

# What do magnetic molecules teach us about magnetism?

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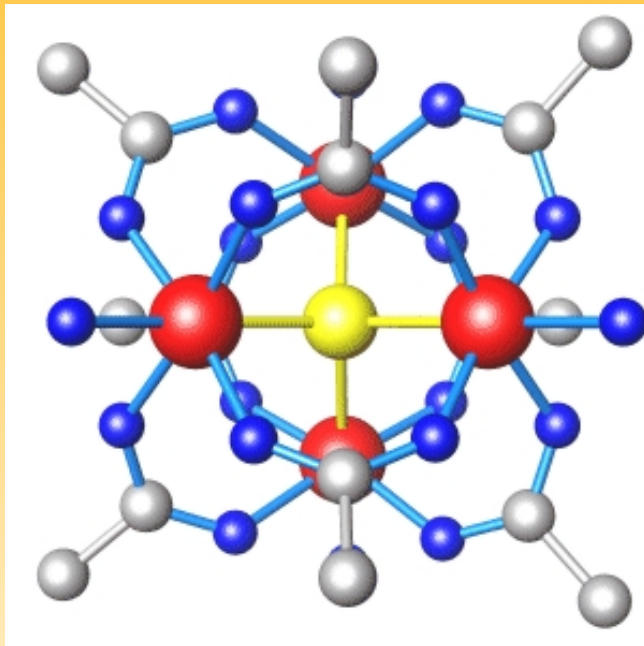
*Theoriekolloquium*

TU Darmstadt, December 8th 2003

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- The beauty of magnetic molecules
- Interesting phenomena: LIESST, magnetization tunneling
- Model Hamiltonian: Heisenberg Hamiltonian & effective Hamiltonians
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- General results: rings, bounds, rotational bands, magnetization jumps
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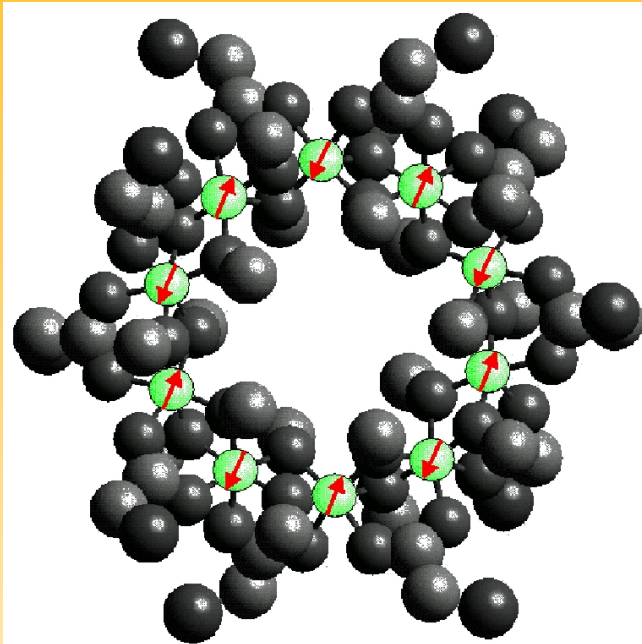
# What are magnetic molecules?



Cr<sub>4</sub>

- macro molecules (polyoxometalates etc.): consist of constituents like Hydrogen (H), Carbon (C), Oxygen (O), and diamagnetic ions (e.g. Mo) as well as paramagnetic ions like Iron (Fe), Chromium (Cr), Copper (Cu), Nickel (Ni) or Manganese (Mn);
- pure organic magnetic molecules: magnetic coupling between high spin units (e.g. free radicals);
- single spin quantum number  $1/2 \leq s \leq 7/2$ ;
- intermolecular interaction relatively small, therefore measurements reflect the thermal behaviour of a single molecule.

# Structure of magnetic molecules

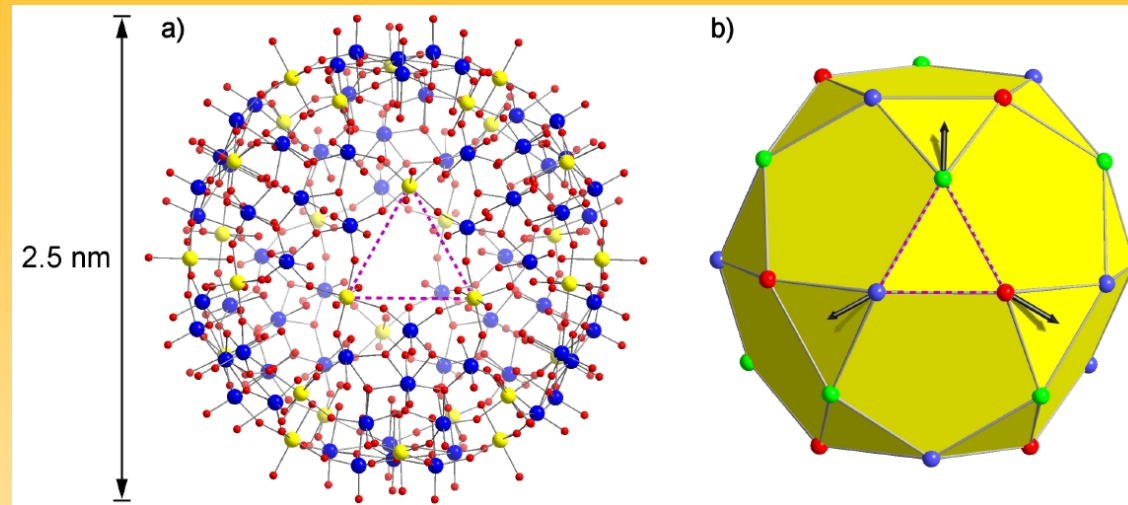


Fe<sub>10</sub>

- dimers (Fe<sub>2</sub>), tetrahedra (Cr<sub>4</sub>), cubes (Cr<sub>8</sub>);
- rings, especially iron rings (Fe<sub>6</sub>, Fe<sub>8</sub>, Fe<sub>10</sub>, ...);
- complex structures (Mn<sub>12</sub>) – drosophila of molecular magnetism;
- soccer balls, more precisely icosidodecahedra (Fe<sub>30</sub>) and other macro molecules;
- chain like and planar structures of interlinked magnetic molecules.

