Magnetism of free and deposited magnetic molecules

Jürgen Schnack

Department of Physics – University of Bielefeld – Germany

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

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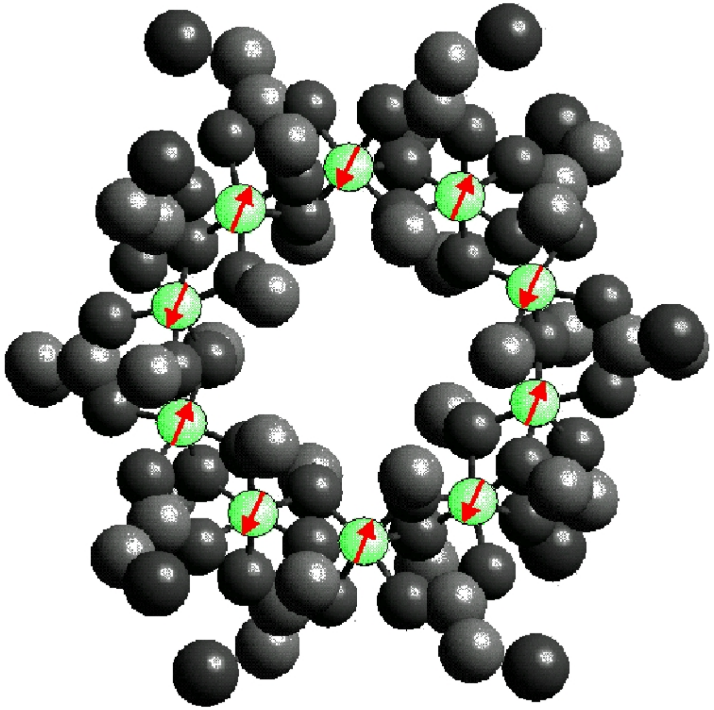
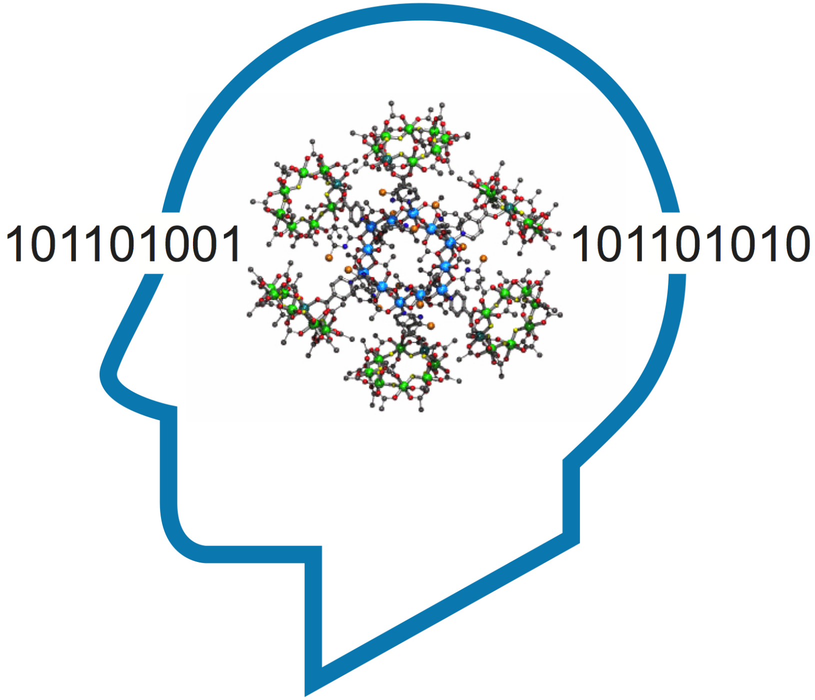
The problem

You have got a molecule!



Congratulations!

You want to build a quantum computer!

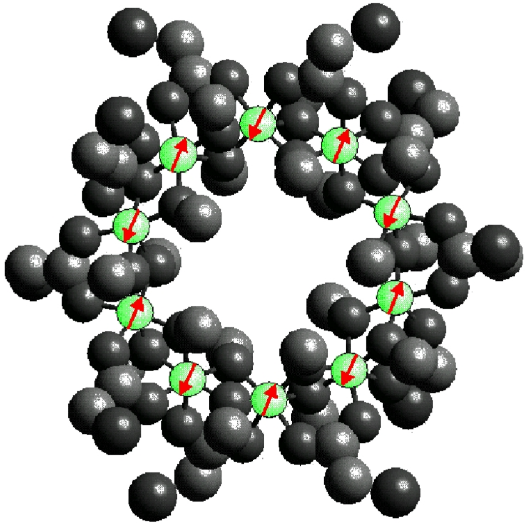


Very smart!

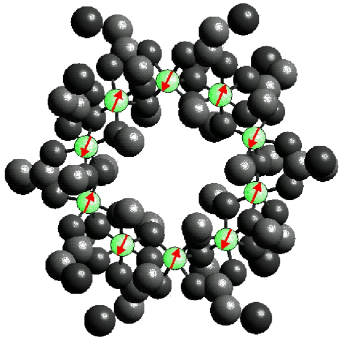
You have got an idea about the modeling!

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

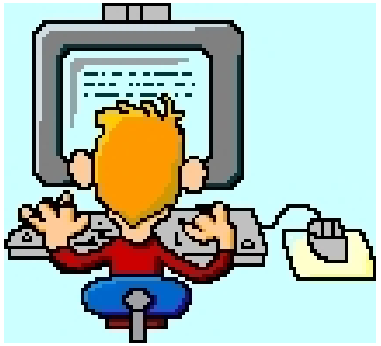
Heisenberg Zeeman



In the end it's always a big matrix!



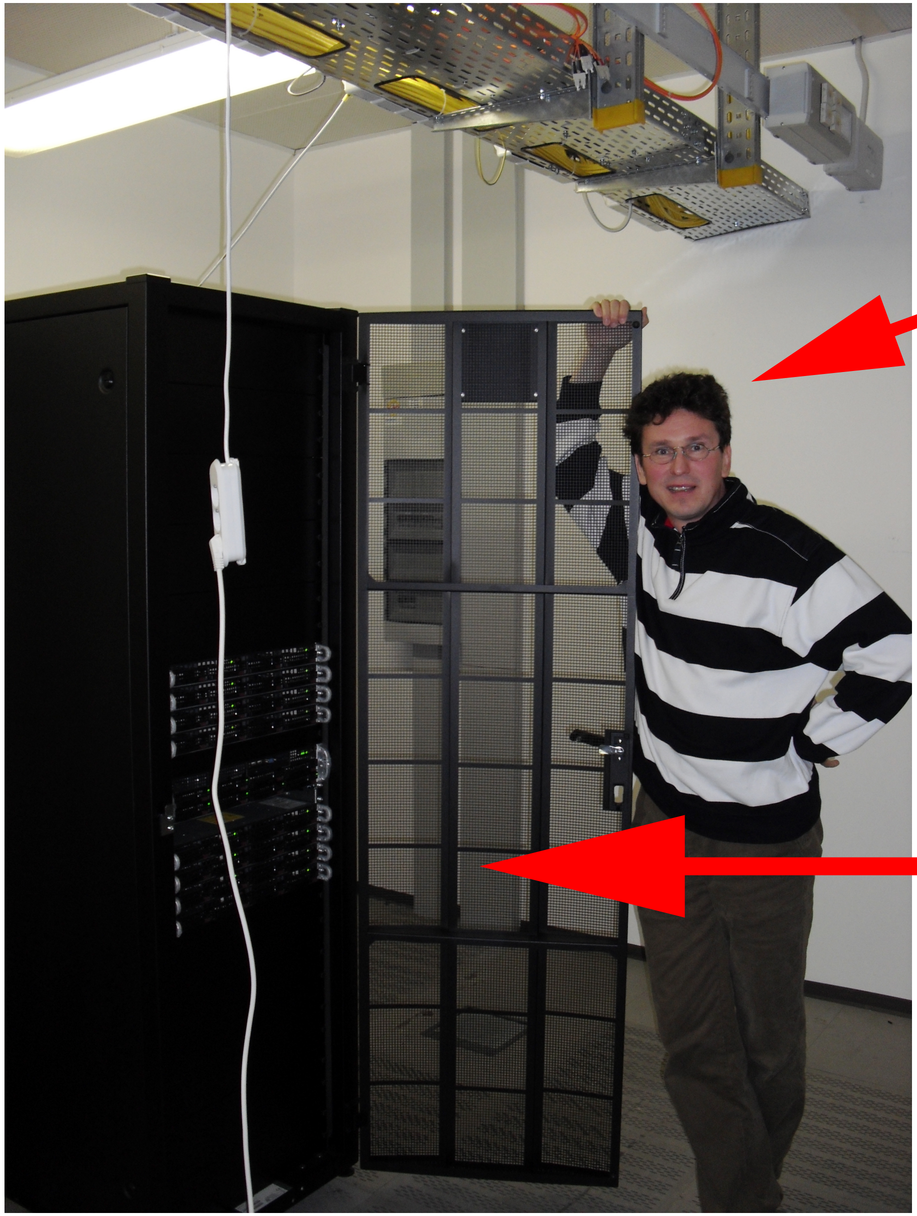
$$\Rightarrow \begin{pmatrix} -27.8 & 3.46 & 0.18 & \cdots \\ 3.46 & -2.35 & -1.7 & \cdots \\ 0.18 & -1.7 & 5.64 & \cdots \\ \vdots & \vdots & \vdots & \cdots \end{pmatrix} \Rightarrow$$



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

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

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

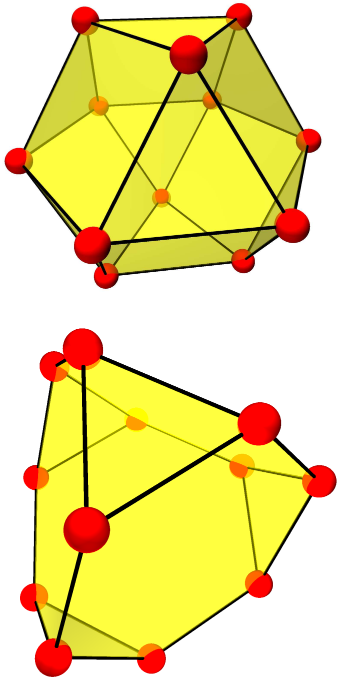
1. Yes, we can
2. A bit on dynamics
3. Deposited spins
4. (Magnetocalorics)

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

Yes, we can!

(Treat spin systems with dimensions up to 10^{10}.)

Irreducible Tensor Operator approach



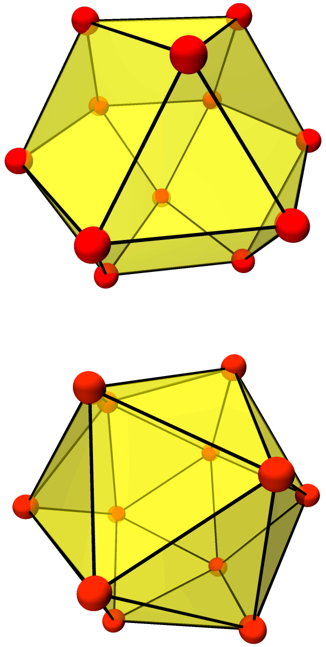
Spin rotational symmetry SU(2):

- $\underset{\sim}{H} = -2\sum_{i<j} J_{ij}\ \underset{\sim}{\vec{s}}_i \cdot \underset{\sim}{\vec{s}}_j + g\mu_B \underset{\sim}{\vec{S}} \cdot \vec{B}$;
- 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

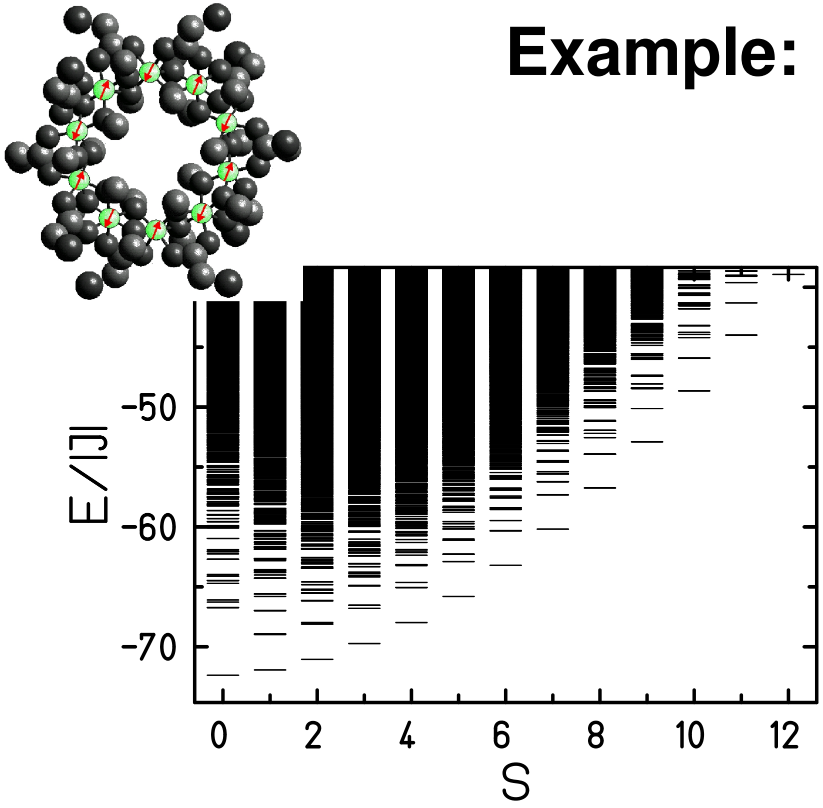


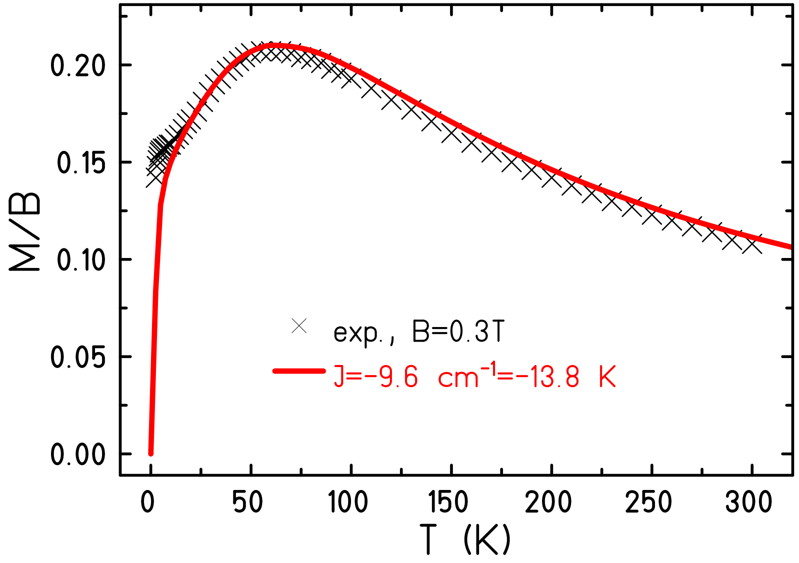
- Point groups, e.g. O_h or I_h, realized as permutations;
- Hamiltonian commutes with all group operations: $\left[\underset{\sim}{H}, \underset{\sim}{G}_i\right] = 0$;
- Construct irreducible representations and related Hamilton matrices;

  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.

