Sub-Kelvin cooling with magnetic molecules

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Here is what I could talk about . . .

Possible contents

Introduction to molecular magnetism

Traditional approach

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

Approximate methods

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

\+ examples: MCE, frustration, SMM, NRG

\+ Outlook

. . . and here is
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Contents for you today

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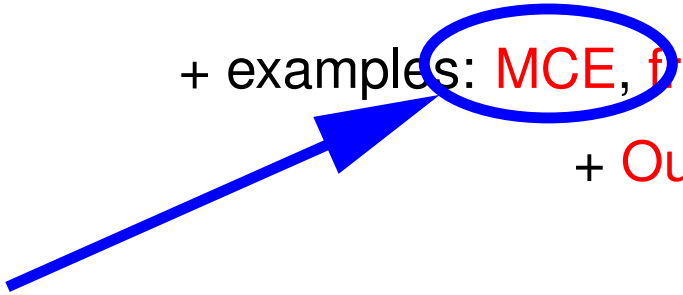
+ Outlook

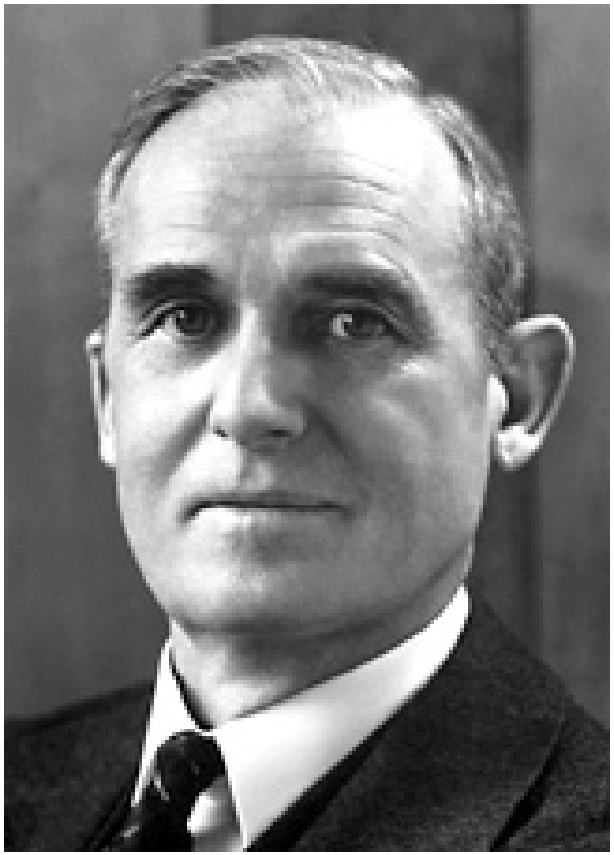


Enhanced magnetocaloric effect

Magnetocaloric effect – Basics

- Heating or cooling in a varying magnetic field. Discovered in pure iron by Emil Warburg in 1881.
- 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.

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

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).

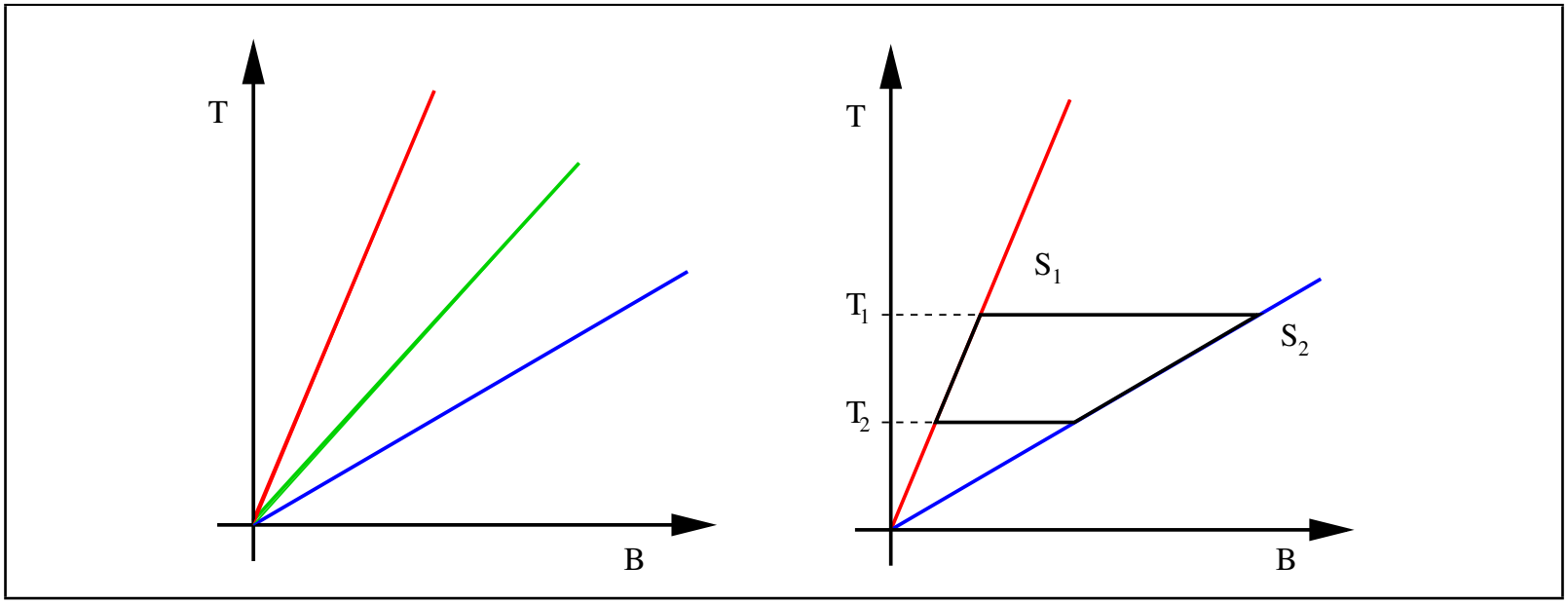
Magnetocaloric effect – cooling rate

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

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

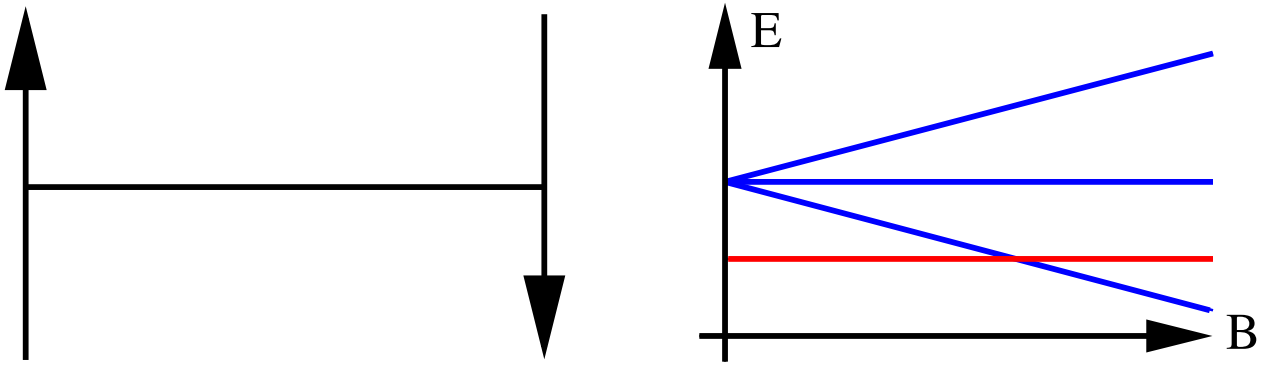
(1) V.K. Pecharsky, K.A. Gschneidner, Jr., A. O. Pecharsky, and A. M. Tishin, Phys. Rev. B **64**, 144406 (2001).
(2) Lijun Zhu, M. Garst, A. Rosch, and Qimiao Si, Phys. Rev. Lett. **91**, 066404 (2003).
B. Wolf, Y. Tsui, D. Jaiswal-Nagar, U. Tutsch, A. Honecker, K. Removic-Langer, G. Hofmann, A. Prokofiev, 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).

Magnetocaloric effect – Paramagnets



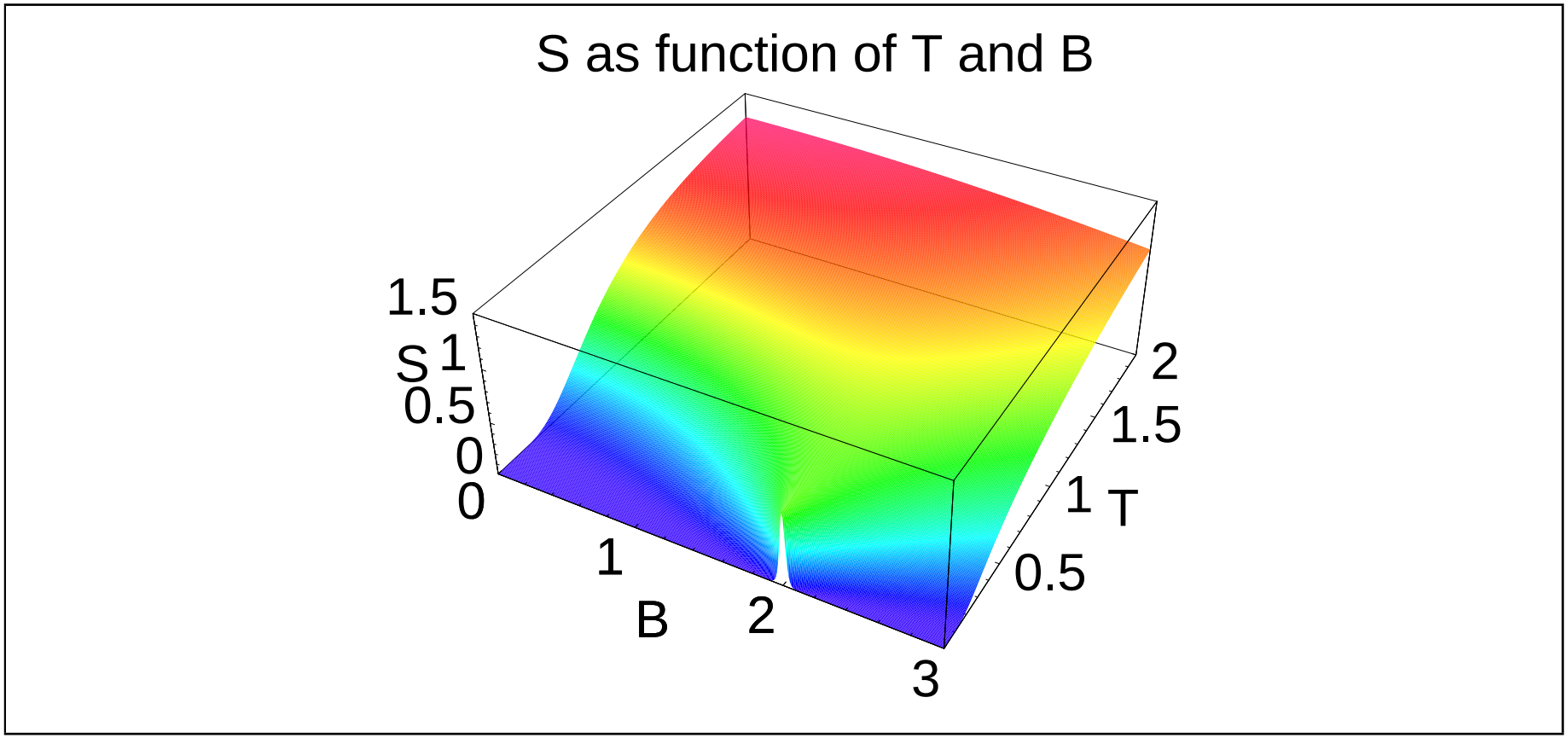
- Ideal paramagnet: $S(T,B) = f(B/T)$, i.e. $S = const \Rightarrow T \propto B$.
- At low T pronounced effects of dipolar interaction prevent further effective cooling.

