

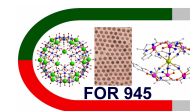
Magnetism of free and deposited magnetic molecules

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Seminar, Johann-Wolfgang-von-Goethe-Universität
Frankfurt am Main, 24. 04. 2015



How can we cool things?

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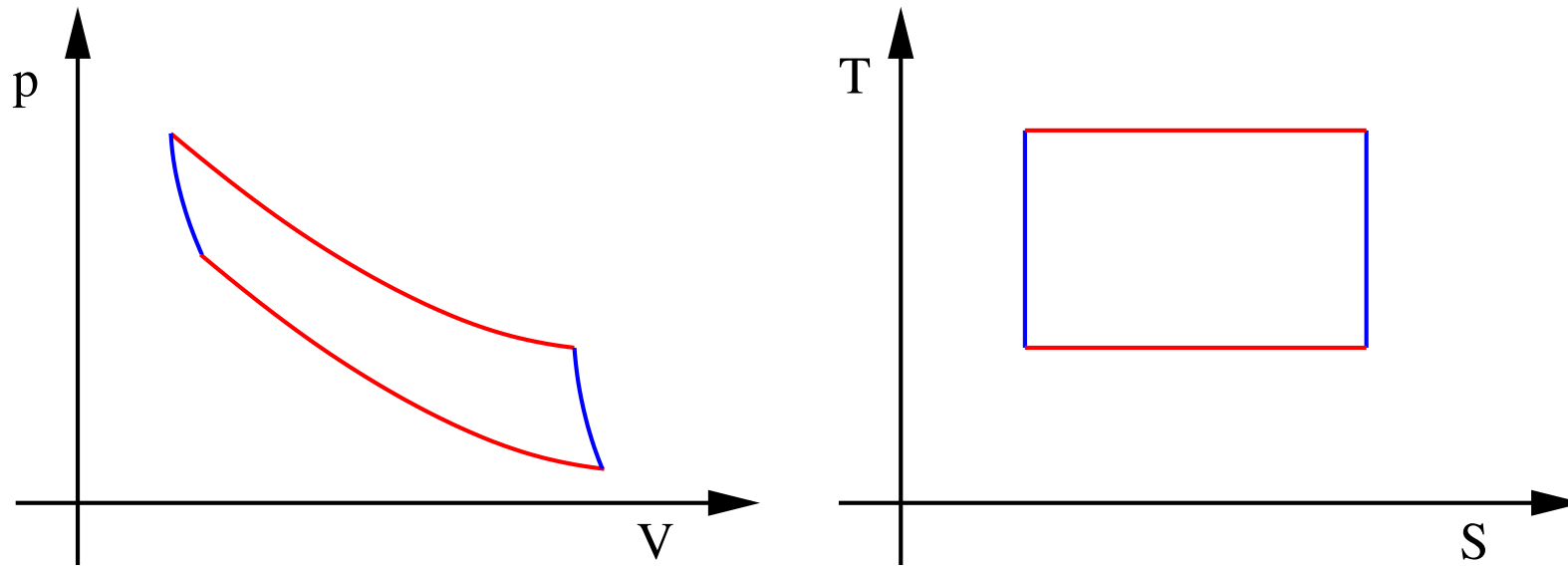
How can we cool things?

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

$C = C_p$: heat capacity at constant pressure

$\left(\frac{\partial T}{\partial p}\right)_S$ adiabatic cooling rate

How can we cool things? – Carnot process



needs work to cool one colder substance by Q_2 and releases heat Q_1 to another hotter substance

Should also work with
magnetic substances!

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. **The magnetocaloric effect**
2. Magnetocalorics of molecules
3. **Finite-Temperature Lanczos**
4. Deposited molecules

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

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 . . . 2 K/T.
- Giant magnetocaloric effect: 3 . . . 4 K/T e.g. in $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ 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).

Magnetocaloric effect – cooling rate

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

$C = C_B = T \left(\frac{\partial S}{\partial T}\right)_B$: heat capacity at constant field

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

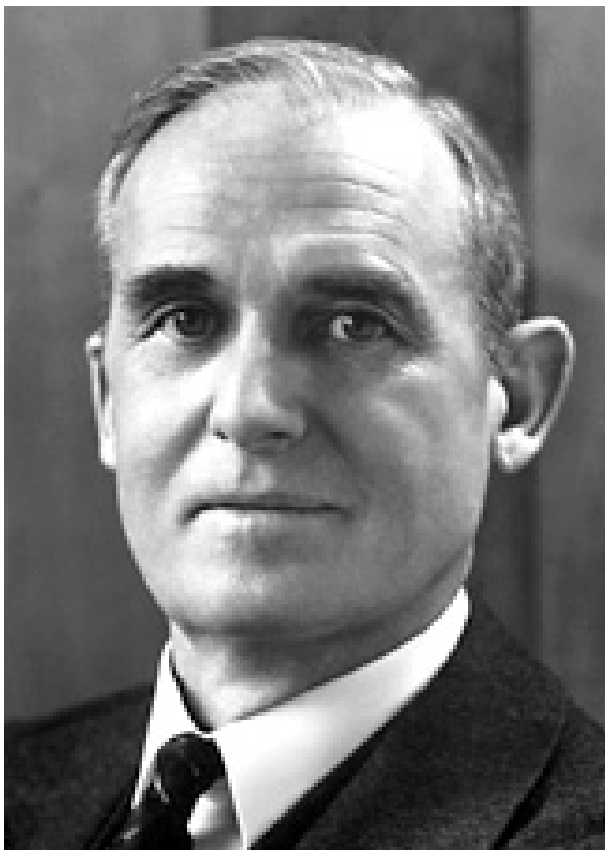
(1) V.K. Pecharsky, K.A. Gschneidner, Jr., A. O. Pecharsky, and A. M. Tishin, Phys. Rev. B **64**, 144406 (2001).

(2) Lijun Zhu, M. Garst, A. Rosch, and Qimiao Si, Phys. Rev. Lett. **91**, 066404 (2003).

B. Wolf, Y. Tsui, D. Jaiswal-Nagar, U. Tutsch, A. Honecker, K. Removic-Langer, G. Hofmann, A. Prokofiev, W. Assmus, G. Donath, M. Lang, Proceedings of the National Academy of Sciences **108**, 6862 (2011).

(3) M.E. Zhitomirsky, A. Honecker, J. Stat. Mech.: Theor. Exp. **2004**, P07012 (2004).

Sub-Kelvin cooling: Nobel prize 1949



The Nobel Prize in Chemistry 1949 was awarded to William F. Giaouque *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

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LETTERS TO THE EDITOR

Attainment of Temperatures Below 1° Absolute by Demagnetization of $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$

We have recently carried out some preliminary experiments on the adiabatic demagnetization of $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ 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 $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ 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.

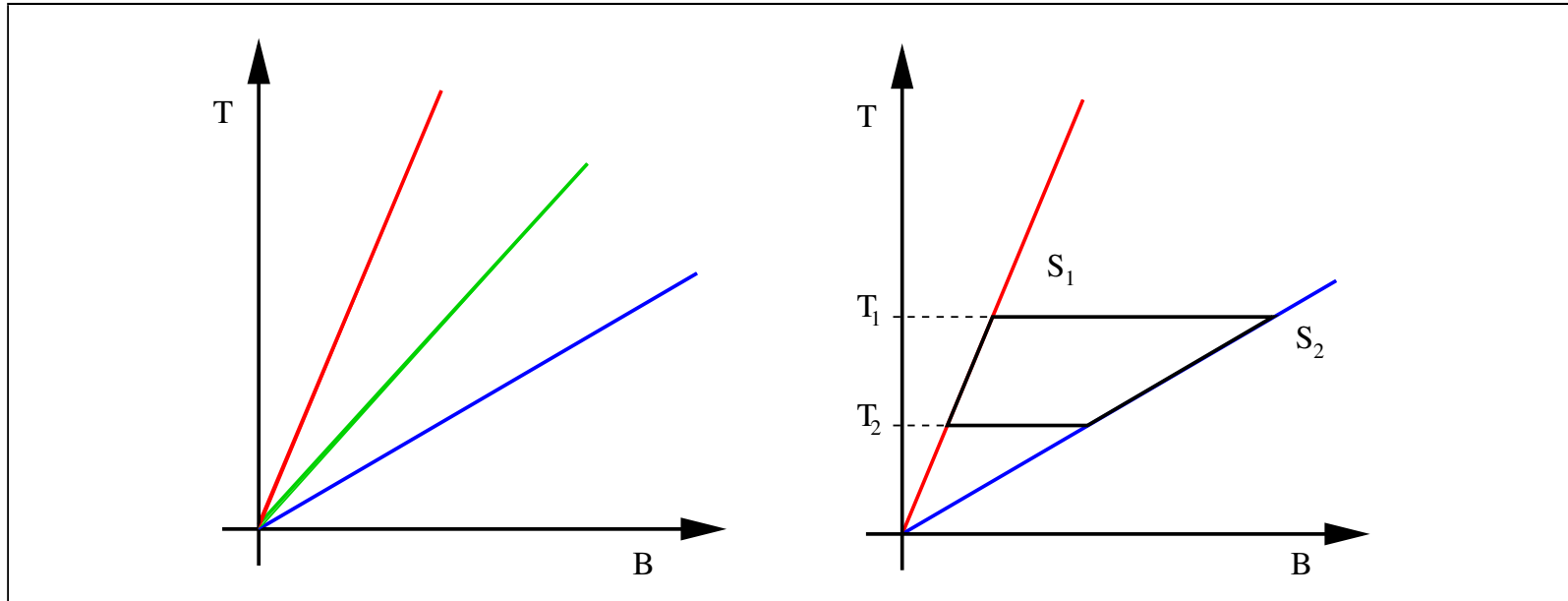
It is apparent that it will be possible to obtain much lower temperatures, especially when successive demagnetizations are utilized.

W. F. GIAUQUE
D. P. MACDOUGALL

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

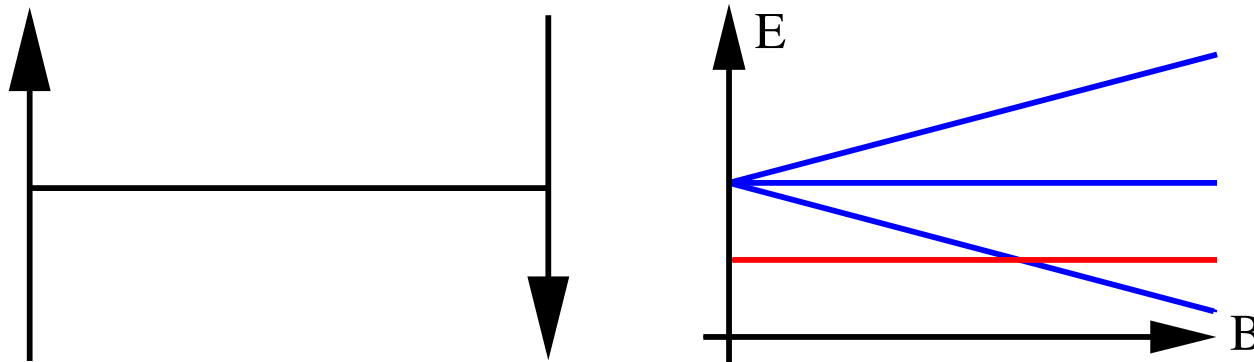
W. F. Giauque and D. MacDougall, *Phys. Rev.* **43**, 768 (1933).

Magnetocaloric effect – Paramagnets



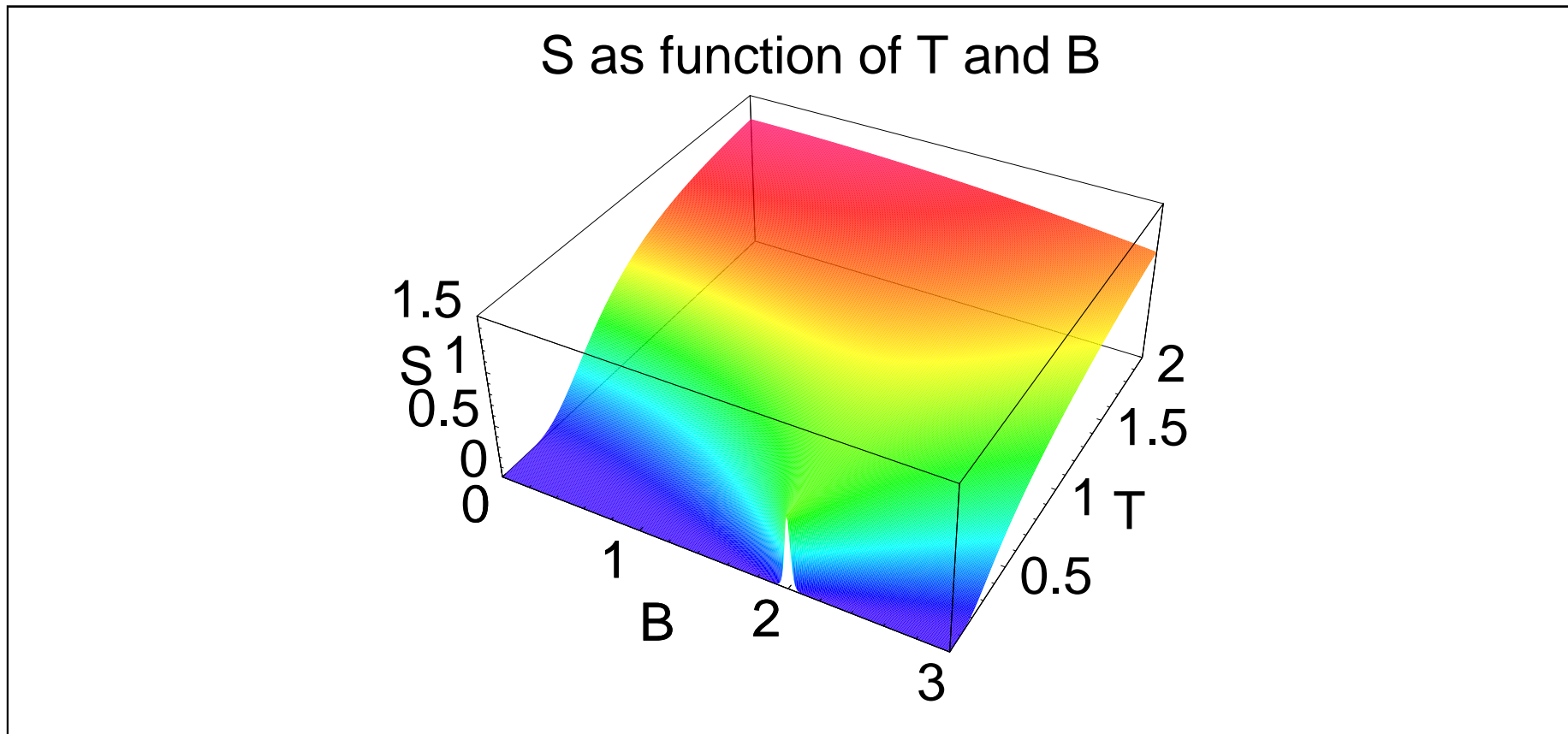
- **Ideal paramagnet: $S(T, B) = f(B/T)$, i.e. $S = const \Rightarrow T \propto B$.**
- At low T pronounced effects of dipolar interaction prevent further effective cooling.