# Example of magnetic macro molecules

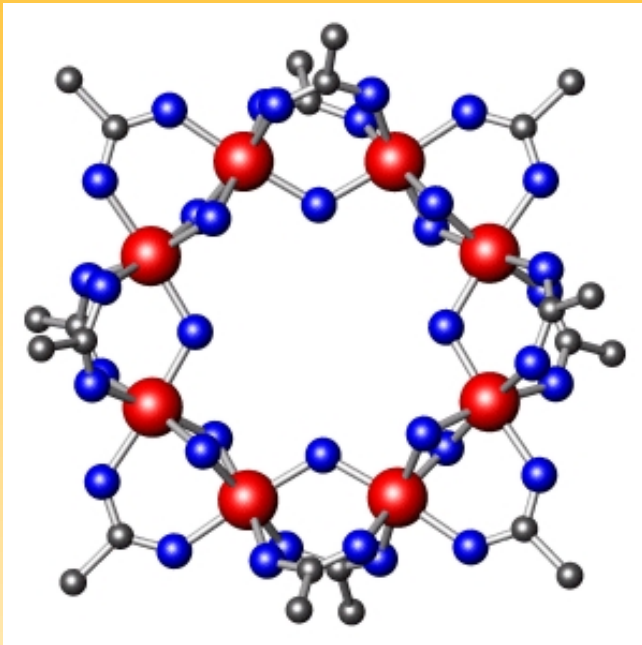
## {Mo<sub>72</sub>Fe<sub>30</sub>}



- structure of {Mo<sub>72</sub>Fe<sub>30</sub>}: Fe - yellow, Mo - blue, O - red,
- antiferromagnetic interaction mediated by O-Mo-O bridges (1).
- classical ground state of {Mo<sub>72</sub>Fe<sub>30</sub>}: three sublattice structure, coplanar spins (2);
- quantum mechanical ground state  $S = 0$  can only be approximated, dimension of Hilbert space  $(2s + 1)^N \approx 10^{23}$ .

(1) A. Müller *et al.*, Chem. Phys. Chem. **2**, 517 (2001) , (2) M. Axenovich and M. Luban, Phys. Rev. B **63**, 100407 (2001)

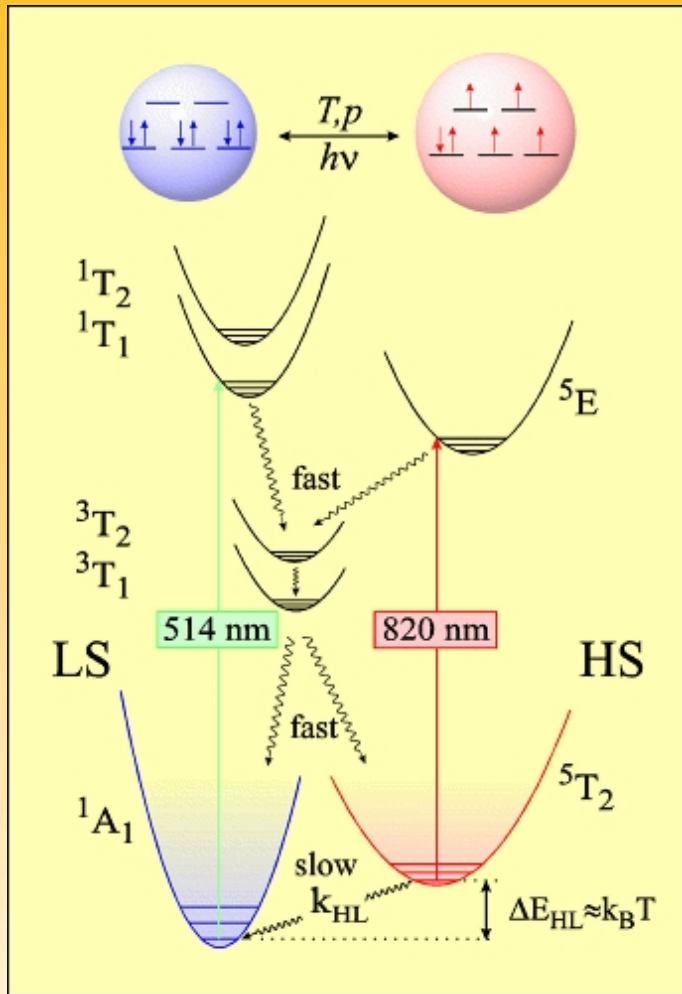
# Why study magnetic molecules?



Cr<sub>8</sub>

- transition few-spin system  $\Rightarrow$  many-spin system, contribution to understanding of bulk magnetism;
- transition quantum spin system ( $s = 1/2$ )  $\Rightarrow$  classical spin system ( $s_{\text{Fe}} = 5/2$ ,  $s_{\text{Gd}} = 7/2$ );
- easy to produce, single crystals with  $> 10^{17}$  identical molecules can be synthesized and practically completely characterized;
- speculative applications: magnetic storage devices, magnets in biological systems, light-induced nano switches, displays, catalysts, qubits for quantum computers.

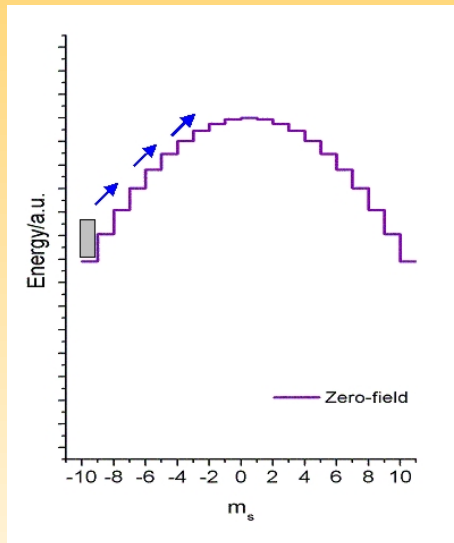
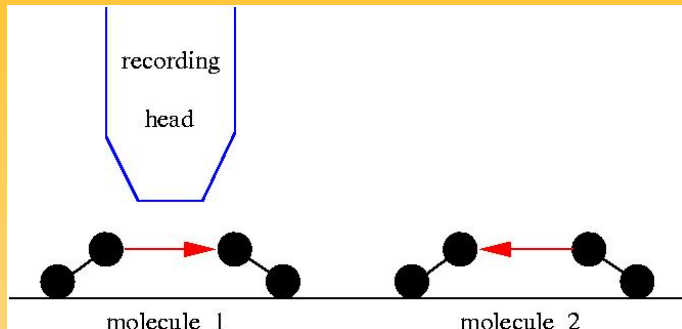
# Light Induced Excited Spin State Trapping (LIESST)



- magnetic molecules may serve as optical switches or displays;
- materials: spin crossover substances which show the LIESST effect;
- example: sixfold coordinated iron, spin-dependent radial harmonic potential;
- principle: reversible change in colour (and structure) when irradiated with laser light or when heated as well as cooled.

