Quantum Theory of Molecular Magnetism

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36th IFF Spring School – Magnetism goes Nano

Jülich, February 23rd 2005

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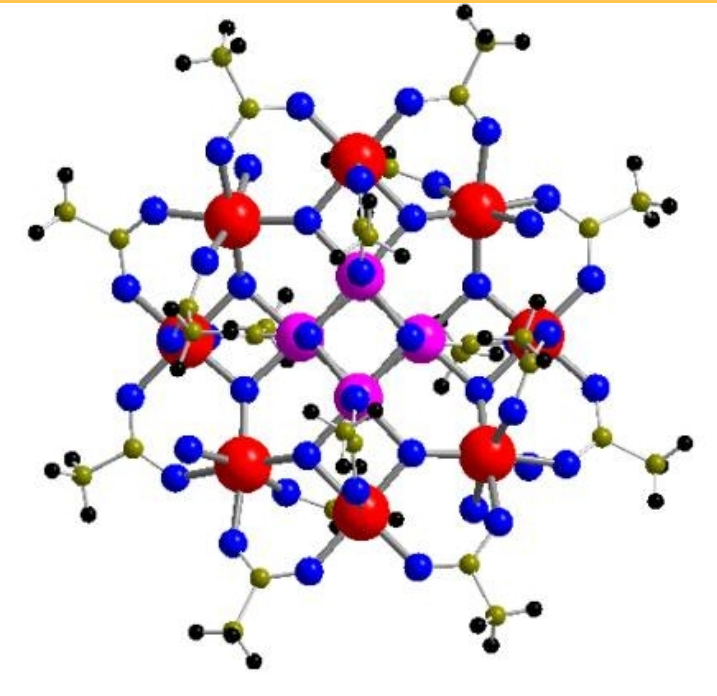
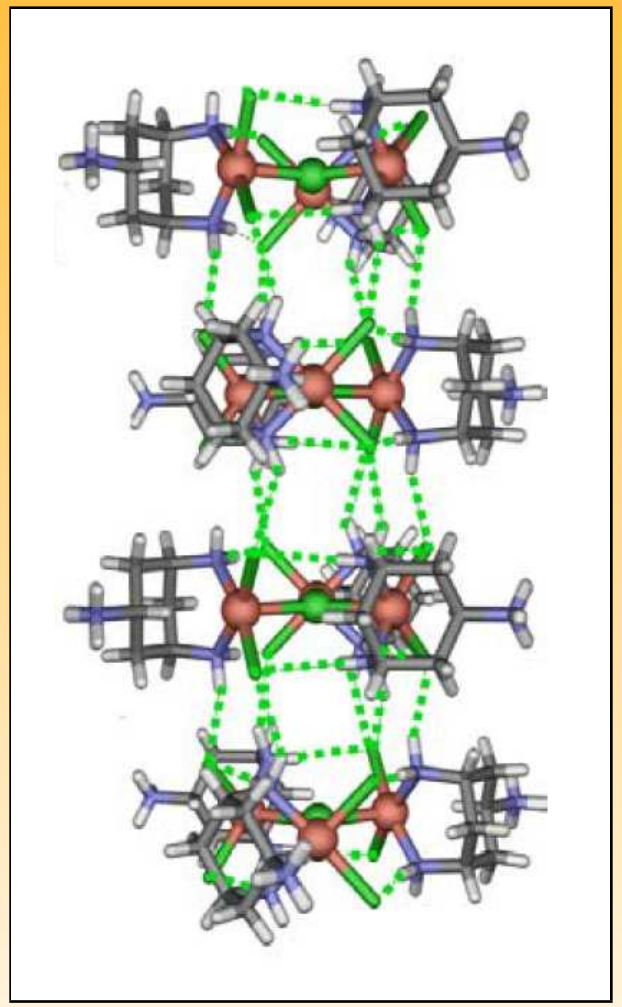
The beauty of magnetic molecules I



Mn_{12}

- 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), Vanadium (V) 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.

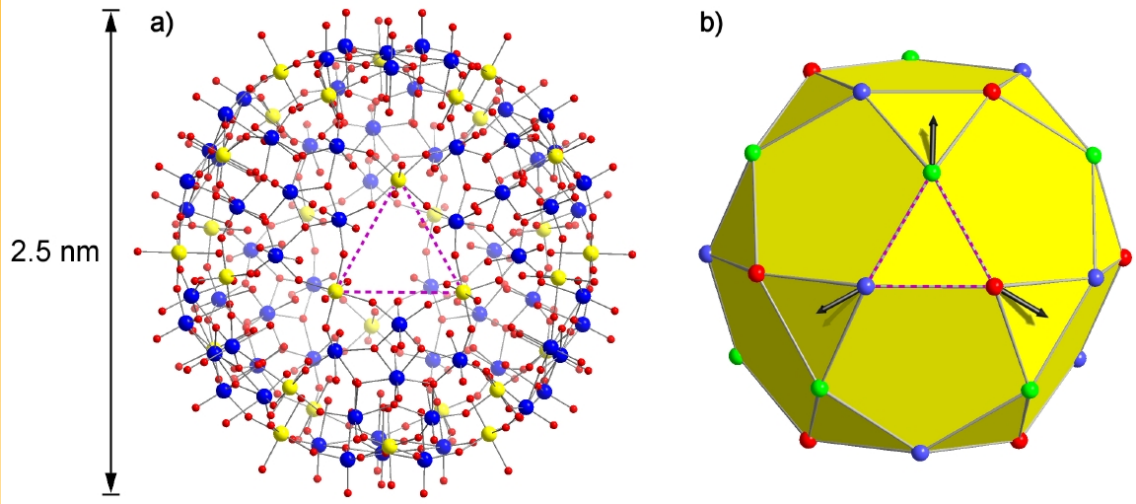
The beauty of magnetic molecules II



- Dimers (Fe_2), tetrahedra (Cr_4), cubes (Cr_8);
- Rings, especially iron rings (Fe_6, Fe_8, Fe_{10}, . . .);
- Complex structures (Mn_{12}) – drosophila of molecular magnetism;
- “Soccer balls”, more precisely icosidodecahedra (Fe_{30}) and other macro molecules;
- Chain like and planar structures of interlinked magnetic molecules, e.g. triangular Cu chain:

  J. Schnack, H. Nojiri, P. Kögerler, G. J. T. Cooper, L. Cronin, Phys. Rev. B 70, 174420 (2004)

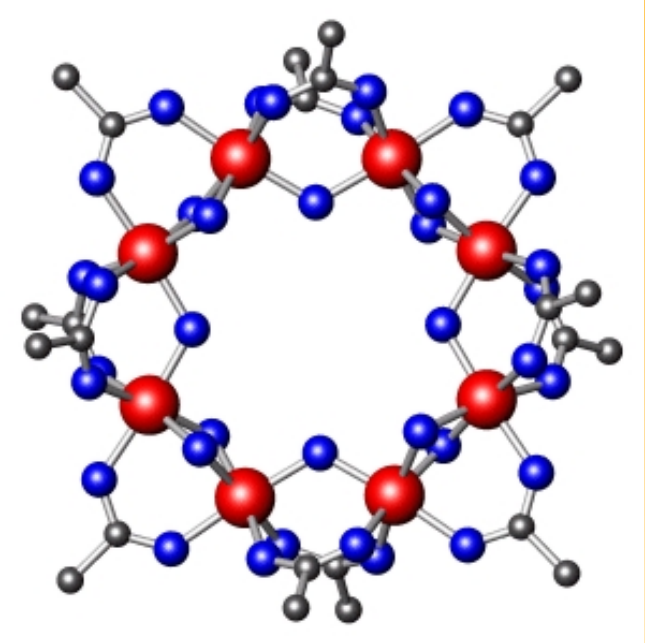
The beauty of magnetic molecules III
$\{Mo_{72}Fe_{30}\}$ – our favorite molecule



- Giant magnetic Keplerate molecule;
- Structure: Fe - yellow, Mo - blue, O - red;
- Antiferromagnetic interaction mediated by O-Mo-O bridges (1).
- Classical ground state of $\{Mo_{72}Fe_{30}\}$: 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)

The beauty of magnetic molecules IV
Why magnetic molecules?