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 ; $S(T = 0, B_c) = k_B \ln 2$, otherwise zero.

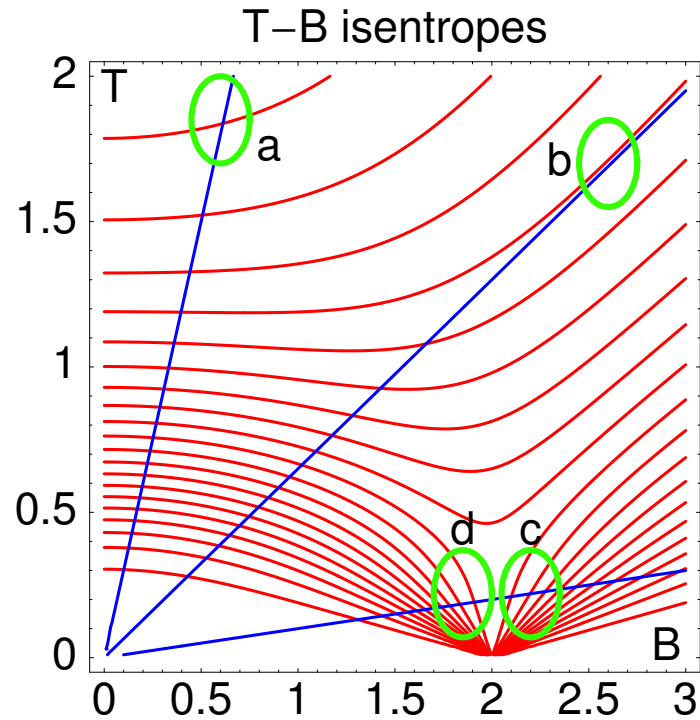
Magnetocaloric effect – at $s = 1/2$ dimer



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

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

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



blue lines: ideal paramagnet, red curves: af dimer

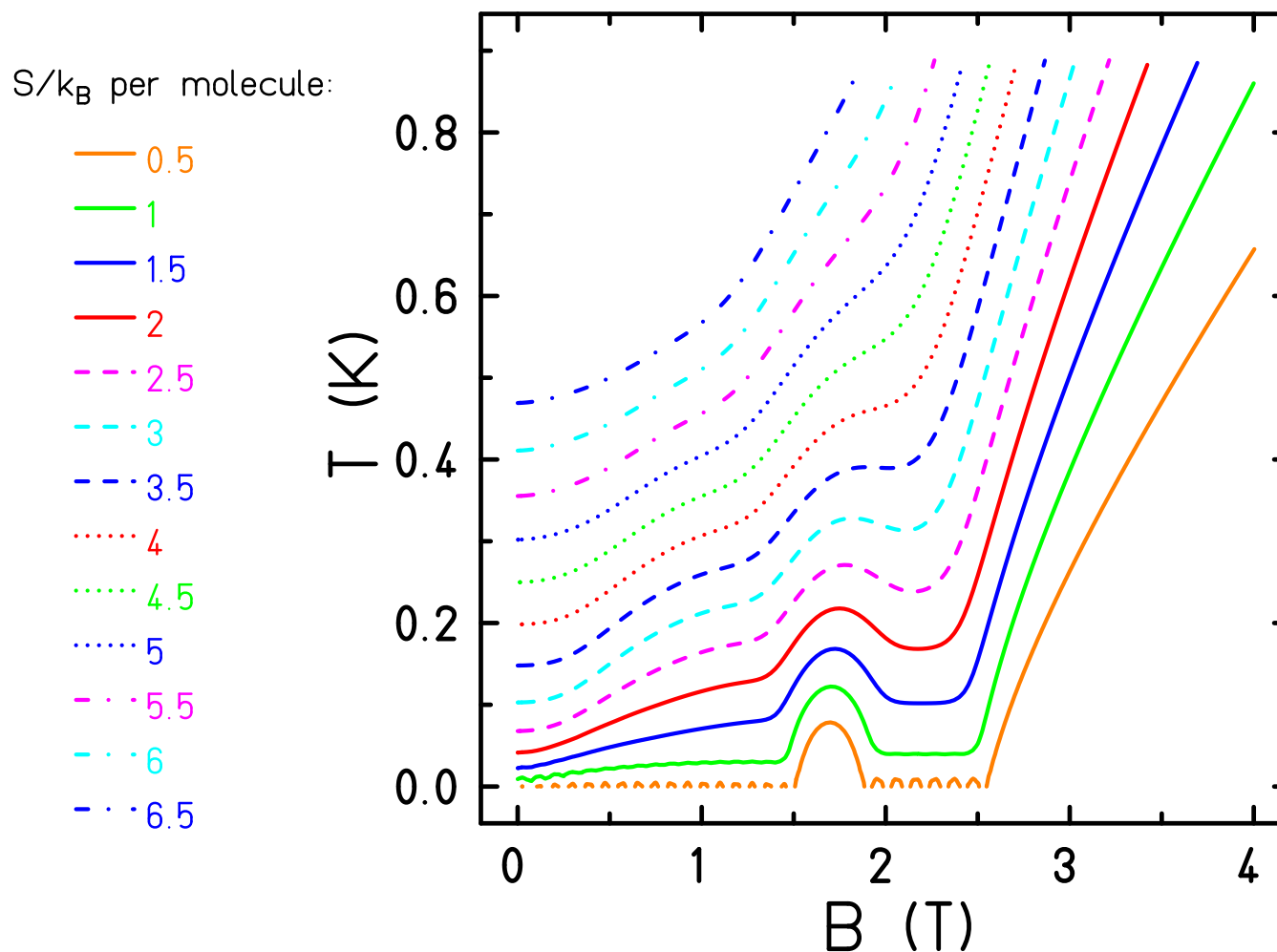
Magnetocaloric effect:

- (a) reduced,
- (b) the same,
- (c) enhanced,
- (d) opposite

when compared to an ideal paramagnet.

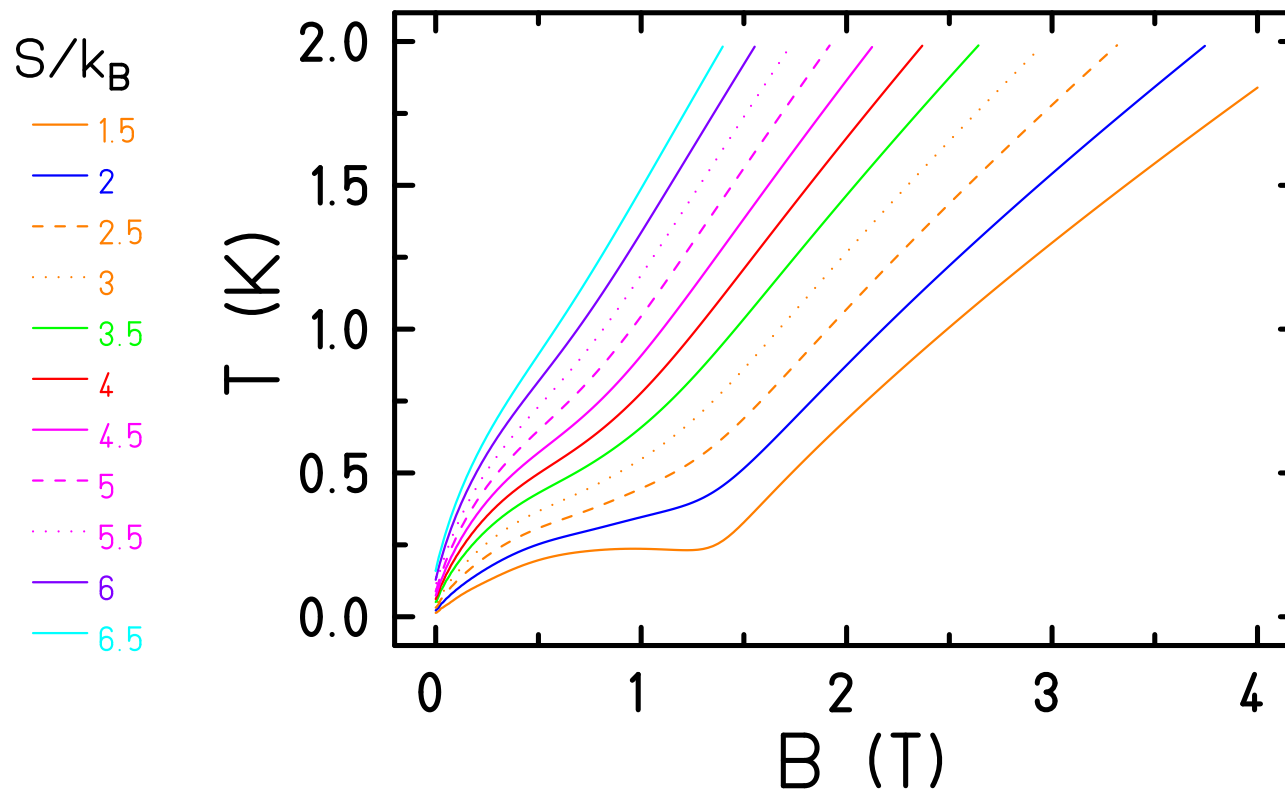
Case (d) does not occur for a paramagnet.

Typical isentropes for af spin system



Level crossings signal antiferromagnetic interactions.

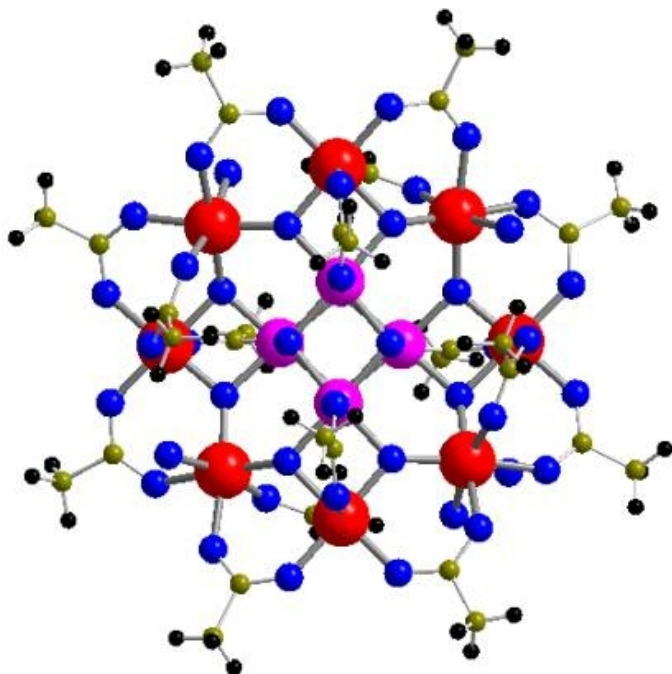
Typical isentropes for high-spin system



Typical for high-spin ground state.

Nice ideas,
but can one measure it?
With magnetic molecules?

The beauty of magnetic molecules I

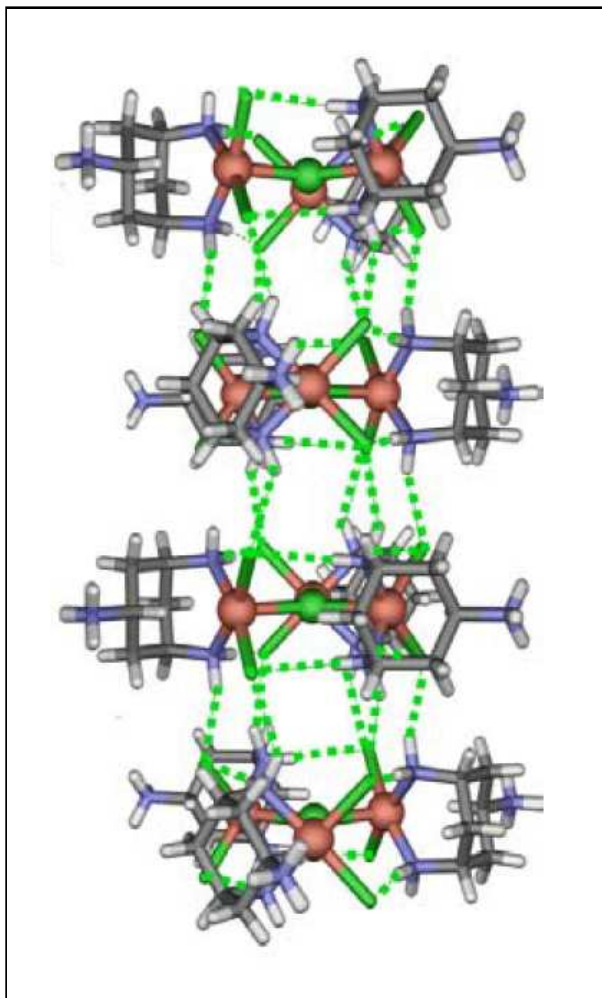


Mn₁₂

- Inorganic or organic macro molecules, e.g. polyoxometalates, where paramagnetic ions such as Iron (Fe), Chromium (Cr), Copper (Cu), Nickel (Ni), Vanadium (V), Manganese (Mn), or rare earth ions are embedded in a host matrix;
- Pure organic magnetic molecules: magnetic coupling between high spin units (e.g. free radicals);
- Single spin quantum number $1/2 \leq s \leq 7/2$;
- Intermolecular interaction relatively small, therefore measurements reflect the thermal behaviour of a single molecule.

