Advanced quantum many-body methods for magnetic molecules: what theory can do for you

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Universität Bielefeld DFG FOR 945 lrz

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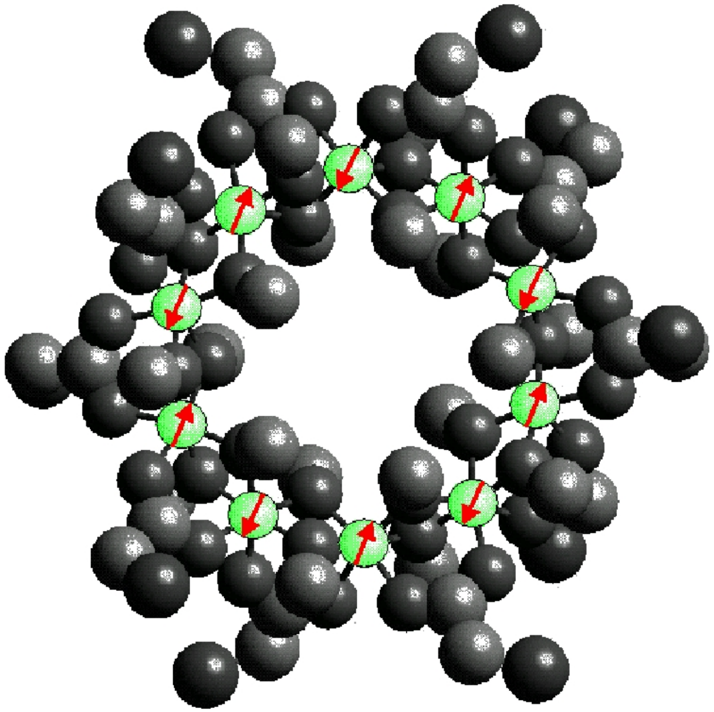
If you have got a question, please ask.

The problem

You have got a molecule!

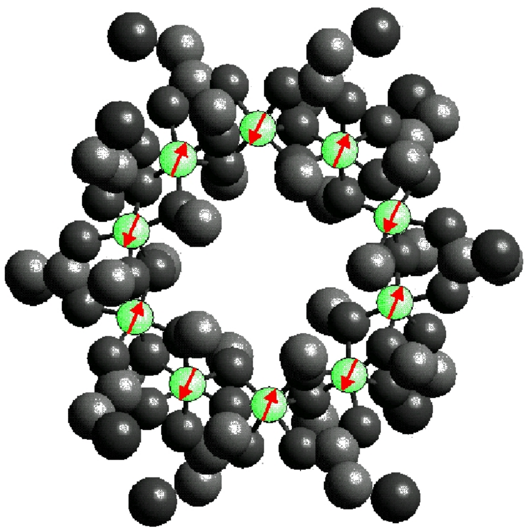


Congratulations!

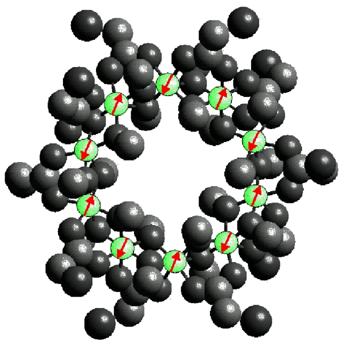
You have got an idea about the modeling!

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

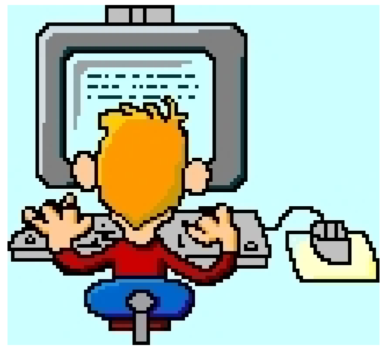
Heisenberg Zeeman



In the end it's always a big matrix!



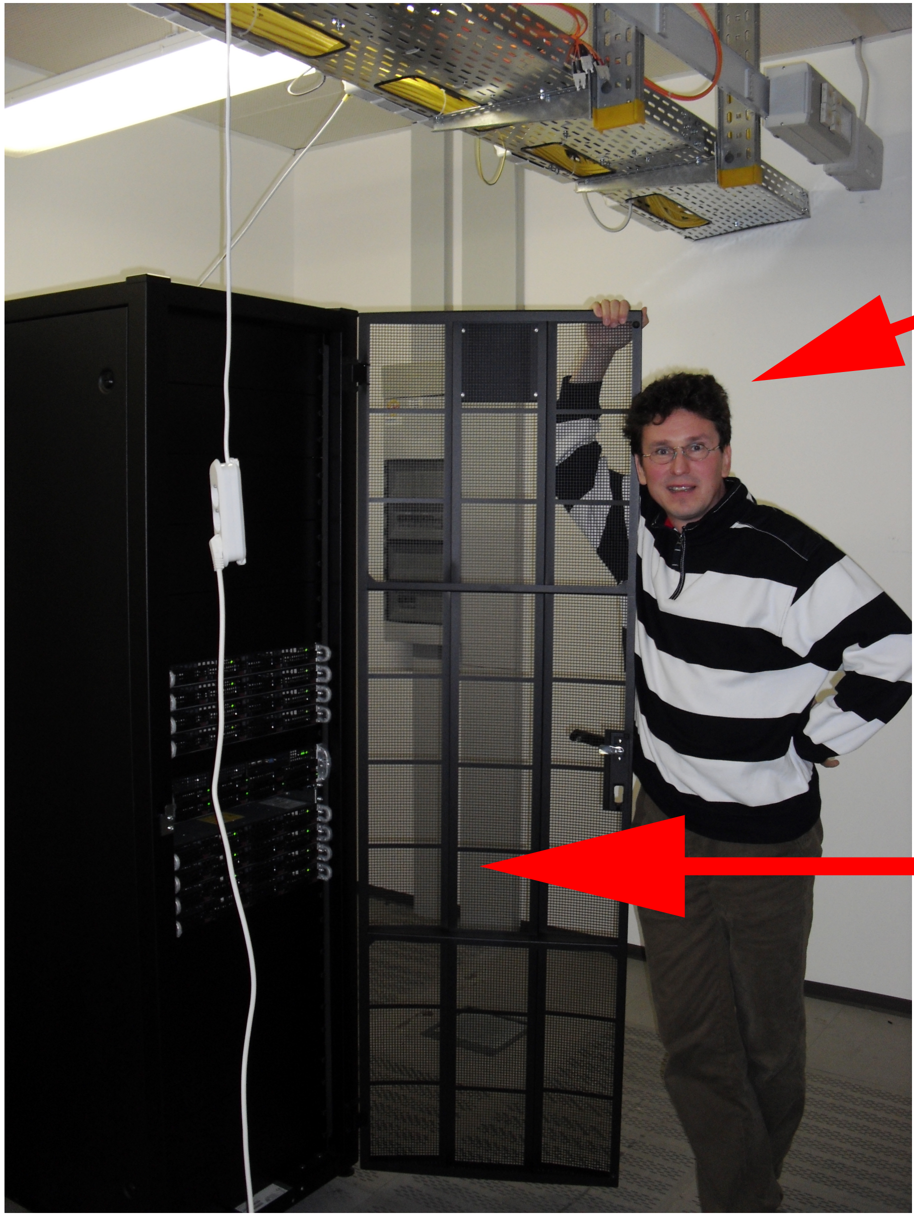
$$\Rightarrow \begin{pmatrix} -27.8 & 3.46 & 0.18 & \cdots \\ 3.46 & -2.35 & -1.7 & \cdots \\ 0.18 & -1.7 & 5.64 & \cdots \\ \vdots & \vdots & \vdots & \cdots \end{pmatrix} \Rightarrow$$



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

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!

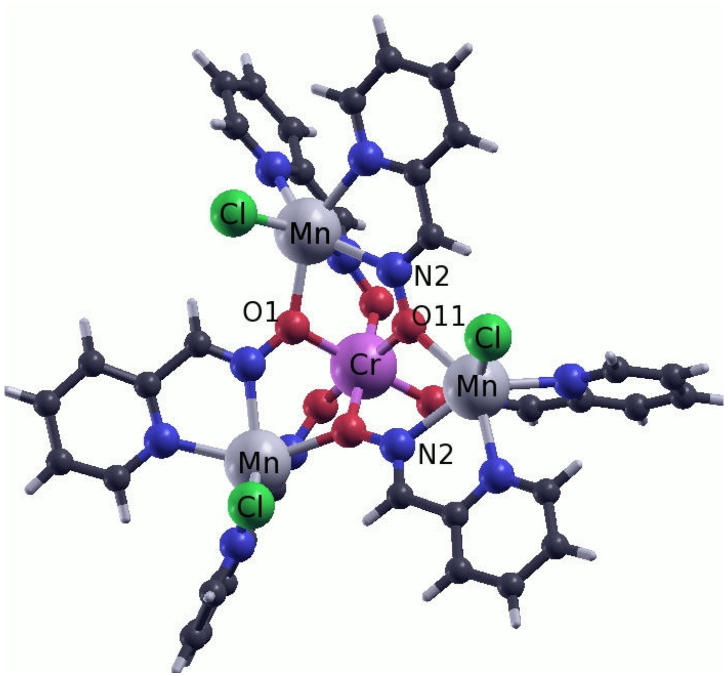
Contents for you today

$$\begin{pmatrix} 3 & 42 & 4711 \\ 42 & 0 & 3.14 \\ 4711 & 3.14 & 8 \\ -17 & 007 & 13 \\ 1.8 & 15 & 081 \end{pmatrix}$$

1. Small: Complete diagonalization
2. Medium: FTLM
3. Big: DDMRG
4. Deposited: NRG
5. Glasgow

We are the sledgehammer team of matrix diagonalization.
Please send inquiries to jschnack@uni-bielefeld.de!

Magnetic molecules in one slide



- Crystals of 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.

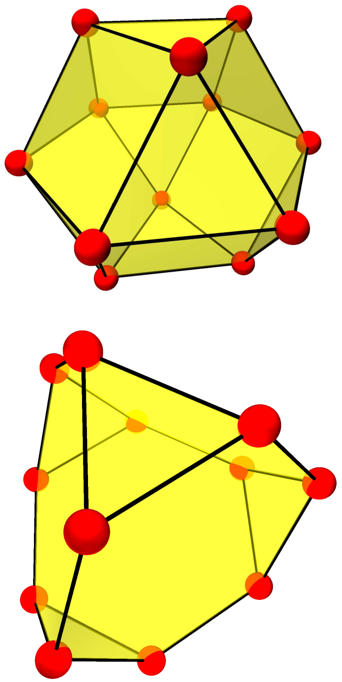
Magnetism goes Nano, Ed. Stefan Blügel, Thomas Brückel, and Claus M. Schneider, FZ Jülich, Institute of Solid State Research, Lecture Notes **36** Jülich 2005

Reminder on 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



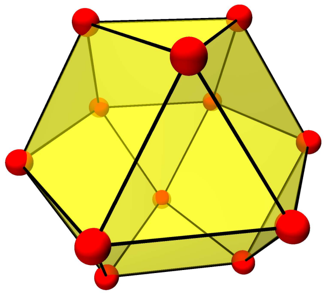
Spin rotational symmetry SU(2):

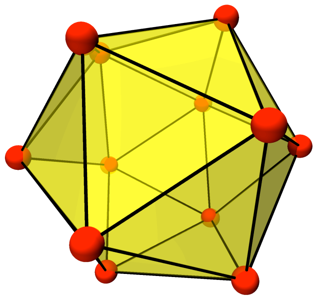
- $\underset{\sim}{H} = -2\sum_{i<j} J_{ij}\ \underset{\sim}{\vec{s}}_i \cdot \underset{\sim}{\vec{s}}_j + g\mu_B \underset{\sim}{\vec{S}} \cdot \vec{B}$;
- Physicists employ: $\left[\underset{\sim}{H}, \underset{\sim}{S}_z\right] = 0$;
- Chemists employ: $\left[\underset{\sim}{H}, \underset{\sim}{\vec{S}}^2\right]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

  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).

Point Group Symmetry



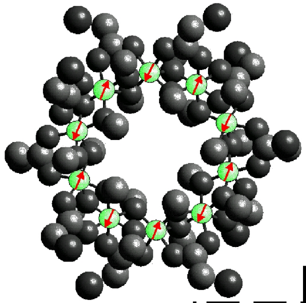


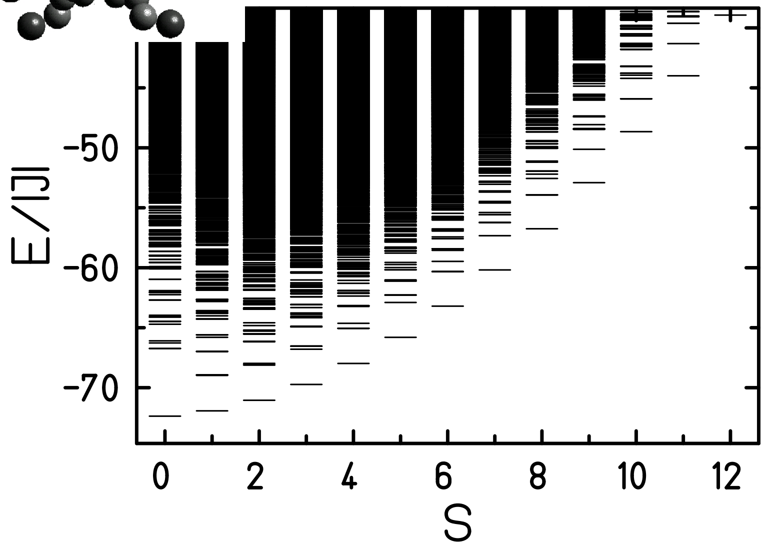
- Point groups, e.g. O_h or I_h, realized as permutations;
- Hamiltonian commutes with all group operations: $\left[\underset{\sim}{H}, \underset{\sim}{G}_i\right] = 0;$
- Construct irreducible representations and related Hamilton matrices;

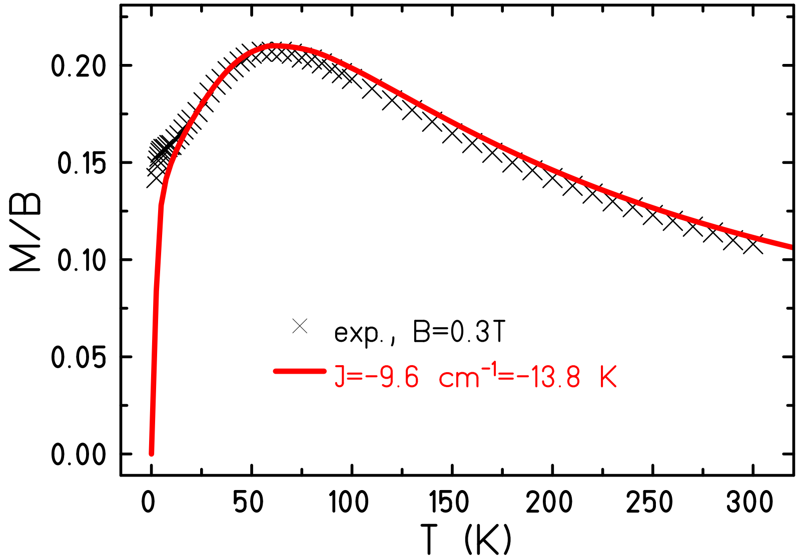
  No free program available (4).