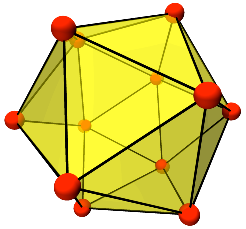
Example: Fe$_{10}$ – SU(2) & D_2



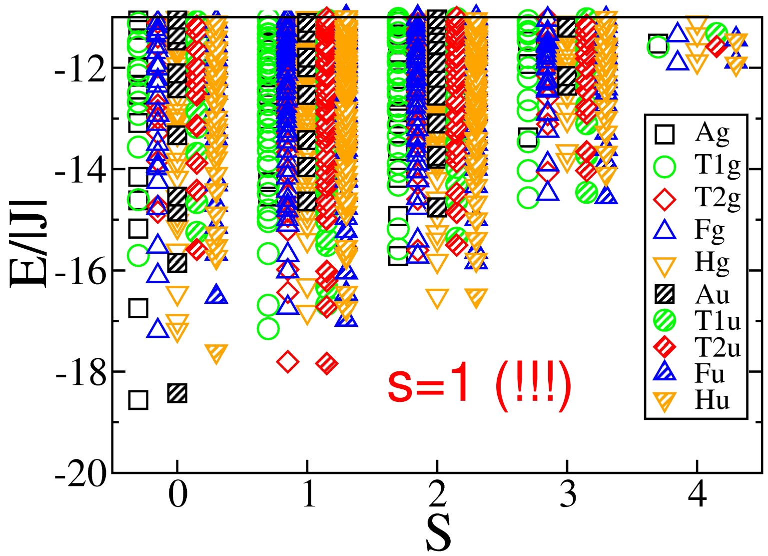


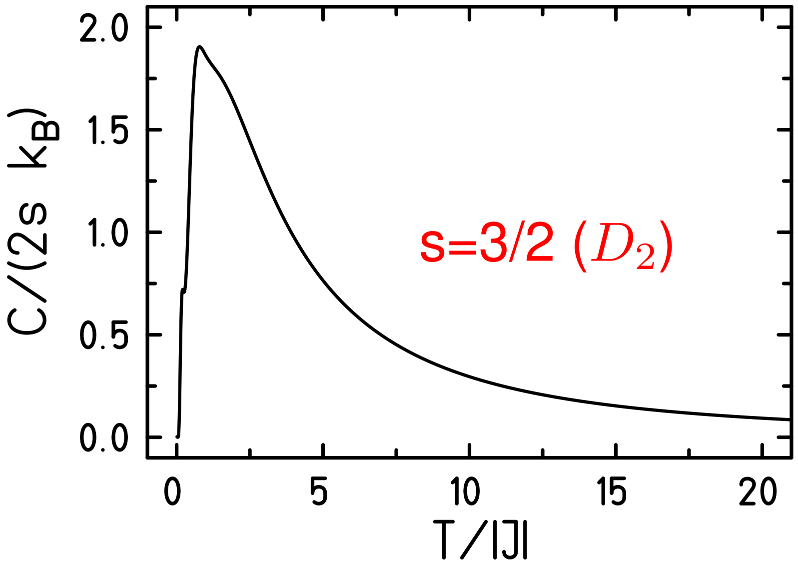
Spin ring, $N = 10$, $s = 5/2$, Hilbert space dimension 60,466,176; symmetry D_2 (1).

(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).

What if your molecule is

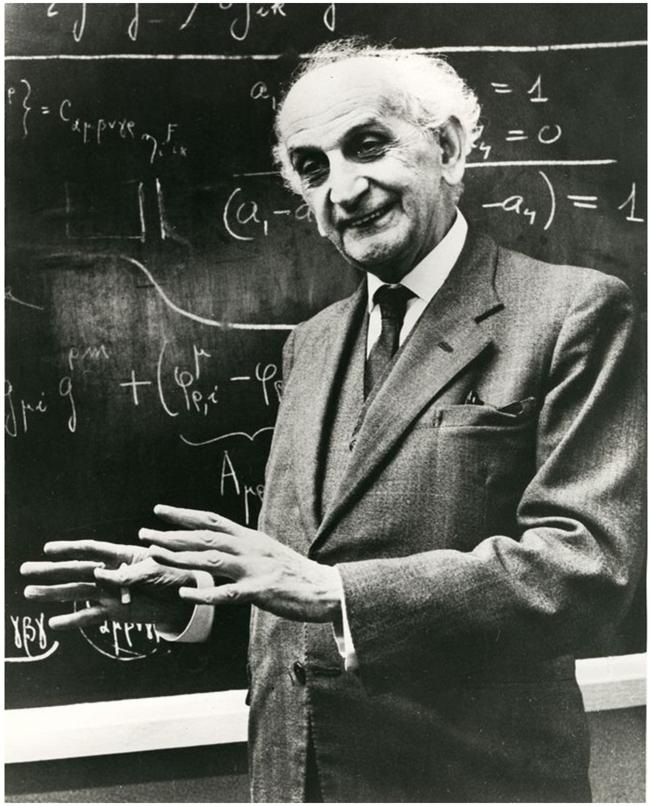
BIGGER?

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

Finite-temperature Lanczos Method I

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

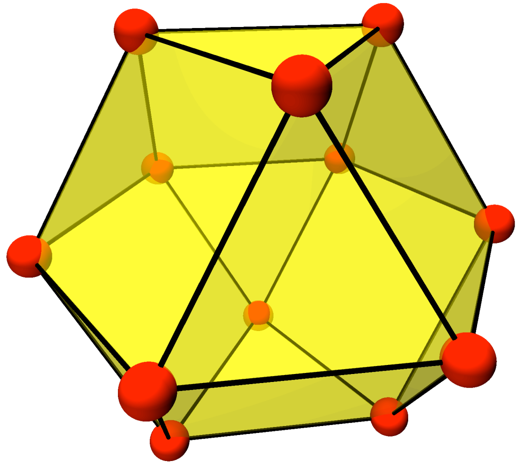
$$\langle\, \nu \,|\, \exp\left\{-\beta \underset{\sim}{H}\right\} |\, \nu \,\rangle \approx \sum_n \langle\, \nu \,|\, n(\nu) \,\rangle \exp\left\{-\beta \epsilon_n\right\} \langle\, n(\nu) \,|\, \nu \,\rangle$$

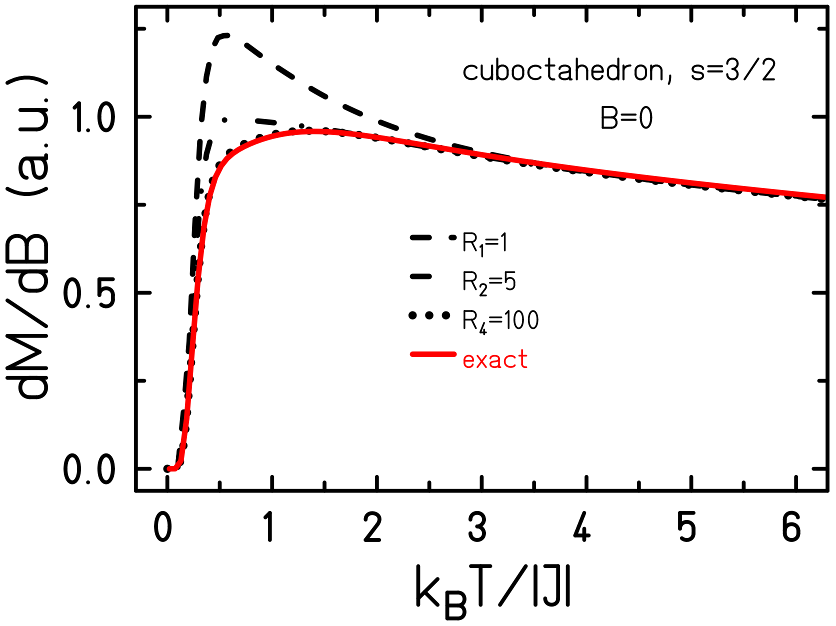
$$Z(T,B) \approx \frac{\text{dim}(\mathcal{H})}{R} \sum_{\nu=1}^{R} \sum_{n=1}^{N_L} \exp\left\{-\beta \epsilon_n\right\} |\langle\, n(\nu) \,|\, \nu \,\rangle|^2$$

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

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

How good is finite-temperature Lanczos?

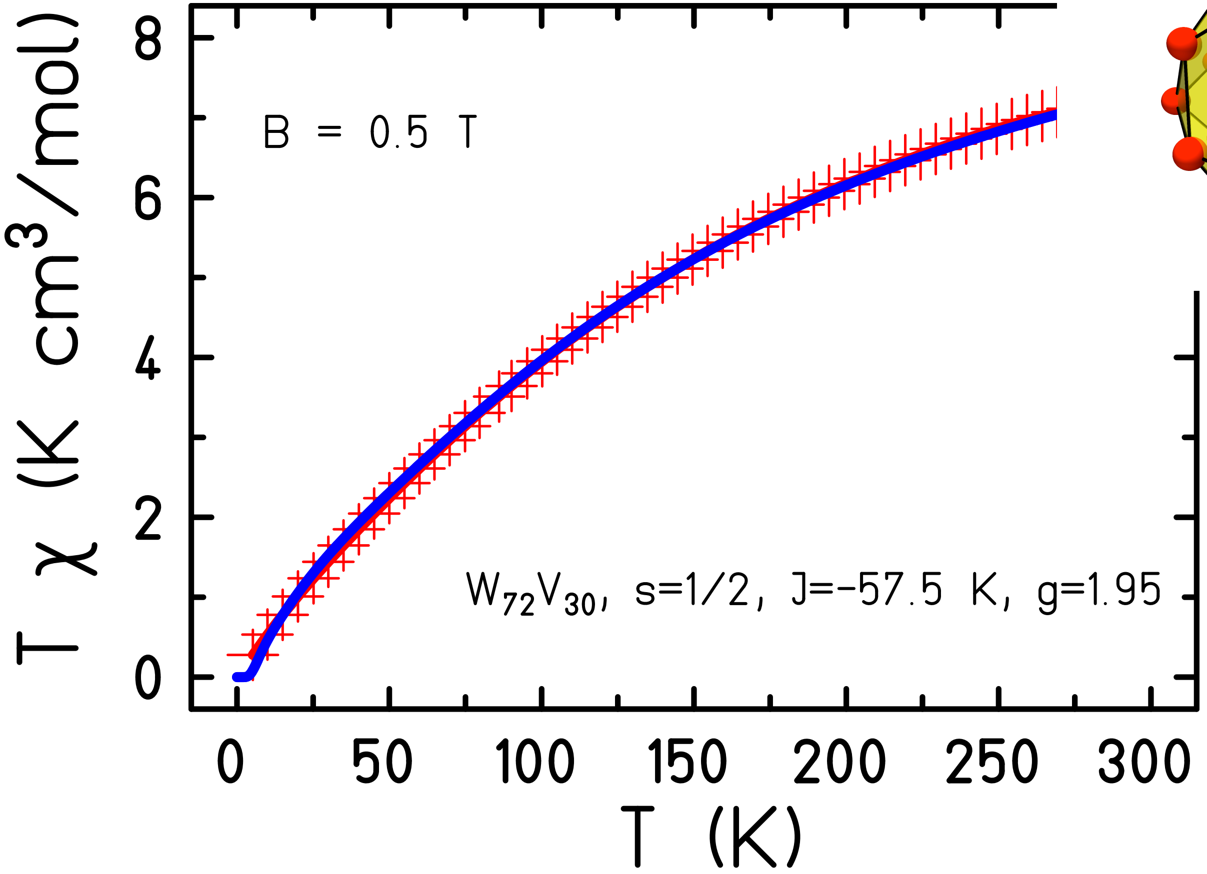


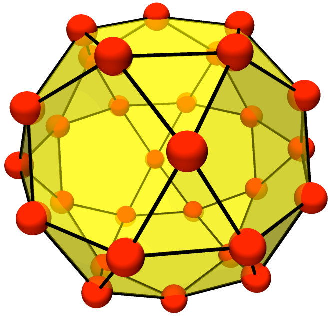


- Works very well: compare frustrated cuboctahedron.
- $N = 12, s = 3/2$: Considered $< 100,000$ states instead of 16,777,216.

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).