<http://ak-guetlich.chemie.uni-mainz.de/toss/liesst.shtml>

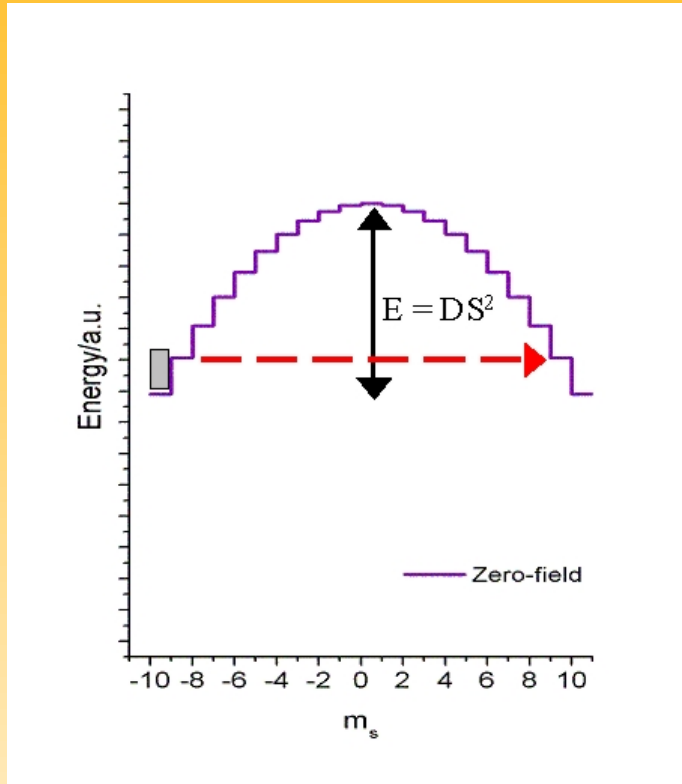
# Magnetic molecules as storage media?



- Single Molecule Magnet (SMM): magnetic molecule with high ground state spin and hysteresis (usually due to large anisotropy);
- every molecule is a domain of its own; very weak intermolecular interactions; high density and nevertheless good separation of magnetic moments;
- high ground state spin possible, e.g.  $S = 10$  for  $Mn_{12}$ ;
- theoretically possible storage density: **40 Tbits per square inch**, today: 20 Gbits per square inch (IBM), 300GB per square inch (Fujitsu 05/2002)



# Magnetic molecules as storage media?

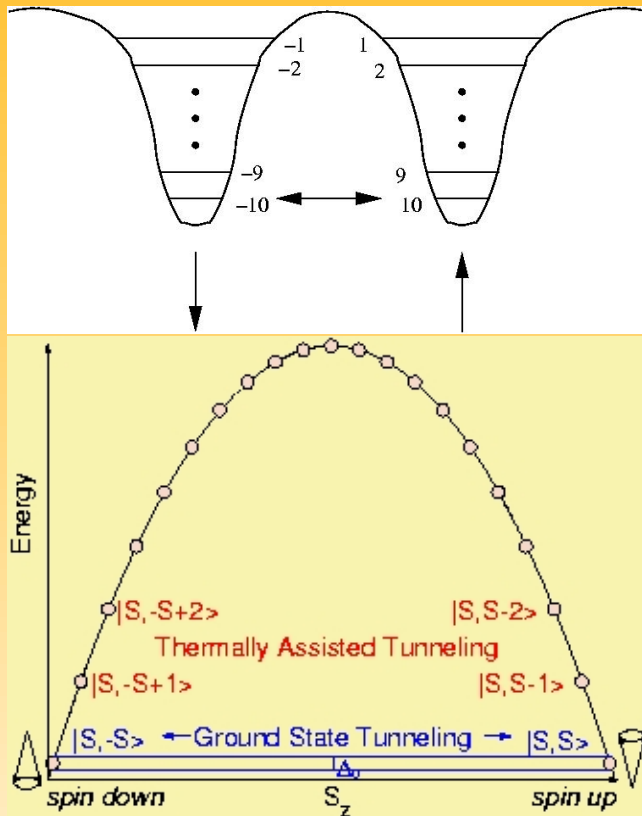


## Disadvantages:

- magnetization tunneling – stabilisation by appropriate substrate?  
Prof. Blügel, Osnabrück/Jülich,  
<http://www.flapw.de>
- often very small coupling ( $J \approx 10$  K), i.e. thermally unstable at room temperature;
- recording head must be very small and needs precise guide.

[http://www.people.man.ac.uk/~mbdssrew/winpeny\\_intro3.html](http://www.people.man.ac.uk/~mbdssrew/winpeny_intro3.html)

# Magnetization tunneling



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- for SMM like  $Mn_{12}$  (l.h.s.) an effective one-spin Hamiltonian can be used:

$$\tilde{H} = -D\tilde{S}_z^2 - D_4\tilde{S}_z^4 + \tilde{H}'$$

$$\tilde{H}' = g\mu_B H_x \tilde{S}_x$$

- tunneling rate depends on initial  $M$ :

$$M = 10 \Rightarrow \omega \approx 10^{-45} \text{ Hz } (H_x = 100 \text{ G})$$

$$M = 2 \Rightarrow \omega \approx 10^5 \text{ Hz } (H_x = 100 \text{ G})$$

- macroscopic magnetization tunneling possible;
- thermally activated tunneling observed.

## Model Hamiltonian – Heisenberg-Model

$$\underline{H} = - \sum_{i,j} J_{ij} \underline{\tilde{S}}(i) \cdot \underline{\tilde{S}}(j) - D \sum_i \left( \underline{\tilde{e}}(i) \cdot \underline{\tilde{S}}(i) \right)^2 + g \mu_B B \sum_i^N \tilde{S}_z(i)$$

Heisenberg
Anisotropy
Zeeman

The Heisenberg model including anisotropy, and dipol-dipol interaction if necessary, as well as a Zeeman term describes the magnetic spectrum of many molecules with high accuracy.

**Reason:** ions of the iron group, Russel-Saunders coupling in the free ion,  $\langle \underline{l} \rangle \approx 0$  due to chemical binding, remaining spin-orbit coupling treated perturbatively with the help of anisotropy terms.

Since the dimension of Hilbert space equals  $(2s + 1)^N$  the Hamiltonian can be diagonalized completely for small molecules. For larger ones approximate methods are used.

## Dimension of the problem

Product basis, total dimension:  $\dim(\mathcal{H}) = (2s + 1)^N$

$$\hat{S}_z(u) |m_1, \dots, m_u, \dots, m_N\rangle = m_u |m_1, \dots, m_u, \dots, m_N\rangle$$

These states span the Hilbert space and are used to construct symmetry-related basis states.

