Yes, we can! Advanced quantum methods for the largest magnetic molecules

Jürgen Schnack

Department of Physics – University of Bielefeld – Germany

http://obelix.physik.uni-bielefeld.de/∼schnack/

Seminar, University of Copenhagen, Chemistry, Kemisk Institute
Copenhagen, Denmark, 3. 10. 2014

Universität Bielefeld

DFG

FOR 945

SPONSORED BY THE
Federal Ministry
of Education
and Research

My relation to Denmark I

My relation to Denmark II

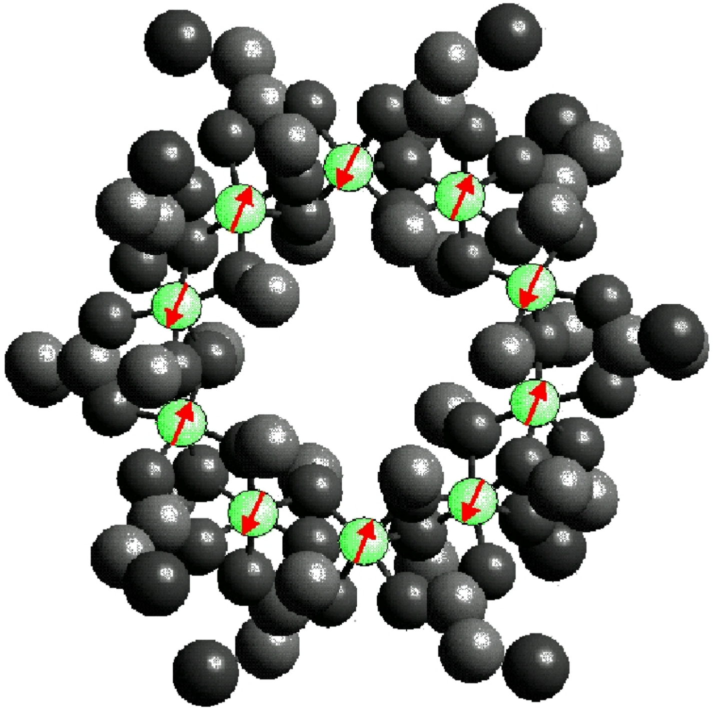
Frustrated, or not frustrated; that is the question:
Whether it’s nobler in the mind to suffer
The difficulties and pain of competing interactions,
Or to take arms against the intractable antiferromagnets?
And by diagonalizing the Hamiltonian? To know;
No more; and to say we understand
The gaps, the plateaus, and the giant jumps

. . .

W.S., Hamlet, early version, about 1599

The problem

You have got a molecule!

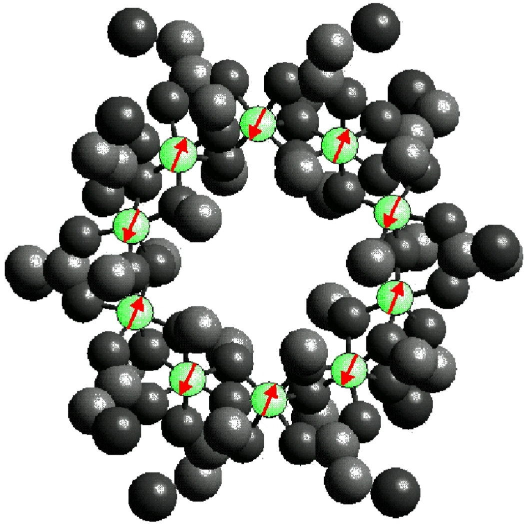


Congratulations!

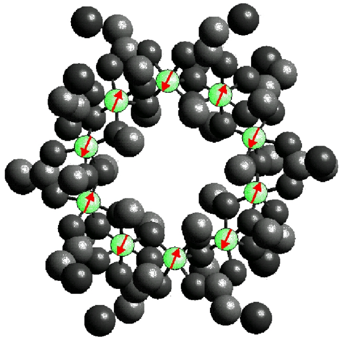
You have got an idea about the modeling!

$$\underset{\sim}{H} = -2\sum_{i<j} J_{ij}\, \underset{\sim}{\vec{s}}(i) \cdot \underset{\sim}{\vec{s}}(j) \quad + \quad g\,\mu_B\, B \sum_{i}^{N} \underset{\sim}{s}_z(i)$$

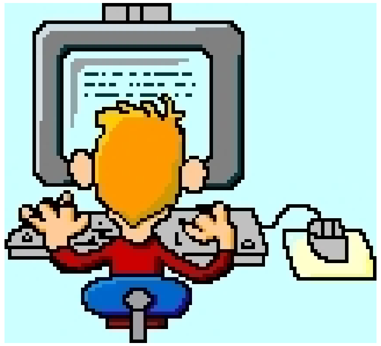
Heisenberg Zeeman



In the end it's always a big matrix!



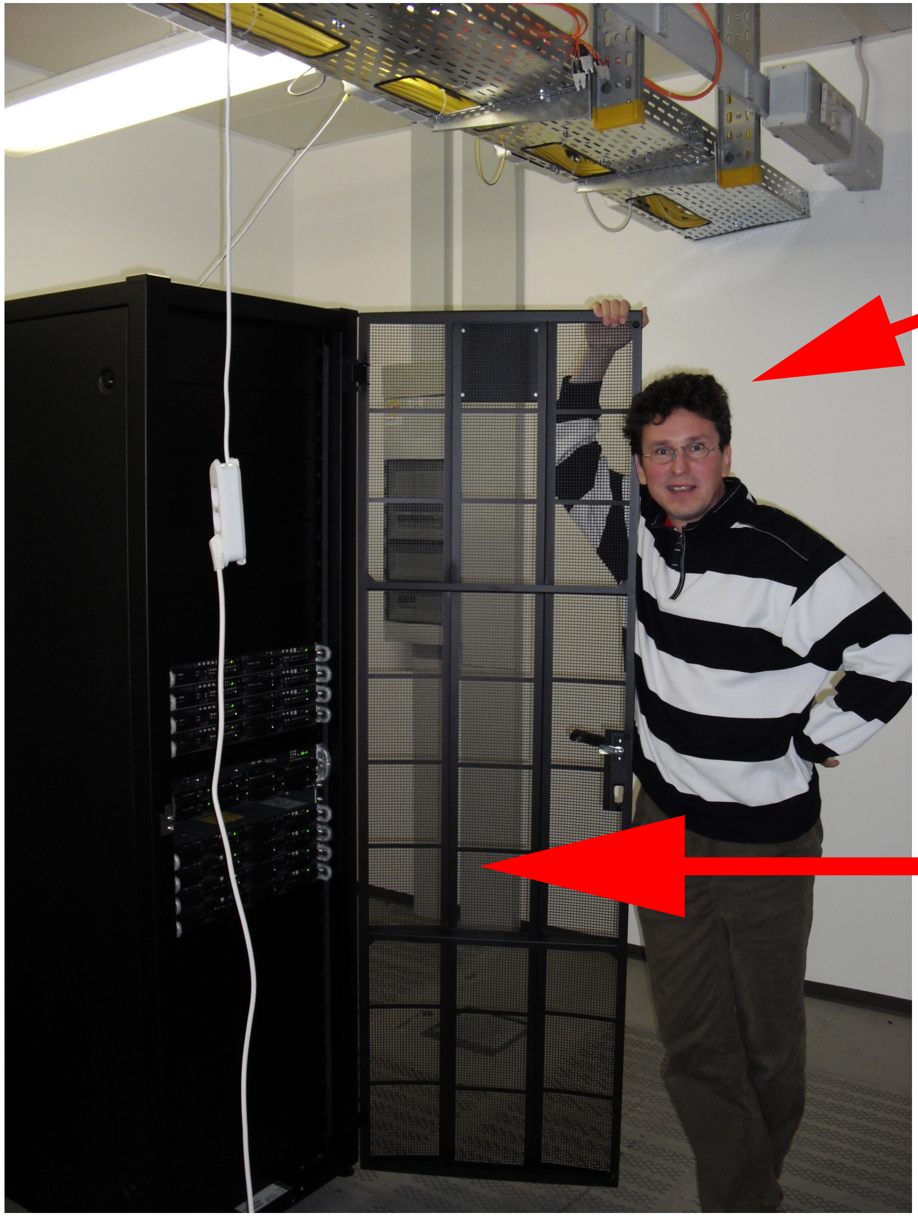
$$\Rightarrow \begin{pmatrix} -27.8 & 3.46 & 0.18 & \cdots \\ 3.46 & -2.35 & -1.7 & \cdots \\ 0.18 & -1.7 & 5.64 & \cdots \\ \vdots & \vdots & \vdots & \cdots \end{pmatrix} \Rightarrow$$



Fe$_{10}^{\text{III}}$: $N = 10, s = 5/2$

Dimension=60,466,176. Maybe **too** big?

Thank God, we have computers



“Espresso-doped multi-core”

128 cores, 384 GB RAM

. . . but that’s not enough!

Contents for you today

~~Introduction to molecular magnetism~~

Traditional approach

1. ~~Complete diagonalization, easy~~
2. Complete diagonalization, SU(2) & point groups

Approximate methods

1. Finite-temperature Lanczos
2. ~~DMRG & DDMRG~~
3. ~~QMC~~

+ examples: MCE, frustration, SMM, NRG

+ Outlook

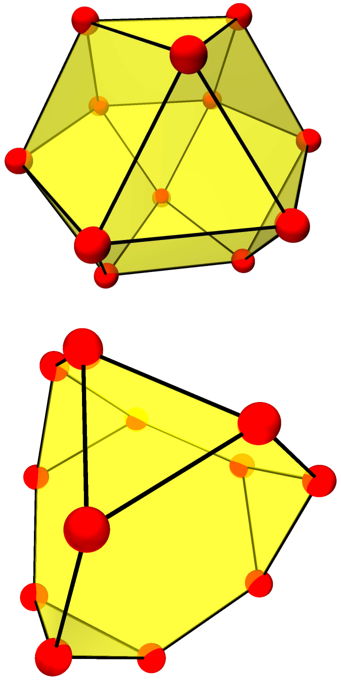
Complete diagonalization:

SU(2) & point group symmetry

Quantum chemists need to be much smarter since they have smaller computers!

(1) D. Gatteschi and L. Pardi, Gazz. Chim. Ital. **123**, 231 (1993).
(2) J. J. Borras-Almenar, J. M. Clemente-Juan, E. Coronado, and B. S. Tsukerblat, Inorg. Chem. **38**, 6081 (1999).
(3) B. S. Tsukerblat, *Group theory in chemistry and spectroscopy: a simple guide to advanced usage*, 2nd ed. (Dover Publications, Mineola, New York, 2006).

Irreducible Tensor Operator approach



Spin rotational symmetry SU(2):

- $\underset{\sim}{H} = -2 \sum_{i<j} J_{ij}\ \underset{\sim}{\vec{s}}_i \cdot \underset{\sim}{\vec{s}}_j + g\mu_B \underset{\sim}{\vec{S}} \cdot \vec{B}$;
- Physicists employ: $\left[\underset{\sim}{H}, \underset{\sim}{S}_z\right] = 0$;
- Chemists employ: $\left[\underset{\sim}{H}, \underset{\sim}{\vec{S}}^2\right] = 0$, $\left[\underset{\sim}{H}, \underset{\sim}{S}_z\right] = 0$;

  Irreducible Tensor Operator (ITO) approach;
  Free program MAGPACK (2) available.

(1) D. Gatteschi and L. Pardi, Gazz. Chim. Ital. **123**, 231 (1993).
(2) J. J. Borras-Almenar, J. M. Clemente-Juan, E. Coronado, and B. S. Tsukerblat, Inorg. Chem. **38**, 6081 (1999).
(3) B. S. Tsukerblat, *Group theory in chemistry and spectroscopy: a simple guide to advanced usage*, 2nd ed. (Dover Publications, Mineola, New York, 2006).

Idea of ITO

$$\begin{aligned} \underset{\sim}{H}_{\text{Heisenberg}} &= -2\sum_{i<j} J_{ij}\; \underset{\sim}{\vec{s}}_i \cdot \underset{\sim}{\vec{s}}_j \\ &= 2\sqrt{3}\sum_{i<j} J_{ij}\, \underset{\sim}{T}^{(0)}(\{k_i\}, \{\bar{k}_i\} | k_i = k_j = 1) \end{aligned}$$

Irreducible Tensor Operator approach

- Express spin operators and functions thereof as ITOs;
- Use vector coupling basis $|\,\alpha\ S\ M\,\rangle$ and recursive recoupling.

(1) Gatteschi, Tsukerblat, Coronado, Waldmann, . . .
(2) R. Schnalle, Ph.D. thesis, Osnabrück University (2009)

Point Group Symmetry

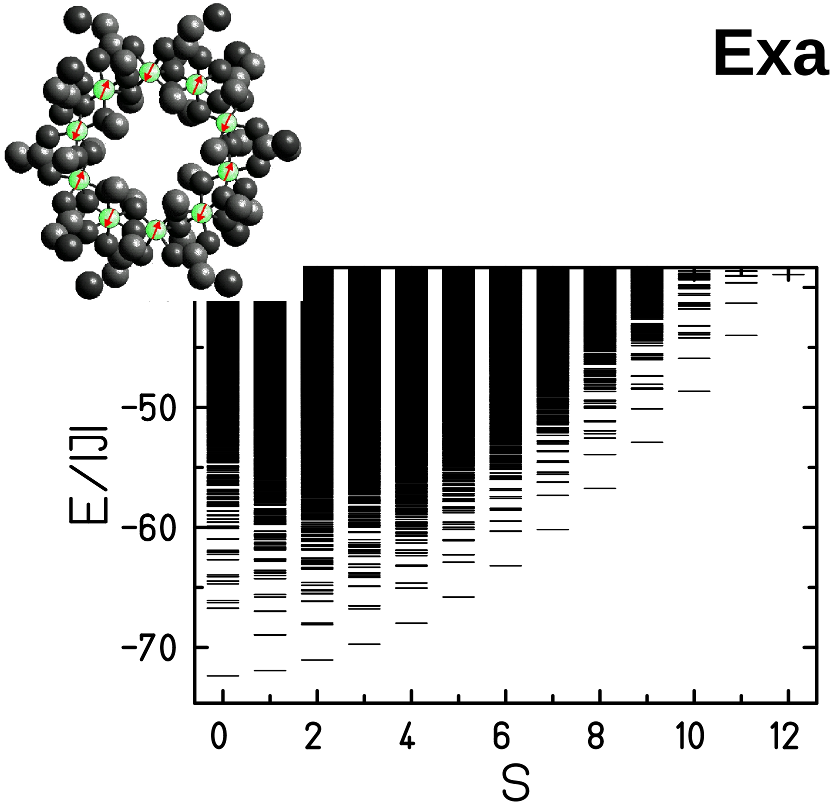
$$|\,\alpha'\,S\,M\,\Gamma\,\rangle = \mathcal{P}^{(\Gamma)}\,|\,\alpha\,S\,M\,\rangle = \left(\frac{l_\Gamma}{h}\sum_R \left(\chi^{(\Gamma)}(R)\right)^{*}\,\underset{\sim}{G}(R)\right)\,|\,\alpha\,S\,M\,\rangle$$

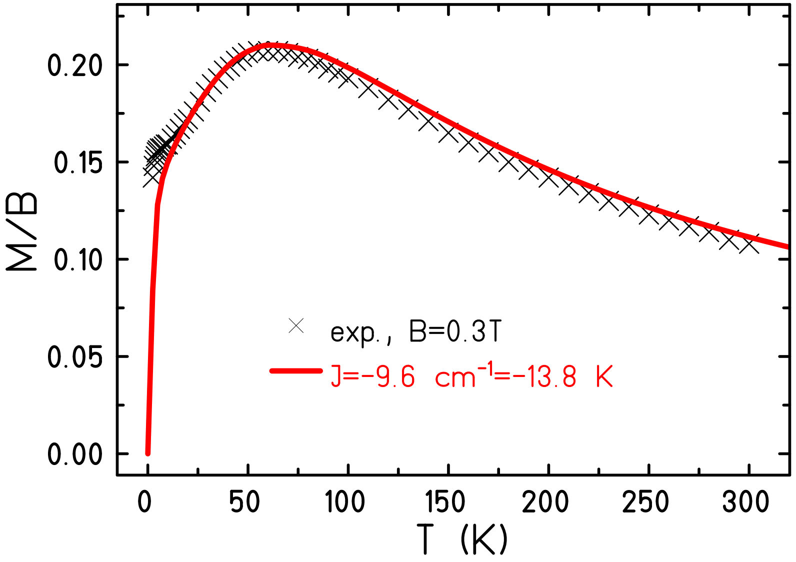
Method:

- Projection onto irreducible representations Γ of the point group (1,2);
- No free program, things are a bit complicated (3,4).

(1) M. Tinkham, *Group Theory and Quantum Mechanics*, Dover.
(2) D. Gatteschi and L. Pardi, Gazz. Chim. Ital. **123**, 231 (1993).
(3) O. Waldmann, Phys. Rev. B **61**, 6138 (2000).
(4) R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403-452 (2010) ⇐ contains EVERYTHING.

Example: Fe$_{10}$





Spin ring, $N = 10$, $s = 5/2$, Hilbert space dimension 60,466,176; symmetry D_2 (1).

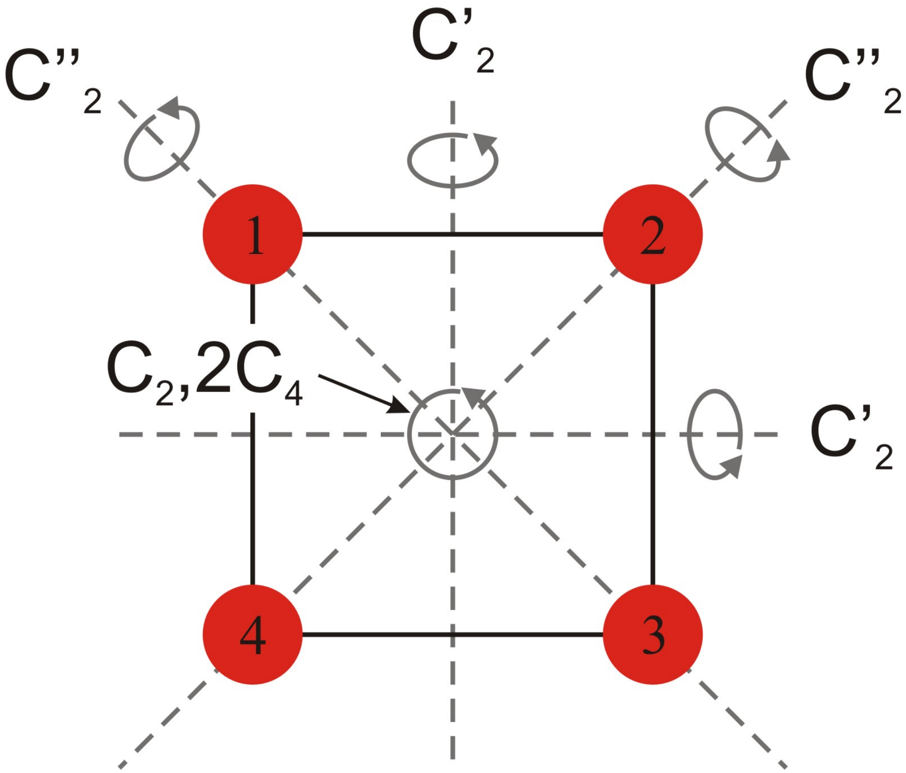
(1) R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403-452 (2010).
(2) C. Delfs *et al.*, Inorg. Chem. **32**, 3099 (1993).

Point Group Symmetry II

$$\underset{\sim}{G}(R)\,|\,\alpha\,S\,M\,\rangle_a = \,|\,\alpha\,S\,M\,\rangle_b = \sum_{\alpha'}\,|\,\alpha'\,S\,M\,\rangle_a\;{}_a\langle\,\alpha'\,S\,M\,|\,\alpha\,S\,M\,\rangle_b$$

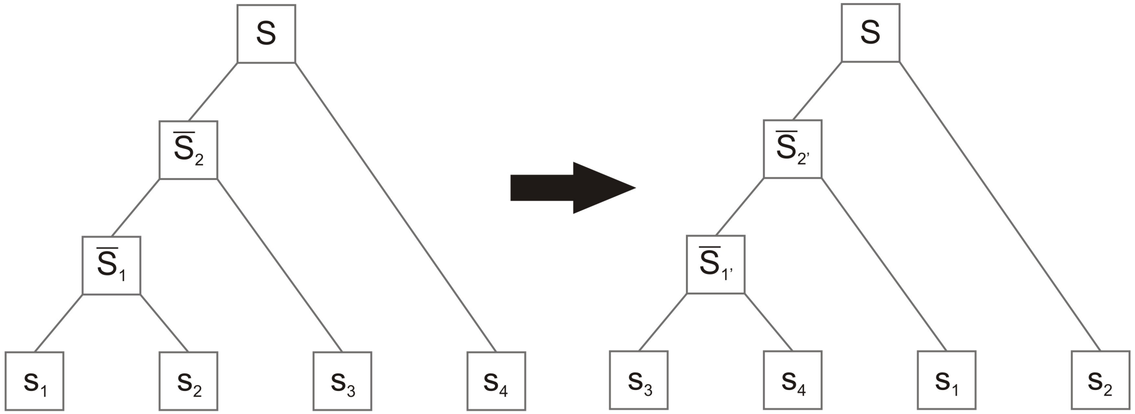
- Serious problem: application of $\underset{\sim}{G}(R)$, i.e. permutation of spins, leads to different coupling schemes: $a \Rightarrow b$;
- Solution: implementation of graph-theoretical results to evaluate recoupling coefficients ${}_a\langle\,\alpha'\,S\,M\,|\,\alpha\,S\,M\,\rangle_b$.

Point Group Symmetry III – example square



$$\left|\, s_1 s_2 \overline{S}_1 s_3 \overline{S}_2 s_4 S M \,\right\rangle \xrightarrow{\underset{\sim}{G}(3\,4\,1\,2)} \left|\, s_3 s_4 \overline{S}_{1'} s_1 \overline{S}_{2'} s_2 S M \,\right\rangle$$

Point Group Symmetry IV – binary trees



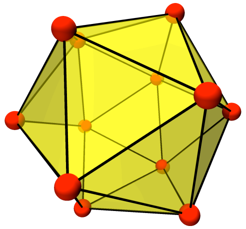
- Recoupling coefficient $\langle\, s_1 s_2 \overline{S}_1 s_3 \overline{S}_2 s_4 S M \mid s_3 s_4 \overline{S}_{1'} s_1 \overline{S}_{2'} s_2 S M \,\rangle$ can be evaluated by a graphical transformation of one binary tree into the other (1,2).

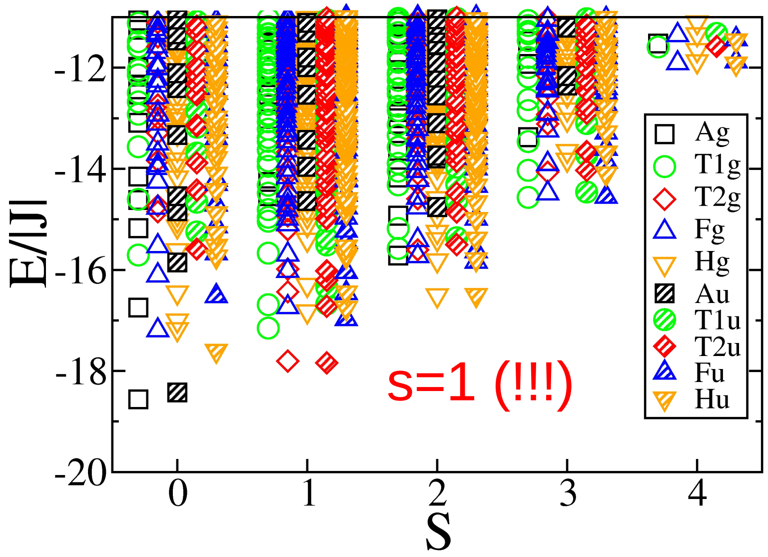
- Exchange and flop operations generate a recoupling formula consisting of square roots, Wigner-6J symbols, and sums over intermediate spins.

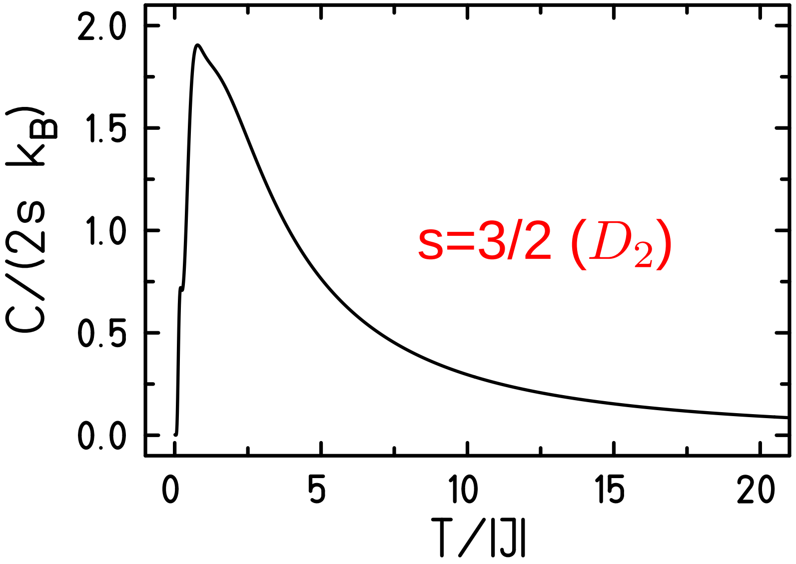
- Open question: optimal coupling for a given symmetry? (3)

(1) V. Fack, S. N. Pitre, and J. van der Jeugt, Comp. Phys. Comm. **86**, 105 (1995).
(2) V. Fack, S. N. Pitre, and J. van der Jeugt, Comp. Phys. Comm. **101**, 155 (1997).
(3) M. Geisler, Bachelor Thesis, Bielefeld University (2010).