Finite-temperature Lanczos Method III

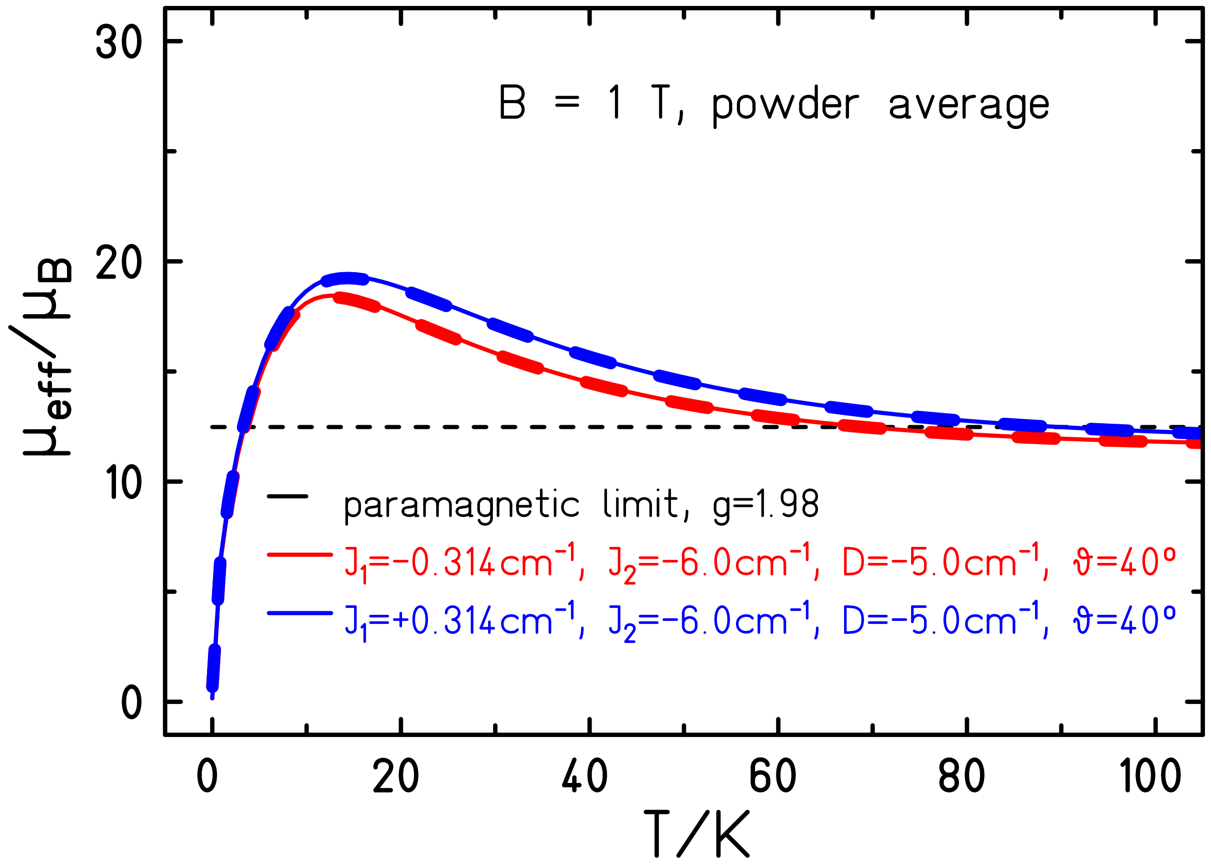
$$\underset{\sim}{H} \;=\; -2\sum_{i<j} \underset{\sim}{\vec{s}}_i \cdot \mathbf{J}_{ij} \cdot \underset{\sim}{\vec{s}}_j + \sum_i \underset{\sim}{\vec{s}}_i \cdot \mathbf{D}_i \cdot \underset{\sim}{\vec{s}}_i + \mu_B\, B \sum_i g_i \underset{\sim}{s}{}_i^z$$

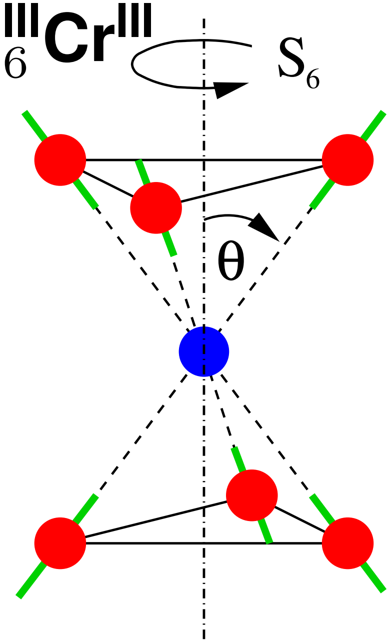
- Problem: for anisotropic Hamiltonians no symmetry left
  → accuracy drops (esp. for high T).

- 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)

Glaser-type molecules: $\mathrm{Mn}_6^{\mathrm{III}}\mathrm{Cr}^{\mathrm{III}}$





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

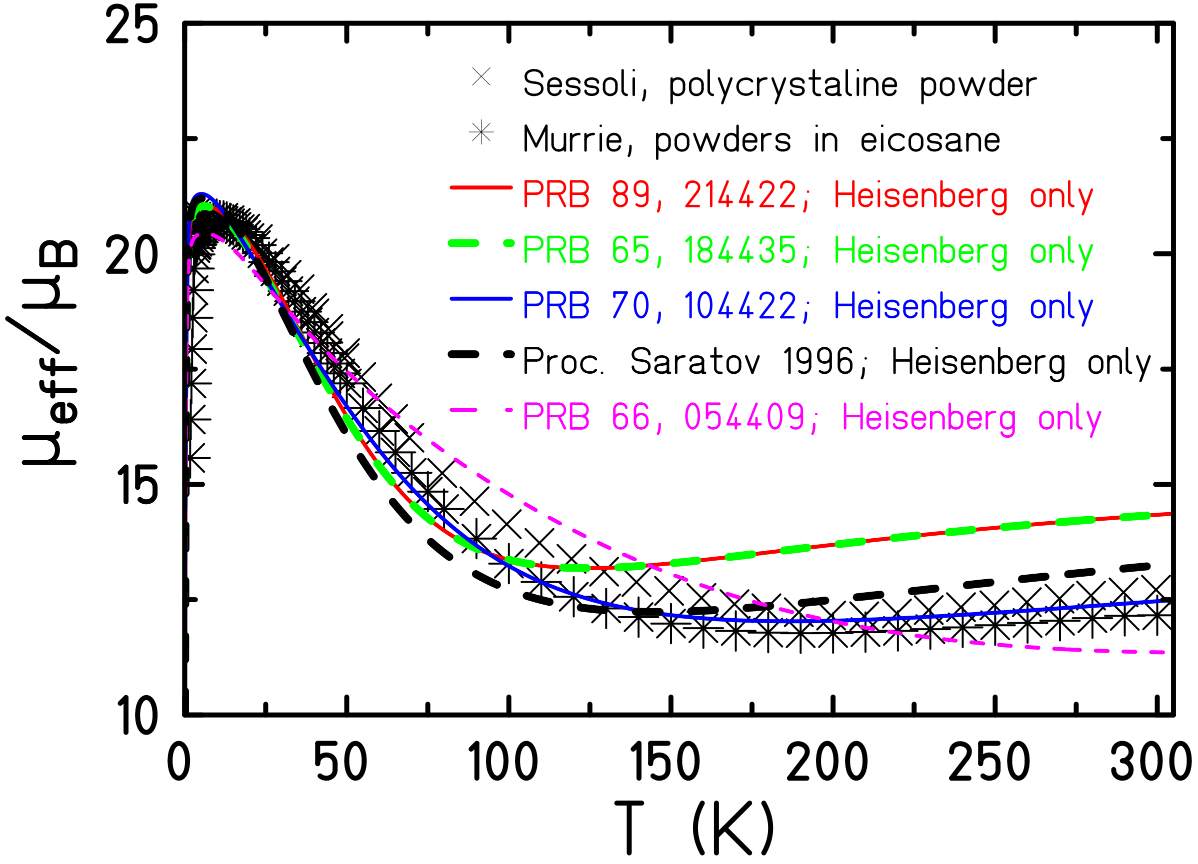
dim$(\mathcal{H}) = 62,500$

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)

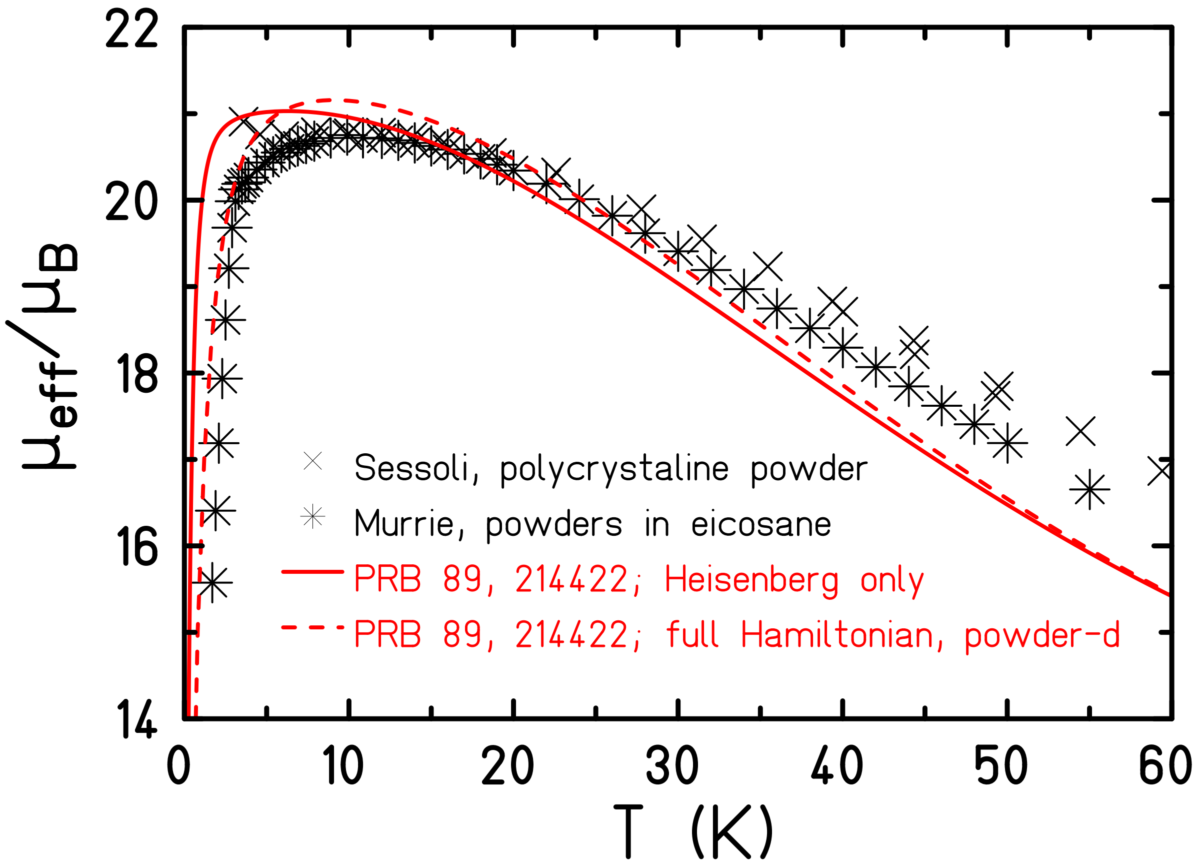
Effective magnetic moment of Mn_{12}-acetate



We can check DFT parameter predictions for large molecules!

O. Hanebaum, J. Schnack, work in progress

Effective magnetic moment of Mn_{12}-acetate



We can check DFT parameter predictions for large molecules!

O. Hanebaum, J. Schnack, work in progress

A bit on dynamics

Quantum master equation

$$\frac{d}{dt}\,\underset{\sim}{\rho}(t) \;=\; \frac{1}{i\hbar}\left[\underset{\sim}{H}(t), \underset{\sim}{\rho}(t)\right] + \hat{L}\underset{\sim}{\rho}(t)$$

$\hat{L}$ – the UNKNOWN super operator (a very dark horse!) models the influence of the environment (bath) on the actual system; depends on the interactions and typ of bath. This term is responsible for thermalization, relaxation, decoherence.

The structure of $\hat{L}$ is such, that the density matrix remains a density matrix (conservation of probability).

(1) N.V. Prokof'ev, P.C.E. Stamp, Rep. Prog. Phys. **63**, 669 (2000); Phys. Rev. Lett. **80**, 5794 (1998).

(2) Heinz-Peter Breuer, *The Theory of Open Quantum Systems*, Oxford University Press (2007).

A simple example

$$\frac{d}{dt}\,\underset{\sim}{\rho}(t) \;=\; \frac{1}{\tau}\left(\underset{\sim}{\rho}^{(\text{eq})}(T,B) - \underset{\sim}{\rho}(t)\right)$$

Describes an exponential relaxation towards thermal equilibrium with a single relaxation time τ. Fully phenomenological.

$$\underset{\sim}{\rho}(t) \;=\; \left(1 - e^{-\frac{t}{\tau}}\right)\underset{\sim}{\rho}^{(\text{eq})}(T,B) + e^{-\frac{t}{\tau}}\underset{\sim}{\rho}(0)\ .$$

Simple quantum dynamics with relaxation/decoherence

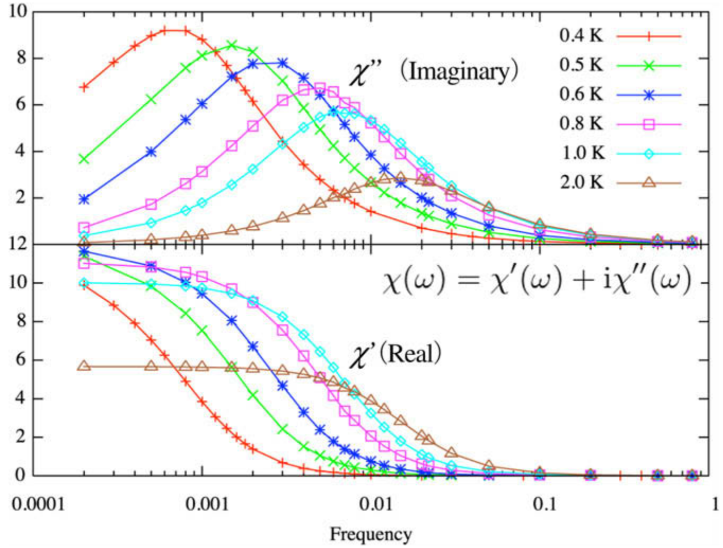
$$\frac{d}{dt}\,\underset{\sim}{\rho}(t) \;=\; \frac{1}{i\hbar}\left[\underset{\sim}{H}(t),\underset{\sim}{\rho}(t)\right] + \frac{1}{\tau}\left(\underset{\sim}{\rho}^{(\text{eq})}(T,B(t)) - \underset{\sim}{\rho}(t)\right)$$

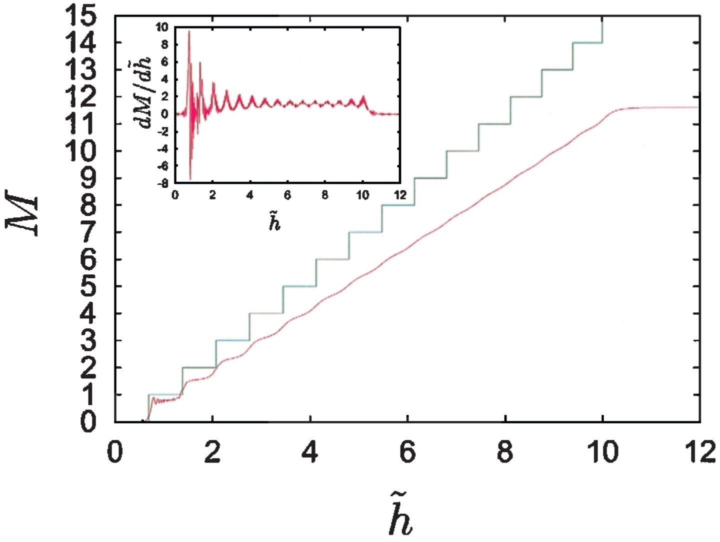
Not a bad start to investigate coherent dynamics under the influence of a heat bath with a single relaxation time τ.

$\underset{\sim}{\rho}^{(\text{eq})}(T,B(t))$ is the equilibrium density matrix for the time-dependent magnetic field at fixed temperature.

related: P. Santini *et al.*, Phys. Rev. Lett. **94**, 077203 (2005).

Realistic bath





Interaction with phonons. AC-susceptibility of a single spin (1). Magnetization dynamics in a pulsed field (2).