Cr_8

- 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.

Hamiltonian and Tools

Model Hamiltonian – Heisenberg-Model

$$\underset{\sim}{H} = -\sum_{i,j} J_{ij}\, \vec{\underset{\sim}{s}}(i) \cdot \vec{\underset{\sim}{s}}(j) + \sum_{i,j} \vec{\underset{\sim}{s}}(i) \cdot \mathbf{D}_{ij} \cdot \vec{\underset{\sim}{s}}(j) + \mu_B\, B \sum_{i}^{N} g_i\, \underset{\sim}{s}_z(i)$$

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 have quenched angular momentum $\langle\, \underset{\sim}{l}\, \rangle \approx 0$ due to chemical binding, remaining spin-orbit coupling treated perturbatively with the help of anisotropy terms. This is different for rare earth ions!

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.

Product basis and symmtries

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

$$\underset{\sim}{s}_z(u) \left| m_1, \ldots, m_u, \ldots, m_N \right\rangle = m_u \left| m_1, \ldots, m_u, \ldots, m_N \right\rangle$$

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

Symmetries of the Heisenberg model without anisotropy

$$\left[\underset{\sim}{H}, \underset{\sim}{\vec{S}}^2\right] = 0 \quad , \qquad \left[\underset{\sim}{H}, \underset{\sim}{S}_z\right] = 0$$

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

Decomposition into mutually orthogonal subspaces

If $\left[\underset{\sim}{H}, \underset{\sim}{S}_z\right] = 0$, the Hilbert space $\mathcal{H}$ can be decomposed into mutually orthogonal subspaces $\mathcal{H}(M)$ (M is the quantum number belonging to $\underset{\sim}{S}_z$)

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

$\mathcal{H}(M)$ containes all states $\left| m_1, \ldots, m_u, \ldots, m_N \right\rangle$ with $\sum_i m_i = M$.

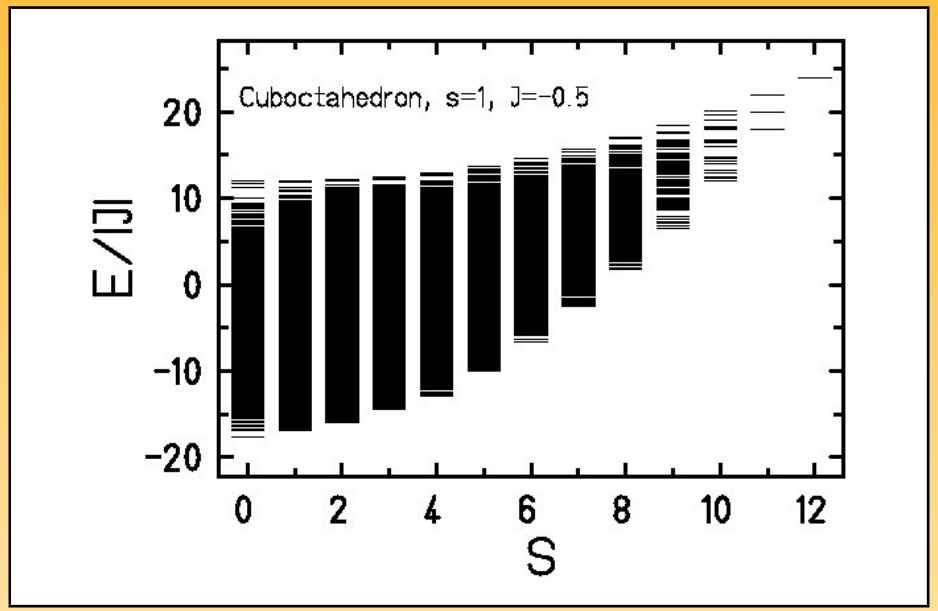
The Hamiltonian is diagonalized in all subspaces separately. The dimension of the largest subspace determines whether a Hamiltonian can diagonalized completely. If further symmetries apply this dimension will be further reduced.

For practical purposes $\vec{\underset{\sim}{s}}(i) \cdot \vec{\underset{\sim}{s}}(j) = \underset{\sim}{s}_z(i)\underset{\sim}{s}_z(j) + \frac{1}{2}\left[\underset{\sim}{s}^+(i)\underset{\sim}{s}^-(j) + \underset{\sim}{s}^-(i)\underset{\sim}{s}^+(j)\right]$.

Example: spin ring with $N = 6, s = 1/2$

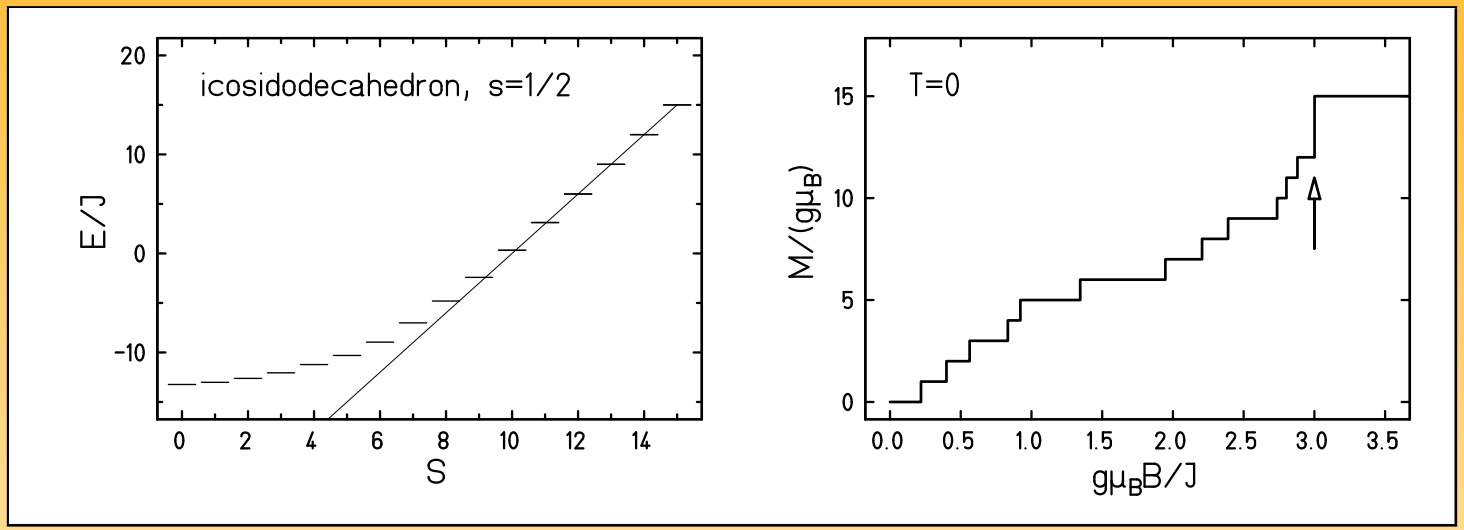
- Total dimension of $\mathcal{H}$: $Dim(\mathcal{H}) = (2 \times 1/2 + 1)^6 = 64$;
- $M = 3$: $|\Omega\rangle = |++++++\rangle$; $Dim(\mathcal{H}(M)) = 1$;
- $M = 2$: $|-+++++\rangle$ and cyclic shifts; $Dim(\mathcal{H}(M)) = 6$;
- $M = 1$: $|--++++\rangle, |-+-+++\rangle, |-++-++\rangle$ and cyclic shifts; $Dim(\mathcal{H}(M)) = 15$;
- $M = 0$: $|---+++\rangle, |--+-++\rangle, |-+--++\rangle, |-+-+-+\rangle$ and cyclic shifts; $Dim(\mathcal{H}(M)) = 20$;
- Dimensional check: $64 = 1 + 6 + 15 + 20 + 15 + 6 + 1$ $\surd$
- Inclusion of translational symmetry leads to orthogonal subspaces $\mathcal{H}(M, k)$ with $k = 0, \ldots, 5$. Then the largest dimension is 4.