(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} – SU(2) & D_2

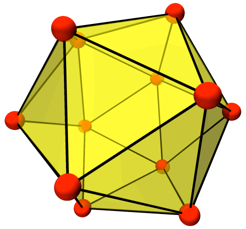




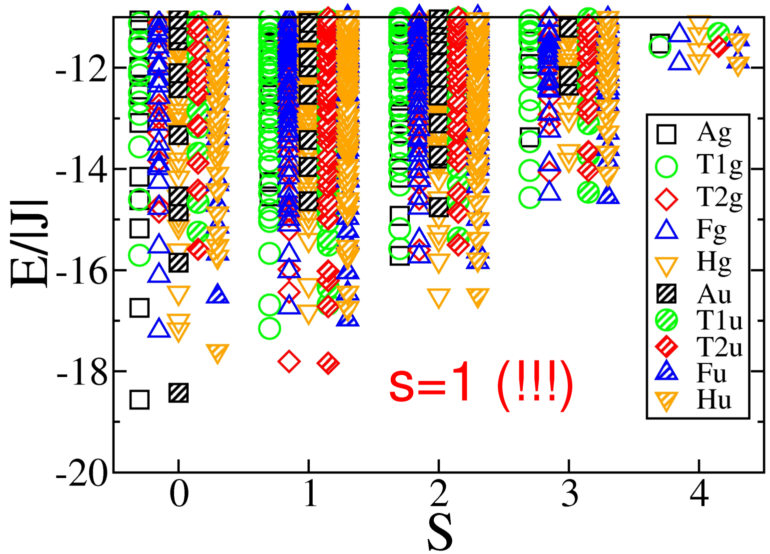


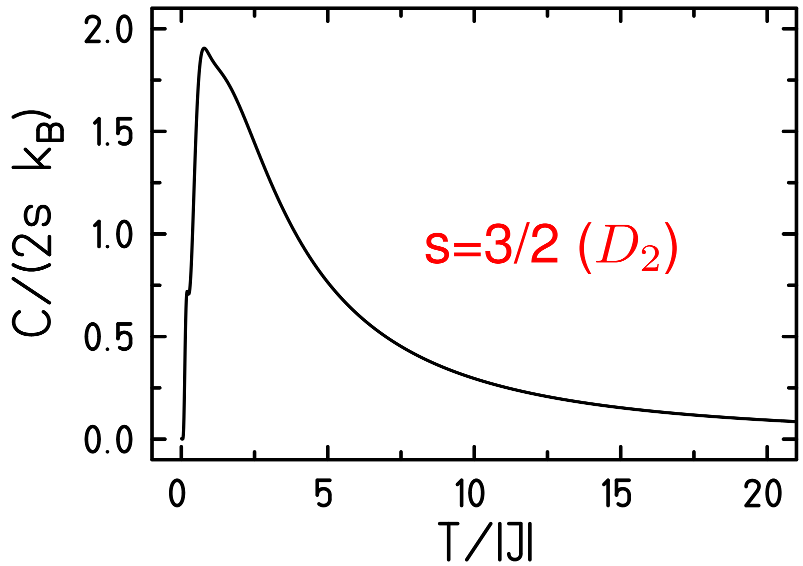
Spin ring, $N = 10$, $s = 5/2$, Hilbert space dimension 60,466,176; symmetry D_2 (1).

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



Example: Icosahedron – SU(2) & I_h

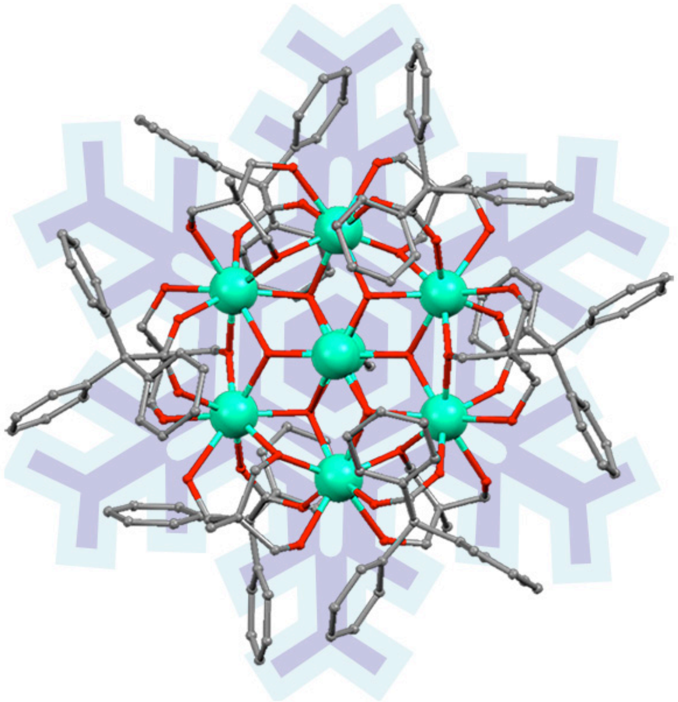




Icosahedron, $s = 3/2$, Hilbert space dimension 16,777,216; symmetry I_h;
Evaluation of recoupling coefficients for $s = 3/2$ in I_h **practically impossible** (1).

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

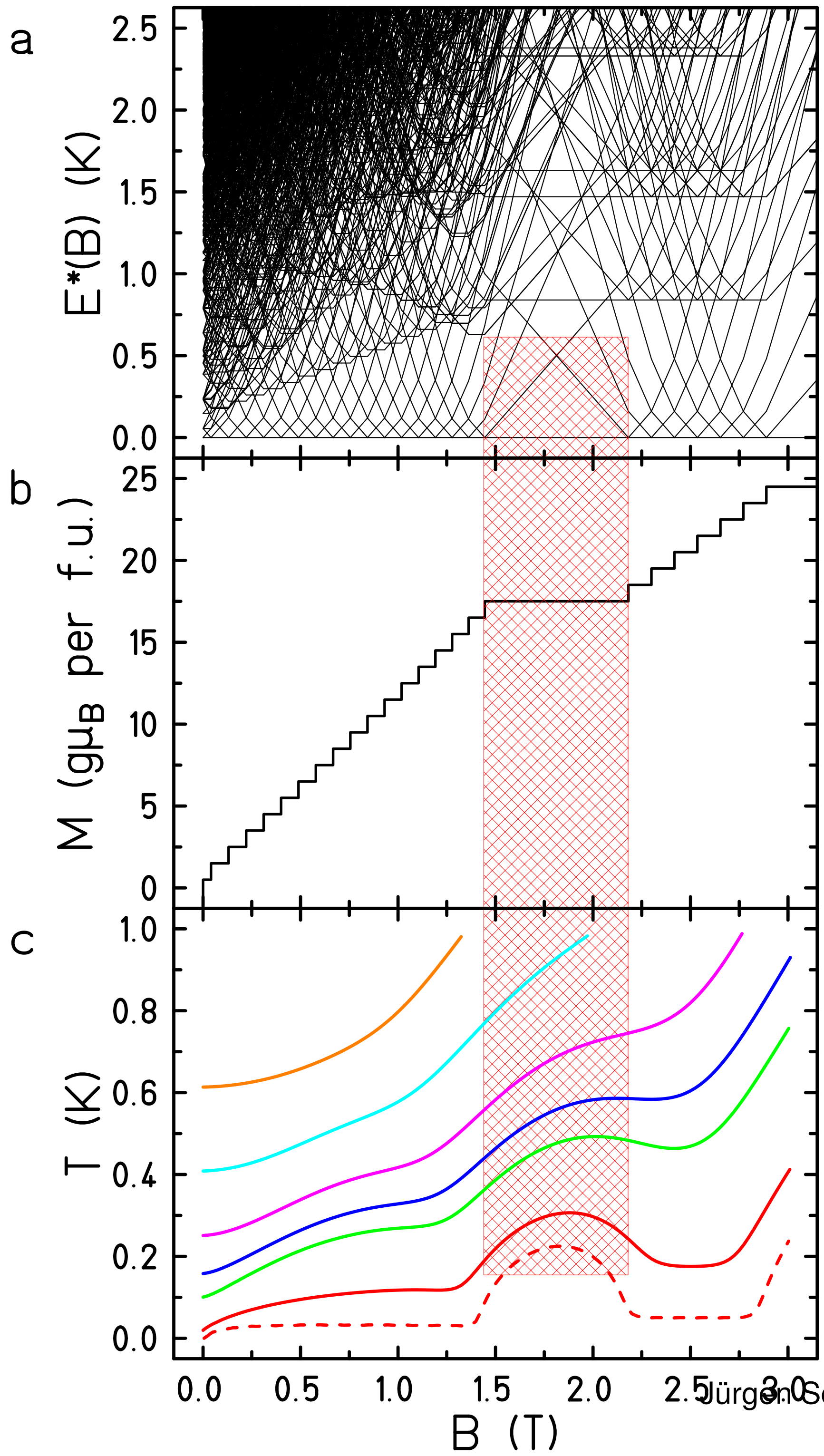
Gd$_7$ – Magnetocalorics

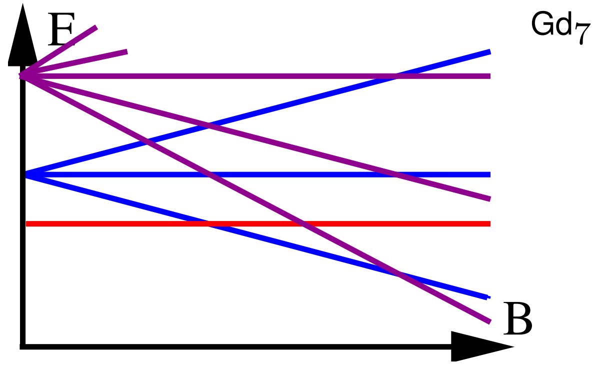


- Often magnetocaloric observables not directly measured, but inferred from Maxwell's relations.
- First real cooling experiment with a molecule.
- $\underset{\sim}{H} = -2\sum_{i<j} J_{ij}\, \underset{\sim}{\vec{s}}_i \cdot \underset{\sim}{\vec{s}}_j + g\,\mu_B\, B \sum_i^N \underset{\sim}{s}_i^z$

  $J_1 = -0.090(5)$ K, $J_2 = -0.080(5)$ K and $g = 2.02$.
- Very good agreement down to the lowest temperatures.

J. W. Sharples, D. Collison, E. J. L. McInnes, J. Schnack, E. Palacios, M. Evangelisti, Nat. Commun. **5**, 5321 (2014).


a
b
c
E*(B) (K)
M (gμB per f.u.)
T (K)
B (T)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
5
10
15
20
25
0.2
0.4
0.6
0.8


Gd7
E
B

What if your molecule is

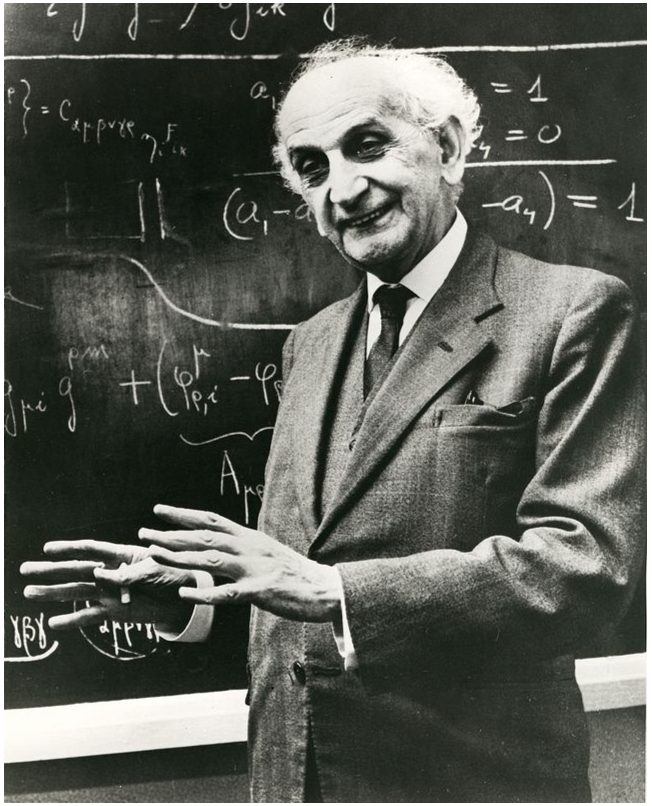
BIGGER?

K-Computer?

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: $\{ \mid \phi \rangle, \underset{\sim}{H} \mid \phi \rangle, \underset{\sim}{H}^2 \mid \phi \rangle, \underset{\sim}{H}^3 \mid \phi \rangle, \dots \}$
- 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).