(1) T. Kawakami *et al.*, Polyhedron **28**, 2092 (2009).

(2) H. Nakano and S. Miyashita, J. Phys. Soc. Jpn. **70**, 2151 (2001).

Why are such calculations so rare?

$$\frac{d}{dt}\,\underset{\sim}{\rho}(t) \;=\; \frac{1}{i\hbar}\left[\underset{\sim}{H}(t), \underset{\sim}{\rho}(t)\right] + \hat{L}\underset{\sim}{\rho}(t)$$

1. $\underset{\sim}{\rho}(t)$ has Dim($\mathcal{H}$)×Dim($\mathcal{H}$) entries!

2. $\hat{L}$ is not really known;
   there are reasonable assumptions such as Lindblad form etc.

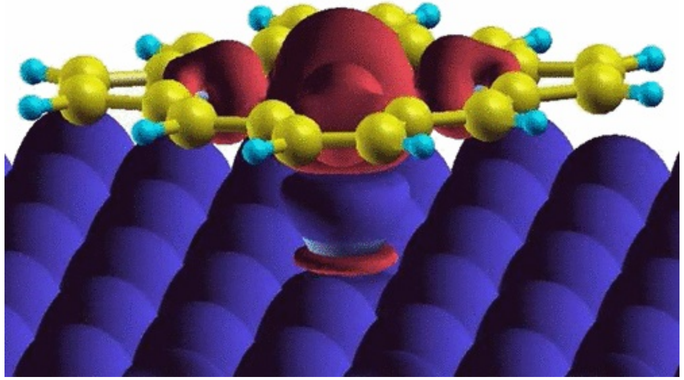
Very encouraging calculations along these lines concerning the question of robustness (1)!

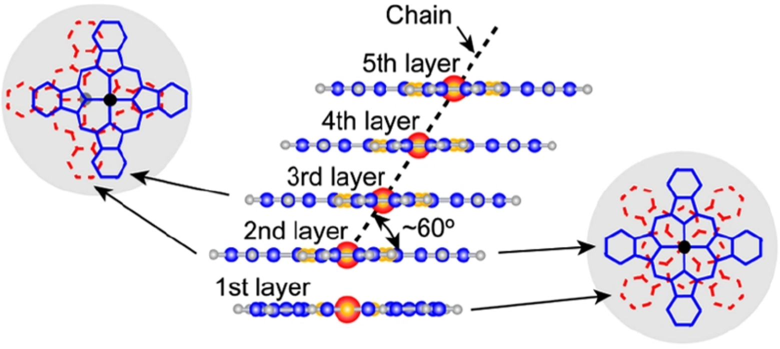
(1) A. Chiesa, D. Gerace, F. Troiani, G. Amoretti, P. Santini, S. Carretta, Phys. Rev. A **89**, 052308 (2014).

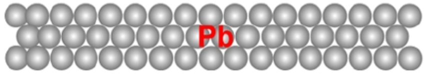
Numerical Renormalization Group calculations

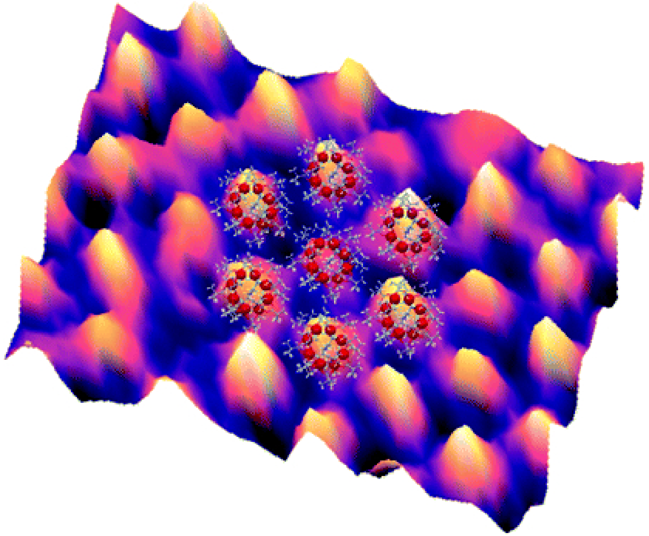
(Good for deposited molecules.)

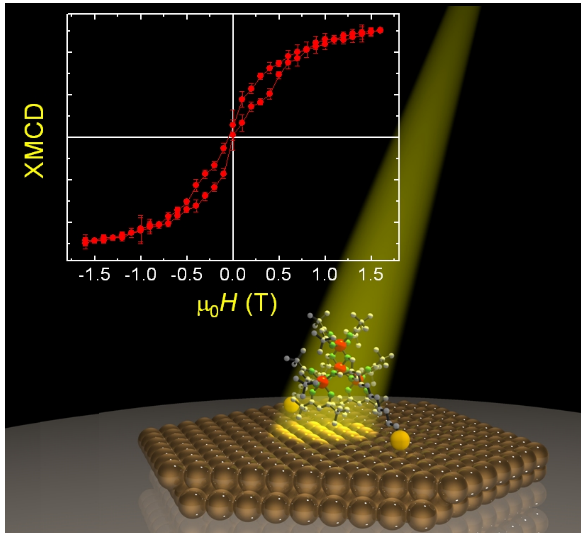
You want to deposite a molecule





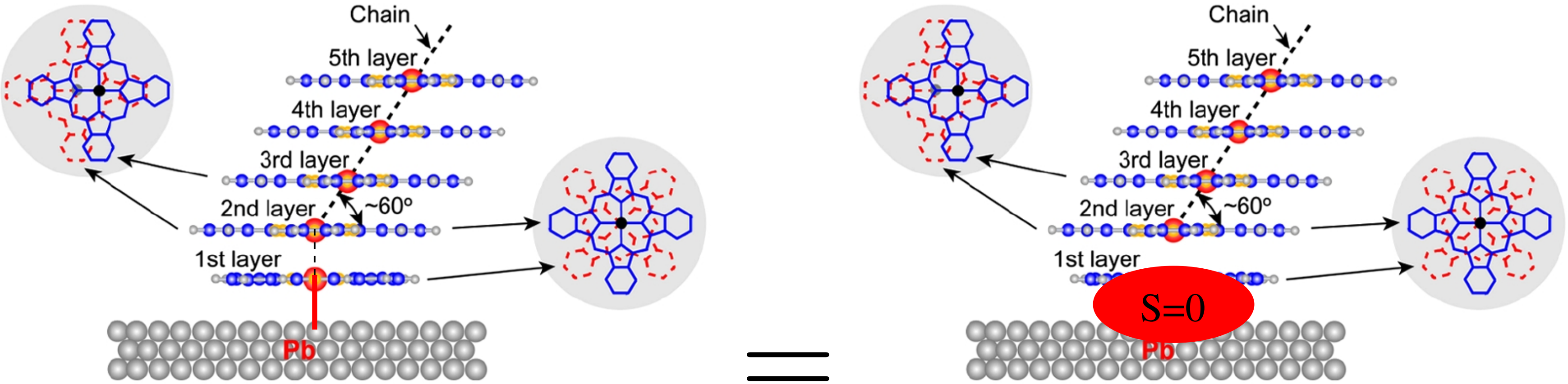






M. Bernien *et al.*, Phys. Rev. Lett. **102**, 047202 (2009); A. Ghirri*et al.*, ACS Nano, **5**, 7090-7099 (2011); X. Chen *et al.*, Phys. Rev. Lett. **101**, 197208 (2008); M. Mannini *et al.*, Nature Materials **8**, 194 - 197 (2009).

Physical example (ICMM 2010)

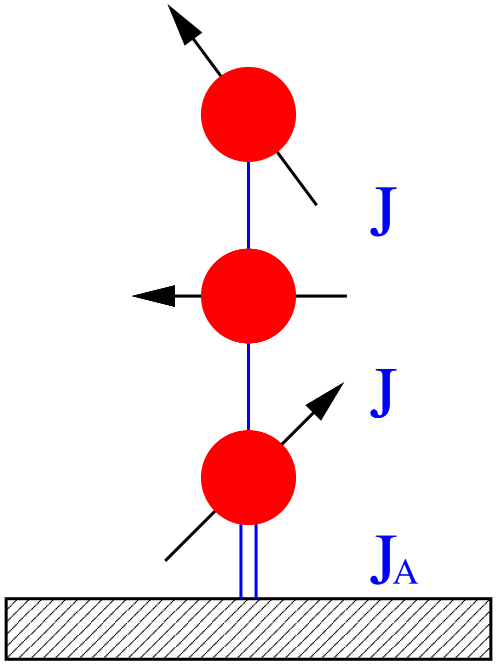


Stack of deposited Cobalt phthalocyanine (CoPc) molecules;
Co^{2+} with spin $s = 1/2$.

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!)



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

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

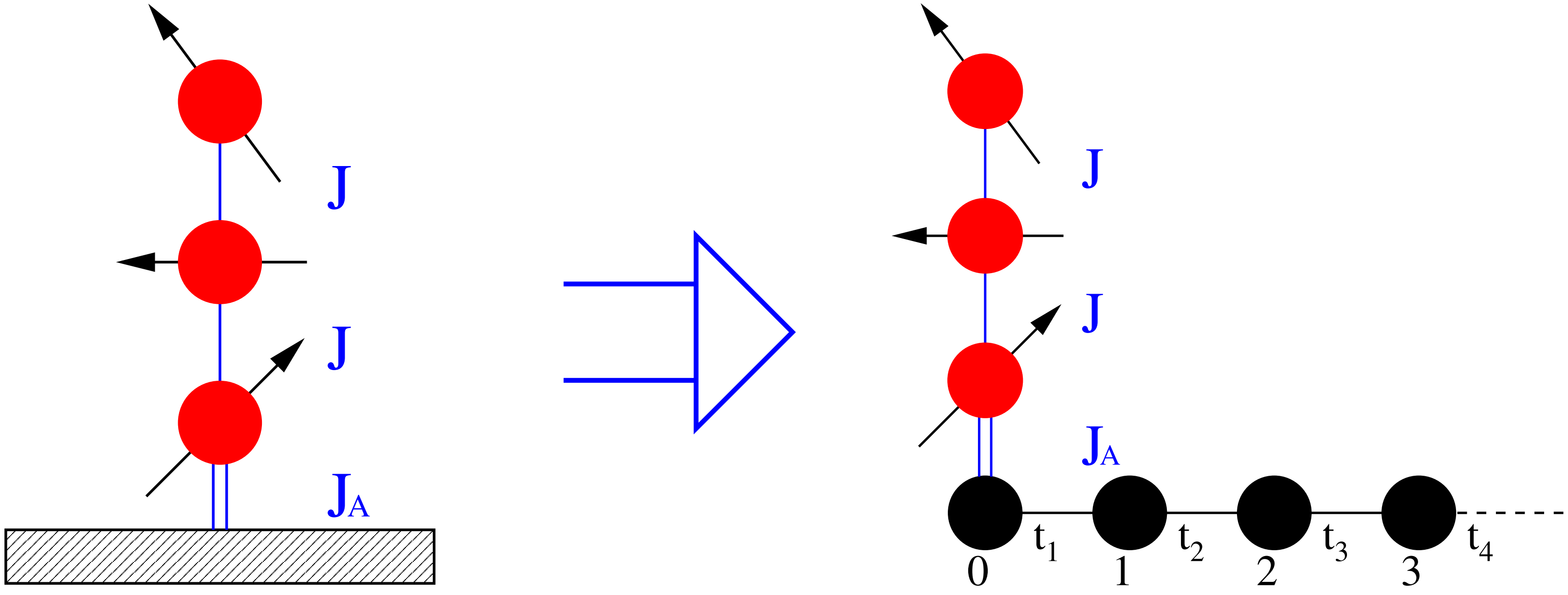
  $\underset{\sim}{H}_{\text{coupling}} = -2 J_A \underset{\sim}{\boldsymbol{S}} \cdot \underset{\sim}{\boldsymbol{s}}_0$, $\underset{\sim}{\boldsymbol{s}}_0$ – spin density at contact

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



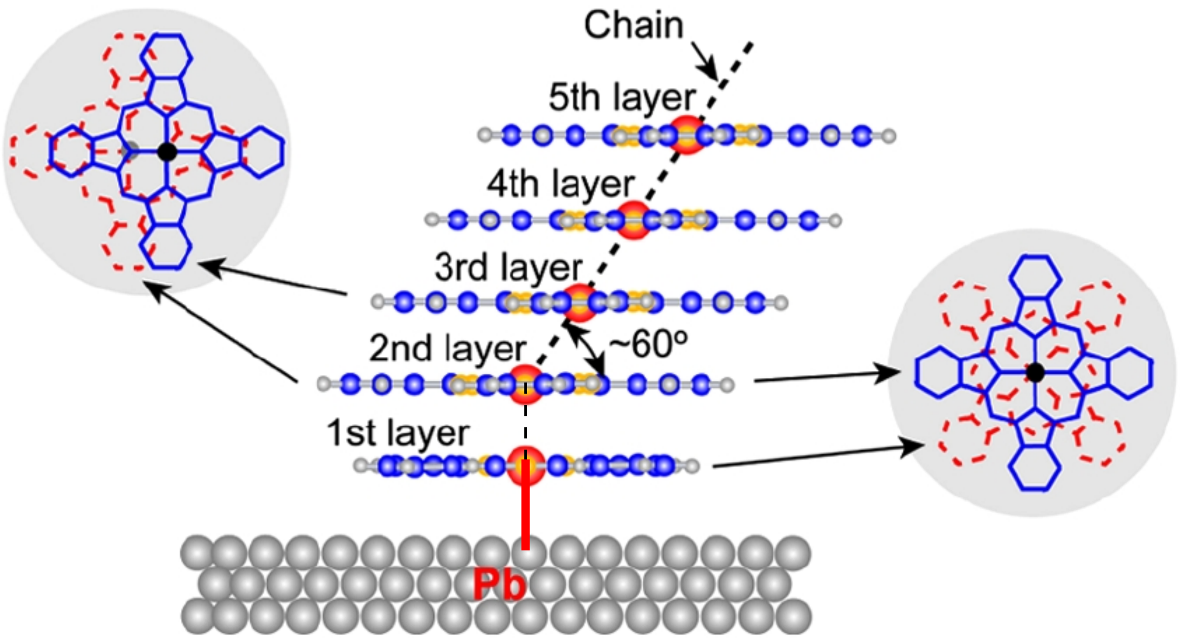
Metallic surface is replaced by semi-infinite Hubbard chain;

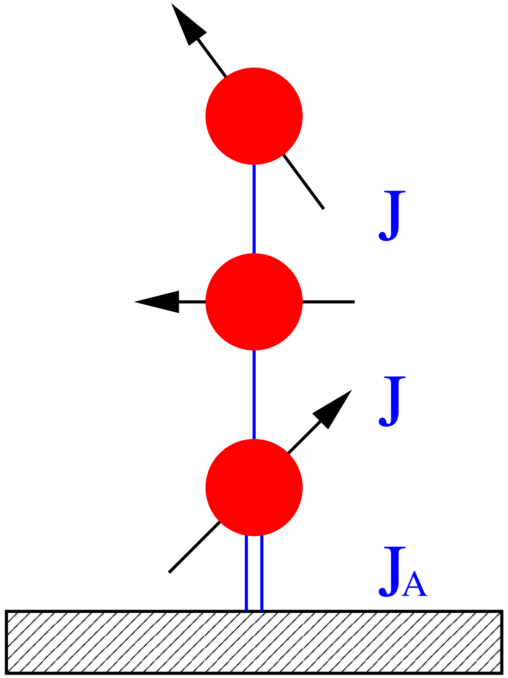
Parameters of the chain: hopping matrix elements and on-site energies;

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

Truncation of basis set when matrices grow too big.