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

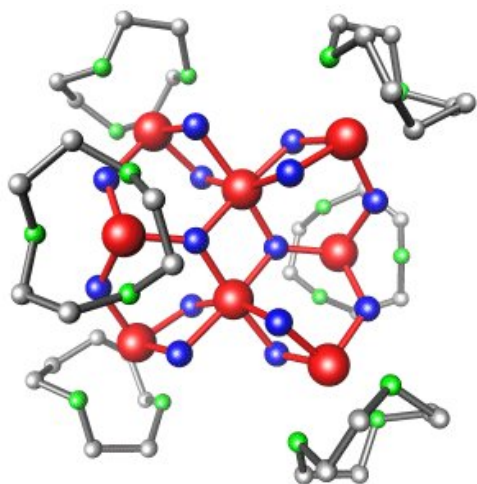
The beauty of magnetic molecules II



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

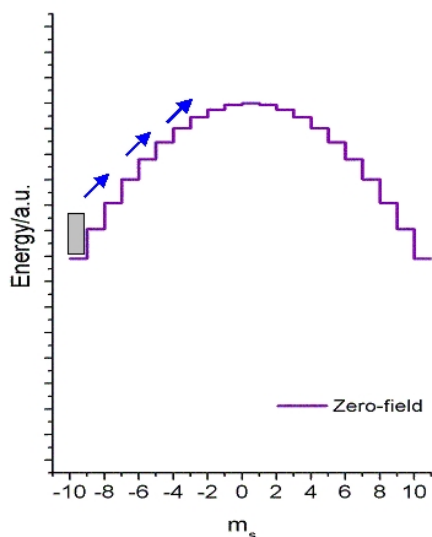
J. Schnack, H. Nojiri, P. Kögerler, G. J. T. Cooper, L. Cronin, Phys. Rev. B 70, 174420 (2004)

The beauty of magnetic molecules III



- Single Molecule Magnets (SMM): magnetic molecules with large ground state moment;
- Example: $S = 10$ for Mn_{12} or Fe_8 ;
- Anisotropy dominates approximate single-spin Hamiltonian:

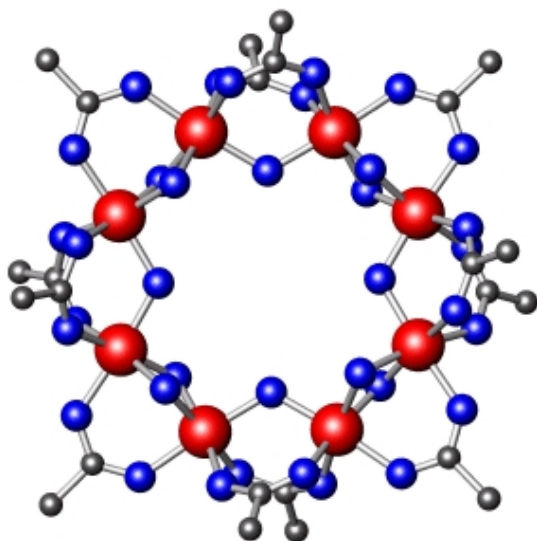
$$\underline{H} = -D\underline{S}_z^2 + \underline{H}', \quad [\underline{S}_z, \underline{H}'] \neq 0$$



- 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

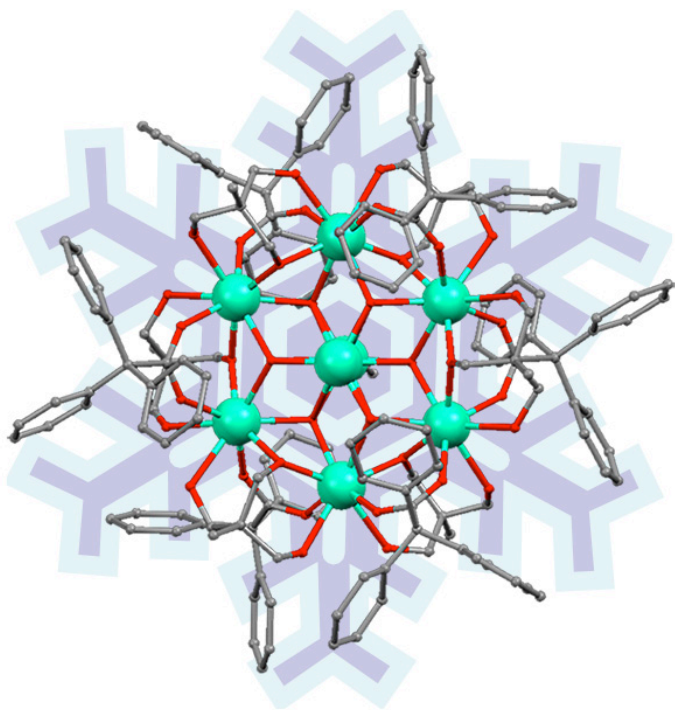
Why magnetic molecules?



Cr₈

- Interacting spin system largely decoupled from remaining degrees of freedom;
- Transition few-spin system \Rightarrow many-spin system, contribution to understanding of bulk magnetism;
- Transition quantum spin system ($s = 1/2$) \Rightarrow classical spin system ($s_{\text{Fe}} = 5/2$, $s_{\text{Gd}} = 7/2$);
- Easy to produce, single crystals with $> 10^{17}$ identical molecules can be synthesized and practically completely characterized;
- **Speculative applications: magnetic storage devices, magnets in biological systems, light-induced nano switches, displays, catalysts, qubits for quantum computers.**

Gd₇ – Basics

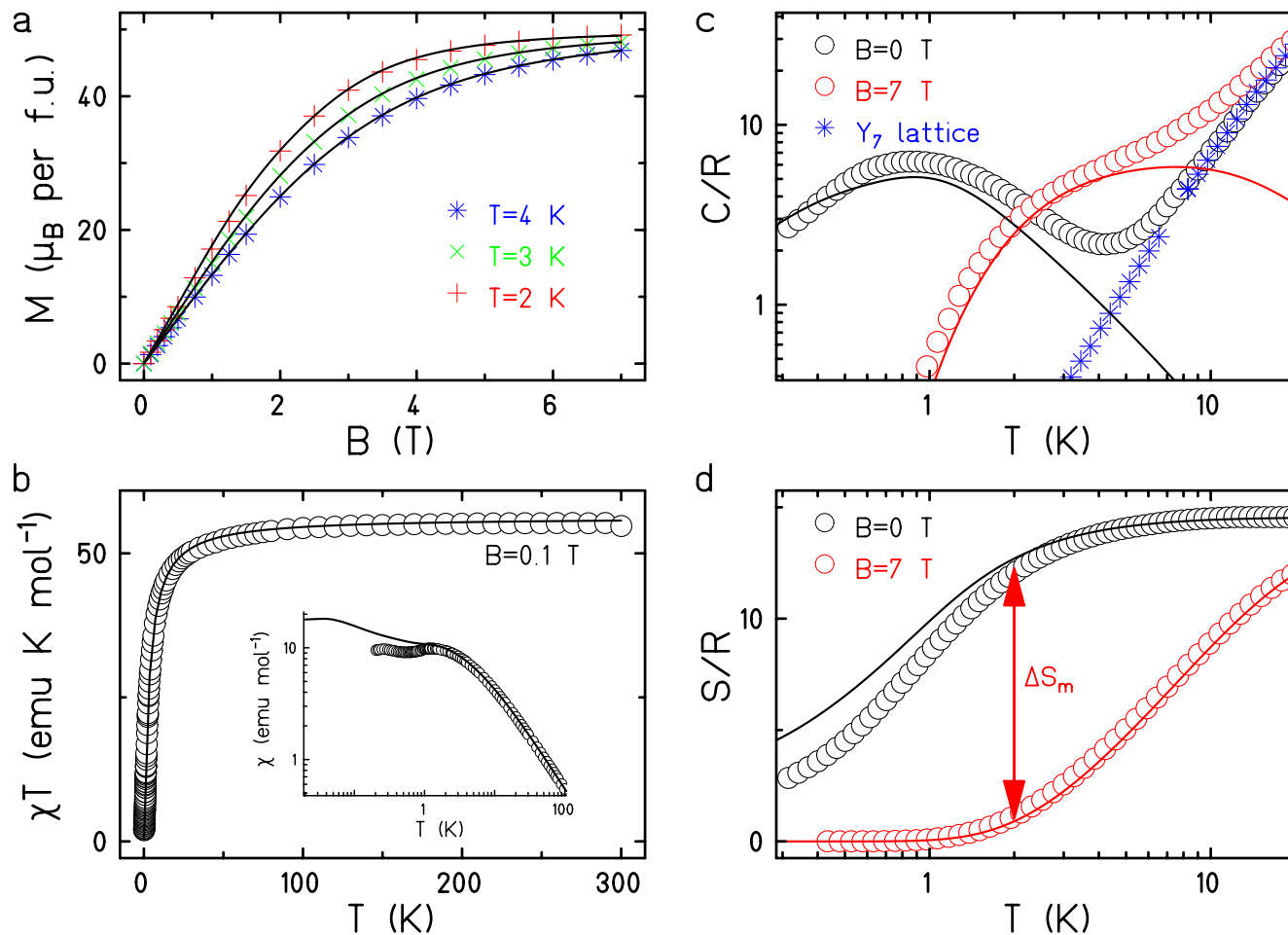


- Often magnetocaloric observables not directly measured, but inferred from Maxwell's relations.
- First real cooling experiment with a molecule.
- $$\underline{H} = -2 \sum_{i < j} J_{ij} \vec{\zeta}_i \cdot \vec{\zeta}_j + g \mu_B B \sum_i^N \zeta_i^z$$

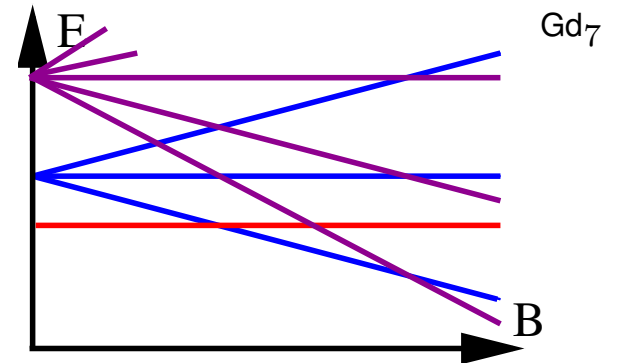
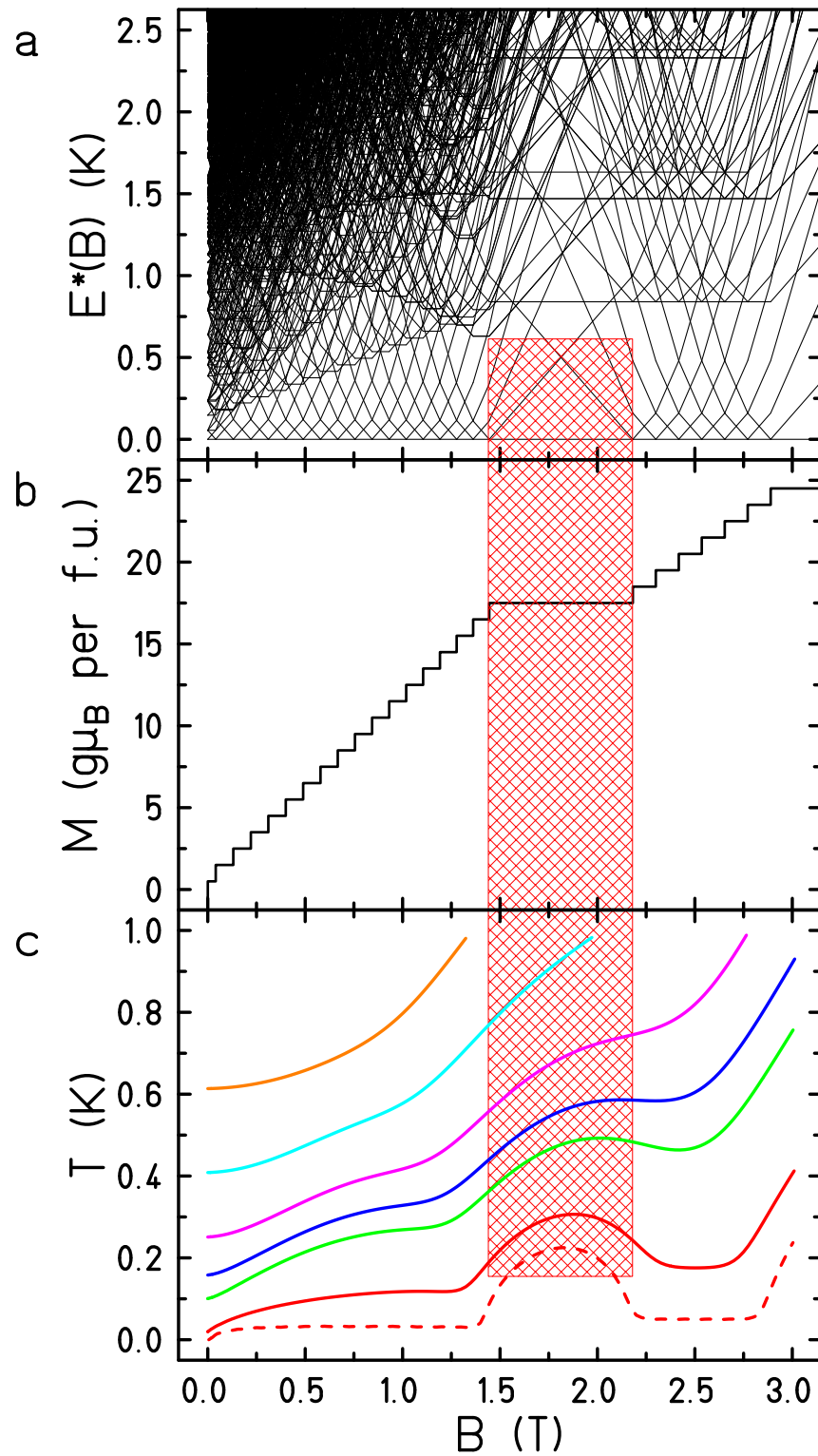
 $J_1 = -0.090(5) \text{ K}, J_2 = -0.080(5) \text{ K}$
 and $g = 2.02$.
- **Very good agreement down to the lowest temperatures.**