Finite-temperature Lanczos Method I

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

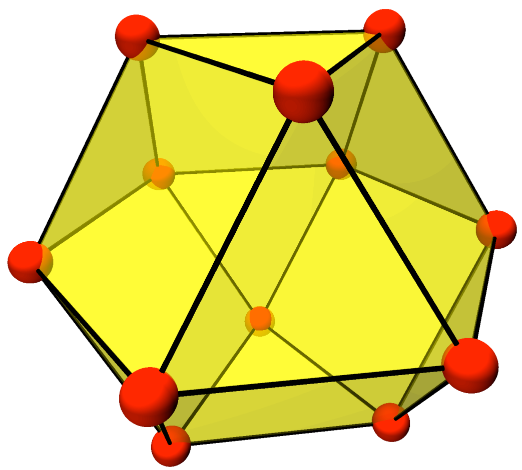
$$\langle \nu \,|\, \exp\left\{-\beta \underset{\sim}{H}\right\} |\, \nu \rangle \approx \sum_n \langle \nu \,|\, n(\nu) \,\rangle \exp\left\{-\beta \epsilon_n\right\} \langle \, n(\nu) \,|\, \nu \,\rangle$$

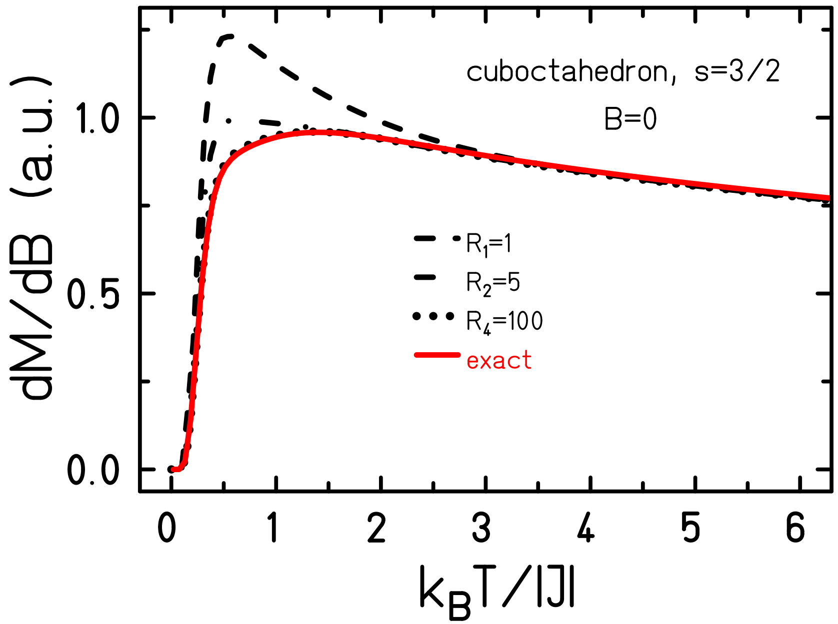
$$Z(T,B) \approx \frac{\text{dim}(\mathcal{H})}{R} \sum_{\nu=1}^{R} \sum_{n=1}^{N_L} \exp\left\{-\beta \epsilon_n\right\} |\langle \, n(\nu) \,|\, \nu \,\rangle|^2$$

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

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

How good is finite-temperature Lanczos?

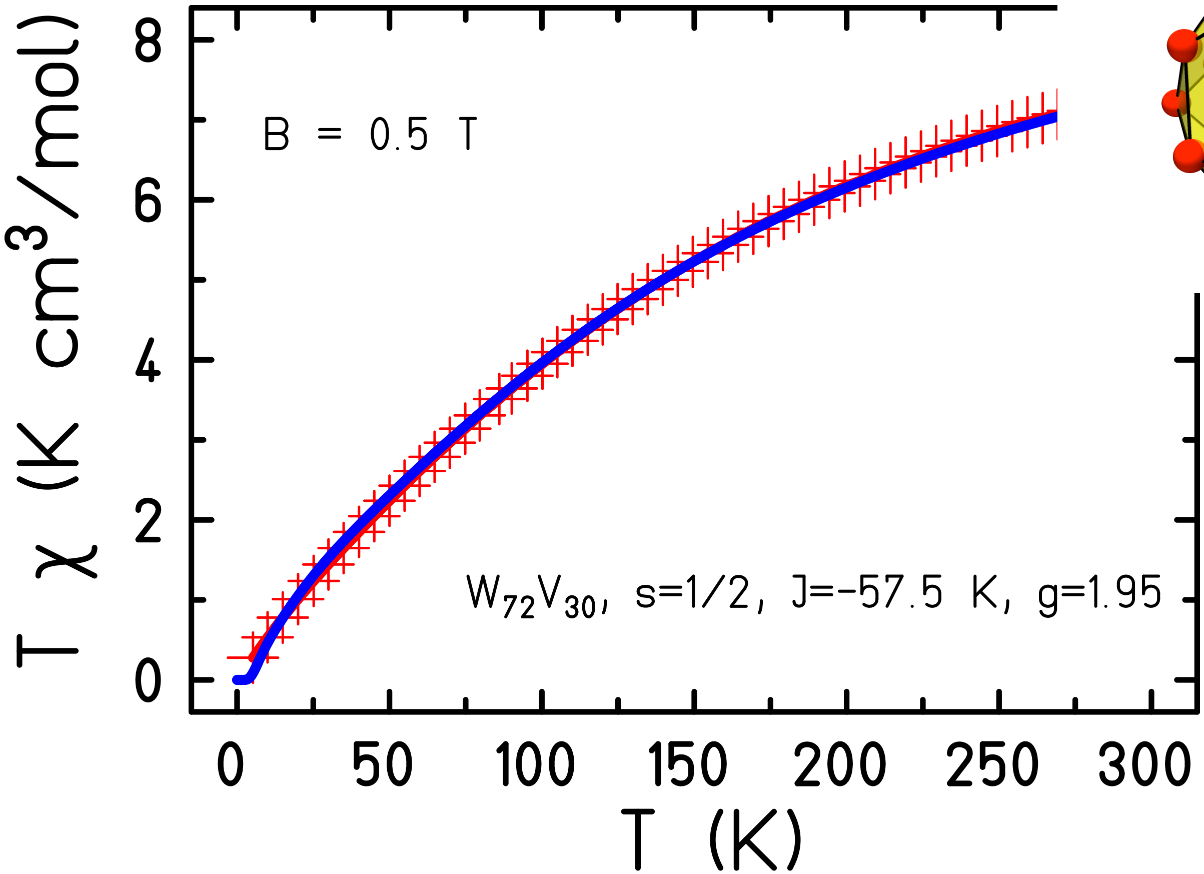


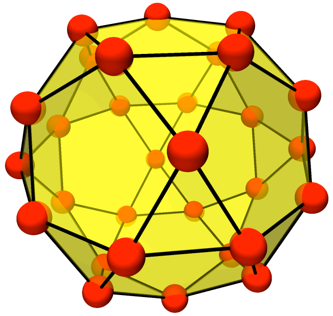


- Works very well: compare frustrated cuboctahedron.
- $N = 12, s = 3/2$: Considered $< 100,000$ states instead of 16,777,216.

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).

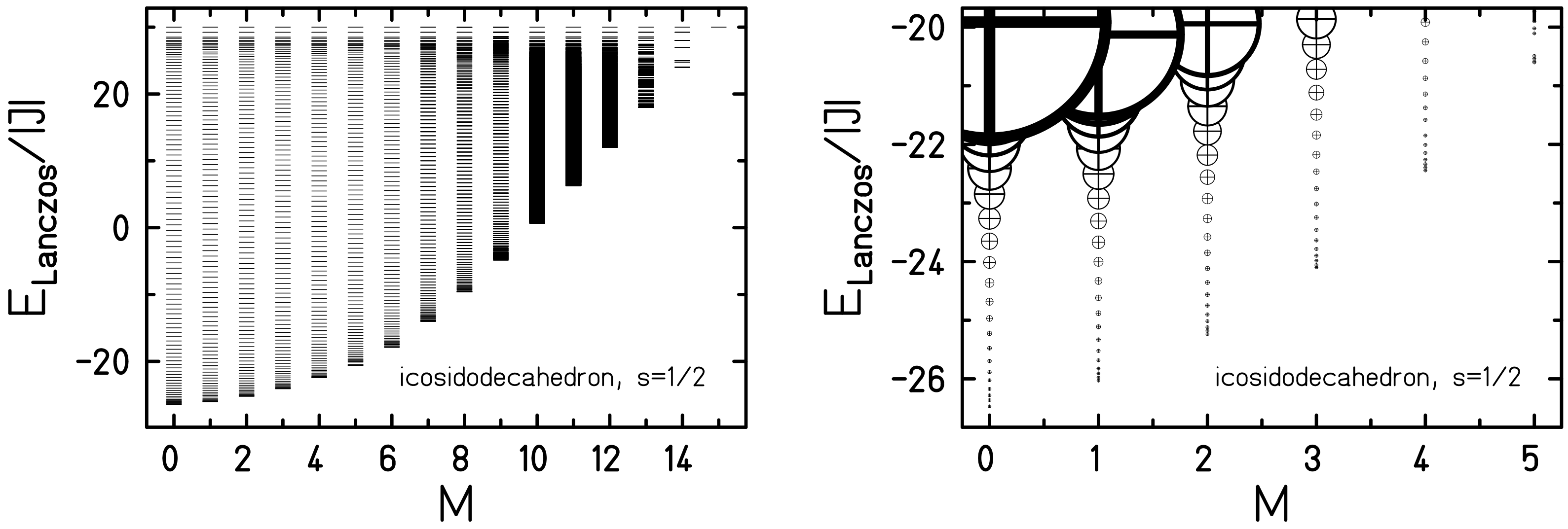
Icosidodecahedron $s = 1/2$





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.

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

Finite-temperature Lanczos Method III

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

- Problem: for anisotropic Hamiltonians no symmetry left $\rightarrow$ accuracy drops (esp. for high T).
- Simple traces such as Tr $\left(\underset{\sim}{S}^z\right) = 0$ tend to be wrong for R not very big.

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

Finite-temperature Lanczos Method IV

Employ very general symmetry (time-reversal invariance)

$$\vec{\mathcal{M}}(T,-\vec{B}) \quad = \quad -\vec{\mathcal{M}}(T,\vec{B})$$

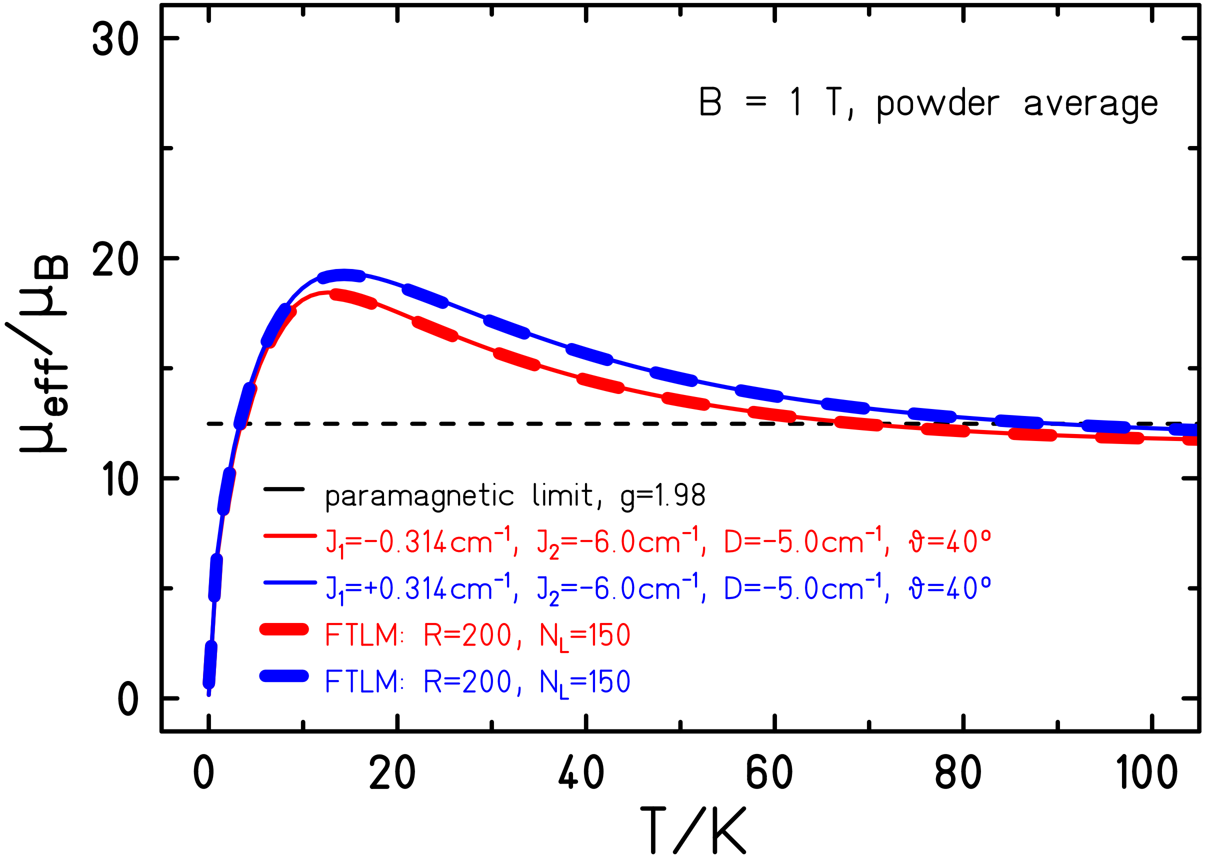
Use Lanczos energy eigenvector $|\,n(\nu)\,\rangle$ and time-reversed counterpart $|\,\tilde{n}(\nu)\,\rangle$

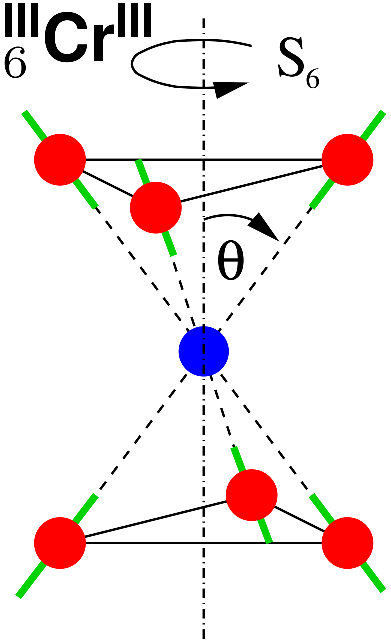
$$|\,n(\nu)\,\rangle = \sum_{\vec{m}} c_{\vec{m}}\,|\,\vec{m}\,\rangle \qquad , \qquad |\,\tilde{n}(\nu)\,\rangle = \sum_{\vec{m}} c^*_{\vec{m}}\,|\,-\vec{m}\,\rangle$$

- Restores $\vec{\mathcal{M}}(T,-\vec{B}) = -\vec{\mathcal{M}}(T,\vec{B})$ and (some) traces.
- More practical: use pairs of time-reversed random vectors; still accurate.