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



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

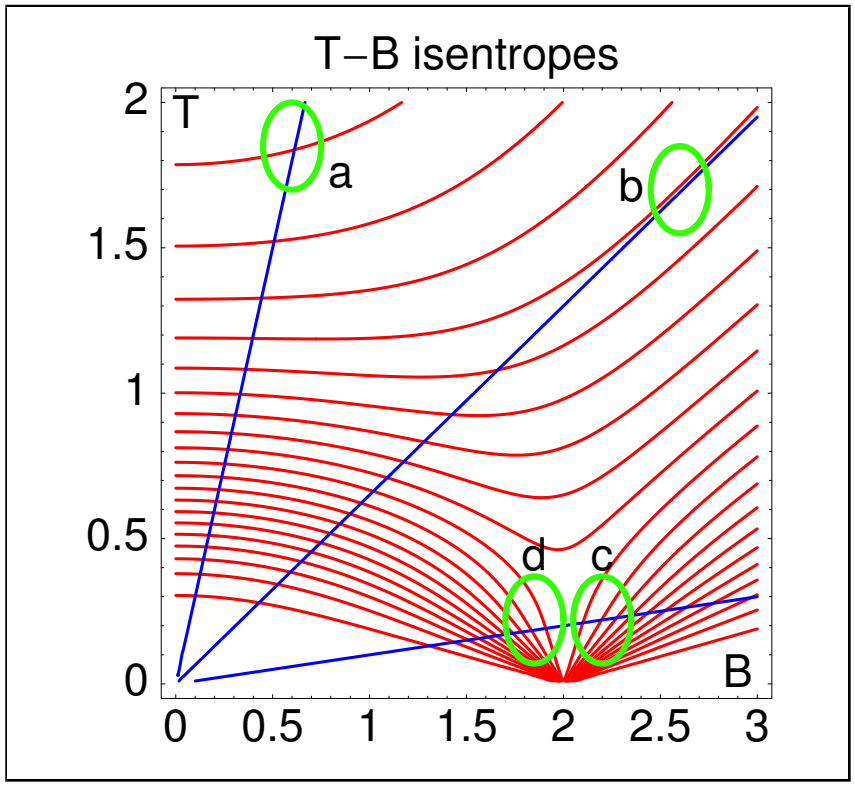
Magnetocaloric effect – af $s = 1/2$ dimer



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

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

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



blue lines: ideal paramagnet, red curves: af dimer

Magnetocaloric effect:

(a) reduced,

(b) the same,

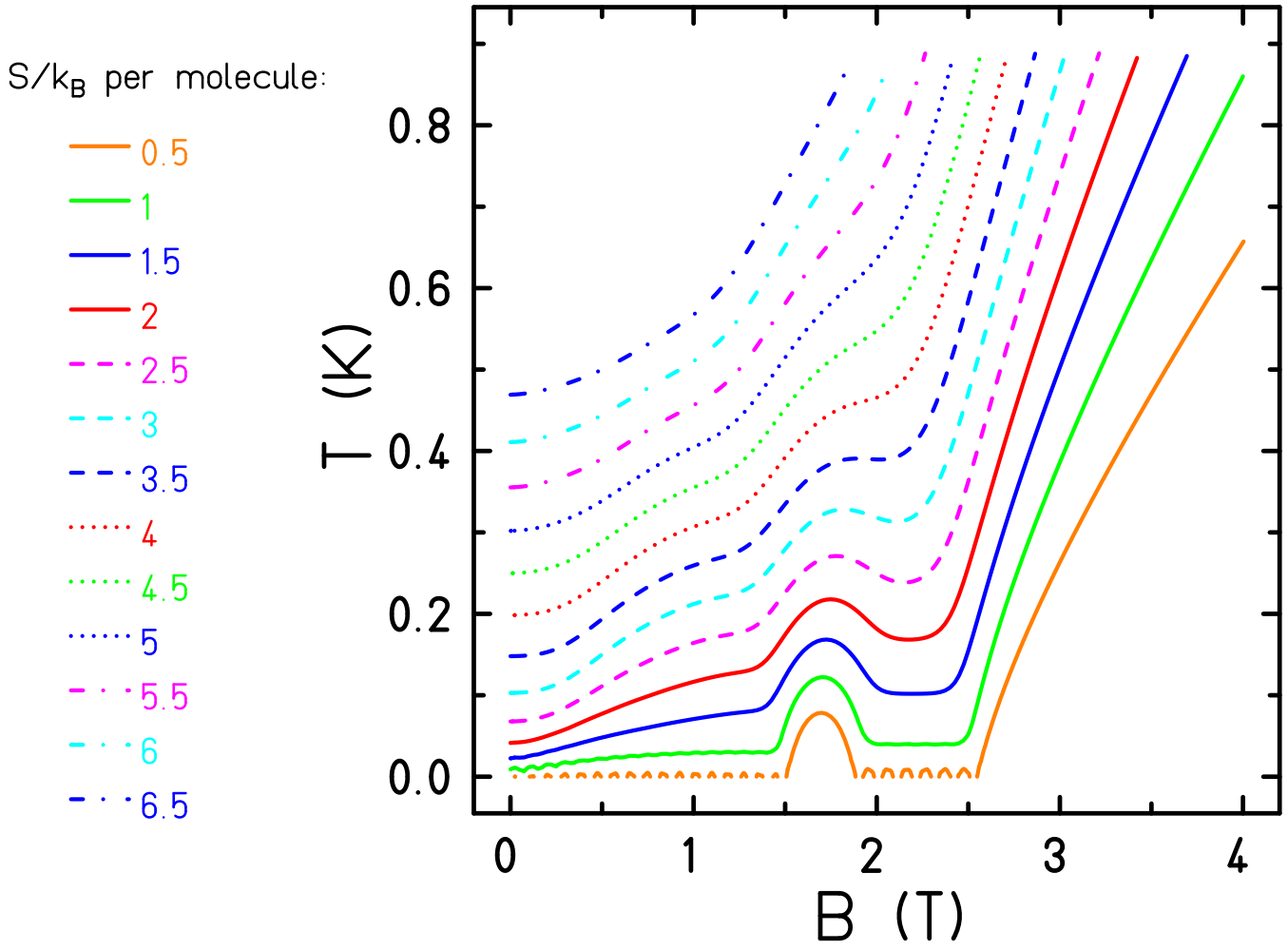
(c) enhanced,

(d) opposite

when compared to an ideal paramagnet.

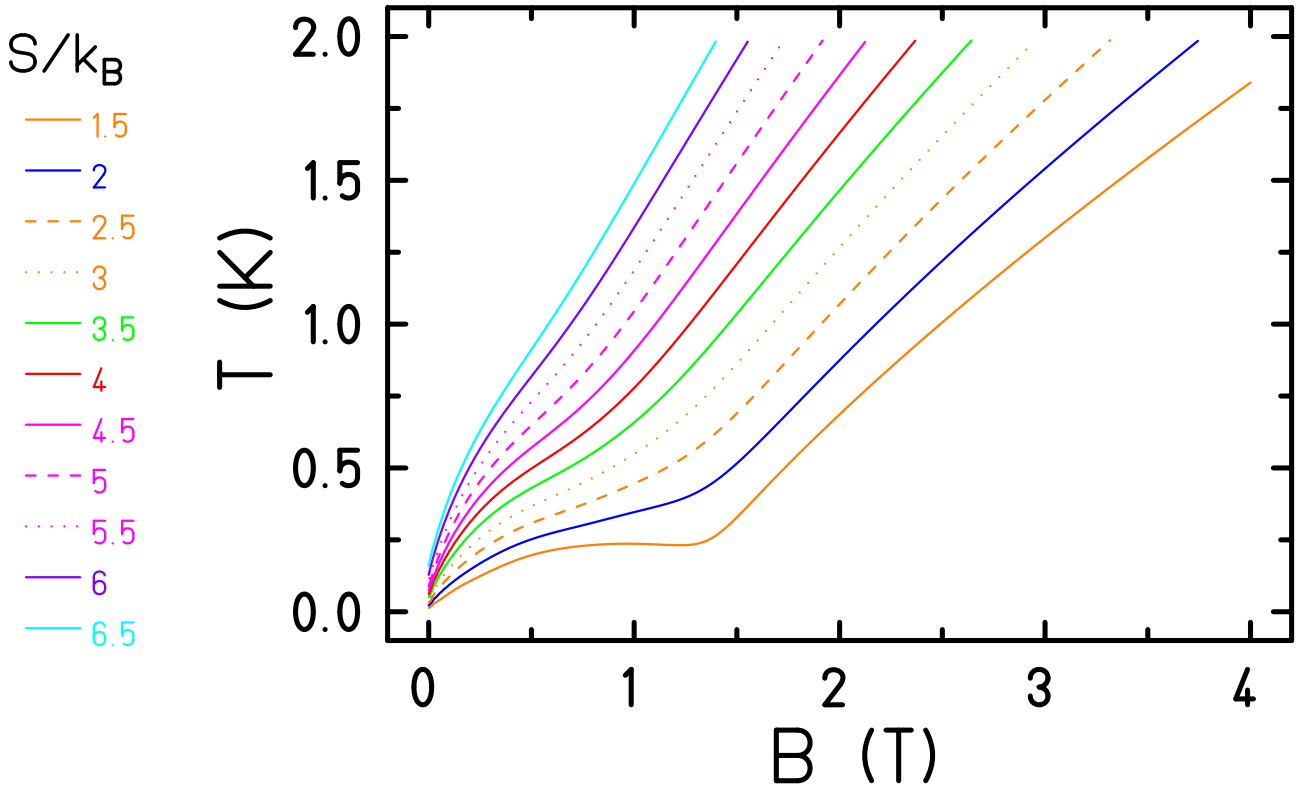
Case (d) does not occur for a paramagnet.

Typical isentropes for af spin system



Level crossings signal antiferromagnetic interactions.

Typical isentropes for high-spin system

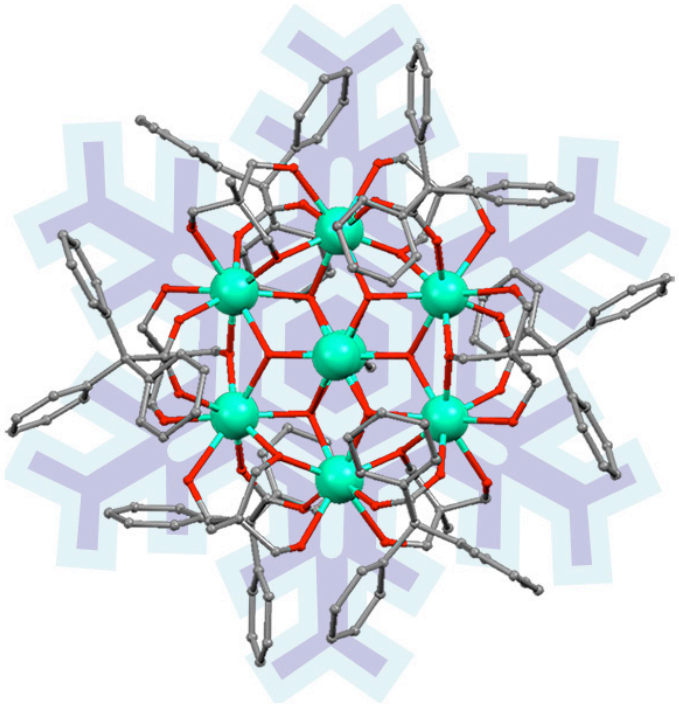


Typical for high-spin ground state.

Nice ideas,

but can one measure it?