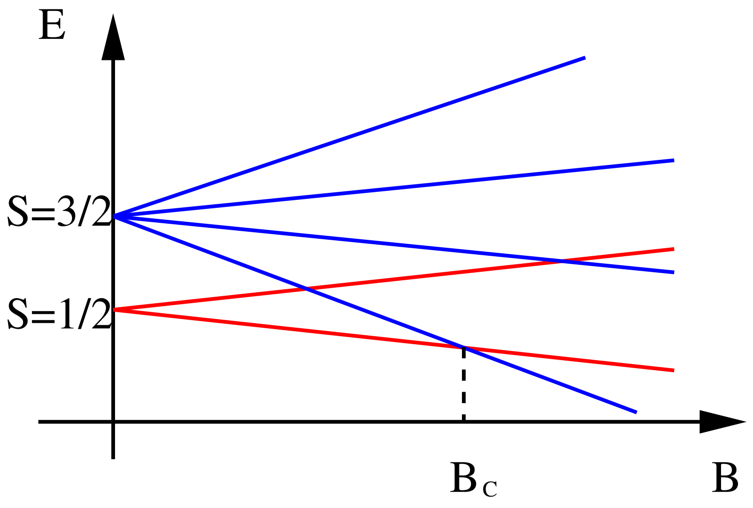
Once more: deposited chain

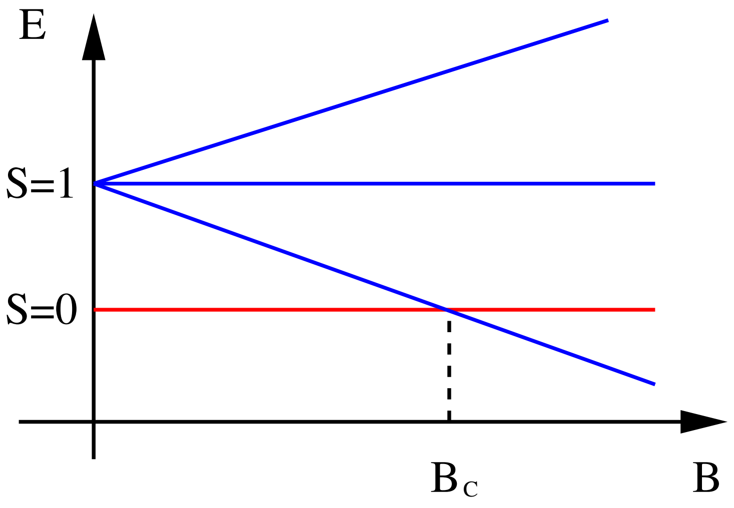




X. Chen *et al.*, Phys. Rev. Lett. **101**, 197208 (2008).

Energy levels of limiting cases for deposited trimer

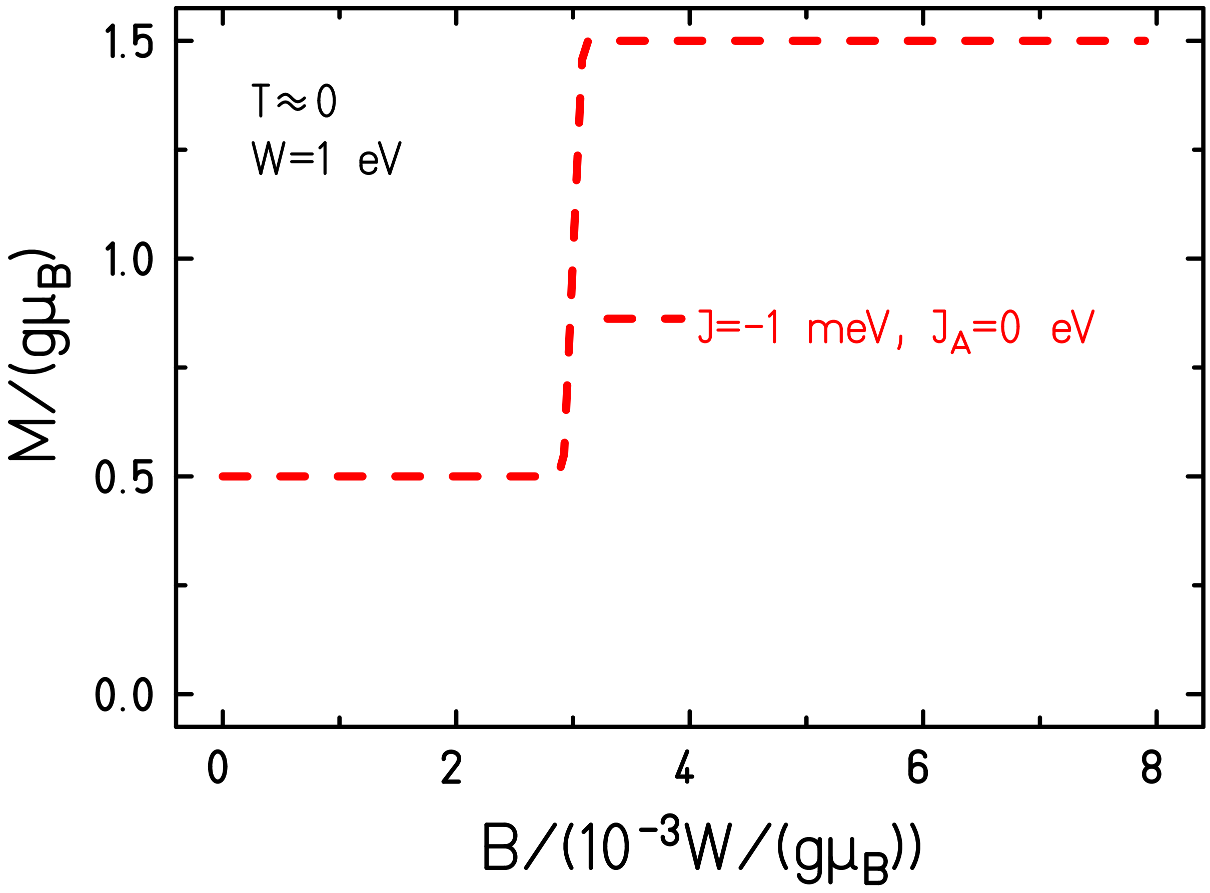


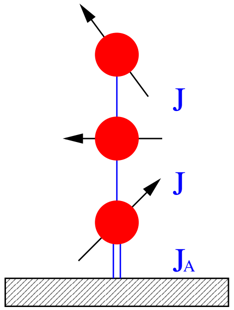


- energy levels of a trimer
- energy levels of a dimer

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.