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, e.g. Mn_{12} (1,2);
- Low-lying states important for quantum phase transitions, e.g. magnetization jumps.
- Several methods available: projection, Lánczos, DMRG.

(1) Regnault *et al.*, Phys. Rev. B **66**, 054409 (2002)
(2) Chaboussant *et al.*, Phys. Rev. B **70**, 104422 (2004)

Lanczos method

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

$$
\begin{aligned}
|\,\psi'_{k+1}\,\rangle &= (1 - |\,\psi_k\,\rangle\langle\,\psi_k\,| - |\,\psi_{k-1}\,\rangle\langle\,\psi_{k-1}\,|\,)\,\underset{\sim}{H}\,|\,\psi_k\,\rangle \\
|\,\psi_{k+1}\,\rangle &= \frac{|\,\psi'_{k+1}\,\rangle}{\sqrt{\langle\,\psi'_{k+1}\,|\,\psi'_{k+1}\,\rangle}}
\end{aligned}
$$

- New Lanczos vector by construction orthogonal 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

- 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

Steven R. White, Phys. Rev. B **48**, 10345 (1993)
Salvatore R. Manmana, Alejandro Muramatsu, Reinhard M. Noack, cond-mat/0502396

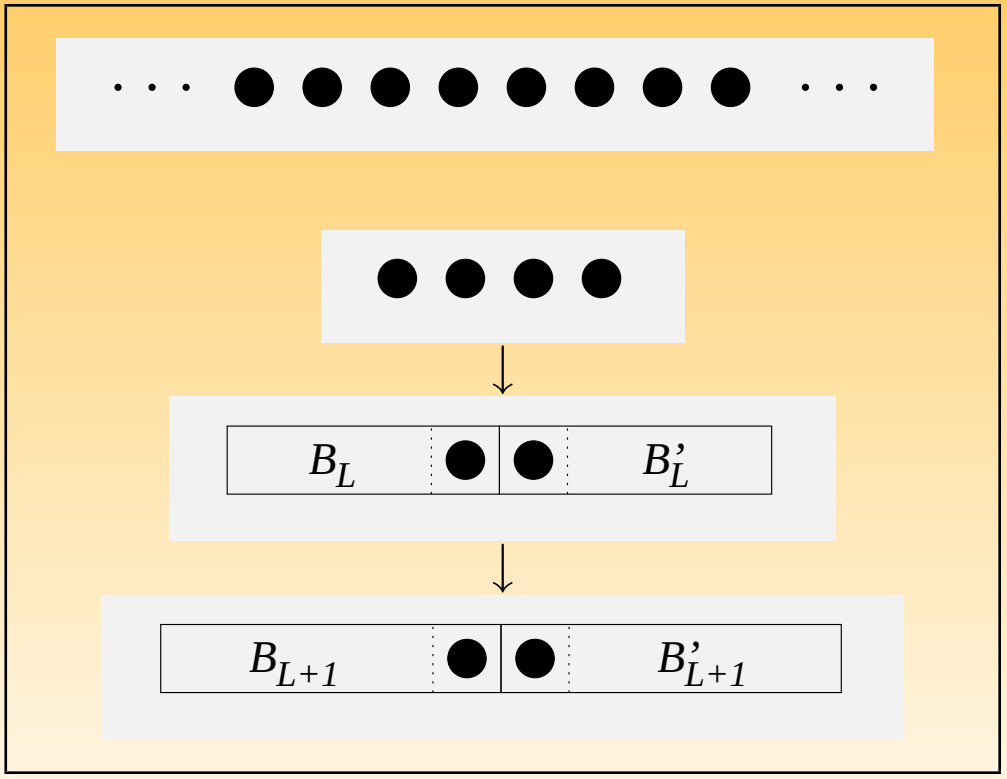
Standard DMRG algorithm schematically

Algorithm was developed and first used to study groundstate properties of infinite systems (1-dimensional)

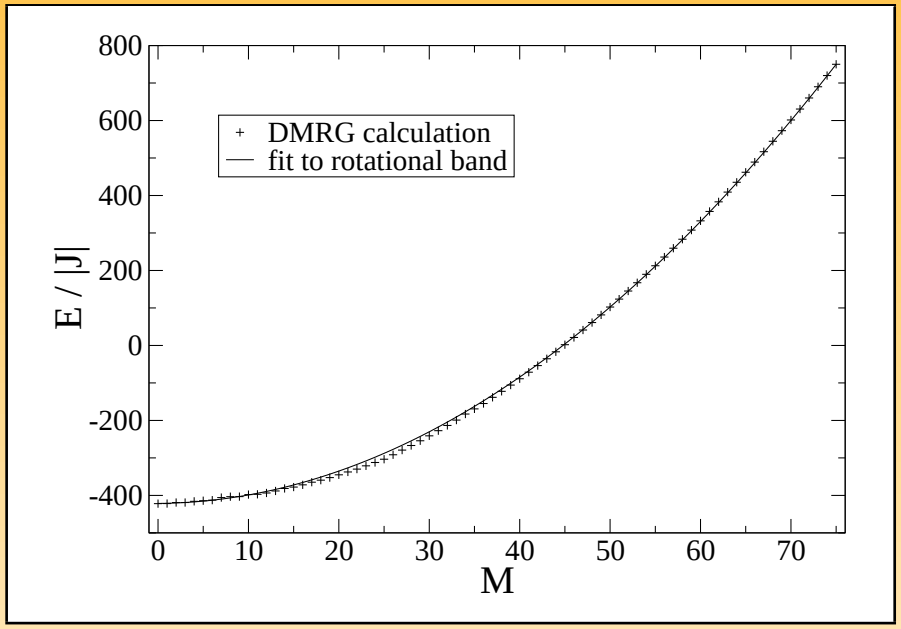
Example: infinite spin chain

1. Begin with 4-spin superblock
2. Combine block B_L and one spin to block B_{L+1}
3. Truncate block B_{L+1} to m states
4. continue with step 2.

