What advanced quantum many-body methods teach us about molecular magnetism
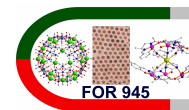
Jürgen Schnack

Department of Physics – University of Bielefeld – Germany

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

Condensed matter seminar, Clarendon Laboratory
Physics, University of Oxford, 9. 2. 2017

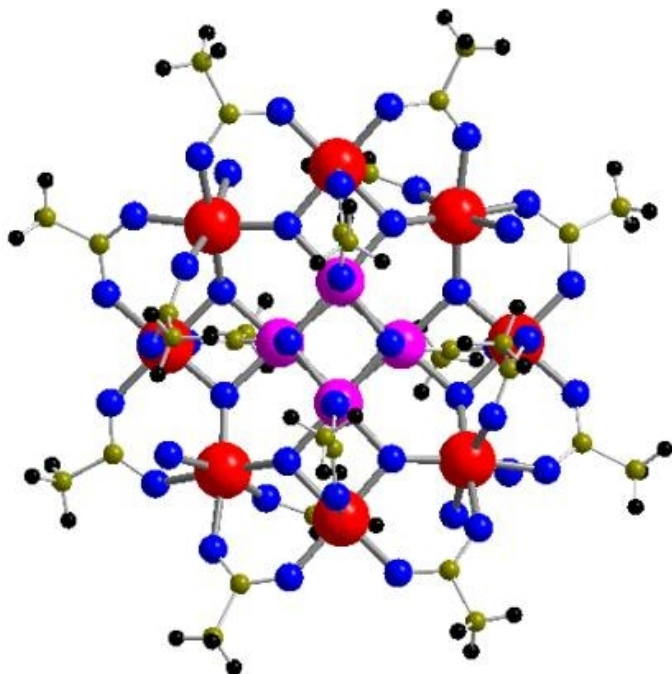Universität Bielefeld

DFG

FOR 945

lrz

If you have got a question, please ask.

Beauty of Magnetic Molecules

The beauty of magnetic molecules I

Mn$_{12}$
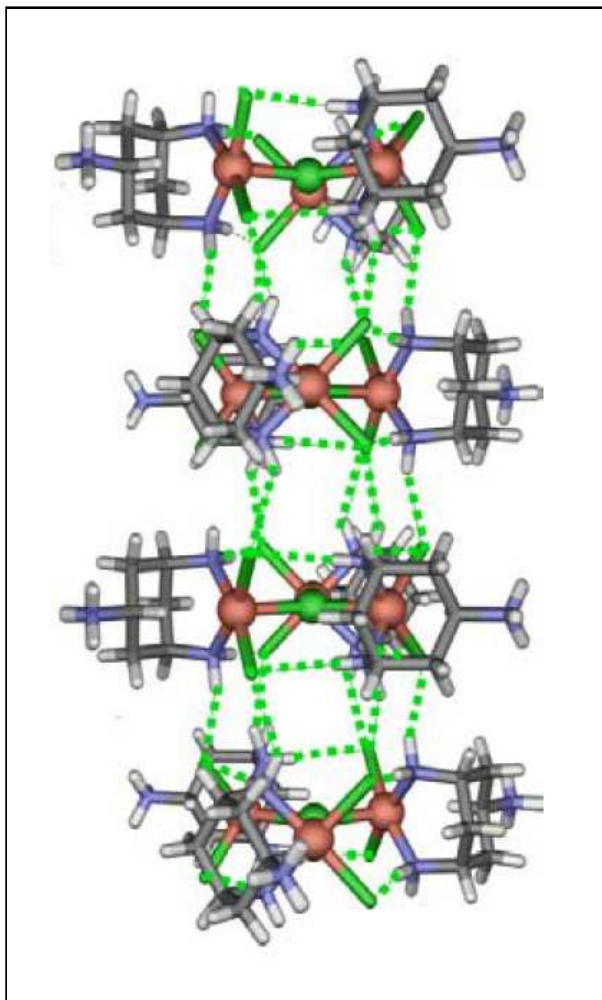
- Inorganic or organic macro molecules, e.g. poly-oxometalates, where paramagnetic ions such as Iron (Fe), Chromium (Cr), Copper (Cu), Nickel (Ni), Vanadium (V), Manganese (Mn), or rare earth ions are embedded in a host matrix;

- 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
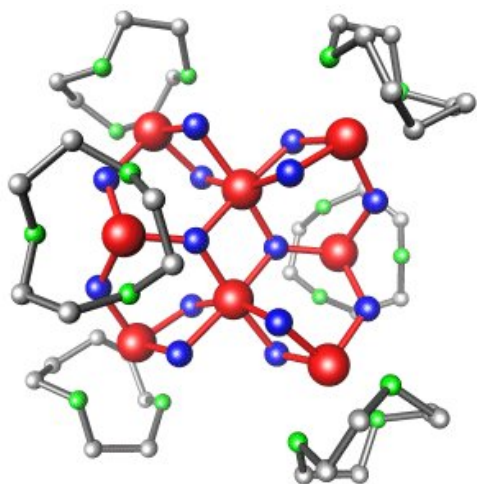
The beauty of magnetic molecules II

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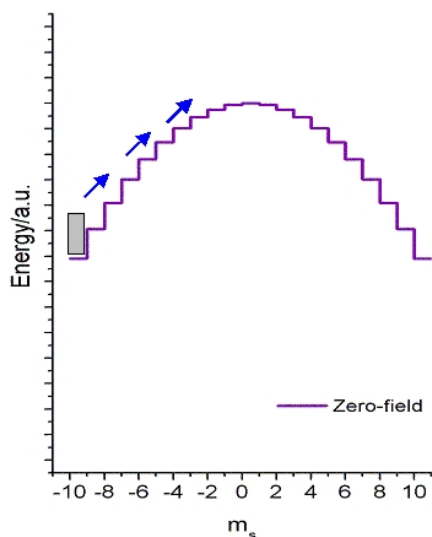
  J. Schnack, H. Nojiri, P. Kögerler, G. J. T. Cooper, L. Cronin, Phys. Rev. B 70, 174420 (2004)

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;

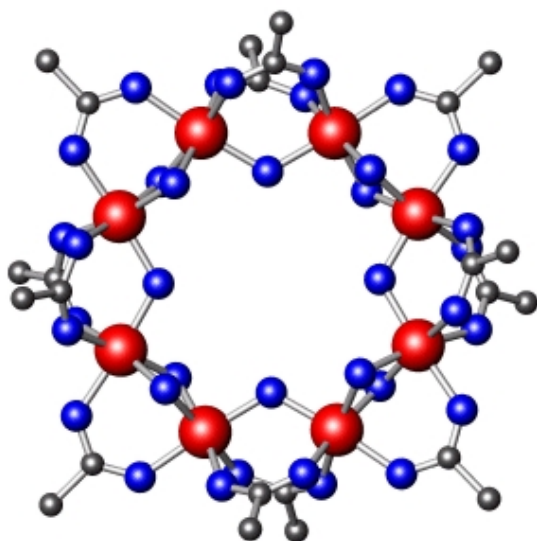- Anisotropy dominates approximate single-spin Hamiltonian:

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

- 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; investigation of frustration effects;

- Transition quantum spin system ($s = 1/2$) $\Rightarrow$ classical spin system ($s_{\mathsf{Fe}} = 5/2$, $s_{\mathsf{Gd}} = 7/2$);

- 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.
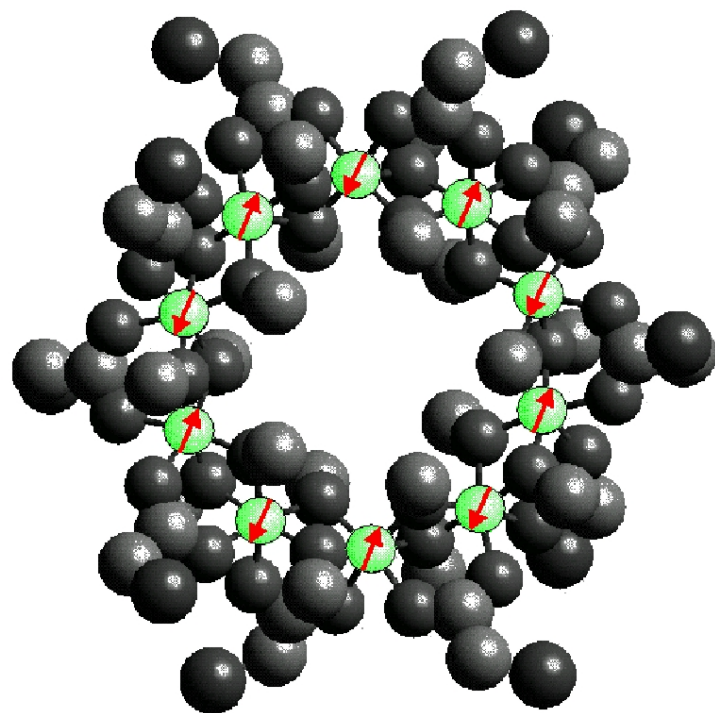
Contents for you today

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

1. Beauty of magnetic molecules $\sqrt{}$

2. Some basic theory

3. Finite-Temperature Lanczos

4. QMC: intermolecular interactions

5. DMRG: neutron scattering

6. NRG: deposited molecules

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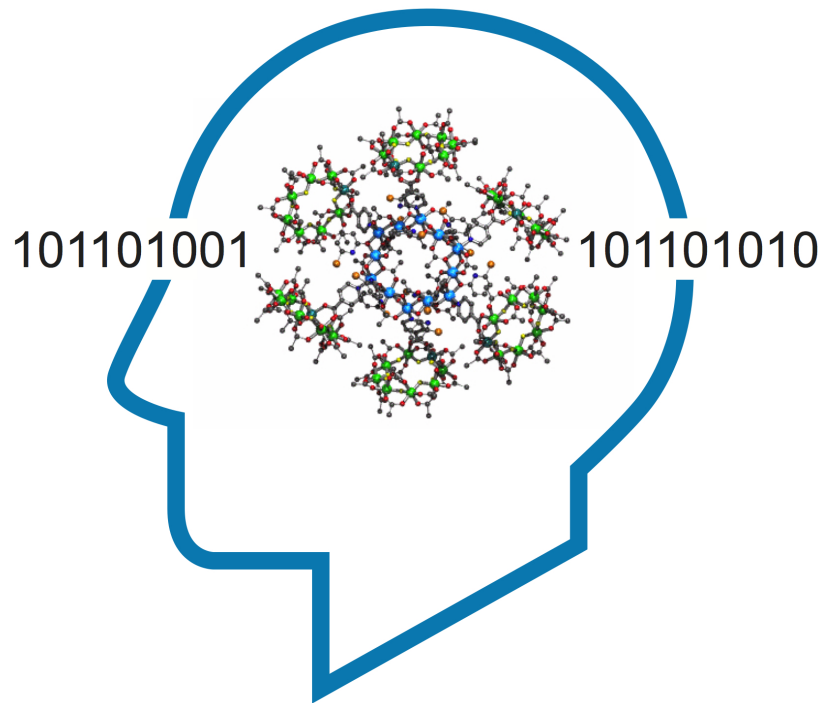Please send inquiries to jschnack@uni-bielefeld.de!
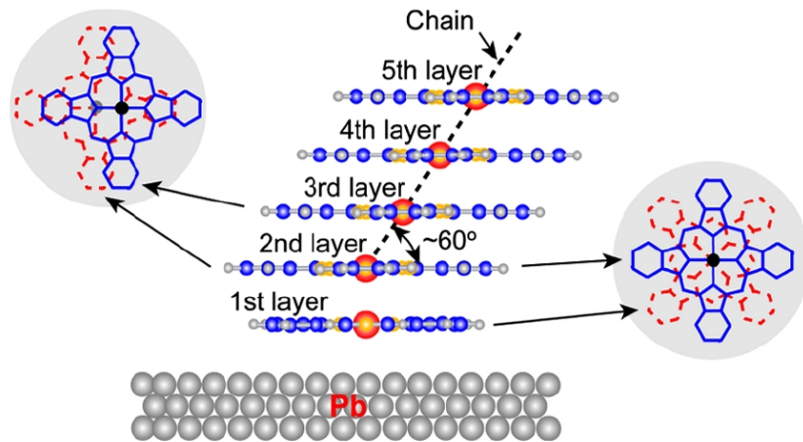
Some basic theory

You have got a molecule!

Congratulations!

You want to build a quantum computer!

101101001 101101010

Very smart!

You want to deposit your molecule!

Next generation magnetic storage!

You have got an idea about the modeling!