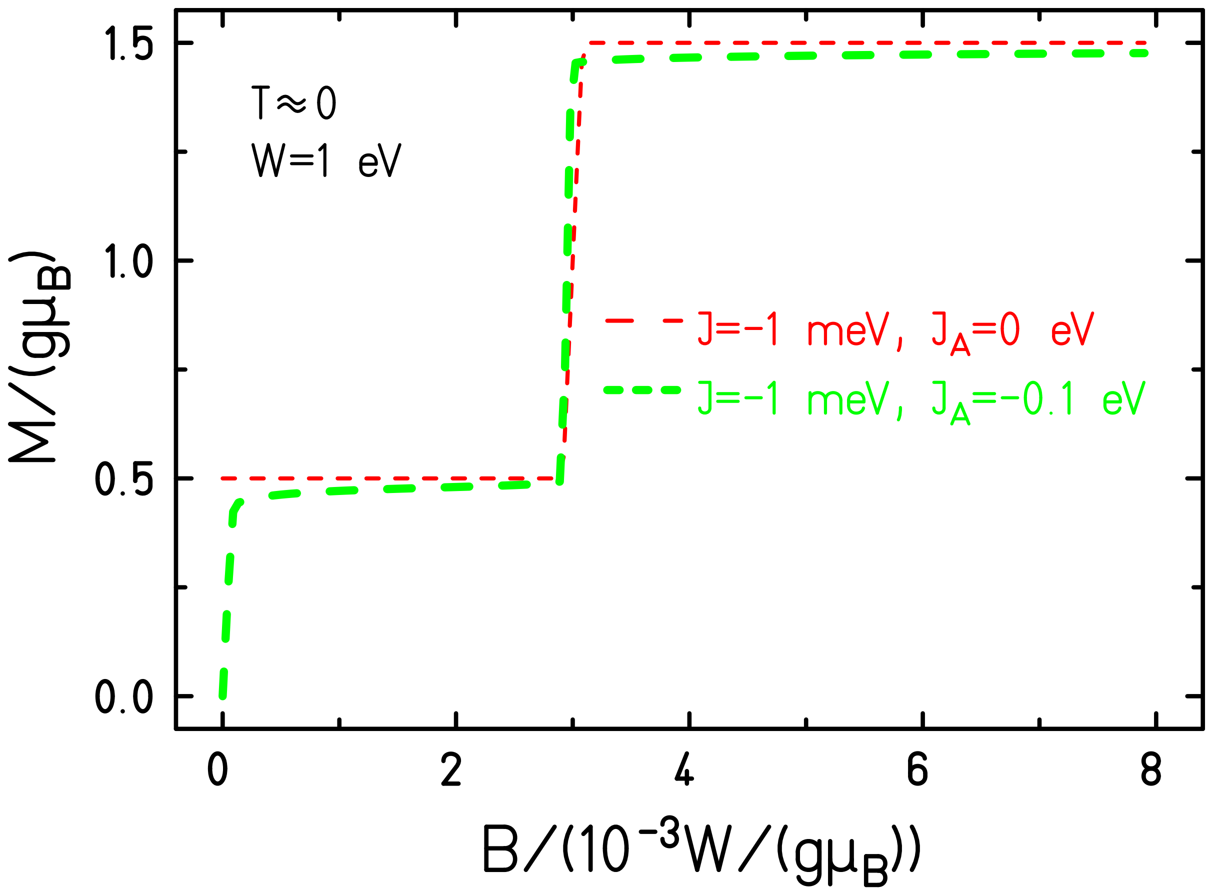
Increasing coupling to the substrate

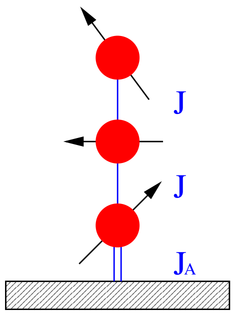




H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

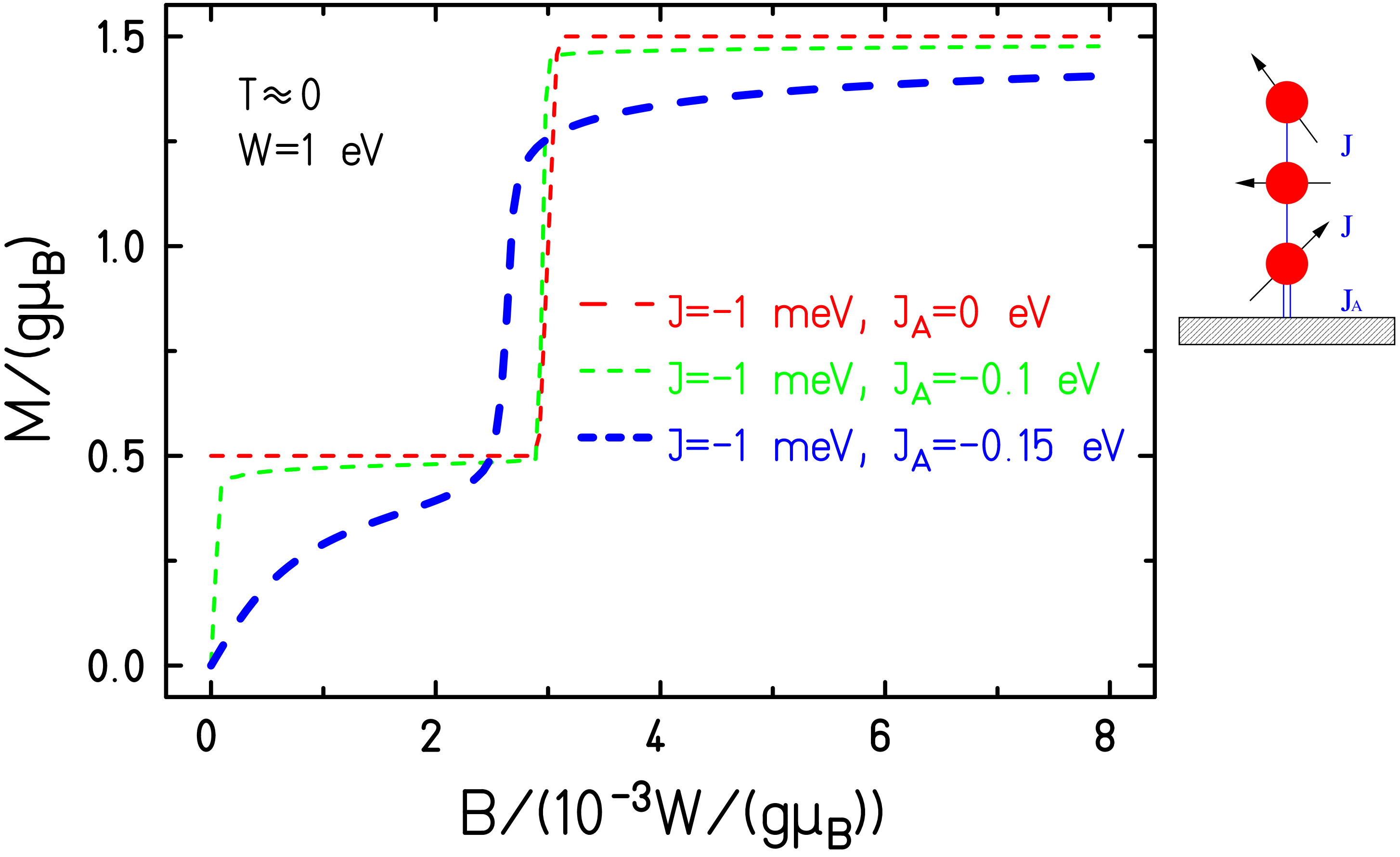
Increasing coupling to the substrate





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

Increasing coupling to the substrate



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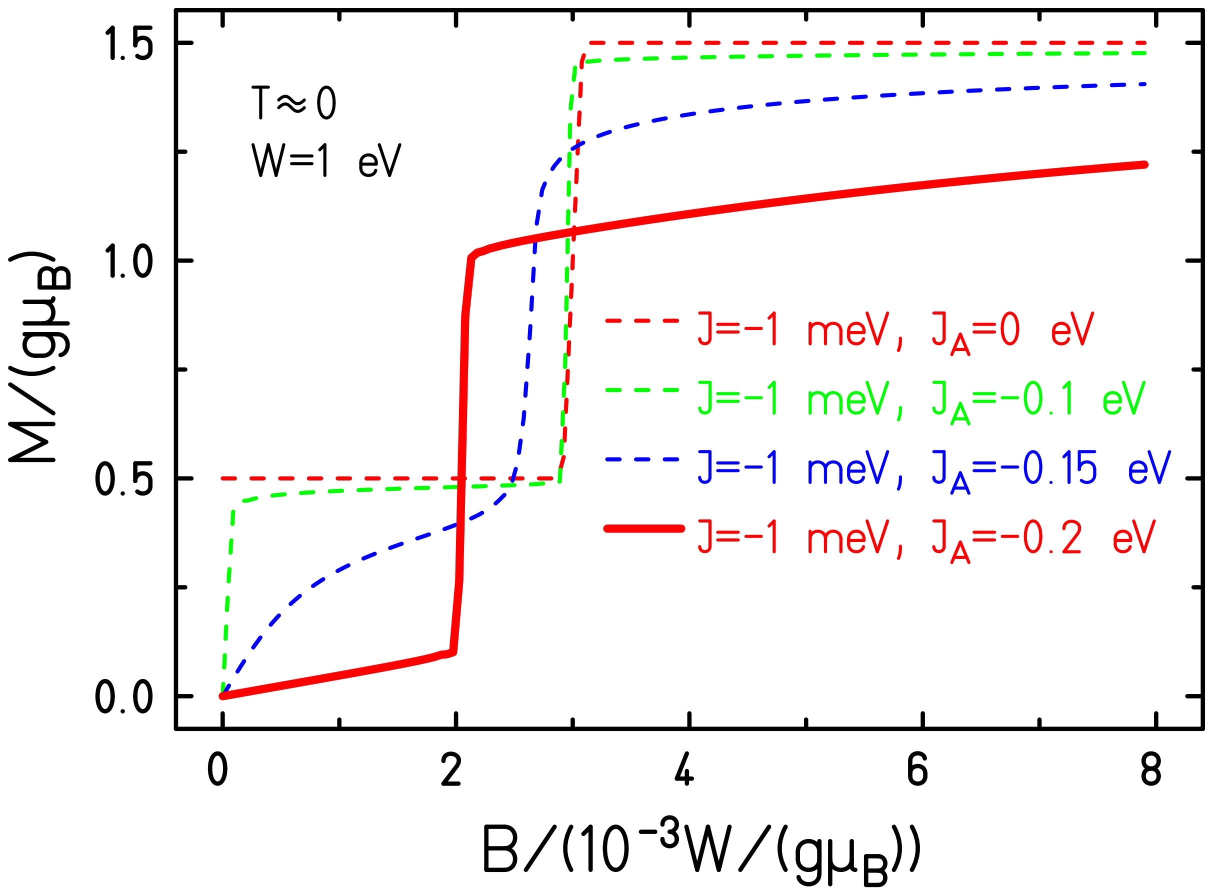
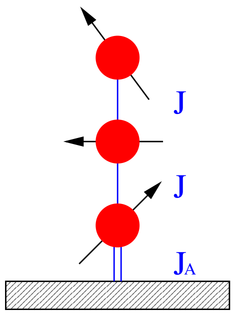
Increasing coupling to the substrate





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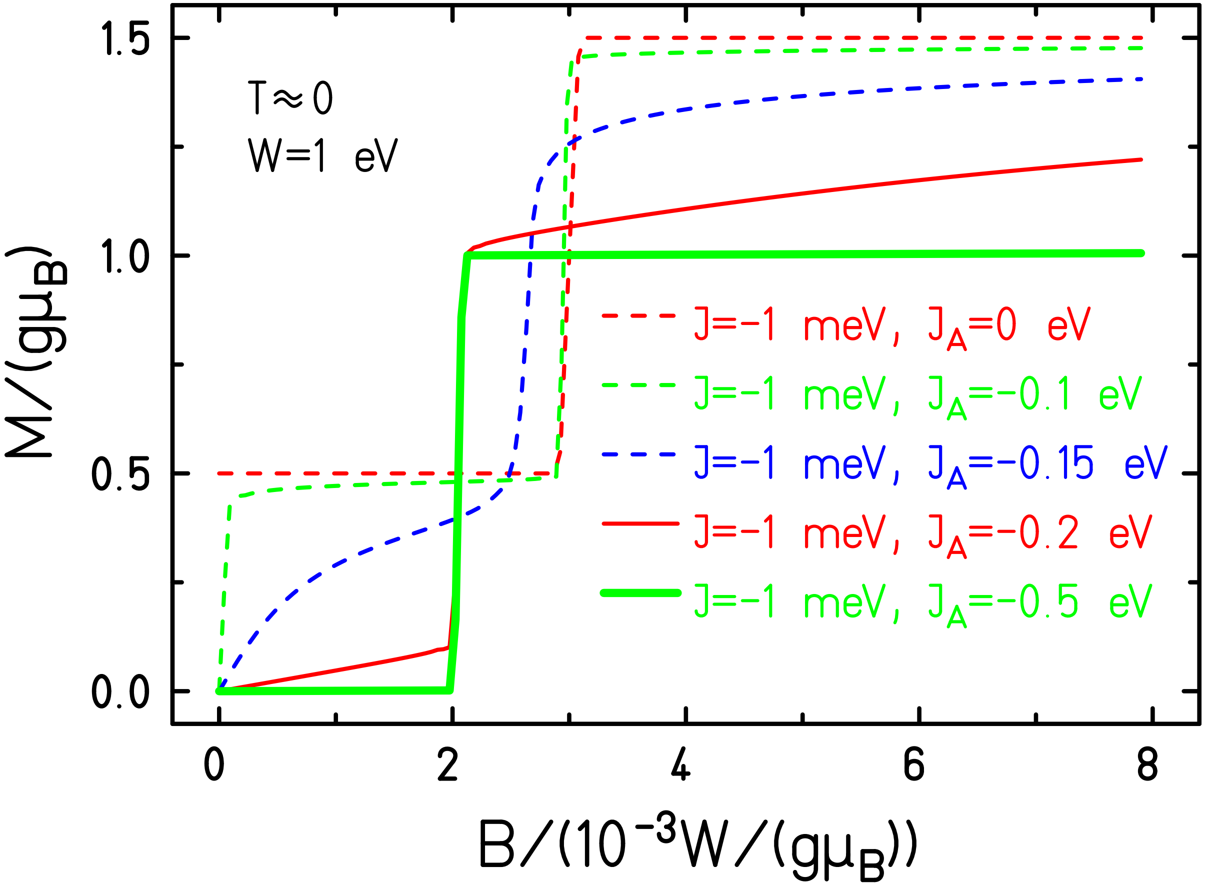
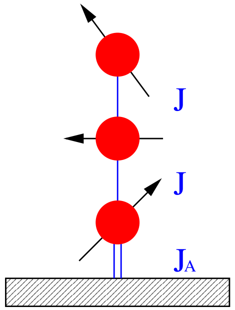
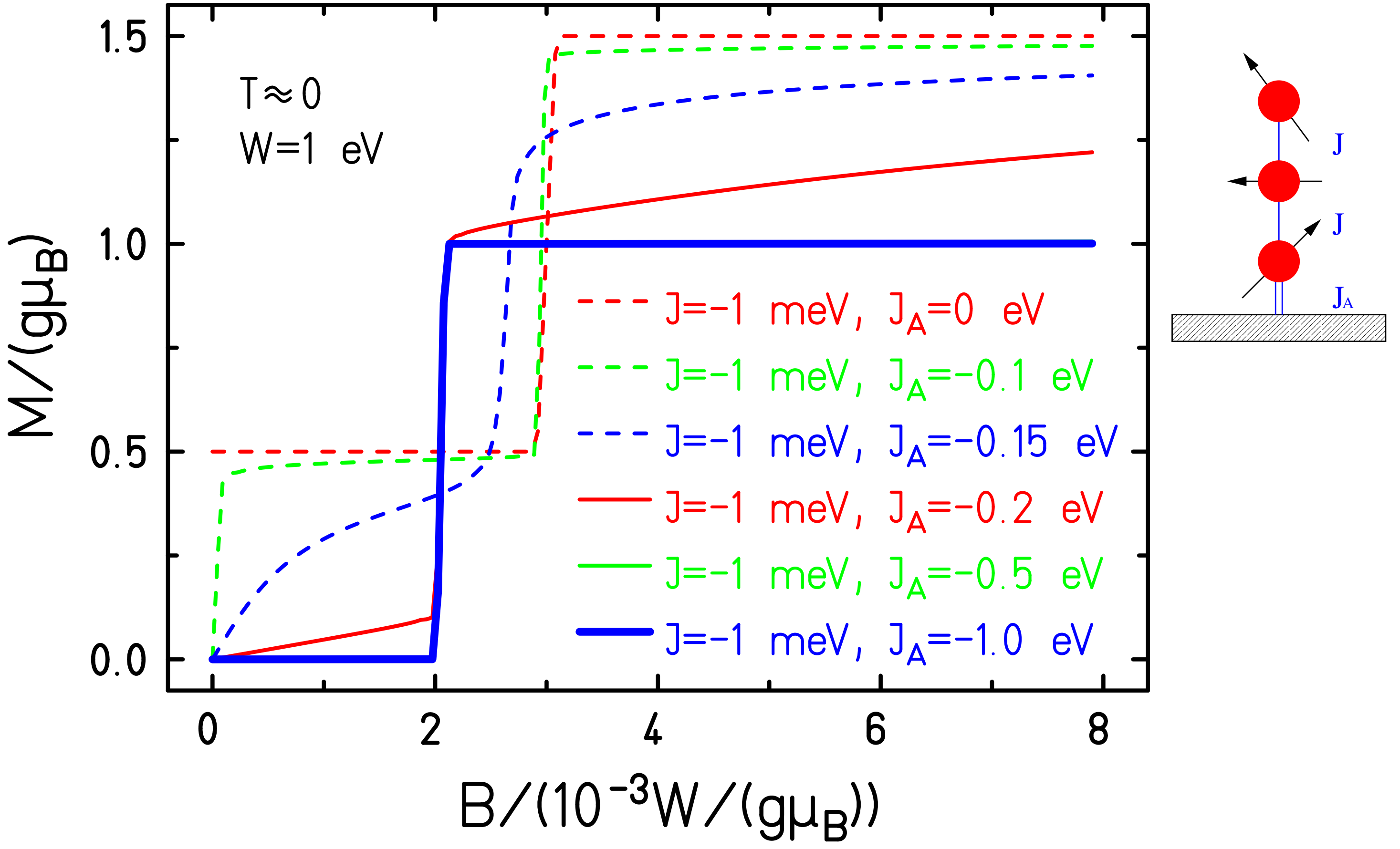
Increasing coupling to the substrate





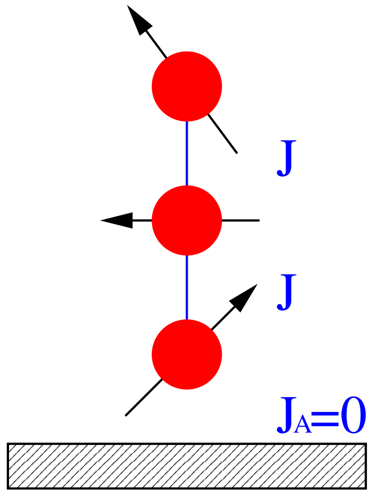
H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

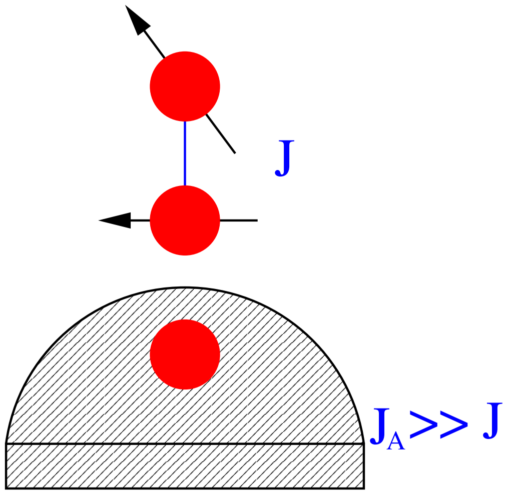
Increasing coupling to the substrate



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

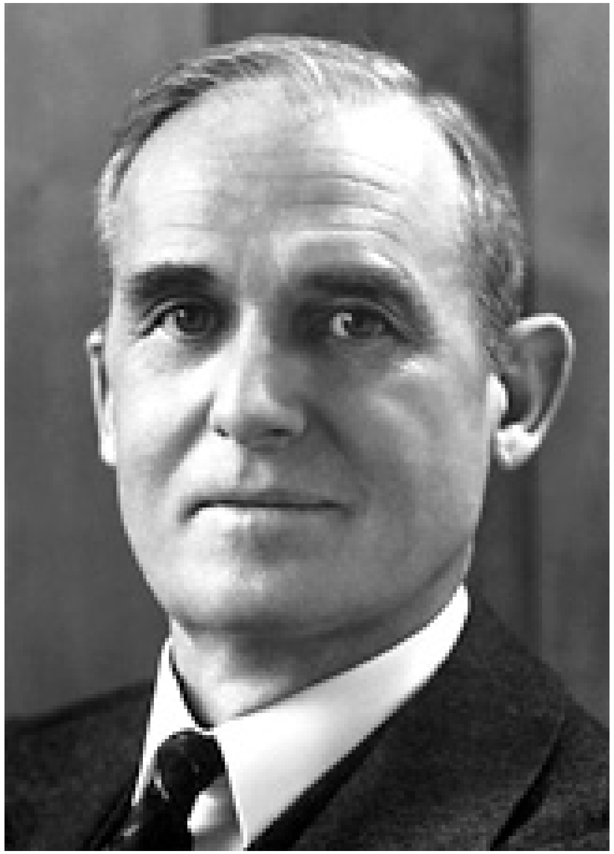
The magnetocaloric effect

Magnetocaloric effect – Basics

- Heating or cooling in a varying magnetic field. Predicted, discussed, discovered by Thomson, Warburg, Weiss, and Piccard (1).
- Typical rates: $0.5 \ldots 2$ K/T.
- Giant magnetocaloric effect: $3 \ldots 4$ 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.