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

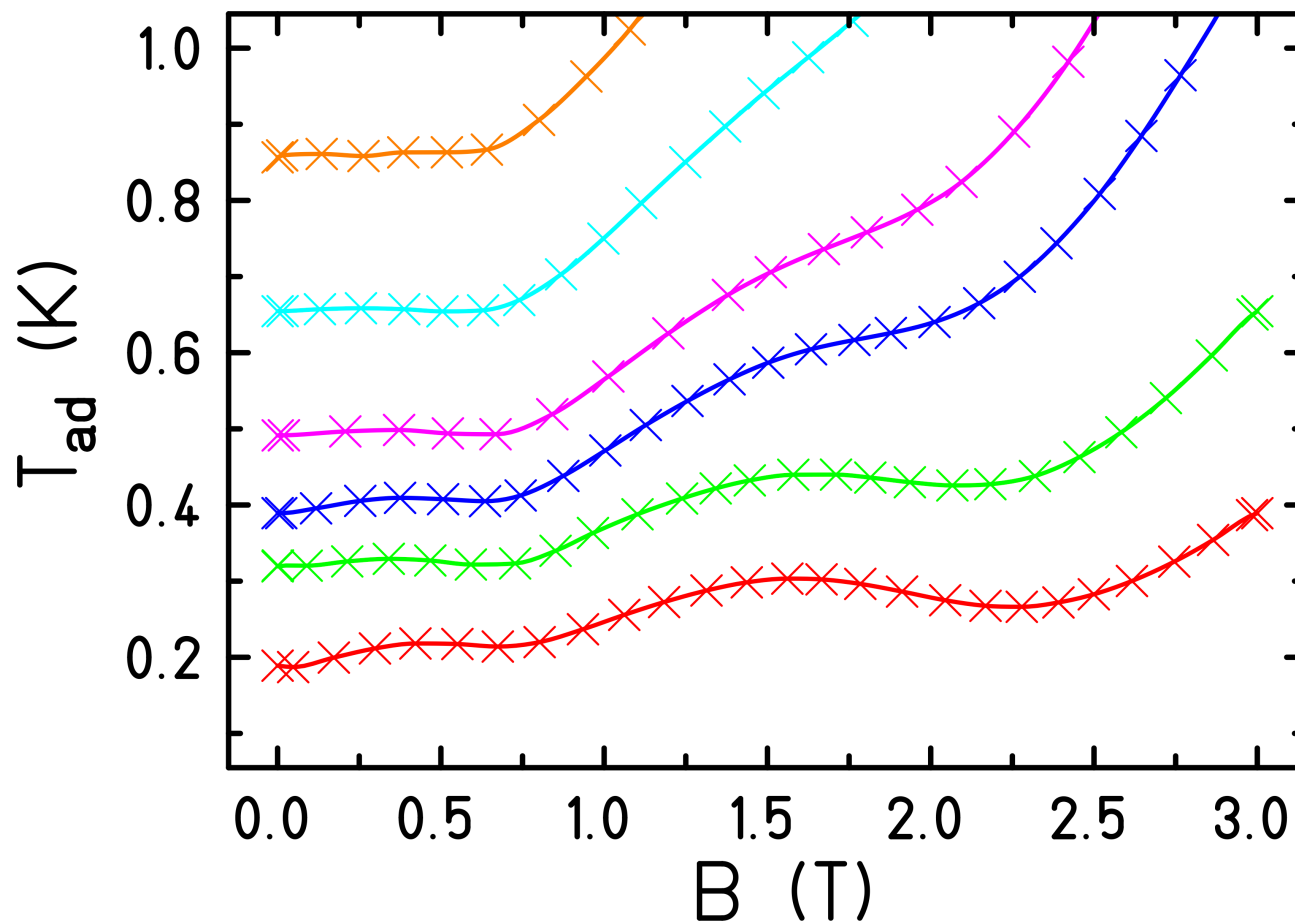
Gd₇ – experiment & theory



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



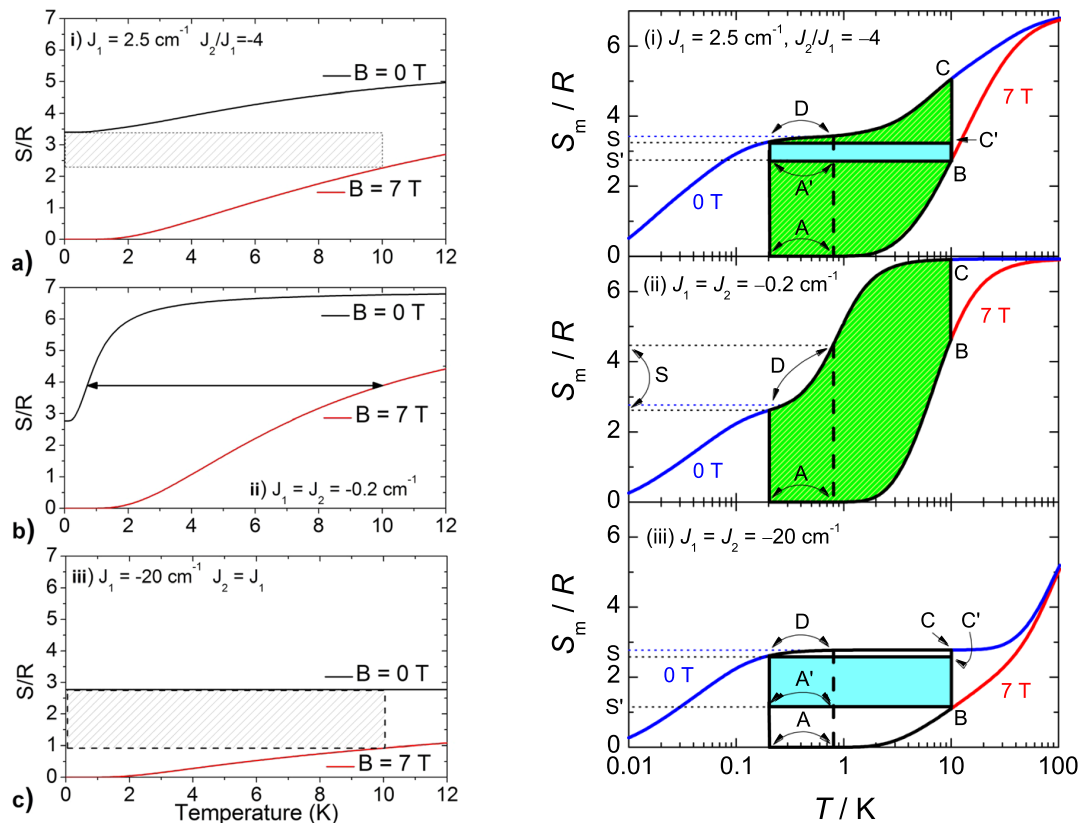
Gd₇ – Experimental cooling



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

Outlook: Design of applications

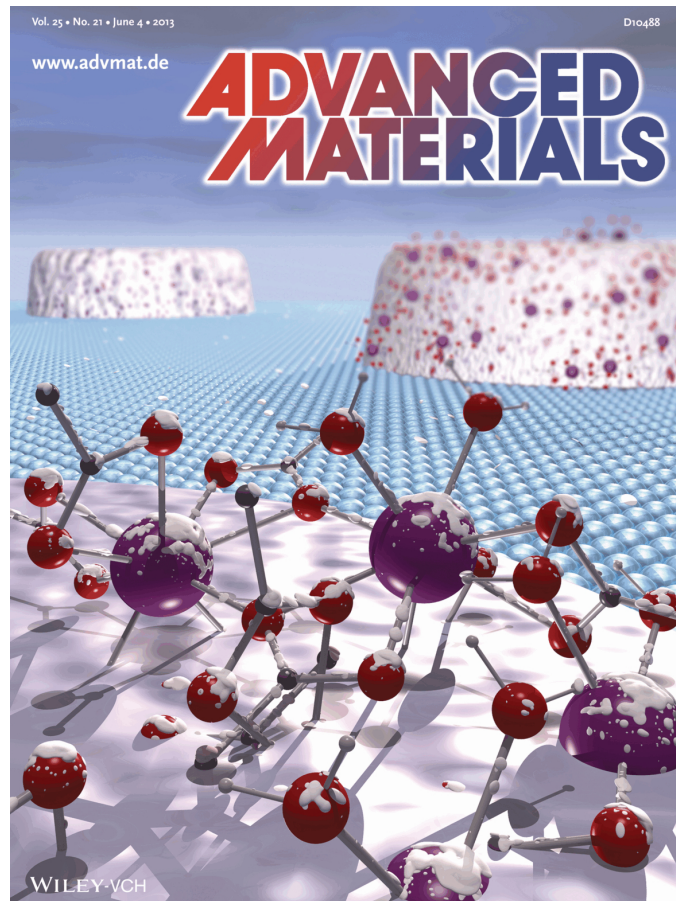
Cycles: Carnot or Ericsson?



Applicable temperature range? Maximum entropy difference at cold temperature?

E. Garlatti, S. Carretta, J. Schnack, G. Amoretti, P. Santini, Appl. Phys. Lett. **103**, (2013); M. Evangelisti, G. Lorusso, and E. Palacios, Applied Physics Letters **105**, (2014); E. Garlatti *et al.*, Applied Physics Letters **105**, 046102 (2014).

MCE surface cooler

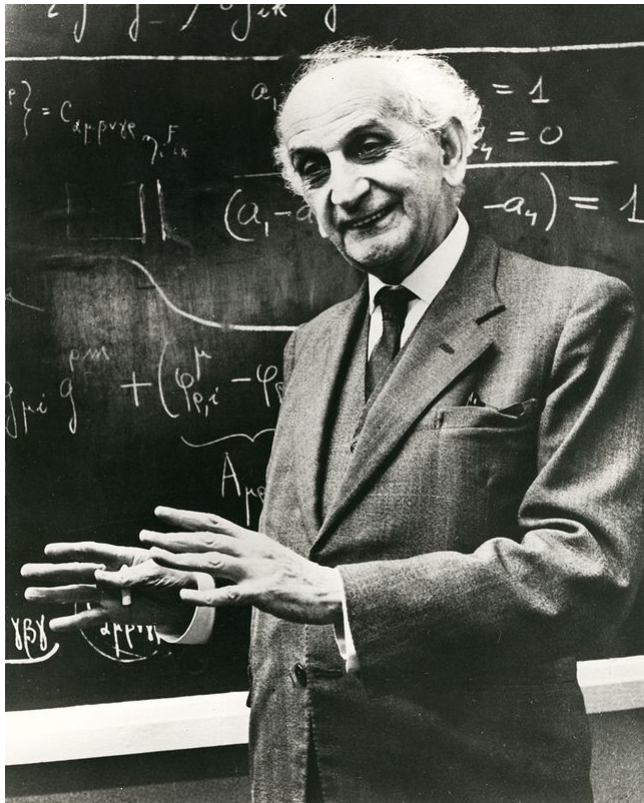


G. Lorusso, M. Jenkins, P. Gonzalez-Monje, A. Arauzo, J. Sese, D. Ruiz-Molina, O. Roubeau, M. Evangelisti, Marco, Adv. Mater. **25**, 2984 (2013); V. Corradini, A. Ghirri, A. Candini, R. Biagi, U. del Pennino, G. Dotti, E. Otero, F. Choueikani, R. J. Blagg, E. J. L. McInnes, M. Affronte, Adv. Mater. **25**, 2816 (2013).

Finite-temperature Lanczos Method

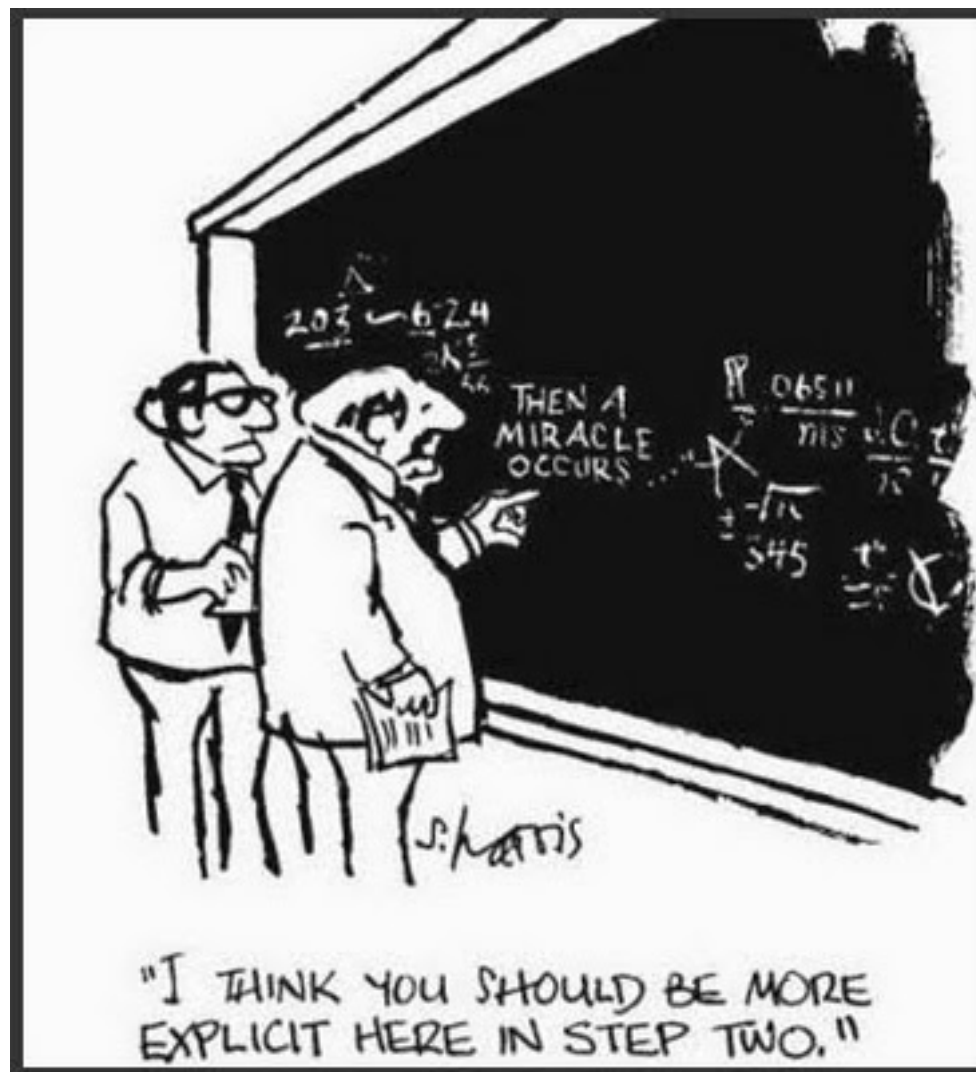
(Good for dimensions up to 10^{10} .)

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:**
 $\{ |\phi\rangle, \tilde{H} |\phi\rangle, \tilde{H}^2 |\phi\rangle, \tilde{H}^3 |\phi\rangle, \dots \}$
- 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

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

$$\langle \nu | \exp \{ -\beta \tilde{H} \} | \nu \rangle \approx \sum_n \langle \nu | n(\nu) \rangle \exp \{ -\beta \epsilon_n \} \langle n(\nu) | \nu \rangle \quad (\text{Step 2})$$

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

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

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

Finite-temperature Lanczos Method II

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

- Approximation better if symmetries taken into account.
- Γ denotes the used irreducible representations; often this is just the S^z symmetry, i.e. $\Gamma \equiv M$

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

Finite-temperature Lanczos Method III

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

- Problem: for anisotropic Hamiltonians no symmetry left
→ accuracy drops (esp. for high T).
- Simple traces such as $\text{Tr} \left(\tilde{S}^z \right) = 0$ 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)

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

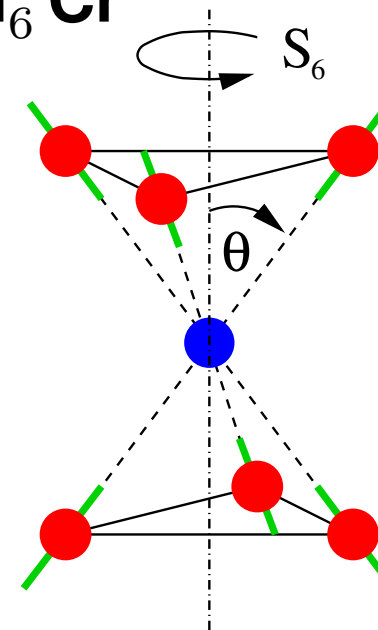
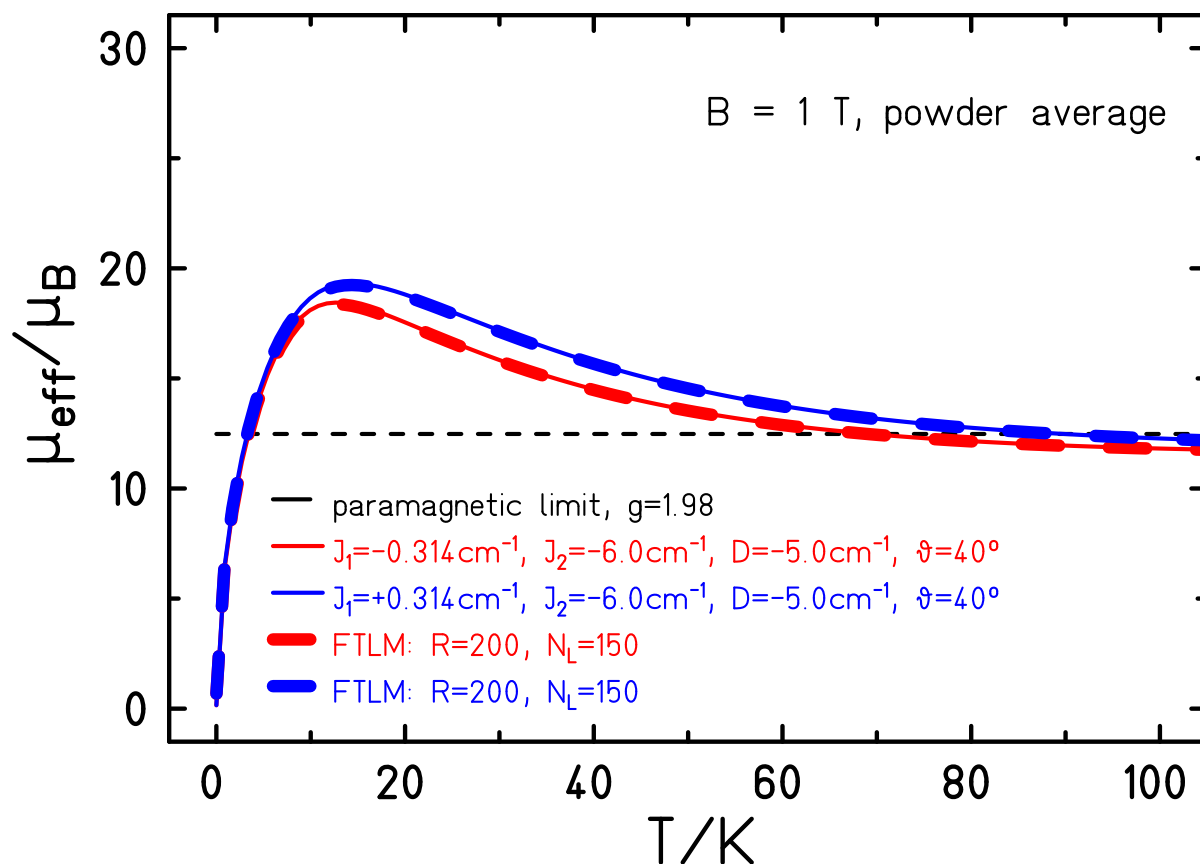
Use Lanczos energy eigenvector $|n(\nu)\rangle$ and time-reversed counterpart $|\tilde{n}(\nu)\rangle$

$$|n(\nu)\rangle = \sum_{\vec{m}} c_{\vec{m}} |\vec{m}\rangle \quad \text{and} \quad |\tilde{n}(\nu)\rangle = \sum_{\vec{m}} c_{\vec{m}}^* |-\vec{m}\rangle$$