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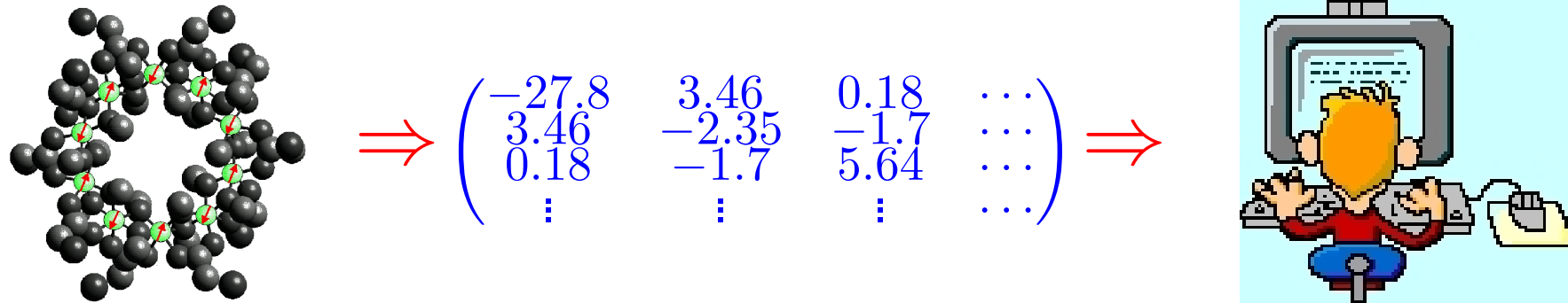
Heisenberg   Zeeman

You have to solve the Schrödinger equation!

$$H \mid \phi_n \rangle = E_n \mid \phi_n \rangle$$

Eigenvalues E_n and eigenvectors $\mid \phi_n \rangle$

- needed for spectroscopy (EPR, INS, NMR);

- needed for thermodynamic functions (magnetization, susceptibility, heat capacity);

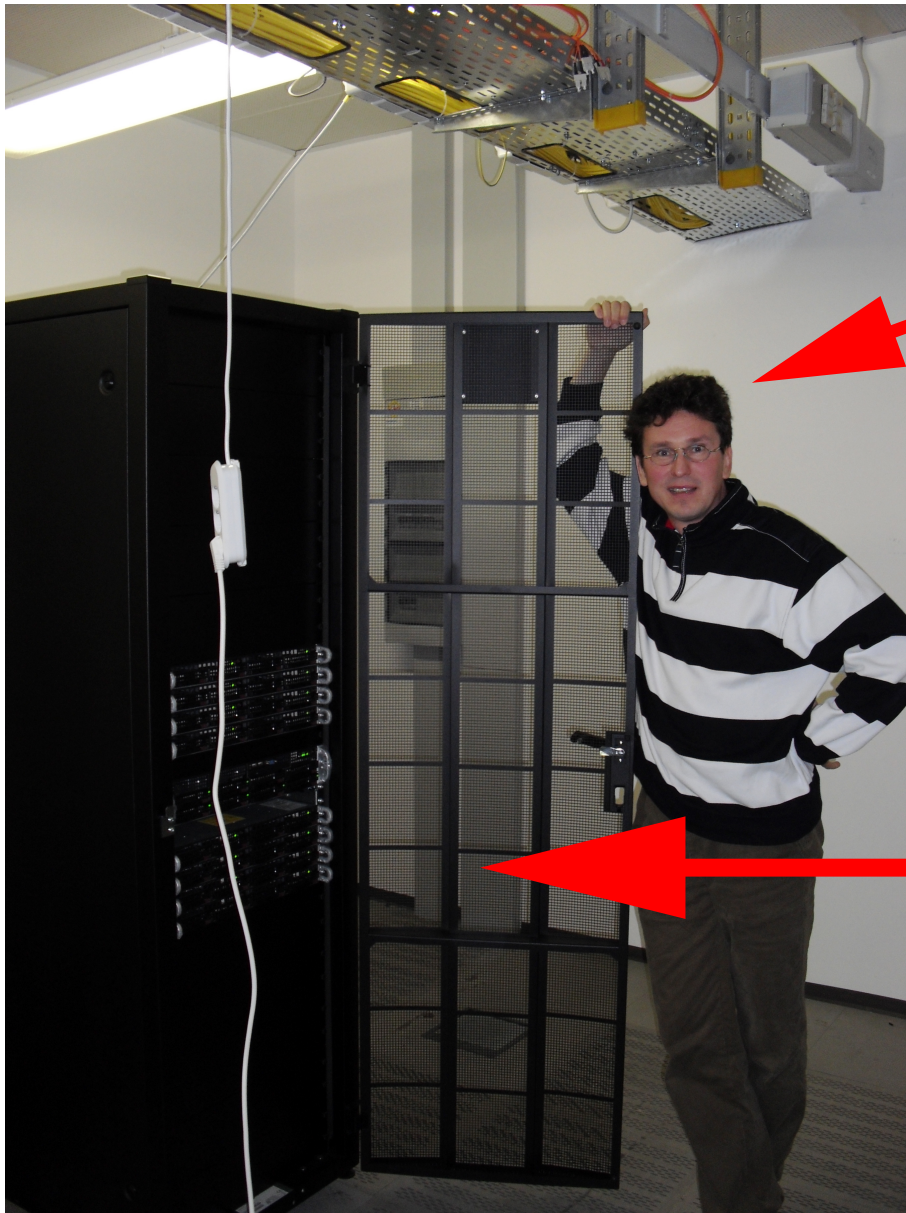- needed for time evolution (pulsed EPR, simulate quantum computing, thermalization).

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

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

Thank God, we have computers

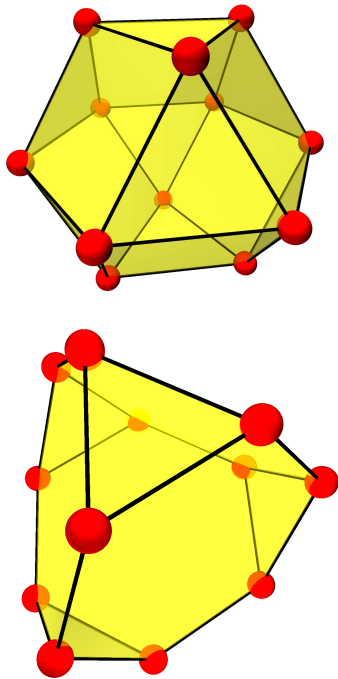"Espresso-doped multi-core"

128 cores, 384 GB RAM

. . . but that's not enough!

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

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

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);
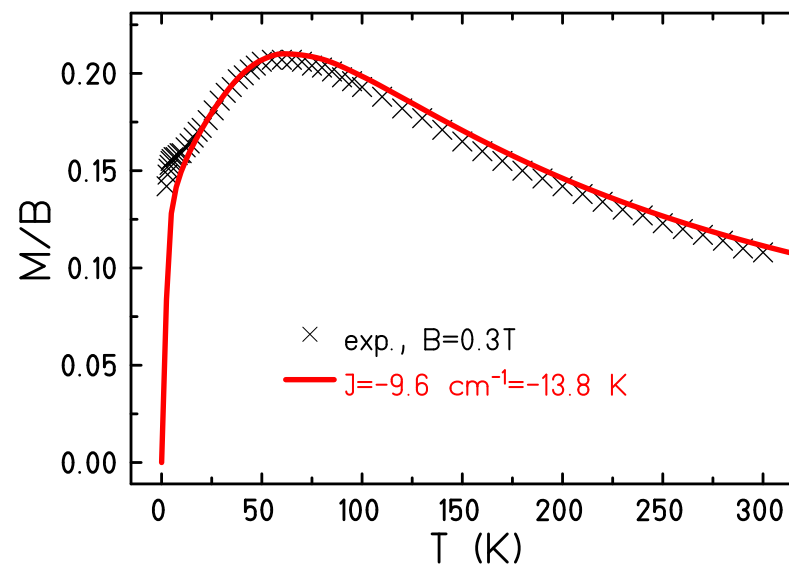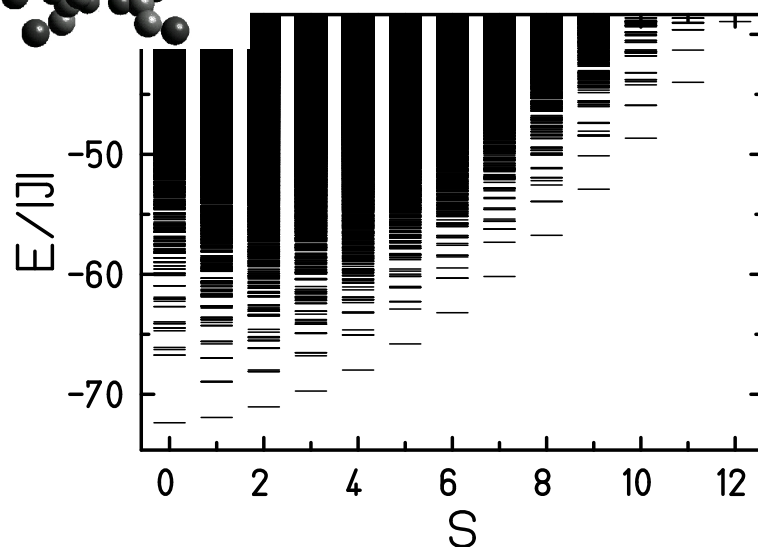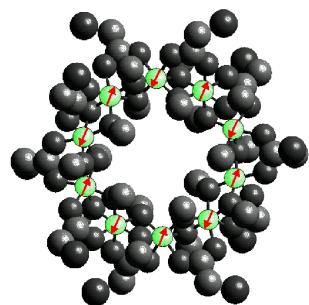
- No free program, things are a bit complicated (3,4).

(1) M. Tinkham, *Group Theory and Quantum Mechanics*, Dover.
(2) D. Gatteschi and L. Pardi, Gazz. Chim. Ital. **123**, 231 (1993).
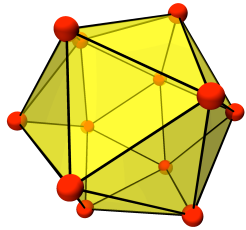(3) O. Waldmann, Phys. Rev. B **61**, 6138 (2000).
(4) R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403-452 (2010) ⇐ contains EVERYTHING.
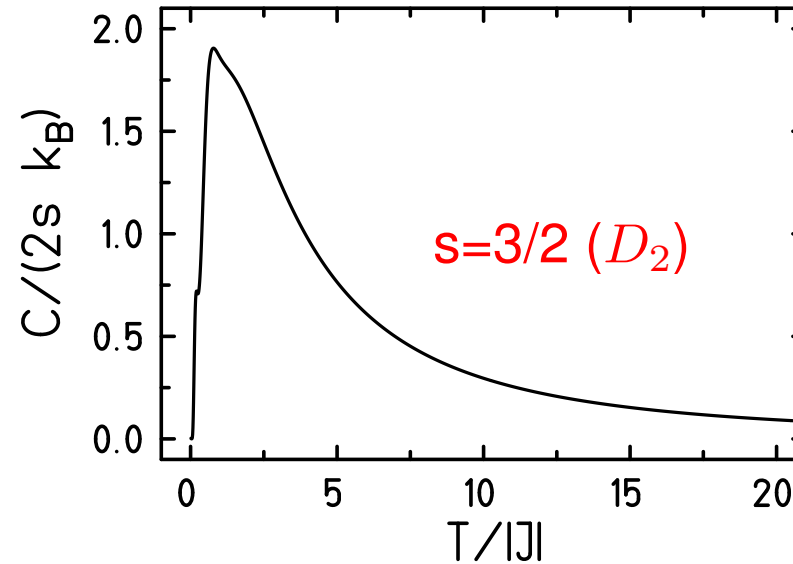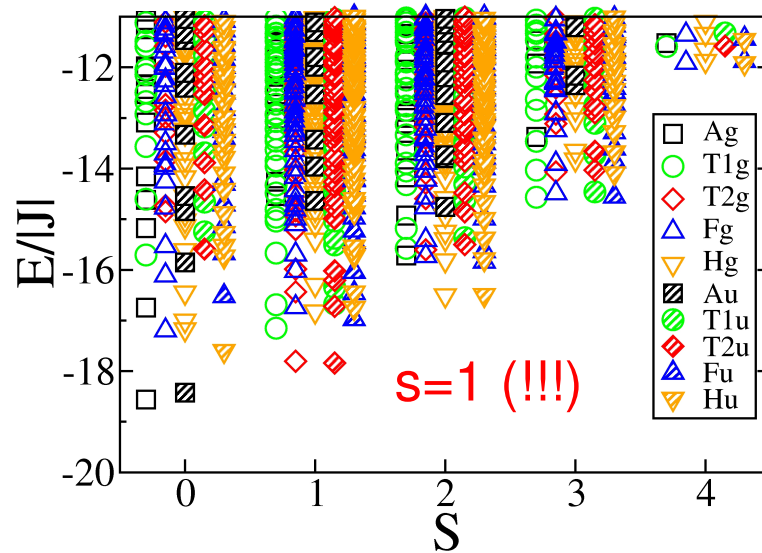
Example: Fe_{10}

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).
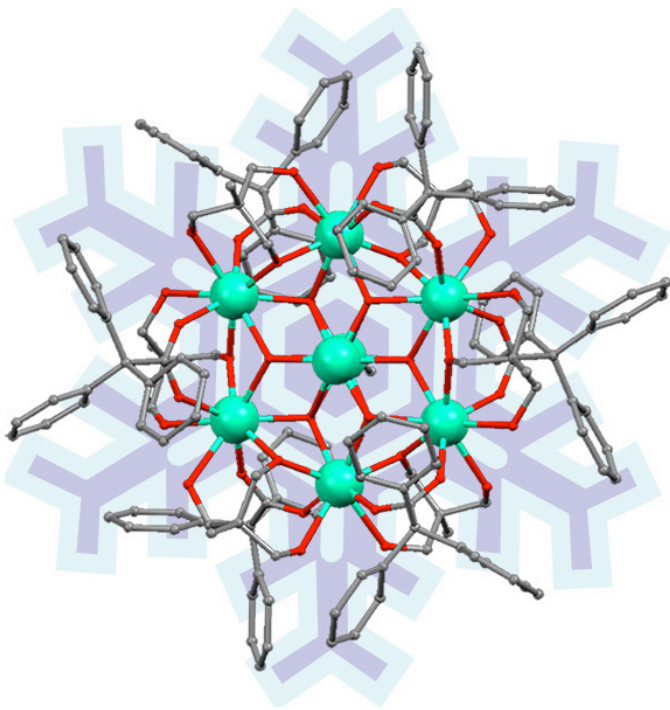(2) C. Delfs *et al.*, Inorg. Chem. **32**, 3099 (1993).

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).