$\rightarrow$ System size increases by 2 spins after each step



$\{Mo_{72}Fe_{30}\}$ – Lowest rotational band with DMRG

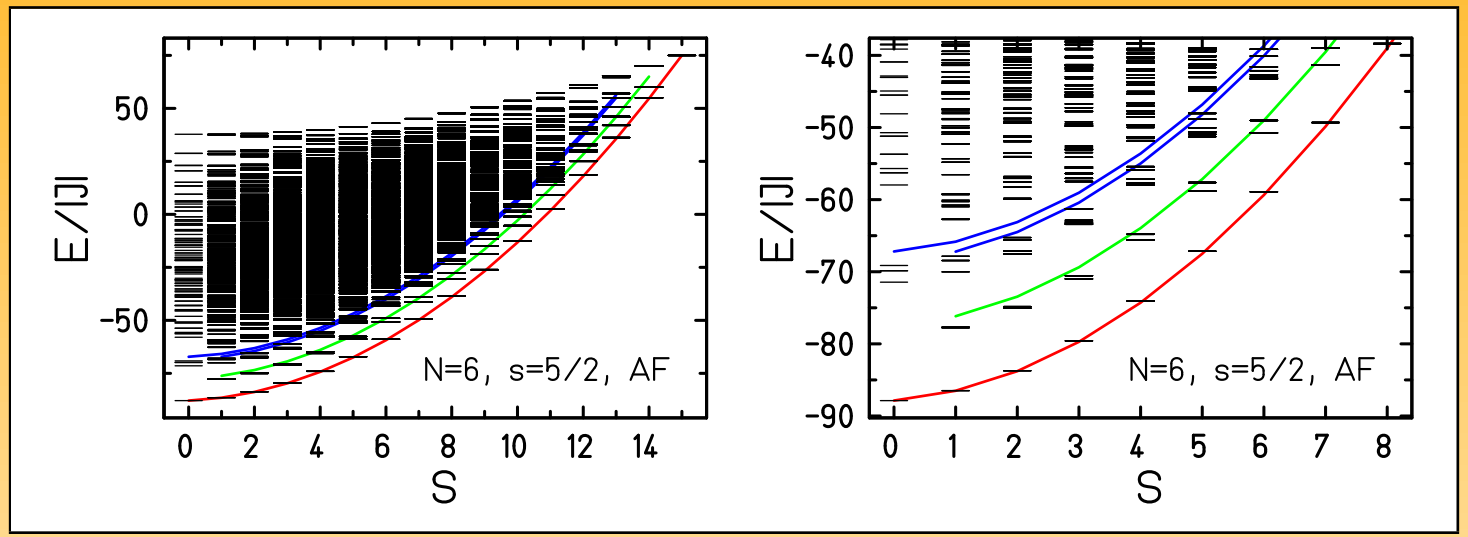


- Dimension of Hilbert space: $(2s+1)^N \approx 10^{23}$;
- Difficult since quasi two-dimensional and finite;
- Slow convergence with $1/m$ instead of $\exp(-m)$;
- Result: relative ground state energies form an almost quadratic band (rotational band hypothesis).

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

General Results

Rotational bands in antiferromagnets I

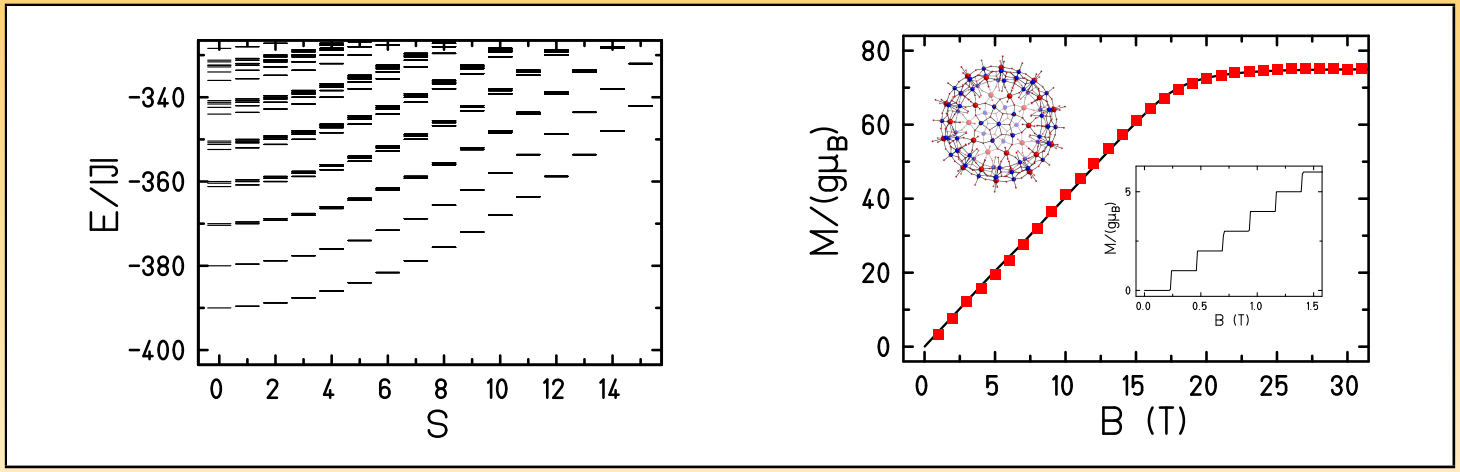


- Often minimal energies $E_{min}(S)$ form a rotational band: Landé interval rule (1);
- Most pronounced for bipartite systems (2), good approximation for more general systems;
- Sometimes low-lying spectrum is a sequence of rotational bands (3).