- 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: $\text{Mn}_6\text{Cr}^{\text{III}}$

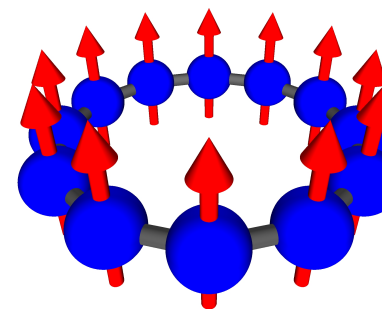
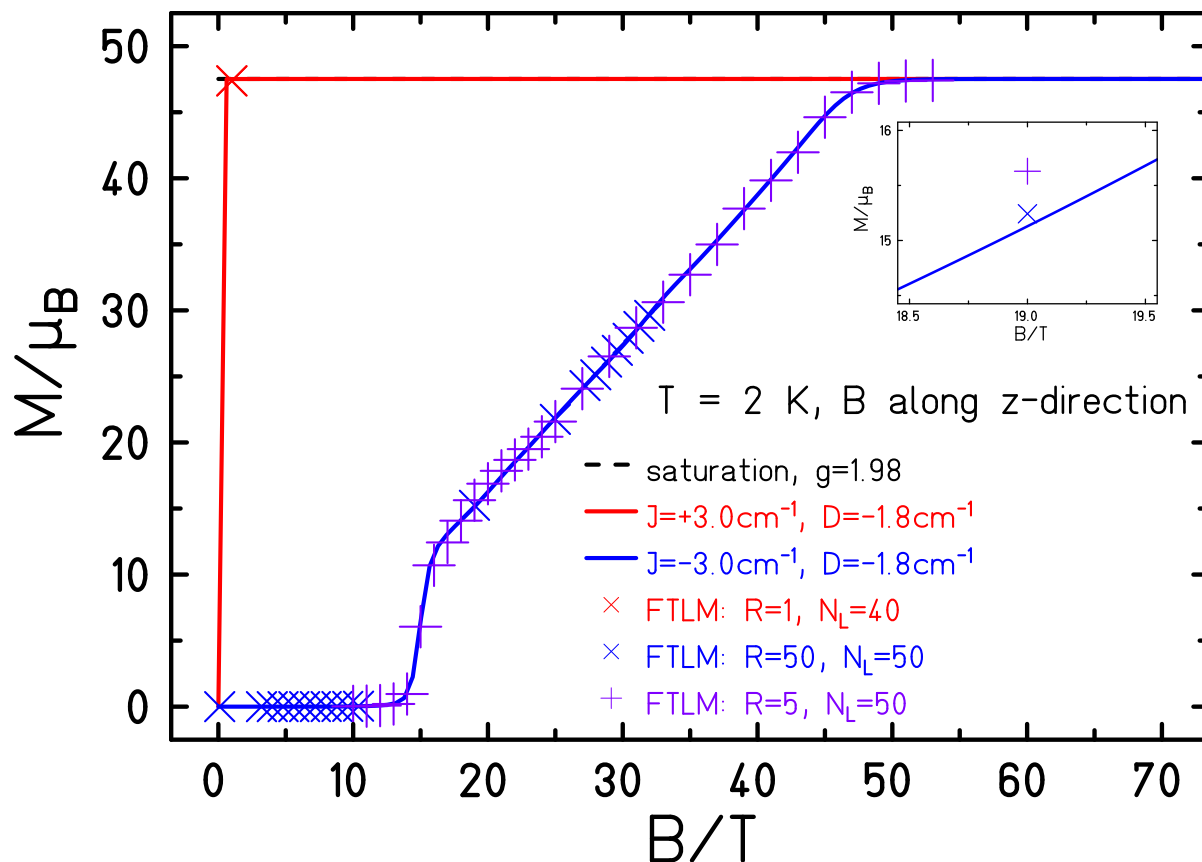


$s = 2, s = 3/2$
 $\dim(\mathcal{H}) = 62,500$
 non-collinear easy axes

Hours compared to days, notebook compared to supercomputer!

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

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

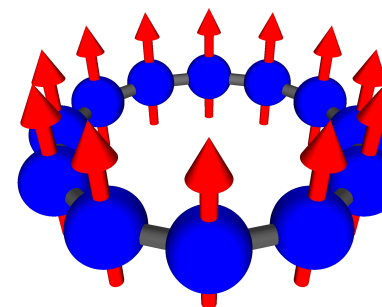
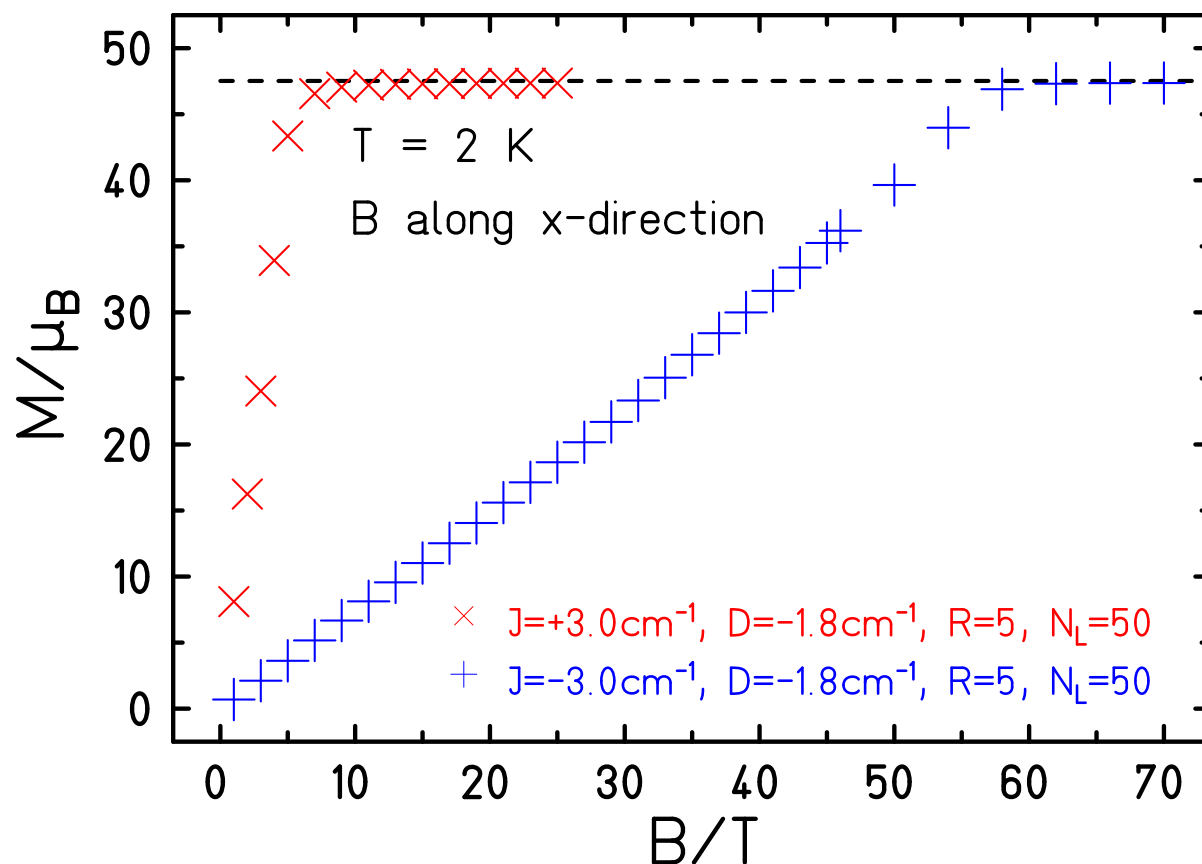


$s = 2$
 $\dim(\mathcal{H}) = 244, 140, 625$
 collinear easy axes

A few days compared to *impossible!*

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

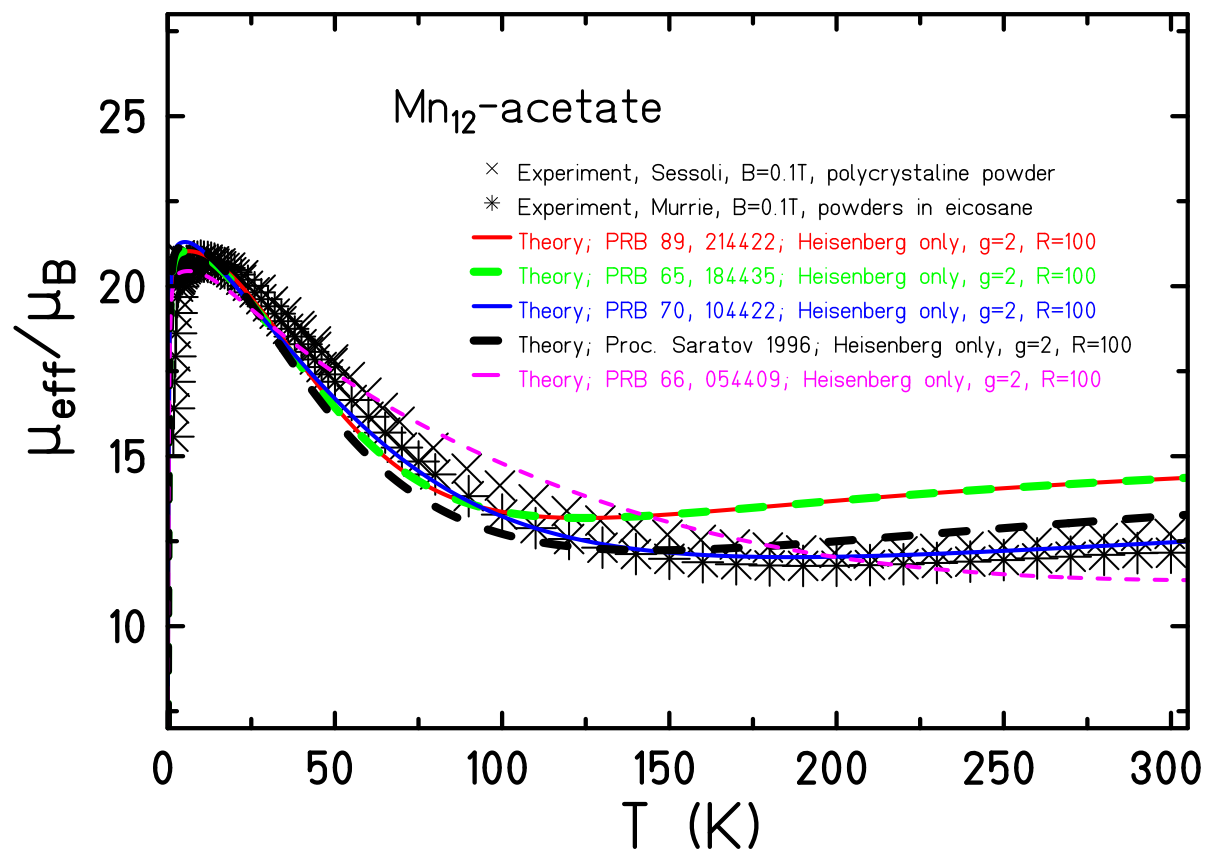
A fictitious $\text{Mn}_{12}^{\text{III}}$ – M_x vs B_x



No other method can deliver these curves!