Gd$_7$ – Basics

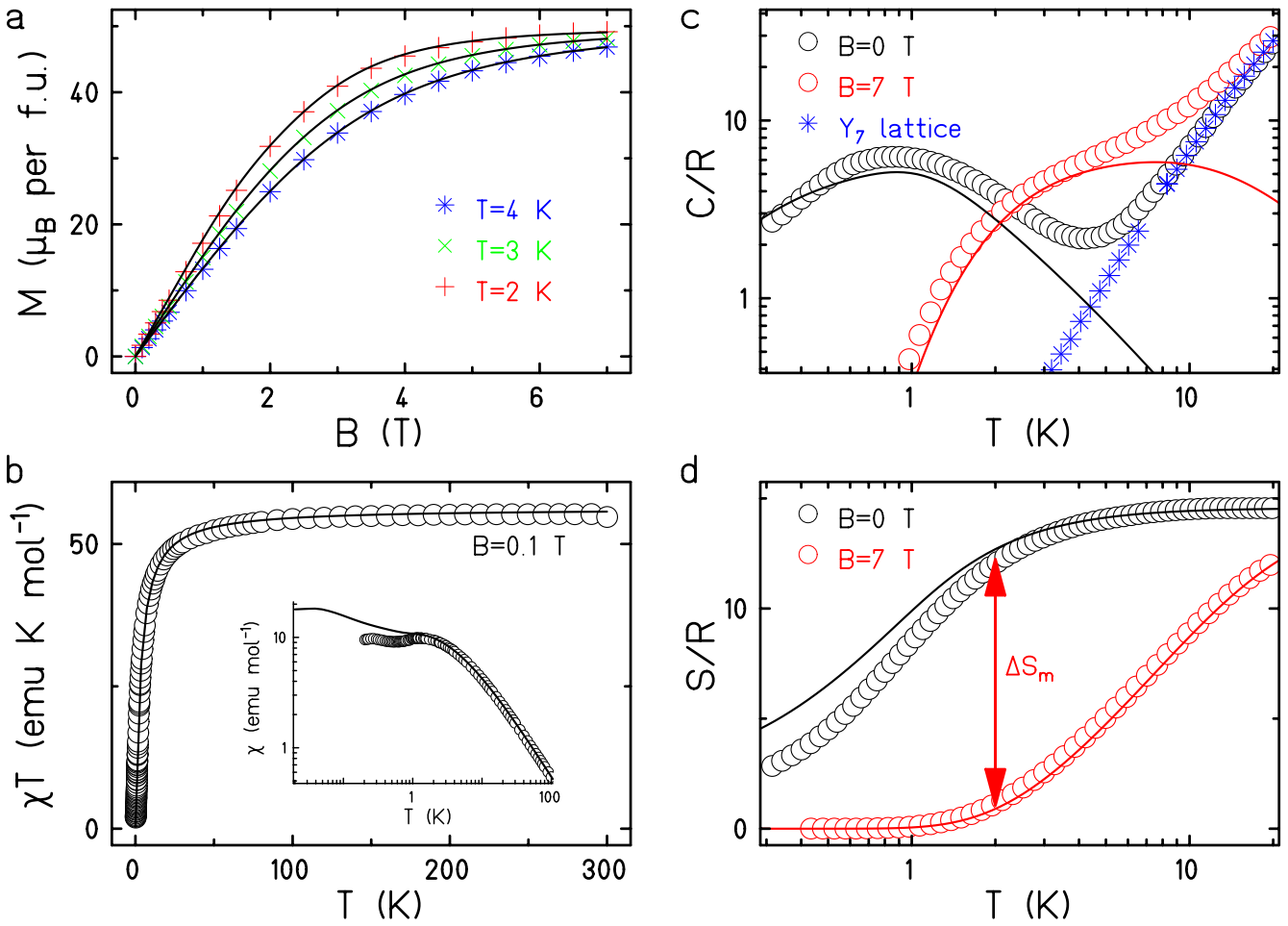


- Often magnetocaloric observables not directly measured, but inferred from Maxwell's relations.
- First real cooling experiment with a molecule.
- $\underset{\sim}{H} = -2 \sum_{i<j} J_{ij}\, \underset{\sim}{\vec{s}}_i \cdot \underset{\sim}{\vec{s}}_j + g\, \mu_B\, B \sum_i^N \underset{\sim}{s}_i^z$

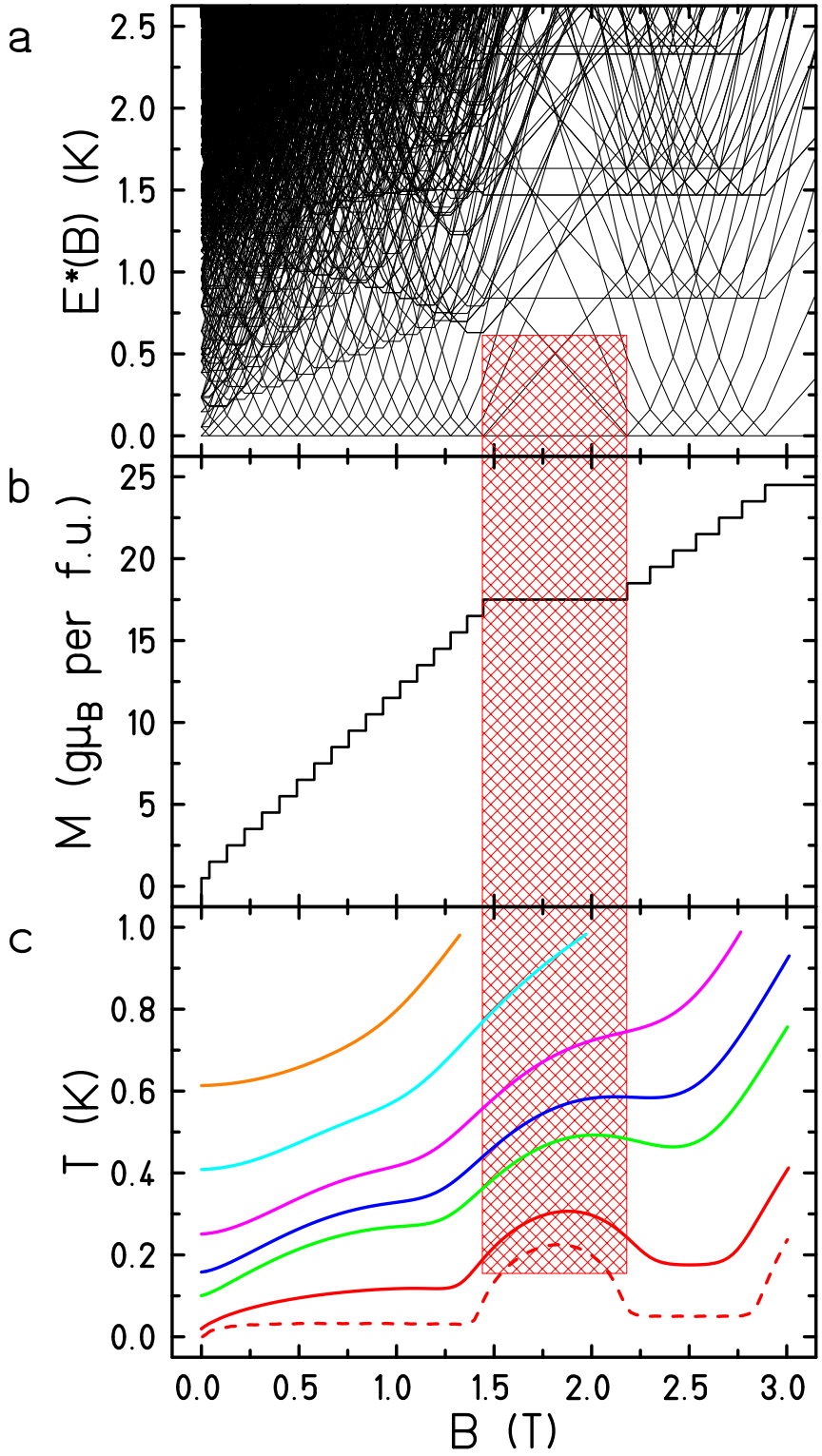
  $J_1 = -0.090(5)$ K, $J_2 = -0.080(5)$ K and $g = 2.02$.
- Very good agreement down to the lowest temperatures.

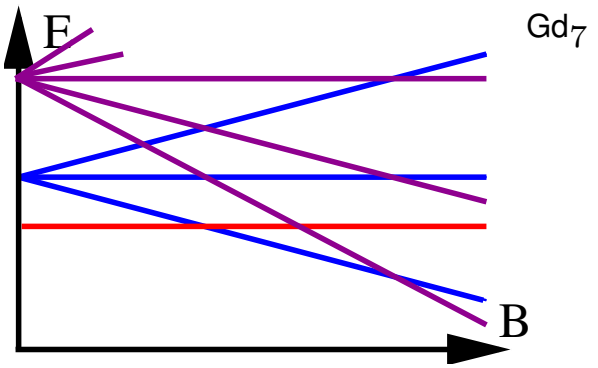
J. W. Sharples, D. Collison, E. J. L. McInnes, J. Schnack, E. Palacios, M. Evangelisti, Nat. Commun. **5**, 5321 (2014).