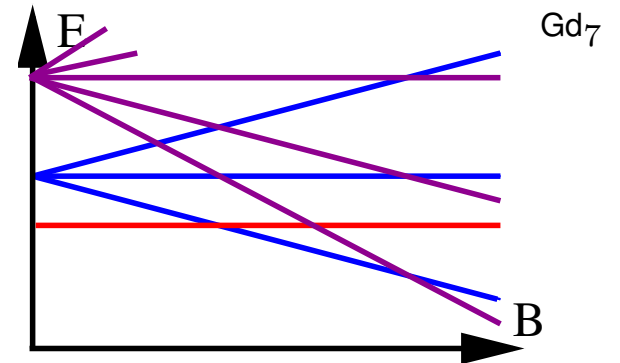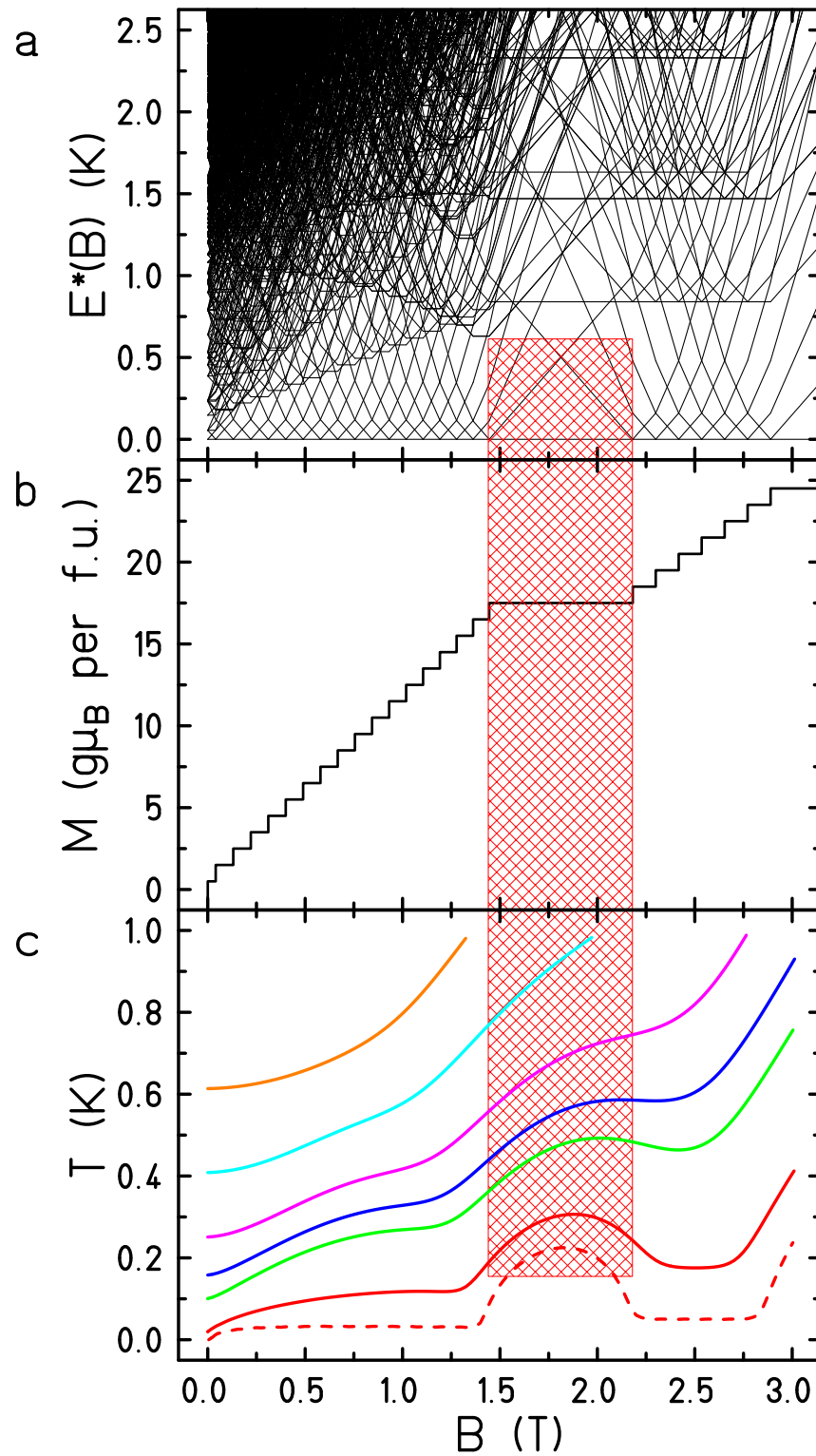(1) R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403-452 (2010).

Gd$_7$ – Magnetocalorics

- Often magnetocaloric observables not directly measured, but inferred from Maxwell's relations.

- First real cooling experiment with a molecule.

- $H = -2 \sum_{i<j} J_{ij}\, \vec{s}_i \cdot \vec{s}_j + g\,\mu_B\,B \sum_i^N s_i^z$

  $J_1 = -0.090(5)$ 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).

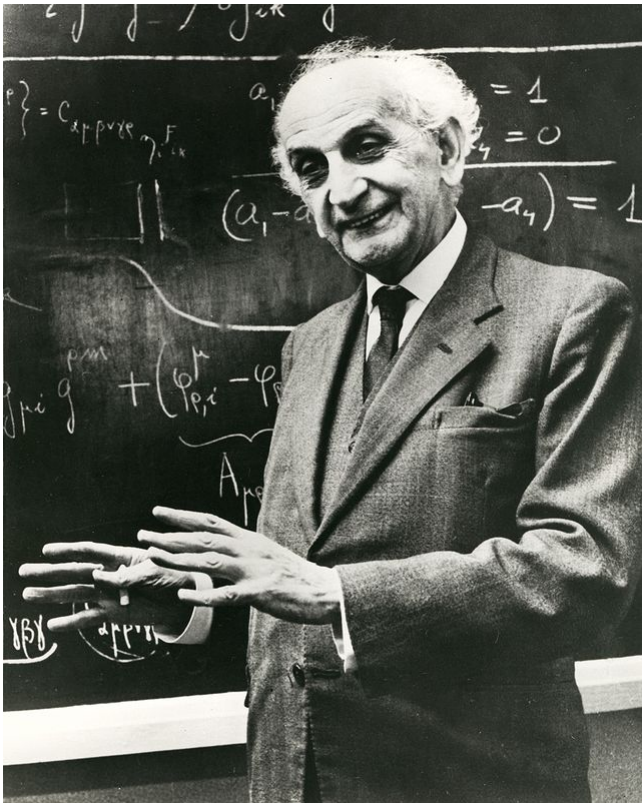# What if your molecule is BIGGER?

rendered on SuperMUC by LRZ

SuperMUC @ LRZ!

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:**
  $$\left\{ |\phi\rangle, \underset{\sim}{H} |\phi\rangle, \underset{\sim}{H}^2 |\phi\rangle, \underset{\sim}{H}^3 |\phi\rangle, \dots \right\}$$

- 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

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

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

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

- $| n(\nu) \rangle$ n-th Lanczos eigenvector starting from $| \nu \rangle$

- Partition function replaced by a small sum: $R = 1 \ldots 10, N_L \approx 100$.

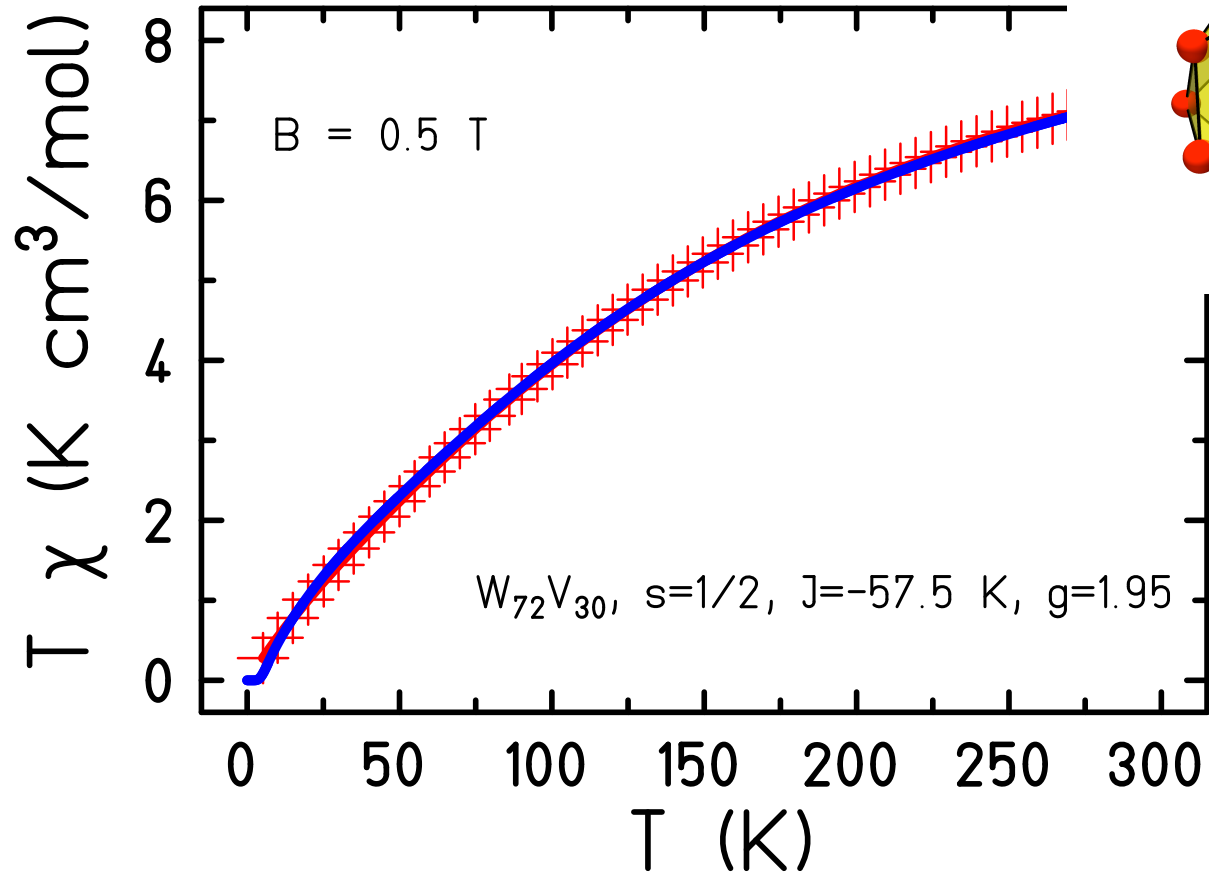J. Jaklic and P. Prelovsek, Phys. Rev. B **49**, 5065 (1994).

Finite-temperature Lanczos Method II

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

- **Approximation better if symmetries taken into account.**

- Γ denotes the used irreducible representations; often this is just the $\underset{\sim}{S^z}$ symmetry, i.e. $\Gamma \equiv M$

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

Icosidodecahedron $s = 1/2$

B = 0.5 T

$W_{72}V_{30}$, s=1/2, J=−57.5 K, g=1.95

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.

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

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 $\mathrm{Tr}\left(\underset{\sim}{S^z}\right) = 0$ 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)

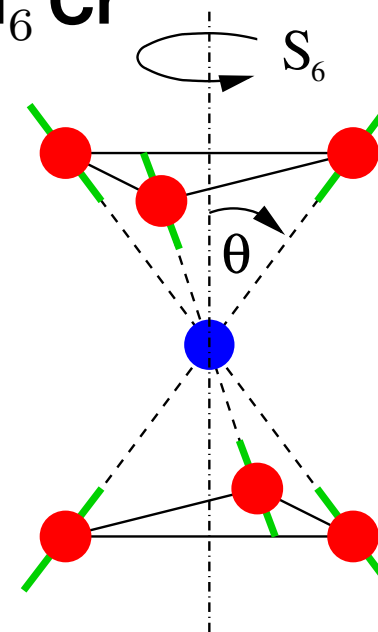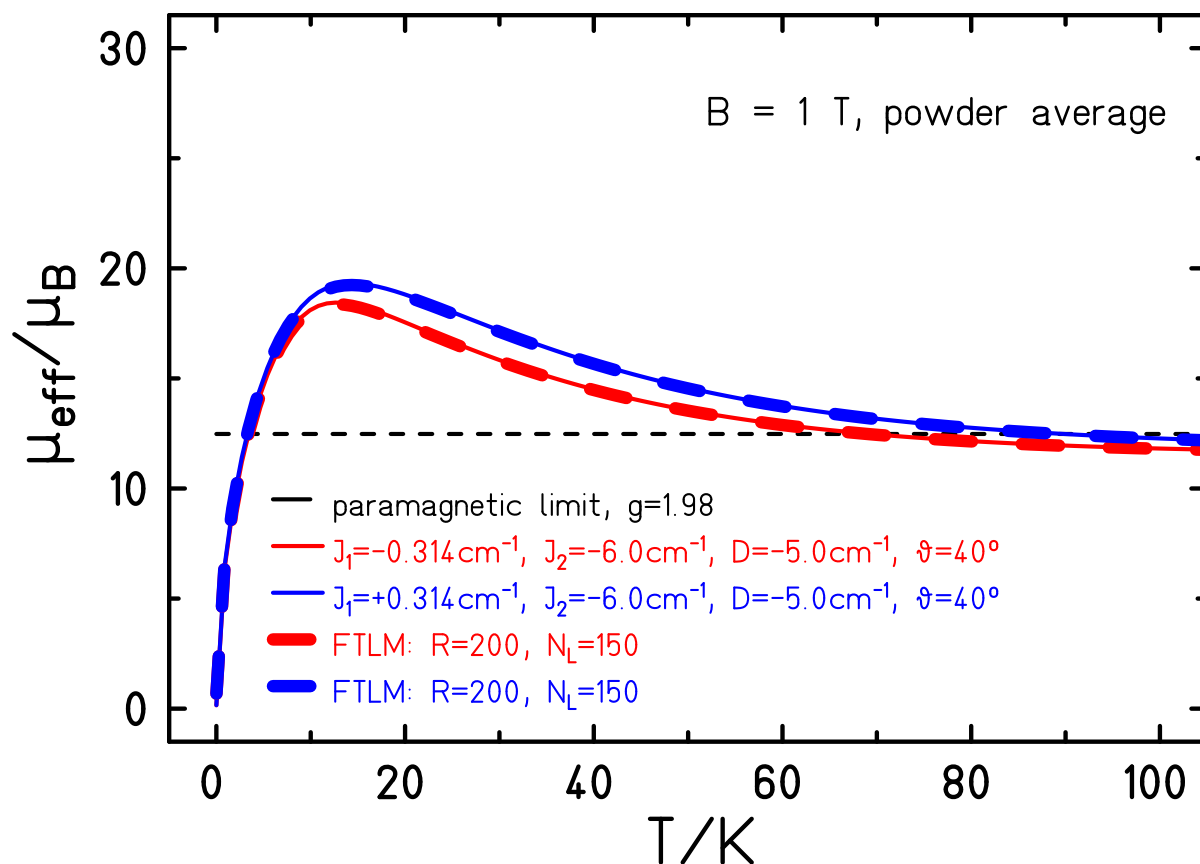$$\vec{\mathcal{M}}(T, -\vec{B}) = -\vec{\mathcal{M}}(T, \vec{B})$$