Symmetries of the Heisenberg model without anisotropy

$$\left[ \tilde{H}, \tilde{S}^2 \right] = 0 \quad , \quad \left[ \tilde{H}, \tilde{S}_z \right] = 0$$

Additional (point group) symmetries are possible, e.g. shifts on a ring molecule.

# Decomposition into mutually orthogonal subspaces

Hilbert space  $\mathcal{H}$  can be decomposed into mutually orthogonal subspaces  $\mathcal{H}(M)$  with  $M = \sum_u m_u$  ( $M$  is the quantum number belonging to  $\tilde{S}_z$ )

$$\left[ \tilde{H}, \tilde{S}_z \right] = 0 \quad : \quad \mathcal{H} = \bigoplus_{M=-S_{\max}}^{+S_{\max}} \mathcal{H}(M), \quad S_{\max} = Ns$$

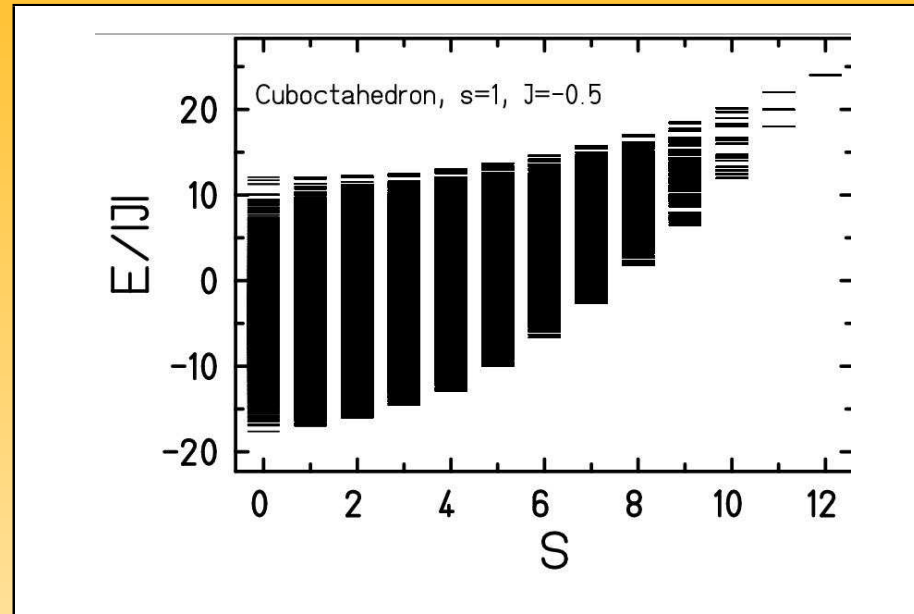
dimension of  $\mathcal{H}(M)$  (de Moivre)

$$\dim(\mathcal{H}(M)) = f(N, 2s + 1, S_{\max} - M)$$

$$\text{with } f(N, \mu, \nu) = \sum_{n=0}^{[\nu/\mu]} (-1)^n \binom{N}{n} \binom{N-1+\nu-n\mu}{N-1}$$

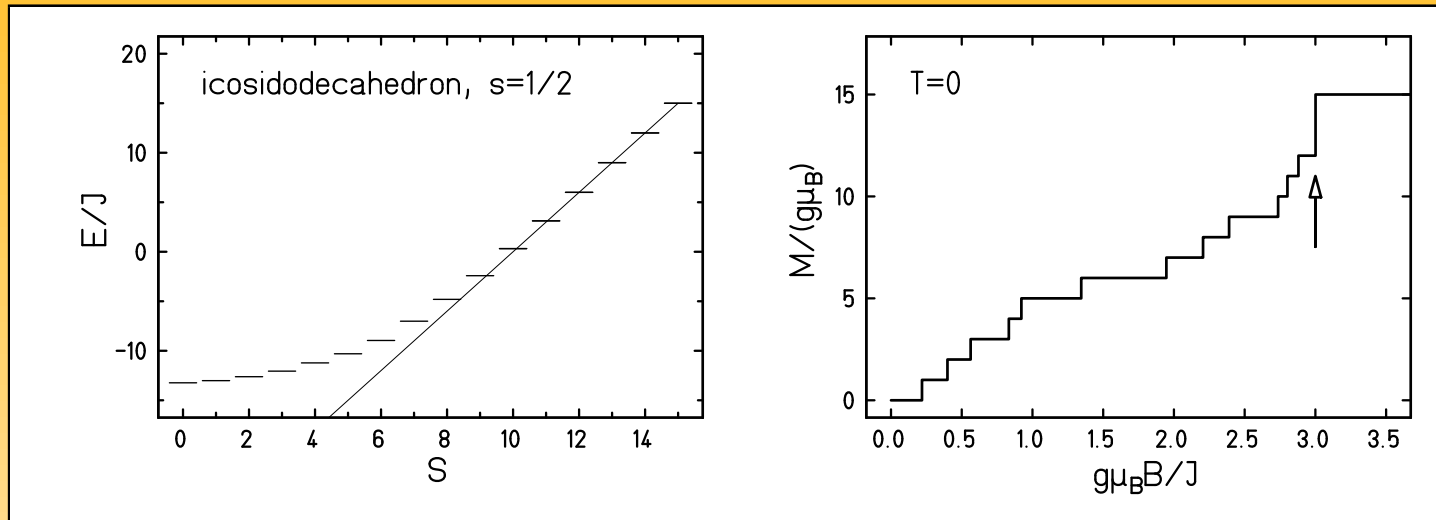
The dimension of the largest subspace is relevant. If more symmetries apply this dimension will be further reduced.

# Exact diagonalization



- Numerically exact diagonalization feasible up to RAM size;
- Example: 10,000x10,000 complex\*16, 1.6 GB RAM needed;
- Not much we can do at this point, wait for more RAM 😊

# The best we can do: Low-lying states



- Low-lying states sufficient for low-temperature physics;
- Low-lying states important for quantum phase transitions, e.g. magnetization jumps.
- Several methods available to obtain extreme eigenvalues: projection, Lánczos, DMRG.

## Lanczos method

Construct tridiagonal matrix starting with an arbitrary vector  $|\psi_1\rangle$

$$|\psi'_{k+1}\rangle = (1 - |\psi_k\rangle\langle\psi_k| - |\psi_{k-1}\rangle\langle\psi_{k-1}|) \underline{H} |\psi_k\rangle$$

$$|\psi_{k+1}\rangle = \frac{|\psi'_{k+1}\rangle}{\sqrt{\langle\psi'_{k+1}|\psi'_{k+1}\rangle}}$$

- New Lanczos vector by construction orthogonal to all previous Lanczos vectors;
- Extremal eigenvalues of tridiagonal matrix converge quickly against true extremal eigenvalues;
- Example: ground state energy approximated to 10 figures with about 300 Lanczos steps although dimension of Hilbert space  $10^8$ ;
- Three Lanczos vectors needed: RAM!