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

Effective magnetic moment of Mn₁₂-acetate



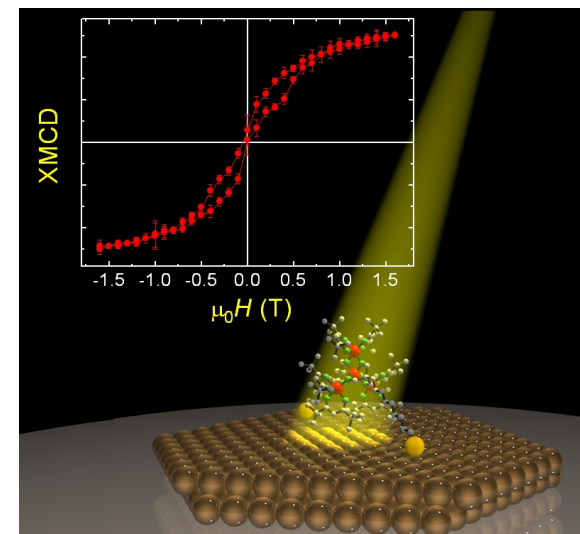
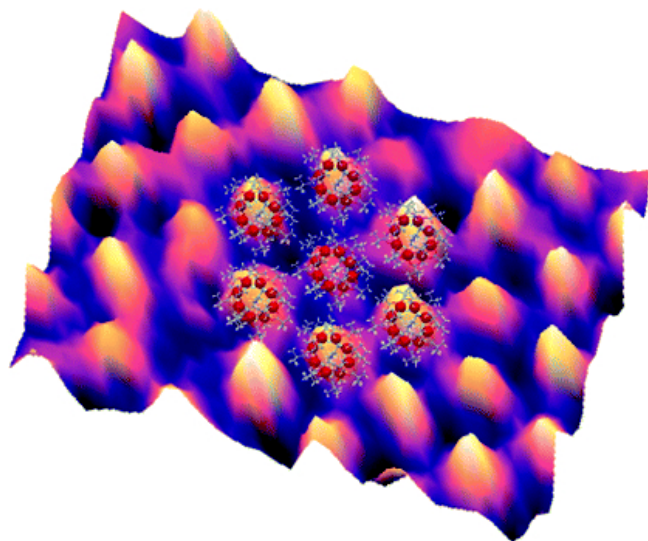
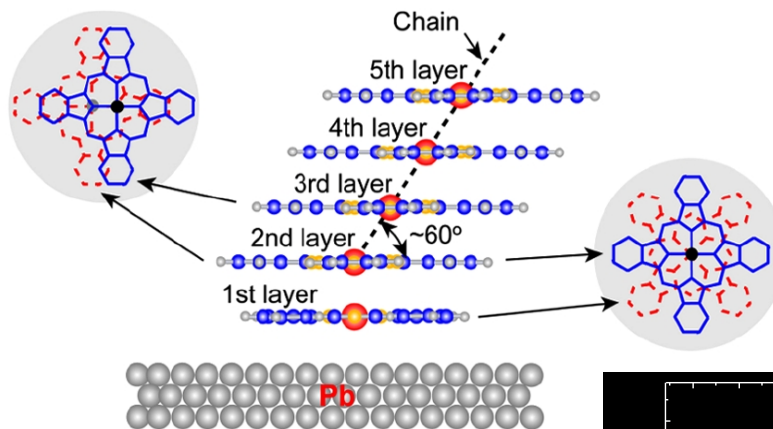
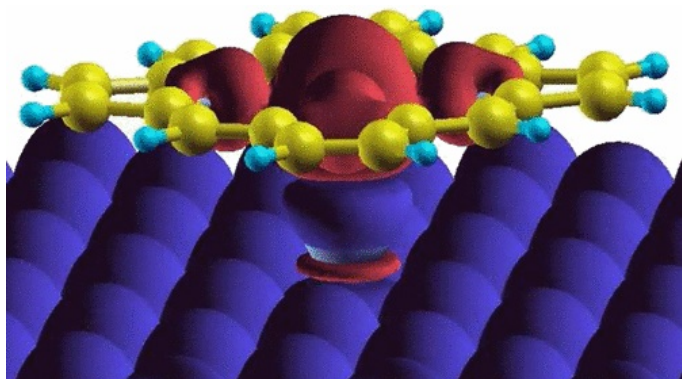
We can check DFT parameter predictions for large molecules!

O. Hanebaum, J. Schnack, work in progress

Numerical Renormalization Group calculations

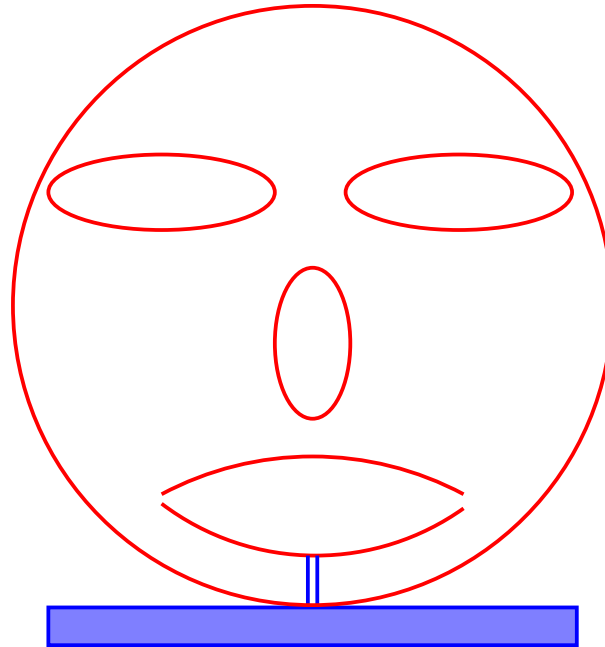
(Good for deposited molecules.)

You want to deposit a molecule



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

From a bloody physicist's perspective ...



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

Properties may change drastically

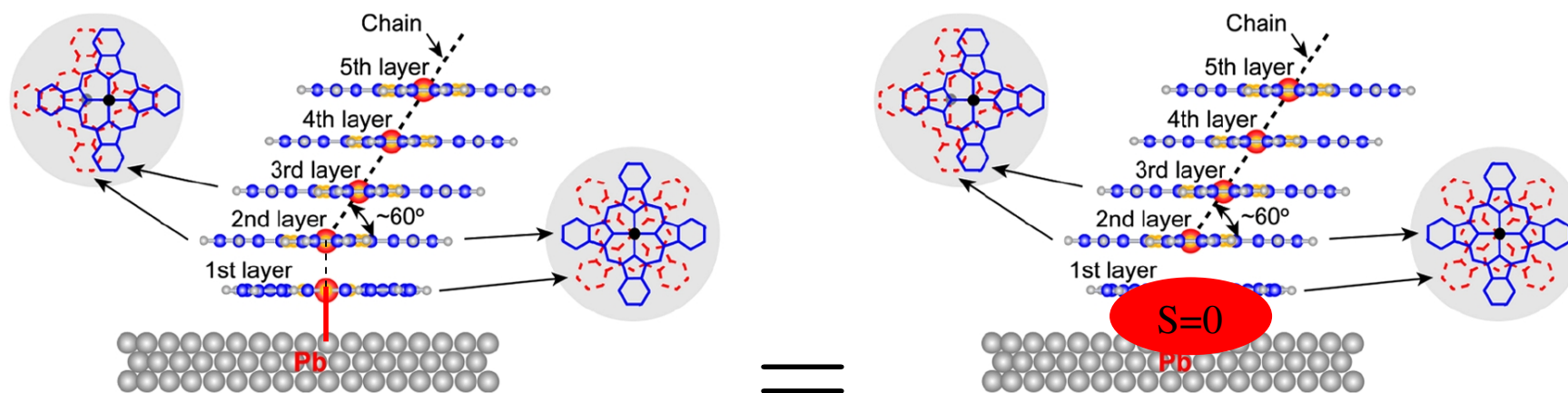


Kondo screening may improve or worsen the magnetic properties;

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

How to calculate such things?

Physical example (ICMM 2010)

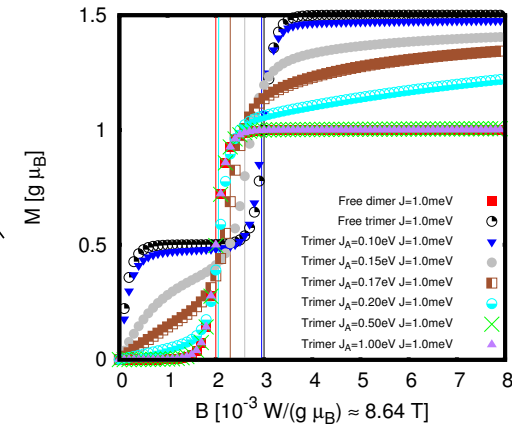
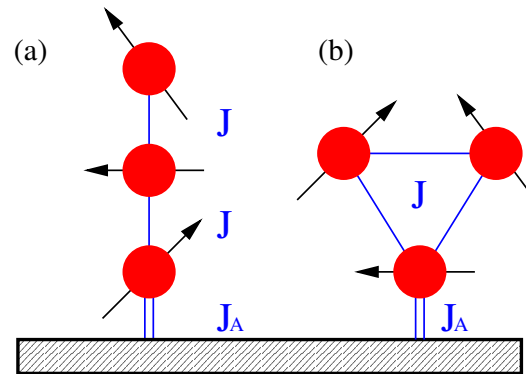


Stack of deposited Cobalt phthalocyanine (CoPc) molecules;
 Co^{2+} with spin $s = 1/2$.

Under which circumstances is the picture of total screening correct?

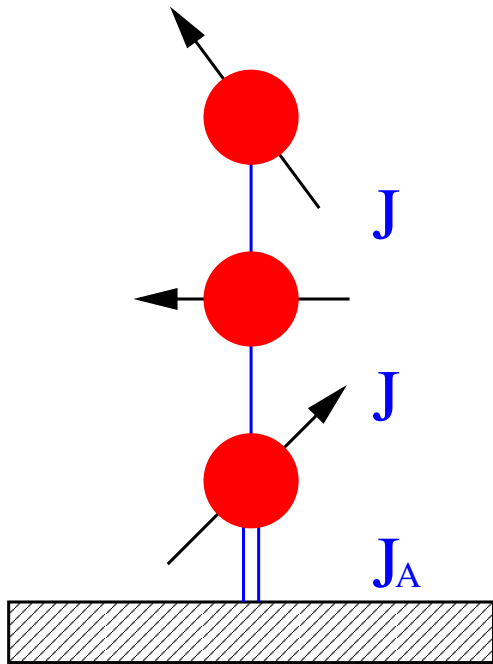
X. Chen *et al.*, Phys. Rev. Lett. **101**, 197208 (2008).

Numerical Renormalization Group (Wilson)



- Magnetic properties of deposited spin systems;
- Martin Höck (until 07/2013): anisotropic single spins (PRB **87**, 184408 (2013));
- Henning-Timm Langwald: deposited Heisenberg systems.

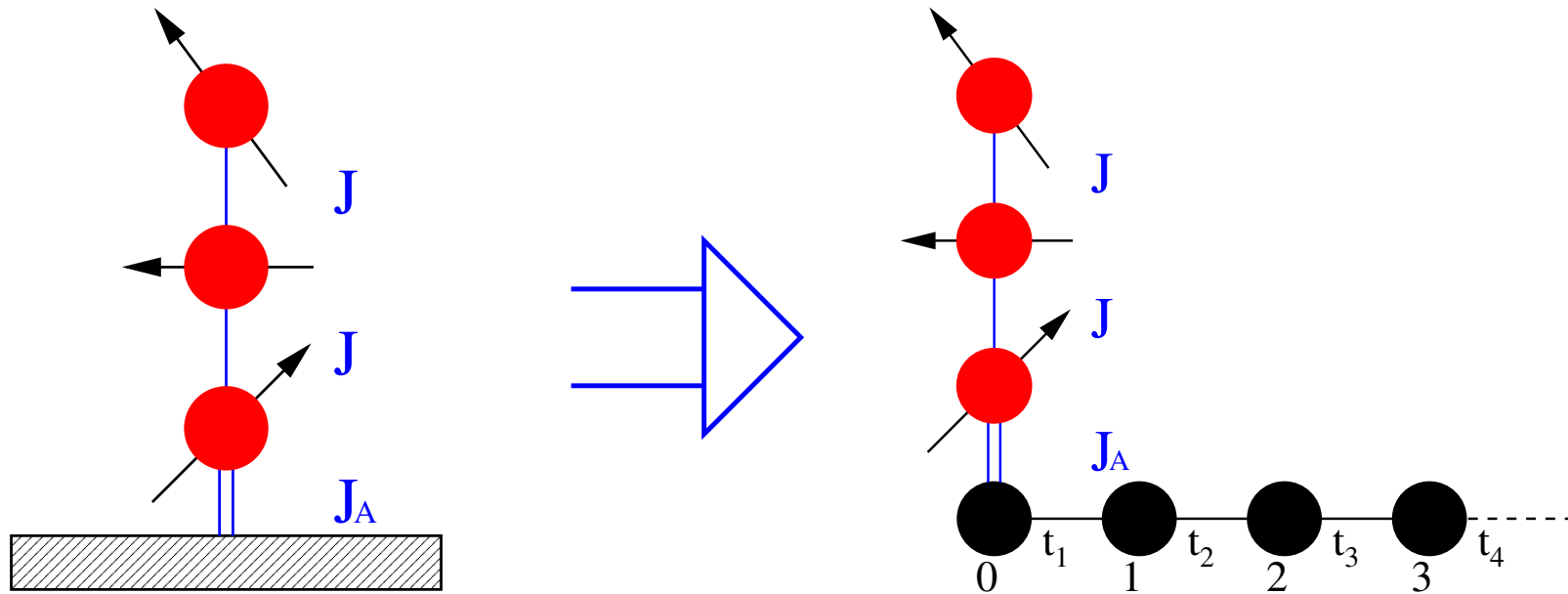
NRG – minimal model (already an approximation!)



- $\underline{H} = \underline{H}_{\text{electrons}} + \underline{H}_{\text{coupling}} + \underline{H}_{\text{impurity}}$
- $\underline{H}_{\text{electrons}} = \sum_{i \neq j, \sigma} t_{ij} d_{i\sigma}^\dagger d_{j\sigma} + g_e \mu_B B \underline{S}^z$
- $\underline{H}_{\text{coupling}} = -2J_A \underline{S} \cdot \underline{s}_0$, \underline{s}_0 – spin density at contact
- $\underline{H}_{\text{impurity}} =$ 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



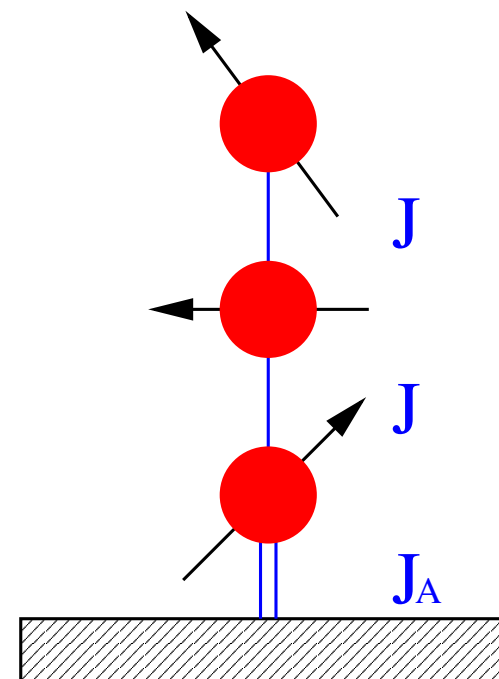
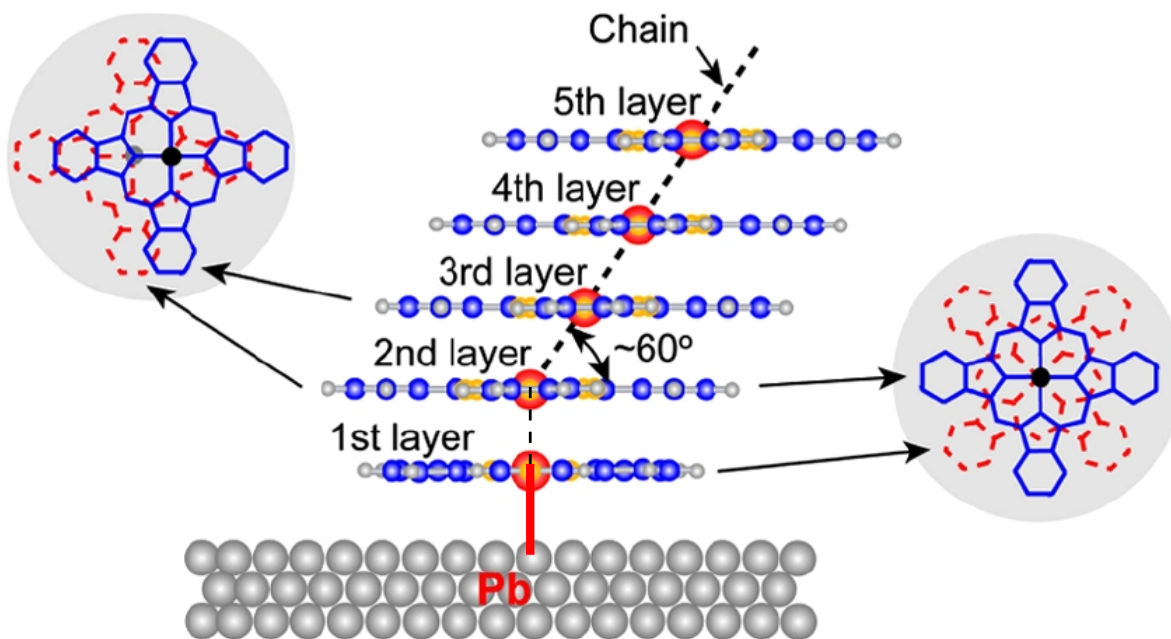
Metallic surface is replaced by semi-infinite Hubbard chain;

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

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

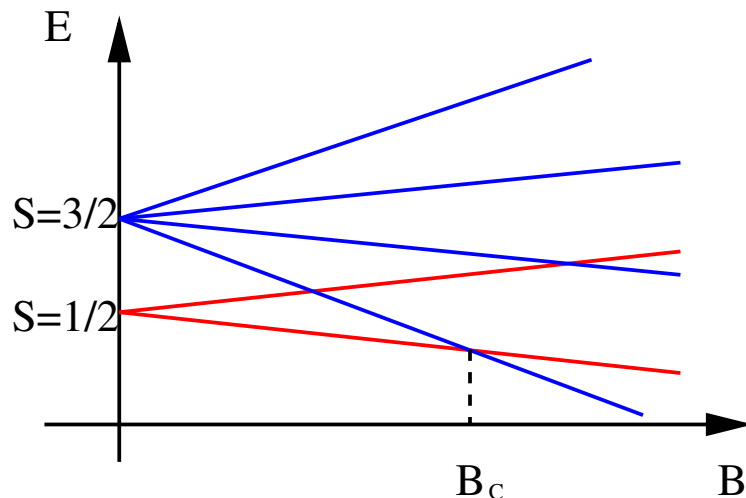
Truncation of basis set when matrices grow too big.