(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)

Rotational bands in antiferromagnets II
Approximate Hamiltonian for $\{\mathbf{Mo}_{72}\mathbf{Fe}_{30}\}$

$$\underset{\sim}{H} = -2\,J \sum_{(u<v)} \vec{\underset{\sim}{s}}(u)\cdot\vec{\underset{\sim}{s}}(v) \quad \approx \quad -\frac{D\,J}{N}\left[\vec{\underset{\sim}{S}}^{2} - \sum_{j=1}^{N_{SL}} \vec{\underset{\sim}{S}}_{j}^{2}\right] = \underset{\sim}{H}^{\text{eff}}$$

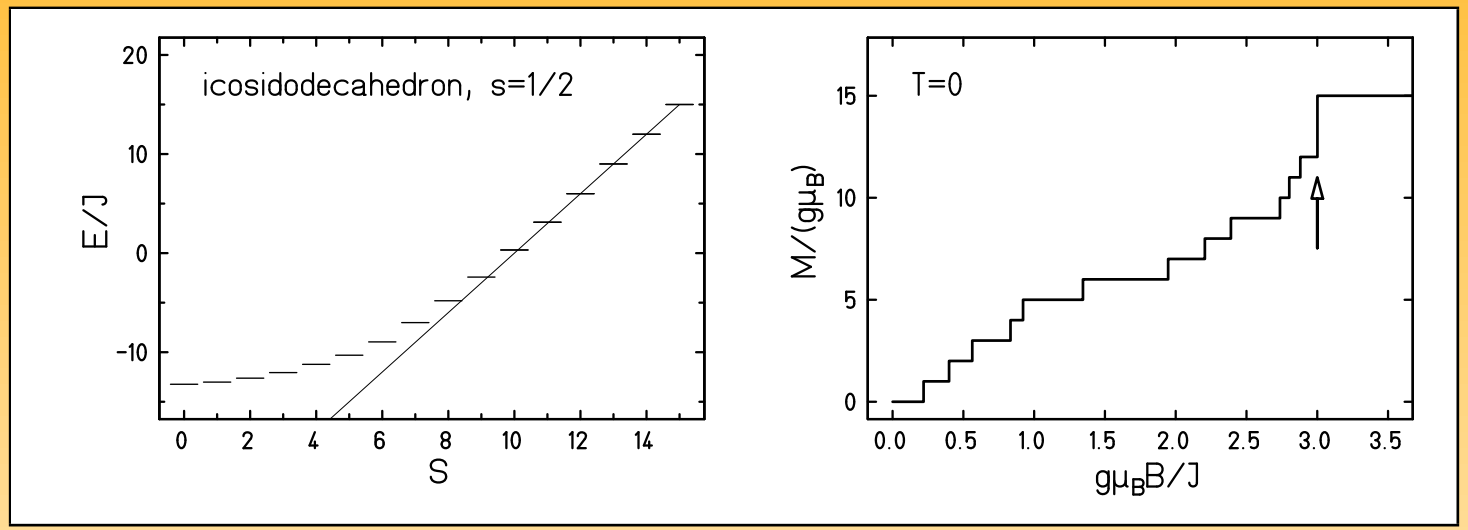


$\vec{\underset{\sim}{S}}_j$ sublattice spins; $D = 6$; INS shows broad peak at band separation.

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

Giant magnetization jumps in frustrated antiferromagnets I

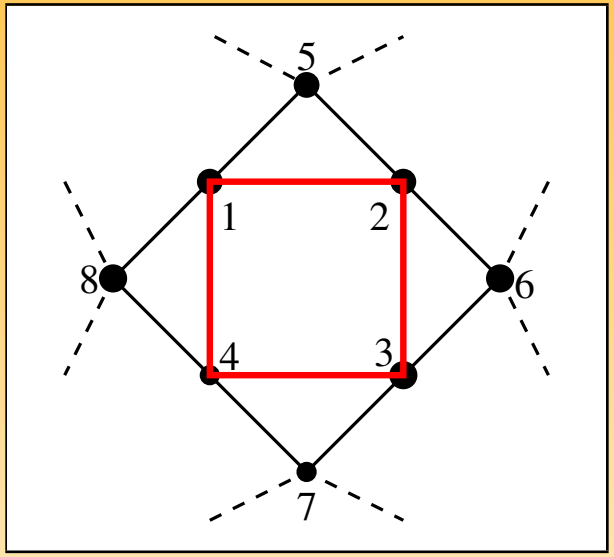
$\{Mo_{72}Fe_{30}\}$



- $E_{\text{min}}(S)$ 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**, 167207 (2002)

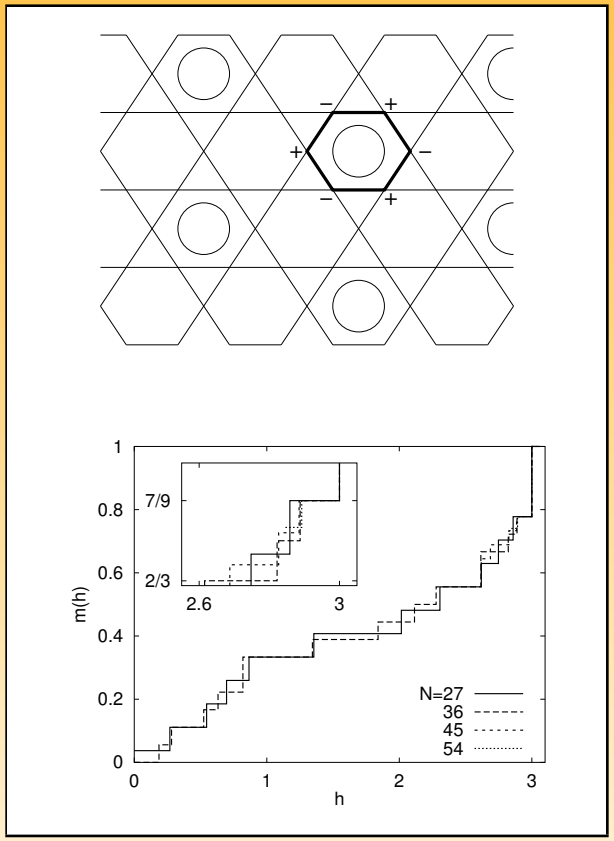
Giant magnetization jumps in frustrated antiferromagnets II
Localized Magnons



- $|\,\text{localized magnon}\,\rangle = \frac{1}{2}(\,|\,1\,\rangle - |\,2\,\rangle + |\,3\,\rangle - |\,4\,\rangle)$
- $|\,1\,\rangle = \underset{\sim}{s}^{-}(1)\,|\uparrow\uparrow\uparrow\ \ldots\rangle$ etc.
- $\underset{\sim}{H}\,|\,1\,\rangle = J\{\,|\,1\,\rangle + 1/2(\,|\,2\,\rangle + |\,4\,\rangle + |\,5\,\rangle + |\,8\,\rangle)\}$
  $\underset{\sim}{H}\,|\,2\,\rangle = J\{\,|\,2\,\rangle + 1/2(\,|\,1\,\rangle + |\,3\,\rangle + |\,5\,\rangle + |\,6\,\rangle)\}$
  $\ldots$
- $\underset{\sim}{H}\,|\,\text{localized magnon}\,\rangle \propto |\,\text{localized magnon}\,\rangle$

- Triangles trap the localized magnon, amplitudes cancel at outer vertices.