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: $Mn_6^{III}Cr^{III}$

B = 1 T, powder average

- — paramagnetic limit, g=1.98
- — J_1=-0.314 cm^{-1}, J_2=-6.0 cm^{-1}, D=-5.0 cm^{-1}, ϑ=40°
- — J_1=+0.314 cm^{-1}, J_2=-6.0 cm^{-1}, D=-5.0 cm^{-1}, ϑ=40°
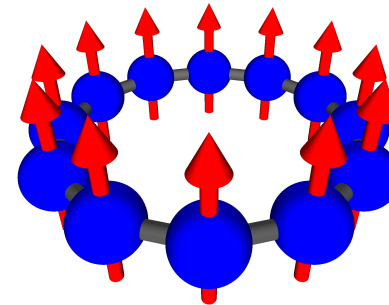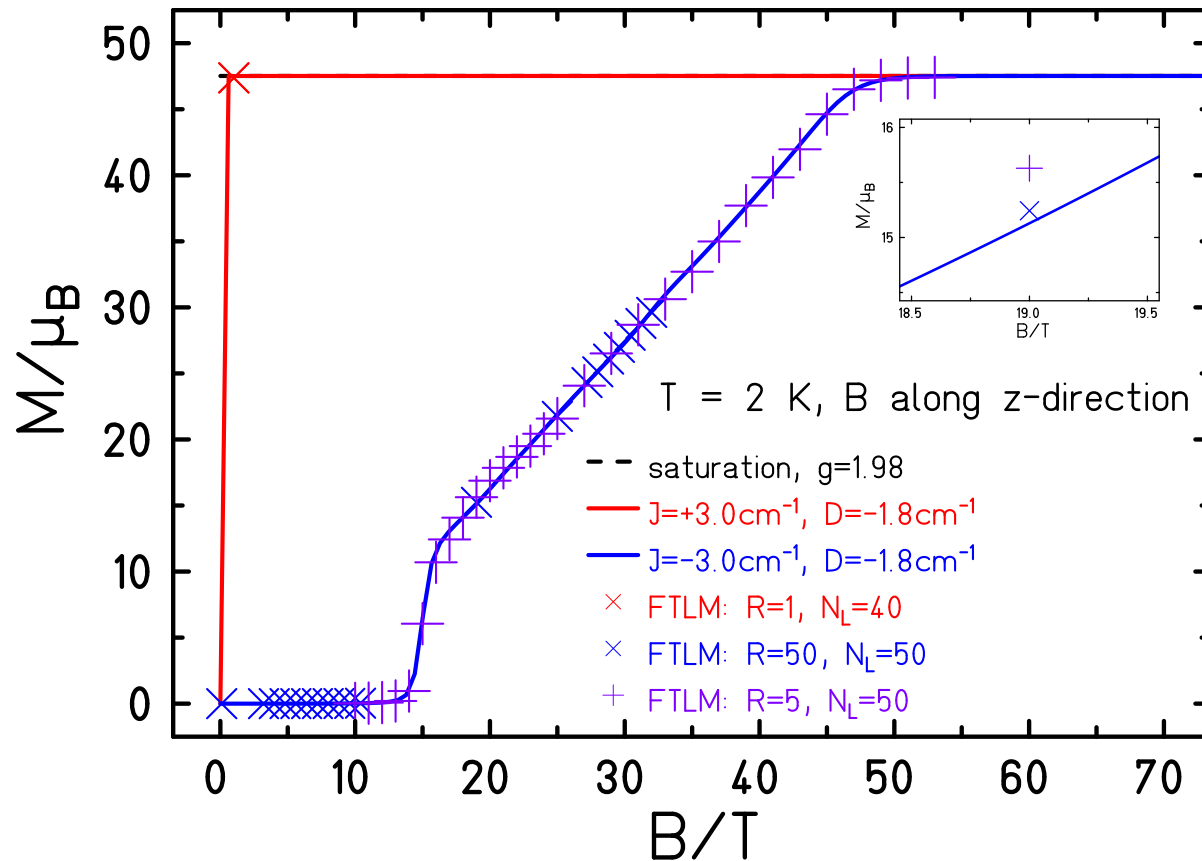- ▬ FTLM: R=200, N_L=150
- ▬ FTLM: R=200, N_L=150

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

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 $\mathbf{Mn}_{12}^{III} - M_z$ vs B_z

$s = 2$

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

collinear easy axes

A few days compared to *impossible*!

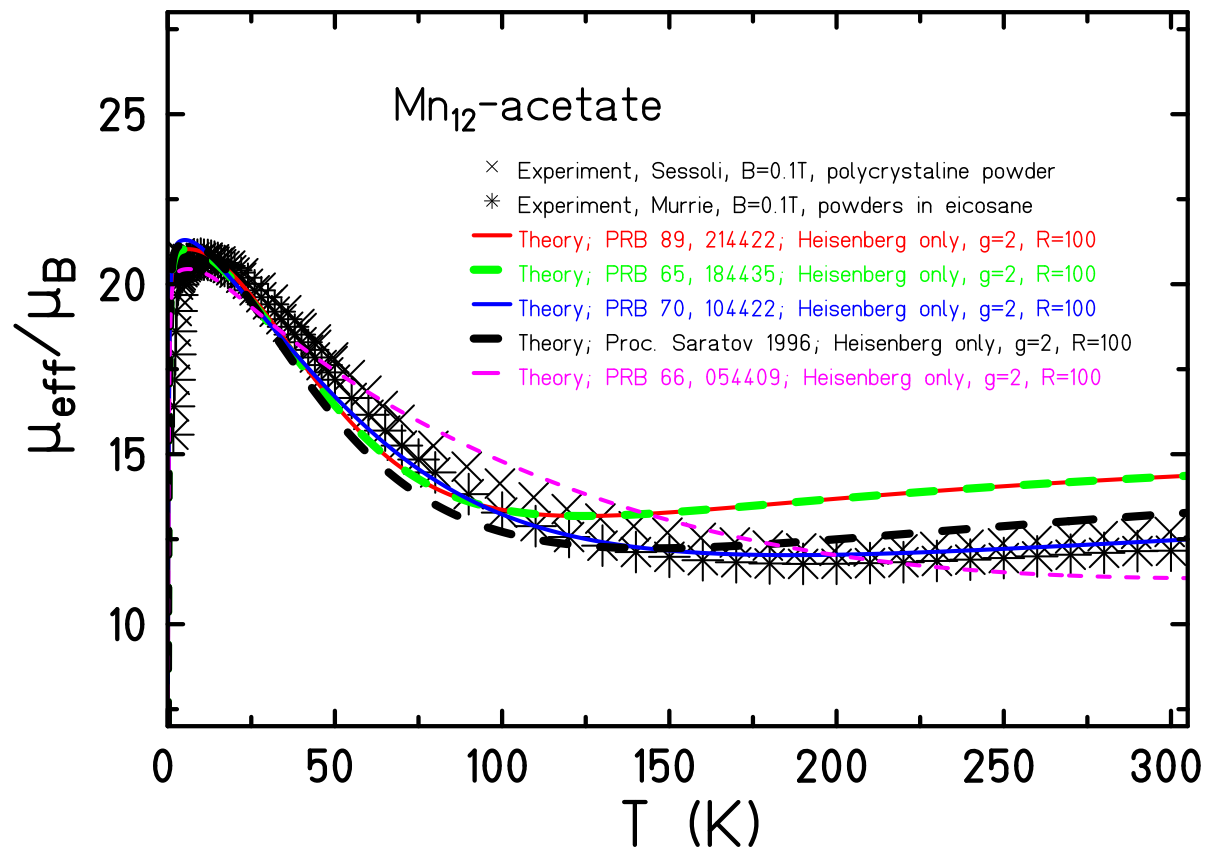O. Hanebaum, J. Schnack, Eur. Phys. J. B **87**, 194 (2014)

A fictitious $\mathbf{Mn}^{\mathsf{III}}_{12} - M_x$ 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
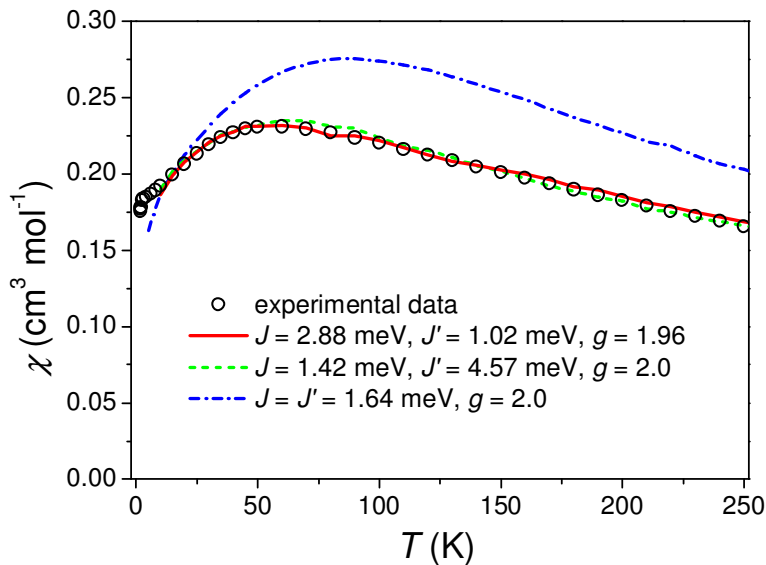
Intermolecular interactions

Quantum Monte Carlo

Chopped (sliced) partition function:

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

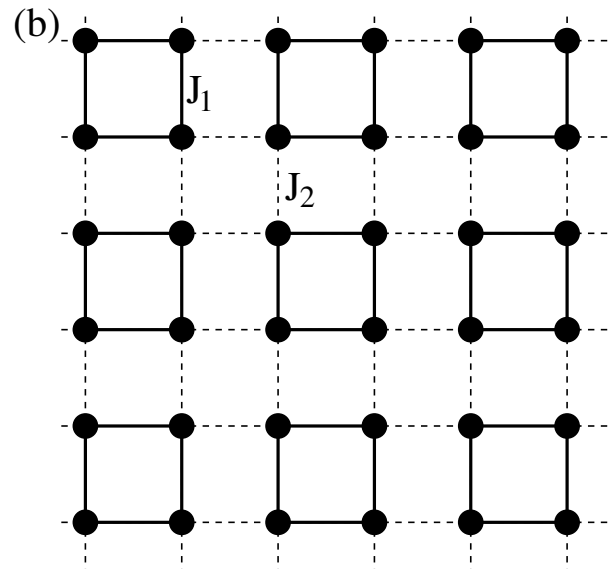 $= \sum_\nu \langle \nu | \left[\exp\left\{-\beta \underset{\sim}{H}/m\right\}\right]^m | \nu \rangle$
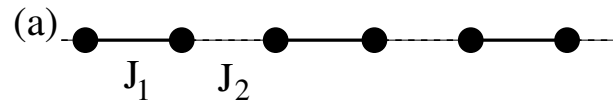
  $= \sum_{\nu, \alpha, \beta, ...} \langle \nu | \exp\left\{-\beta \underset{\sim}{H}/m\right\} | \alpha \rangle \langle \alpha | \cdots$

  $\approx \sum_{\nu, \alpha, \beta, ...} \langle \nu | \left\{1 - \beta \underset{\sim}{H}/m\right\} | \alpha \rangle \langle \alpha | \cdots$

- Bad/no convergence for frustrated systems (negative sign problem).

Legend:
- ○ experimental data
- $J = 2.88$ meV, $J' = 1.02$ meV, $g = 1.96$
- $J = 1.42$ meV, $J' = 4.57$ meV, $g = 2.0$
- $J = J' = 1.64$ meV, $g = 2.0$

x-axis: T (K); y-axis: χ (cm^3 mol^{-1})

(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).
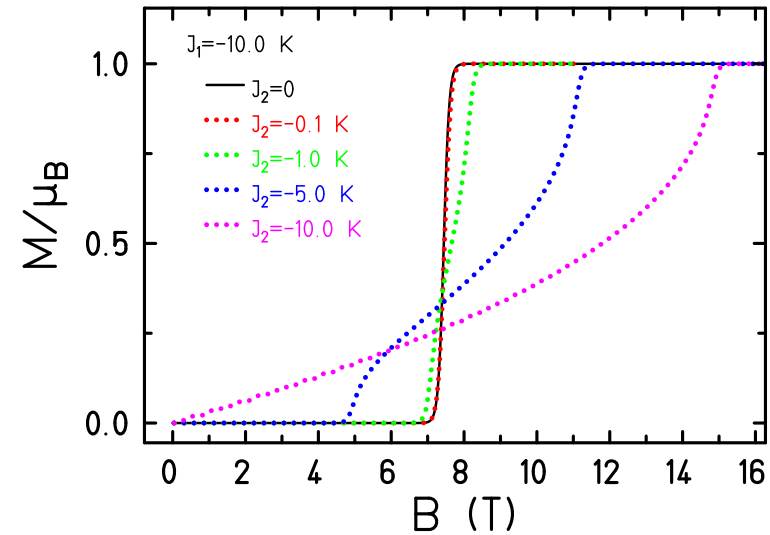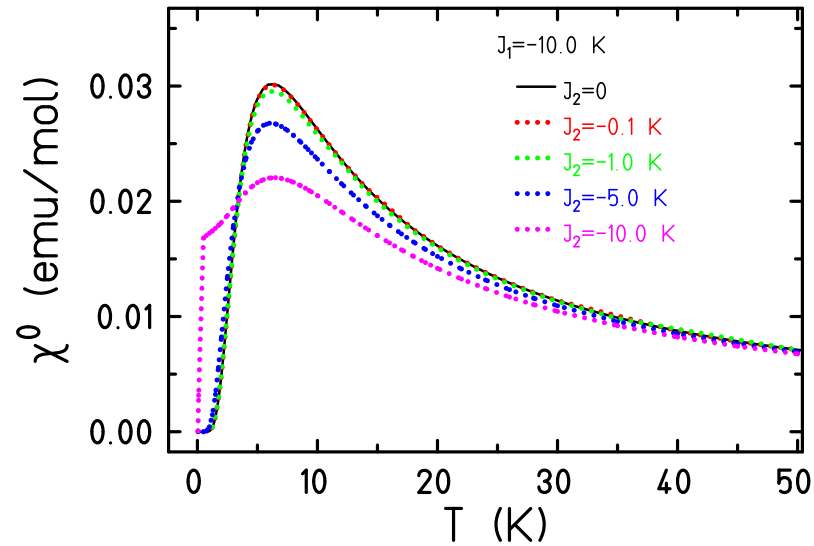(4) J. Ummethum *et al.*, Phys. Rev. B **86**, 104403 (2012).

Intermolecular interactions – systems

(a) J_1 J_2

(b) J_1 J_2 J_1 J_2

QMC investigation: Dimers in 1-d, squares in 2-d, cubes in 3-d.
All interactions antiferromagnetic, all spins $s = 1/2$. $N = 100 \ldots 1000$. PBC.