Once more: deposited chain

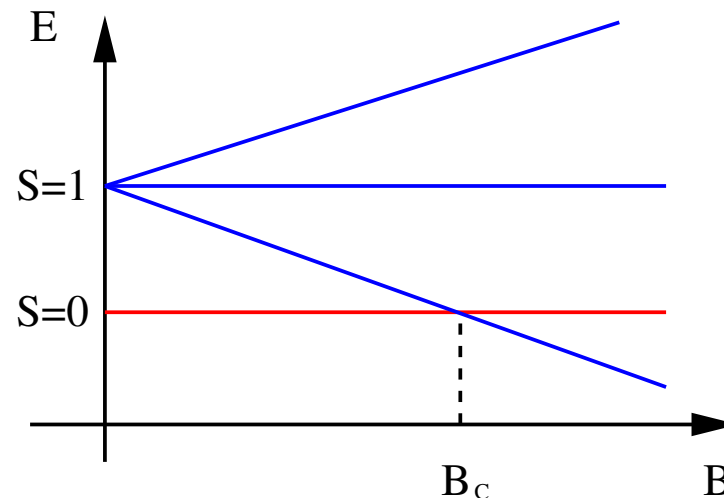


X. Chen *et al.*, Phys. Rev. Lett. **101**, 197208 (2008).

Energy levels of limiting cases for deposited trimer



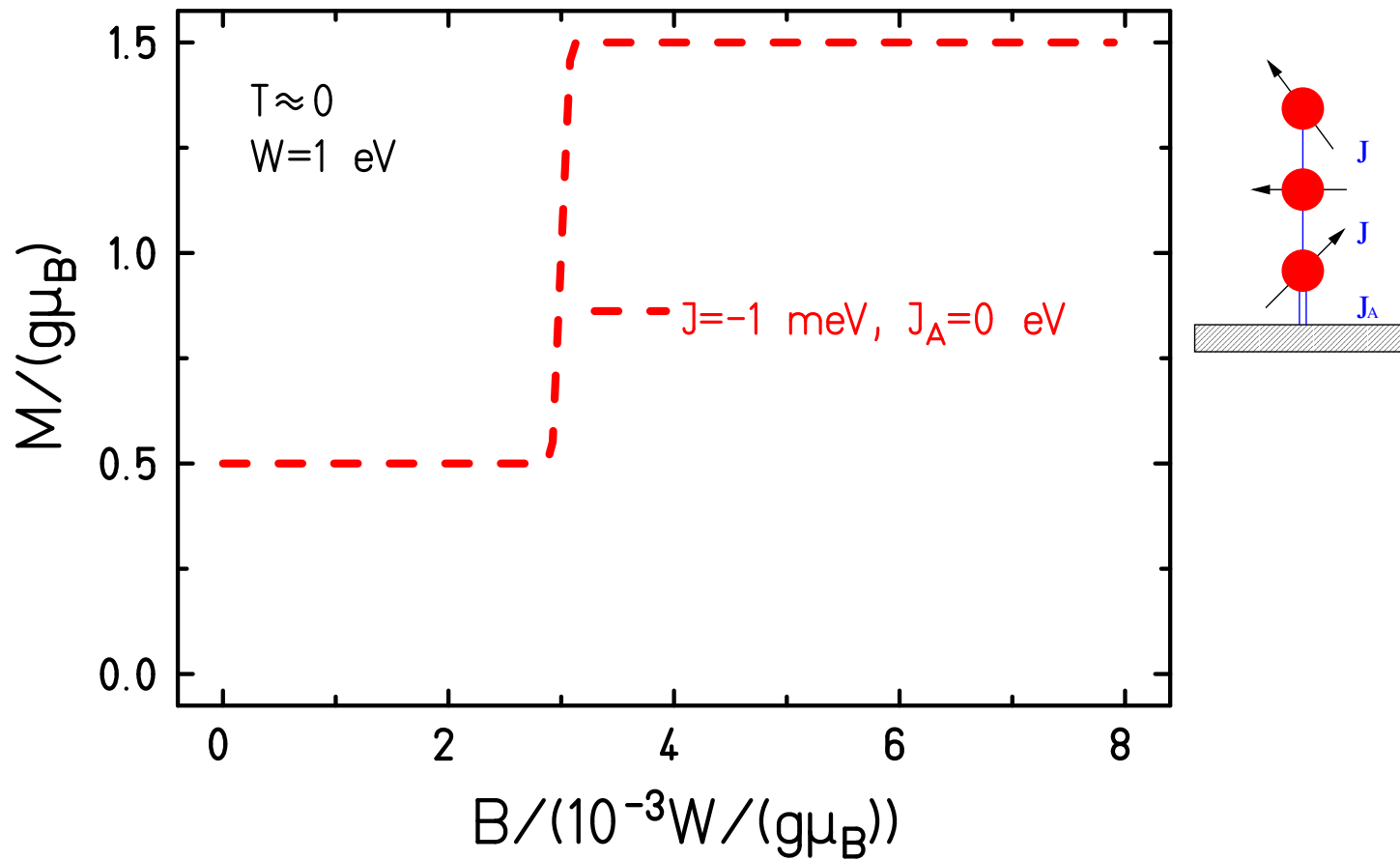
- energy levels of a trimer



- energy levels of a dimer

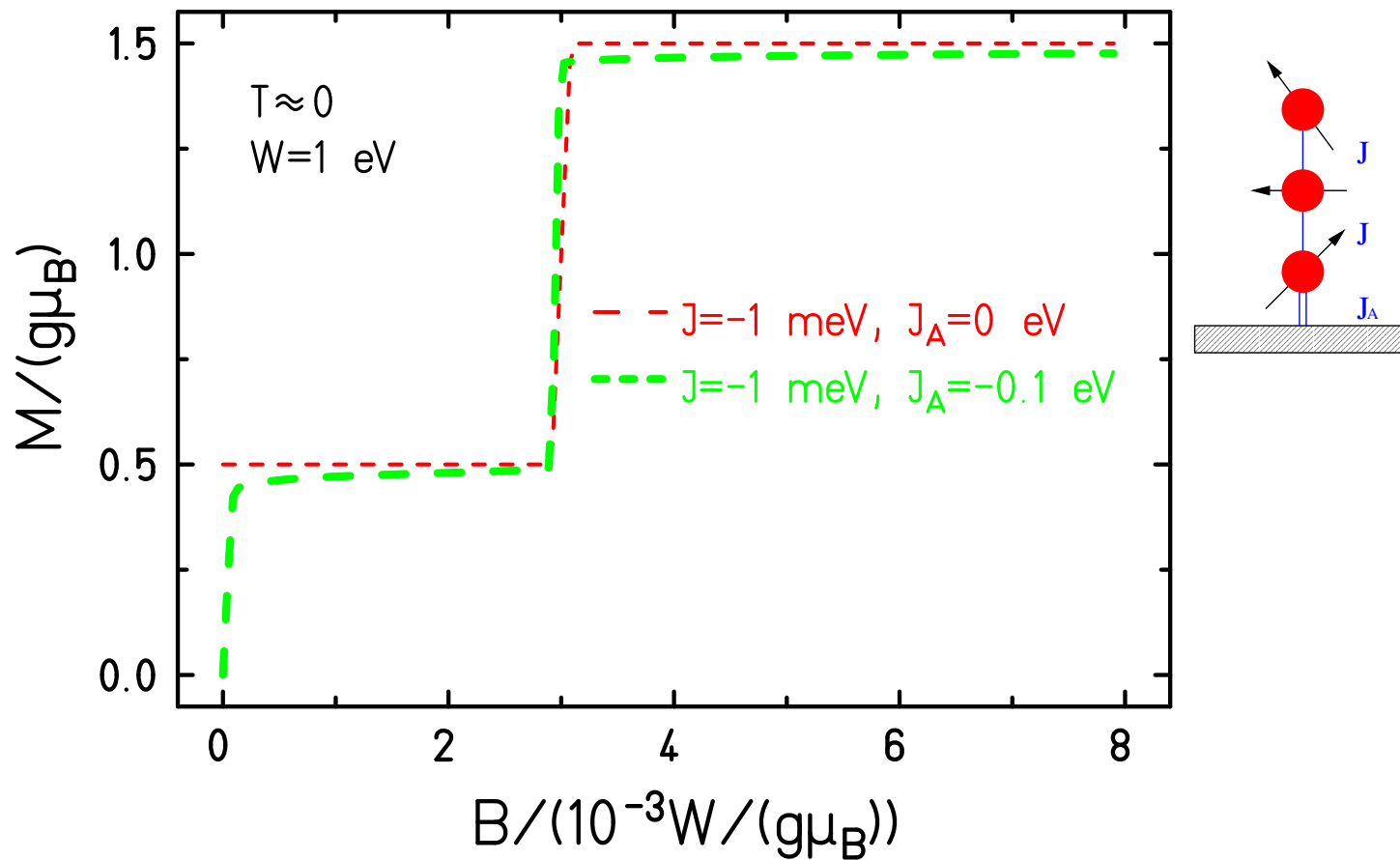
Magnetization curves different; could be seen in XMCD.
 NRG calculates observables also between limiting cases
 and can thus tell under which circumstances a limiting case applies.

Increasing coupling to the substrate



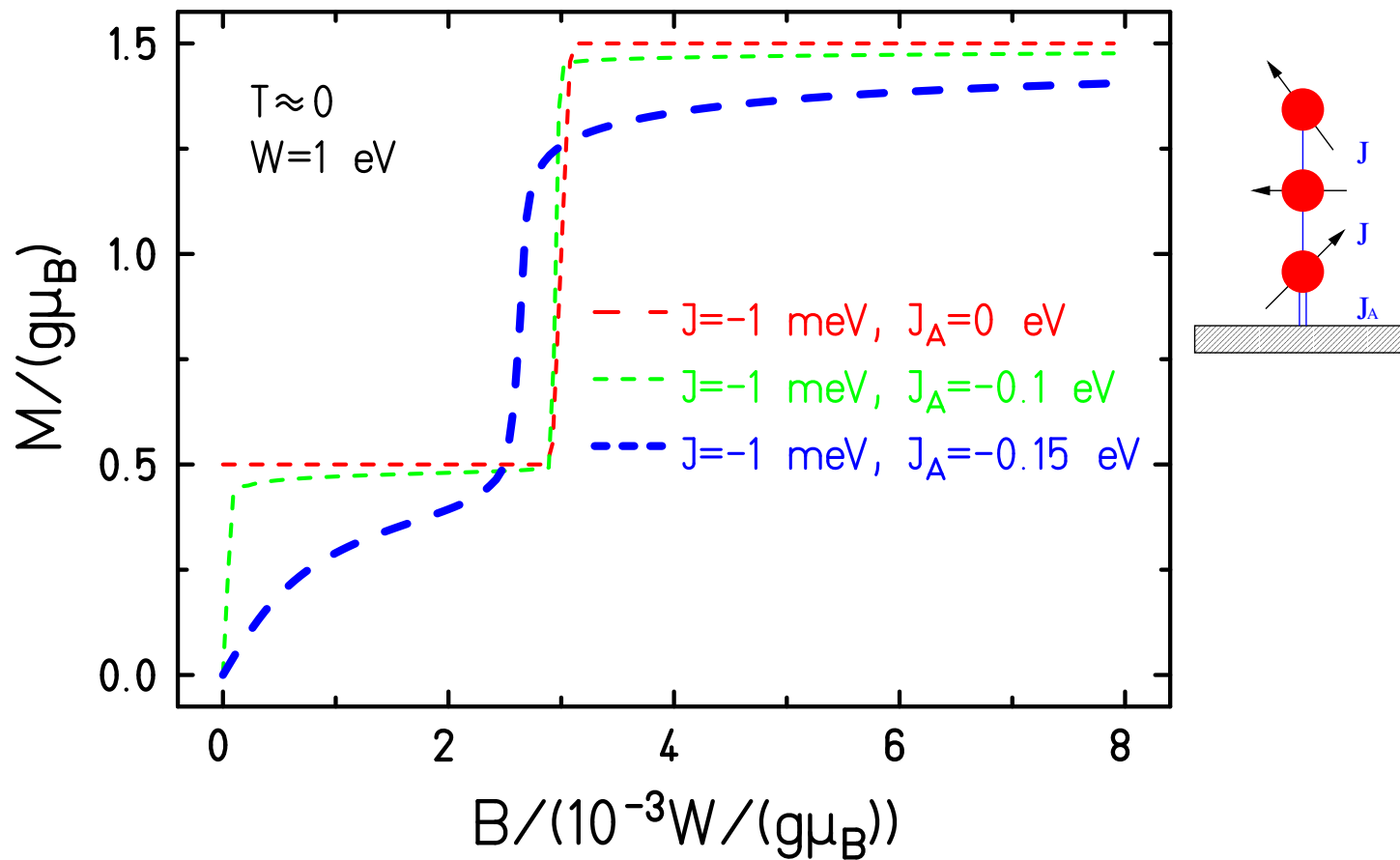
H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