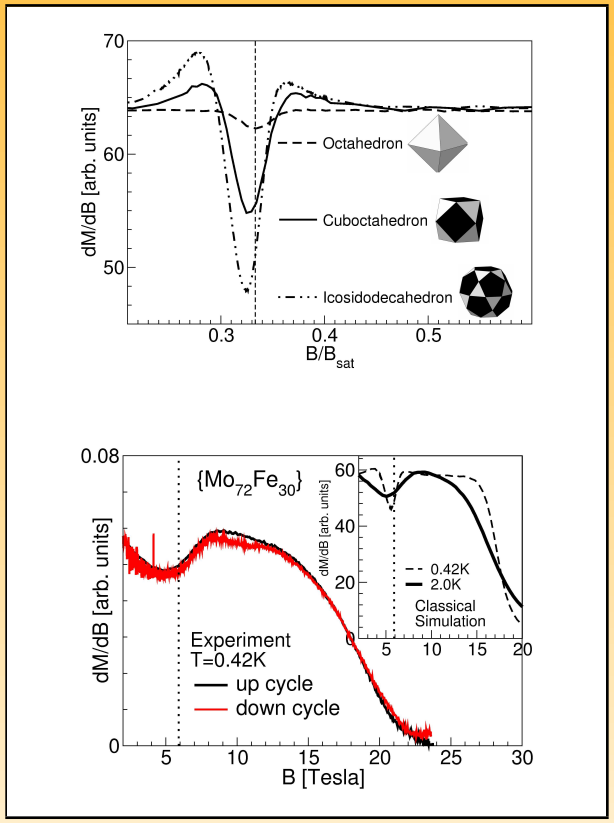
Giant magnetization jumps in frustrated antiferromagnets III
Kagome Lattice



- Non-interacting one-magnon states can be placed on various lattices, e. g. the kagome lattice;
- Each state of n independent magnons is the ground state in the Hilbert subspace with $M = Ns - n$;
- Linear dependence of E_{min} on M
  $\Rightarrow$ magnetization jump;
- Maximal number of independent magnons: N/9;
- Jump is a macroscopic quantum effect!

J. Schulenburg, A. Honecker, J. Schnack, J. Richter, H.-J. Schmidt, Phys. Rev. Lett. **88**, 167207 (2002)
J. Richter, J. Schulenburg, A. Honecker, J. Schnack, H.-J. Schmidt, J. Phys.: Condens. Matter **16**, S779 (2004)

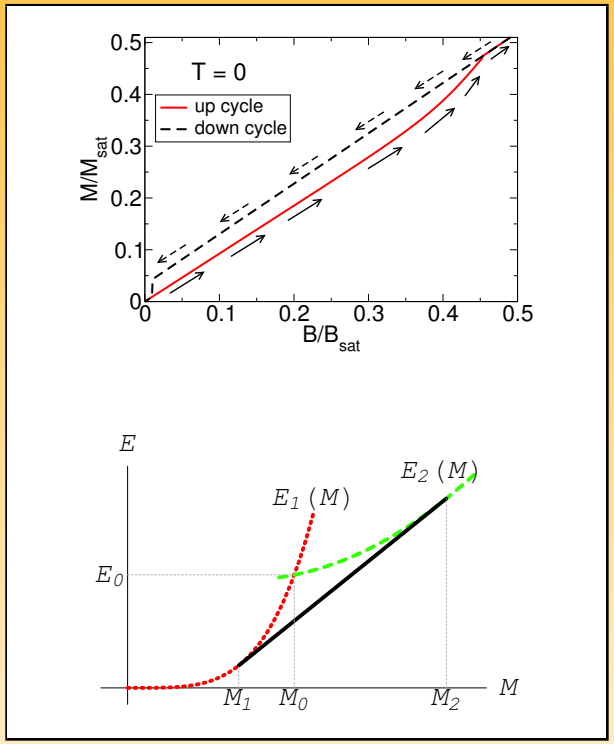
Magnetization plateaus and susceptibility minima



- Octahedron, Cubocthedron, Icosidodecahedron – little (polytope) brothers of the kagome lattice with increasing frustration.
- Cubocthedron & Icosidodecahedron realized as magnetic molecules.
- Cubocthedron & Icosidodecahedron feature plateaus, e.g. at $\mathcal{M}_{\text{sat}}/3$ and independent magnons.
- Susceptibility shows a pronounced dip at $B_{\text{sat}}/3$ (classical calculations and quantum calculations for the cuboctahedron).
- Experimentally verified with $\{\text{Mo}_{72}\text{Fe}_{30}\}$.

C. Schröder, H. Nojiri, J. Schnack, P. Hage, M. Luban, P. Kögerler, Phys. Rev. Lett. **94**, 017205 (2005)

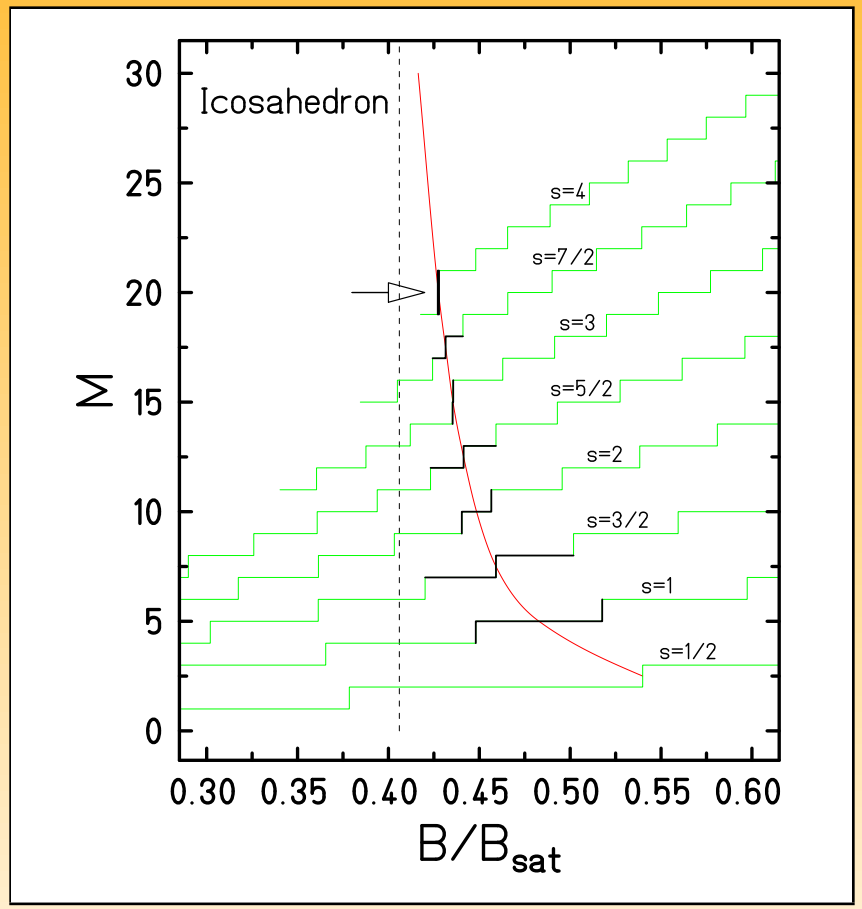
Metamagnetic phase transition I



- Normally hysteretic behavior of SMM is an outcome of magnetic anisotropy.
- The classical AF Heisenberg Icosahedron exhibits a pronounced hysteresis loop.
- It shows a first order phase transition at $T = 0$ as function of B.
- The minimal energies are realized by two families of spin configurations (movie by C. Schröder).
- The overall minimal energy curve is not convex $\Rightarrow$ magnetization jump.