Example: Icosahedron







Icosahedron, $s = 3/2$, Hilbert space dimension 16,777,216; symmetry I_h;
Evaluation of recoupling coefficients for $s = 3/2$ in I_h **practically impossible** (1).

(1) R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403-452 (2010).

World-leading, but . . .

This world-leading method was developed in Osnabrück, unfortunately . . .

World-leading, but . . .

. . . too late!

There are more powerful and easy to program methods.

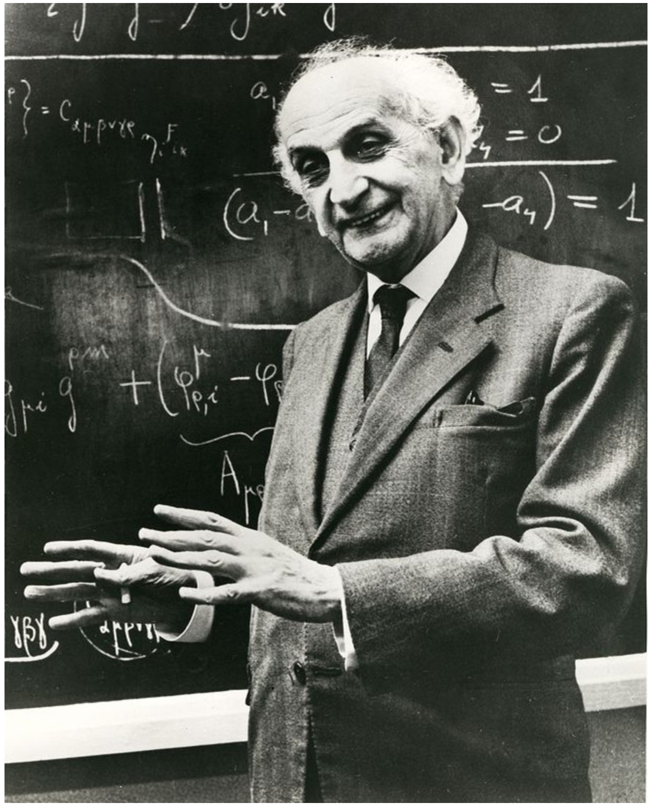
Nevertheless, matrix theory goes on . . .

. . . at the Hessische Landesbank!

Finite-temperature Lanczos Method

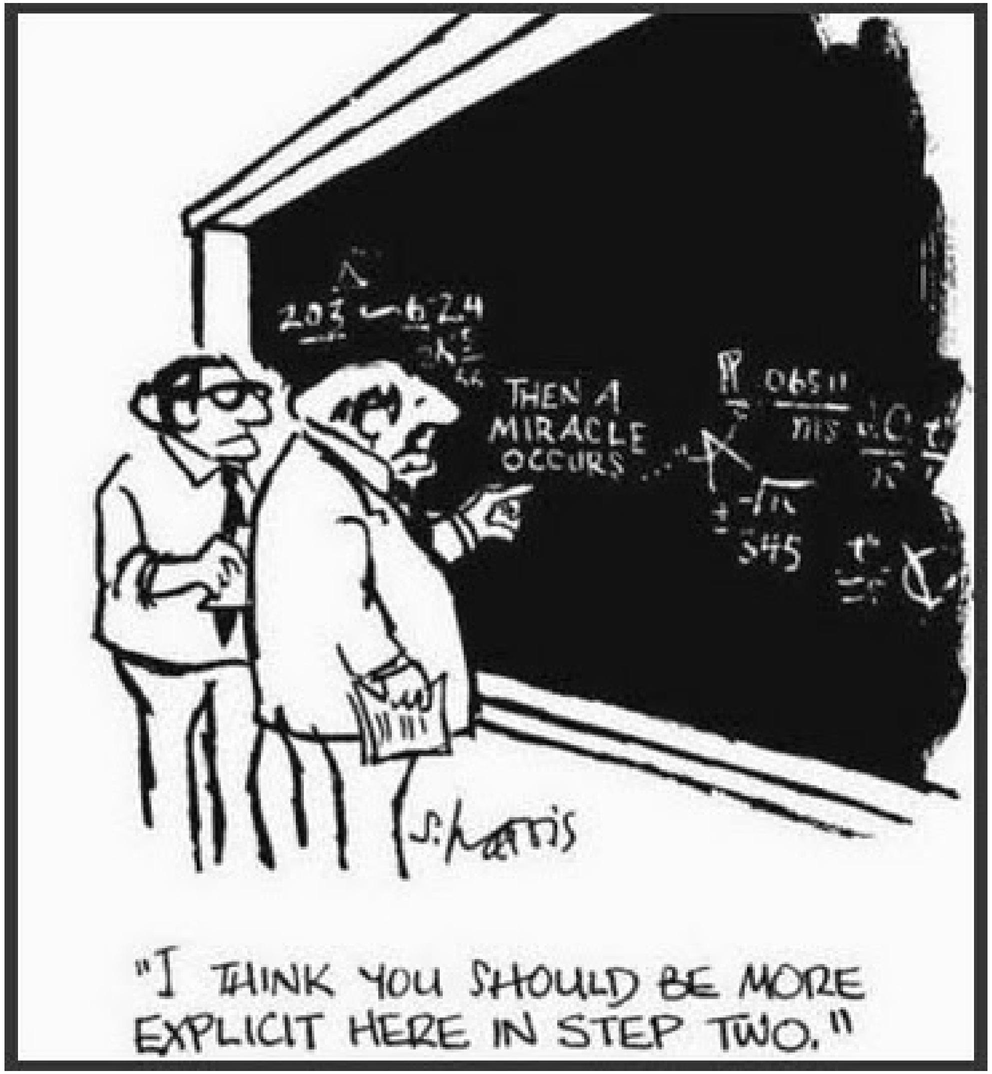
(Good for dimensions up to 10^{10}.)

Lanczos – a Krylov space method



- Idea: exact diagonalization in reduced basis sets.
- But which set to choose???
- Idea: generate the basis set with the operator you want to diagonalize: $\{\,|\,\phi\,\rangle, \underset{\sim}{H}\,|\,\phi\,\rangle, \underset{\sim}{H}^2\,|\,\phi\,\rangle, \underset{\sim}{H}^3\,|\,\phi\,\rangle, \dots\,\}$
- But which starting vector to choose???
- Idea: almost any will do!
- Cornelius Lanczos (Lánczos Kornél, 1893-1974)

(1) C. Lanczos, J. Res. Nat. Bur. Stand. **45**, 255 (1950).


THEN A MIRACLE OCCURS
S. Harris
"I THINK YOU SHOULD BE MORE EXPLICIT HERE IN STEP TWO."

Finite-temperature Lanczos Method I

$$Z(T,B) = \sum_{\nu} \langle\, \nu \,|\, \exp\left\{ -\beta \underset{\sim}{H} \right\} |\, \nu \,\rangle$$

$$\langle\, \nu \,|\, \exp\left\{ -\beta \underset{\sim}{H} \right\} |\, \nu \,\rangle \approx \sum_{n} \langle\, \nu \,|\, n(\nu) \,\rangle \exp\left\{ -\beta \epsilon_n \right\} \langle\, n(\nu) \,|\, \nu \,\rangle \qquad \text{(Step 2)}$$

$$Z(T,B) \approx \frac{\dim(\mathcal{H})}{R} \sum_{\nu=1}^{R} \sum_{n=1}^{N_L} \exp\left\{ -\beta \epsilon_n \right\} |\langle\, n(\nu) \,|\, \nu \,\rangle|^2$$

- $|\, n(\nu) \,\rangle$ n-th Lanczos eigenvector starting from $|\, \nu \,\rangle$
- Partition function replaced by a small sum: $R = 1 \dots 10, N_L \approx 100$.

J. Jaklic and P. Prelovsek, Phys. Rev. B **49**, 5065 (1994).

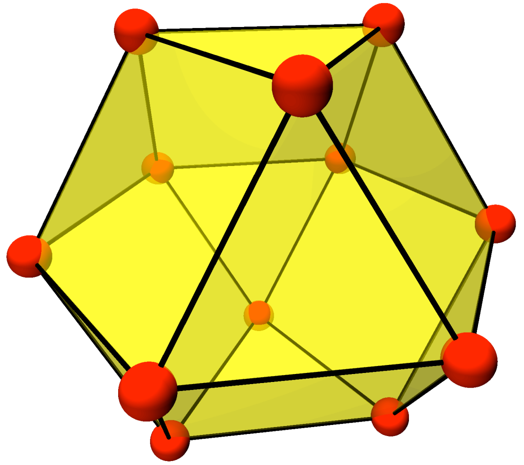
Finite-temperature Lanczos Method II

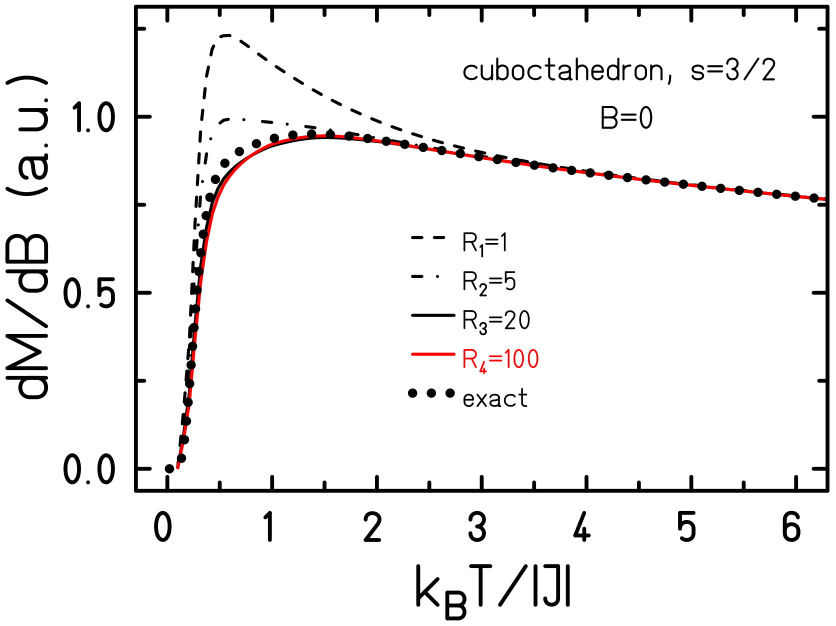
$$Z(T,B) \approx \sum_{\Gamma} \frac{\text{dim}(\mathcal{H}(\Gamma))}{R_\Gamma} \sum_{\nu=1}^{R_\Gamma} \sum_{n=1}^{N_L} \exp\left\{-\beta\epsilon_n\right\} |\langle\, n(\nu,\Gamma)\,|\,\nu,\Gamma\,\rangle|^2$$

- Approximation better if symmetries taken into account.
- Γ denotes the used irreducible representations.

J. Schnack and O. Wendland, Eur. Phys. J. B **78** (2010) 535-541

How good is finite-temperature Lanczos?

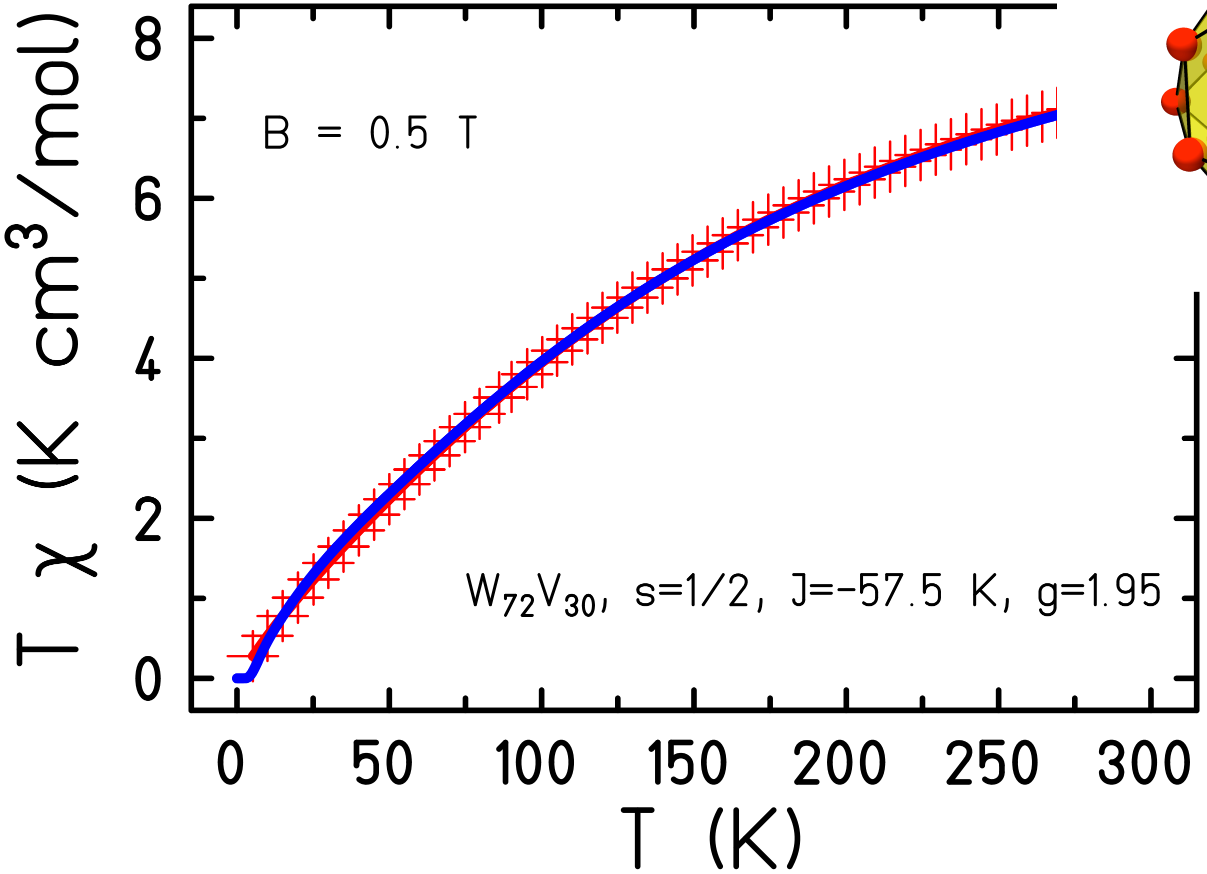


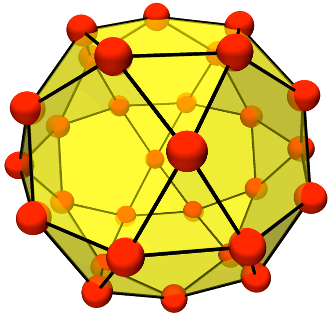


- Works very well: compare frustrated cuboctahedron.
- $N = 12, s = 3/2$: Considered $< 100,000$ states instead of 16,777,216.

Exact results: R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403-452 (2010).
FTLM: J. Schnack and O. Wendland, Eur. Phys. J. B **78**, 535-541 (2010).

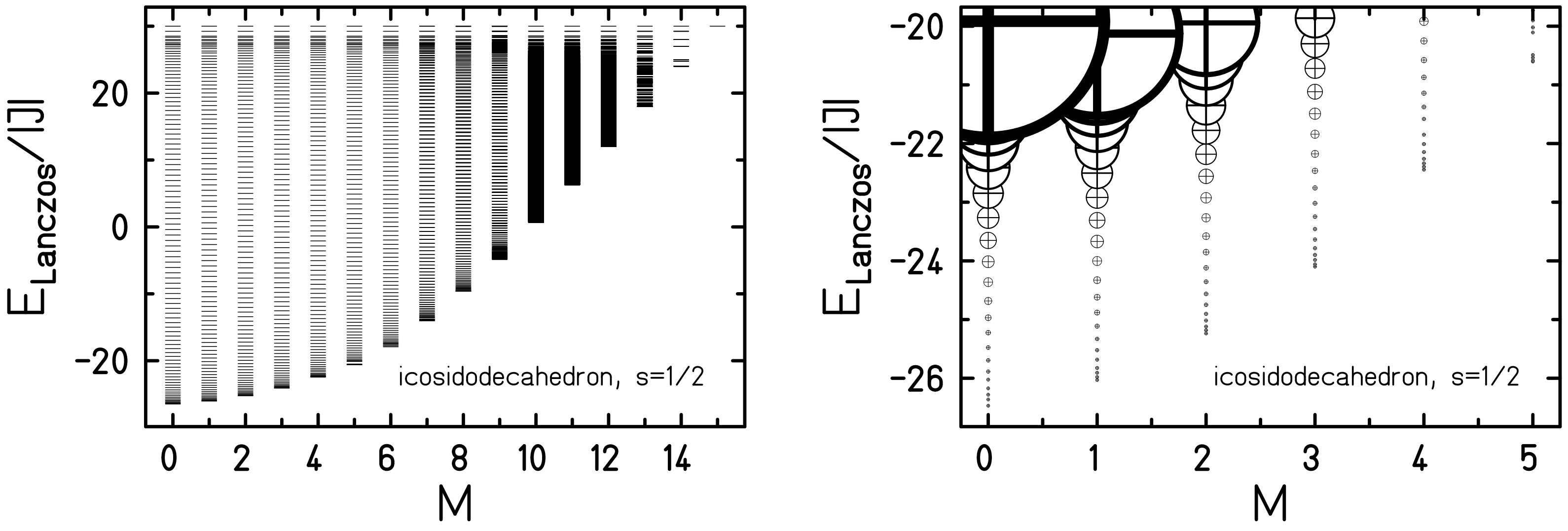
Icosidodecahedron $s = 1/2$





Exp. data: A. M. Todea, A. Merca, H. Bögge, T. Glaser, L. Engelhardt, R. Prozorov, M. Luban, A. Müller, Chem. Commun., 3351 (2009).

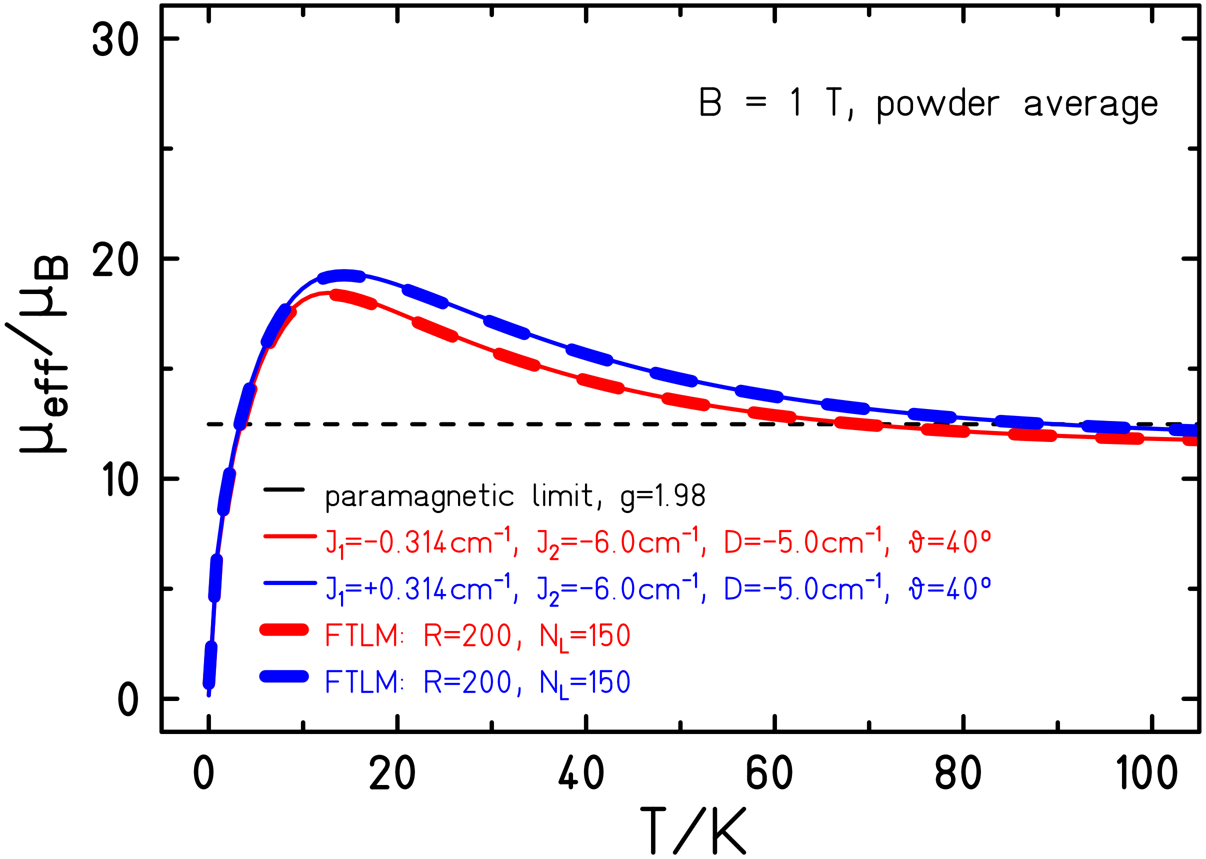
Icosidodecahedron $s = 1/2$

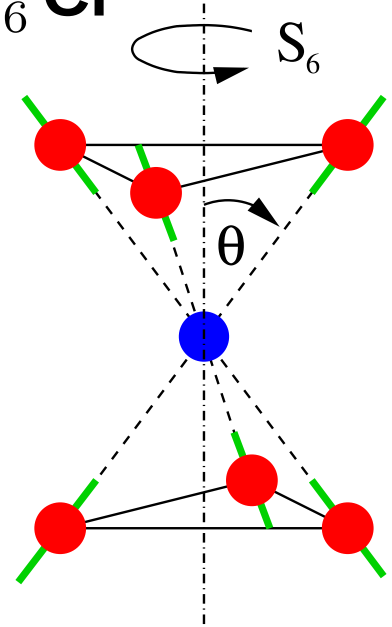


- The true spectrum will be much denser. This is miraculously compensated for by the weights.

$$Z(T,B) \approx \frac{\text{dim}(\mathcal{H})}{R} \sum_{\nu=1}^{R} \sum_{n=1}^{N_L} \exp\left\{-\beta\epsilon_n\right\} |\langle\, n(\nu,\Gamma) \,|\, \nu,\Gamma\,\rangle|^2$$

Glaser-type molecules: $Mn_6^{III}Cr^{III}$





$s = 2$, $s = 3/2$

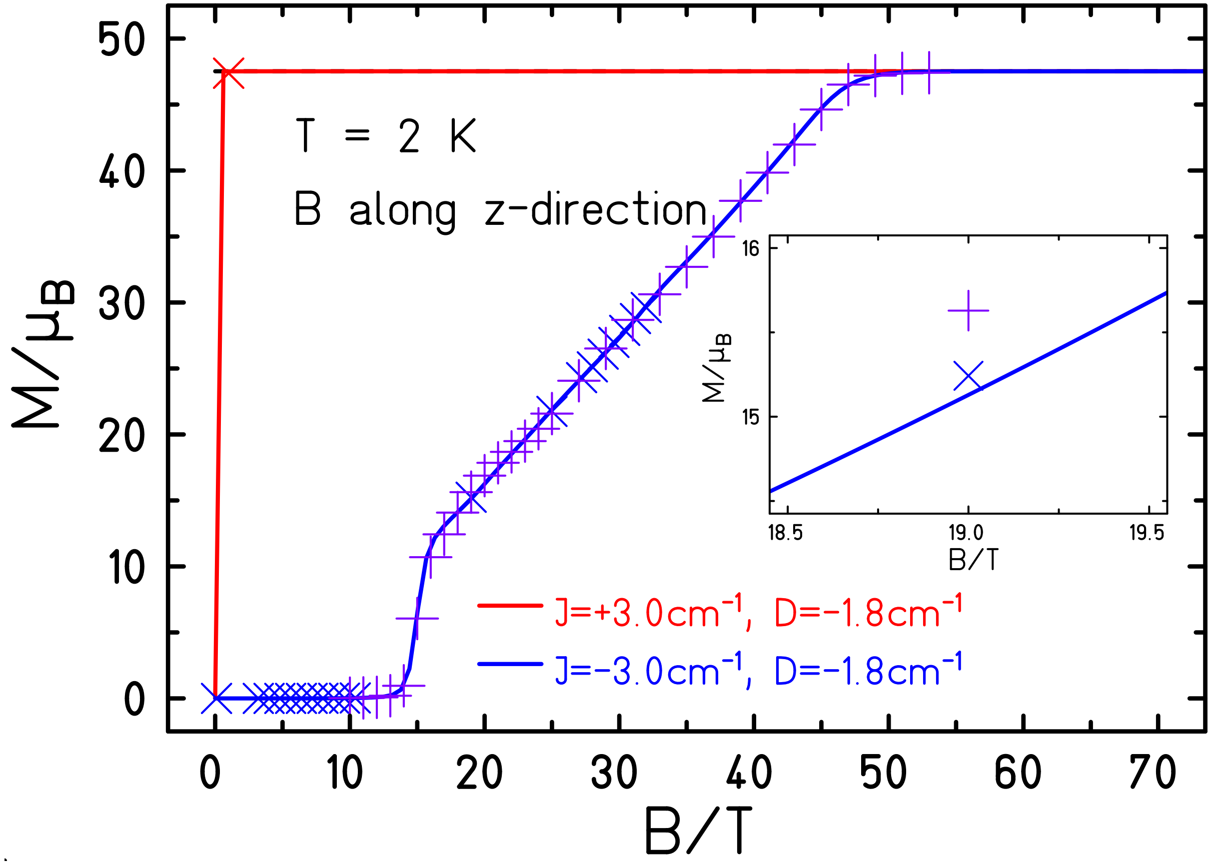
dim$(\mathcal{H}) = 62,500$

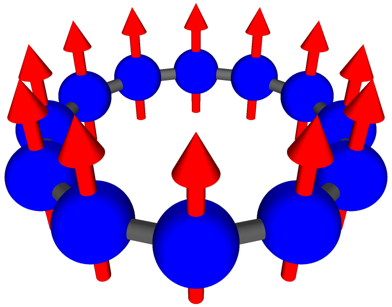
non-collinear easy axes

Hours compared to days, notebook compared to supercomputer!