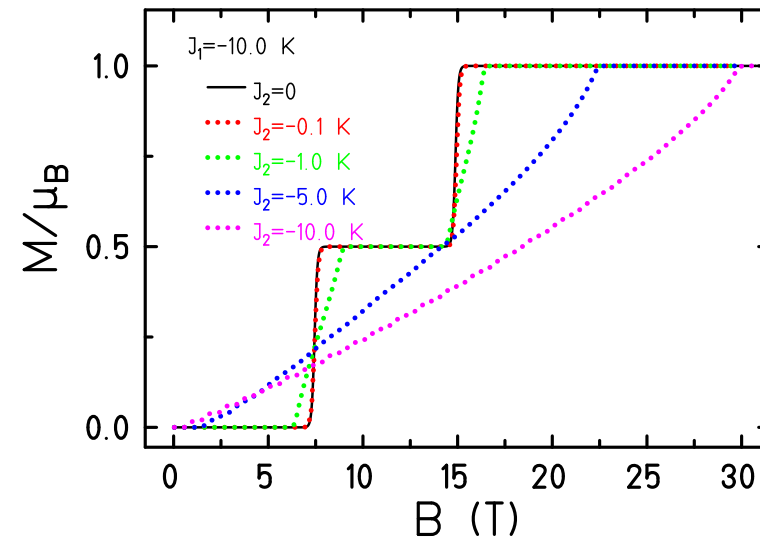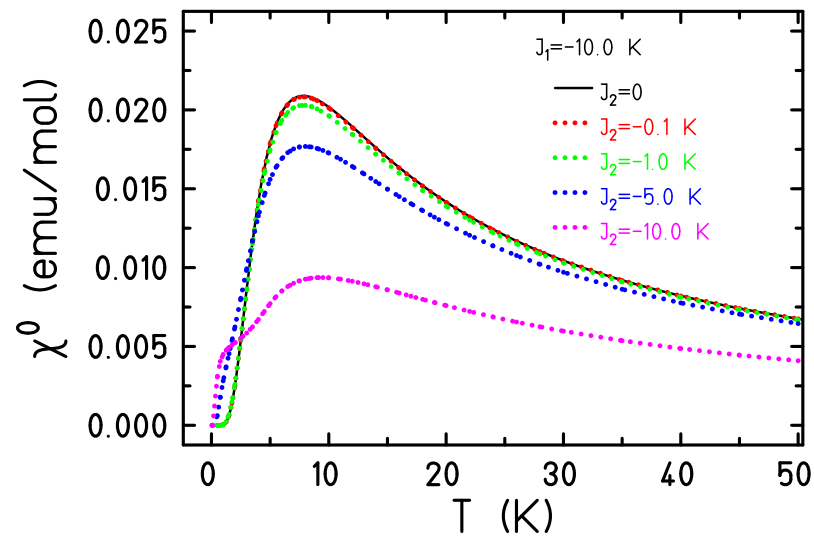(1) J. Schnack, Phys. Rev. B **93**, 054421 (2016).

Intermolecular interactions – 1-d

Gradually af dimers turn into gapless af chain.
Even at 50 % gap still large.

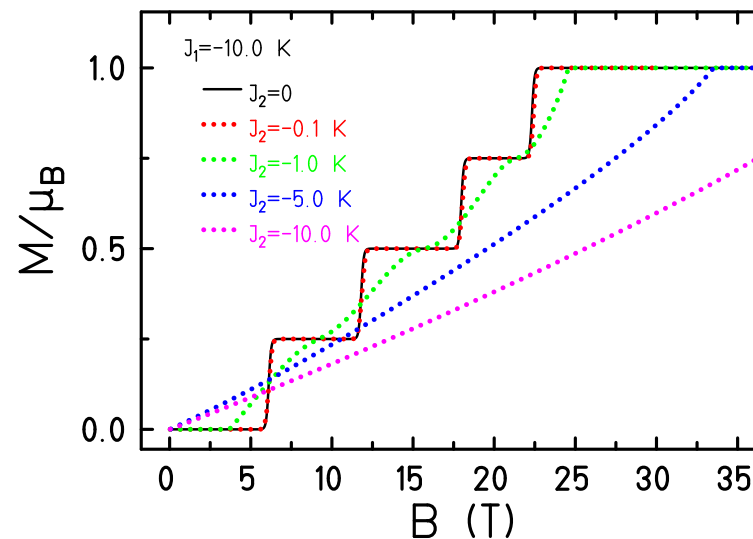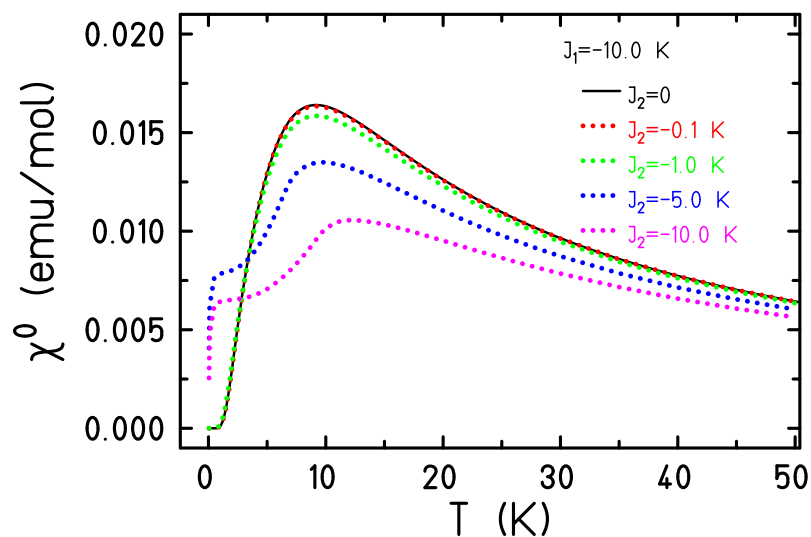(1) J. Schnack, Phys. Rev. B **93**, 054421 (2016).

Intermolecular interactions – 2-d

The two magnetization steps vanish more rapidly with intermolecular interactions in 2-d.

(1) J. Schnack, Phys. Rev. B **93**, 054421 (2016).

Intermolecular interactions – 3-d

In 3-d 10 % intermolecular interactions sufficient to wash out magnetization steps.

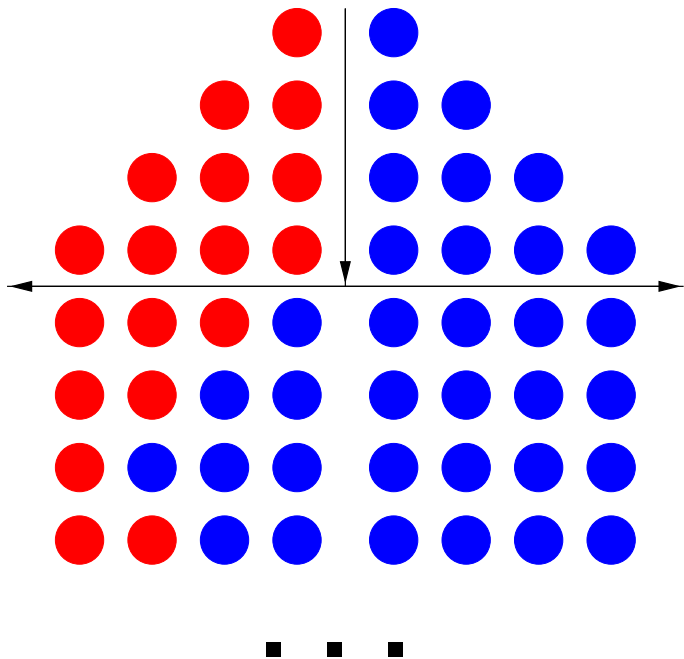(1) J. Schnack, Phys. Rev. B **93**, 054421 (2016).

Take home:

10 % intermolecular interactions in 3-d is enough

(. . . to spoil static molecular magnetic observables.)

Density Matrix Renormalization Group

(Best for one-dimensional systems, even for huge sizes.)
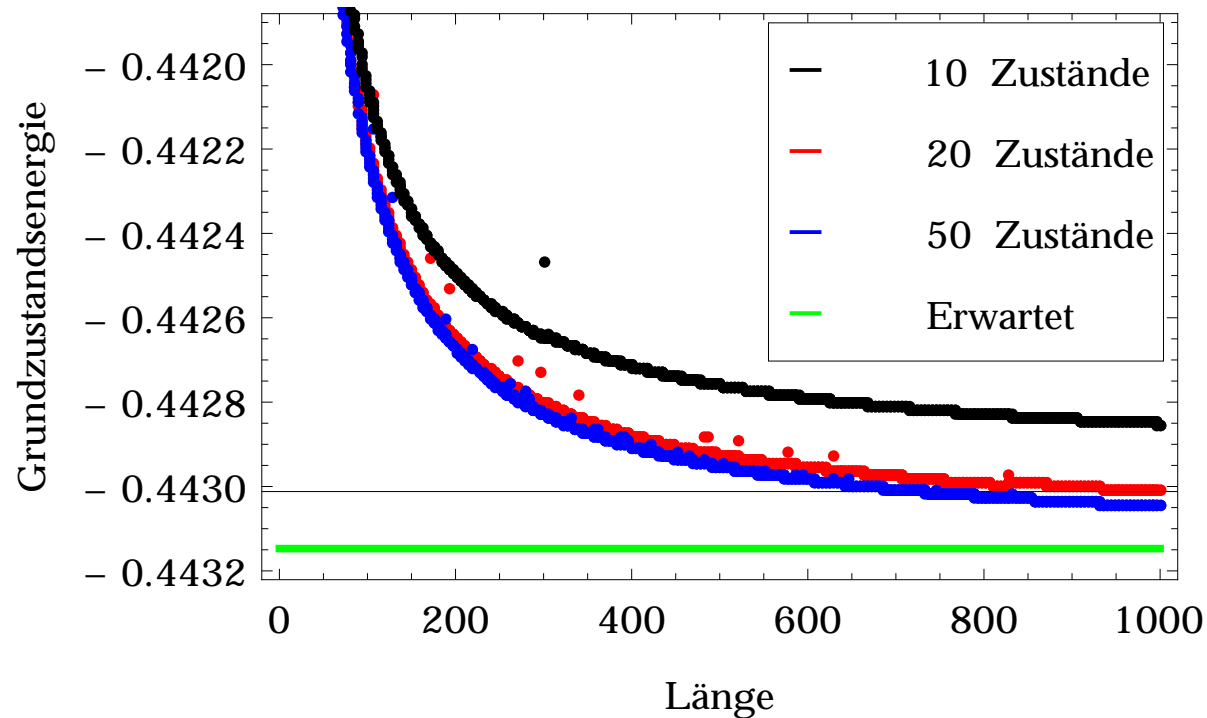
Density Matrix Renormatization Group

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).

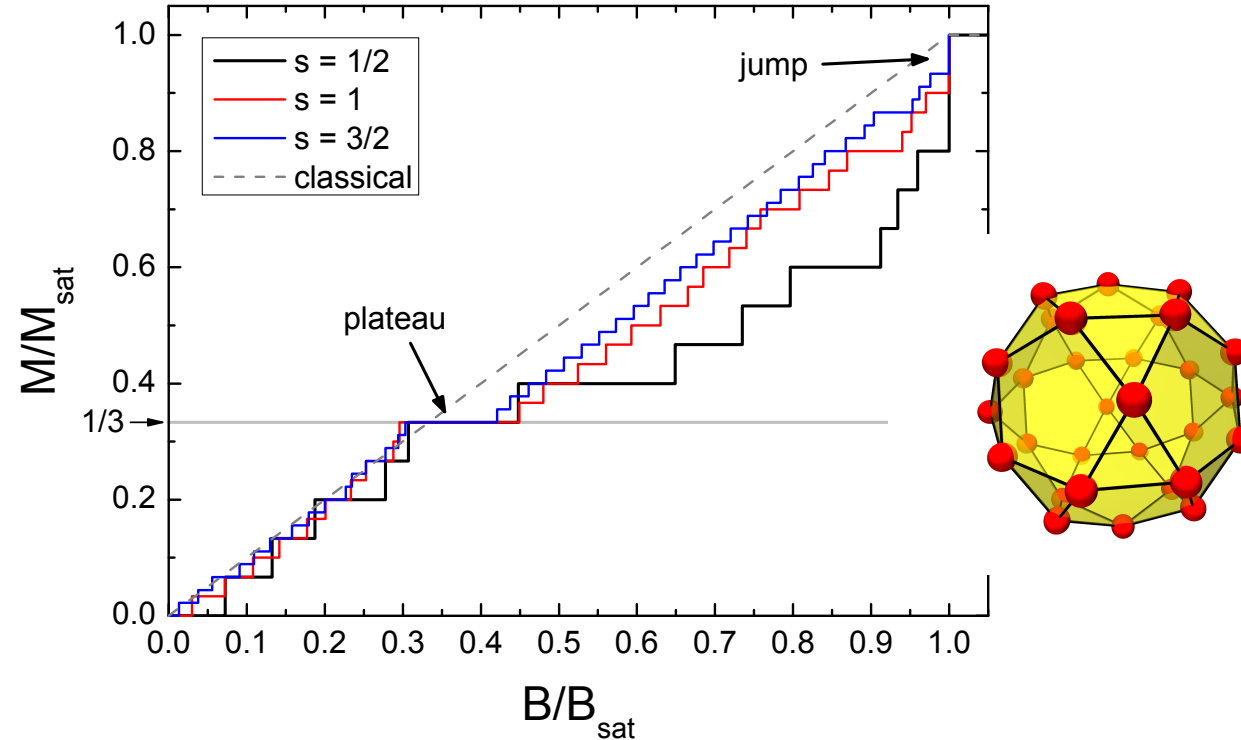- Technical procedure: growth of system & sweeps.

(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 $2^{1000} \approx 10^{301}$.