Gd$_7$ – experiment & theory

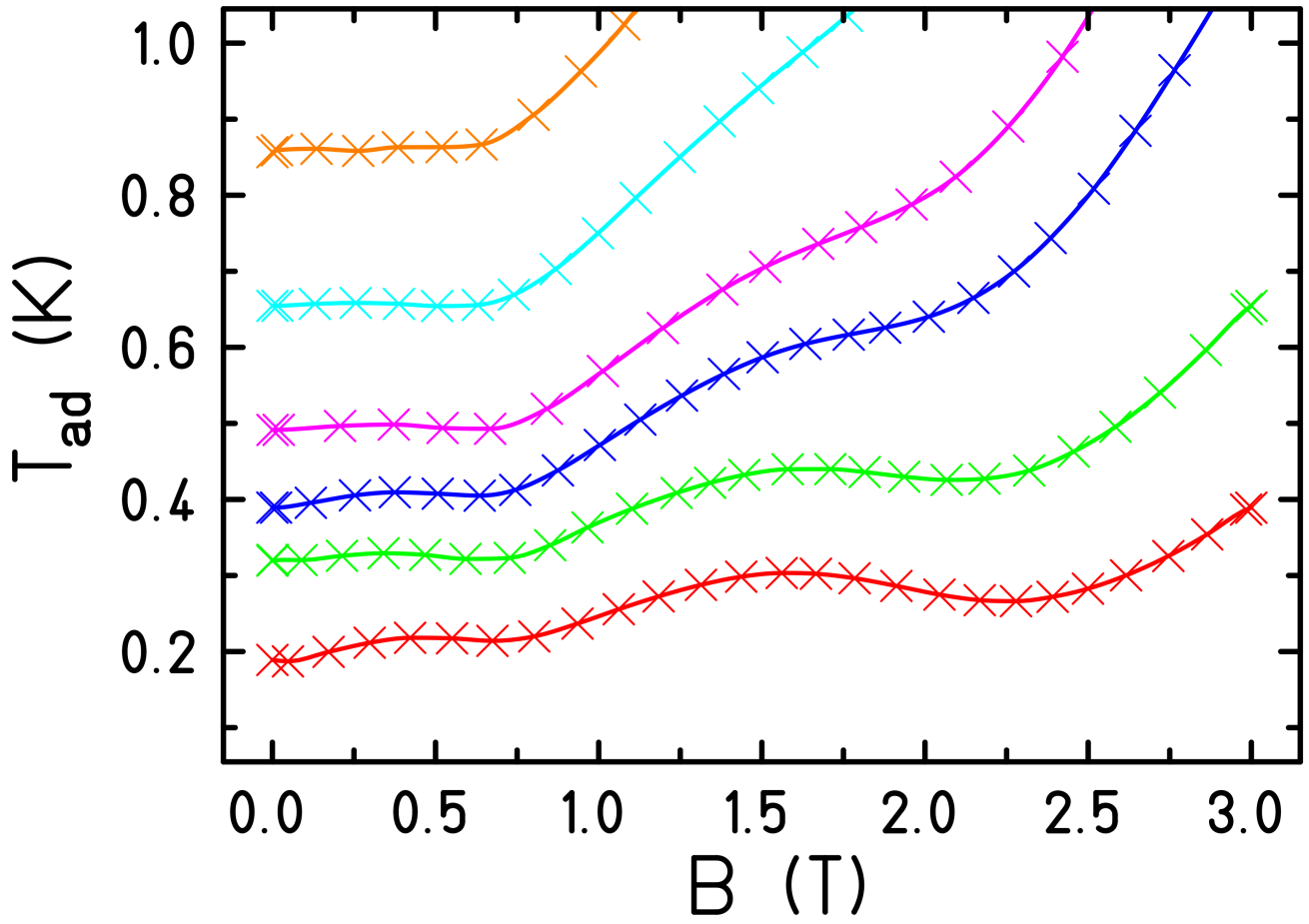


J. W. Sharples, D. Collison, E. J. L. McInnes, J. Schnack, E. Palacios, M. Evangelisti, Nat. Commun. **5**, 5321 (2014).


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


E
B
Gd7

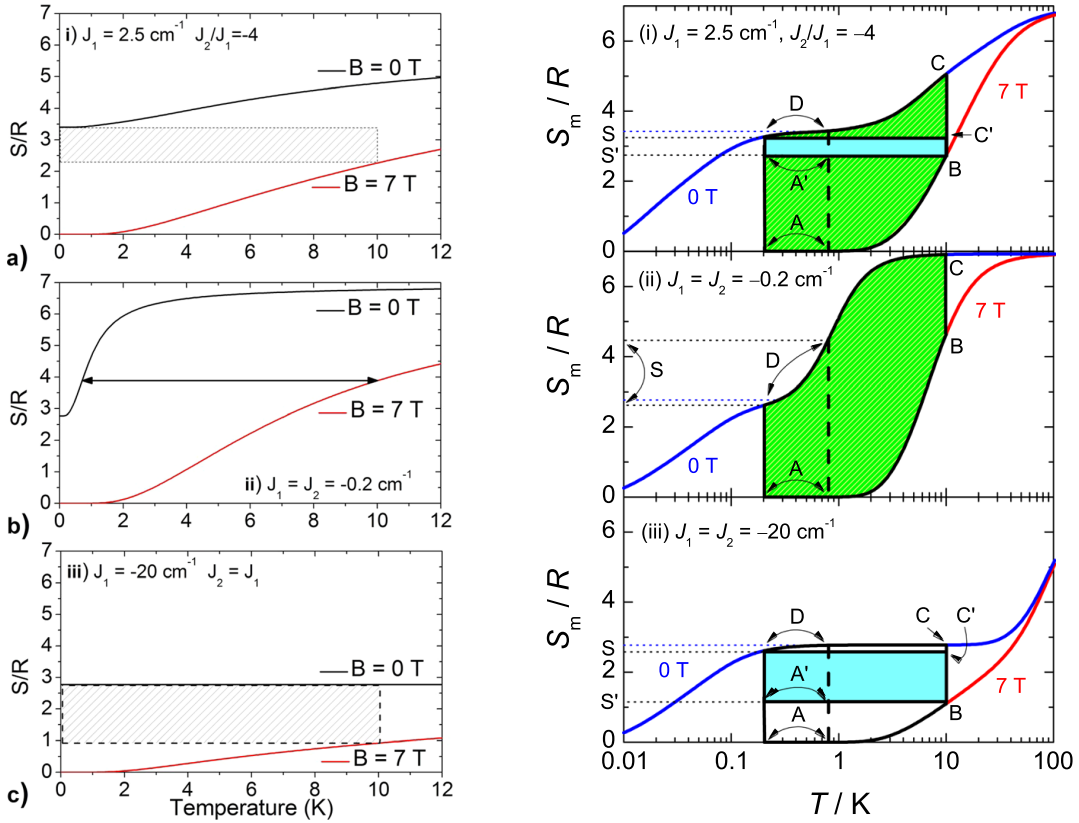
Gd$_7$ – Experimental cooling



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

Can we now design thermodynamic cycles?

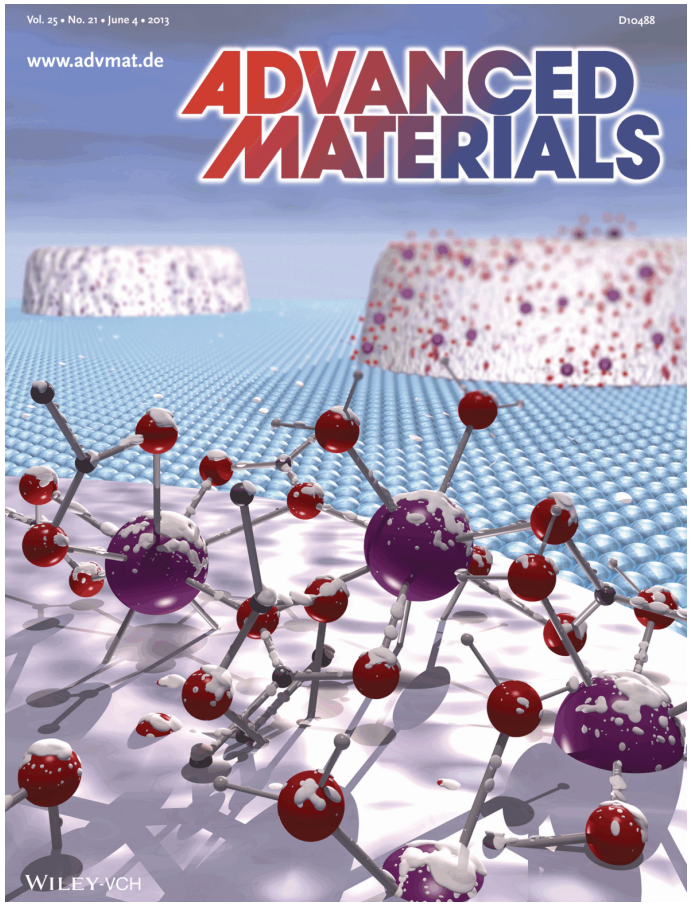
Cycles: Carnot or Ericsson?



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).

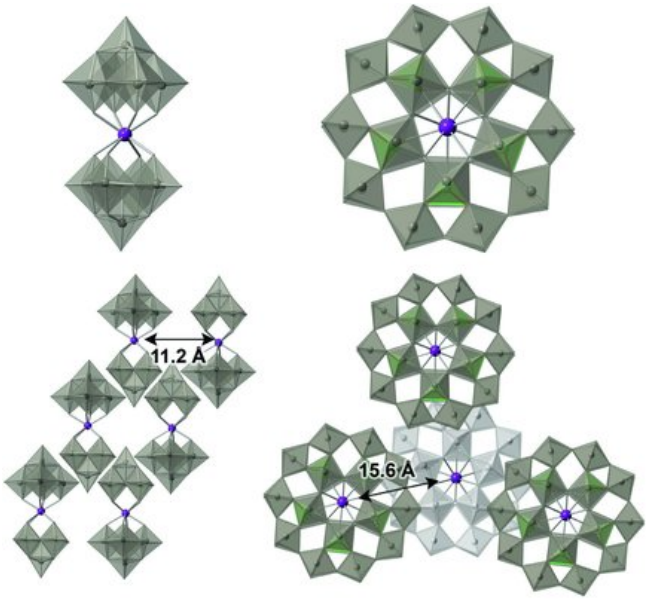
MCE surface cooler



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).

Weird ideas about dipolar interactions

Dipolar Interactions

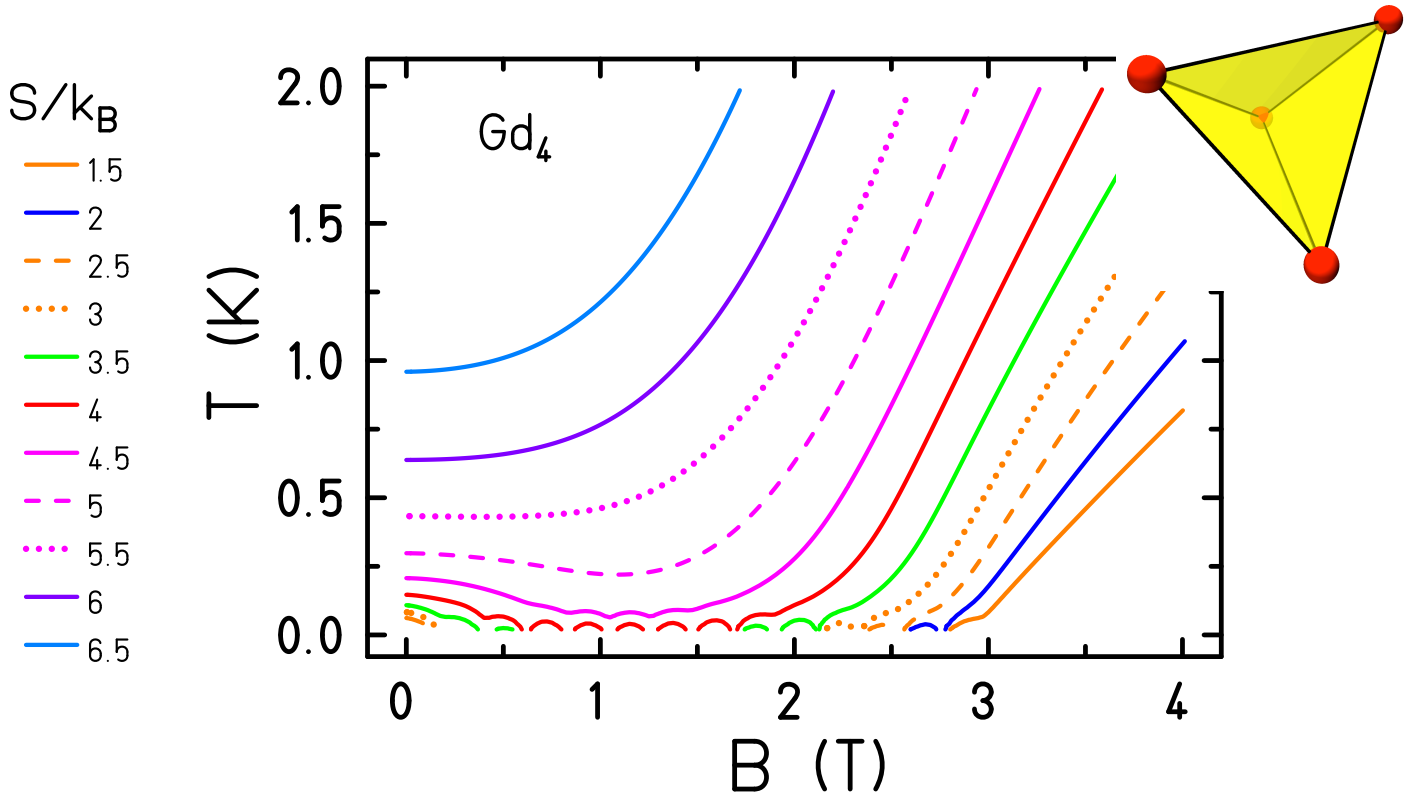


- Dipole-dipole interactions disturb/prevent sub-Kelvin cooling.
- Experimental solution: dilution of magnetic centers (1).
- Theoretical solution: Create low-energy entropy without magnetic moment (2)!

(1) M.-J. Martinez-Perez, O. Montero, M. Evangelisti, F. Luis, J. Sese, S. Cardona-Serra, E. Coronado, Adv. Mater. **24** (2012) 4301-4305.

(2) J. Schnack and C. Heesing, Eur. Phys. J. B **86**, 46 (2013).

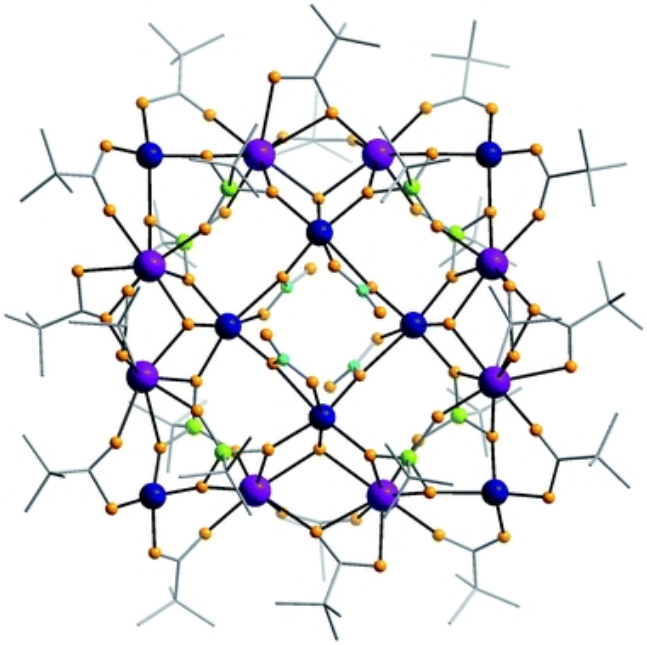
A fictitious af Gd_4 tetrahedron



Ground state with $S = 0$ 8-fold degenerate!