O. Hanebaum, J. Schnack, Eur. Phys. J. B **87**, 194 (2014)

A fictitious $\mathrm{Mn}^{\mathrm{III}}_{12}$ – M_z vs B_z





$s = 2$

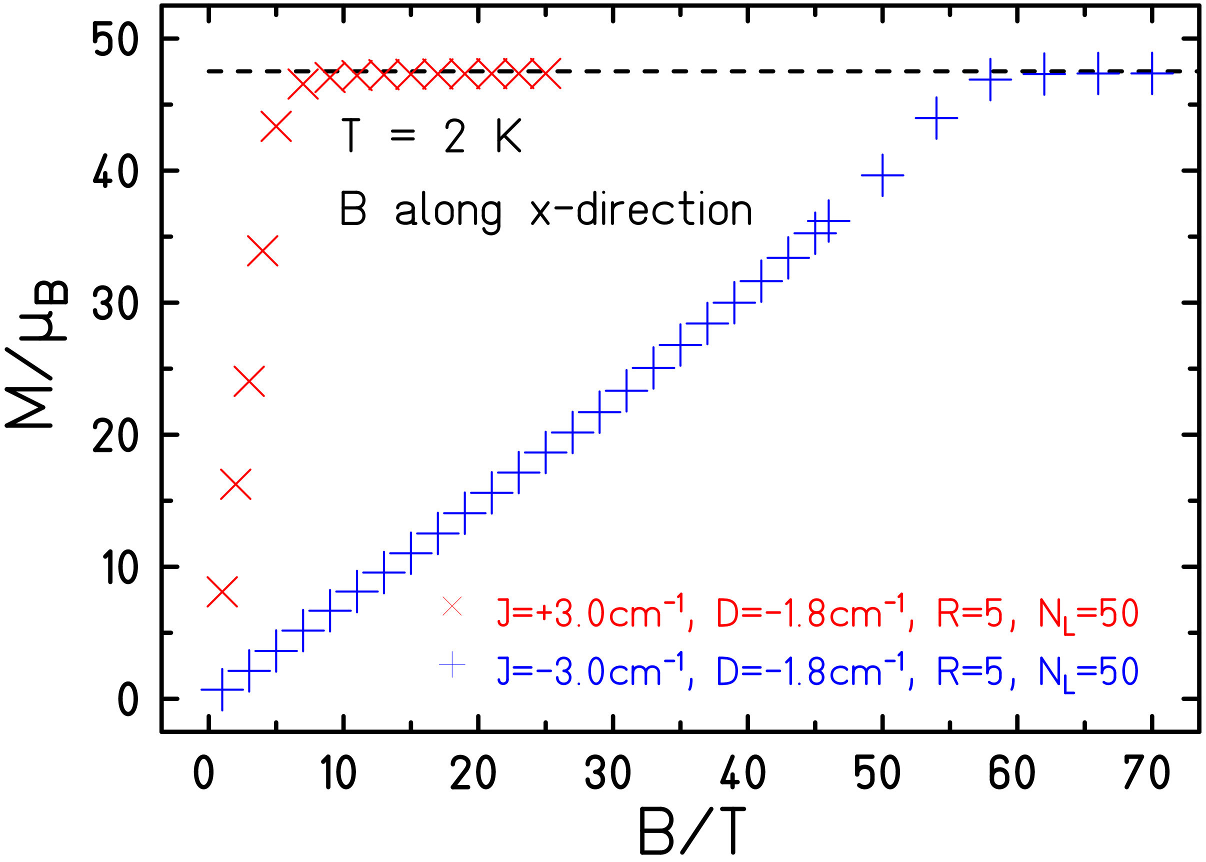
dim$(\mathcal{H}) = 244,140,625$

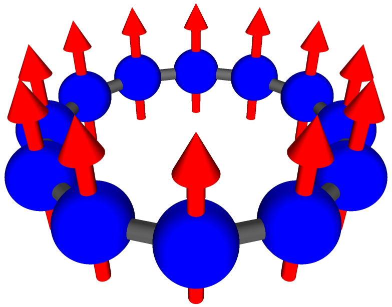
collinear easy axes

A few days compared to *impossible*!

O. Hanebaum, J. Schnack, Eur. Phys. J. B **87**, 194 (2014)

A fictitious $\mathrm{Mn}_{12}^{\mathrm{III}}$ – M_x vs B_x



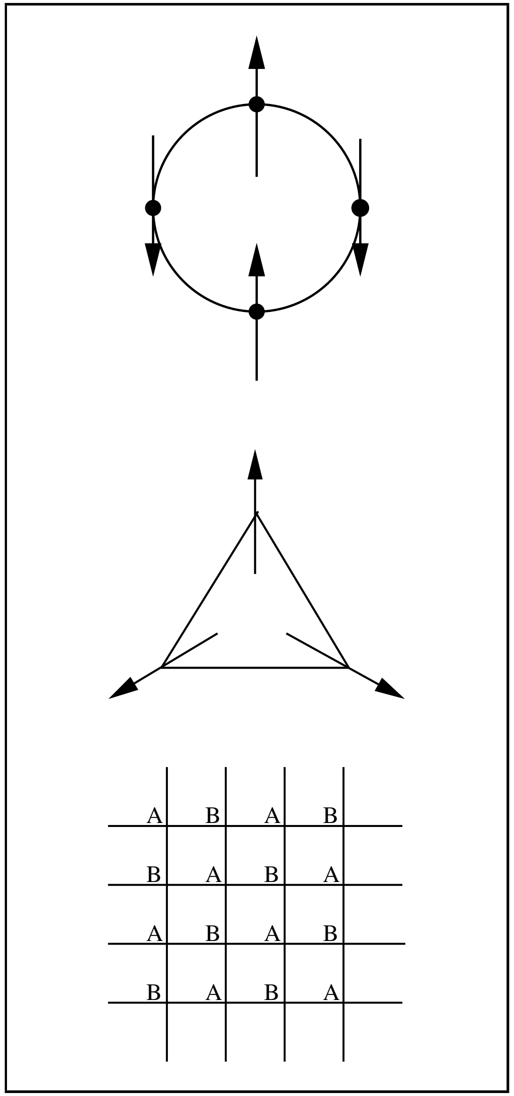


No other method can deliver these curves!

O. Hanebaum, J. Schnack, Eur. Phys. J. B **87**, 194 (2014)

Frustration effects

Definition of frustration

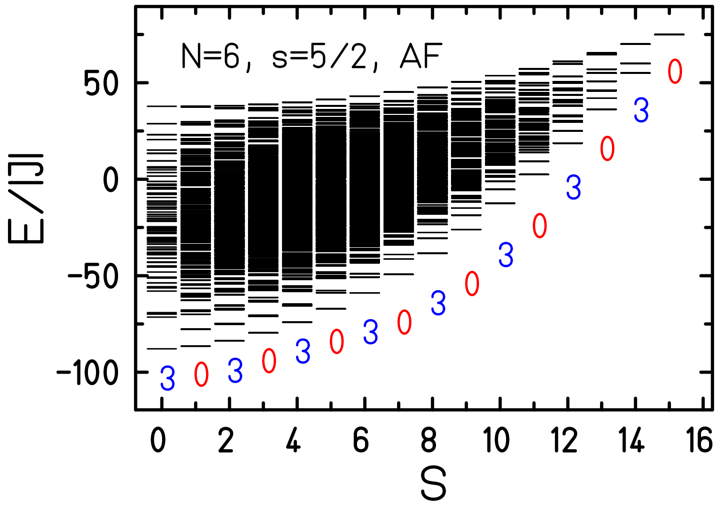


- Simple: A spin system is frustrated if in the ground state of the corresponding classical spin system not all interactions can be minimized simultaneously.

- Advanced: A non-bipartite antiferromagnet is frustrated. A bipartite spin system can be decomposed into two sublattices A and B such that for all exchange couplings:
$J(x_A, y_B) \leq g^2 \; , J(x_A, y_A) \geq g^2 \; , J(x_B, y_B) \geq g^2$, cmp. (1,2).

(1) E.H. Lieb, T.D. Schultz, and D.C. Mattis, Ann. Phys. (N.Y.) **16**, 407 (1961)
(2) E.H. Lieb and D.C. Mattis, J. Math. Phys. **3**, 749 (1962)

Marshall-Peierls sign rule for even rings



- Expanding the ground state in $\mathcal{H}(M)$ in the product basis yields a sign rule for the coefficients

$$|\,\Psi_0\,\rangle = \sum_{\vec{m}} c(\vec{m})\;|\,\vec{m}\,\rangle \qquad \text{with } \sum_{i=1}^{N} m_i = M$$

$$c(\vec{m}) = (-1)^{\left(\frac{Ns}{2} - \sum_{i=1}^{N/2} m_{2i}\right)} a(\vec{m})$$

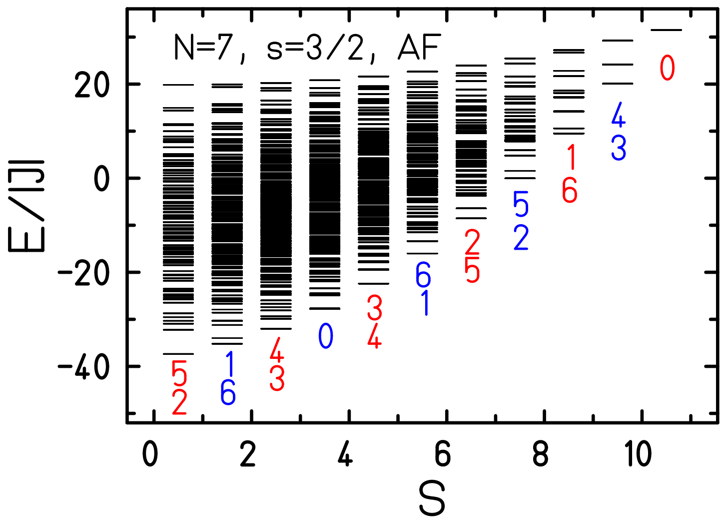
All $a(\mathbf{m})$ are non-zero, real, and of equal sign.

- Yields eigenvalues for the shift operator $\underset{\sim}{T}$:

$$\exp\left\{-i\frac{2\pi k}{N}\right\} \text{ with } k \equiv a\,\frac{N}{2} \mod N\ , \qquad a = Ns - M$$

(1) W. Marshall, Proc. Royal. Soc. A (London) **232**, 48 (1955)

Numerical findings for odd rings



- For odd N and half integer s, i.e. $s = 1/2, 3/2, 5/2, \dots$ we find that (1)
  - the ground state has total spin $S = 1/2$;
  - the ground state energy is **fourfold** degenerate.
- Reason: In addition to the (trivial) degeneracy due to $M = \pm 1/2$, a degeneracy with respect to k appears (2):
  $k = \lfloor \frac{N+1}{4} \rfloor$ and $k = N - \lfloor \frac{N+1}{4} \rfloor$
- For the first excited state similar rules could be numerically established (3).

---

(1) K. Bärwinkel, H.-J. Schmidt, J. Schnack, J. Magn. Magn. Mater. **220**, 227 (2000)
(2) $\lfloor \cdot \rfloor$ largest integer, smaller or equal
(3) J. Schnack, Phys. Rev. B **62**, 14855 (2000)

k-rule for odd rings

- An extended k-rule can be inferred from our numerical investigations which yields the k quantum number for relative ground states of subspaces $\mathcal{H}(M)$ for even as well as odd spin rings, i.e. for all rings (1)

$$k \equiv \pm a \left\lceil \frac{N}{2} \right\rceil \quad \mathrm{mod}\ N\ , \qquad a = Ns - M$$

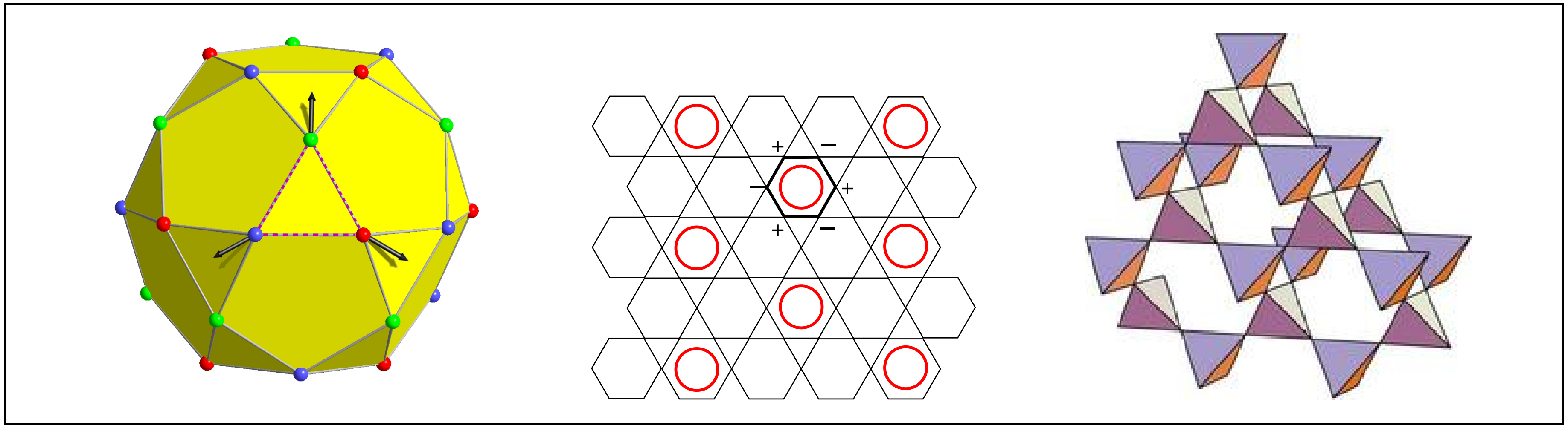
k is independent of s for a given N and a. The degeneracy is minimal ($N \neq 3$).

		a									
N	s	0	1	2	3	4	5	6	7	8	9
8	1/2	0	4	$8 \equiv 0$	$12 \equiv 4$	$16 \equiv 0$	-	-	-	-	-
9	1/2	0	$5 \equiv 4$	$10 \equiv 1$	$15 \equiv 3$	$20 \equiv 2$	-	-	-	-	-
9	1	0	$5 \equiv 4$	$10 \equiv 1$	$15 \equiv 3$	$20 \equiv 2$	$25 \equiv 2$	$30 \equiv 3$	$35 \equiv 1$	$40 \equiv 4$	$45 \equiv 0$

No general, but partial proof yet.

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

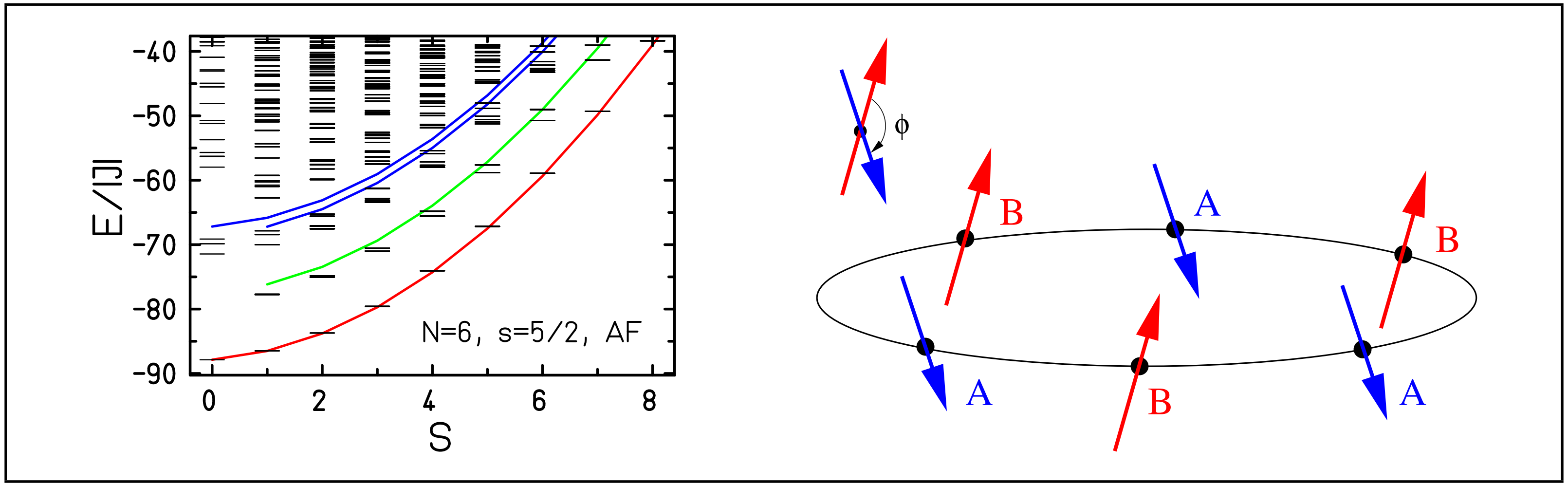
Fe$_{30}$ and friends
Corner sharing triangles and tetrahedra



- Several frustrated antiferromagnets show an unusual magnetization behavior, e.g. plateaus and jumps.

- Example systems: icosidodecahedron, kagome lattice, pyrochlore lattice.

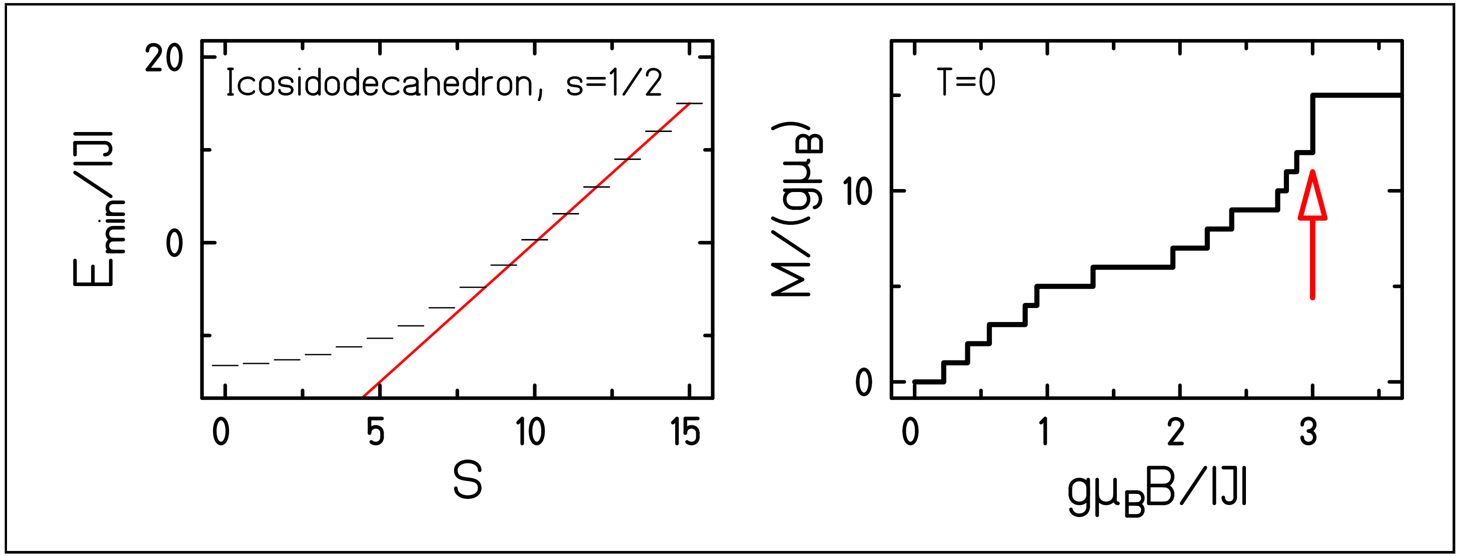
Rotational bands in non-frustrated antiferromagnets



- Often minimal energies $E_{min}(S)$ form a rotational band: Landé interval rule (1);
- For bipartite systems (2,3): $\underset{\sim}{H}^{\text{eff}} = -2\,J_{\text{eff}}\,\underset{\sim}{\vec{S}}_A \cdot \underset{\sim}{\vec{S}}_B$;
- Lowest band – rotation of Néel vector, second band – spin wave excitations (4).

(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)
(4) P.W. Anderson, Phys. Rev. B **86**, 694 (1952), O. Waldmann *et al.*, Phys. Rev. Lett. **91**, 237202 (2003).

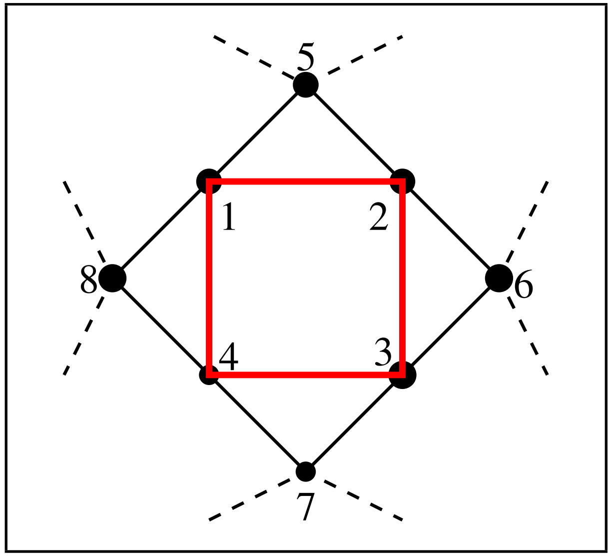
Giant magnetization jumps in frustrated antiferromagnets I
the icosidodecahedron



- Close look: $E_{\text{min}}(S)$ 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

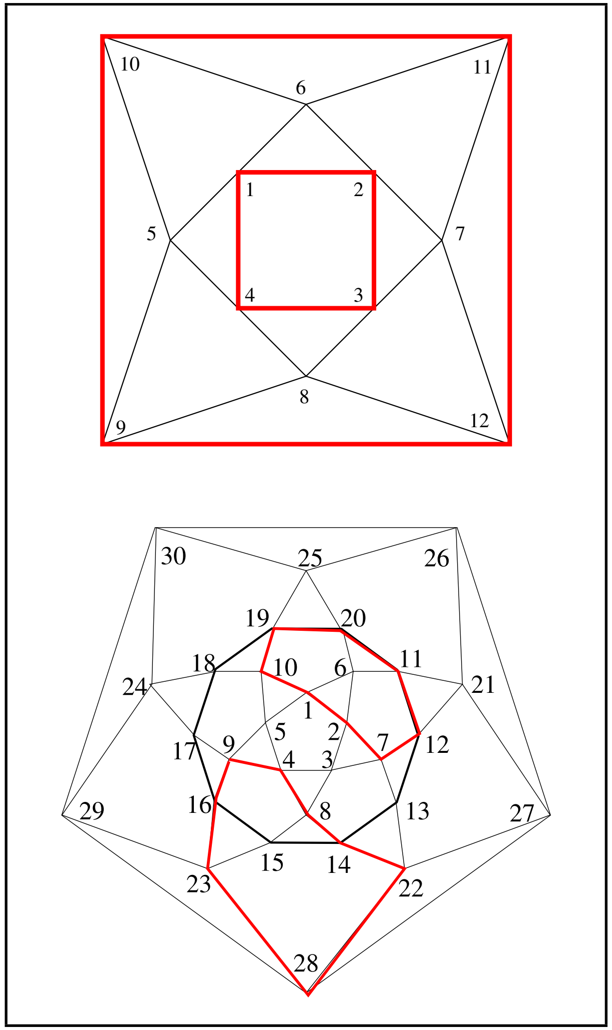


- $|\,\text{localized magnon}\,\rangle = \frac{1}{2}(\,|\,1\,\rangle - |\,2\,\rangle + |\,3\,\rangle - |\,4\,\rangle)$
- $|\,1\,\rangle = \underset{\sim}{s}^{-}(1)\,|\uparrow\uparrow\uparrow\;\dots\rangle$ etc.
- $\underset{\sim}{H}\,|\,\text{localized magnon}\,\rangle \propto |\,\text{localized magnon}\,\rangle$
- Localized magnon is state of lowest energy (1,2).