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

Glaser-type molecules: $Mn^{III}_6Cr^{III}$





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

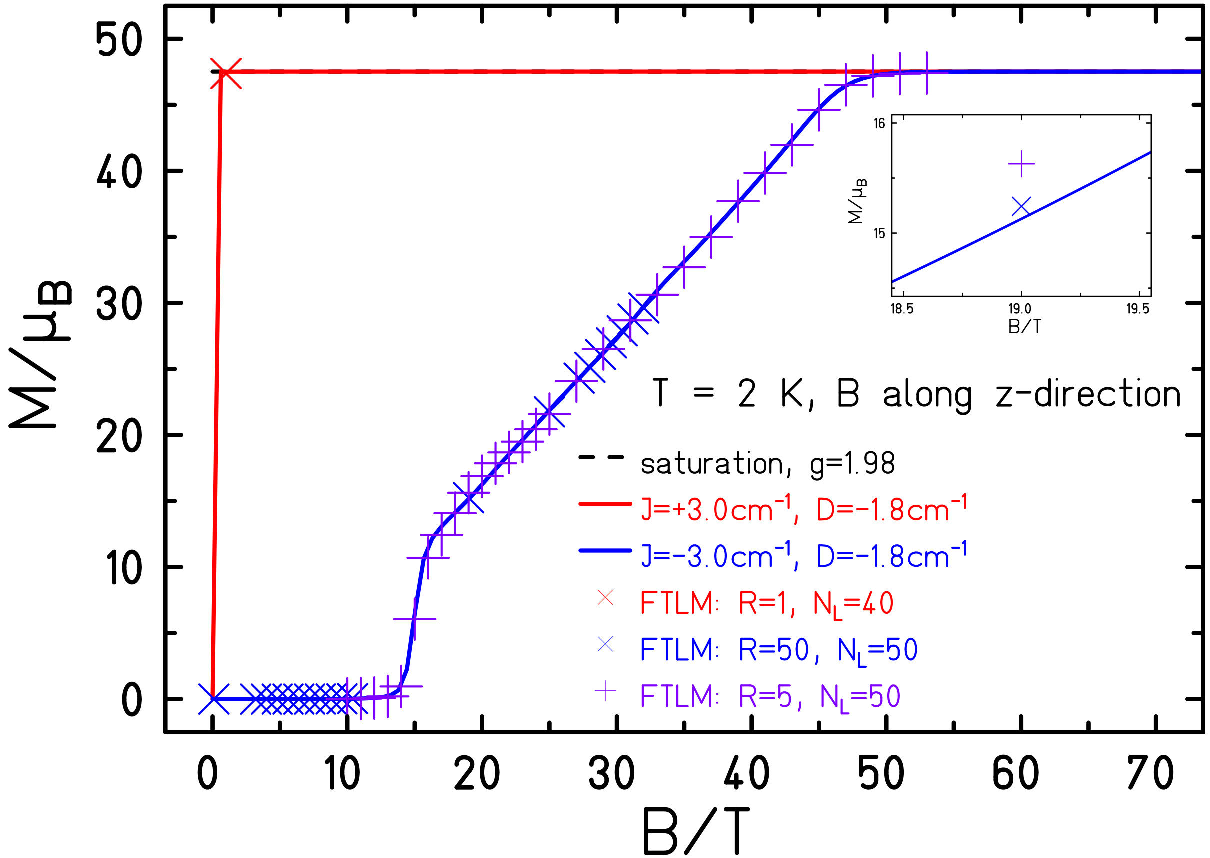
$\dim(\mathcal{H}) = 62,500$

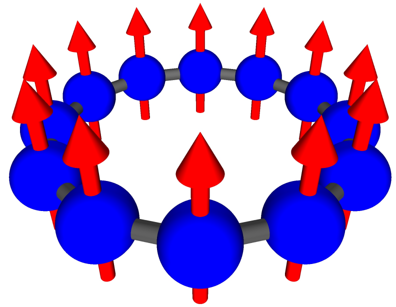
non-collinear easy axes

Hours compared to days, notebook compared to supercomputer!

O. Hanebaum, J. Schnack, Eur. Phys. J. B **87**, 194 (2014)
T. Glaser, Chem. Commun. **47**, 116-130 (2011)

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





$s = 2$

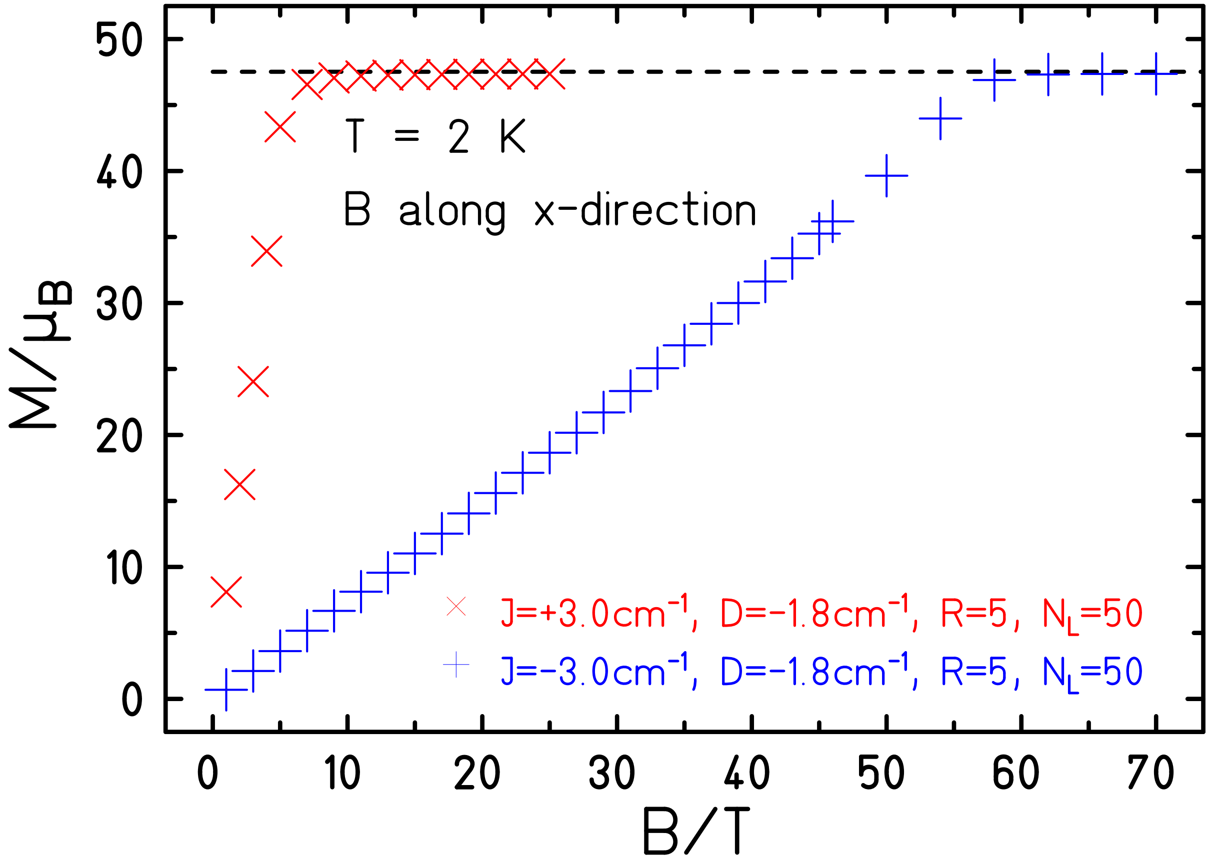
dim$(\mathcal{H}) = 244,140,625$

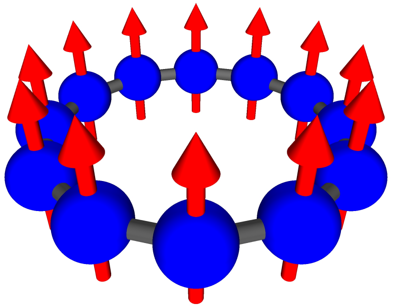
collinear easy axes

A few days compared to *impossible*!

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

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

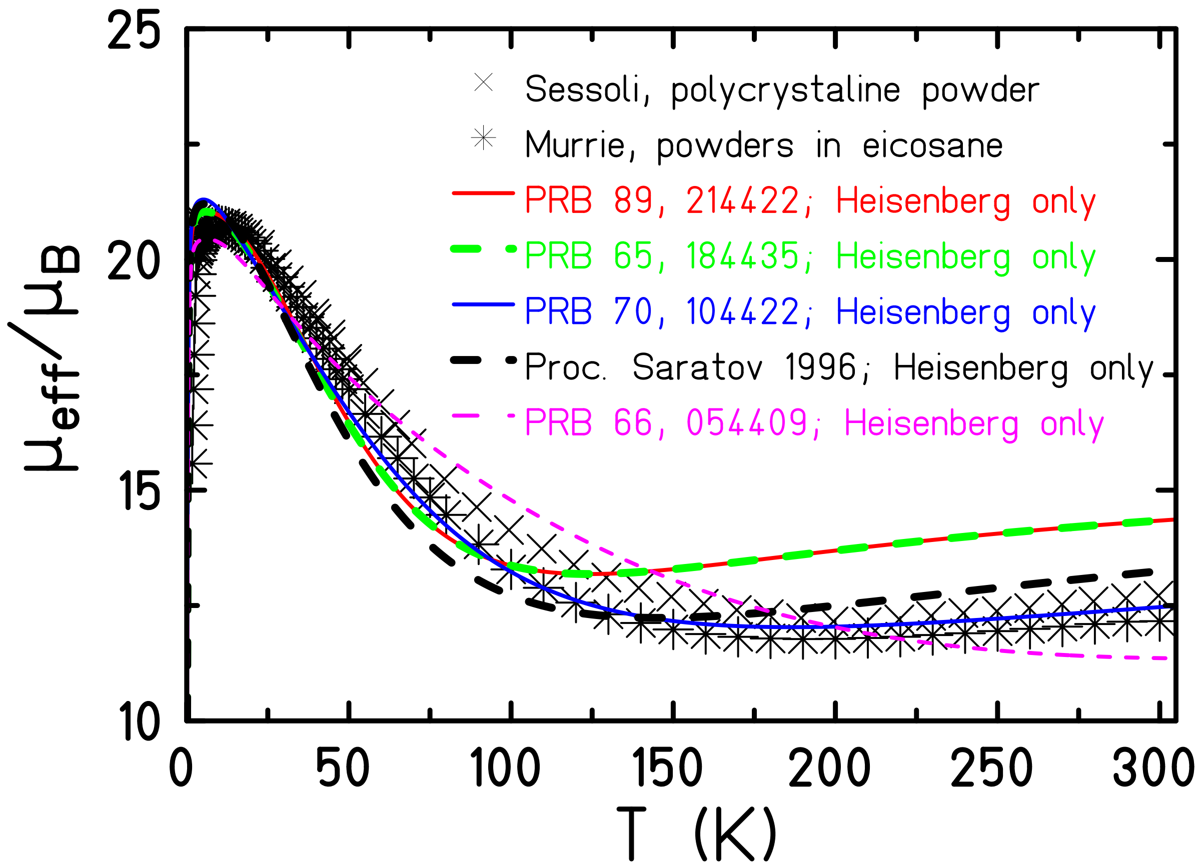




No other method can deliver these curves!

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

Effective magnetic moment of Mn_{12}-acetate



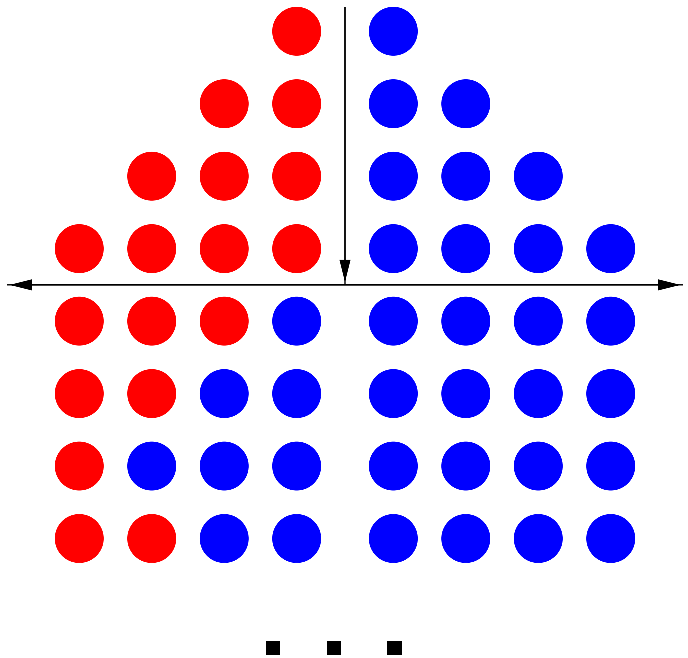
We can check DFT parameter predictions for large molecules!

