q=0* magnon. Scattering of the *q=0* mode off thermal magnons leads to a decay of oscillations. The corresponding decay time can be both measured and calculated.

Scattering of the q=0 mode off thermal magnons

The lowest order processes that, in principle, can conserve both energy and momentum here are 4-magnon processes:

does not change
# of magnons

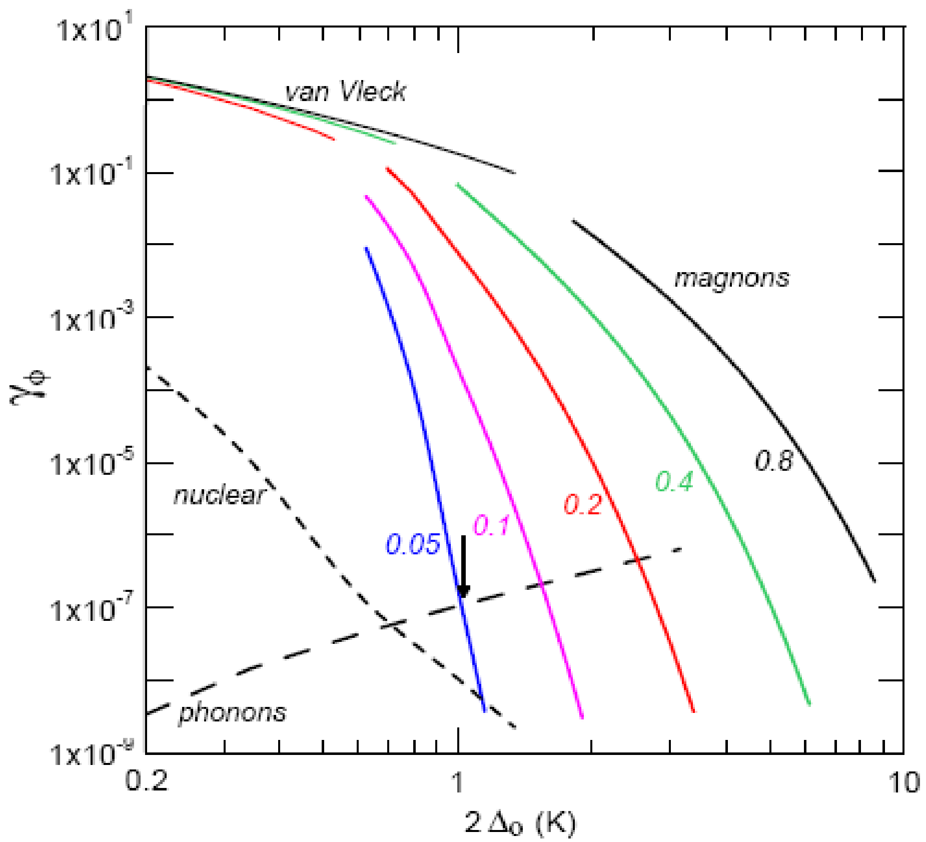


change
# of magnons

Fe_8 – sample averaged rates
(triclinic lattice, spherical sample)

$$\frac{1}{\tau_\phi^{(4)}} = \frac{2\pi}{\hbar} \sum_{\mathbf{q},\mathbf{q}'} |\Gamma^{(4)}_{\mathbf{q}\mathbf{q}'}|^2 \; F[n] \; \delta(\hbar\omega_0 + \hbar\omega_{\mathbf{q}} - \hbar\omega_{\mathbf{q}'} - \hbar\omega_{\mathbf{q}-\mathbf{q}'})$$

$$F[n] = [\overline{n}_{\mathbf{q}}(\overline{n}_{\mathbf{q}'} + 1)(\overline{n}_{\mathbf{q}-\mathbf{q}'} + 1) - (\overline{n}_{\mathbf{q}} + 1)\overline{n}_{\mathbf{q}'}\overline{n}_{\mathbf{q}-\mathbf{q}'}]$$



$$\gamma_\phi = \hbar/(\Delta_o \tau_\phi)$$

Fe_8

Except at very low T, dipolar decoherence completely dominates over nuclear and phonon decoherence, unless H_Y>2.7 T.

A. Morello, P.C.E. Stamp, and I.S. Tupitsyn, PRL 97 (2006)