All isentropes with $S \leq k_B \log(8) = 2.08 k_B$ head for absolute zero.

Magnetocaloric effect – Why Gd compounds?



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

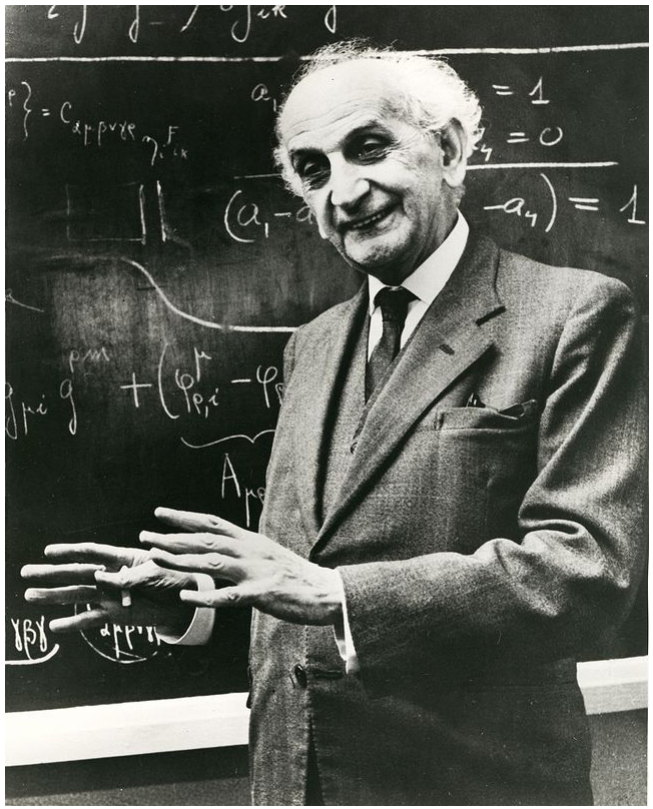
Yan-Zhen Zheng, Marco Evangelisti, Richard E. P. Winpenny, Chem. Sci. **2**, 99-102 (2011)

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

Finite-temperature Lanczos Method

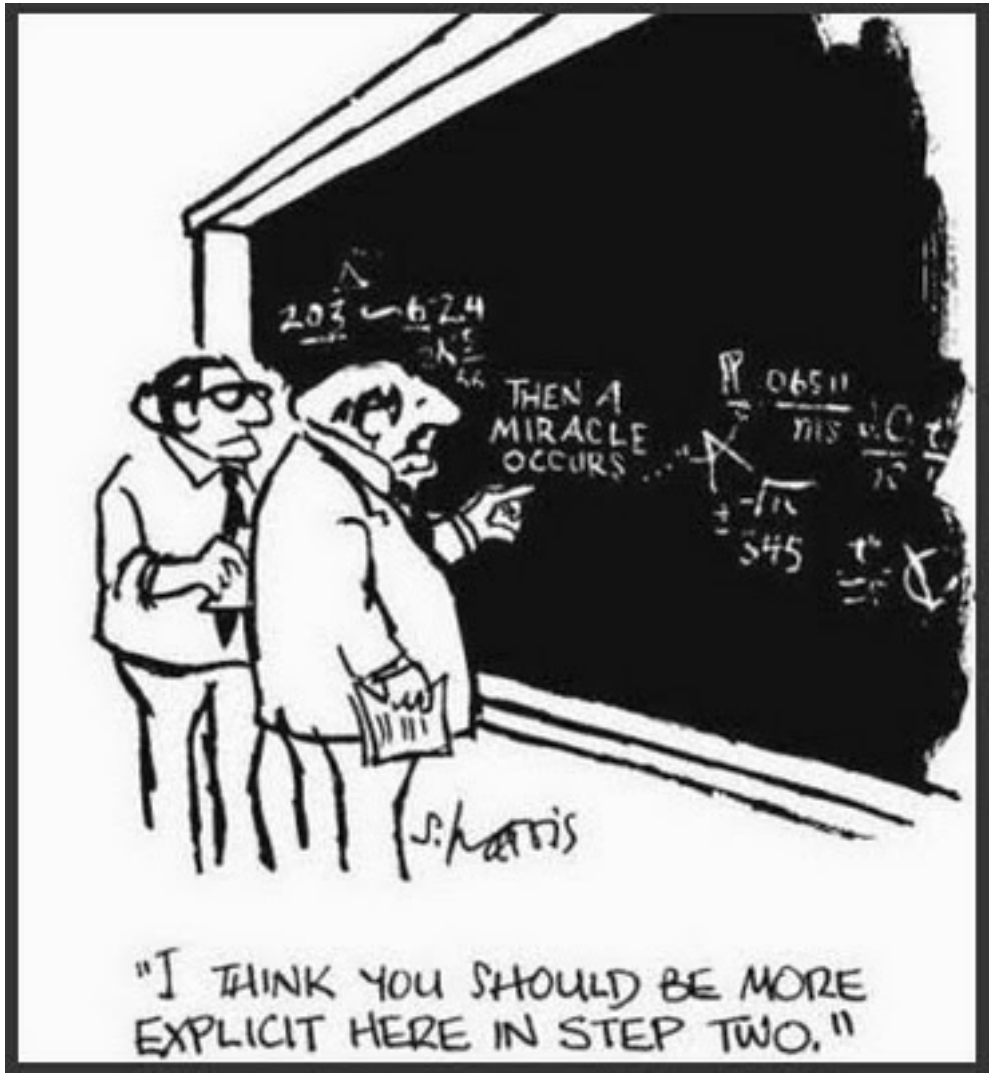
(Good for dimensions up to 10^{10}.)

Lanczos – a Krylov space method



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

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


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

Finite-temperature Lanczos Method I

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

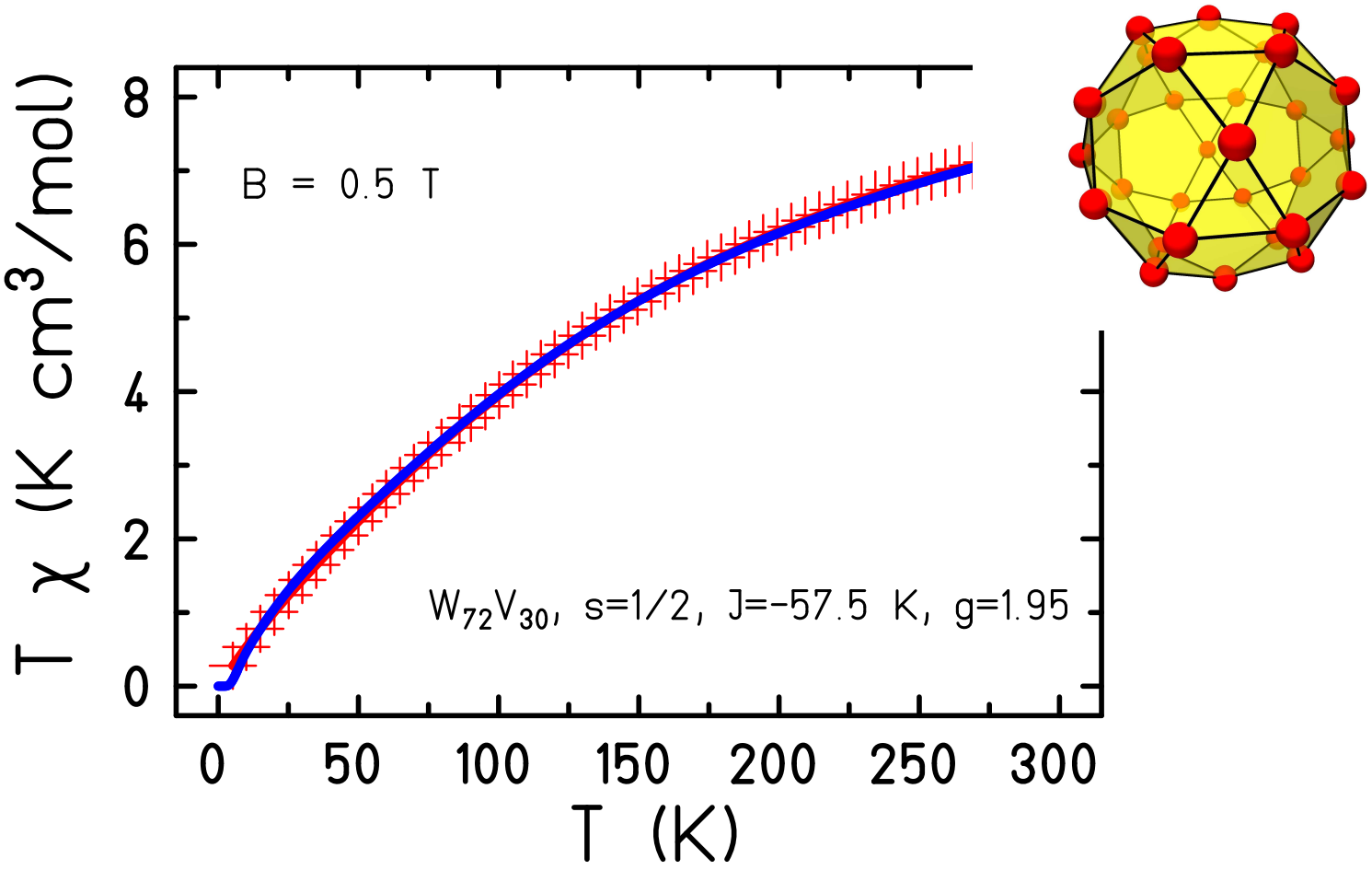
$$\langle \nu | \exp\left\{-\beta \underset{\sim}{H}\right\} | \nu \rangle \approx \sum_{n} \langle \nu | n(\nu) \rangle \exp\{-\beta\epsilon_n\} \langle n(\nu) | \nu \rangle \qquad \text{(Step 2)}$$

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

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

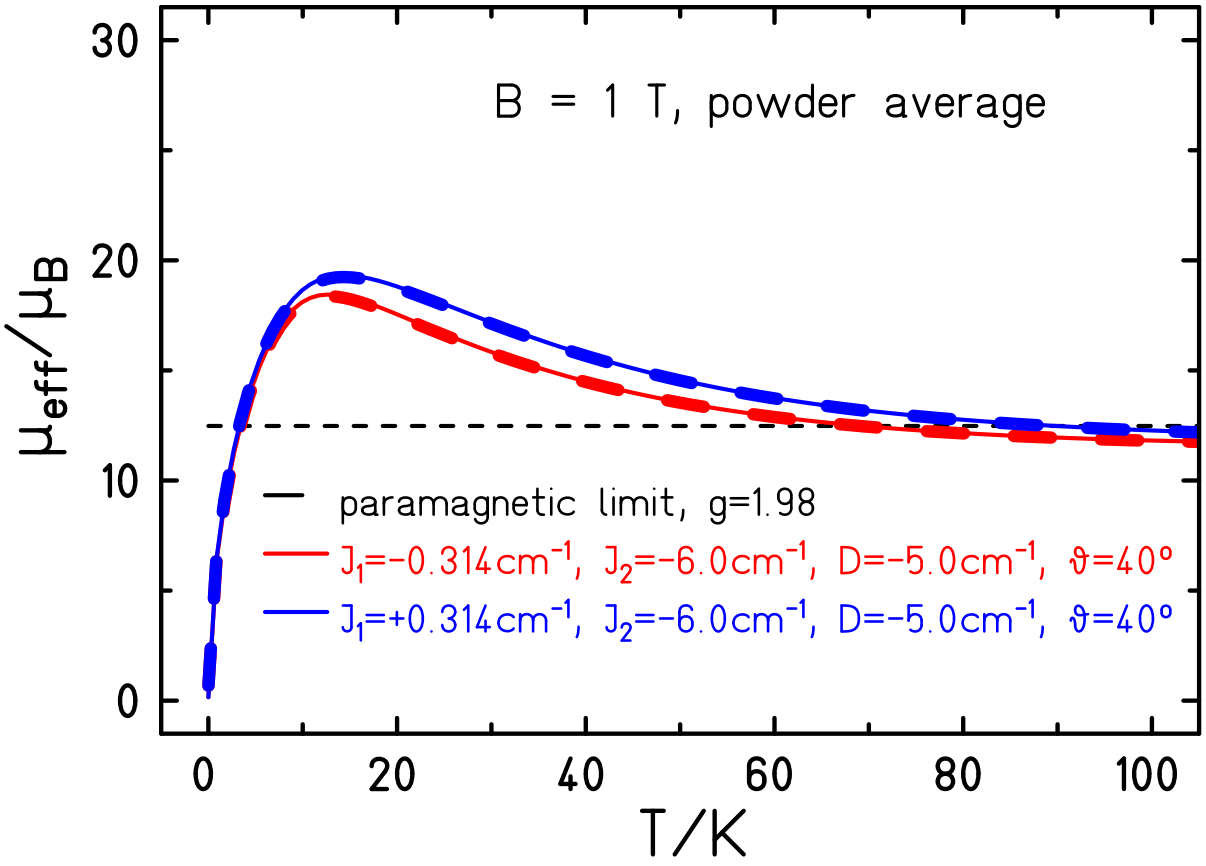
J. Jaklic and P. Prelovsek, Phys. Rev. B **49**, 5065 (1994).