O. Hanebaum, J. Schnack, Phys. Rev. B **92** (2015) 064424

Density Matrix Renormalization Group

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

Density Matrix Renormatization Group

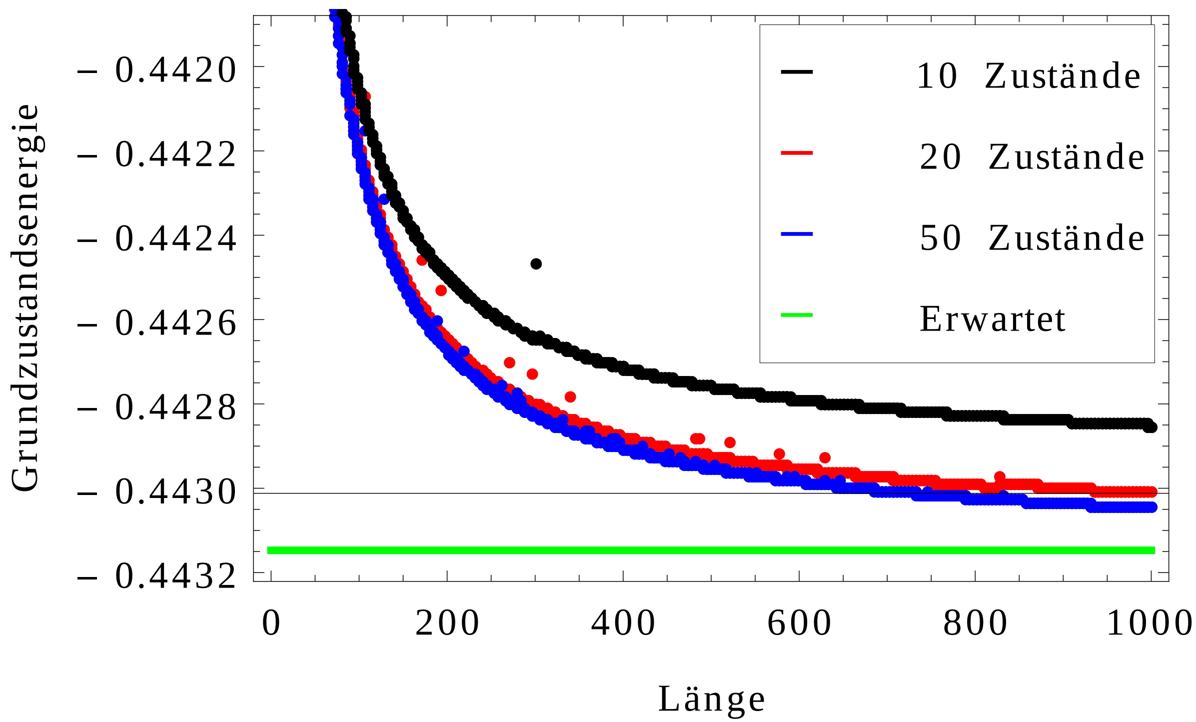


Again: build your appropriate reduced basis set

- 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.

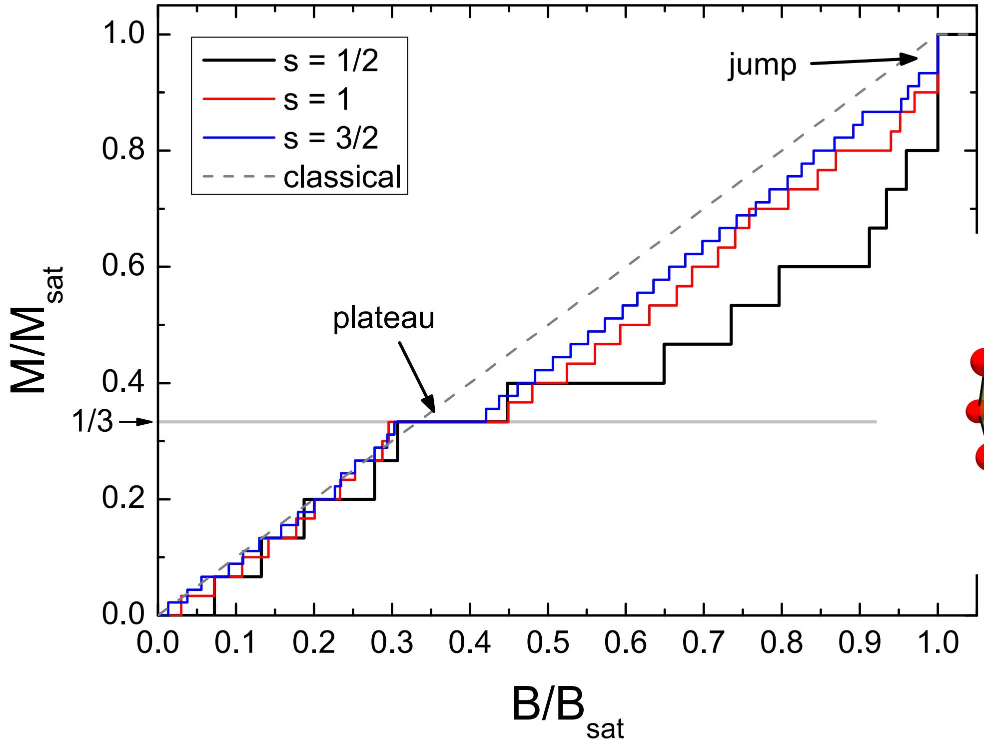
(1) S. R. White, Phys. Rev. Lett. **69**, 2863 (1992).
(2) S. R. White, Phys. Rev. B **48**, 10345 (1993).
(3) U. Schollwöck, Rev. Mod. Phys. **77**, 259 (2005).

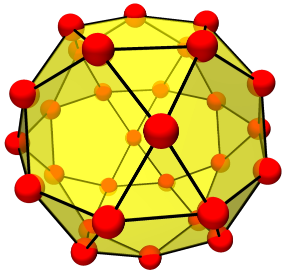
DMRG spin chain $s = 1/2$



- 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

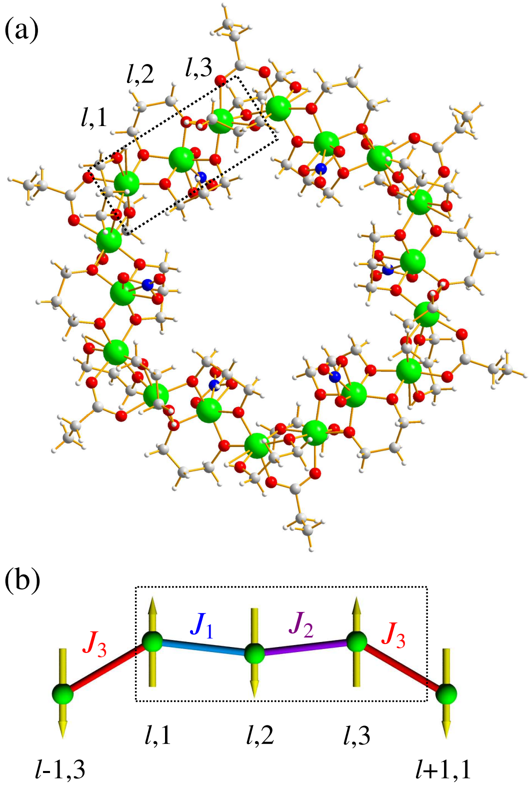




- DMRG yields ground states + very few low-lying states in orthogonal subspaces.
- Magnetization curve for $T = 0$, resonance energies for spectroscopy.

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

Dynamical Density Matrix Renormatization Group

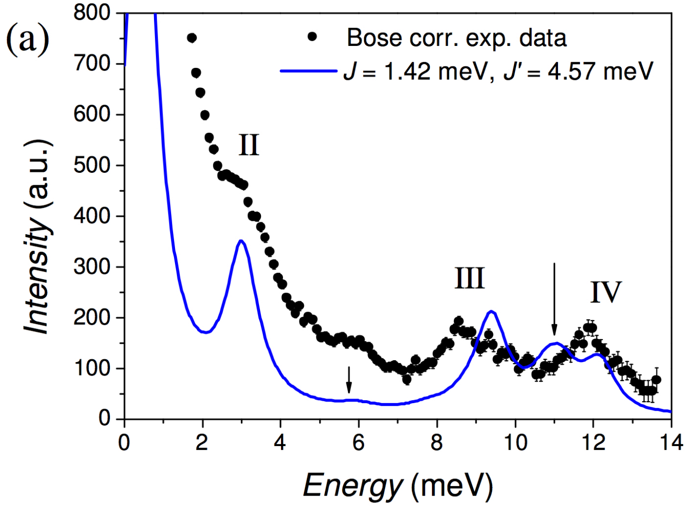


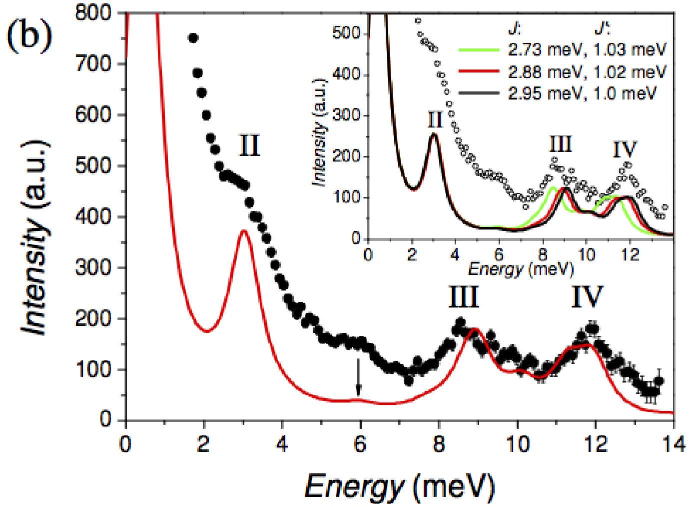
Evaluation of correlation functions, e.g. for INS:

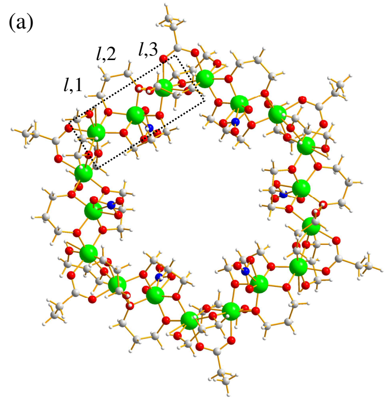
- $S^{zz}_{jj'}(\omega) \equiv \sum_n \langle 0|\underset{\sim}{s}^z_j|n\rangle\langle n|\underset{\sim}{s}^z_{j'}|0\rangle\, \delta(\hbar\omega - E_n + E_0)$; transitions from the ground state;
- $S^{zz}_{jj'}(\omega) \approx \frac{1}{\pi}\langle 0|\underset{\sim}{s}^z_j \frac{\eta}{(E_0+\hbar\omega-\underset{\sim}{H})^2+\eta^2}\underset{\sim}{s}^z_{j'}|0\rangle$;
- 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}.

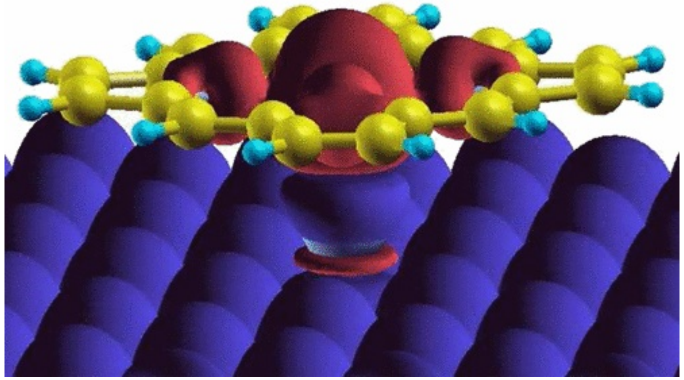
- Determination of model parameters.

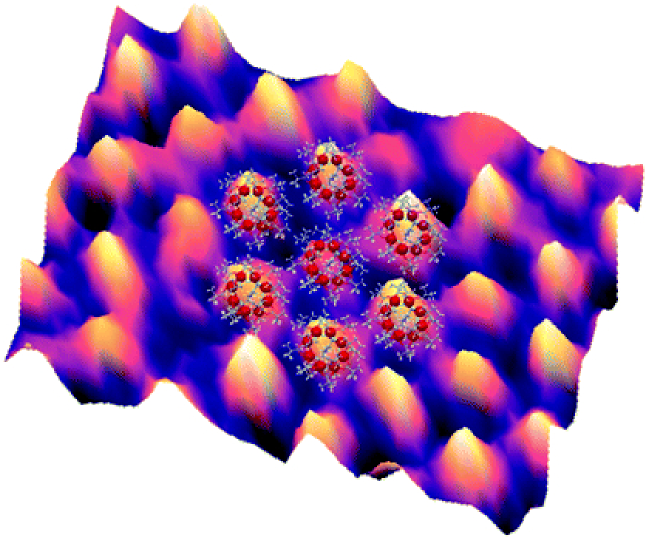
(1) J. Ummethum, J. Nehrkorn, S. Mukherjee, N. B. Ivanov, S. Stuiber, Th. Strässle, P. L. W. Tregenna-Piggott, H. Mutka, G. Christou, O. Waldmann, J. Schnack, Phys. Rev. B **86**, 104403 (2012).