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

(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)

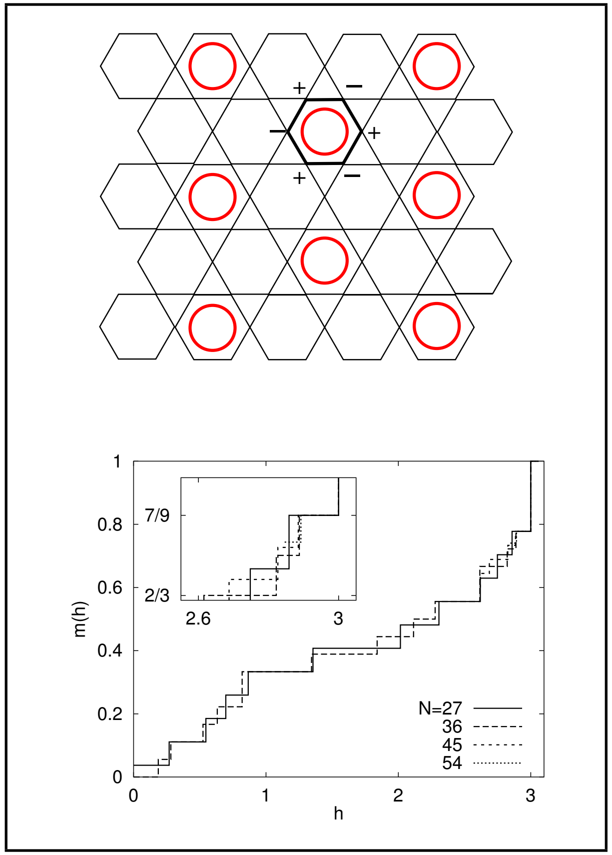
Giant magnetization jumps in frustrated antiferromagnets III



- Non-interacting one-magnon states can be placed on various molecules, e. g. 2 on the cuboctahedron and 3 on the icosidodecahedron (3rd delocalized);
- 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 $\Rightarrow$ $(T=0)$ magnetization jump;
- A rare example of analytically known many-body states!

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

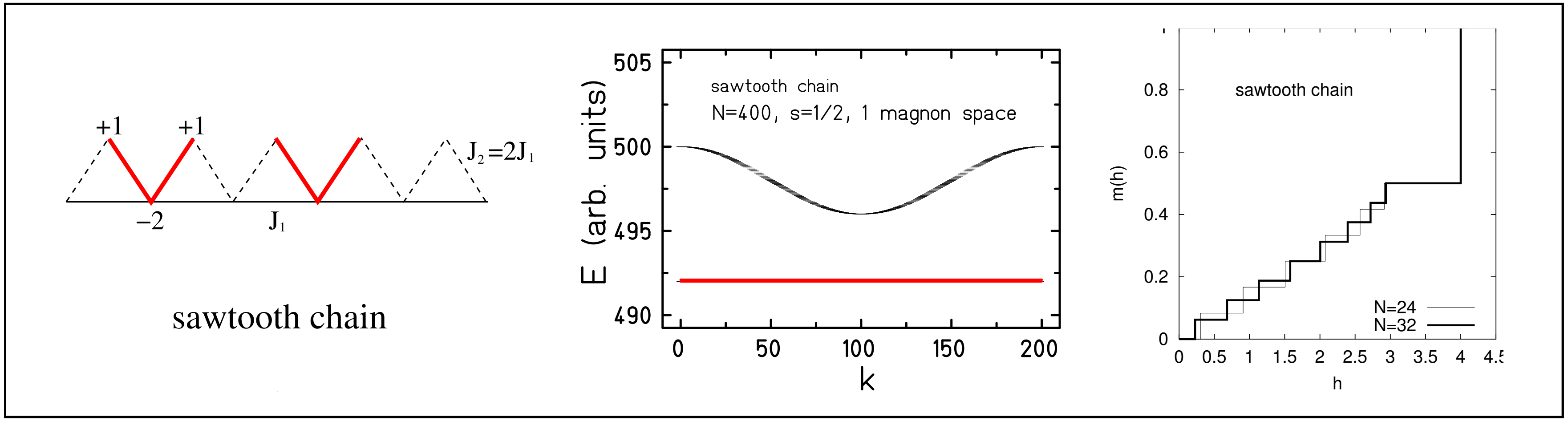
Giant magnetization jumps in frustrated antiferromagnets III
Kagome Lattice



- Non-interacting one-magnon states can be placed on various lattices, e. g. kagome or pyrochlore;
- Each state of n independent magnons is the ground state in the Hilbert subspace with $M = Ns - n$; Kagome: max. number of indep. magnons is N/9;
- Linear dependence of E_{min} on M $\Rightarrow$ $(T=0)$ magnetization jump;
- Jump is a macroscopic quantum effect!
- A rare example of analytically known many-body states!

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)

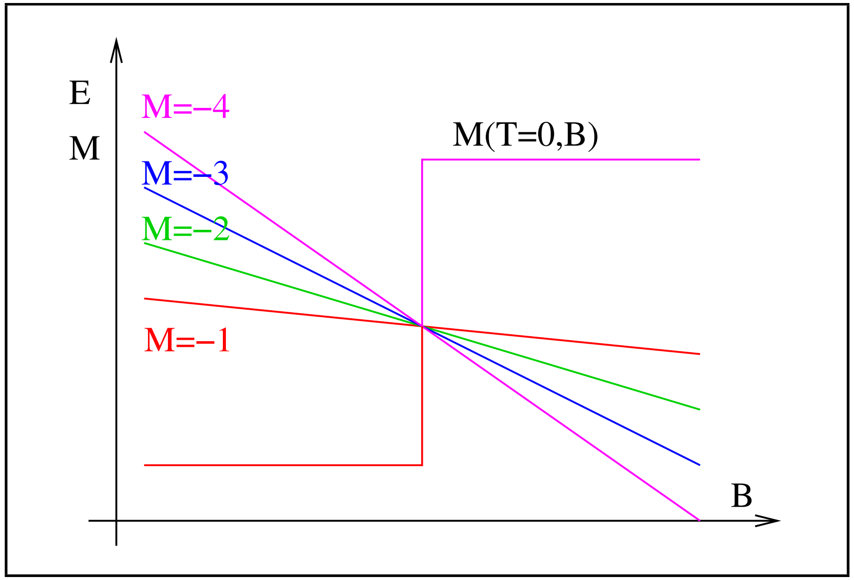
Condensed matter physics point of view: Flat band



- Flat band of minimal energy in one-magnon space; localized magnons can be built from delocalized states in the flat band.
- Entropy can be evaluated using hard-object models (1); universal low-temperature behavior.
- Same behavior for Hubbard model; flat band ferromagnetism (Tasaki & Mielke), jump of N with μ (2).

(1) H.-J. Schmidt, J. Richter, R. Moessner, J. Phys. A: Math. Gen. **39**, 10673 (2006)
(2) A. Honecker, J. Richter, Condens. Matter Phys. **8**, 813 (2005)

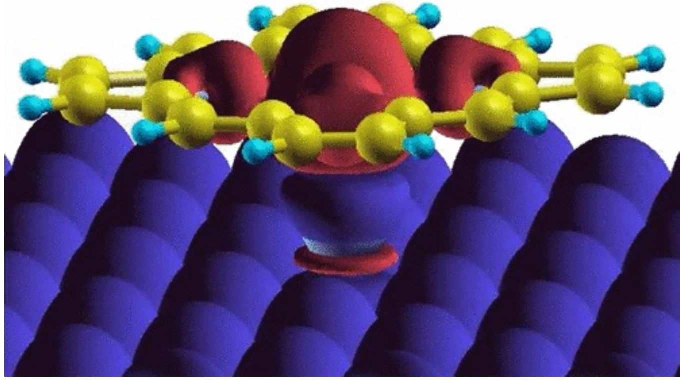
Magnetocaloric effect I
Giant jumps to saturation

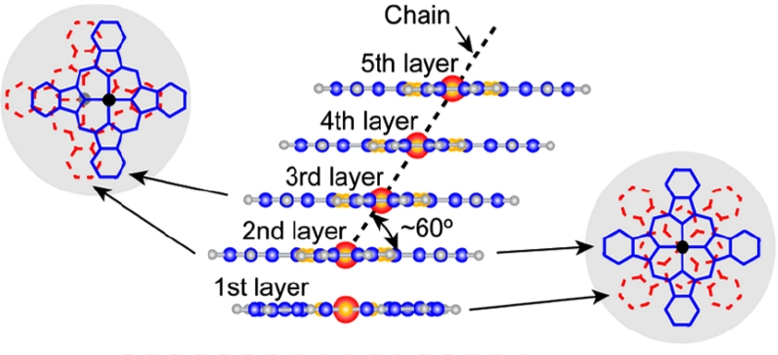


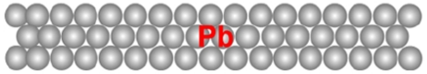
- Many Zeeman levels cross at one and the same magnetic field.
- You know this for a giant spin at $B=0$.
- High degeneracy of ground state levels $\Rightarrow$ large residual entropy at $T=0$.
- $$\left(\frac{\partial T}{\partial B}\right)_S = -\frac{T}{C}\left(\frac{\partial S}{\partial B}\right)_T$$

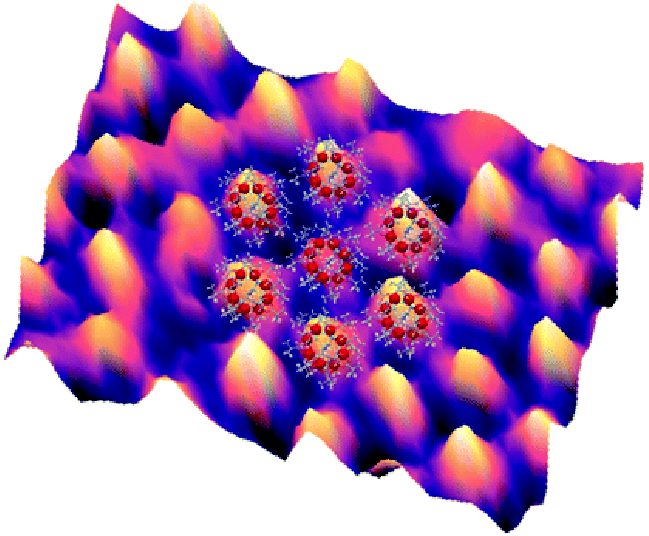
M. Evangelisti *et al.*, Appl. Phys. Lett. **87**, 072504 (2005).
J. Schulenburg, A. Honecker, J. Schnack, J. Richter, H.-J. Schmidt, Phys. Rev. Lett. **88**, 167207 (2002)
M. E. Zhitomirsky, Phys. Rev. B **67**, 104421 (2003).
M. E. Zhitomirsky and A. Honecker, J. Stat. Mech.: Theor. Exp. **2004**, P07012 (2004).

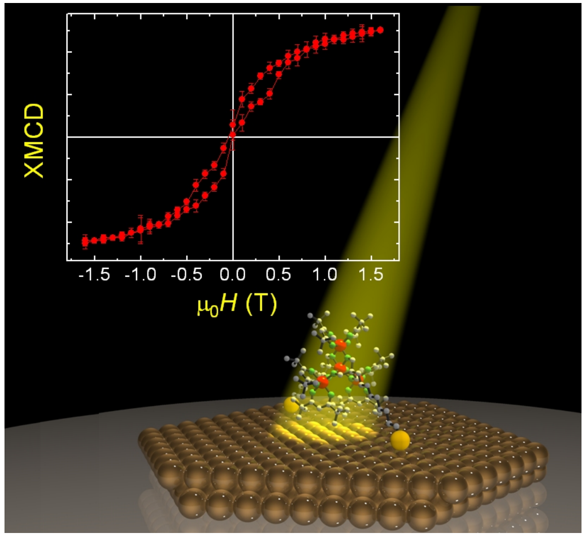
You want to deposite a molecule





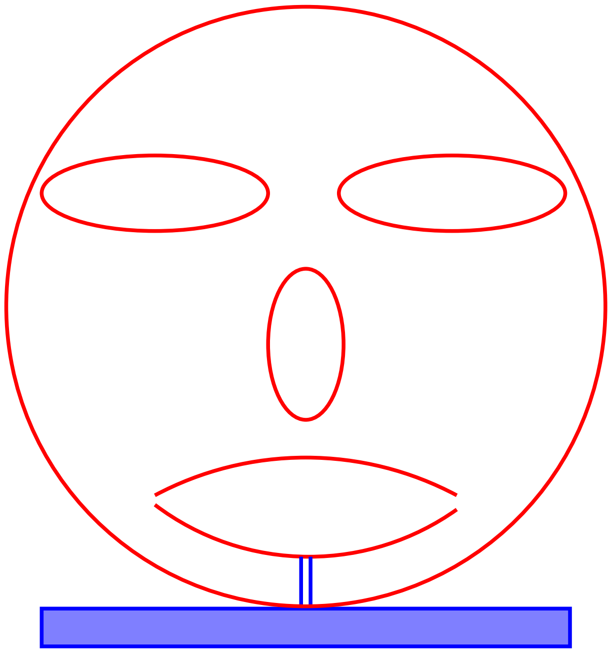






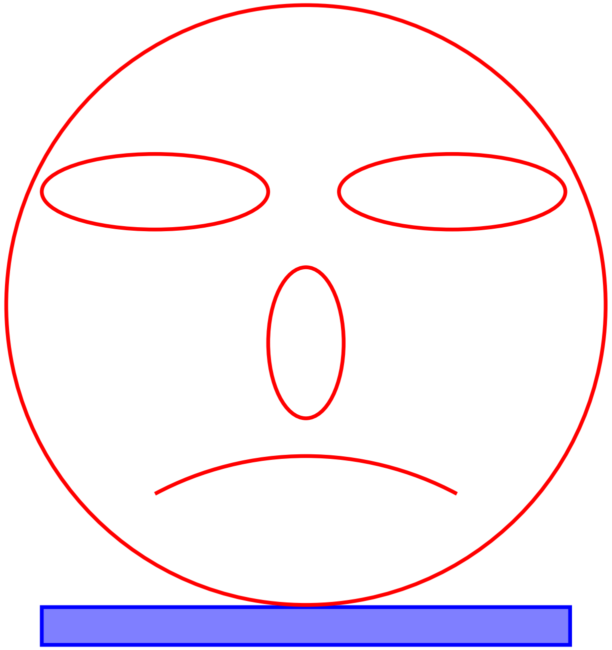
M. Bernien *et al.*, Phys. Rev. Lett. **102**, 047202 (2009); A. Ghirri*et al.*, ACS Nano, **5**, 7090-7099 (2011); X. Chen *et al.*, Phys. Rev. Lett. **101**, 197208 (2008); M. Mannini *et al.*, Nature Materials **8**, 194 - 197 (2009).

From a bloody physicist’s perspective . . .



Molecule with nice properties deposited on non-magnetic metal substrate;
Exchange coupled to metal spins;
Kondo screening may . . .

Properties may change drastically

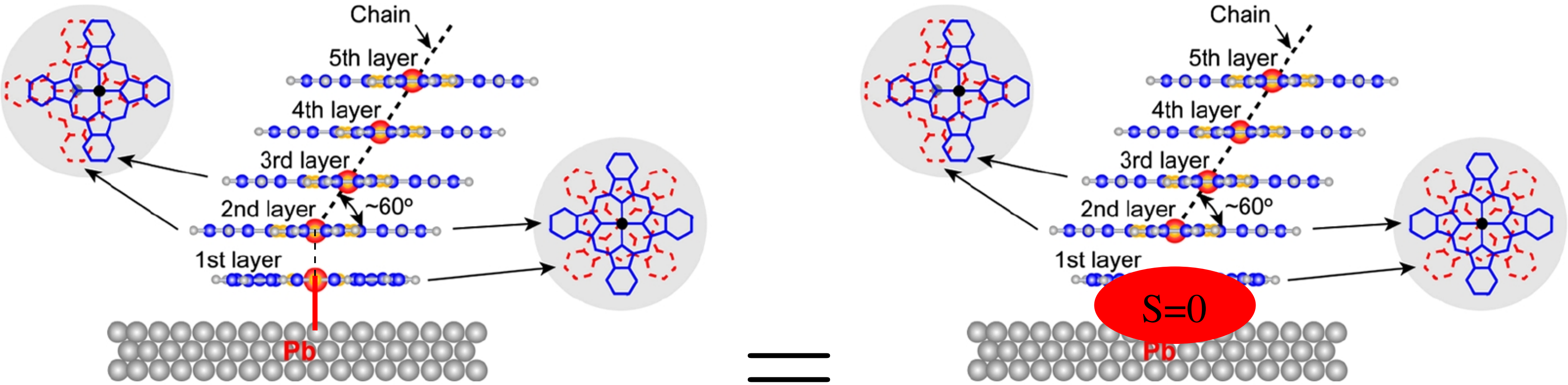


Kondo screening may improve or worsen the magnetic properties;

How does the exchange coupling to the metal influence the magnetic properties?

How to calculate such things?

Physical example (ICMM 2010)



Stack of deposited Cobalt phthalocyanine (CoPc) molecules;
Co^{2+} with spin $s = 1/2$.

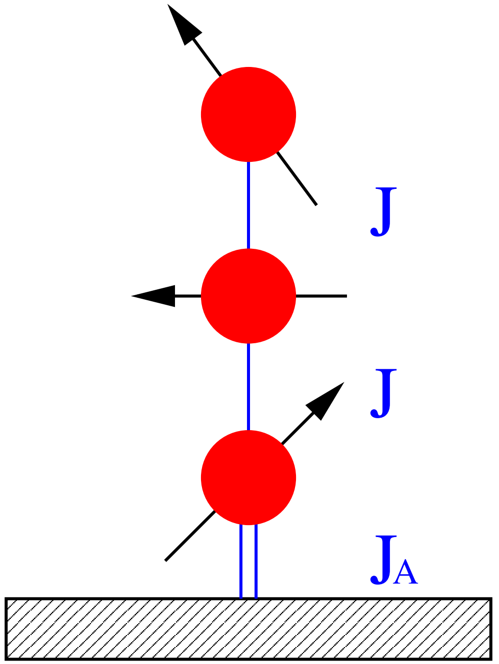
Under which circumstances is the picture of total screening correct?

X. Chen *et al.*, Phys. Rev. Lett. **101**, 197208 (2008).

Numerical Renormalization Group calculations

(Good for deposited molecules.)

NRG – minimal model (already an approximation!)



- $\underset{\sim}{H} = \underset{\sim}{H}_{\text{electrons}} + \underset{\sim}{H}_{\text{coupling}} + \underset{\sim}{H}_{\text{impurity}}$

  $\underset{\sim}{H}_{\text{electrons}} = \sum_{i\neq j,\,\sigma} t_{ij}\, \underset{\sim}{d}^{\dagger}_{i\sigma} \underset{\sim}{d}_{j\sigma} + g_e \mu_B B \underset{\sim}{S}^{z}$

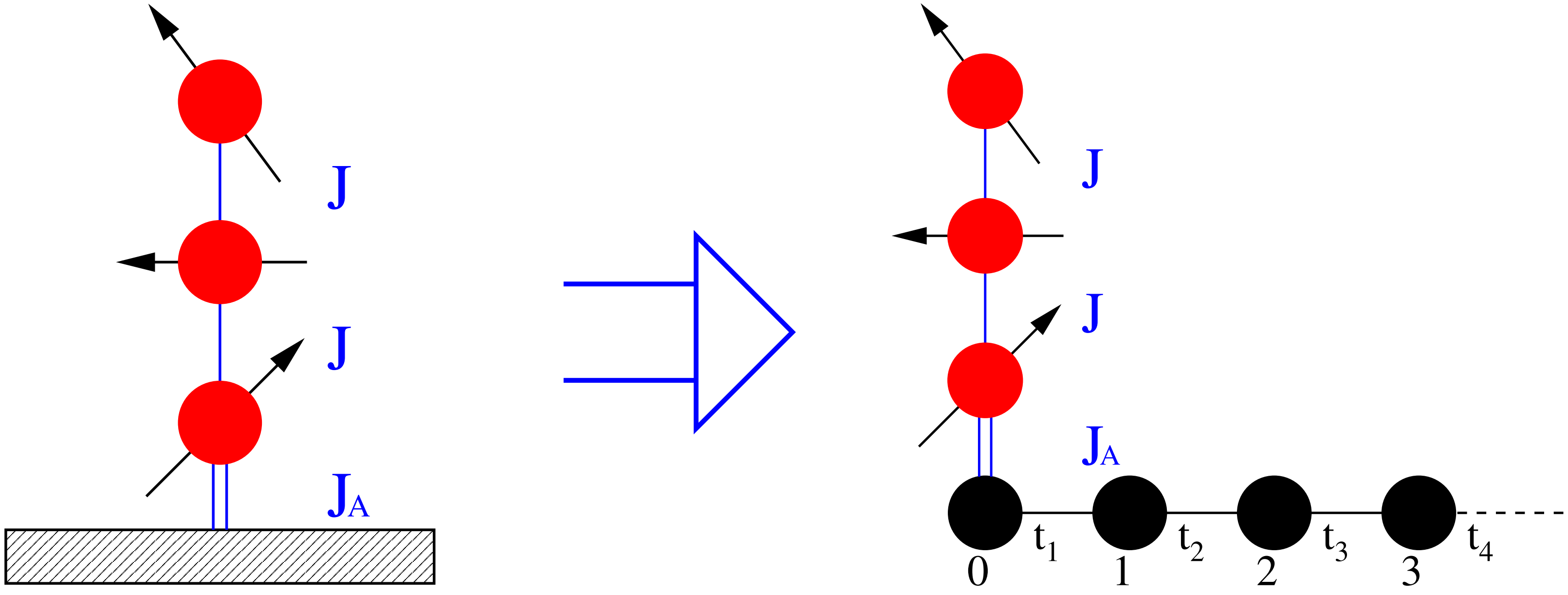
  $\underset{\sim}{H}_{\text{coupling}} = -2J_A \underset{\sim}{\boldsymbol{S}} \cdot \underset{\sim}{\boldsymbol{s}}_0$, $\underset{\sim}{\boldsymbol{s}}_0$ – spin density at contact

- $\underset{\sim}{H}_{\text{impurity}} =$ Hamiltonian of your molecule!

- NRG $\equiv$ construction of a small (!) effective model in order to evaluate properties of the deposited cluster, the impurity (3).

(1) K. G. Wilson, Rev. Mod. Phys. **47**, 773 (1975)
(2) M. Höck, J. Schnack, Phys. Rev. B **87**, 184408 (2013)
(3) *Impurity* is a technical term in this context and not an insult to chemists.

NRG in a cartoon



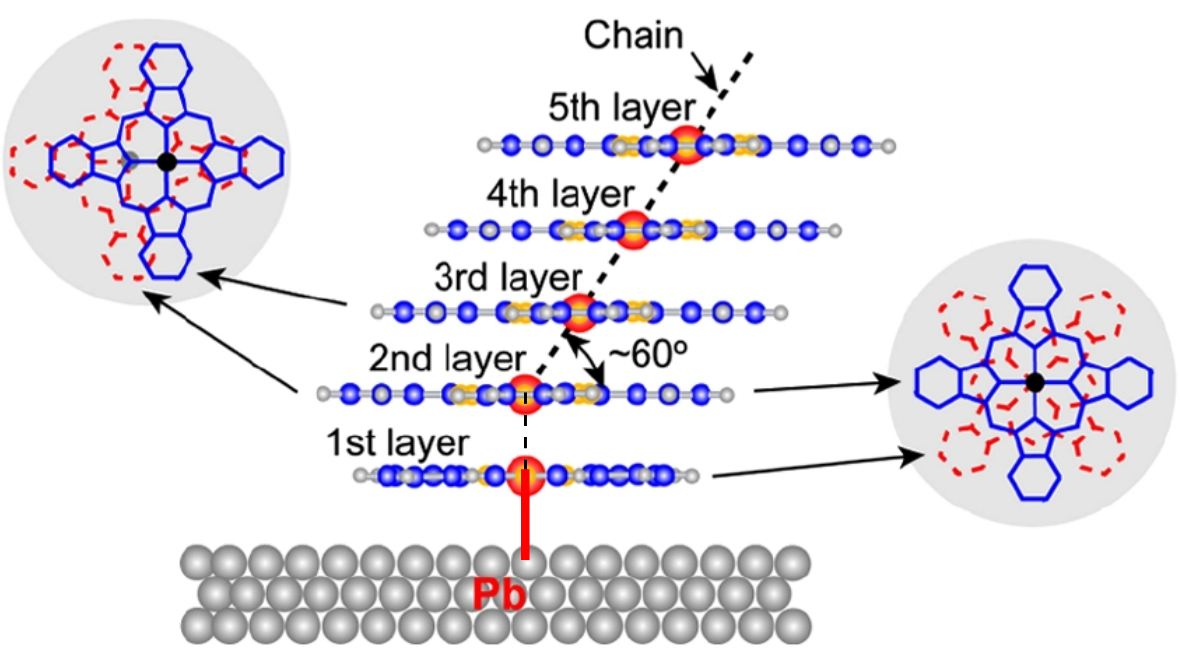
Metallic surface is replaced by semi-infinite Hubbard chain;

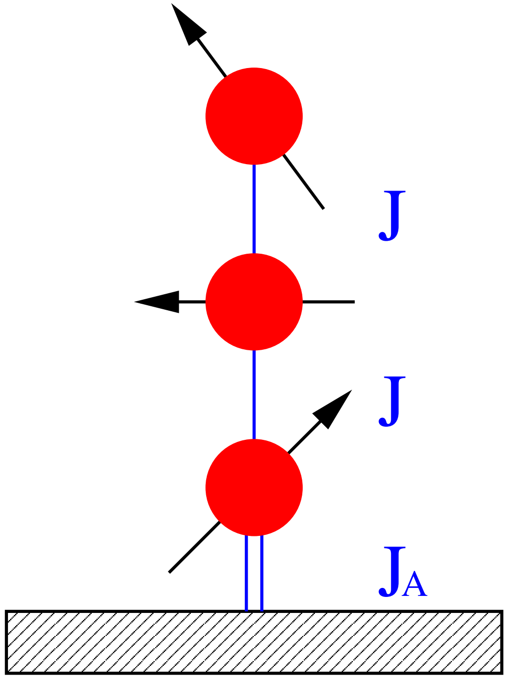
Parameters of the chain: hopping matrix elements and on-site energies;

Stepwise enlargement of the chain ($t_1 > t_2 > t_3 \ldots$);

Truncation of basis set when matrices grow too big.