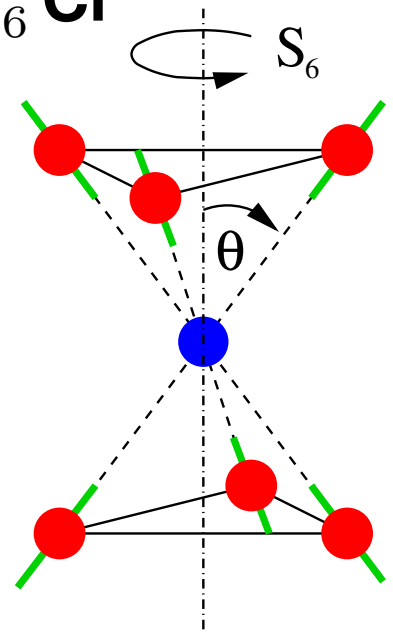
Icosidodecahedron $s = 1/2$



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

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





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

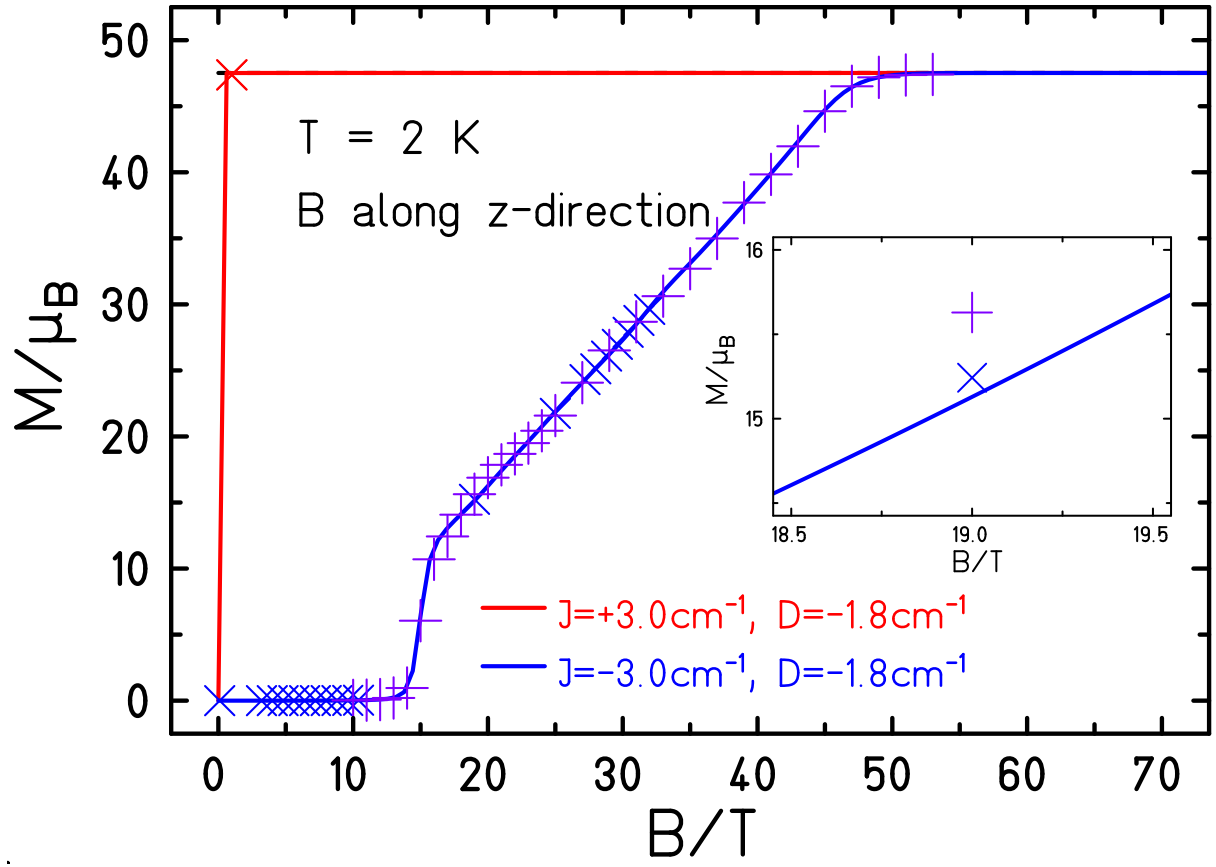
$\dim(\mathcal{H}) = 62,500$

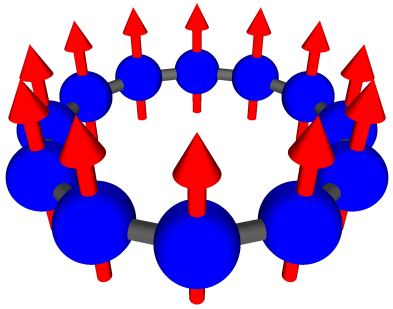
non-collinear easy axes

Hours compared to days, notebook compared to supercomputer!

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

A fictitious Mn_{12}^{III} – M_z vs B_z





$s = 2$

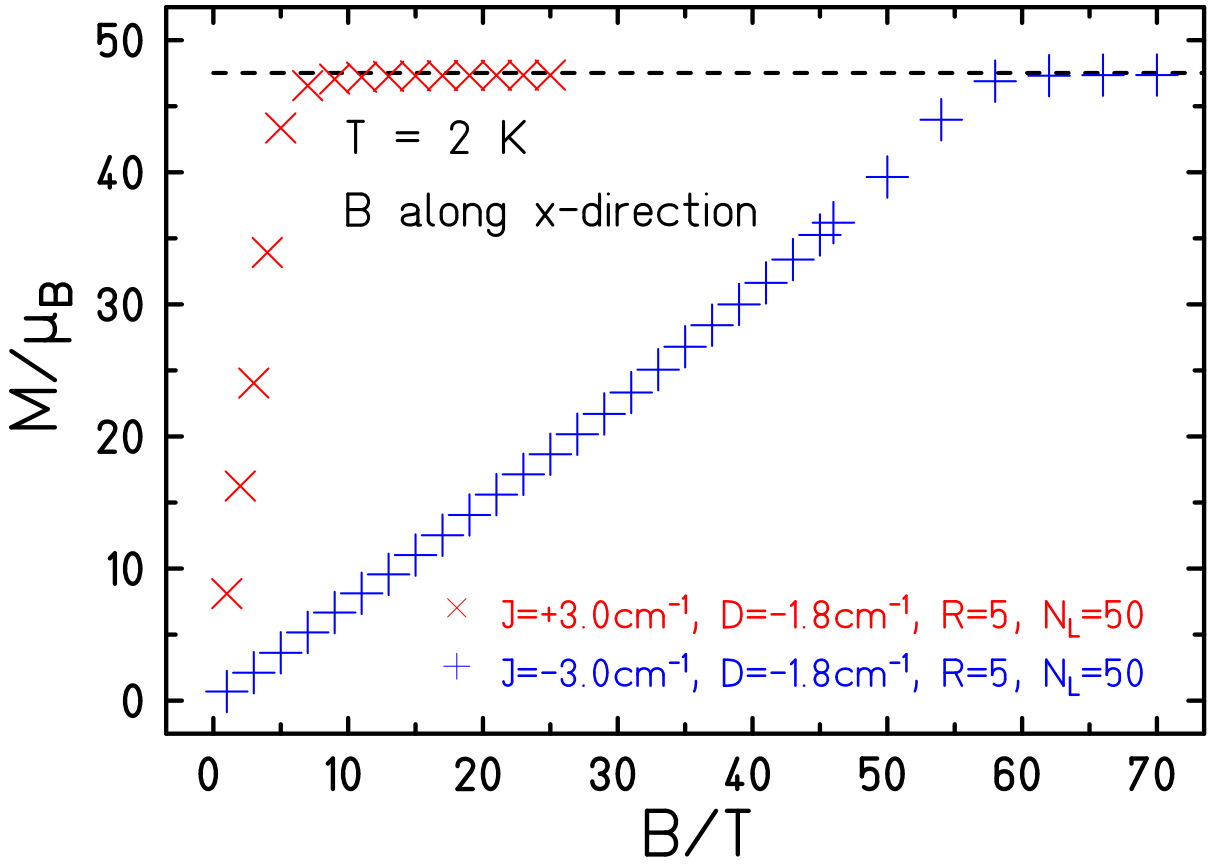
$\dim(\mathcal{H}) = 244,140,625$

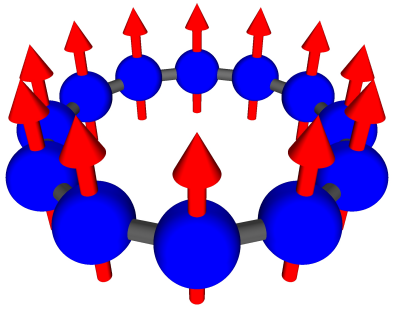
collinear easy axes

A few days compared to *impossible*!