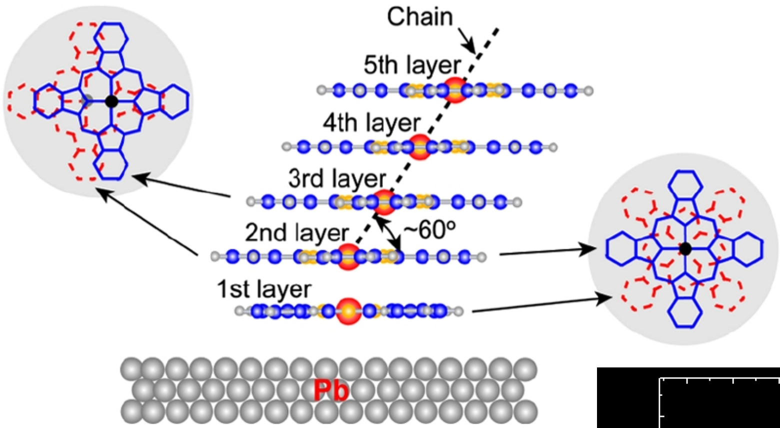
Numerical Renormalization Group calculations

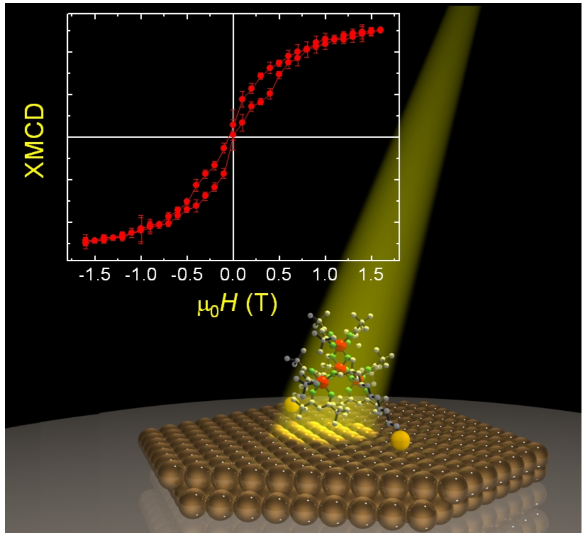
(Good for deposited molecules.)

You want to deposite a molecule



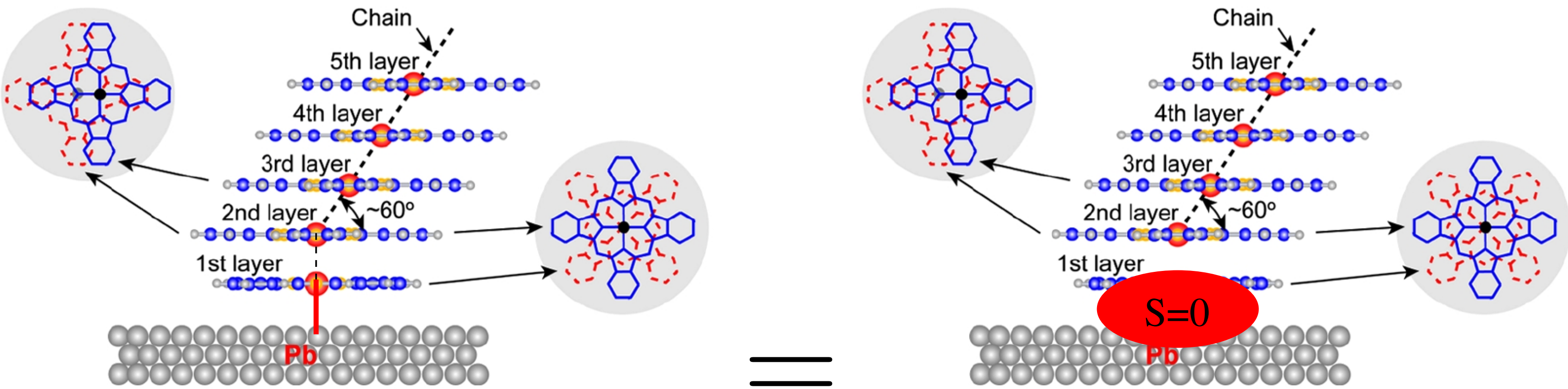






M. Bernien *et al.*, Phys. Rev. Lett. **102**, 047202 (2009); A. Ghirri*et al.*, ACS Nano, **5**, 7090-7099 (2011); X. Chen *et al.*, Phys. Rev. Lett. **101**, 197208 (2008); M. Mannini *et al.*, Nature Materials **8**, 194 - 197 (2009).

Physical example (ICMM 2010)

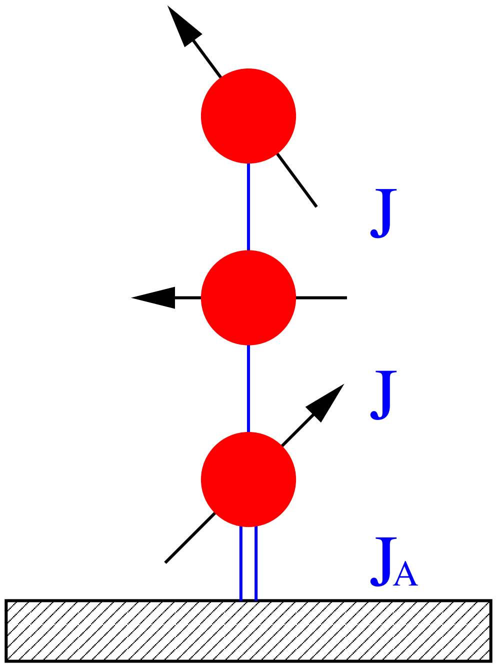


Stack of deposited Cobalt phthalocyanine (CoPc) molecules;
Co^{2+} with spin $s = 1/2$.

Under which circumstances is the picture of total screening correct?

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

NRG – minimal model (already an approximation!)



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

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

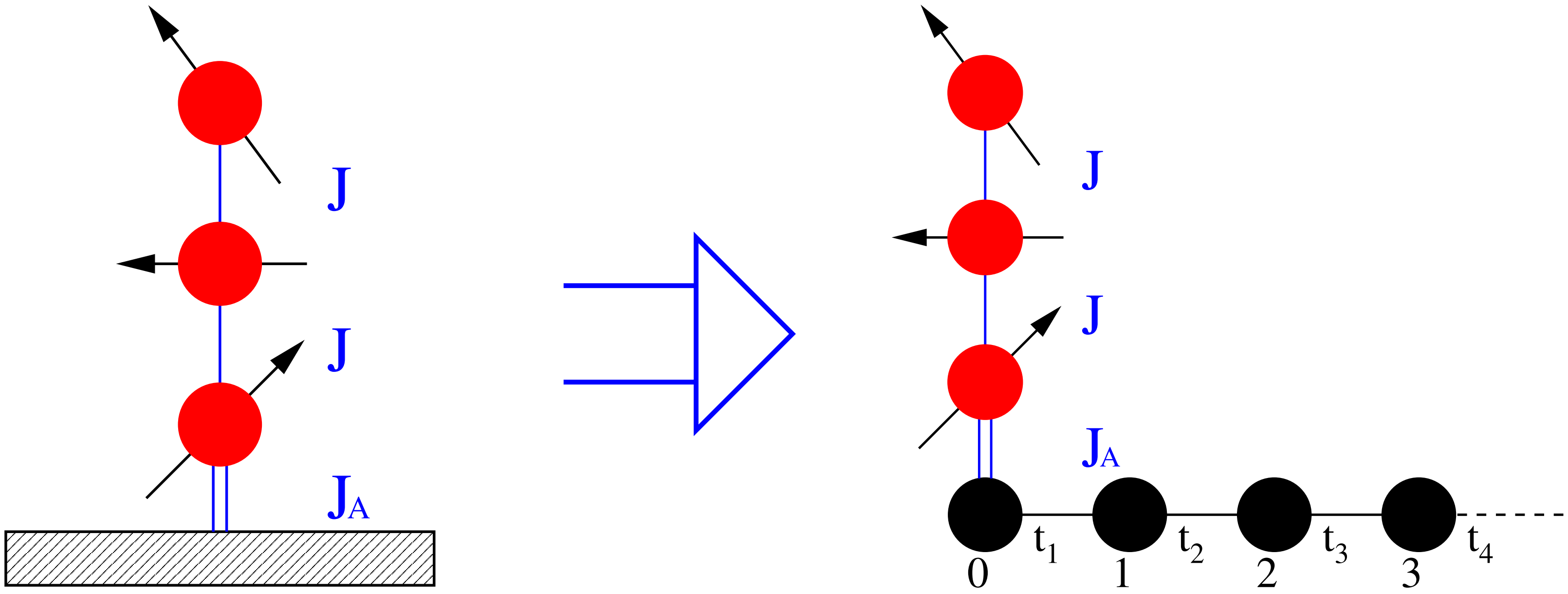
  $\underset{\sim}{H}_{\text{coupling}} = -2 J_A \underset{\sim}{\boldsymbol{S}} \cdot \underset{\sim}{\boldsymbol{s}}_0$, $\underset{\sim}{\boldsymbol{s}}_0$ – spin density at contact

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

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

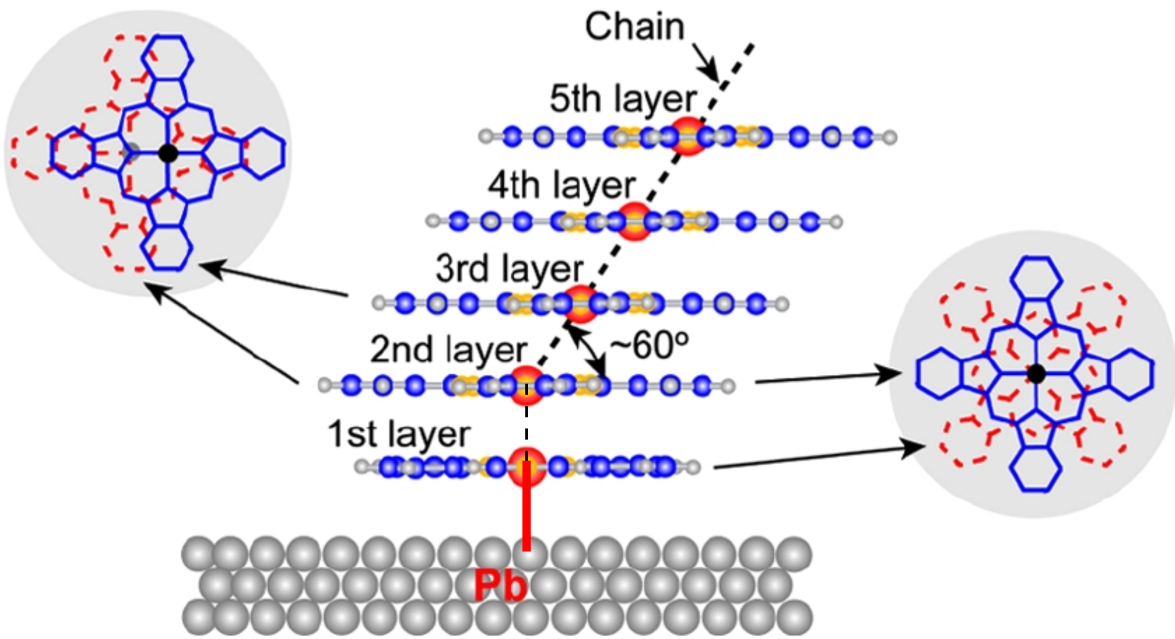
(1) K. G. Wilson, Rev. Mod. Phys. **47**, 773 (1975)
(2) M. Höck, J. Schnack, Phys. Rev. B **87**, 184408 (2013)
(3) *Impurity* is a technical term in this context and not an insult to chemists.

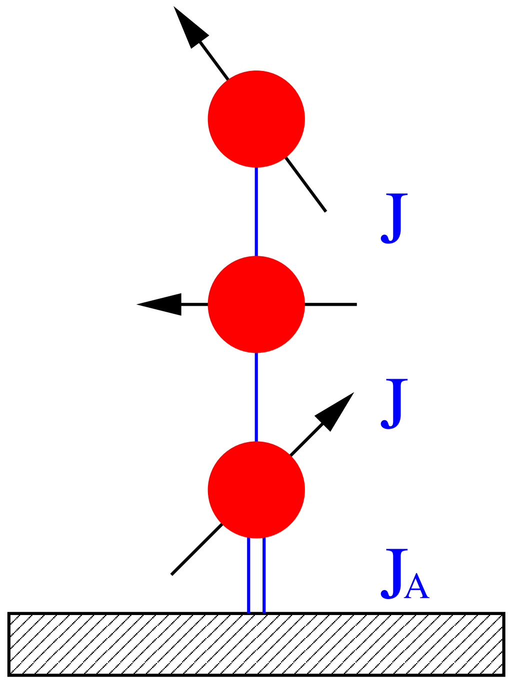
NRG in a cartoon



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.