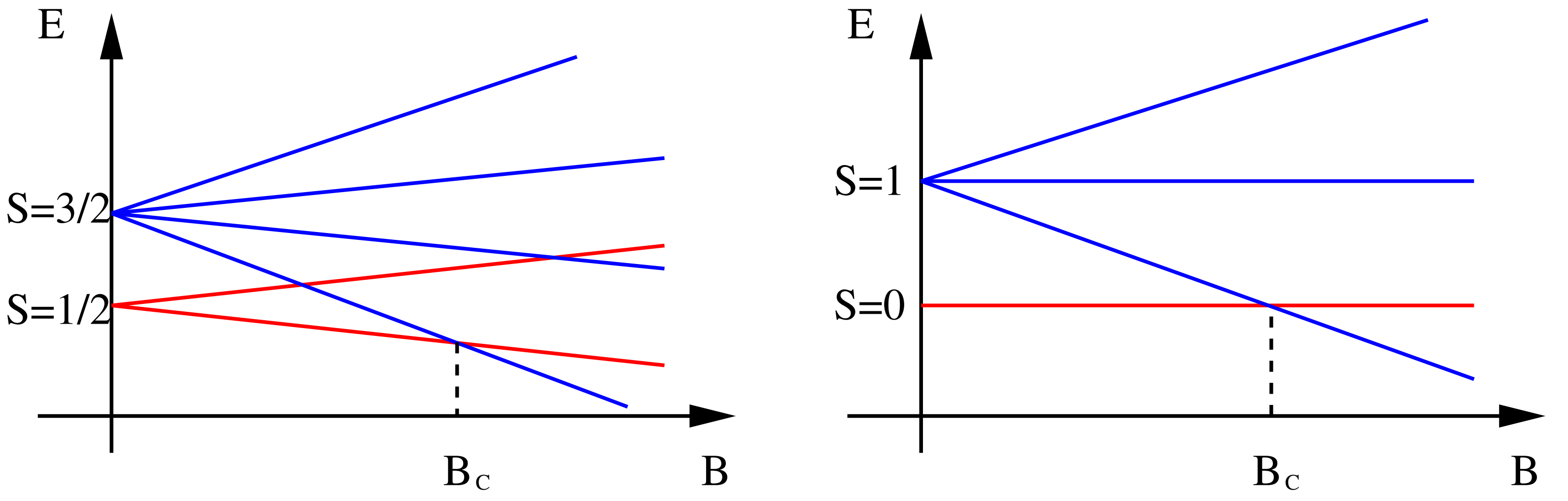
Once more: deposited chain





X. Chen *et al.*, Phys. Rev. Lett. **101**, 197208 (2008).

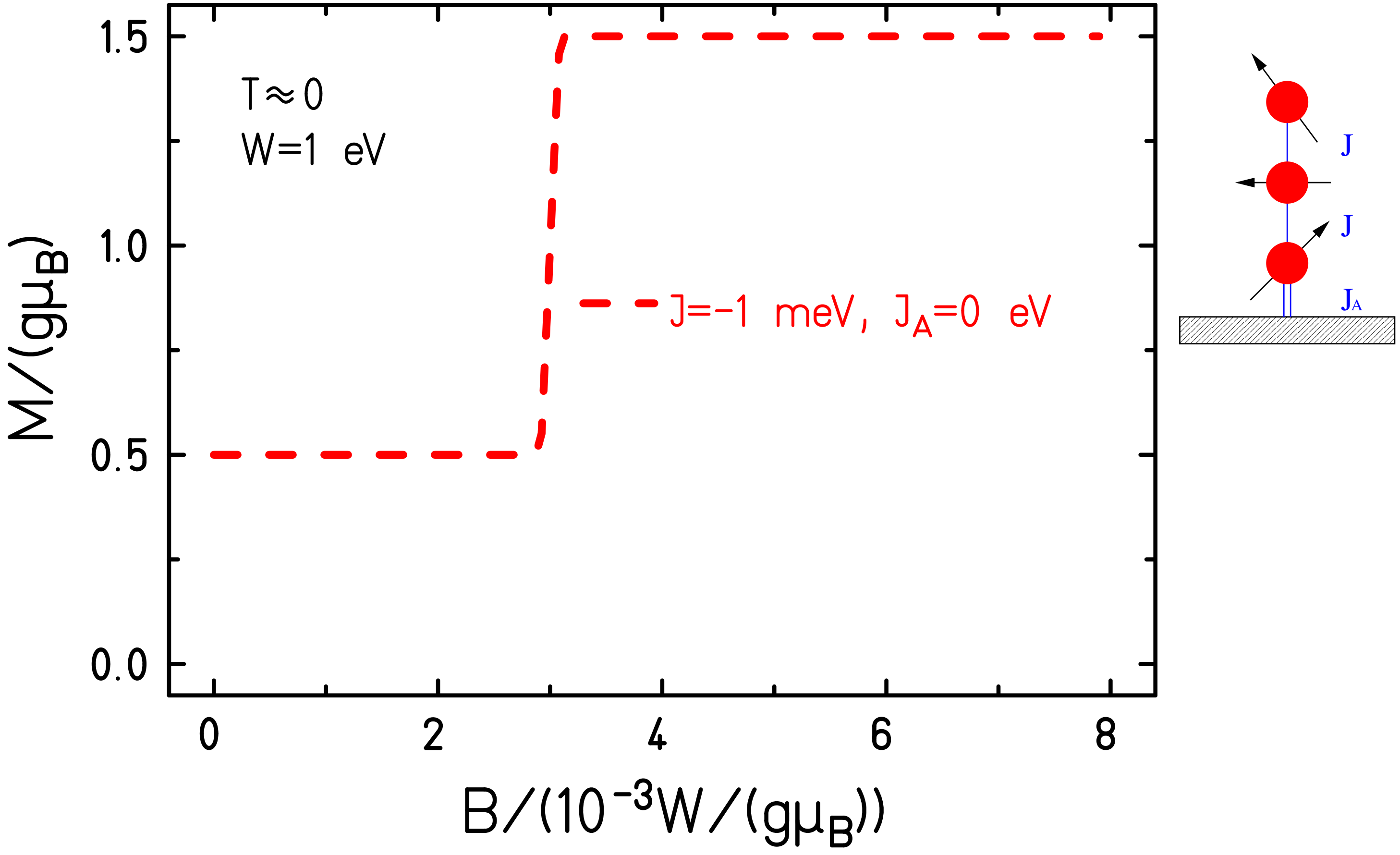
Energy levels of limiting cases for deposited trimer



- energy levels of a trimer
- energy levels of a dimer

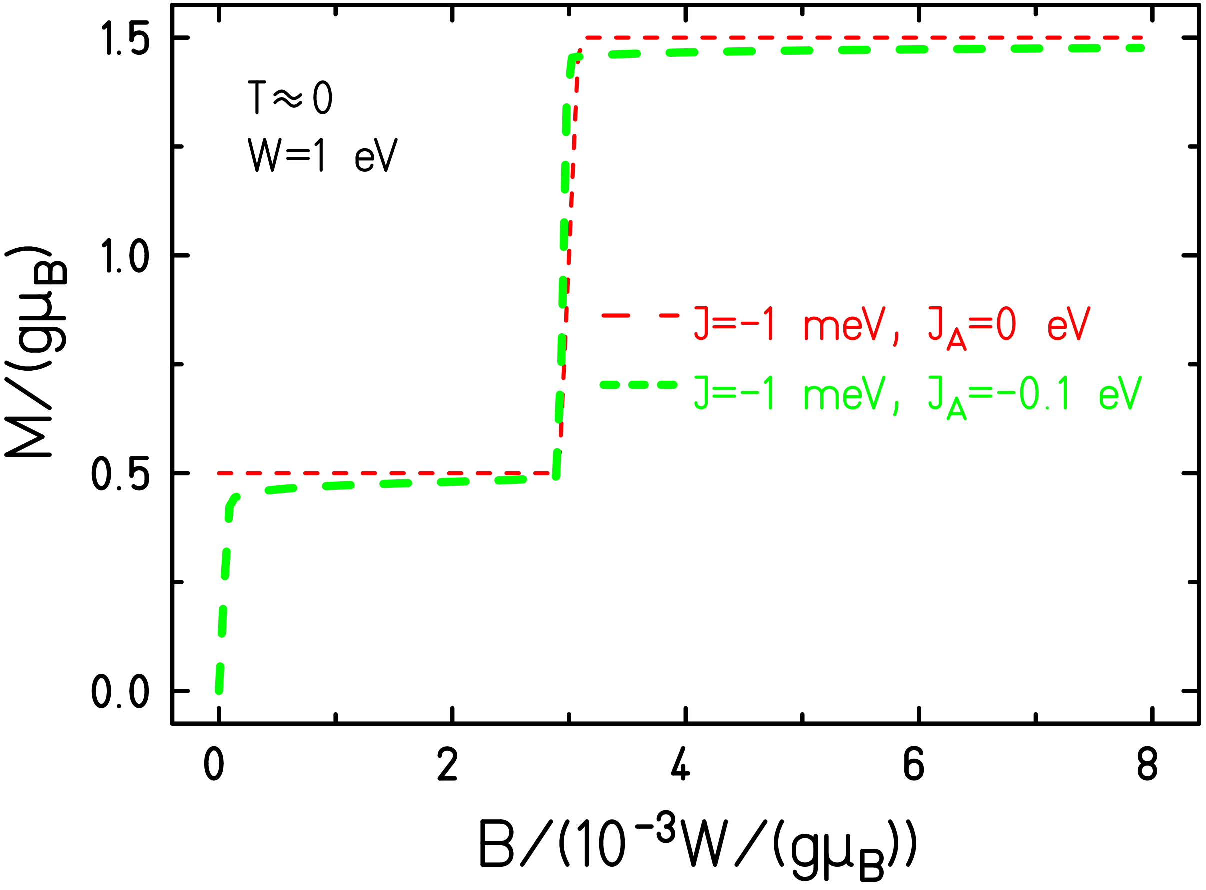
Magnetization curves different; could be seen in XMCD.
NRG calculates observables also between limiting cases
and can thus tell under which circumstances a limiting case applies.

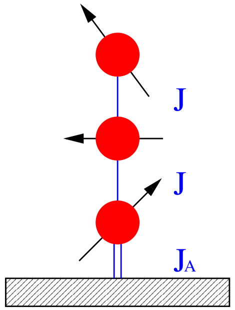
Increasing coupling to the substrate



H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

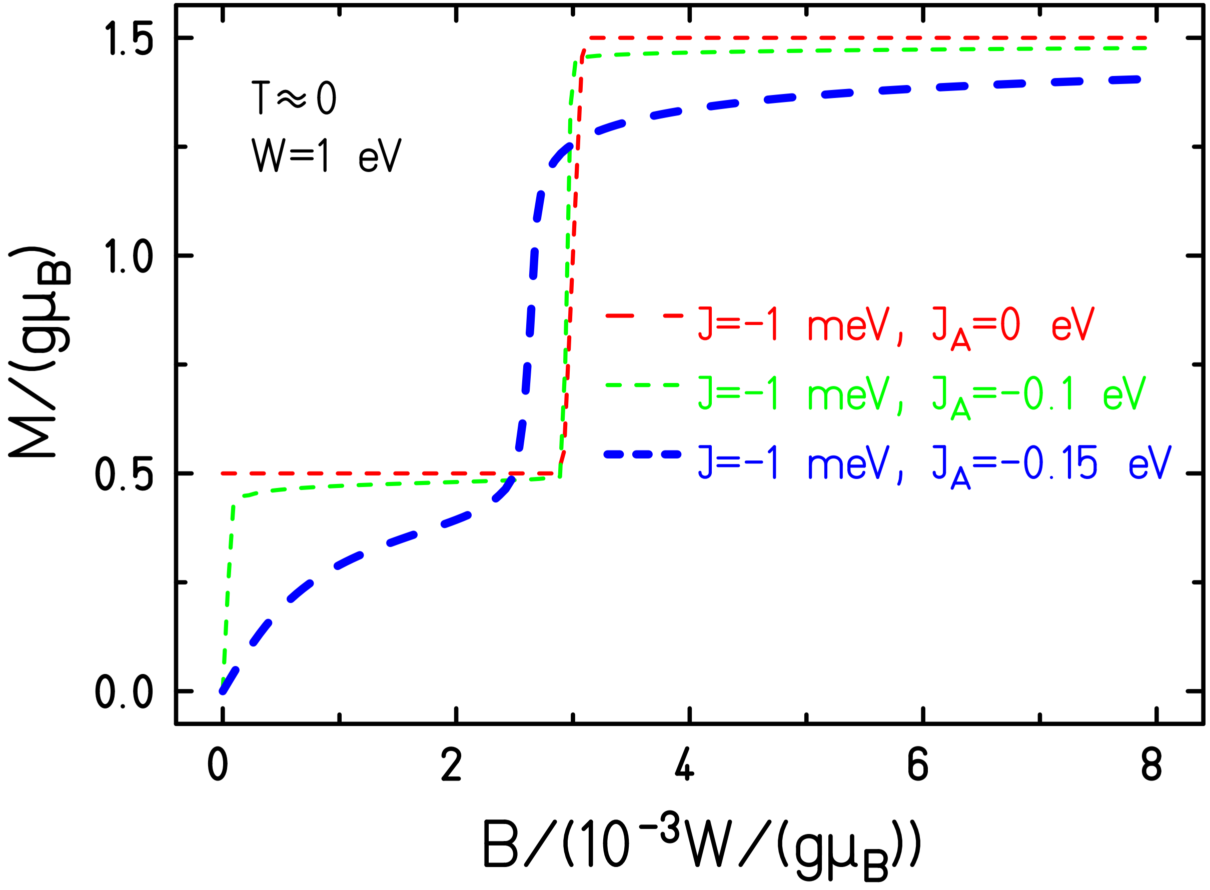
Increasing coupling to the substrate

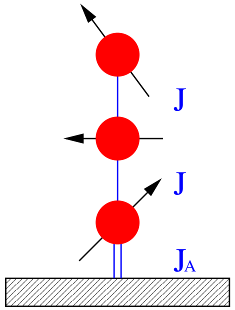




H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

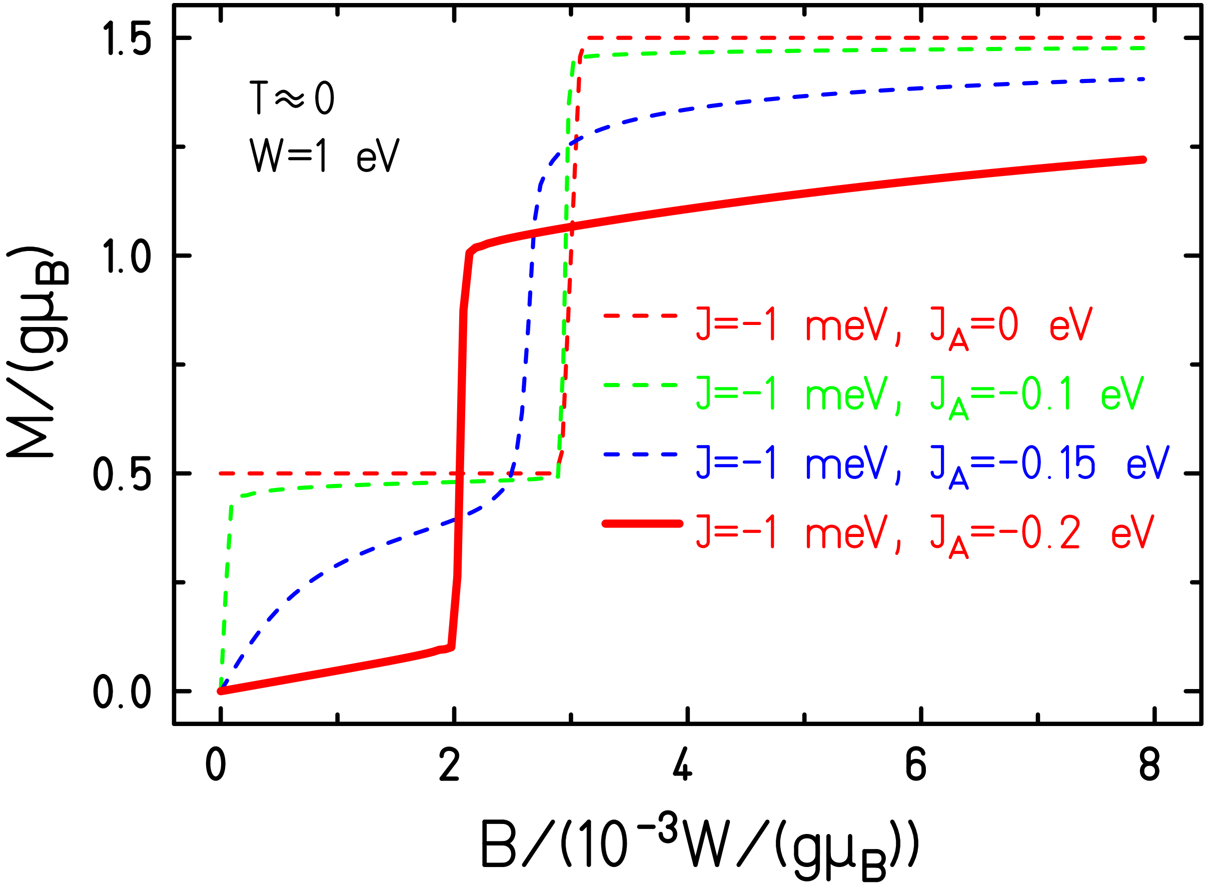
Increasing coupling to the substrate

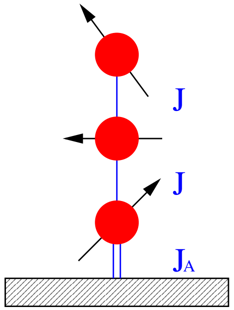




H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

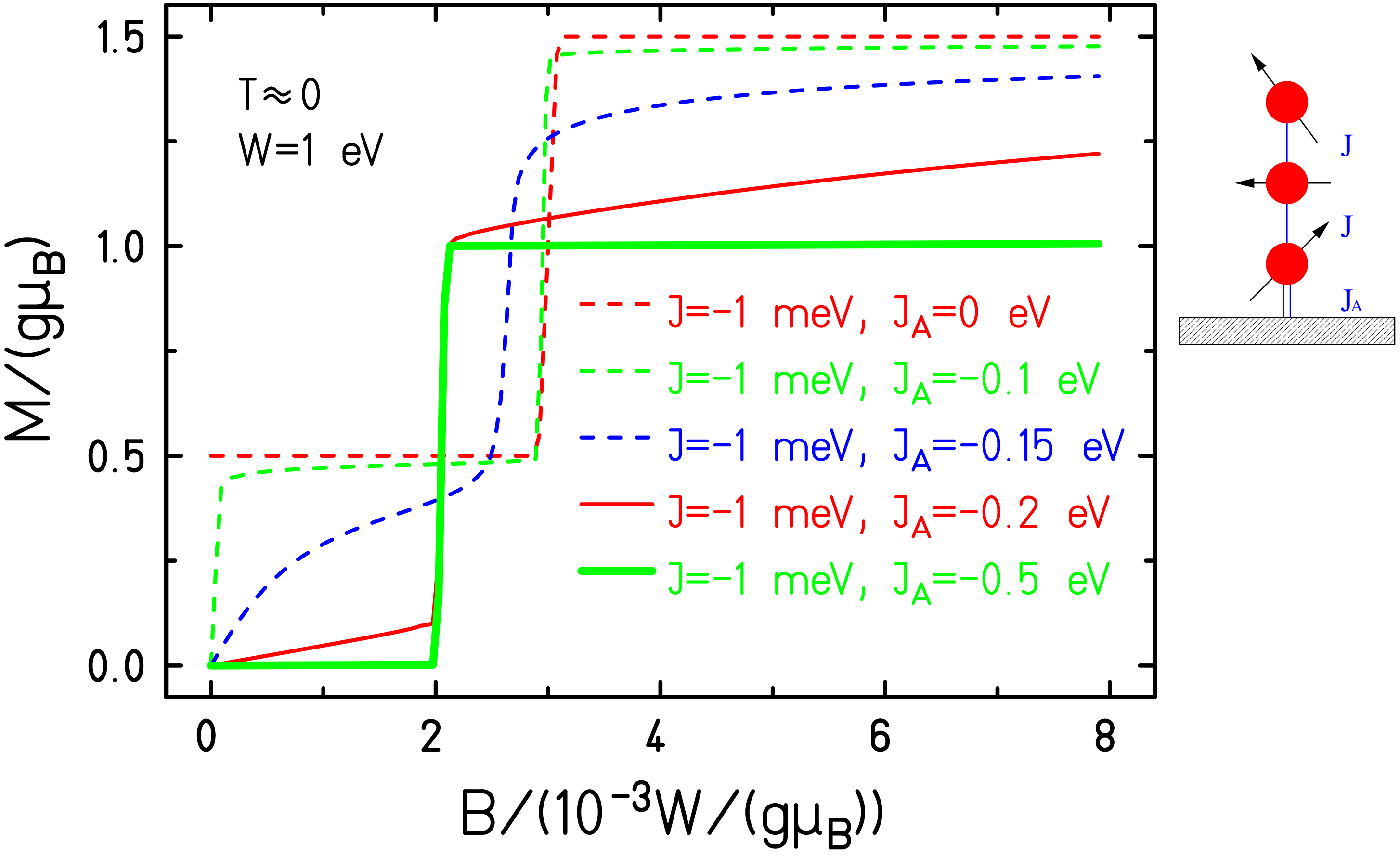
Increasing coupling to the substrate





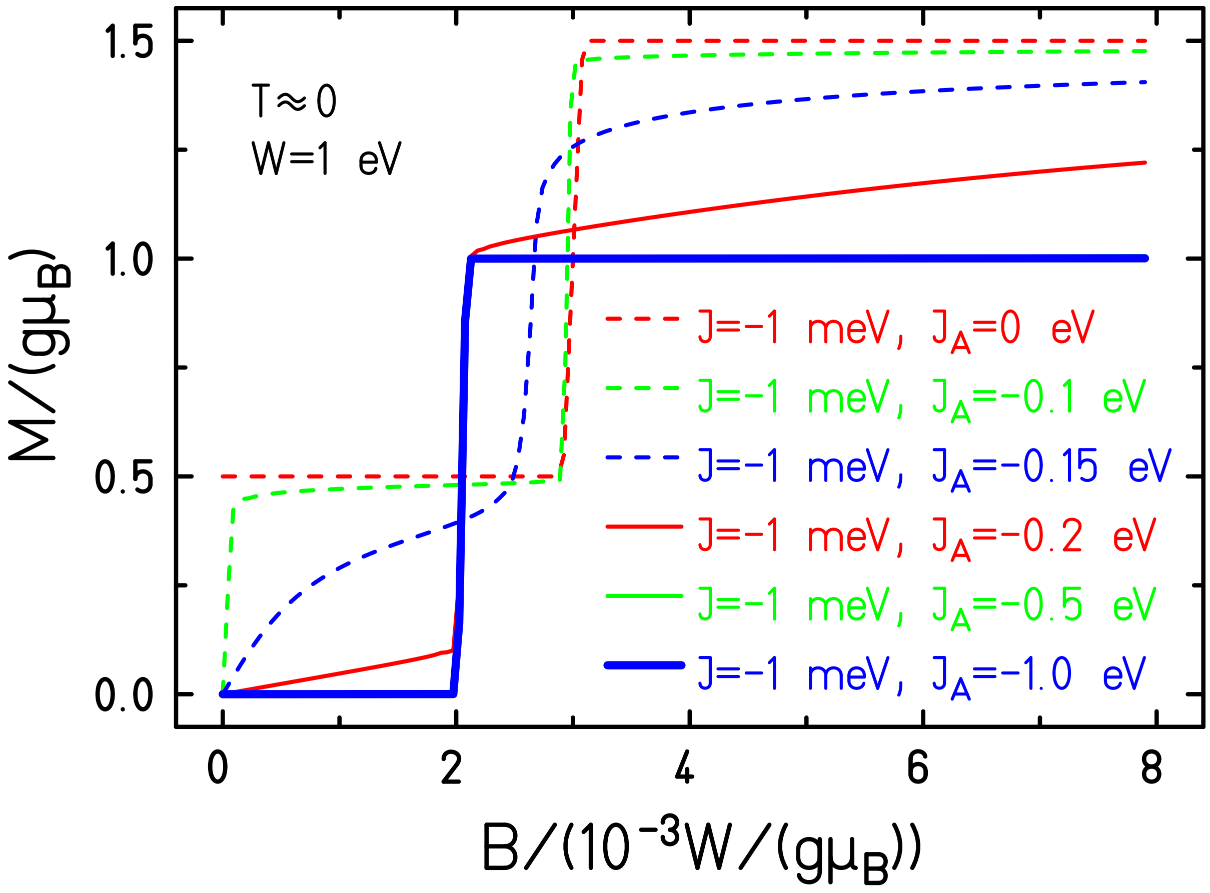
H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