# Density Matrix Renormalization Group technique

Procedure to construct subspaces that contain low-lying trial states, developed to calculate groundstate properties of (infinite) 1D spin systems (S. White 1992).

- Split system into subsystems (e.g. spin chain into single spin sites)
- Iteratively increase system size but keep only a fixed number of states

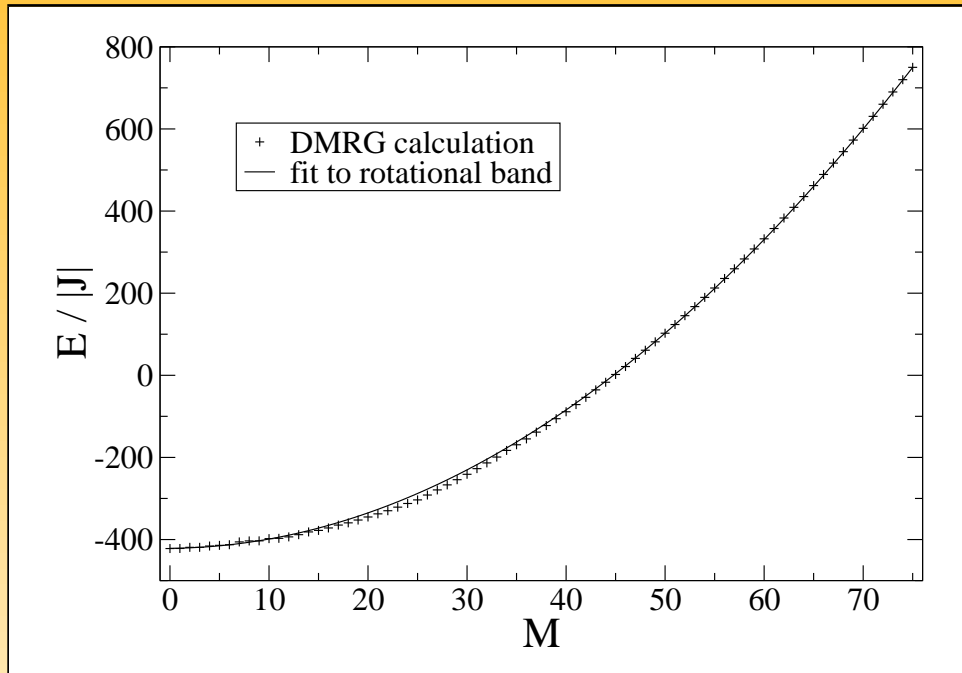
→ Truncation of the Hilbert space

- Question: Which states are best suited to be kept?

→ Use density matrix of “target state” to determine most important states

- Calculate physical properties in reduced Hilbert spaces

# {Mo<sub>72</sub>Fe<sub>30</sub>} - lowest rotational band with DMRG



- difficult to calculate since quasi two-dimensional and finite;
- convergence with  $1/m$  instead of  $\exp(-m)$ ;
- accuracy tested with an icosidodecahedron of  $s = 1/2$ ;
- relative ground state energies form an almost quadratic band (rotational band hypothesis).

M. Exler, J. Schnack, Phys. Rev. B **67** (2003) 094440

# Spin-coherent states

Overcomplete set of “basis” states

$$|\theta, \phi\rangle = \sum_{p=0}^{2s} \sqrt{\binom{2s}{p}} [\cos(\theta/2)]^{(2s-p)} [e^{i\phi} \sin(\theta/2)]^p |s, m = s - p\rangle$$

$$\langle \theta, \phi | \vec{s} | \theta, \phi \rangle = s \begin{pmatrix} \sin(\theta) \cos(\phi) \\ \sin(\theta) \sin(\phi) \\ \cos(\theta) \end{pmatrix}$$

- Spin-coherent states intuitive due to classical correspondence;
- Use reduced set of trial states to approximate low-lying levels.

# Theoretical findings

- Improvement of the theorem of Lieb, Schultz, and Mattis for spin rings;
- Construction of general bounds for the minimal energies of antiferromagnetic spin systems;
- Approximation of the low-lying spectrum by rotational bands;
- Discovery of giant magnetization jumps on certain frustrated spin lattices.

# Spin rings I

Shift operator commutes with Heisenberg Hamiltonian  $\left[ \tilde{H}, \tilde{T} \right] = 0$ :

$$\tilde{T} |m_1, \dots, m_{N-1}, m_N\rangle = |m_N, m_1, \dots, m_{N-1}\rangle$$

$$\tilde{H} |\phi_\nu\rangle = E_\nu |\phi_\nu\rangle, \quad \tilde{T} |\phi_\nu\rangle = \exp\left\{-i\frac{2\pi k_\nu}{N}\right\} |\phi_\nu\rangle, \quad k_\nu = 0, \dots, N-1$$

Properties of the  $k$ -quantum number of the ground state are known for rings of even  $N$  (Marshall, Peierls, Lieb, Schultz, Mattis).

Numerical investigations revealed that the  $k$  quantum number fulfills certain rules for all spin rings, also those of odd  $N$ .

K. Bärwinkel, H.-J. Schmidt, and J. Schnack, J. Magn. Magn. Mater. **220**, 227 (2000);  
J. Schnack, Phys. Rev. B **62**, 14855 (2000)