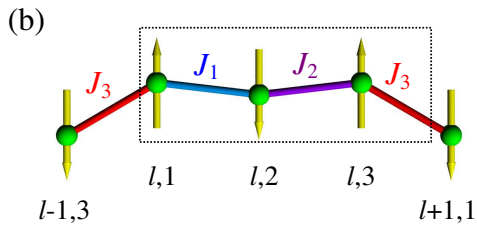- Approaches result known from Bethe ansatz with matrices as small as 50×50!
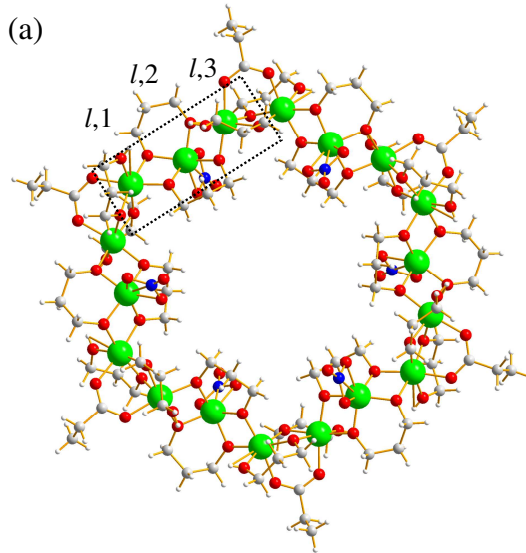
Density Matrix Renormatization Group

- 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
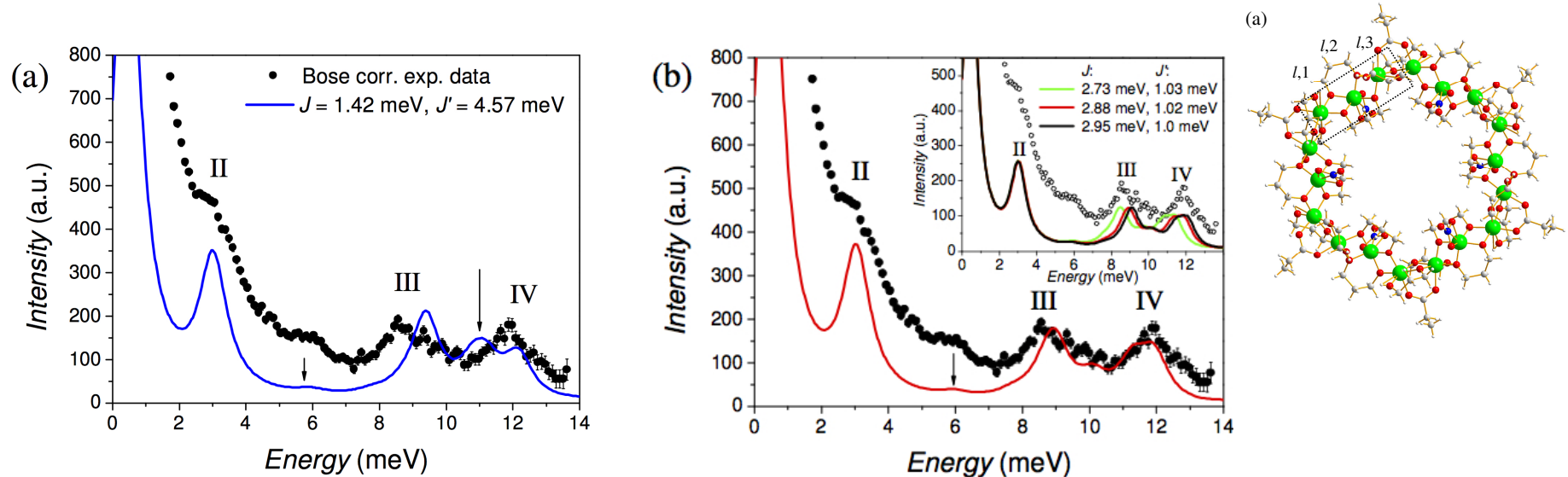
Dynamical Density Matrix Renormatization Group

(a)

(b)

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

- $S_{jj'}^{zz}(\omega) \equiv \sum_n \langle 0|\underset{\sim}{s}_j^z|n\rangle\langle n|\underset{\sim}{s}_{j'}^z|0\rangle\,\delta(\hbar\omega - E_n + E_0)$; transitions from the ground state;

- $S_{jj'}^{zz}(\omega) \approx \frac{1}{\pi}\langle 0|\underset{\sim}{s}_j^z\frac{\eta}{(E_0+\hbar\omega-\underset{\sim}{H})^2+\eta^2}\underset{\sim}{s}_{j'}^z|0\rangle$;

- 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).
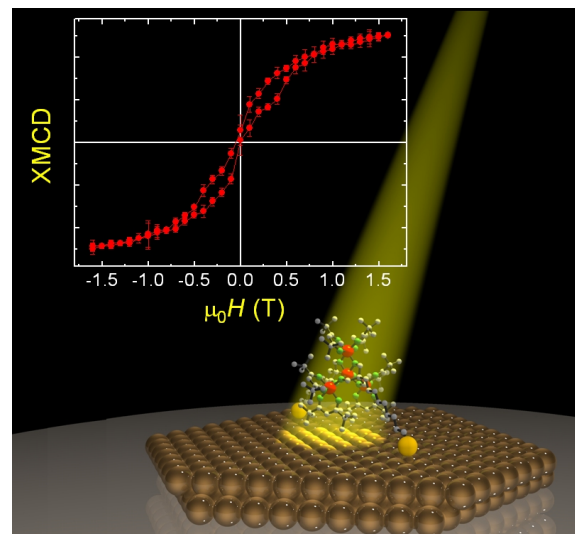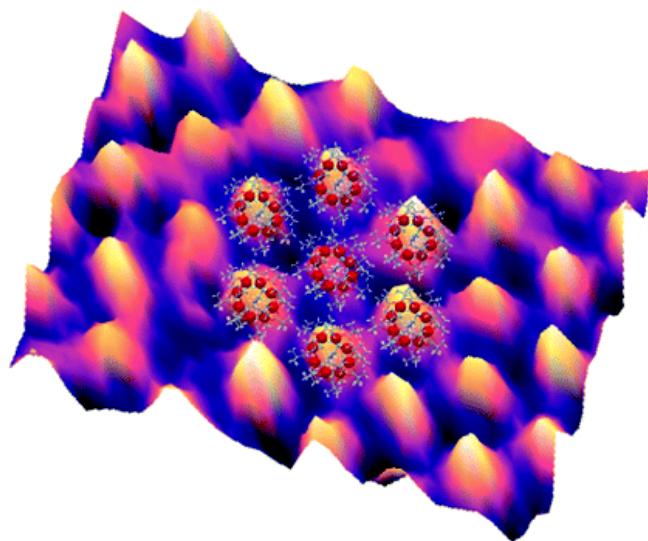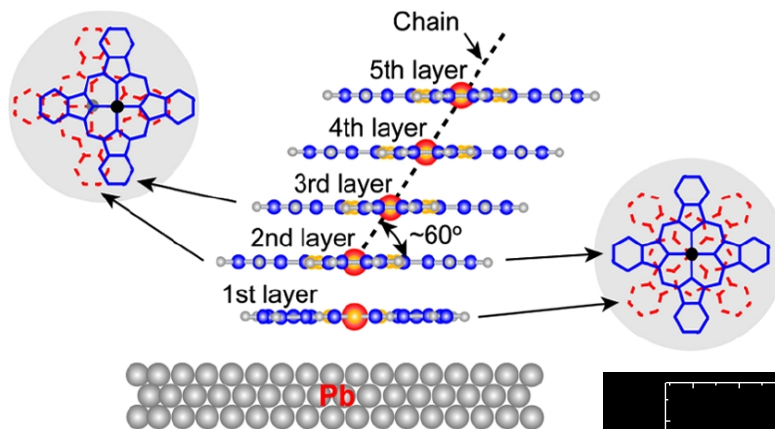
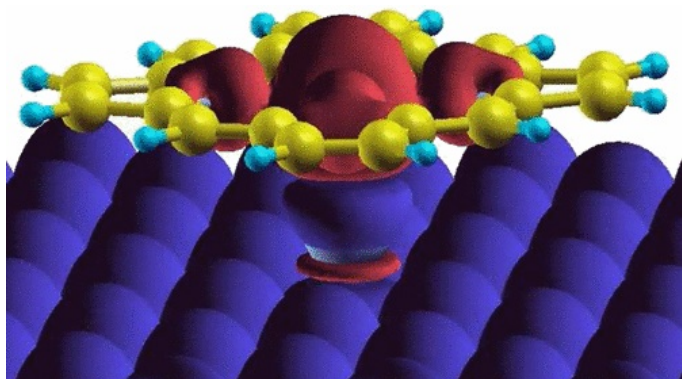# Dynmical Density Matrix Renormatization Group

- **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).

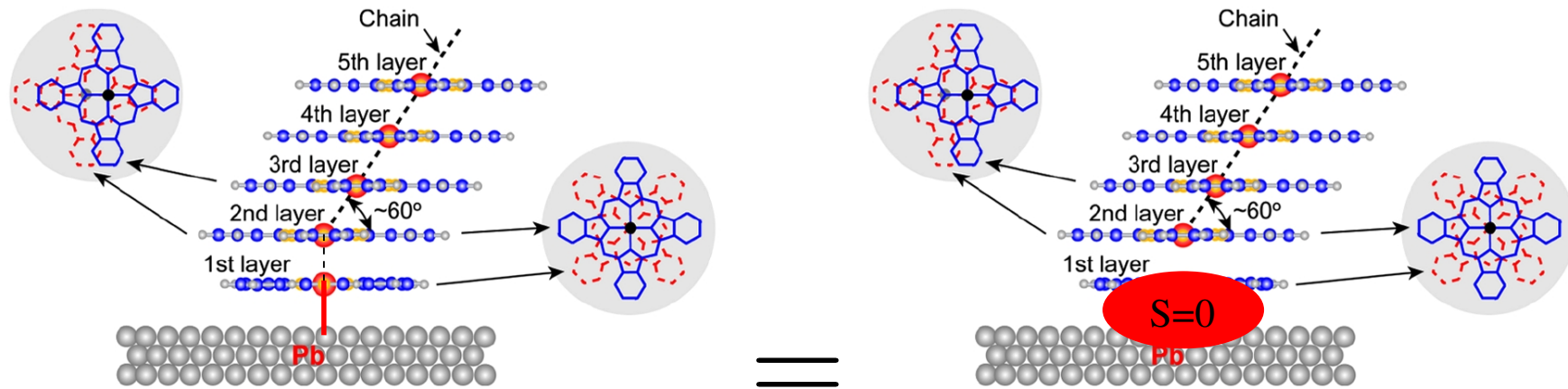# Numerical Renormalization Group calculations

(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).

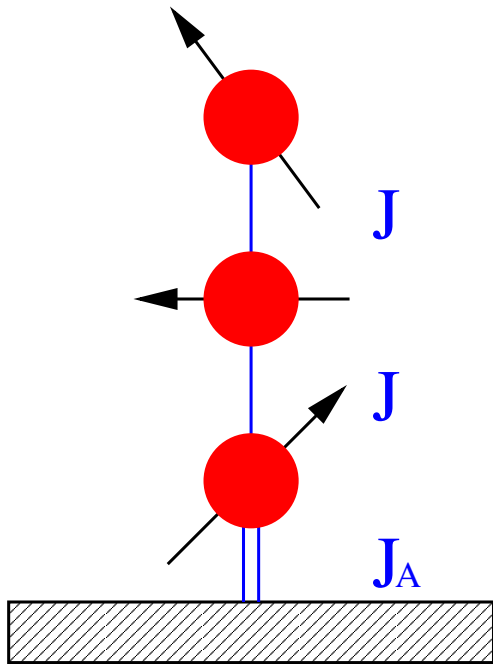# Physical example (ICMM 2010)

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).
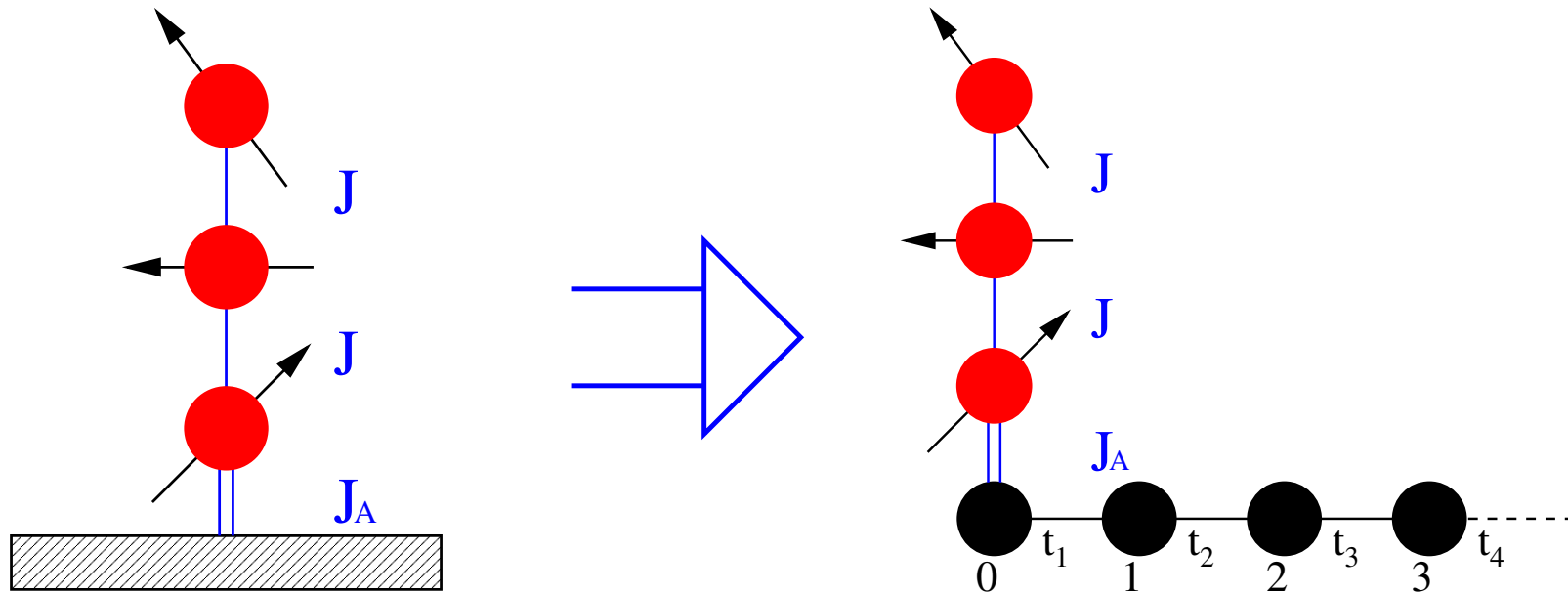
NRG – minimal model (already an approximation!)

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

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

  $\underset{\sim}{H}_{\text{coupling}} = -2 J_A \underset{\sim}{S} \cdot \underset{\sim}{s}_0$, $\underset{\sim}{s}_0$ – 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).