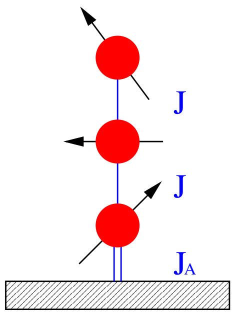
Increasing coupling to the substrate



H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

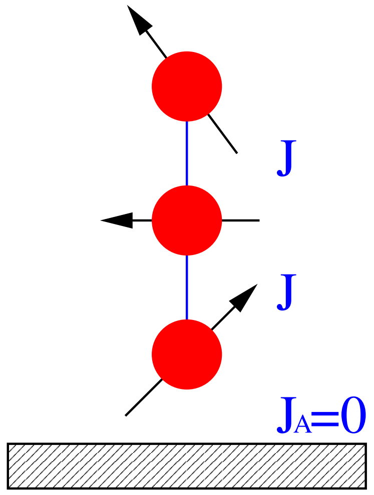
Increasing coupling to the substrate

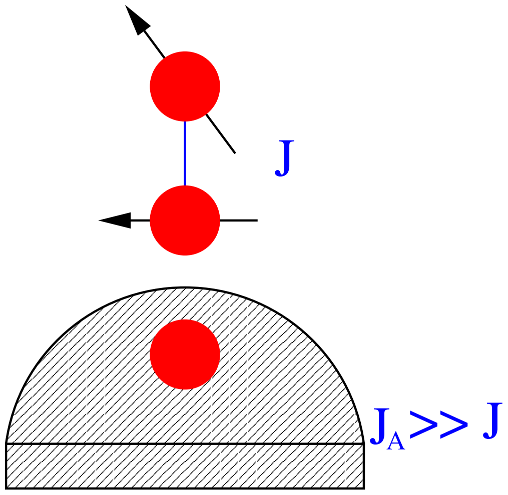




H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

Weak vs. strong coupling



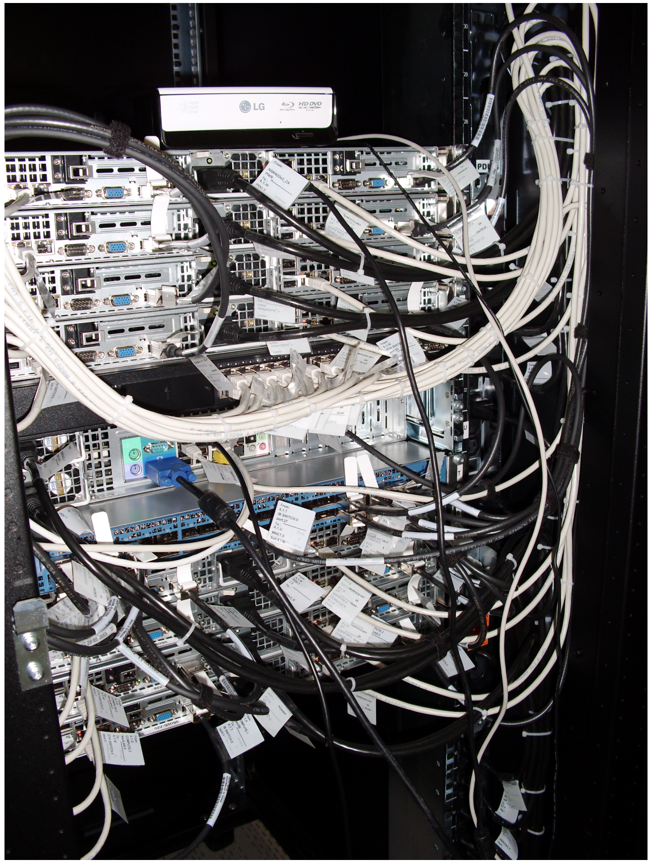


- weak coupling limit:
  unperturbed molecule (trimer)
- $|J_A| \lessapprox 0.1W$

- strong coupling limit:
  effective remainder (dimer)
- $|J_A| \gtrapprox 0.5W$

Inbetween: no simple characterization $+$ further sequential screening possible

Summary



- Exact diagonalization is great but limited.
- Finite-temperature Lanczos is a good approximate method for Hilbert space dimensions smaller than 10^{10}. DMRG for big 1-d systems. QMC for non-frustrated systems. ALPS!
- Magnetic molecules for storage, q-bits, MCE, and since they are nice.
- Often, the juice is in the anisotropic terms.

(1) A. Albuquerque *et al.*, J. Magn. Magn. Mater. **310**, 1187 (2007).
(2) http://alps.comp-phys.org (English, Japanese, Chinese)

Many thanks to my collaborators worldwide

- T. Glaser, Chr. Heesing, M. Höck, N.B. Ivanov, S. Leiding, A. Müller, R. Schnalle, Chr. Schröder, J. Ummethum, O. Wendland (Bielefeld)
- K. Bärwinkel, H.-J. Schmidt, M. Neumann (Osnabrück)
- M. Luban (Ames Lab, USA); P. Kögerler (Aachen, Jülich, Ames); R.E.P. Winpenny, E.J.L. McInnes (Man U, UK); L. Cronin, M. Murrie (Glasgow, UK); E. Brechin (Edinburgh, UK); H. Nojiri (Sendai, Japan); A. Postnikov (Metz, France); M. Evangelisti (Zaragosa, Spain)
- J. Richter, J. Schulenburg (Magdeburg); A. Honecker (Göttingen); U. Kortz (Bremen); A. Tennant, B. Lake (HMI Berlin); B. Büchner, V. Kataev, H.-H. Klauß (Dresden); P. Chaudhuri (Mühlheim); J. Wosnitza (Dresden-Rossendorf); J. van Slageren (Stuttgart); R. Klingeler (Heidelberg); O. Waldmann (Freiburg)

Thank you very much for your attention.

The end.

Molecular Magnetism Web

www.molmag.de

Highlights. Tutorials. Who is who. Conferences.

Contents for you today

~~Introduction to molecular magnetism~~

Traditional approach

1. ~~Complete diagonalization, easy~~
2. Complete diagonalization, SU(2) & point groups

Approximate methods

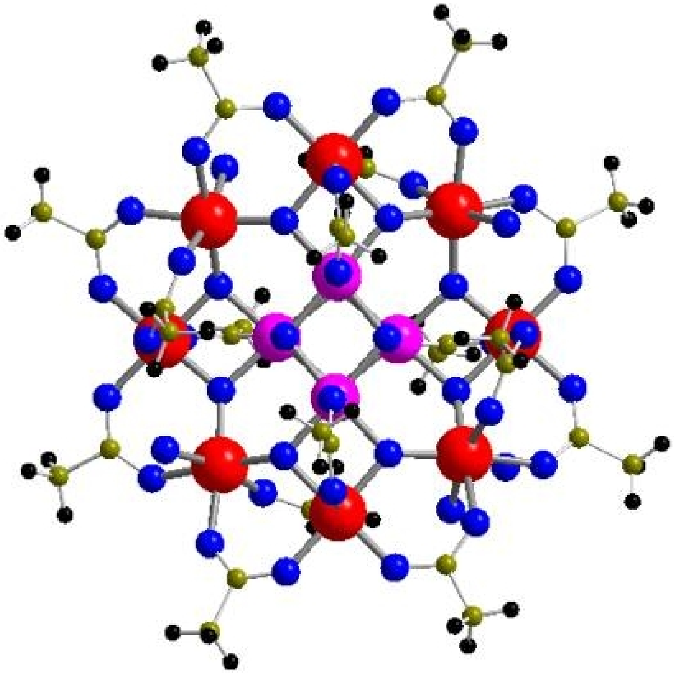
1. Finite-temperature Lanczos
2. ~~DMRG & DDMRG~~
3. ~~QMC~~

+ examples: MCE, frustration, SMM, NRG

+ Outlook

Beauty of Magnetic Molecules

The beauty of magnetic molecules I

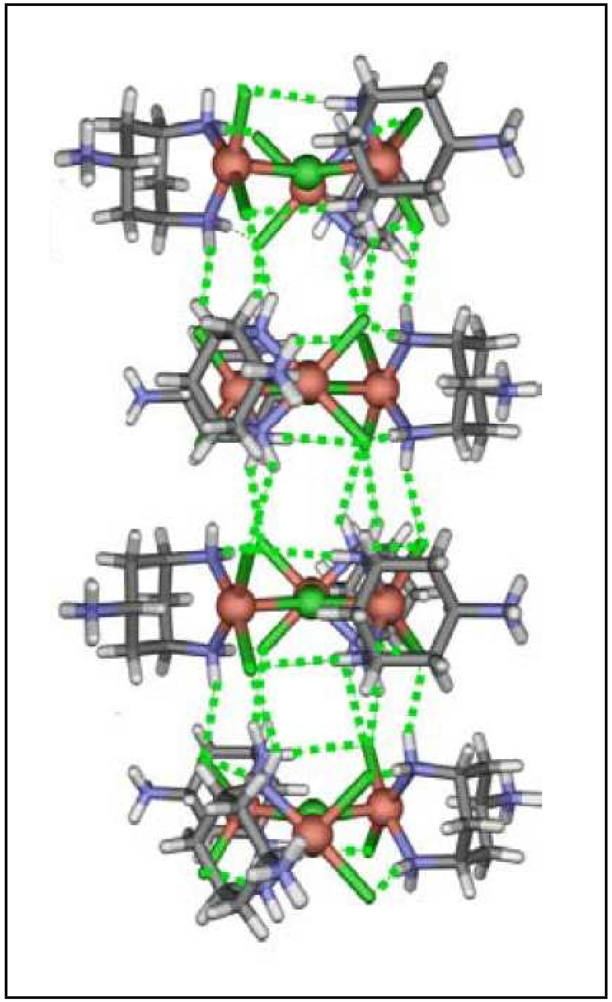


Mn_{12}

- Inorganic or organic macro molecules, e.g. polyoxometalates, where paramagnetic ions such as Iron (Fe), Chromium (Cr), Copper (Cu), Nickel (Ni), Vanadium (V), Manganese (Mn), or rare earth ions are embedded in a host matrix;
- 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.

Magnetism goes Nano, Ed. Stefan Blügel, Thomas Brückel, and Claus M. Schneider, FZ Jülich, Institute of Solid State Research, Lecture Notes **36** Jülich 2005

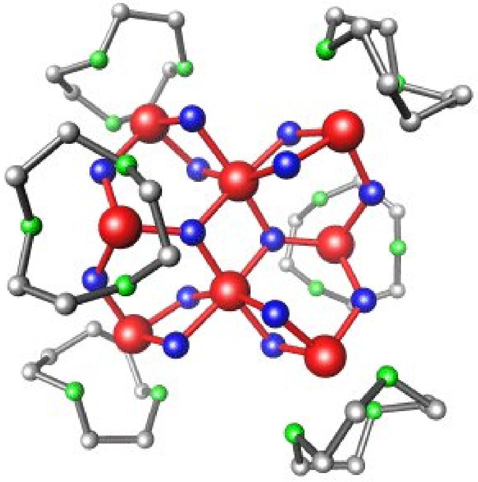
The beauty of magnetic molecules II

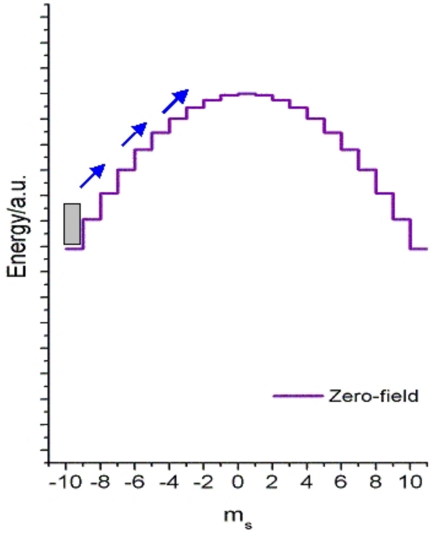


- Dimers (Fe_2), tetrahedra (Cr_4), cubes (Cr_8);
- Rings, especially iron rings (Fe_6, Fe_8, Fe_{10}, . . .);
- Complex structures (Mn_{12}) – drosophila of molecular magnetism;
- “Soccer balls”, more precisely icosidodecahedra (Fe_{30}) and other macro molecules;
- Chain like and planar structures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



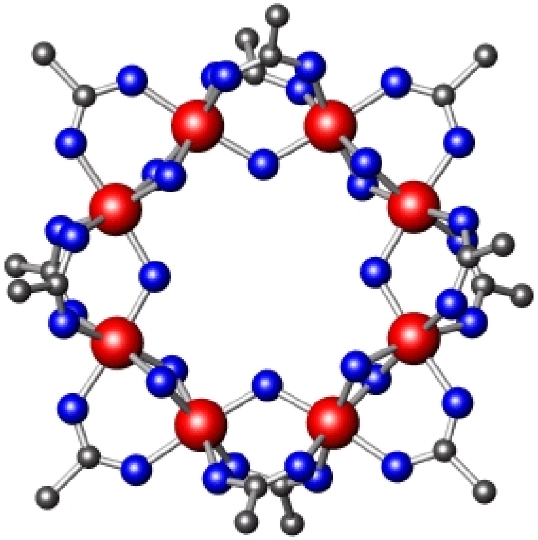


- Single Molecule Magnets (SMM): magnetic molecules with large ground state moment;
- Example: $S = 10$ for Mn$_{12}$ or Fe$_8$;
- Anisotropy dominates approximate single-spin Hamiltonian:

$$\underset{\sim}{H} = -D\underset{\sim}{S}_z^2 + \underset{\sim}{H}', \qquad \left[\underset{\sim}{S}_z, \underset{\sim}{H}'\right] \neq 0$$

- Single molecule shows: metastable magnetization, hysteresis, ground state magnetization tunneling, thermally and phonon assisted tunneling.
- Today's major efforts: improve stability of magnetization; investigate on surfaces.

The beauty of magnetic molecules IV
Why magnetic molecules?



Cr$_8$

- Interacting spin system largely decoupled from remaining degrees of freedom;
- 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.

Complete diagonalization:

The easy version

Most physicists do this!

Model Hamiltonian – Heisenberg and more

$$\underset{\sim}{H} \; = \; -2\sum_{i<j} J_{ij}\,\underset{\sim}{\vec{s}}_i \cdot \underset{\sim}{\vec{s}}_j + \sum_{i,j} \underset{\sim}{\vec{s}}_i \cdot \mathbf{D}_{ij} \cdot \underset{\sim}{\vec{s}}_j + \mu_B\, B \sum_{i}^{N} g_i\, \underset{\sim}{s}_i^z$$

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 $(\mathcal{H}) = (2s+1)^N$

$$\underset{\sim}{s}^z_u \mid m_1, \dots, m_u, \dots, m_N \,\rangle = m_u \mid m_1, \dots, m_u, \dots, m_N \,\rangle$$

These states span the Hilbert space and are used to construct symmetry-related basis states. Use $a_u = s_u - m_u$ for computation (integer).

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 $\underset{\sim}{S}_z$)

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

$\mathcal{H}(M)$ containes all states $\mid m_1, \dots, m_u, \dots, m_N\,\rangle$ with $\sum_i m_i = M$.

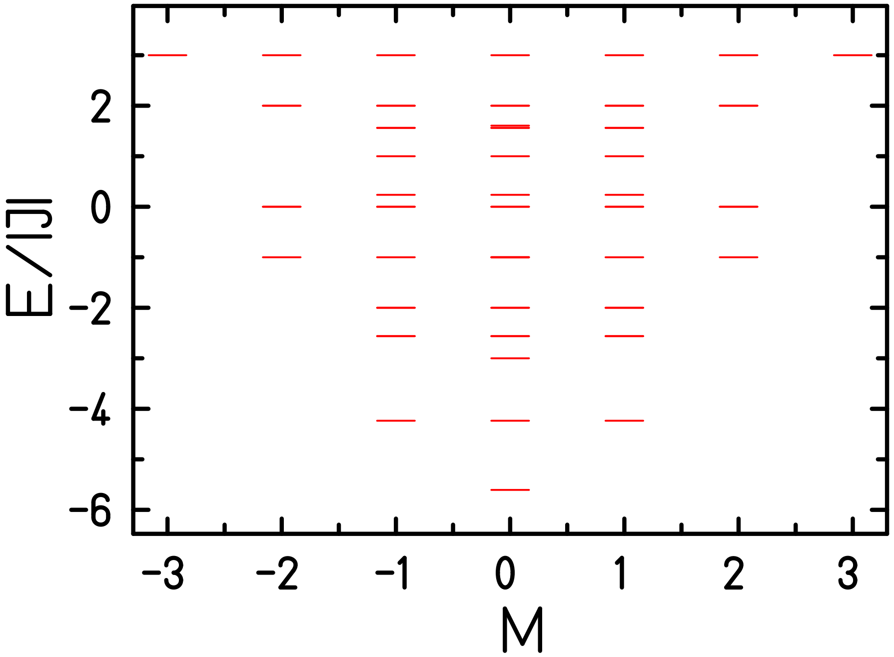
The Hamiltonian is diagonalized in all subspaces separately. The dimension of the largest subspace determines whether a Hamiltonian can diagonalized completely. If further symmetries apply this dimension will be further reduced.

For practical purposes $\underset{\sim}{\vec{s}}_i \cdot \underset{\sim}{\vec{s}}_j = \underset{\sim}{s}^z_i \underset{\sim}{s}^z_j + \frac{1}{2}\left[\underset{\sim}{s}^+_i \underset{\sim}{s}^-_j + \underset{\sim}{s}^-_i \underset{\sim}{s}^+_j\right]$.

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

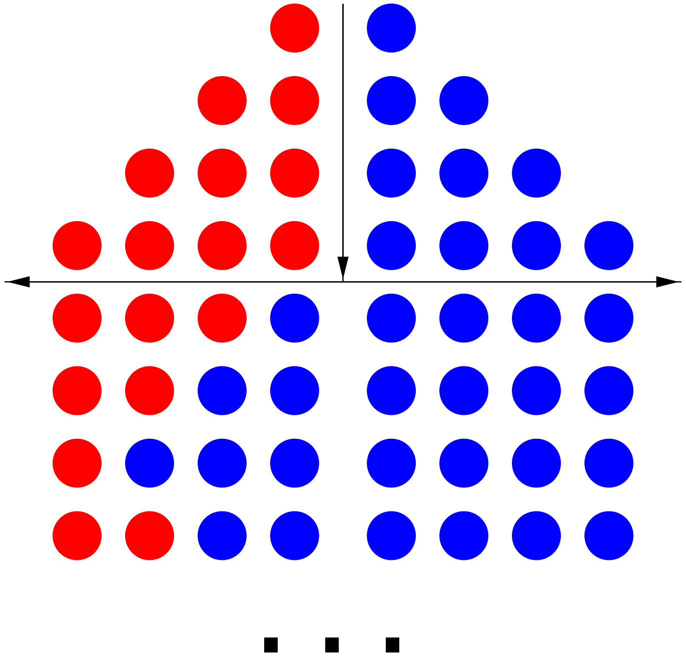


- Numerically exact diagonalization feasible up to RAM size;
- Example: 10,000x10,000 complex*16, 1.6 GB RAM needed;
- Not much we can do at this point, wait for more RAM 😉

Density Matrix Renormalization Group

(Best for one-dimensional systems, even for huge sizes.)

Density Matrix Renormatization Group



Again: build your appropriate reduced basis set

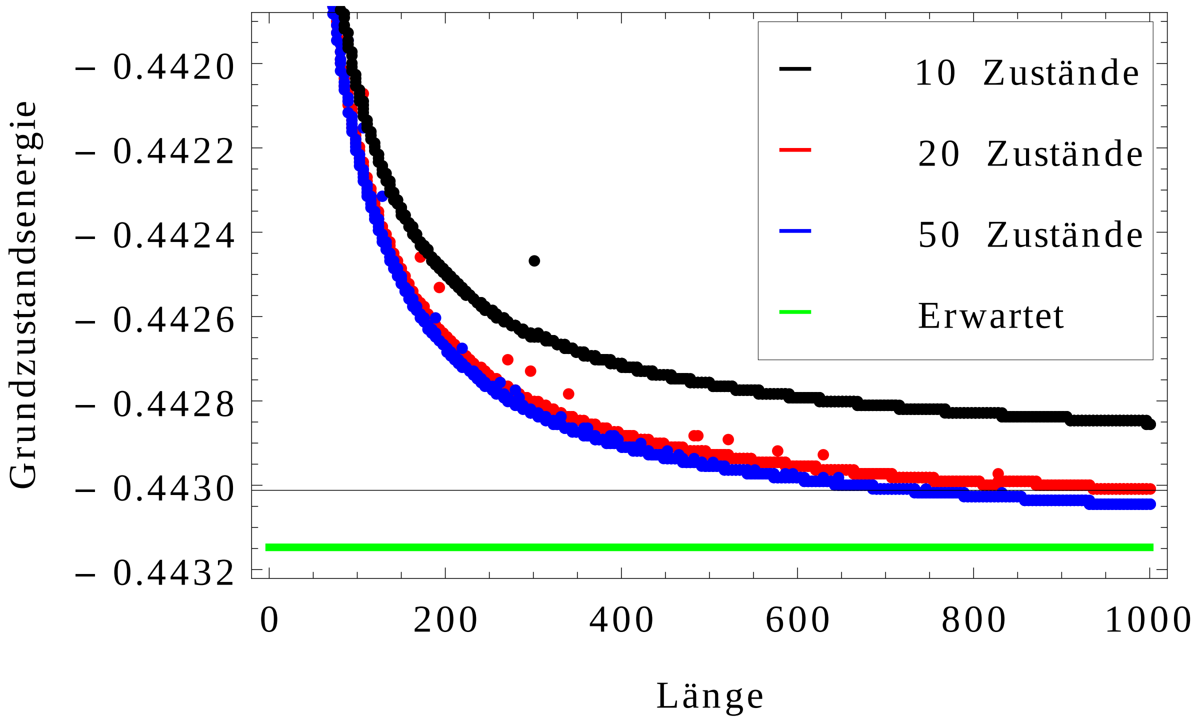
- Naive idea: start with small system, diagonalize $\underset{\sim}{H}$, keep only m lowest states, enlarge system, diagonalize $\underset{\sim}{H}$, keep only m lowest states, . . .

- Better: similar idea, use low-lying eigenstates of density matrix of part of system (1,2,3).

- Technical procedure: growth of system & sweeps.

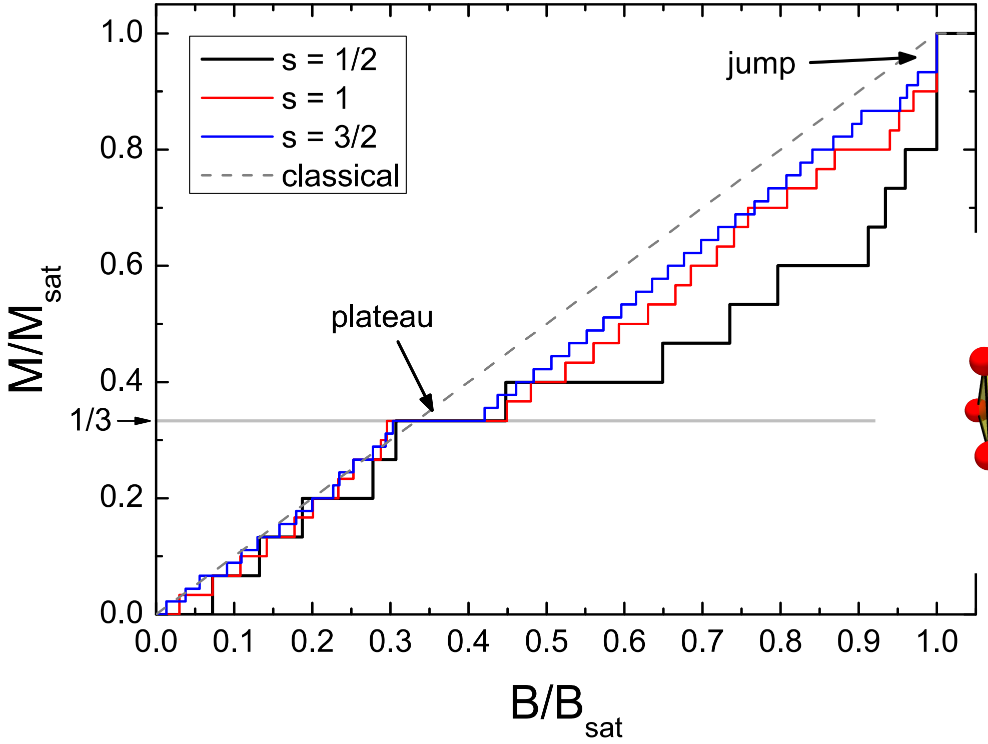
(1) S. R. White, Phys. Rev. Lett. **69**, 2863 (1992).
(2) S. R. White, Phys. Rev. B **48**, 10345 (1993).
(3) U. Schollwöck, Rev. Mod. Phys. **77**, 259 (2005).