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

A fictitious Mn_{12}^{III} – M_x vs B_x

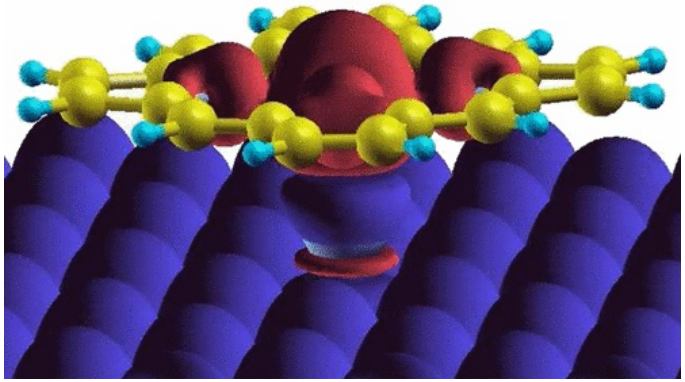


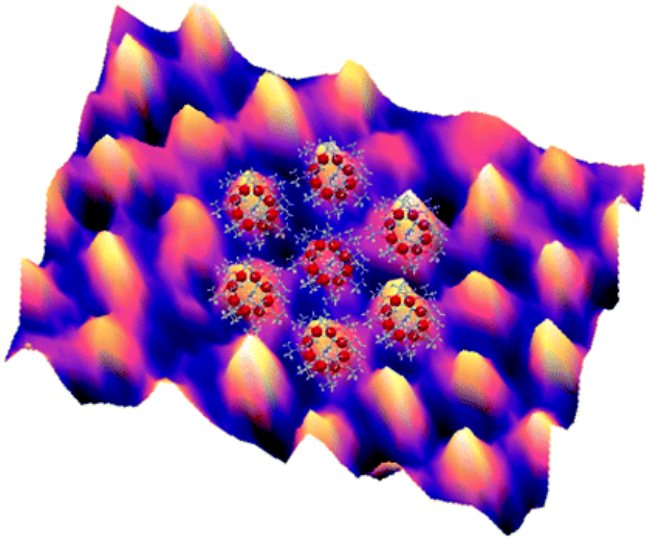


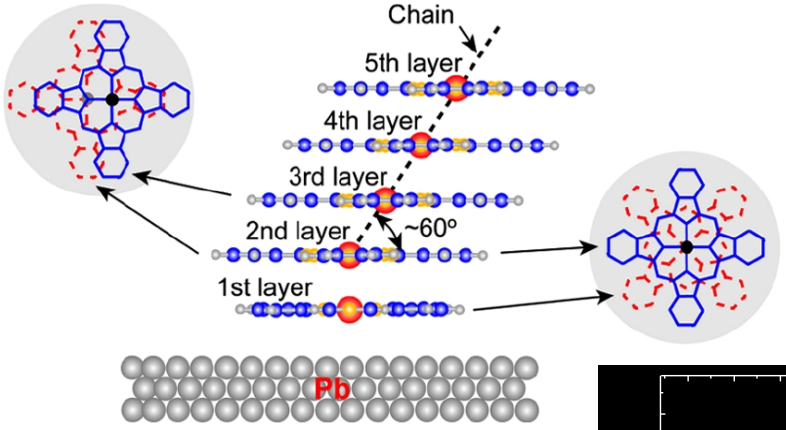
No other method can deliver these curves!

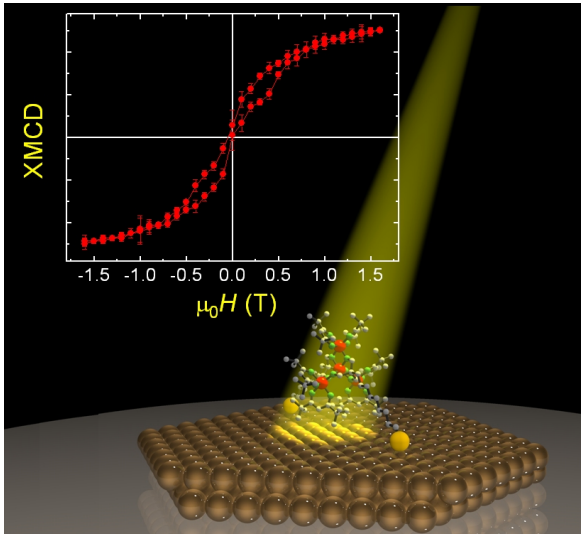
O. Hanebaum, J. Schnack, Eur. Phys. J. B **87**, 194 (2014)

You want to deposite a molecule



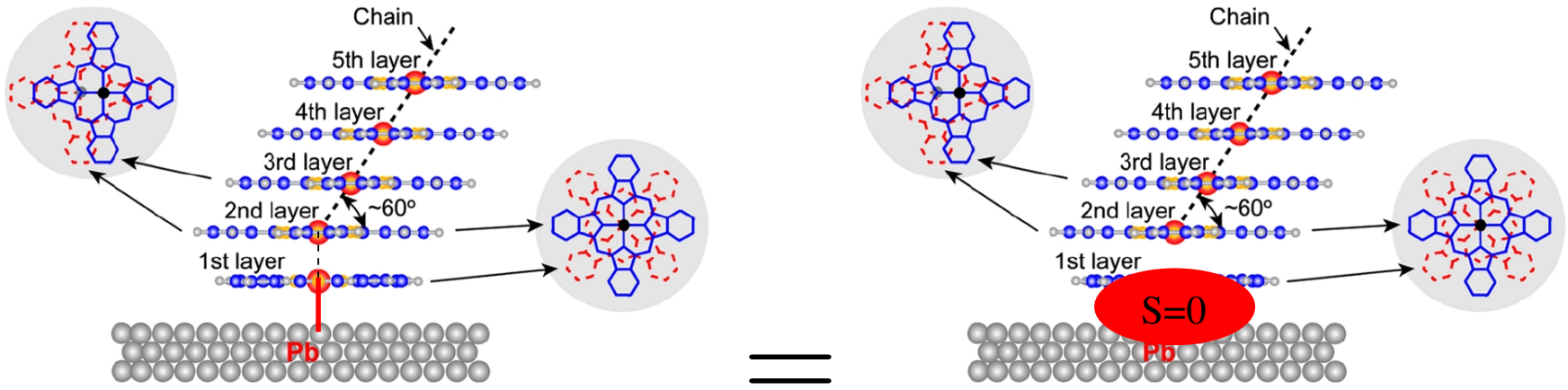






M. Bernien *et al.*, Phys. Rev. Lett. **102**, 047202 (2009); A. Ghirri*et al.*, ACS Nano, **5**, 7090-7099 (2011); X. Chen *et al.*, Phys. Rev. Lett. **101**, 197208 (2008); M. Mannini *et al.*, Nature Materials **8**, 194 - 197 (2009).

Physical example (ICMM 2010)



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

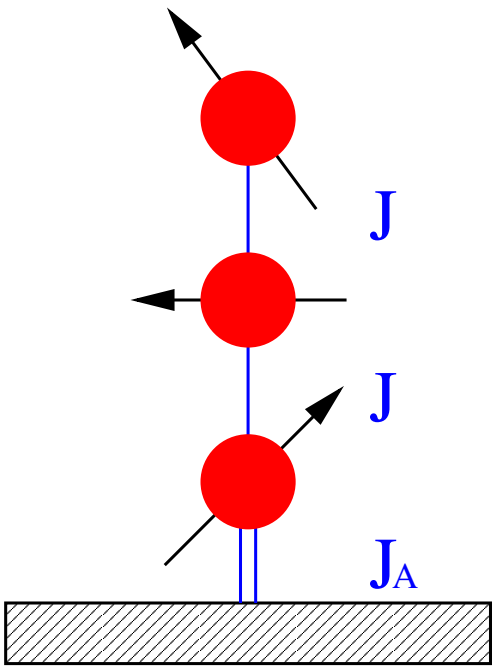
Under which circumstances is the picture of total screening correct?

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

Numerical Renormalization Group calculations

(Good for deposited molecules.)

NRG – minimal model (already an approximation!)



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

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

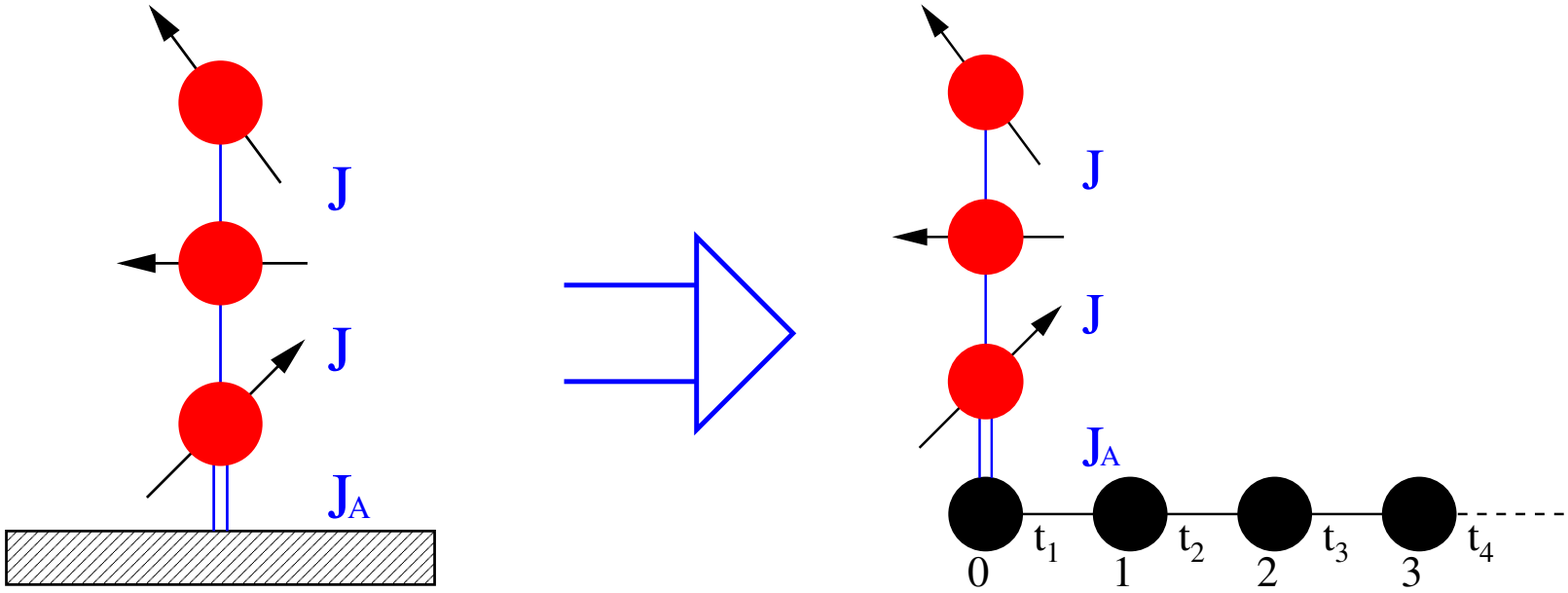
  $\underset{\sim}{H}_{\text{coupling}} = -2 J_A \underset{\sim}{\boldsymbol{S}} \cdot \underset{\sim}{\boldsymbol{s}}_0 \quad , \quad \underset{\sim}{\boldsymbol{s}}_0$ – spin density at contact

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

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

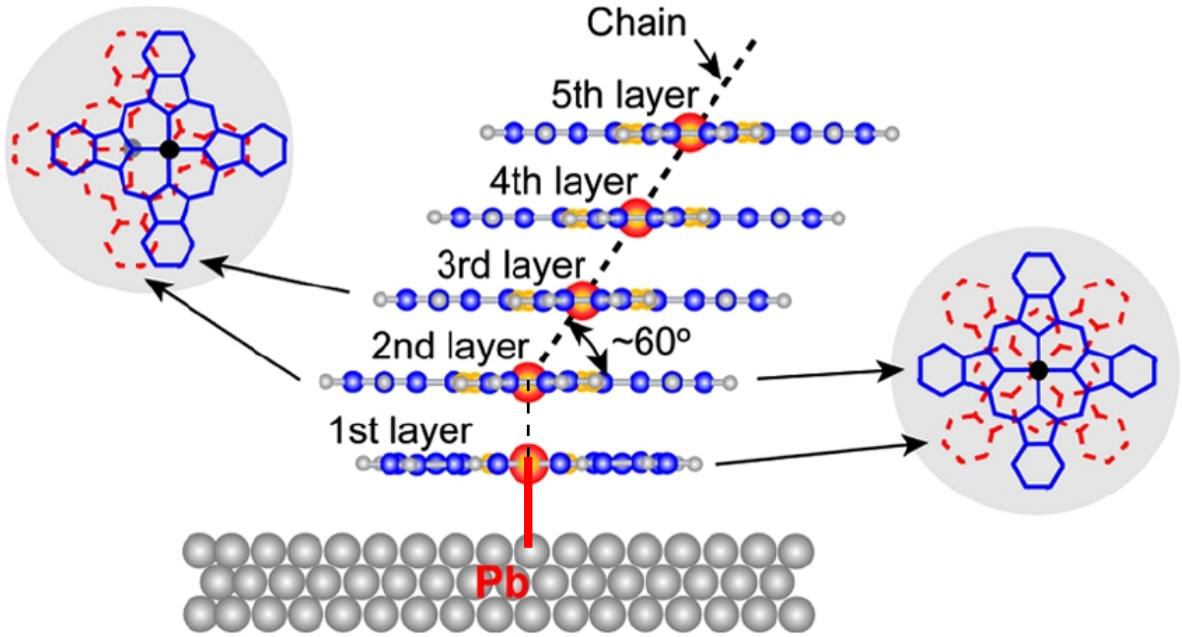
(1) K. G. Wilson, Rev. Mod. Phys. **47**, 773 (1975)
(2) M. Höck, J. Schnack, Phys. Rev. B **87**, 184408 (2013)
(3) *Impurity* is a technical term in this context and not an insult to chemists.