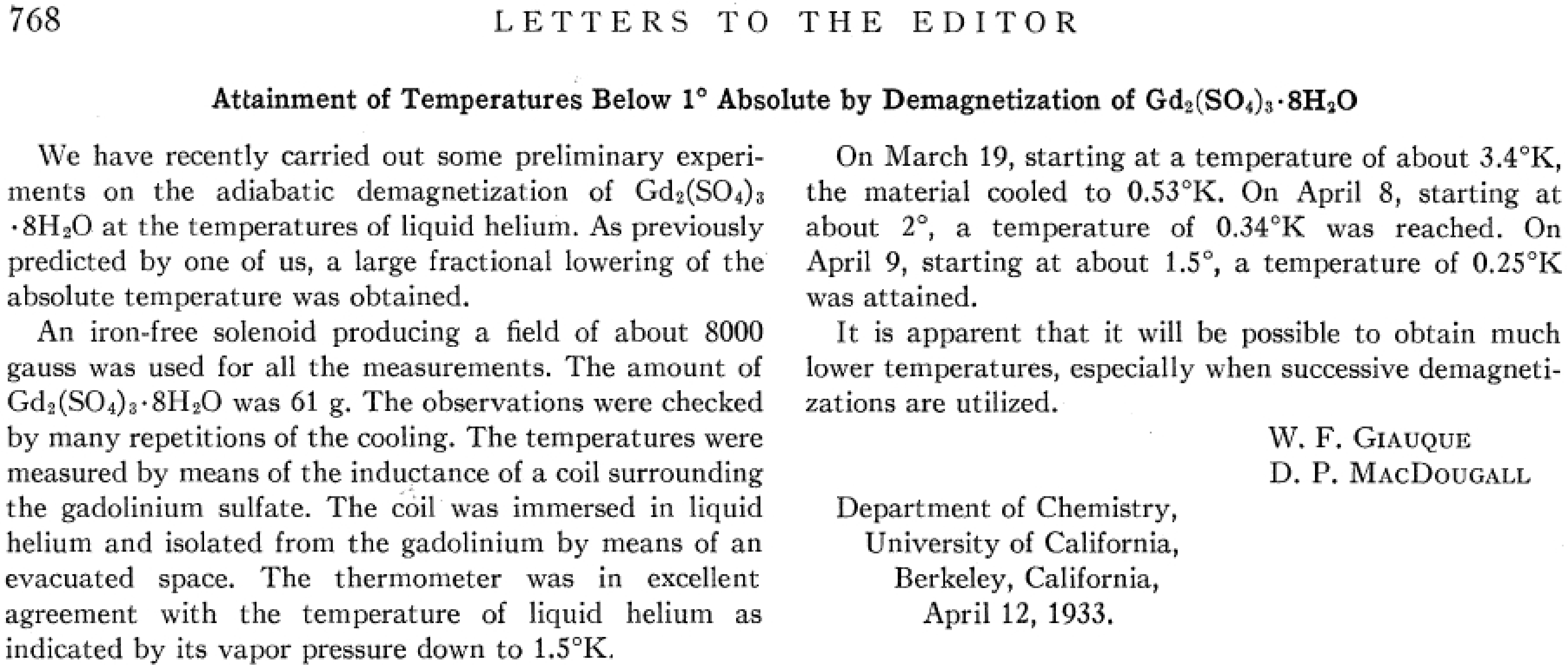
(1) A. Smith, Eur. Phys. J. H **38**, 507 (2013).

Sub-Kelvin cooling: Nobel prize 1949



The Nobel Prize in Chemistry 1949 was awarded to William F. Giauque *for his contributions in the field of chemical thermodynamics, particularly concerning the behaviour of substances at extremely low temperatures*.

Sub-Kelvin cooling: Nobel prize 1949



768 LETTERS TO THE EDITOR

Attainment of Temperatures Below 1° Absolute by Demagnetization of $Gd_2(SO_4)_3 \cdot 8H_2O$

We have recently carried out some preliminary experiments on the adiabatic demagnetization of $Gd_2(SO_4)_3 \cdot 8H_2O$ at the temperatures of liquid helium. As previously predicted by one of us, a large fractional lowering of the absolute temperature was obtained.

An iron-free solenoid producing a field of about 8000 gauss was used for all the measurements. The amount of $Gd_2(SO_4)_3 \cdot 8H_2O$ was 61 g. The observations were checked by many repetitions of the cooling. The temperatures were measured by means of the inductance of a coil surrounding the gadolinium sulfate. The coil was immersed in liquid helium and isolated from the gadolinium by means of an evacuated space. The thermometer was in excellent agreement with the temperature of liquid helium as indicated by its vapor pressure down to 1.5°K.

On March 19, starting at a temperature of about 3.4°K, the material cooled to 0.53°K. On April 8, starting at about 2°, a temperature of 0.34°K was reached. On April 9, starting at about 1.5°, a temperature of 0.25°K was attained.

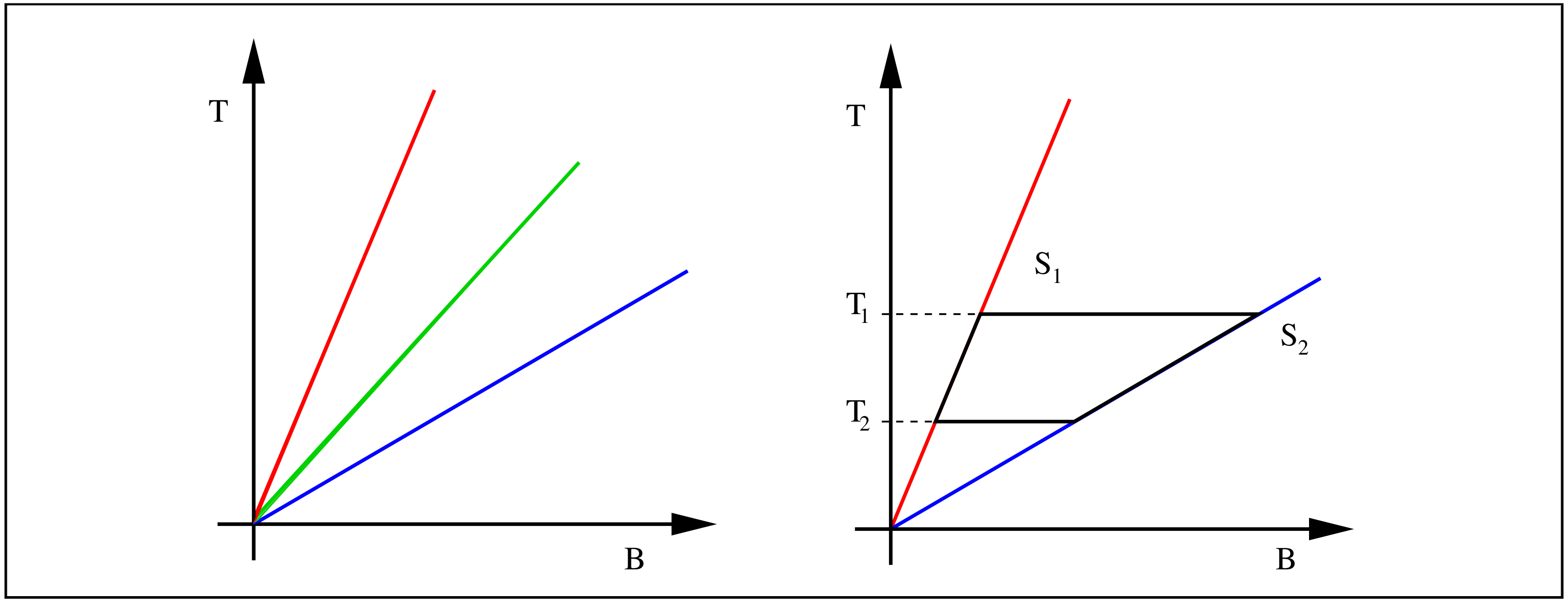
It is apparent that it will be possible to obtain much lower temperatures, especially when successive demagnetizations are utilized.

W. F. GIAUQUE
D. P. MACDOUGALL

Department of Chemistry,
University of California,
Berkeley, California,
April 12, 1933.

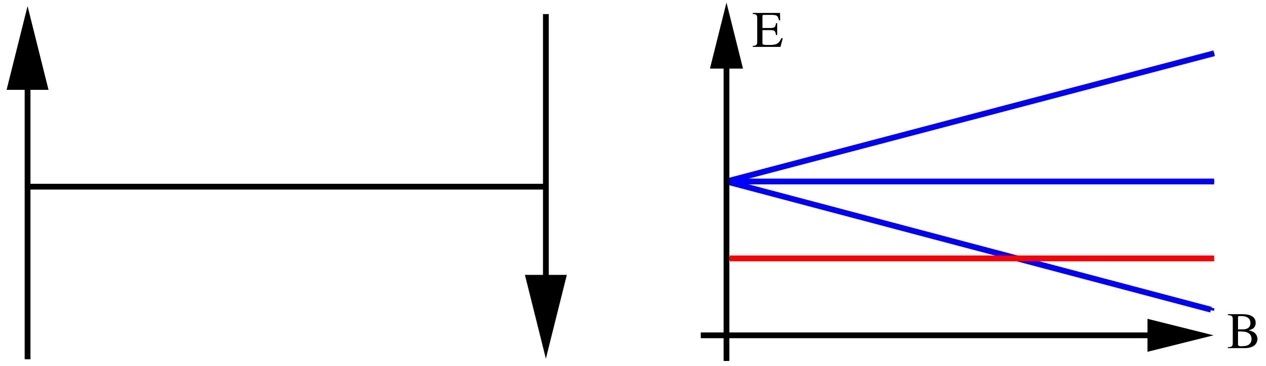
W. F. Giauque and D. MacDougall, Phys. Rev. **43**, 768 (1933).

Magnetocaloric effect – Paramagnets



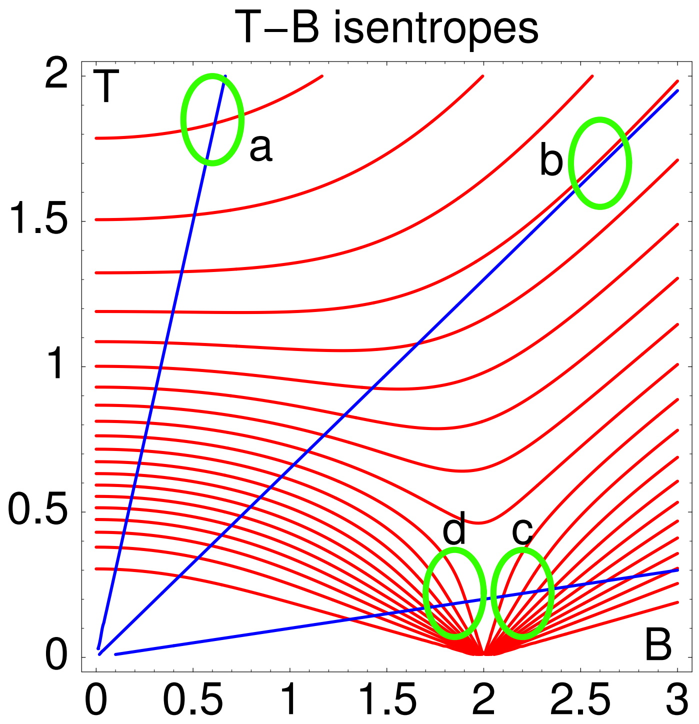
- Ideal paramagnet: $S(T,B) = f(B/T)$, i.e. $S = const \Rightarrow T \propto B$.
- At low T pronounced effects of dipolar interaction prevent further effective cooling.

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



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.

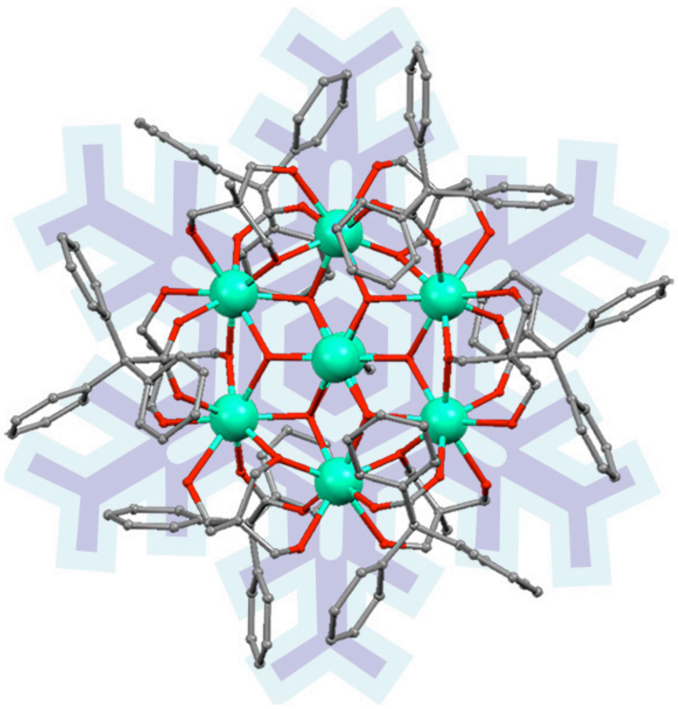
Case (d) does not occur for a paramagnet.

Nice ideas,

but can one measure it?

With magnetic molecules?