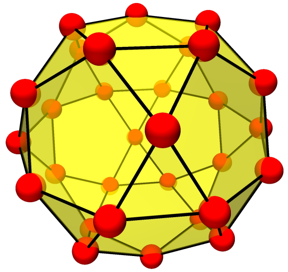
DMRG spin chain $s = 1/2$



- Simple example: 1000 spins with $s = 1/2$; Hilbert space dimension $2^{1000} \approx 10^{301}$.
- Approaches result known from Bethe ansatz with matrices as small as 50×50!

Density Matrix Renormatization Group

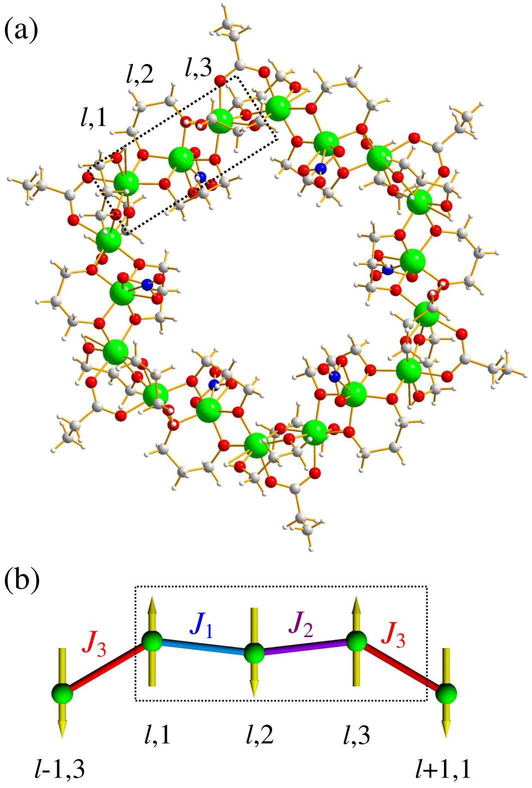




- DMRG yields ground states + very few low-lying states in orthogonal subspaces.
- Magnetization curve for $T = 0$, resonance energies for spectroscopy.

(1) J. Ummethum, J. Schnack, and A. Laeuchli, J. Magn. Magn. Mater. **327** (2013) 103

Dynamical Density Matrix Renormatization Group

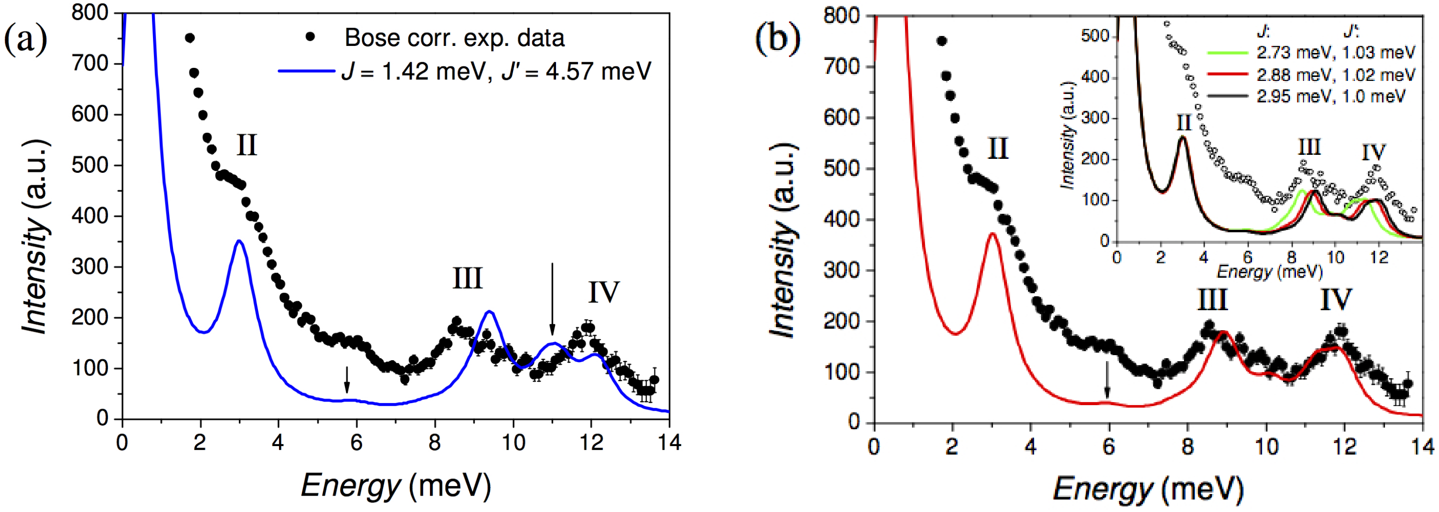


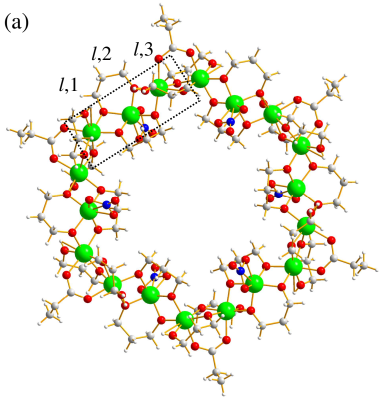
Evaluation of correlation functions, e.g. for INS:

- $S^{zz}_{jj'}(\omega) \equiv \sum_n \langle 0|\underset{\sim}{s}^{z}_{j}|n\rangle\langle n|\underset{\sim}{s}^{z}_{j'}|0\rangle\,\delta(\hbar\omega - E_n + E_0)$; transitions from the ground state;
- $S^{zz}_{jj'}(\omega) \approx \frac{1}{\pi}\langle 0|\underset{\sim}{s}^{z}_{j}\frac{\eta}{(E_0+\hbar\omega-\underset{\sim}{H})^2+\eta^2}\underset{\sim}{s}^{z}_{j'}|0\rangle$;
- Use DMRG ground state and DMRG representation of $\underset{\sim}{H}$ (1,2); η – finite broadening.

(1) T. D. Kühner and S. R. White, Phys. Rev. B **60**, 335 (1999).
(2) E. Jeckelmann, Phys. Rev. B **66**, 045114 (2002).
(3) P. King, T. C. Stamatatos, K. A. Abboud, and G. Christou, Angew. Chem. Int. Ed. **45**, 7379 (2006).
(4) O. Waldmann *et al.*, Phys. Rev. Lett. **102**, 157202 (2009).

Dynmical Density Matrix Renormatization Group





- Accurate description of low-lying excitations for the giant ferric wheel Fe_{18}. Hilbert space dimension 10^{14}.

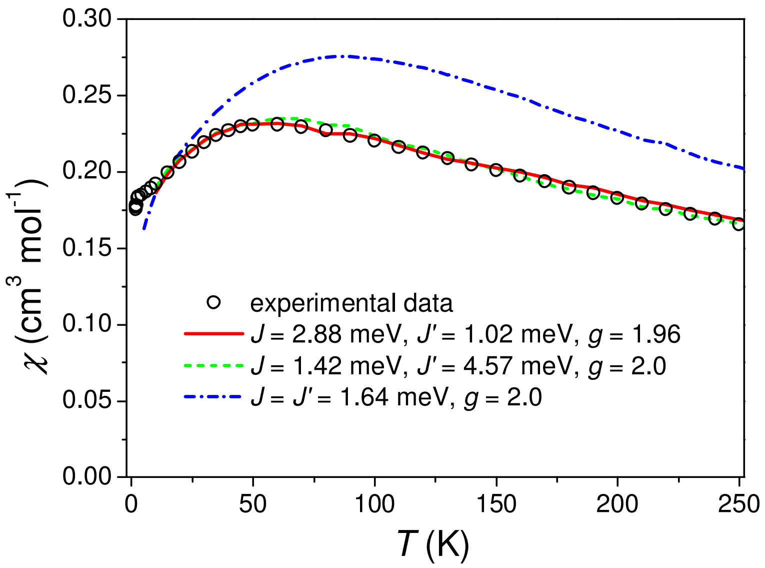
- Determination of model parameters.

(1) J. Ummethum, J. Nehrkorn, S. Mukherjee, N. B. Ivanov, S. Stuiber, Th. Strässle, P. L. W. Tregenna-Piggott, H. Mutka, G. Christou, O. Waldmann, J. Schnack, Phys. Rev. B **86**, 104403 (2012).

Quantum Monte Carlo

(Very good for non-frustrated systems, even for huge sizes.)

Quantum Monte Carlo

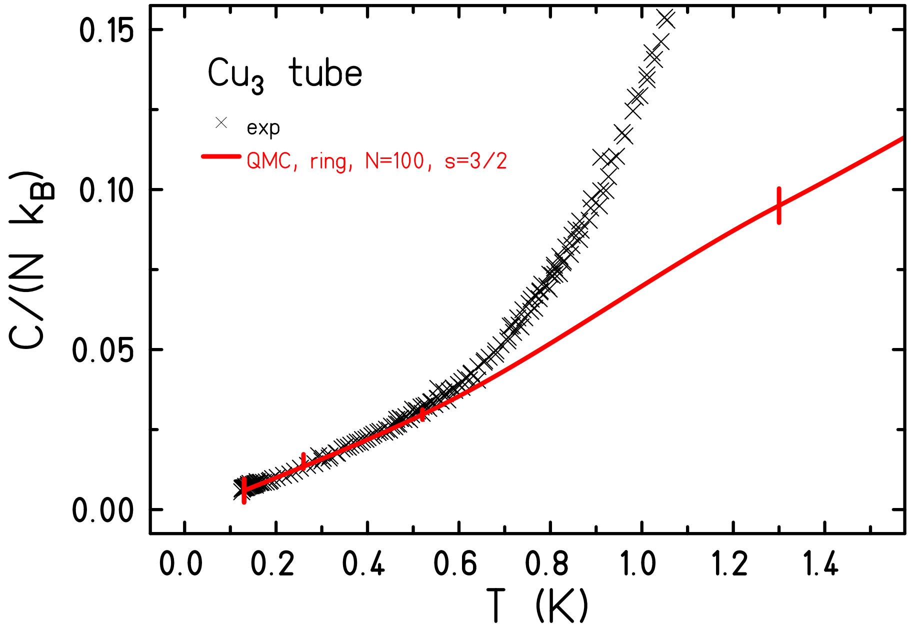


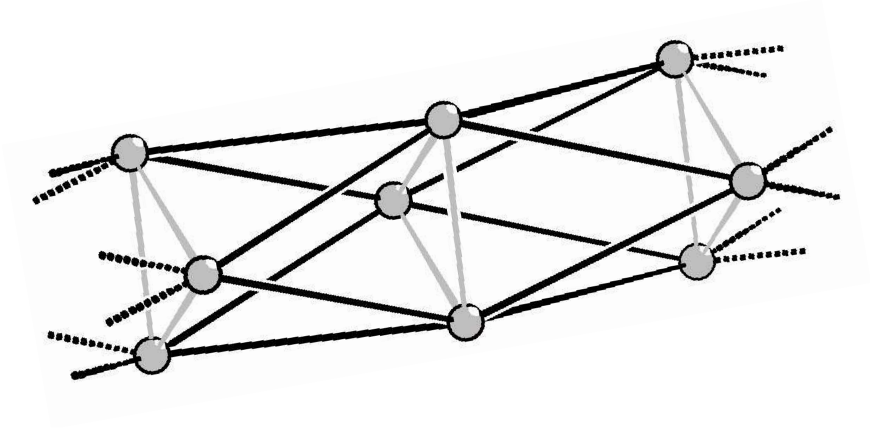
Chopped (sliced) partition function:

- $$\begin{aligned} Z(T,B) &= \sum_\nu \langle\,\nu\,|\,\exp\left\{-\beta \underset{\sim}{H}\right\}\,|\,\nu\,\rangle \\ &= \sum_\nu \langle\,\nu\,|\,\left[\exp\left\{-\beta \underset{\sim}{H}/m\right\}\right]^m\,|\,\nu\,\rangle \\ &= \sum_{\nu,\alpha,\beta,\dots} \langle\,\nu\,|\,\exp\left\{-\beta \underset{\sim}{H}/m\right\}\,|\,\alpha\,\rangle\langle\,\alpha\,|\,\cdots \\ &\approx \sum_{\nu,\alpha,\beta,\dots} \langle\,\nu\,|\,\left\{1-\beta \underset{\sim}{H}/m\right\}\,|\,\alpha\,\rangle\langle\,\alpha\,|\,\cdots \end{aligned}$$
- Bad/no convergence for frustrated systems (negative sign problem).

(1) A. W. Sandvik and J. Kurkijärvi, Phys. Rev. B **43**, 5950 (1991).
(2) A. W. Sandvik, Phys. Rev. B **59**, R14157 (1999).
(3) L. Engelhardt and M. Luban, Phys. Rev. B **73**, 054430 (2006); L. Engelhardt *et al.*, Phys. Rev. B **79**, 014404 (2009).
(4) J. Ummethum *et al.*, Phys. Rev. B **86**, 104403 (2012).

Quantum Monte Carlo





- [(CuCl$_2$tachH)$_3$Cl]Cl$_2$: spins on triangles effectively coupled to $s = 3/2$, treatment as chain $\Rightarrow$ Luttinger liquid behavior, i.e. $C \propto T$.
- 100 spins $s = 3/2$ are no problem for QMC.

(1) N. B. Ivanov, J. Schnack, R. Schnalle, J. Richter, P. Kögerler, G.N. Newton, L. Cronin, Y. Oshima, Hiroyuki Nojiri, Phys. Rev. Lett. **105**, 037206 (2010).

Magnetocalorics

Magnetocaloric effect – Basics

- Heating or cooling in a varying magnetic field. Discovered in pure iron by Emil Warburg in 1881.
- Typical rates: $0.5 \dots 2$ K/T.
- Giant magnetocaloric effect: $3 \dots 4$ K/T e.g. in $Gd_5(Si_xGe_{1-x})_4$ alloys ($x \leq 0.5$).
- Scientific goal I: room temperature applications.
- Scientific goal II: sub-Kelvin cooling.

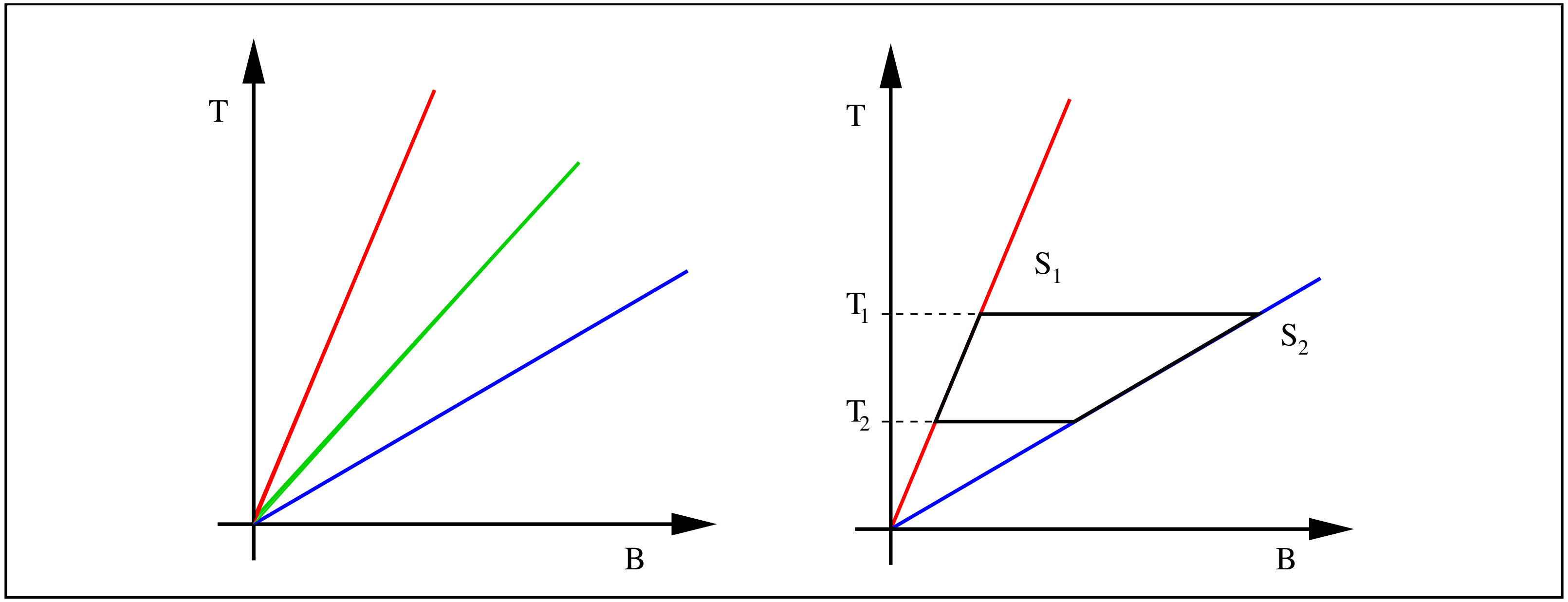
Magnetocaloric effect – cooling rate

$$\left(\frac{\partial T}{\partial B}\right)_S = -\frac{T}{C}\left(\frac{\partial S}{\partial B}\right)_T$$

MCE especially large at large isothermal entropy changes, i.e. at phase transitions (1), close to quantum critical points (2), or due to the condensation of independent magnons (3).

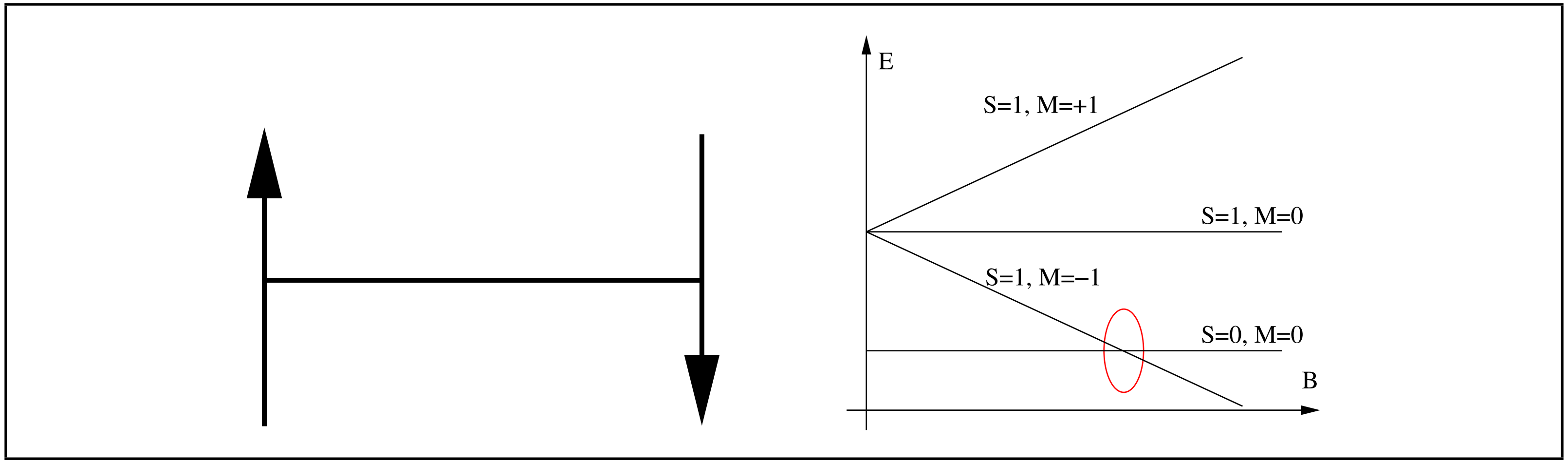
(1) V.K. Pecharsky, K.A. Gschneidner, Jr., A. O. Pecharsky, and A. M. Tishin, Phys. Rev. B **64**, 144406 (2001)
(2) Lijun Zhu, M. Garst, A. Rosch, and Qimiao Si, Phys. Rev. Lett. **91**, 066404 (2003)
(3) M.E. Zhitomirsky, A. Honecker, J. Stat. Mech.: Theor. Exp. **2004**, P07012 (2004)

Magnetocaloric effect – Paramagnets



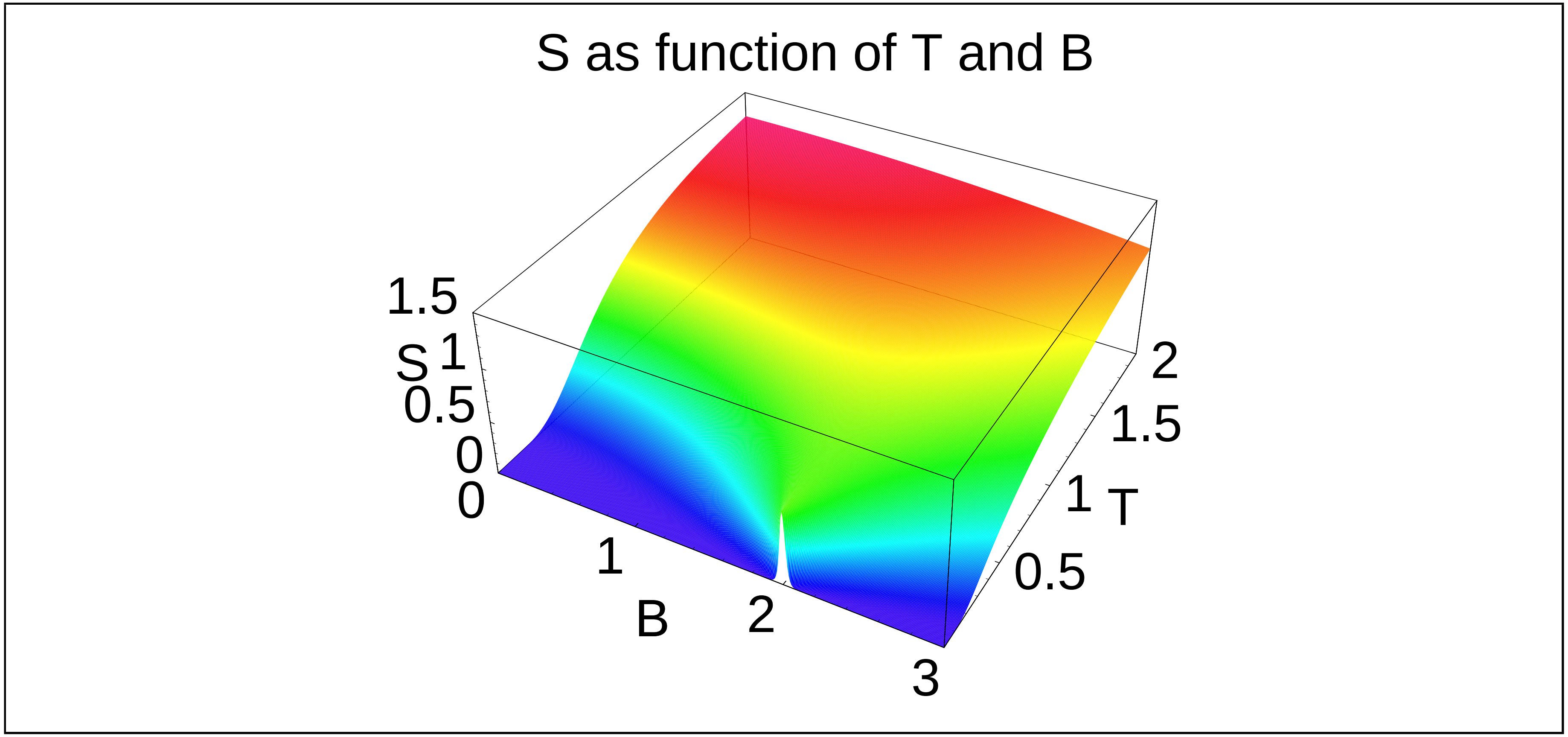
- Ideal paramagnet: $S(T,B) = f(B/T)$, i.e. $S = const \Rightarrow T \propto B$.
- At low T pronounced effects of dipolar interaction prevent further effective cooling.

Magnetocaloric effect – af $s = 1/2$ dimer



- Singlet-triplet level crossing causes a peak of S at $T \approx 0$ as function of B.
- $M(T=0,B)$ and $S(T=0,B)$ not analytic as function of B.
- $M(T=0,B)$ jumps at B_c; $\quad S(T=0,B_c) = k_B \ln 2$, otherwise zero.