Increasing coupling to the substrate



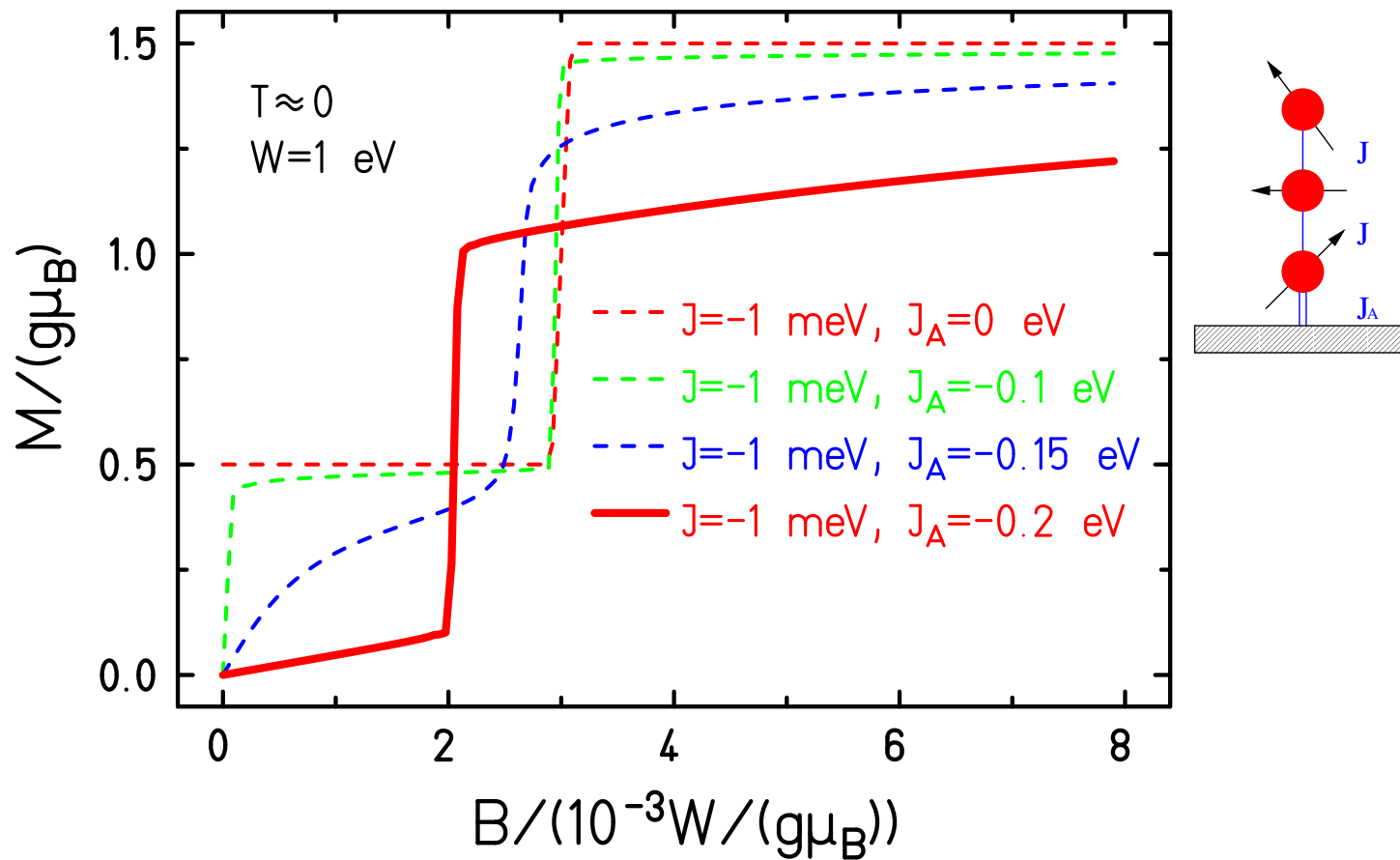
H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

Increasing coupling to the substrate



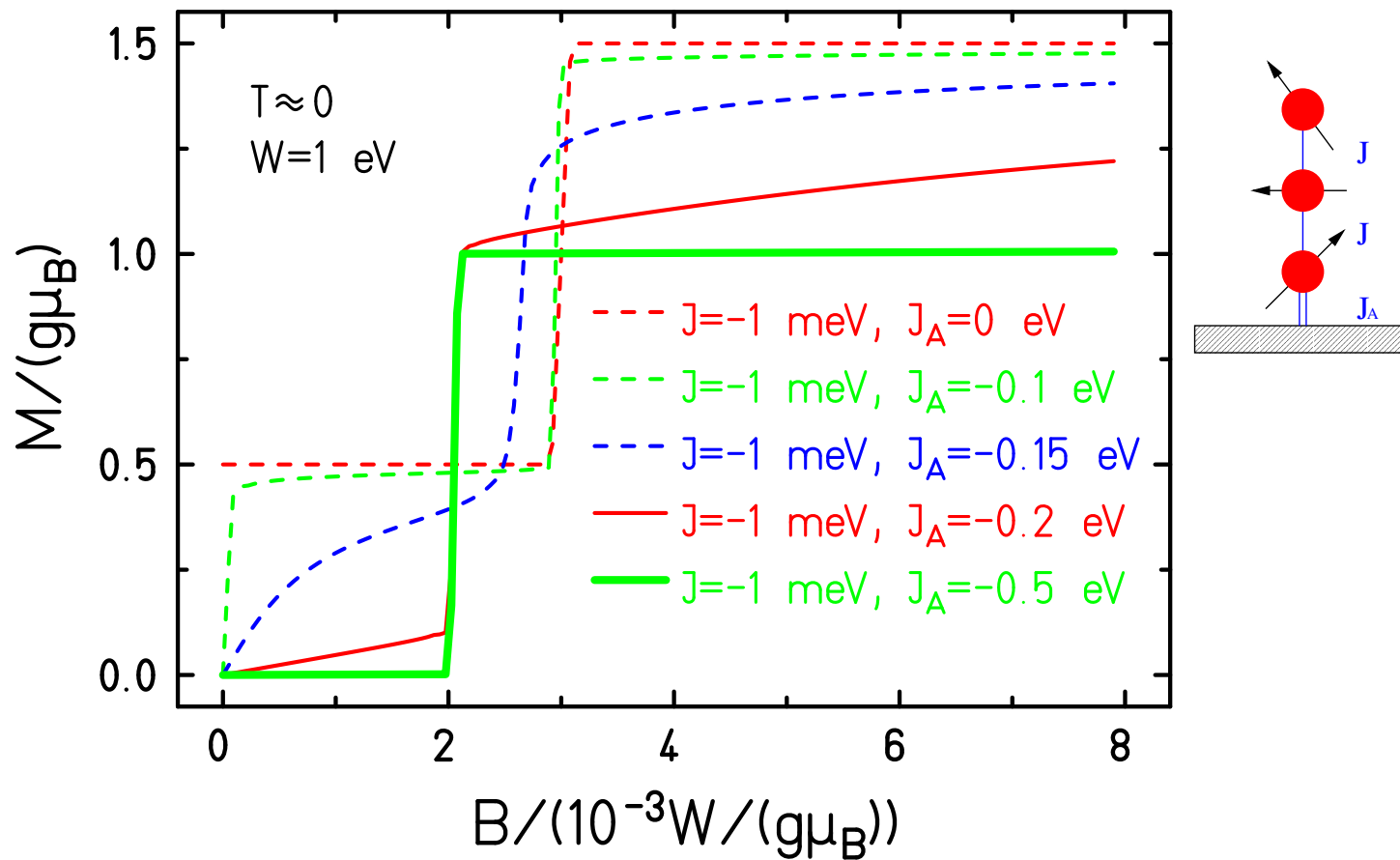
H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

Increasing coupling to the substrate



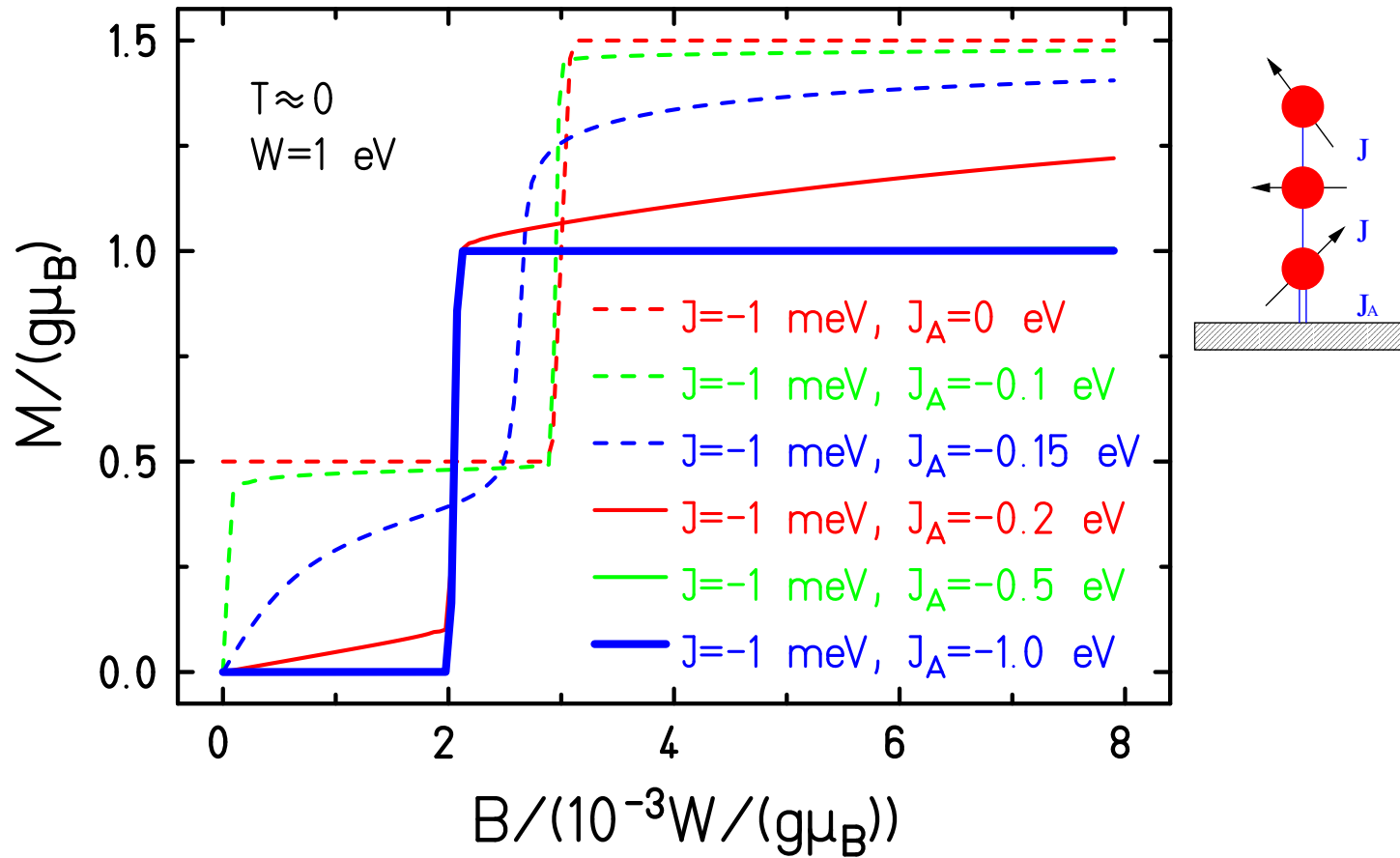
H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

Increasing coupling to the substrate



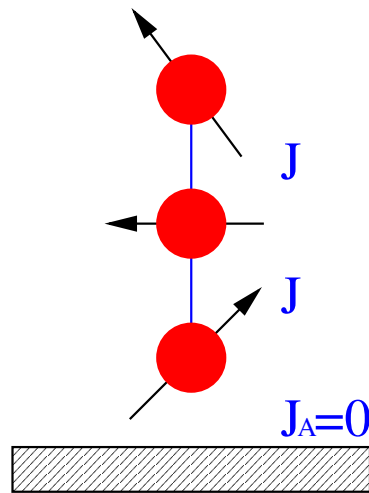
H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

Increasing coupling to the substrate



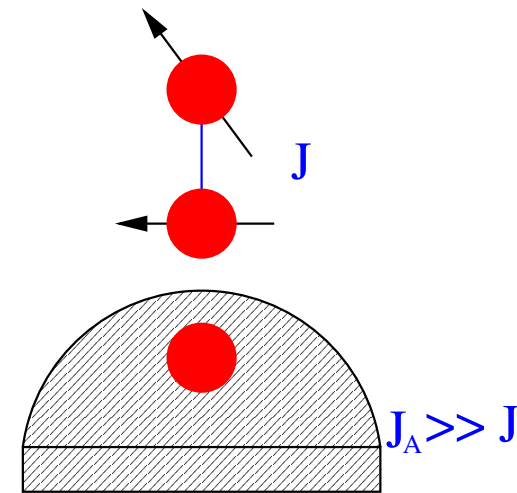
H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

Weak vs. strong coupling



- weak coupling limit:
unperturbed molecule (trimer)

- $|J_A| \lesssim 0.1W$

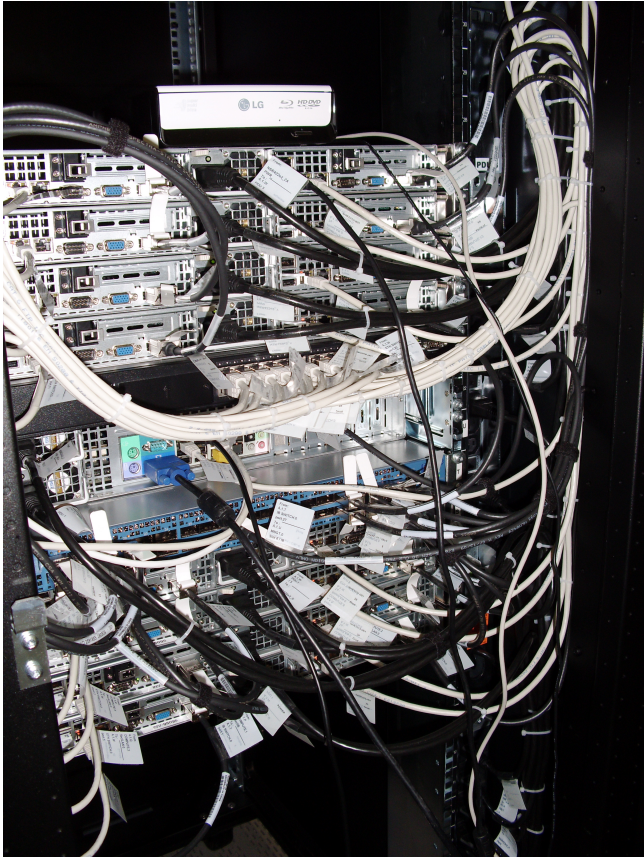


- strong coupling limit:
effective remainder (dimer)

- $|J_A| \gtrsim 0.5W$

Inbetween: no simple characterization + further sequential screening possible

Summary



- Magnetic molecules for storage, q-bits, MCE, and since they are nice.
- Finite-temperature Lanczos is a good approximate method for Hilbert space dimensions smaller than 10^{10} .
- Isentropes for interacting systems are much richer than for paramagnets. Good for applications away from $(T = 0, B = 0)$.
- NRG delivers local observables, such as magnetization, which can be compared with XMCD results.
- Screening can lead to interesting limiting cases, which might show different (worse/better) behavior compared to the free molecule.

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 (Zaragoza); 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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