J

J

J$_A$

(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

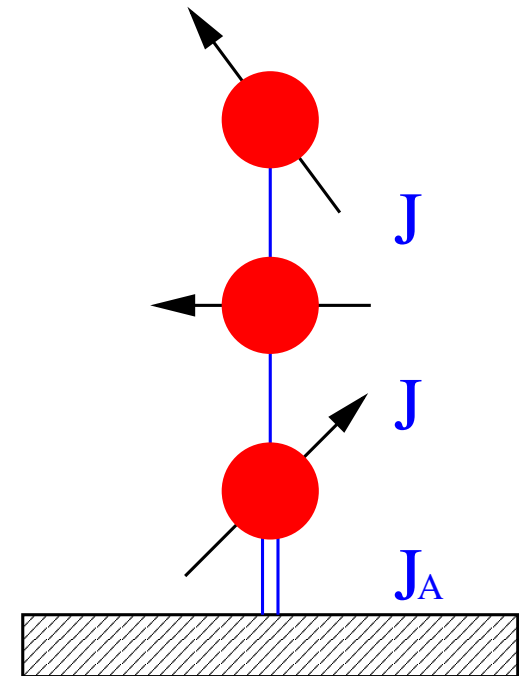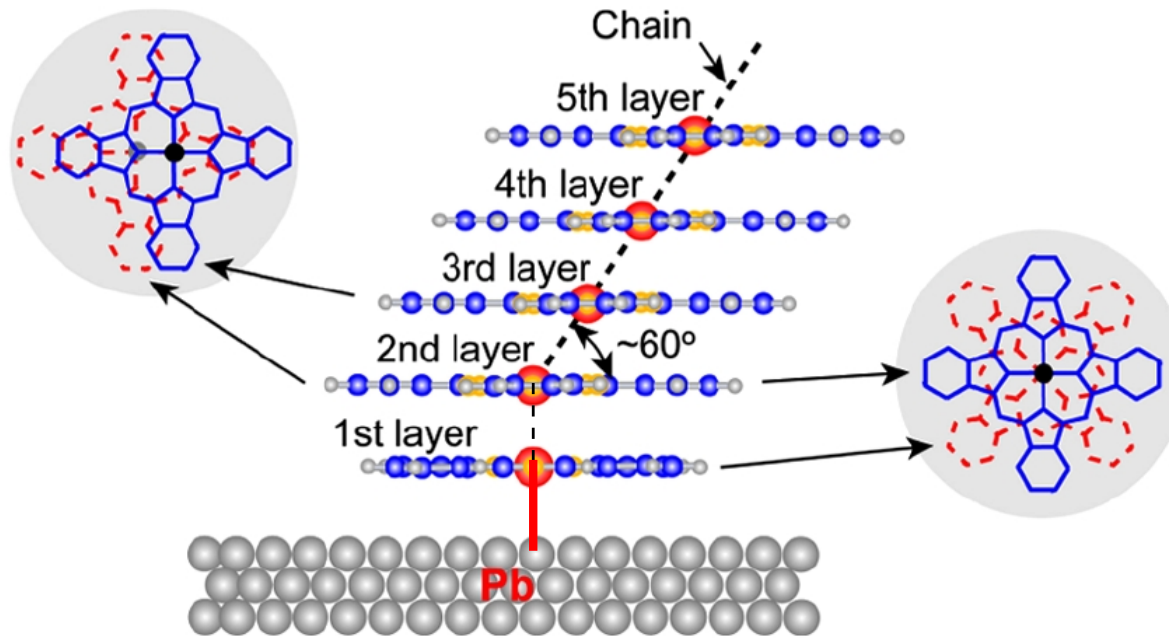
Metallic surface is replaced by semi-infinite Hubbard chain;
Parameters of the chain: hopping matrix elements and on-site energies;
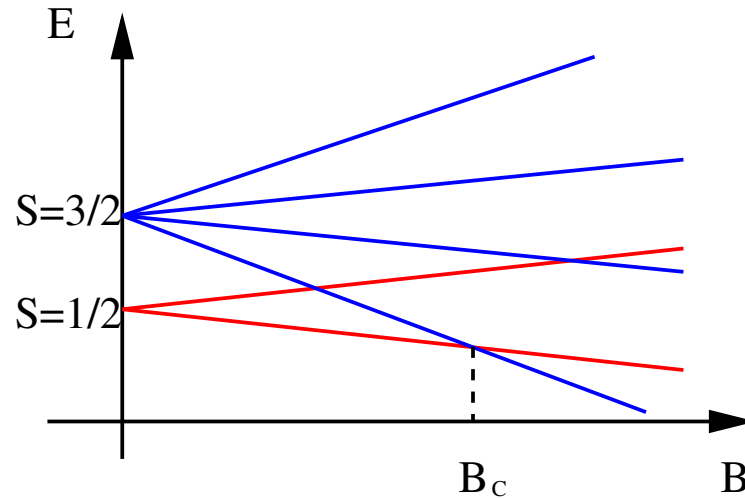Stepwise enlargement of the chain $(t_1 > t_2 > t_3 \ldots)$;
Truncation of basis set when matrices grow too big.
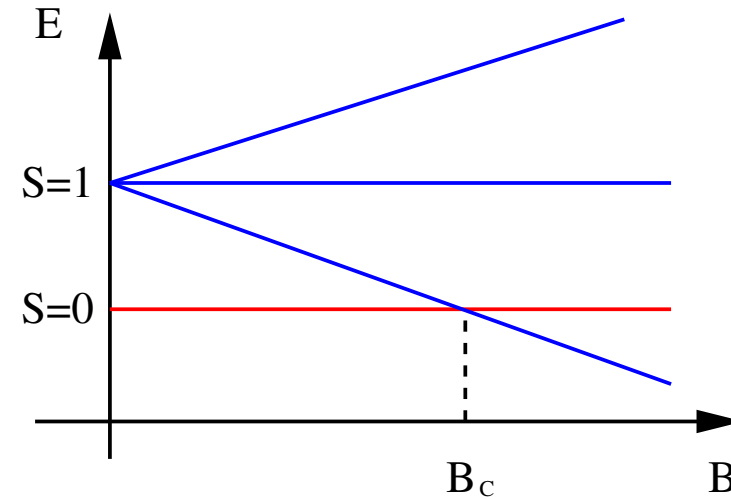
Once more: deposited chain

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

Energy levels of limiting cases for deposited trimer
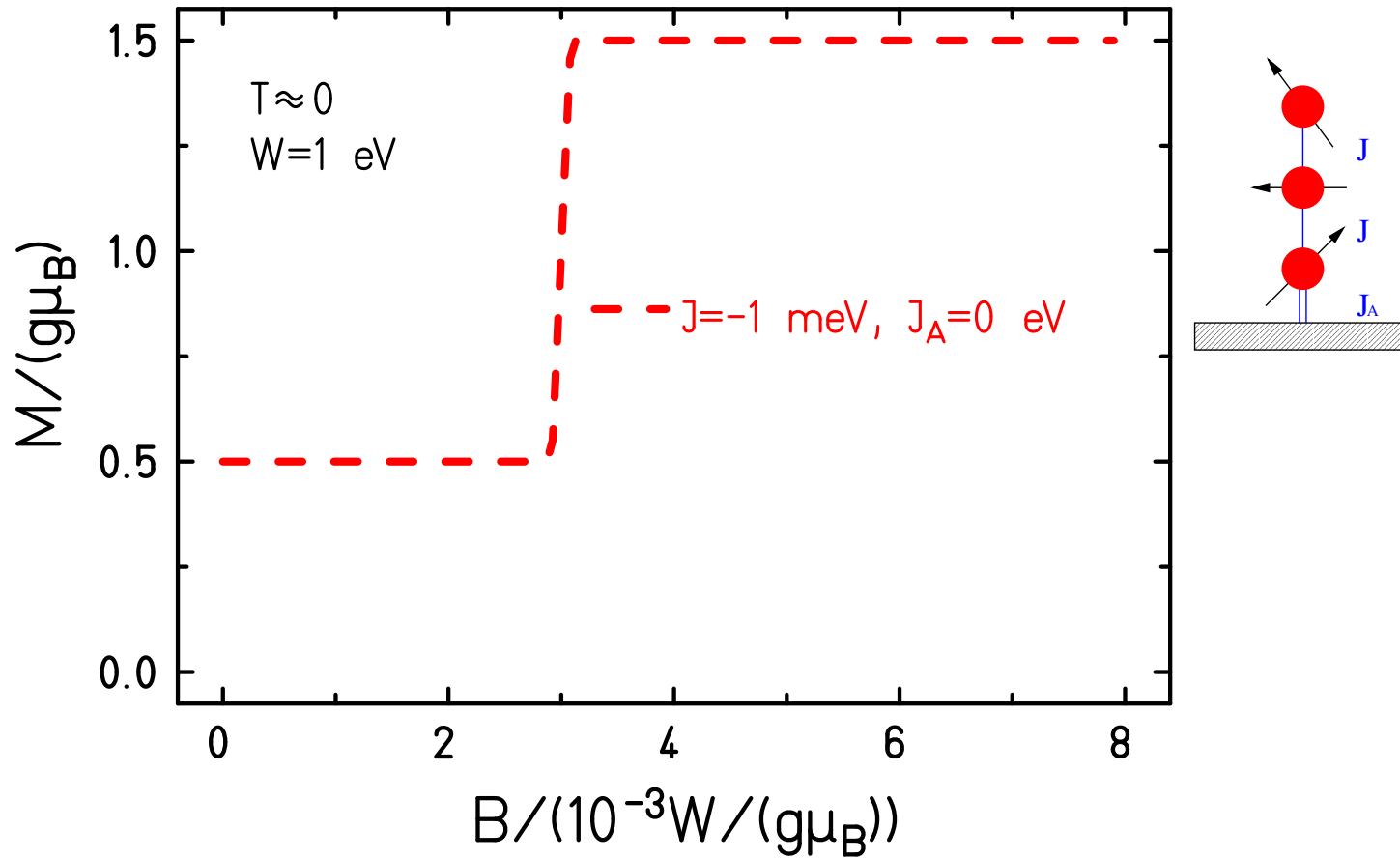

- energy levels of a trimer

- 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

$T \approx 0$
$W = 1$ eV

$- - -$ $J = -1$ meV, $J_A = 0$ eV
$- - -$ $J = -1$ meV, $J_A = -0.1$ eV

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

Increasing coupling to the substrate

$T \approx 0$
$W = 1$ eV

- - - $J=-1$ meV, $J_A=0$ eV
- - - $J=-1$ meV, $J_A=-0.1$ eV
- - - $J=-1$ meV, $J_A=-0.15$ eV
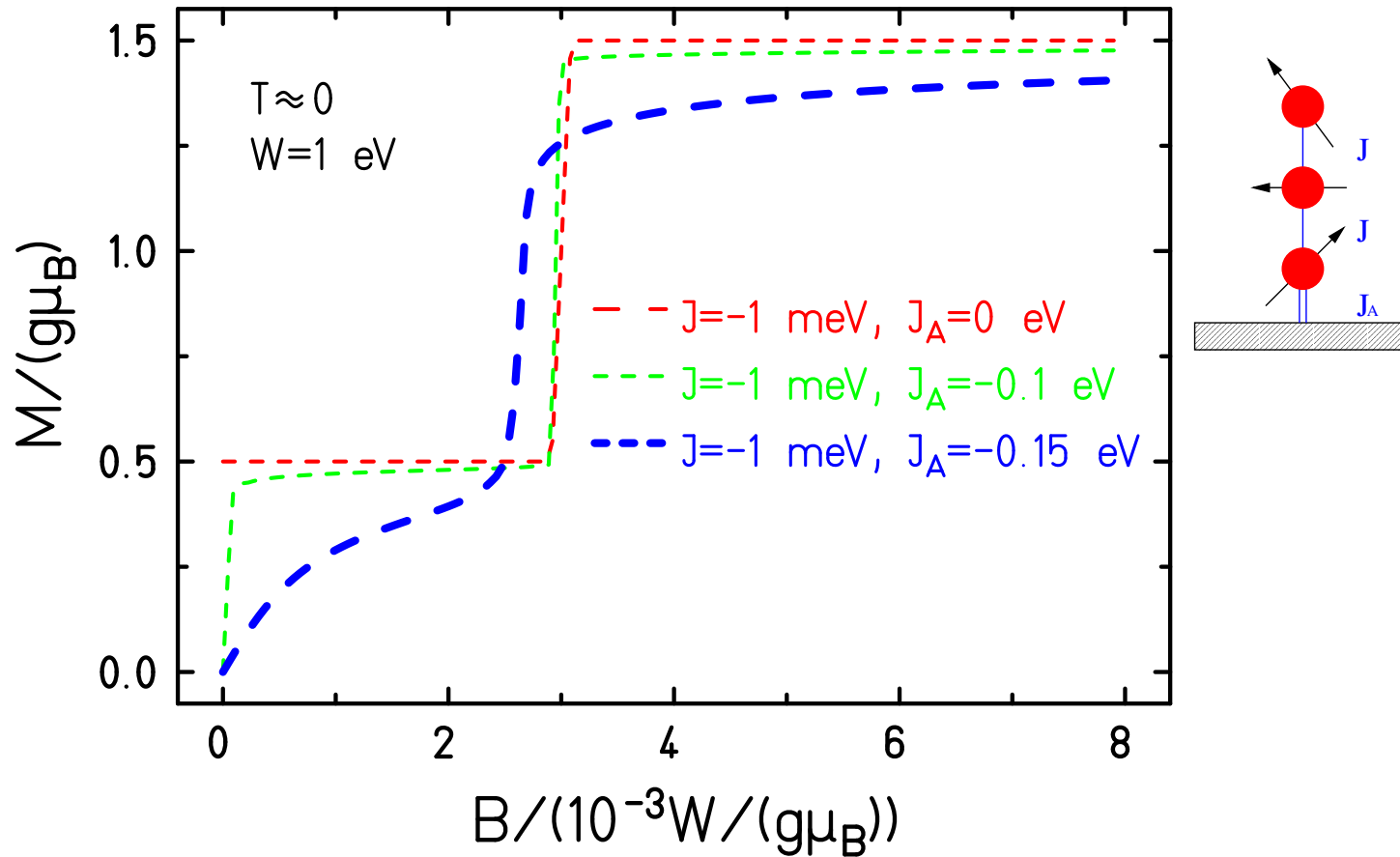
M/(gμ_B) vs B/(10^{-3}W/(gμ_B))