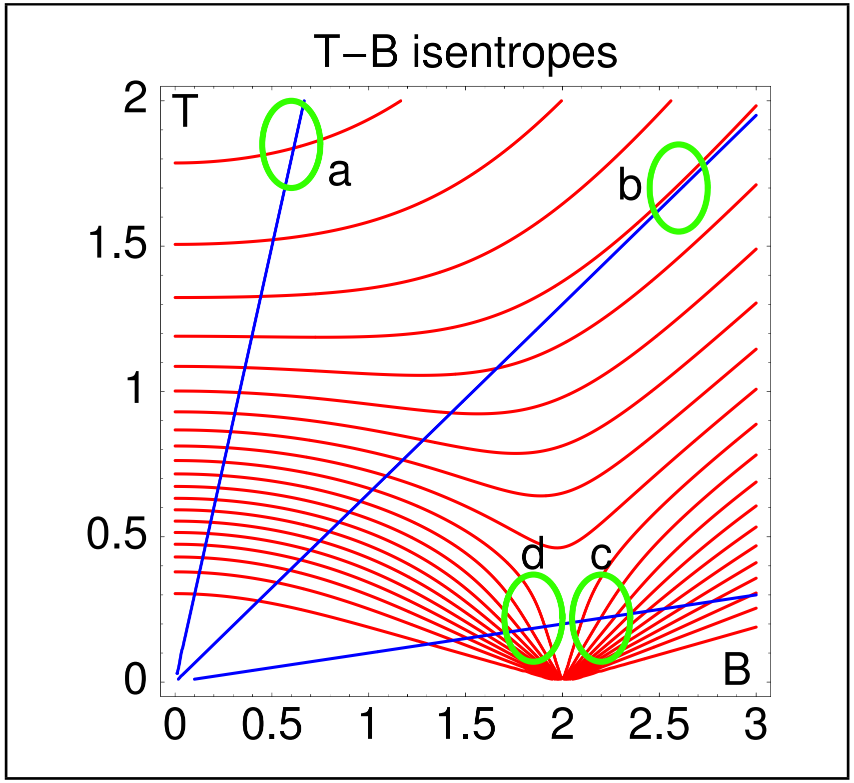
Magnetocaloric effect – af $s = 1/2$ dimer



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

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

Magnetocaloric effect – af $s = 1/2$ dimer



blue lines: ideal paramagnet, red curves: af dimer

Magnetocaloric effect:

(a) reduced,

(b) the same,

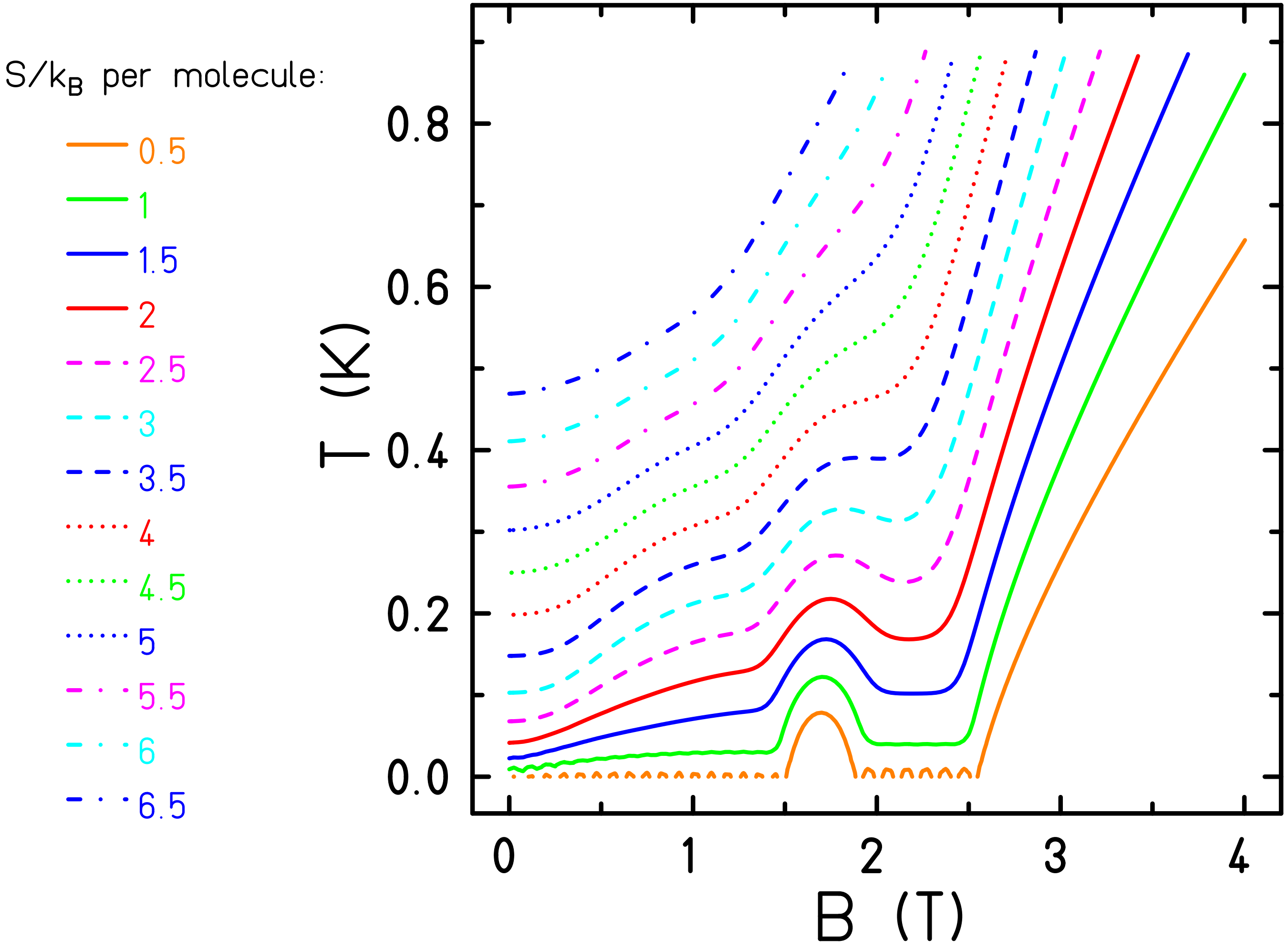
(c) enhanced,

(d) opposite

when compared to an ideal paramagnet.

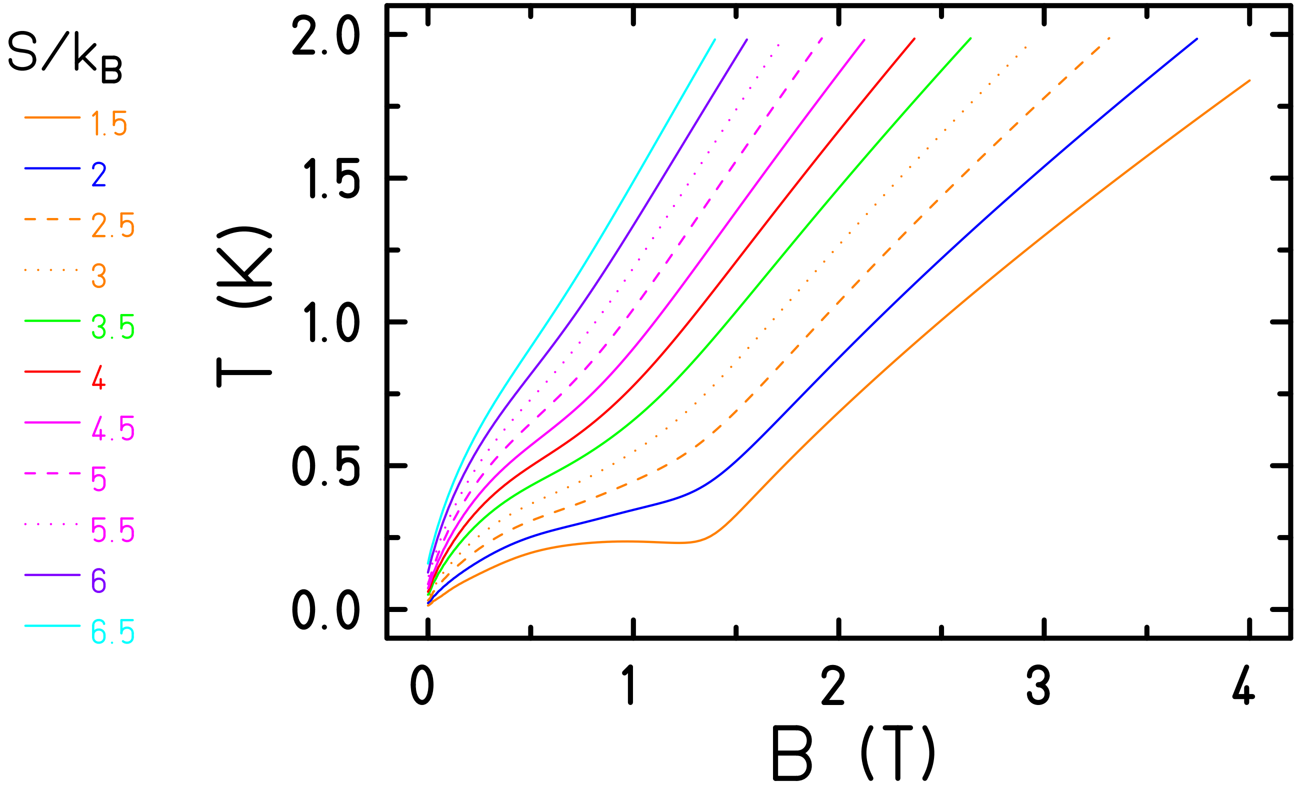
Case (d) does not occur for a paramagnet.

Typical isentropes for af spin system



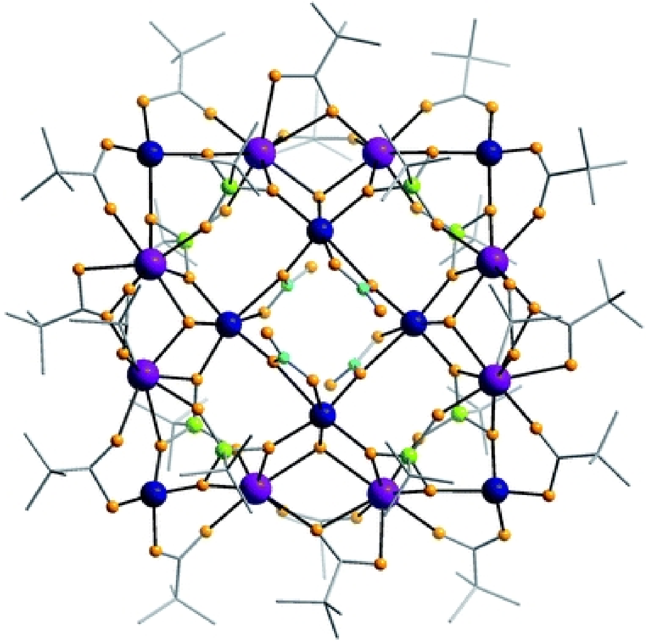
Level crossings signal antiferromagnetic interactions.

Typical isentropes for high-spin system



Typical for high-spin ground state. Cooling rate depends on T and B.

Magnetocaloric effect – Why Gd compounds?



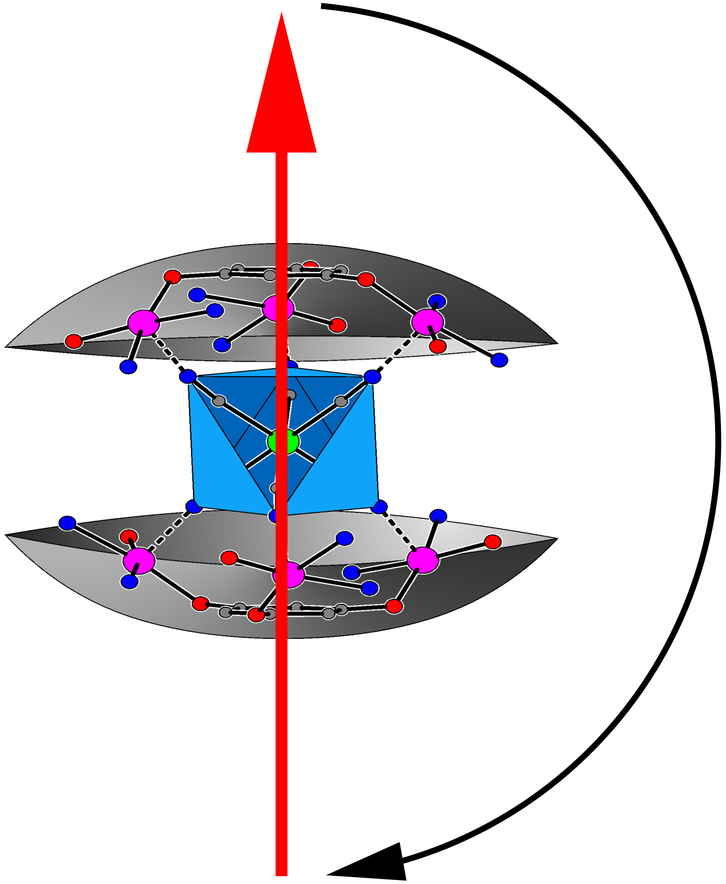
- High spin of $s = 7/2$;
- Weak exchange ⇒ high density of states;
- Can vary the entropy with moderate fields.
- But large Hilbert spaces!
  Exact modeling impossible.
  ⇒ Lanczos

Yan-Zhen Zheng, Marco Evangelisti, Richard E. P. Winpenny, Chem. Sci. **2**, 99-102 (2011)

T. N. Hooper, J. Schnack, St. Piligkos, M. Evangelisti, E. K. Brechin, Angew. Chem. Int. Ed. **51** (2012) 4633-4636.

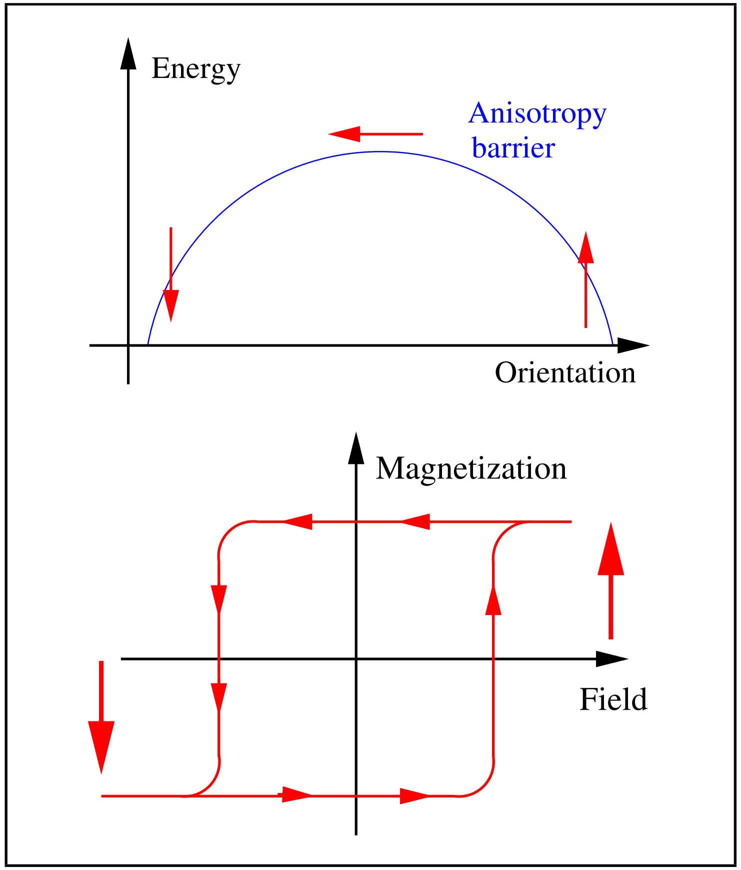
Single Molecule Magnets

Single Molecule Magnets I



- Magnetic Molecules may possess a large ground state spin, e.g. $S = 10$ for Mn_{12} or Fe_8;
- Ground state spin can be stabilized by anisotropy (easy axis).

Single Molecule Magnets II



- Single Molecule Magnets (SMM): large ground state moment; anisotropy barrier dominates at low T.

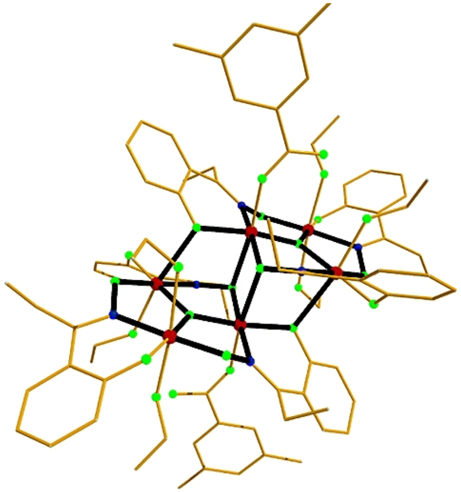
$$\underset{\sim}{H} \approx D S_z^2$$

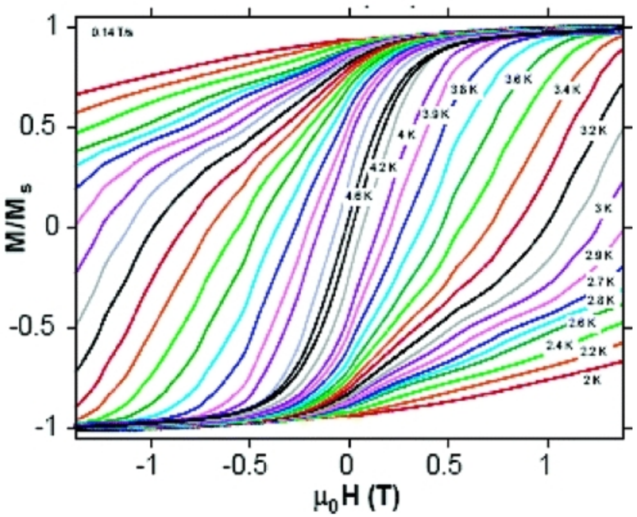
- Metastable magnetization and hysteresis;

- But also magnetization tunneling due to non-commuting terms, e.g. E, B_x, B_y.

$$\underset{\sim}{H} \approx D S_z^2 + E(S_x^2 - S_y^2)$$

Single Molecule Magnets III





$[Mn^{III}_6O_2(Et\text{-}sao)_6(O_2CPh(Me_2))_2(EtOH)_6]$:

- $S = 12$ ground state with $D = -0.43$ cm^{-1}
- $U_{\text{eff}} = 86.4$ K and a blocking temperature of about 4.5 K.
- A record molecule from the group of Euan Brechin (Edinburgh).

C. J. Milios *et al.*, J. Am. Chem. Soc. **129**, 2754 (2007)
S. Carretta *et al.*, Phys. Rev. Lett. **100**, 157203 (2008)

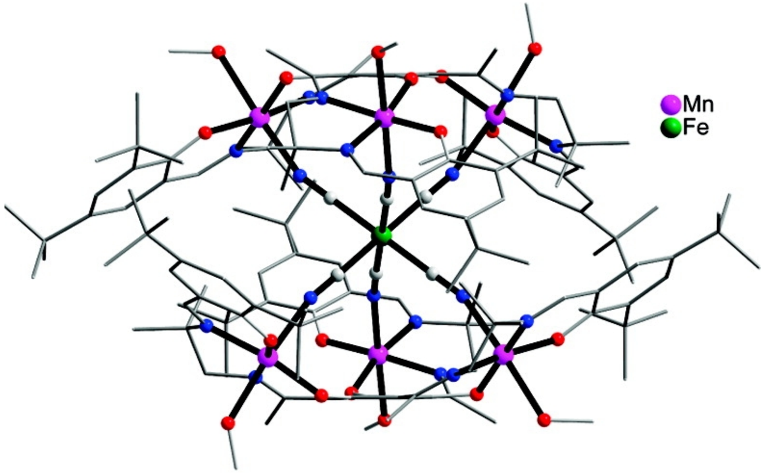
Single Molecule Magnets IV

- "Magnitude of the anisotropy barrier is mainly determined by the strength of the spin-orbit coupling and cannot be engineered by independently optimizing D and S."(1)
- "From this point of view systems with larger energy barriers should be obtained in the case of perfect alignment of the Jahn-Teller axes . . .
  However, the challenge here will be the control of the ferromagnetic exchange."(1)
- ". . . the widely considered design rule to increase S is not as efficient as suggested by $\underset{\sim}{H} = DS^2$,. . . the increase is on the order of unity and not S^2."(2)
- "For obtaining better SMMs, it hence seems most promising to work on the local ZFS tensors D_i or to work in a limit where the Heisenberg term is not dominant (i.e., to break the strong-exchange limit)."(2)

(1) E. Ruiz *et al.*, Chem. Commun. 52 (2008).

(2) O. Waldmann, Inorg. Chem. **46**, 10035 (2007).

Single Molecule Magnets V



Rational design of strict C_3 symmetry:

- Idea of Thorsten Glaser (Bielefeld): C_3 symmetric alignment of local easy axes (easy axis $\equiv$ Jahn-Teller axis);
- Various ions could be used so far, e.g. Mn_6Cr (1), Mn_6Fe (2), . . .
- Advantage: no E-terms, i.e. no (less) tunneling;
- Problem: exchange interaction sometimes antiferromagnetic.

T. Glaser *et al.*, Angew. Chem.-Int. Edit. **45**, 6033 (2006).
T. Glaser *et al.*, Inorg. Chem. **48**, 607 (2009).

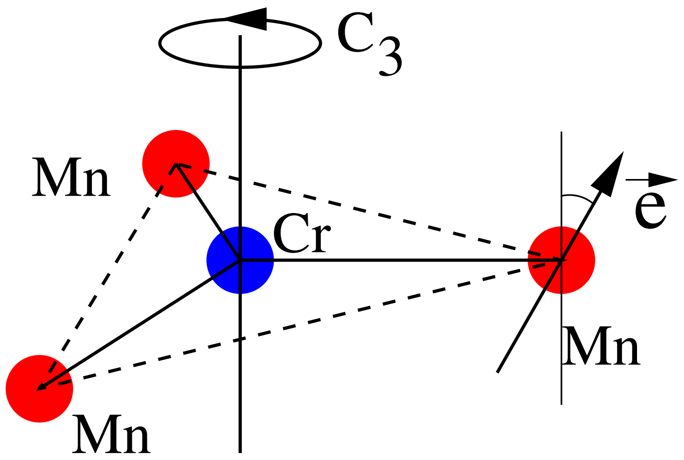
Anisotropic magnetic molecules I – Theory

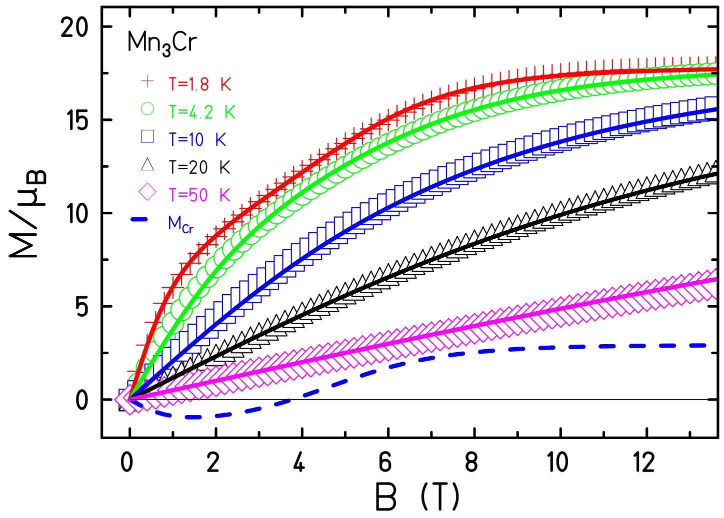
$$\underset{\sim}{H}(\vec{B}) = -\sum_{i,j} J_{ij}\,\underset{\sim}{\vec{s}}(i)\cdot\underset{\sim}{\vec{s}}(j) + \sum_{i} d_i \left(\vec{e}_i\cdot\underset{\sim}{\vec{s}}(i)\right)^2 + \mu_B\,\vec{B}\cdot\sum_{i}^{N}\mathbf{g}_i\cdot\underset{\sim}{\vec{s}}(i)$$

- $\left[\underset{\sim}{H},\underset{\sim}{\vec{S}}^2\right]\neq 0$, $\left[\underset{\sim}{H},\underset{\sim}{S}_z\right]\neq 0$;
- You have to diagonalize $\underset{\sim}{H}(\vec{B})$ for every field (direction and strength)!
  $\Rightarrow$ Orientational average.
- If you are lucky, point group symmetries still exist. Use them!
- Easy: dim$(\mathcal{H}) < 30,000$; possible: $30,000 <$ dim$(\mathcal{H}) < 140,000$

T. Glaser *et al.* *et* J. Schnack, Inorg. Chem. **48**, 607 (2009).

Anisotropic magnetic molecules II – Example





What can be achieved? Mn_3Cr:

- Two couplings: J_1 to central Cr, J_2 between Mn; Mn: s=5/2, g=2.0; Cr: s=3/2, g=1.95
- Model Mn anisotropy by local axis $\vec{e}(\vartheta, \phi)$. Due to C_3 symmetry $\vartheta_{\text{Mn1}} = \vartheta_{\text{Mn2}} = \vartheta_{\text{Mn3}}$. Only relative $\phi = 120^\circ$ determined.
- Model Cr anisotropy by local axis $\vec{e}(\vartheta, \phi)$. Due to C_3 symmetry $\vartheta_{\text{Cr}} = 0, \phi_{\text{Cr}} = 0$.
- Result: $J_1 = -0.29$ cm^{-1}, $J_2 = -0.08$ cm^{-1}, $d_{\text{Mn}} = -1.21$ cm^{-1}, $\vartheta_{\text{Mn}} = 22^\circ$, $d_{\text{Cr}} = +0.17$ cm^{-1}.
- ab initio calculations needed.