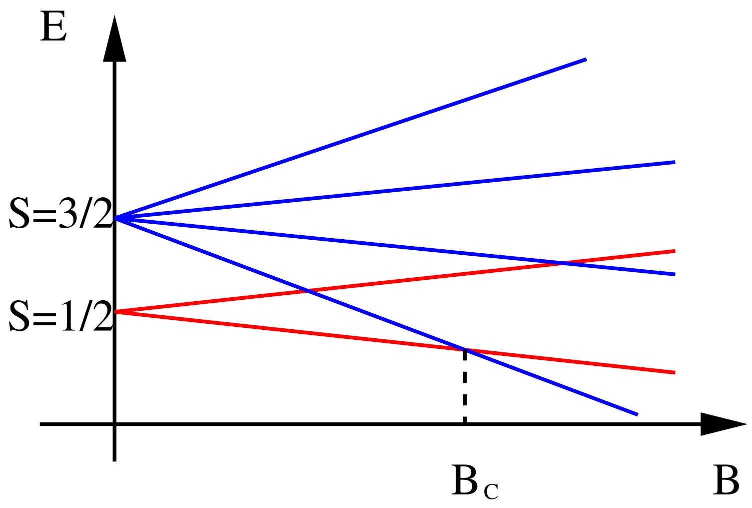
Once more: deposited chain



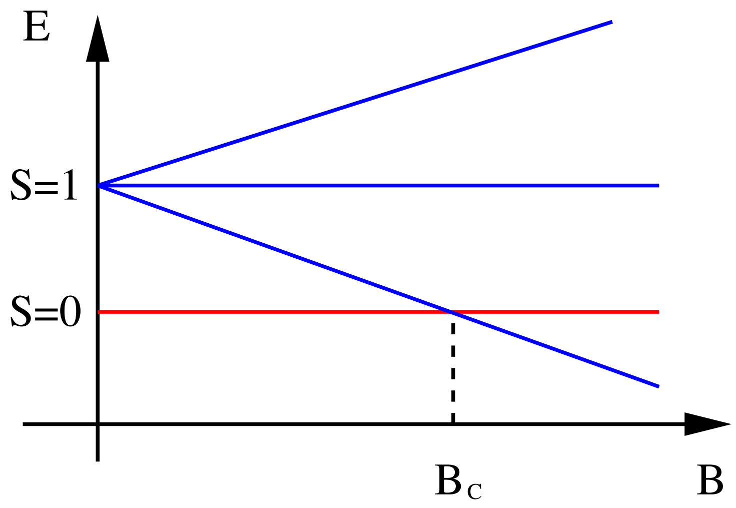


X. Chen *et al.*, Phys. Rev. Lett. **101**, 197208 (2008).

Energy levels of limiting cases for deposited trimer



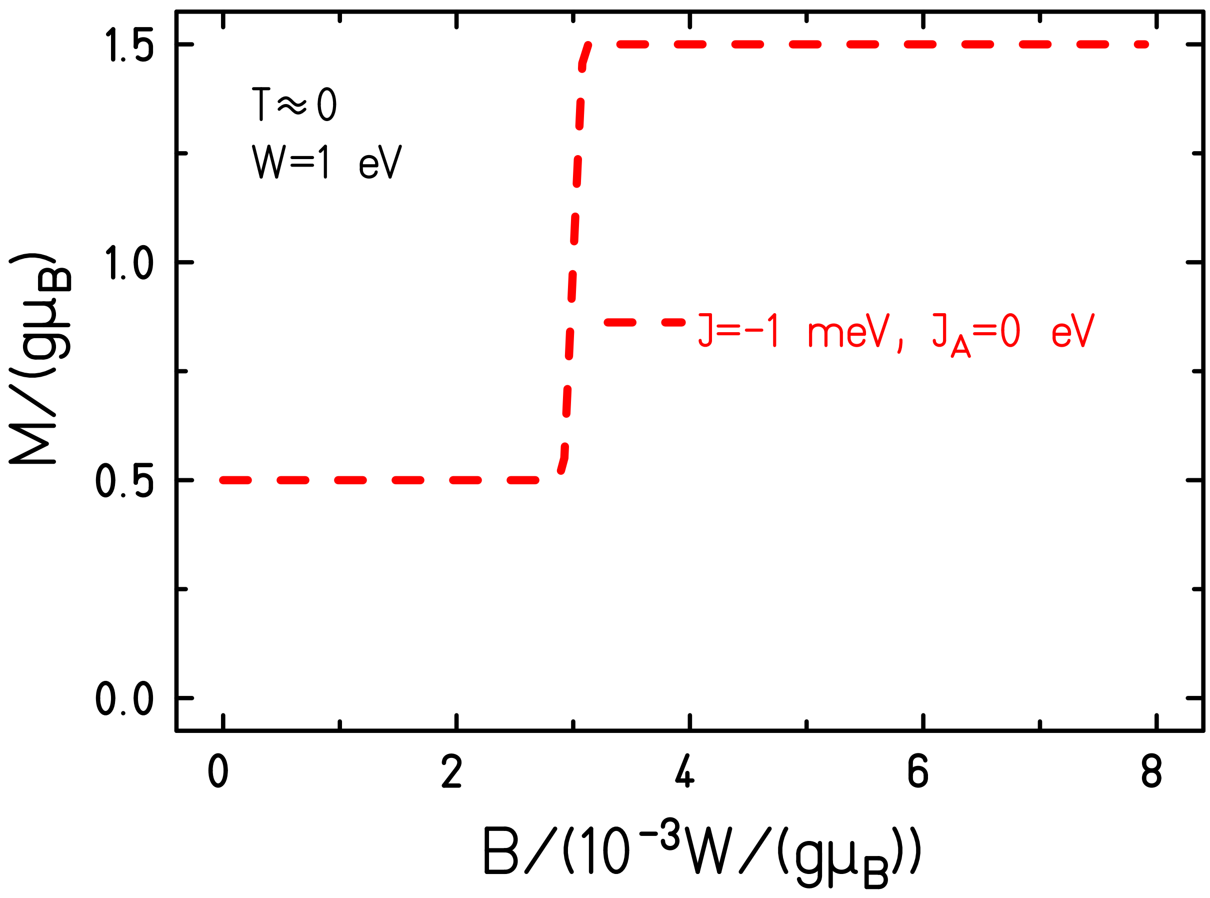
- energy levels of a trimer

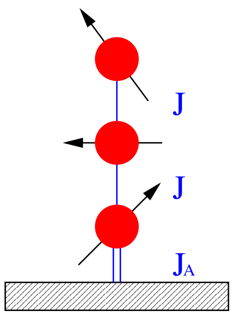


- energy levels of a dimer

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.

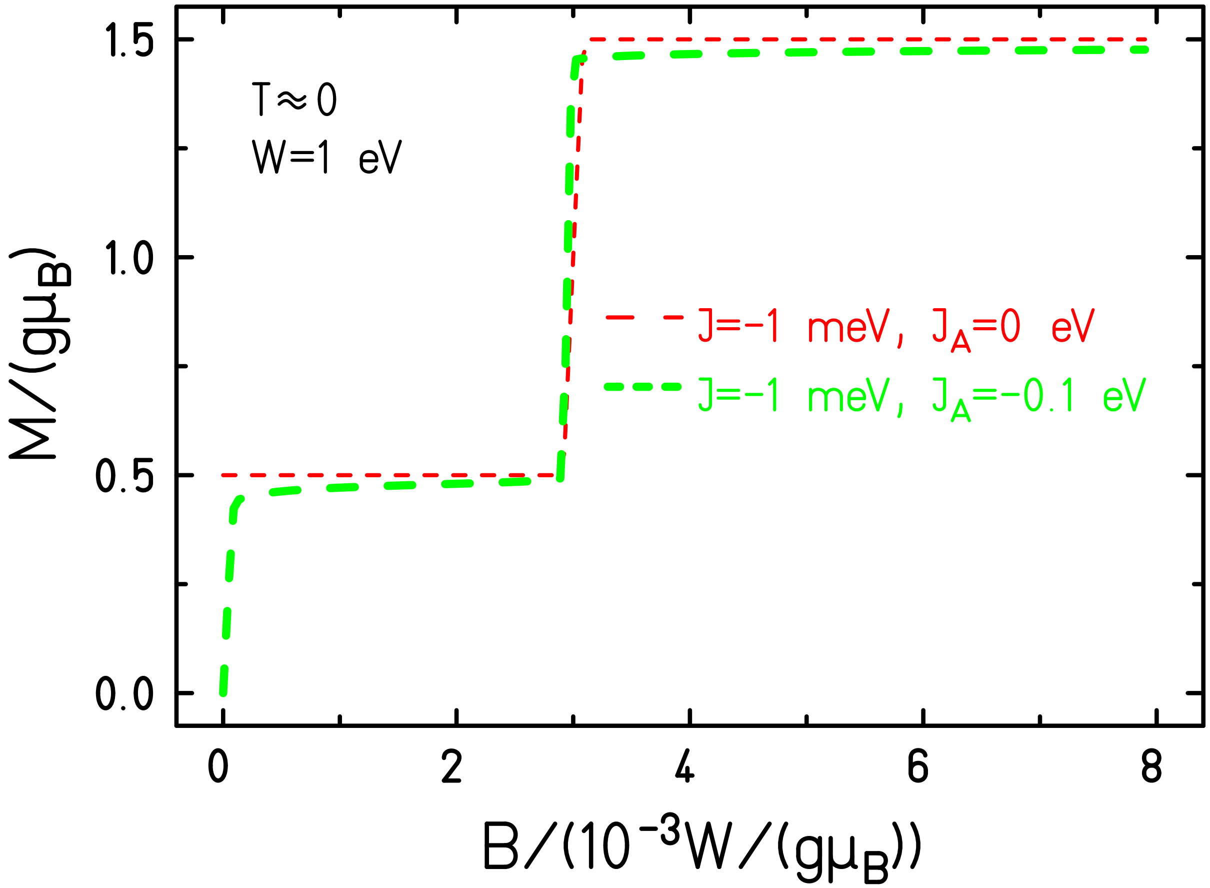
Increasing coupling to the substrate

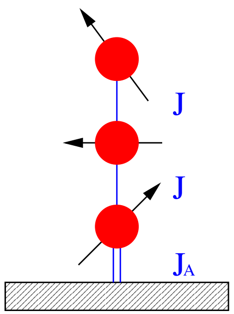




H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

Increasing coupling to the substrate





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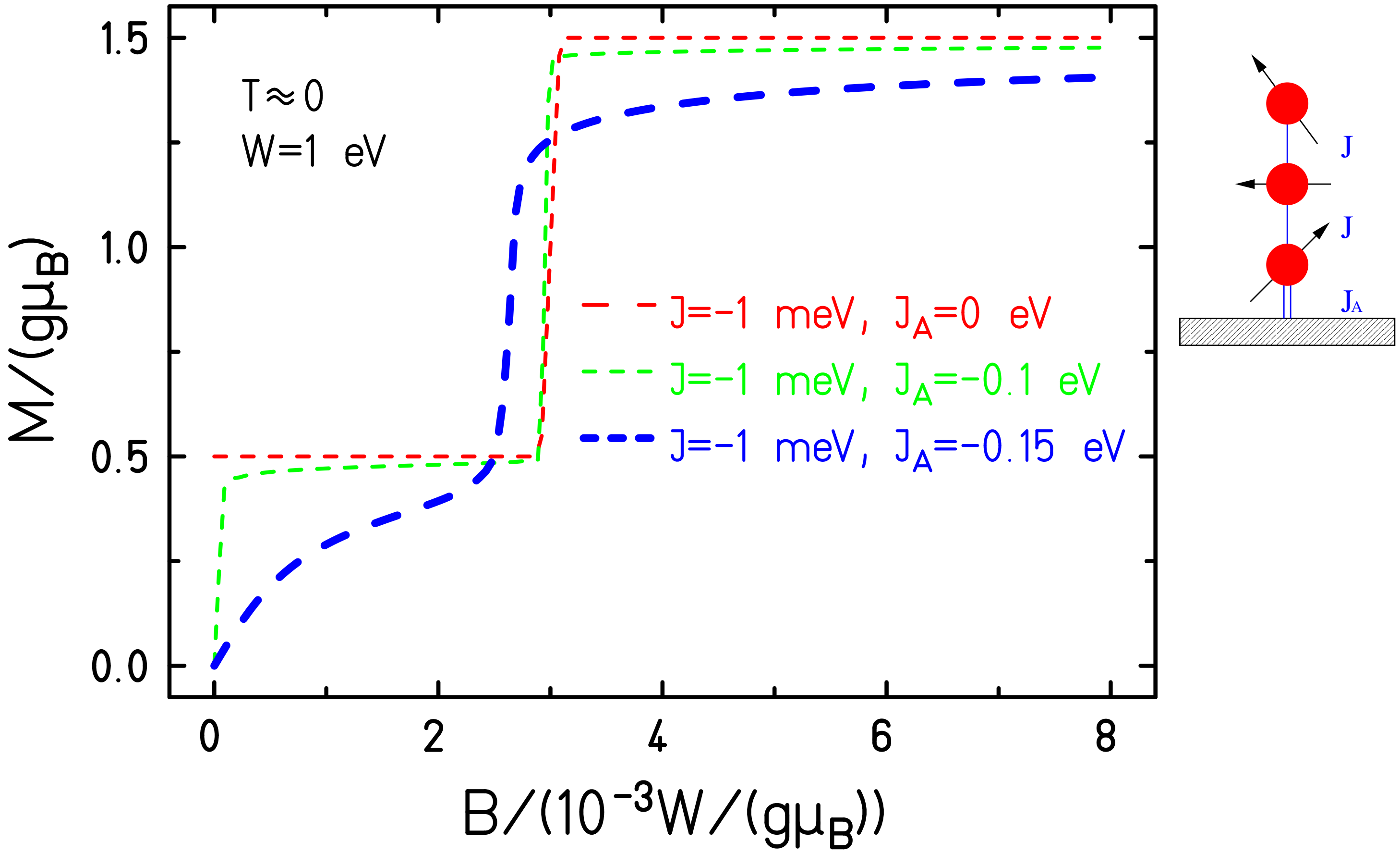