## Spin rings II

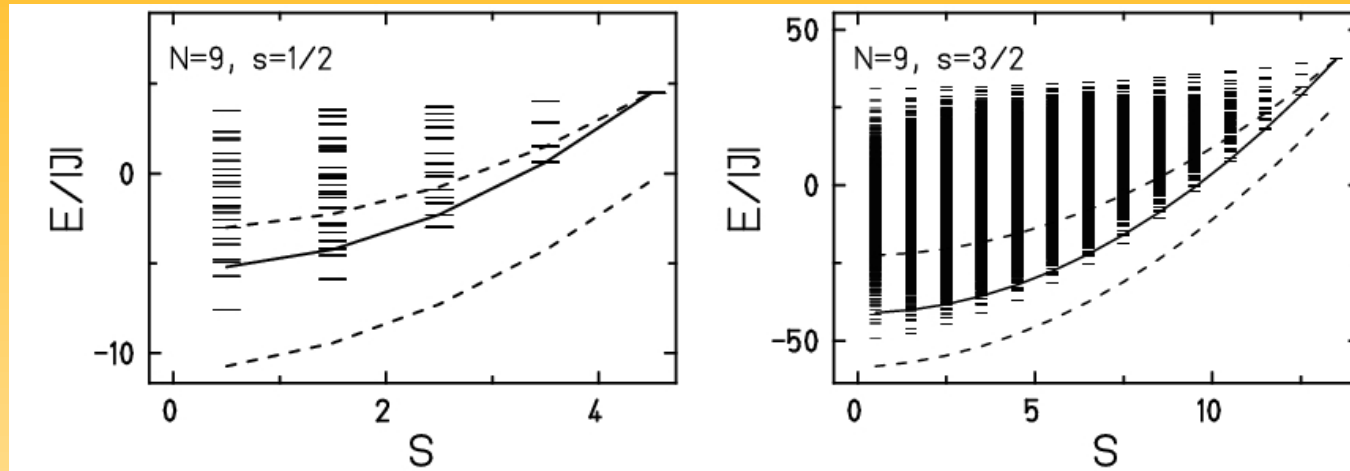
### Extended k-rule for relative ground states in subspaces $\mathcal{H}(M)$

$$\text{If } N \neq 3 \quad \text{then} \quad k \equiv \pm a \lceil \frac{N}{2} \rceil \pmod{N} .$$

- Moreover the degeneracy of the relative ground state is minimal, i.e. twofold degenerate if there are two different shift quantum numbers  $(k, N - k)$  and non-degenerate if  $k = 0 \pmod{N}$  or  $k = N/2 \pmod{N}$ , the latter for even  $N$ ;
- $a = Ns - M$ ; shift quantum numbers do not depend on  $s$ ;
- $\lceil N/2 \rceil$  denotes the smallest integer greater than or equal to  $N/2$ ;
- for  $N = 3$  extraordinary shift quantum numbers exist due to an additional degeneracy.

K. Bärwinkel, P. Hage, H.-J. Schmidt, and J. Schnack, Phys. Rev. B, **68** (2003) 054422

# Bounds



- confine minimal energies as function of  $M$  or  $S$ , improve bounds by Berezin and Lieb (1) and our first try (2);
- bounds must be obeyed by approximations like DMRG; (parabolic) bounds may serve as approximation of lowest (rotational) band.

(1) E. H. Lieb, Commun. Math. Phys. **31**, 327 (1973)  
 F. Berezin, Commun. Math. Phys. **40**, 153 (1975)  
 (2) H.-J. Schmidt, J. Schnack, and M. Luban, Europhys. Lett. **55**, 105 (2001)

## Make use of $n$ -cyclicity for upper bounds

- $n$ -cyclicity: directed graph of interactions can be mapped onto oriented cyclic graph with  $n$  vertices; 2-cyclicity is related to bi-partiteness;
- e.g.: rings –  $N$ -cyclic, triangular lattice – 3-cyclic, square lattice – 4-cyclic, cubic lattice – 2-cyclic, kagomé lattice – 3-cyclic;
- transform  $\underline{H}$  with generalized “Bloch” operator  $\underline{U}$  (1);
- variational state:  $|\phi\rangle = C_M \underline{U}(S^-)^a |\Omega\rangle$ ,  $|\Omega\rangle \equiv |s, s, s, \dots\rangle$  magnon vacuum.

$$E_{\min}(M) \leq \langle \phi | \underline{H} | \phi \rangle = c|\Gamma|s^2 + \left(1 - \frac{c}{\delta}\right) \frac{\delta|\Gamma|}{N} \left( Ns^2 - \frac{2sa(2Ns - a)}{2Ns - 1} \right),$$

where  $c = -1$  in the case of even  $n$  (bipartite) and  $c = -\cos \frac{\pi}{n}$  for odd  $n$ .

(1) I. Affleck, E. H. Lieb, Lett. Math. Phys. **12** (1986) 57

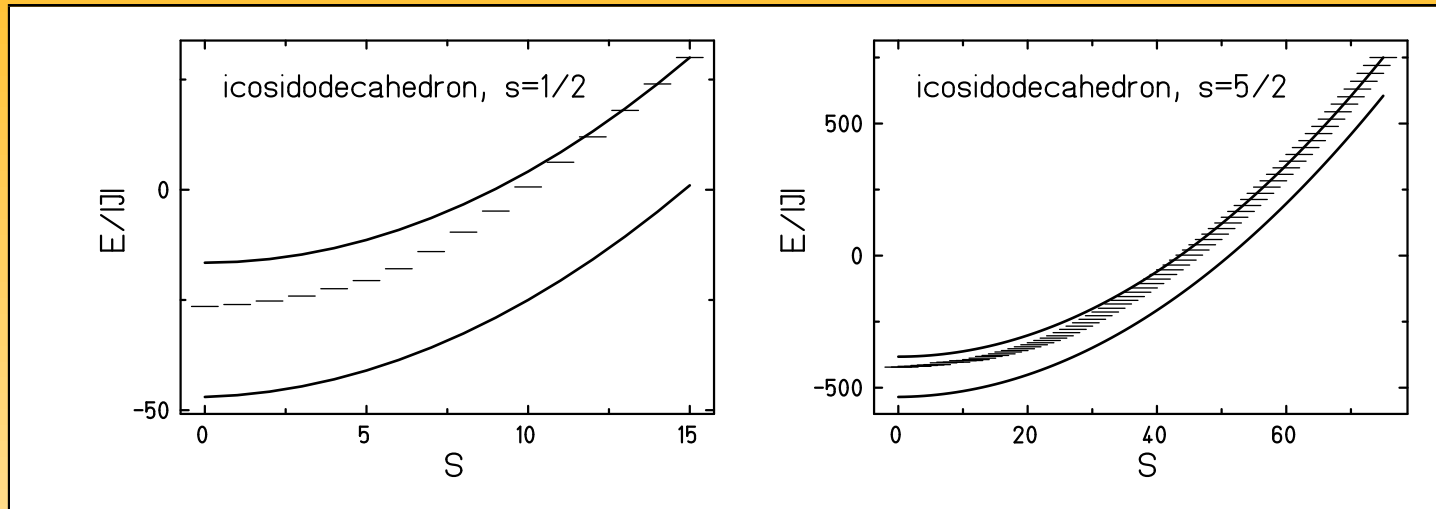


## Lower bounds for $n$ -homogeneous systems

$$\tilde{H} = \sum_{\mu\nu} J_{\mu\nu} \vec{S}_{\mu} \cdot \vec{S}_{\nu} , \quad \sum_{b \in \mathcal{A}_{\mu}} J_{ab} = \begin{cases} j^{\text{in}} & \text{if } a \in \mathcal{A}_{\mu} \\ j^{\text{ex}} & \text{if } a \notin \mathcal{A}_{\mu} \end{cases}$$