C. Schröder, H.-J. Schmidt, J. Schnack, M. Luban, Phys. Rev. Lett., submitted, cond-mat/0501558

Metamagnetic phase transition II



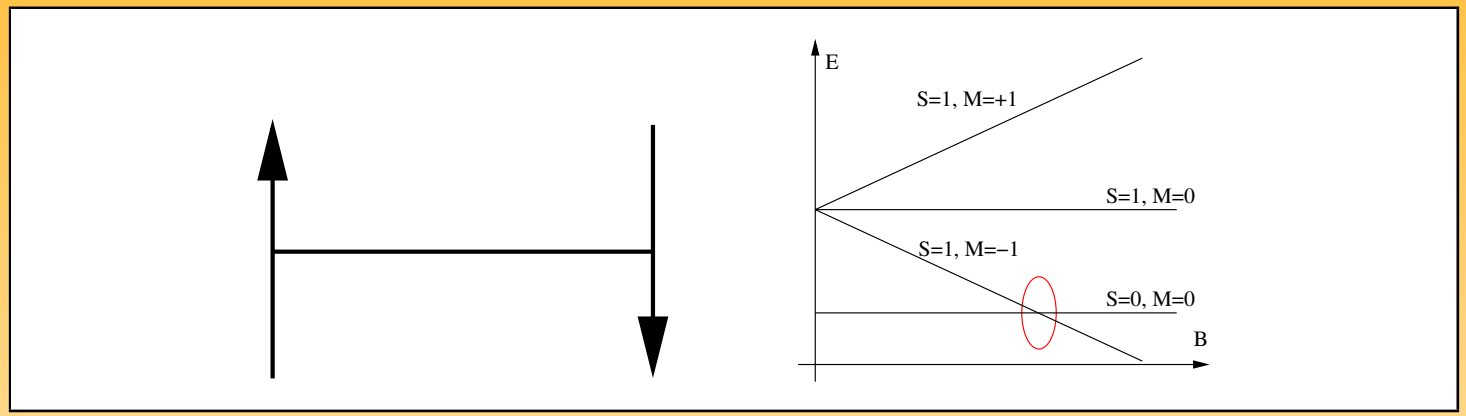
- Quantum analog:
  Non-convex minimal energy levels
  $\Rightarrow$ magnetization jump of $\Delta M > 1$.
- Lanczos diagonalization for various s.
- True jump of $\Delta M = 2$ for $s = 4$.
- Polynomial fit in $1/s$ yields the classically observed transition field.

C. Schröder, H.-J. Schmidt, J. Schnack, M. Luban, Phys. Rev. Lett., submitted, cond-mat/0501558

Enhanced magnetocaloric effect I
Basics

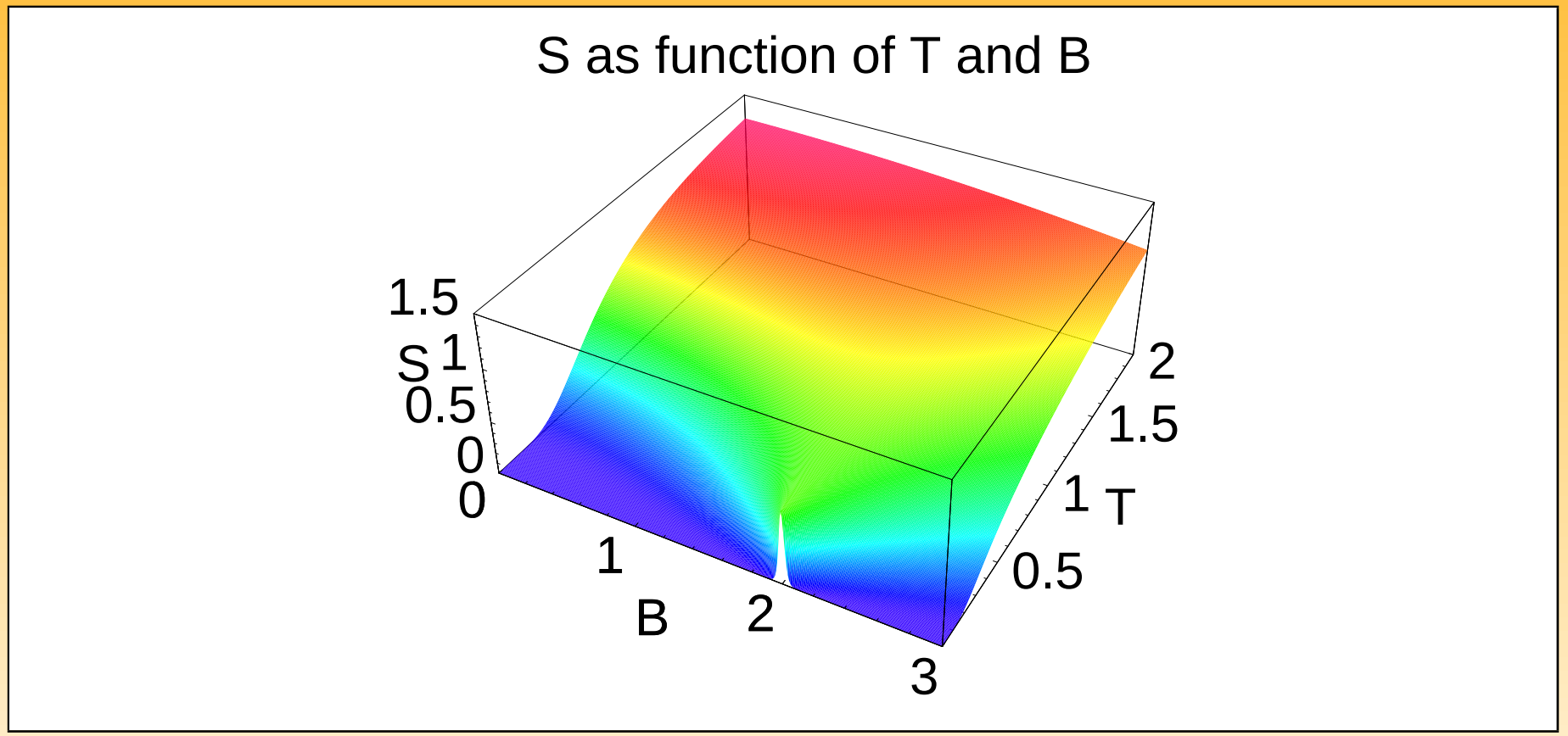
- Discovered in pure iron by E. Warburg in 1881.
- Heating or cooling in a varying magnetic field.
- Typical rates: $0.5 \ldots 2$ K/T (adiabatic temperature change).
- Giant magnetocaloric effect: $3 \ldots 4$ K/T e.g. in $Gd_5(Si_xGe_{1-x})_4$ alloys ($x \leq 0.5$).
- MCE especially large: due to condensation of a macroscopic number of soft modes (Zhitomirsky), due to condensation of independent magnons (Zhitomirsky, Honecker, Richter), close to quantum critical points (Rosch).

Enhanced magnetocaloric effect II
Simple af $s = 1/2$ dimer



- Singlet-triplet level crossing causes a “quantum phase transition” at $T = 0$ as a function of B.
- $M(T = 0, B)$ and $S(T = 0, B)$ not analytic as function of B.
- $C(T, B)$ varies strongly as function of B for low T.