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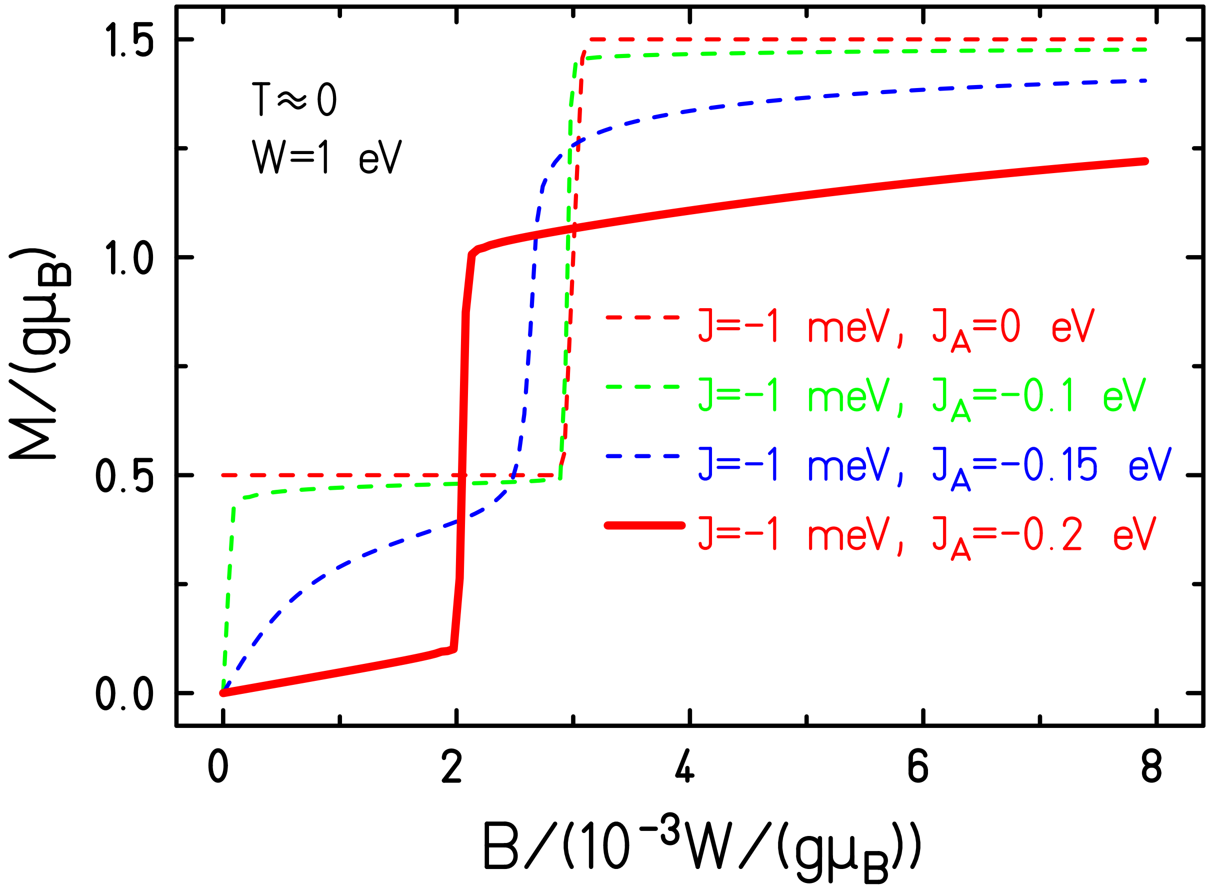

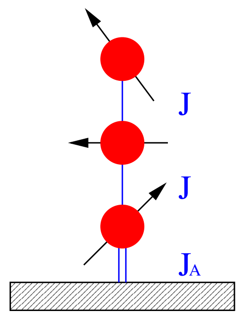

H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

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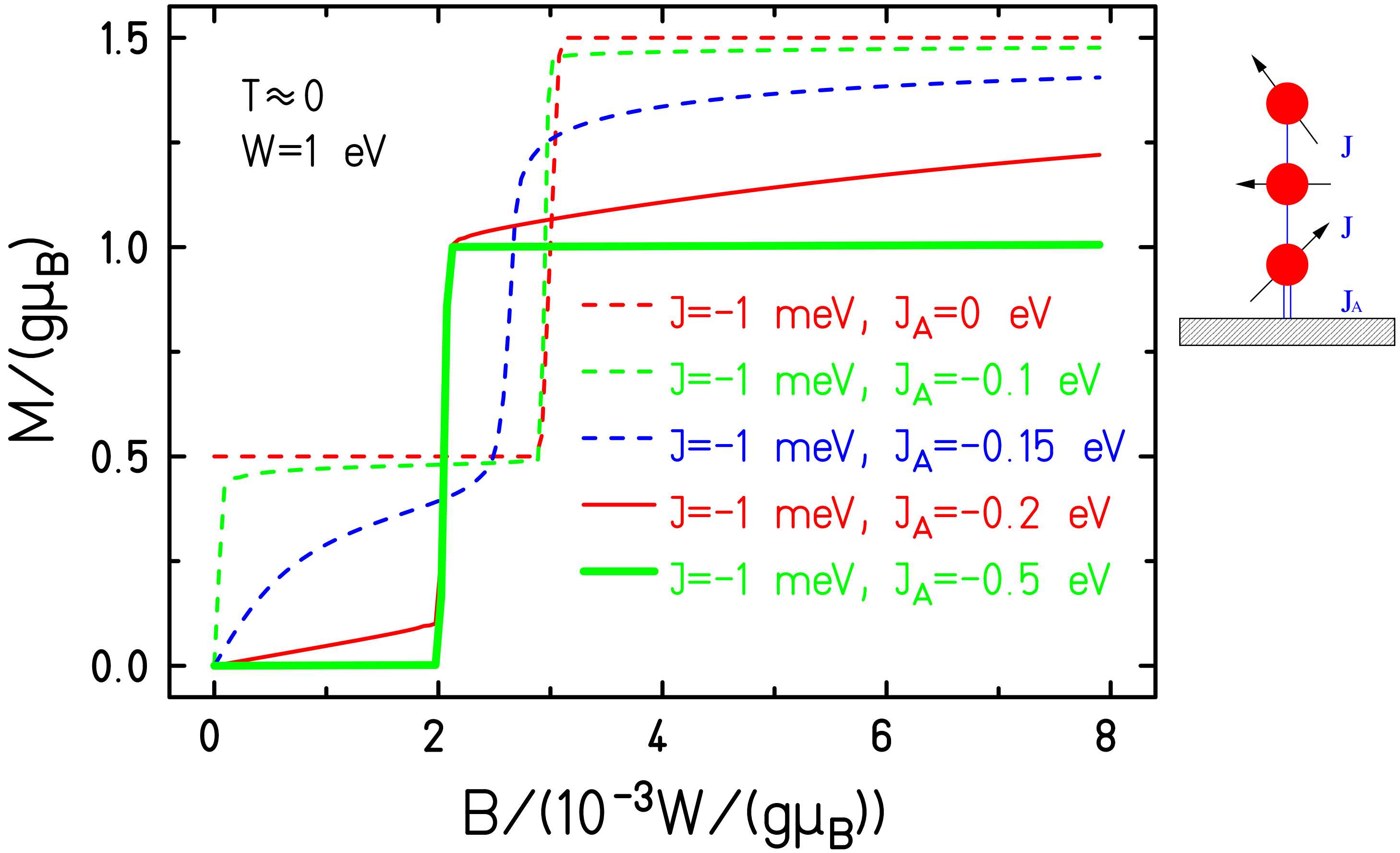

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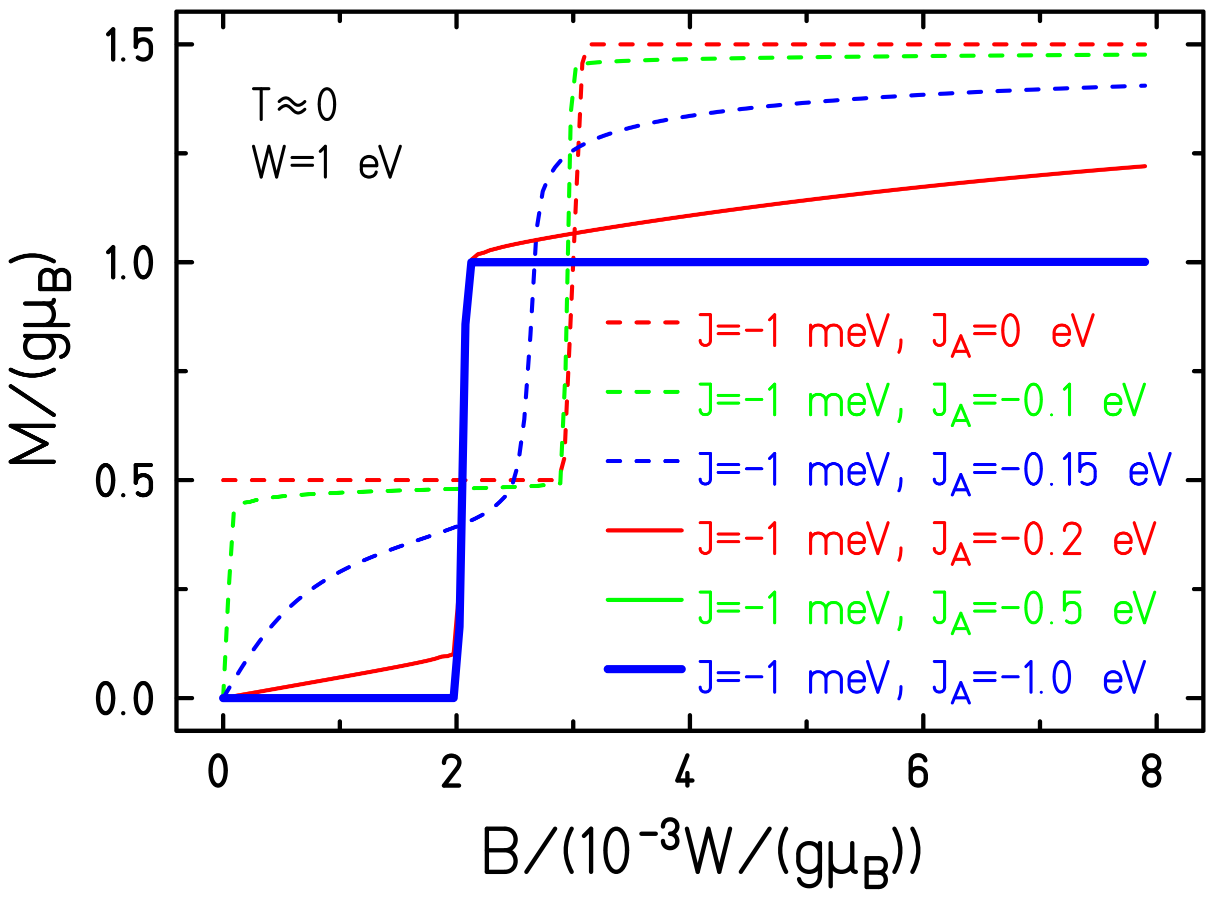
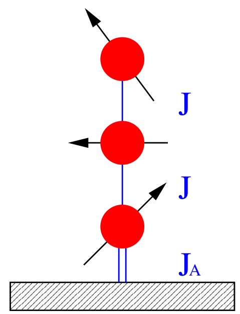
Increasing coupling to the substrate





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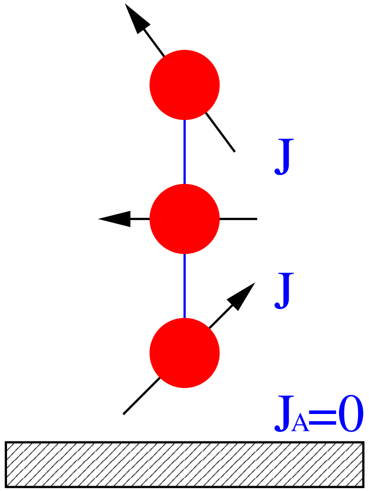
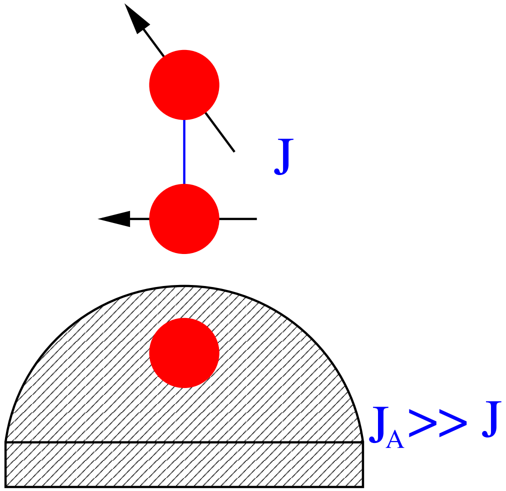
Weak vs. strong coupling



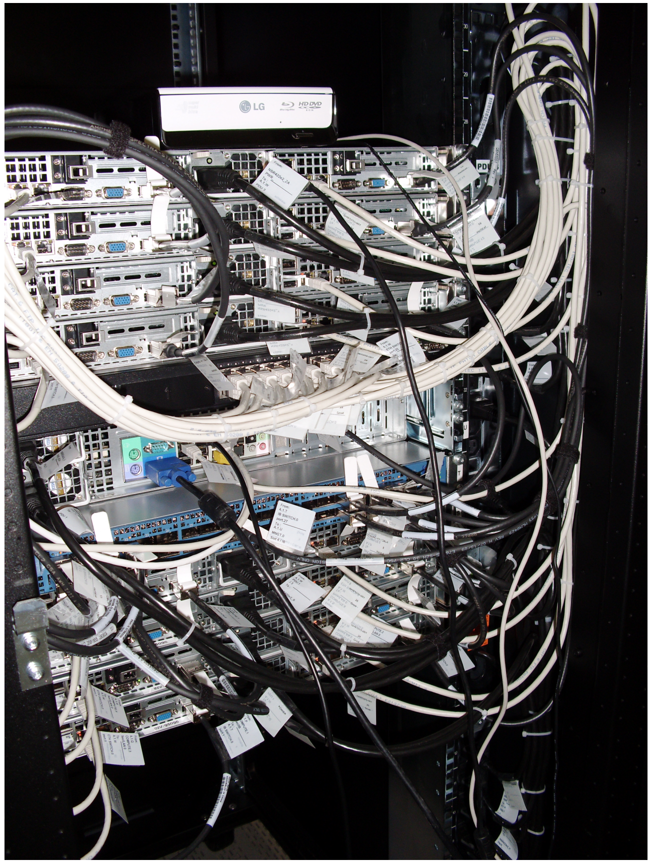


- weak coupling limit:
  unperturbed molecule (trimer)
- strong coupling limit:
  effective remainder (dimer)

- $|J_A| \lessapprox 0.1W$
- $|J_A| \gtrapprox 0.5W$

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}. The accuracy is amazing!
- FTLM works for anisotropic spin systems.
- Magnetic molecules for storage, q-bits, MCE, and since they are nice.

Many thanks to my collaborators worldwide

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Thank you very much for your attention.

The end.

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