- Matrix  $\mathbb{J} \equiv (J_{\mu\nu})$  be symmetric and have constant row sums  $j$ ;
- $n$ -homogeneous: set of spin sites be divided into  $n$  disjoint subsets of equal size  $m$ ,  $\{1, \dots, N\} = \bigcup_{\nu=1}^n \mathcal{A}_{\nu}$ ;  
within each  $\mathcal{A}_{\nu}$ :  $J_{\mu\nu} \leq 0$ , but  $\geq 0$  between  $\mathcal{A}_{\nu}$  and  $\mathcal{A}_{\mu}$  for  $\nu \neq \mu$ ;
- smallest eigenvalue  $j_{\min}$  at least  $(n - 1)$ -times degenerate because of  $n$ -homogeneity,  $j_2$  is the remaining smallest eigenvalue;
- construction of a coupling matrix  $\tilde{\mathbb{J}}$  with eigenvalues  $j$  (1),  $j_{\min}$  ( $n - 1$ ),  $j_2$  ( $N - n$ );
- $\mathbb{J} \geq \tilde{\mathbb{J}} \Rightarrow \tilde{H} \geq \frac{j - j_{\min}}{N} S(S + 1) + N j_{\min} s(s + 1) + (N - n)(j_2 - j_{\min})s$  .

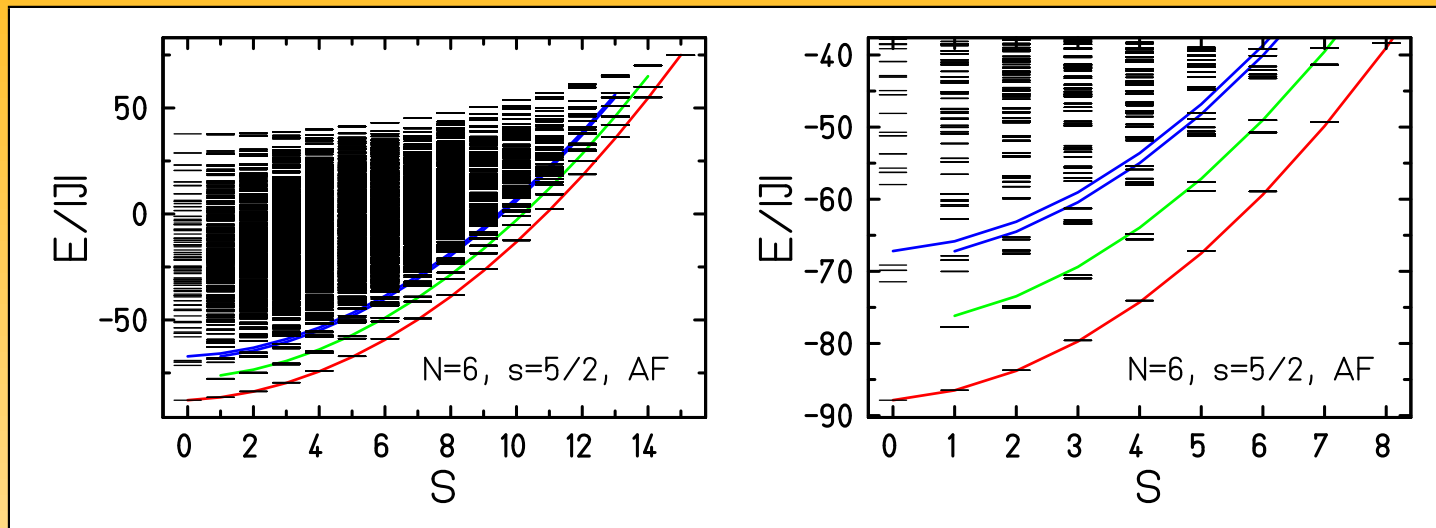
# Bounds for the icosidodecahedron



- minimal energies for the icosidodecahedron:  
 $s = 1/2$  from J. Richter (2),  $s = 5/2$  DMRG (3);
- upper bound rather close to true minimal energies, the better the larger  $s$ .

(1) K. Bärwinkel, H.-J. Schmidt, and J. Schnack, Eur. Phys. J. B **33** (2003) 285  
 (2) J. Schnack, H.-J. Schmidt, J. Richter, J. Schulenburg, Eur. Phys. J. B **24** (2001) 475  
 (3) M. Exler, J. Schnack, Phys. Rev. B **67** (2003) 094440

# Rotational bands



- often minimal energies  $E_{min}(S)$  form a rotational band: Landé interval rule (1);
- most pronounced for bipartite systems (2), good approximation for more general systems;
- sometimes low-lying spectrum is a sequence of rotational bands (3).

(1) A. Caneschi *et al.*, Chem. Eur. J. **2**, 1379 (1996), G. L. Abbati *et al.*, Inorg. Chim. Acta **297**, 291 (2000)

(2) J. Schnack and M. Luban, Phys. Rev. B **63**, 014418 (2001)

(3) O. Waldmann, Phys. Rev. B **65**, 024424 (2002)

## {Mo<sub>72</sub>Fe<sub>30</sub>} - rotational band hypothesis

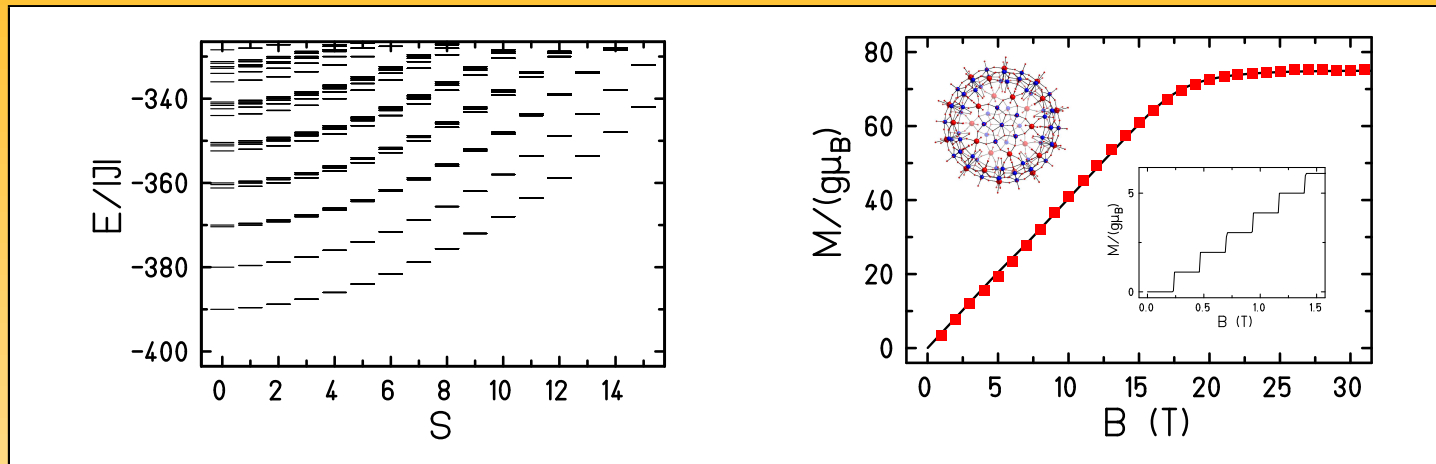
$$\tilde{H} = -2J \sum_{(u < v)} \vec{\tilde{s}}(u) \cdot \vec{\tilde{s}}(v) \approx -\frac{DJ}{N} \left[ \vec{\tilde{S}}^2 - \sum_{j=1}^{N_{SL}} \vec{\tilde{S}}_j^2 \right] = \tilde{H}^{\text{eff}}$$