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

$T \approx 0$
$W = 1$ eV

Legend:
- – – – $J = -1$ meV, $J_A = 0$ eV
- – – – $J = -1$ meV, $J_A = -0.1$ eV
- – – – $J = -1$ meV, $J_A = -0.15$ eV
- ── $J = -1$ meV, $J_A = -0.2$ eV
- ── $J = -1$ meV, $J_A = -0.5$ eV

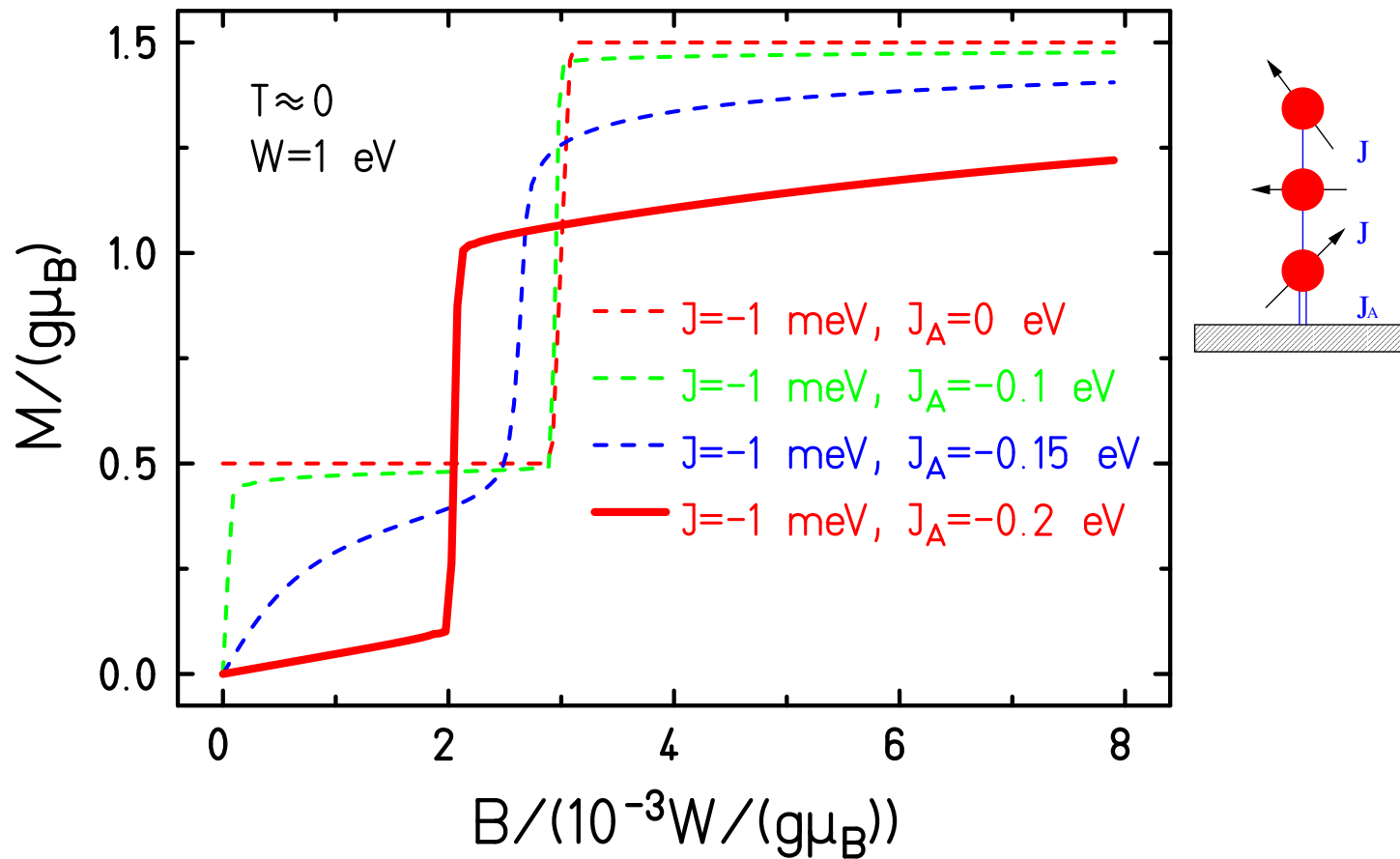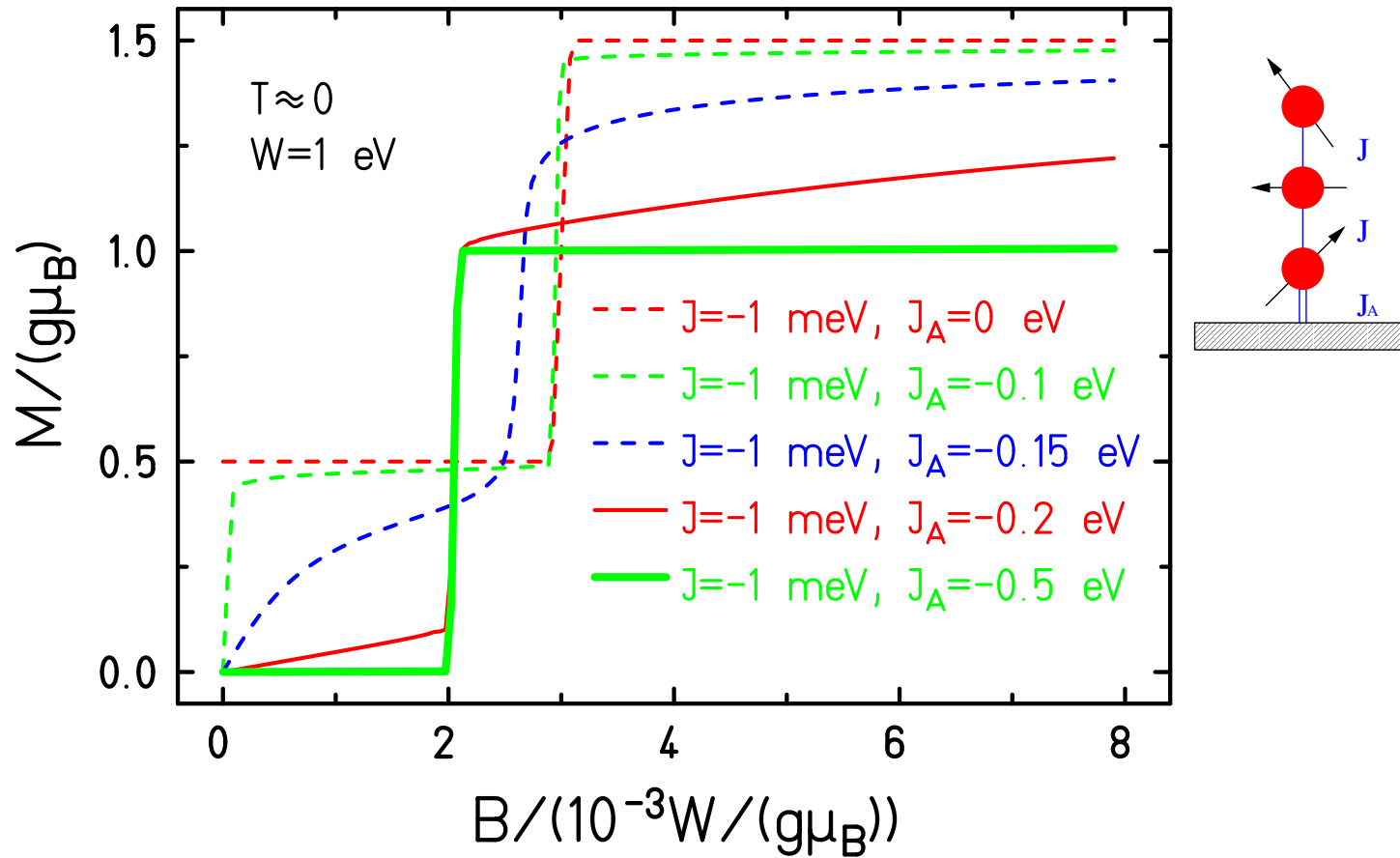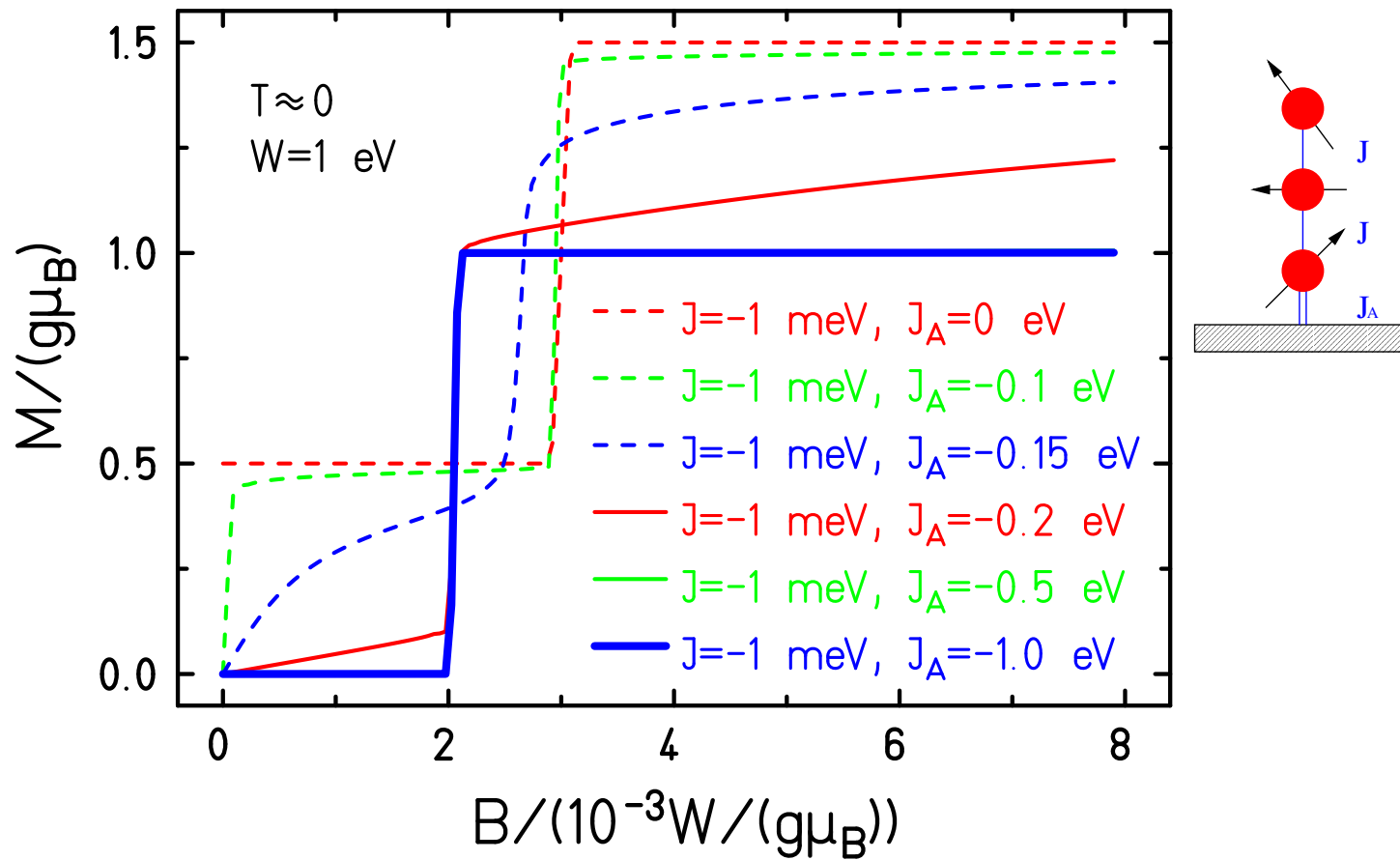Axes: $M/(g\mu_B)$ versus $B/(10^{-3}W/(g\mu_B))$

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

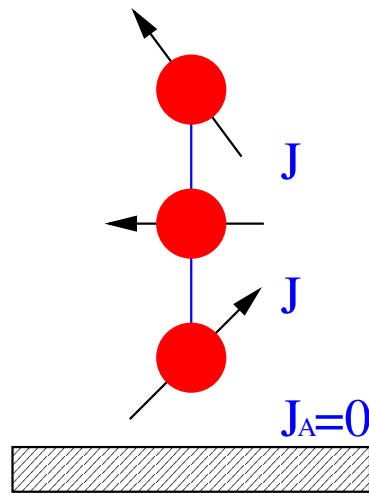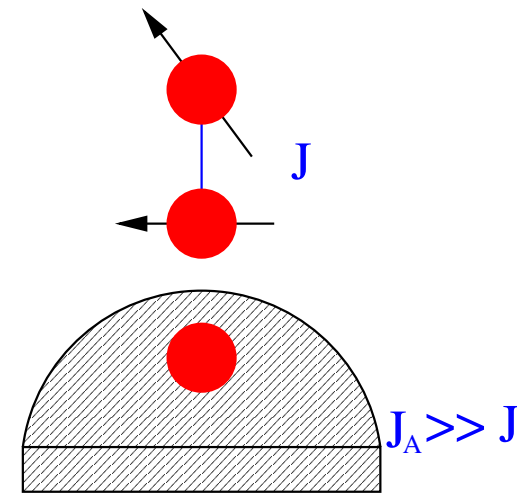- weak coupling limit:
  unperturbed molecule (trimer)

- $|J_A| \lesssim 0.1W$

- strong coupling limit:
  effective remainder (dimer)

- $|J_A| \gtrsim 0.5W$

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

Summary: theory methods

- Complete diagonalization: exact; spectra, transitions, observables, time-evolution; Dimension of largest Hilbert space $< 10^5$.

- Finite Temperature Lanczos Method (FTLM): pseudo-spectrum, low-lying levels good, transitions, observables, time-evolution; DoH $< 10^{10}$.

- Quantum Monte Carlo (QMC): observables; bad/no convergence for competing interactions (frustration) due to negative sign problem; otherwise HUGE systems possible.

- Density Matrix Renormalization Group (DMRG): low-lying target states, correlation functions, short time evolution, maybe thermodynamics; best for 1-d; HUGE systems possible.

- Numerical Renormalization Group (NRG): Kondo or Anderson impurity problems; logarithmic discretization of density of states of conduction electrons; observables as function of T and B.

Many thanks to my collaborators worldwide

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Thank you very much for your attention.

The end.

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