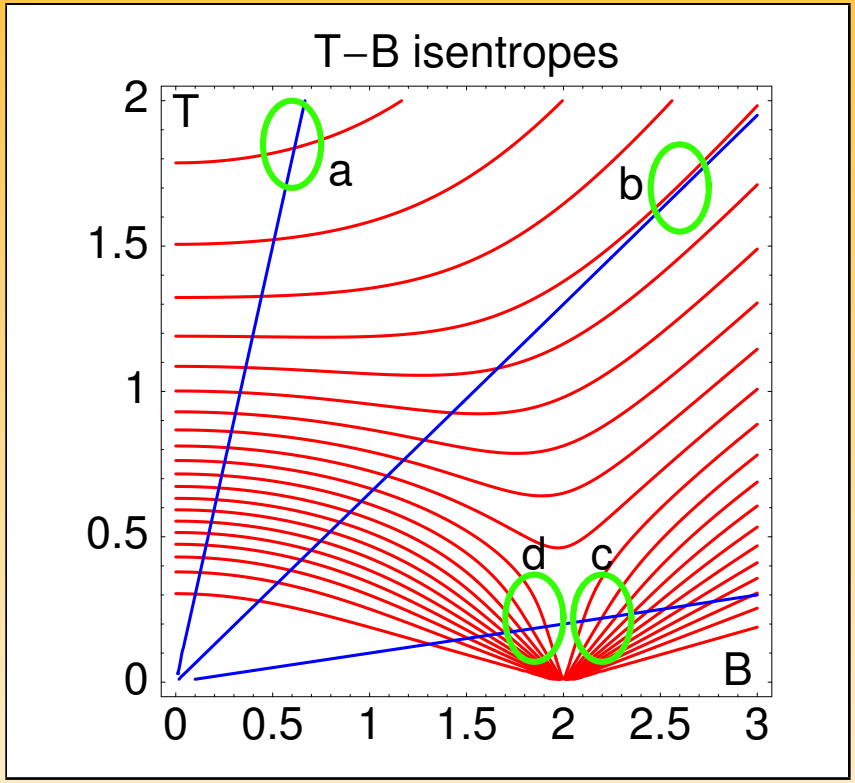
Enhanced magnetocaloric effect III
Entropy of af $s = 1/2$ dimer



$S(T = 0, B) \neq 0$ at level crossing due to degeneracy

O. Derzhko, J. Richter, Phys. Rev. B **70**, 104415 (2004)

Enhanced magnetocaloric effect IV
Isentrops of af $s = 1/2$ dimer



Magnetocaloric effect:

(a) reduced,

(b) the same,

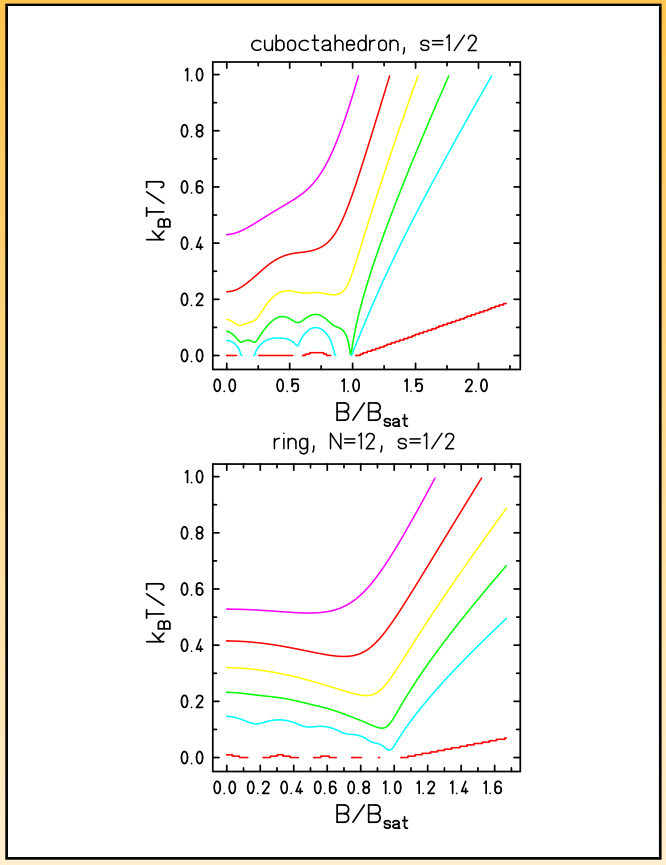
(c) enhanced,

(d) opposite

when compared to an ideal paramagnet.

Case (d) does not occur for a paramagnet.

Enhanced magnetocaloric effect V
Two molecular spin systems



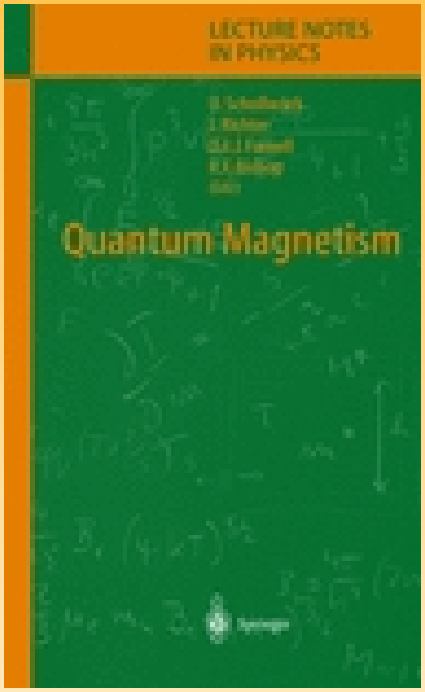
- Graphics: isentrops of the frustrated cuboctahedron and a $N = 12$ ring molecule;
- Cuboctahedron features independent magnons and extraordinarily high jump to saturation;
- Degeneracy and $(T = 0)$–entropy at saturation field higher for the cuboctahedron;
- Adiabatic (de-) magnetization more efficient for the frustrated spin system.

Collaboration

- K. Bärwinkel, H.-J. Schmidt, M. Allalen, M. Brüger, D. Mentrup, M. Exler, P. Hage, F. Hesmer, F. Ouchni, P. Shechelokovskyy (Uni Osnabrück);
- M. Luban, R. Modler, P. Kögerler, D. Vaknin, . . . (Ames Lab, Iowa, USA);
- Chr. Schröder (FH Bielefeld & Ames Lab, Iowa, USA);
- H. Nojiri (Tohoku University, Japan);
- R.E.P. Winpenny (Man U); L. Cronin (University of Glasgow)
- J. Richter, J. Schulenburg (Uni Magdeburg);
- S. Blügel (FZ Jülich); A. Honecker (Uni Braunschweig).
- E. Rentschler (Uni Mainz);

Thank you very much for your attention.

Buy now!



Quantum Magnetism

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Mikeska, Kolezhuk, *One-dimensional magnetism*
Richter, Schulenburg, Honecker, *Q. Mag. in 2-D*
Schnack, *Molecular Magnetism*
Ivanov, Sen, *Spin Wave Analysis*
Laflorencie, Poilblanc, *Low-Dim. Gapped Systems*
Cabra, Pujol, *Field-Theoretical Methods*
Farnell, Bishop, *Coupled Cluster Method*
Klümper, *Integrability of Quantum Chains*
Sachdev, *Mott Insulators*
Lemmens, Millet, *Spin Orbit Topology, a Triptych*