- Aim: approximate low-lying spectrum by rotational bands;
- Fe<sub>30</sub>:  $N_{SL} = 3$ ;  $S_A, S_B, S_C = 0, 1, \dots, 25$ ;  $S = 0, 1, \dots, 75$ ;
- $D = 6$  either from classical counterpart or symmetry considerations or properties of coupling matrix;

J. Schnack, M. Luban, R. Modler, Europhys. Lett. **56** 863 (2001)

H.-J. Schmidt, J. Schnack, and M. Luban, Europhys. Lett. **55**, 105 (2001)

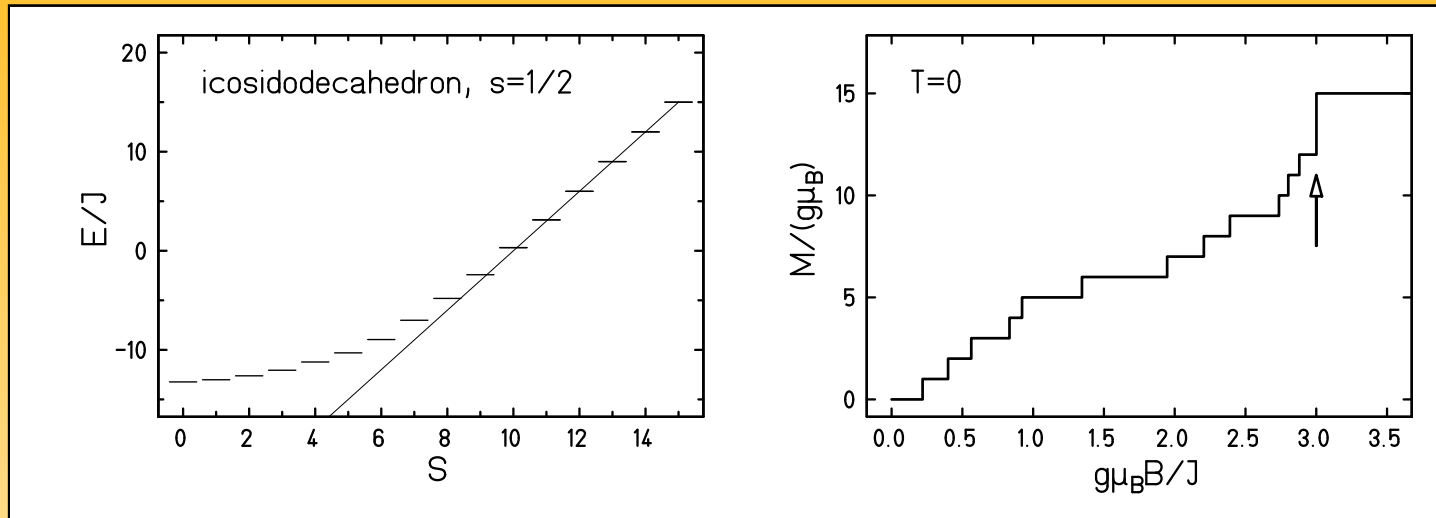
# {Mo<sub>72</sub>Fe<sub>30</sub>} - magnetization



- sequence of rotational bands rather unrealistic for this frustrated system;
- nevertheless magnetization at  $T = 0.46$  K very well reproduced.

J. Schnack, M. Luban, R. Modler, *Europhys. Lett.* **56** 863 (2001) 863  
 A. Müller *et al.*, *Chem. Phys. Chem.* **2**, 517 (2001)

# {Mo<sub>72</sub>Fe<sub>30</sub>} - magnetization jump



- $E_{\min}(S)$  linear in  $S$  for high  $S$  instead of being quadratic (1);
- Heisenberg model: property depends only on the structure but not on  $s$  (2);
- alternative formulation: independent localized magnons (3);

(1) J. Schnack, H.-J. Schmidt, J. Richter, J. Schulenburg, Eur. Phys. J. B **24**, 475 (2001)

(2) H.-J. Schmidt, J. Phys. A: Math. Gen. **35**, 6545 (2002)

(3) J. Schulenburg, A. Honecker, J. Schnack, J. Richter, H.-J. Schmidt, Phys. Rev. Lett. **88** (2002) 167207

# Outlook



- magnetic molecules is a booming field:  
ICCM-2000: 200 participants,  
ICCM-2002: 425 participants;  
DFG-SPP 1137
- huge advances in coordination chemistry, it seems to be possible to synthesize “every” structure;
- dynamics plays a bigger and bigger role: relaxation, hysteresis, magneto-optical switching.
- interesting molecules: complicated couplings + anisotropy, bigger and bigger  $\Rightarrow$  huge Hilbert spaces;
- systematics which connects structure and properties of observables highly required;
- interlinked structures of magnetic molecules are beyond nowadays computing - what to do?

# Thank you very much for your attention.

## Collaboration

- Prof. K. Bärwinkel, Prof. H.-J. Schmidt, M. Allalen, M. Brüger, D. Mentrup, M. Exler, P. Hage, F. Hesmer, F. Ouchni, P. Shechelokovskyy (Uni Osnabrück);
- Prof. M. Luban, Prof. R. Modler, Dr. P. Kögerler, Dr. Chr. Schröder (Ames Lab, Iowa, USA);
- Prof. H. Nojiri (Okayama University, Japan);
- Prof. S. Blügel (FZ Jülich);
- Prof. J. Richter, J. Schulenburg (Uni Magdeburg);
- Dr. A. Honecker (Uni Braunschweig).