Gd$_7$ – Basics

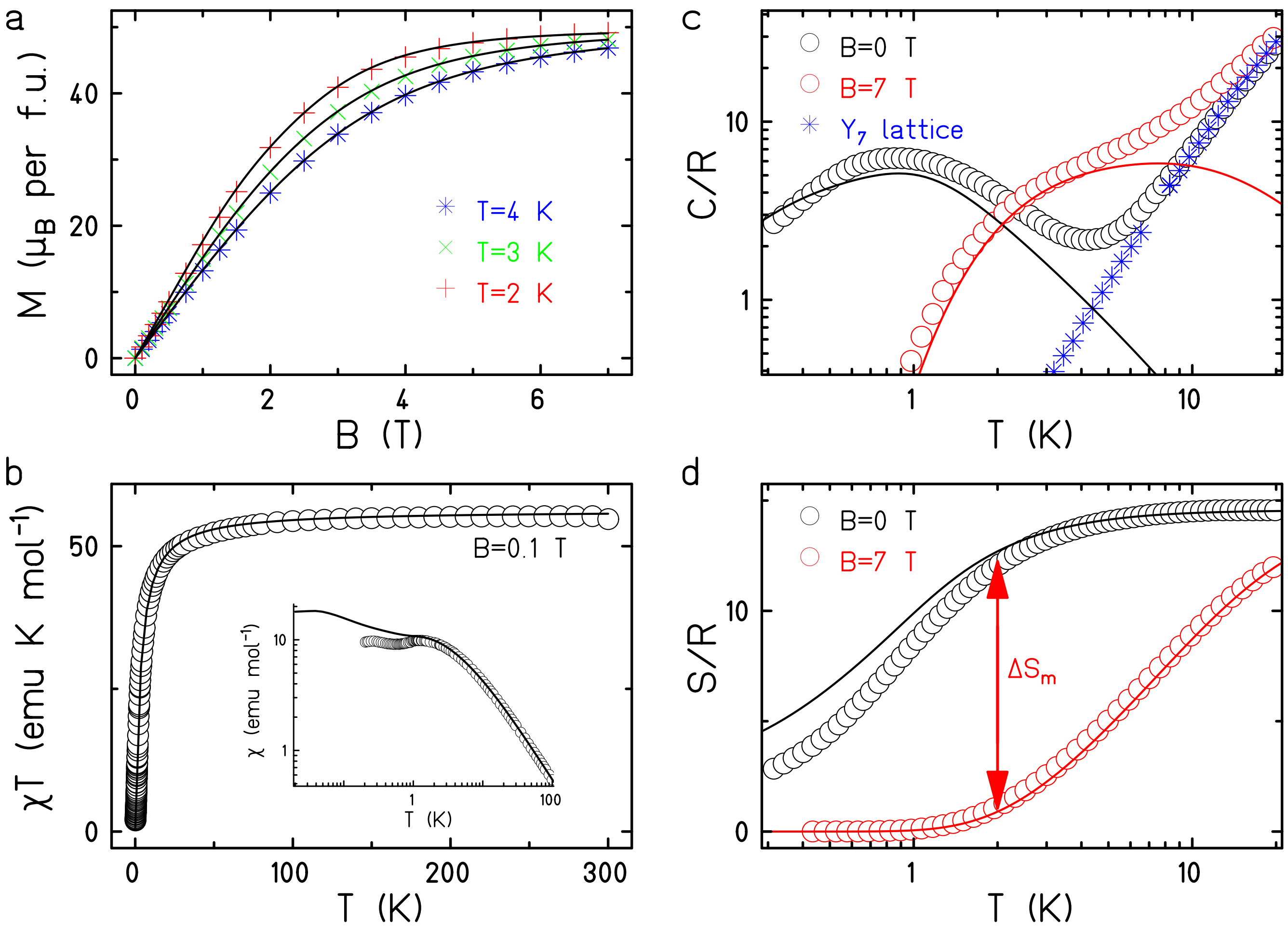


- Often magnetocaloric observables not directly measured, but inferred from Maxwell's relations.
- First real cooling experiment with a molecule.
- $\underset{\sim}{H} = -2 \sum_{i<j} J_{ij}\, \underset{\sim}{\vec{s}}_i \cdot \underset{\sim}{\vec{s}}_j + g\, \mu_B\, B \sum_i^N \underset{\sim}{s}_i^z$

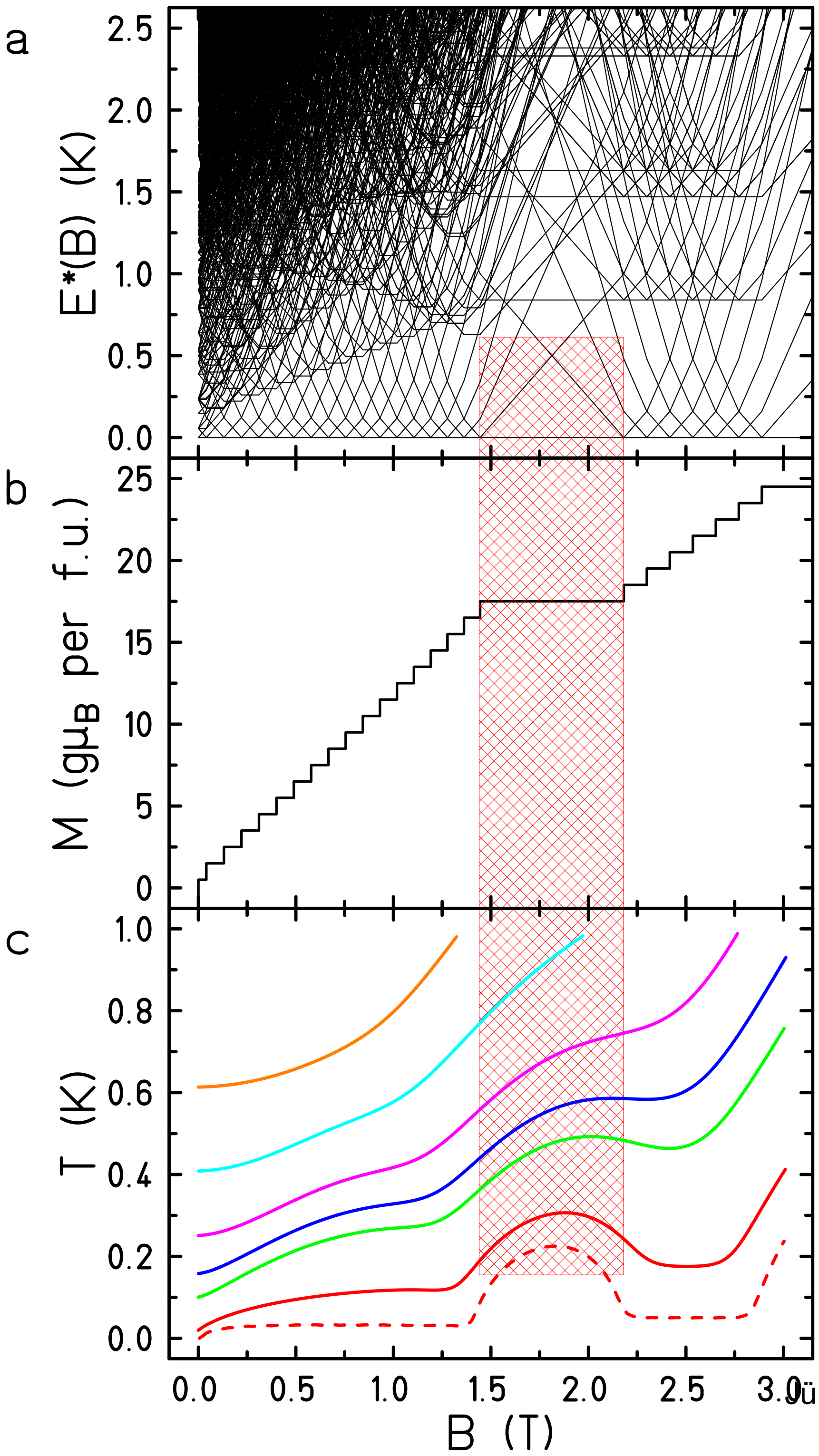
  $J_1 = -0.090(5)$ K, $J_2 = -0.080(5)$ K and $g = 2.02$.
- Very good agreement down to the lowest temperatures.

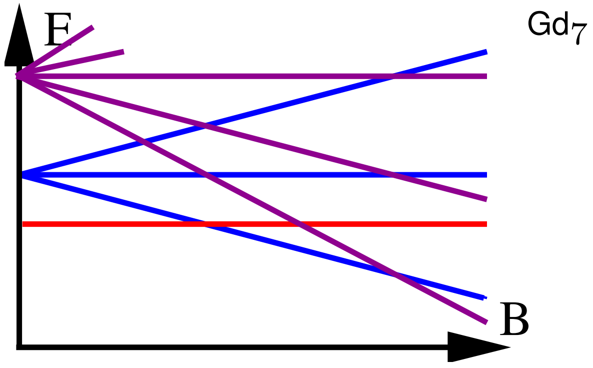
J. W. Sharples, D. Collison, E. J. L. McInnes, J. Schnack, E. Palacios, M. Evangelisti, Nat. Commun. **5**, 5321 (2014).

Gd$_7$ – experiment & theory

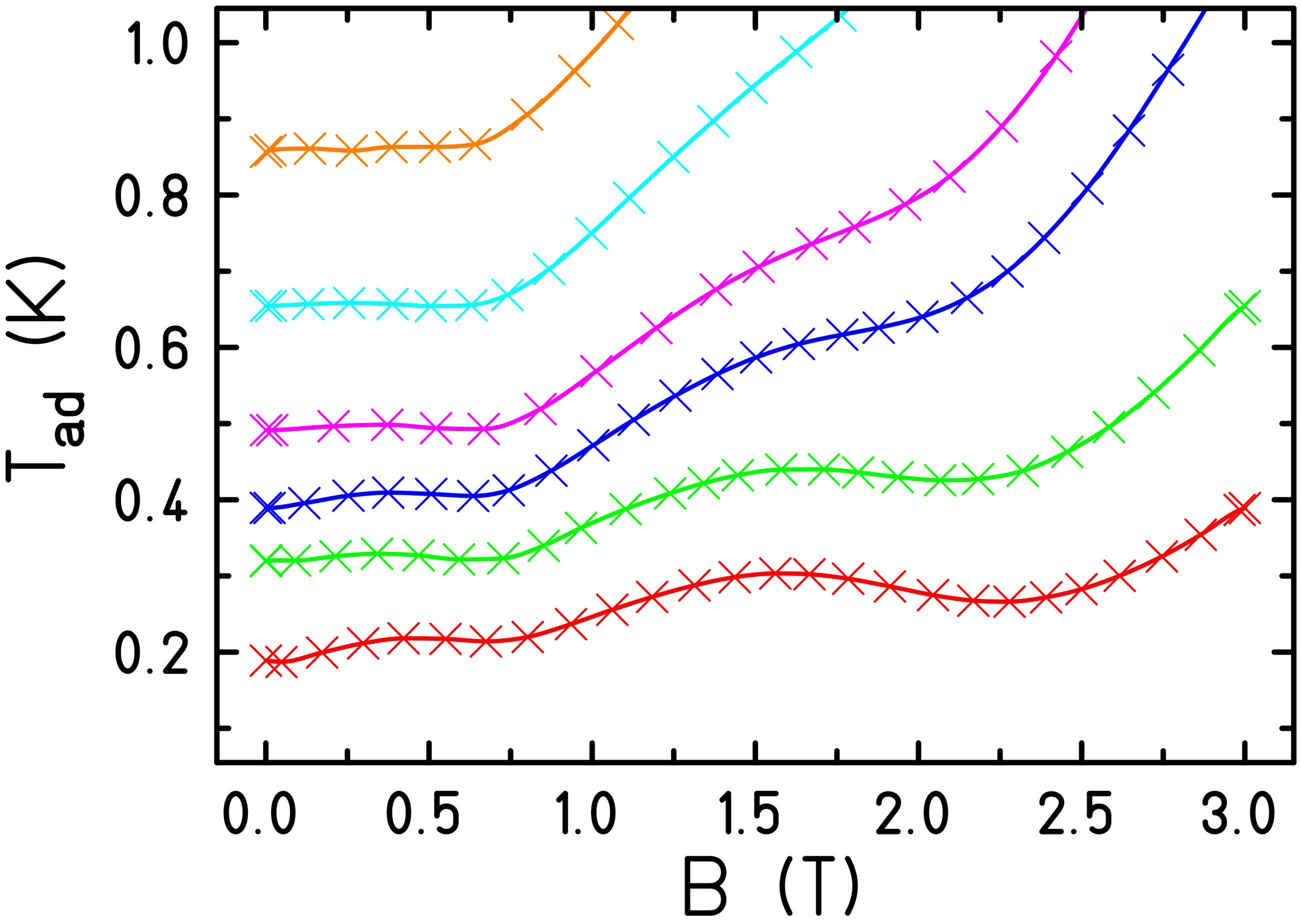


J. W. Sharples, D. Collison, E. J. L. McInnes, J. Schnack, E. Palacios, M. Evangelisti, Nat. Commun. **5**, 5321 (2014).


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

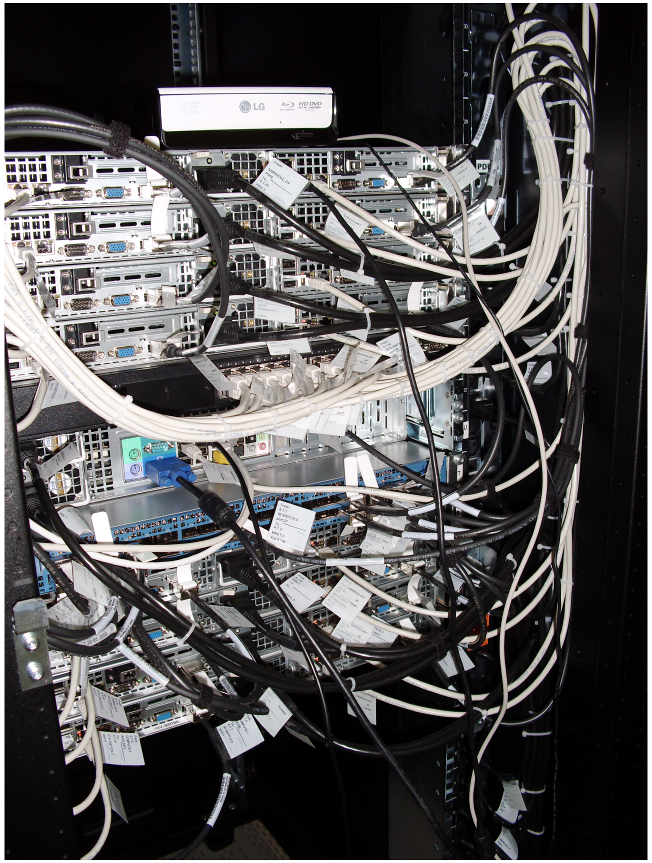

E
B
Gd7

Gd$_7$ – Experimental cooling



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

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

- M. Czopnik, T. Glaser, O. Hanebaum, Chr. Heesing, M. Höck, N.B. Ivanov, F. Kaiser, H.-T. Langwald, S. Leiding, A. Müller, R. Schnalle, Chr. Schröder, J. Ummethum (Bielefeld)
- K. Bärwinkel, H.-J. Schmidt, M. Neumann (Osnabrück)
- M. Luban (Ames Lab, USA); P. Kögerler (Aachen, Jülich, Ames); D. Collison, R.E.P. Winpenny, E.J.L. McInnes, F. Tuna (Man U); L. Cronin, M. Murrie (Glasgow); E. Brechin (Edinburgh); H. Nojiri (Sendai, Japan); A. Postnikov (Metz); W. Wernsdorfer (Grenoble); M. Evangelisti (Zaragosa); E. Garlatti, S. Carretta, G. Amoretti, P. Santini (Parma); Gopalan Rajaraman (Mumbai)
- 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.

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