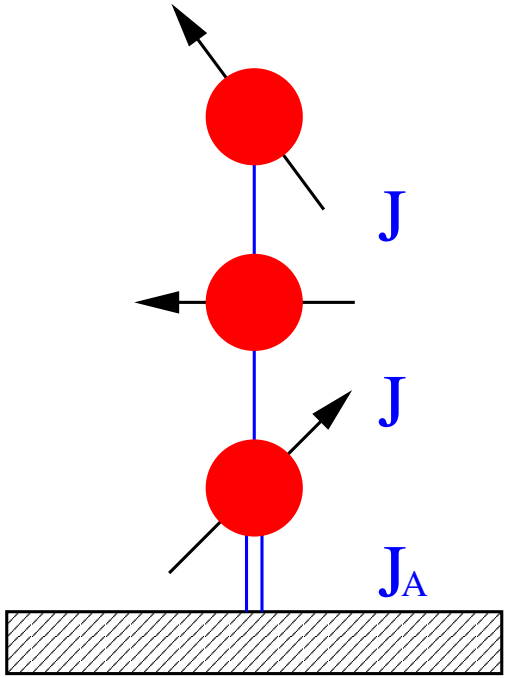
NRG in a cartoon



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

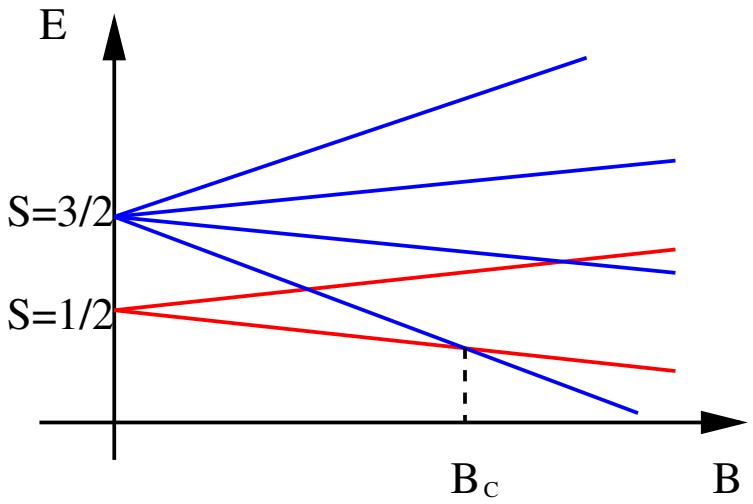
Once more: deposited chain



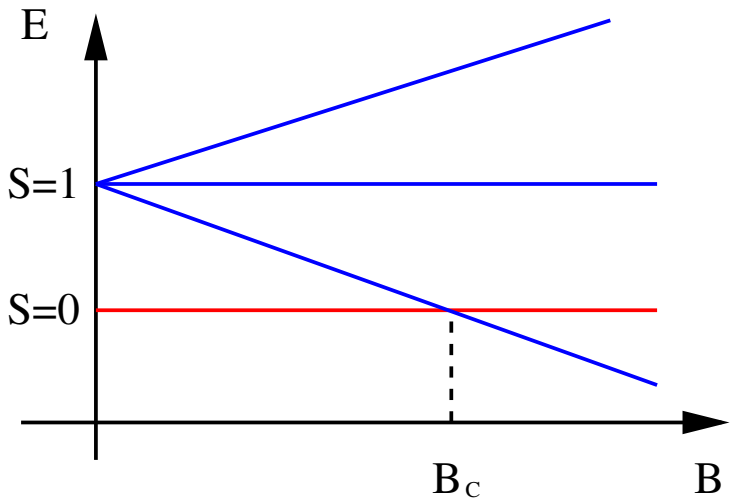


X. Chen *et al.*, Phys. Rev. Lett. **101**, 197208 (2008).

Energy levels of limiting cases for deposited trimer



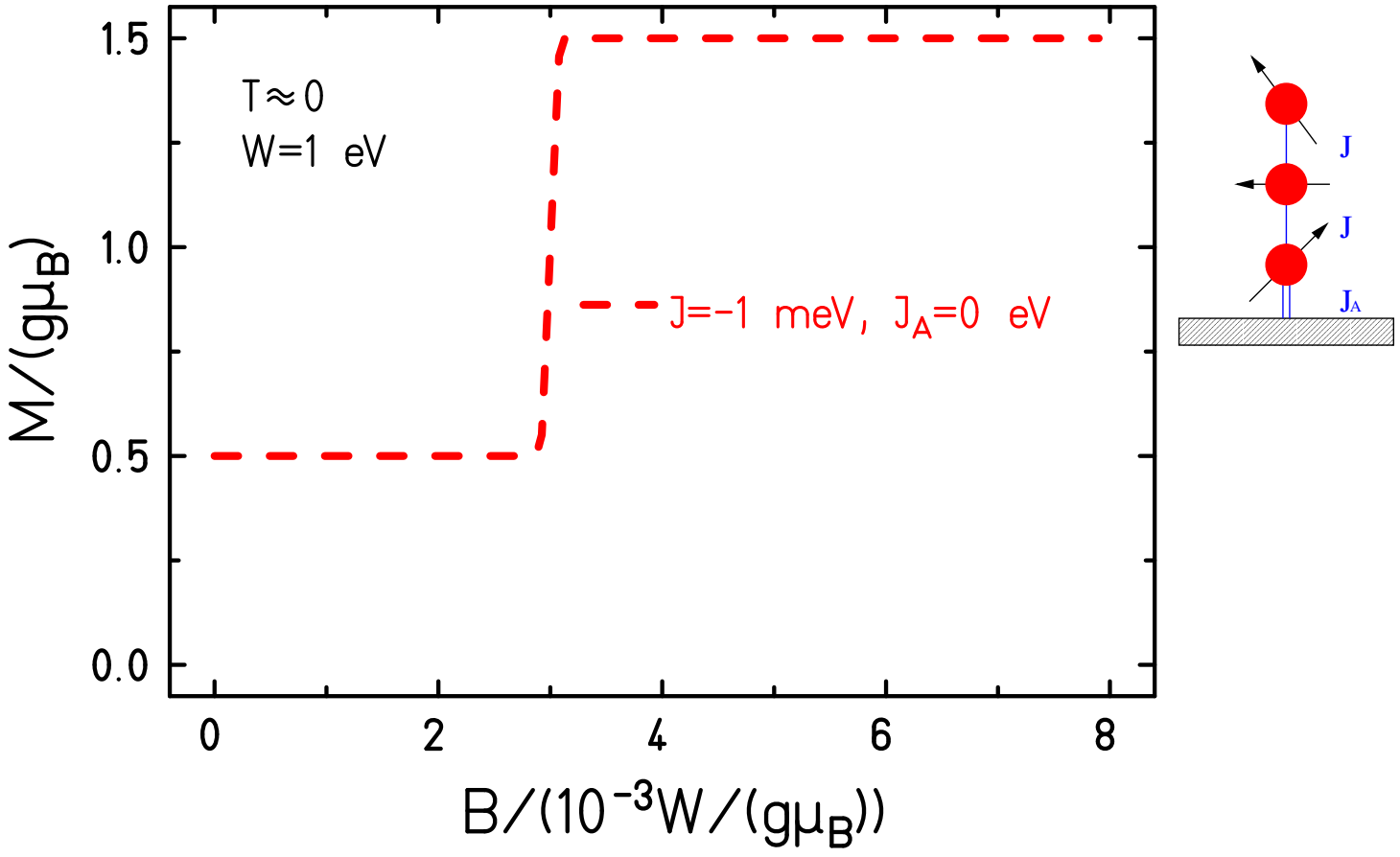
- energy levels of a trimer



- energy levels of a dimer

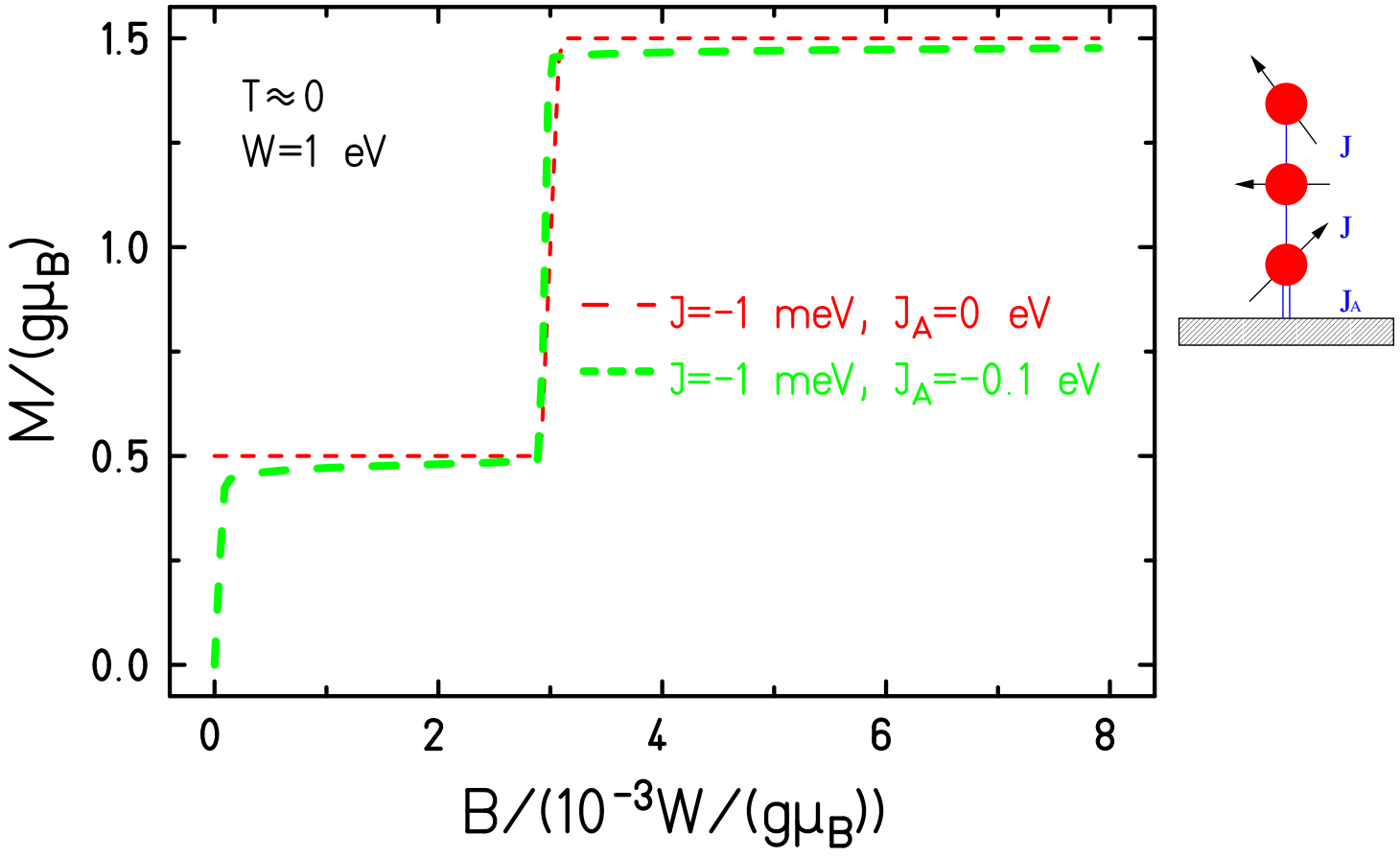
Magnetization curves different; could be seen in XMCD.
NRG calculates observables also between limiting cases
and can thus tell under which circumstances a limiting case applies.

Increasing coupling to the substrate



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

Increasing coupling to the substrate



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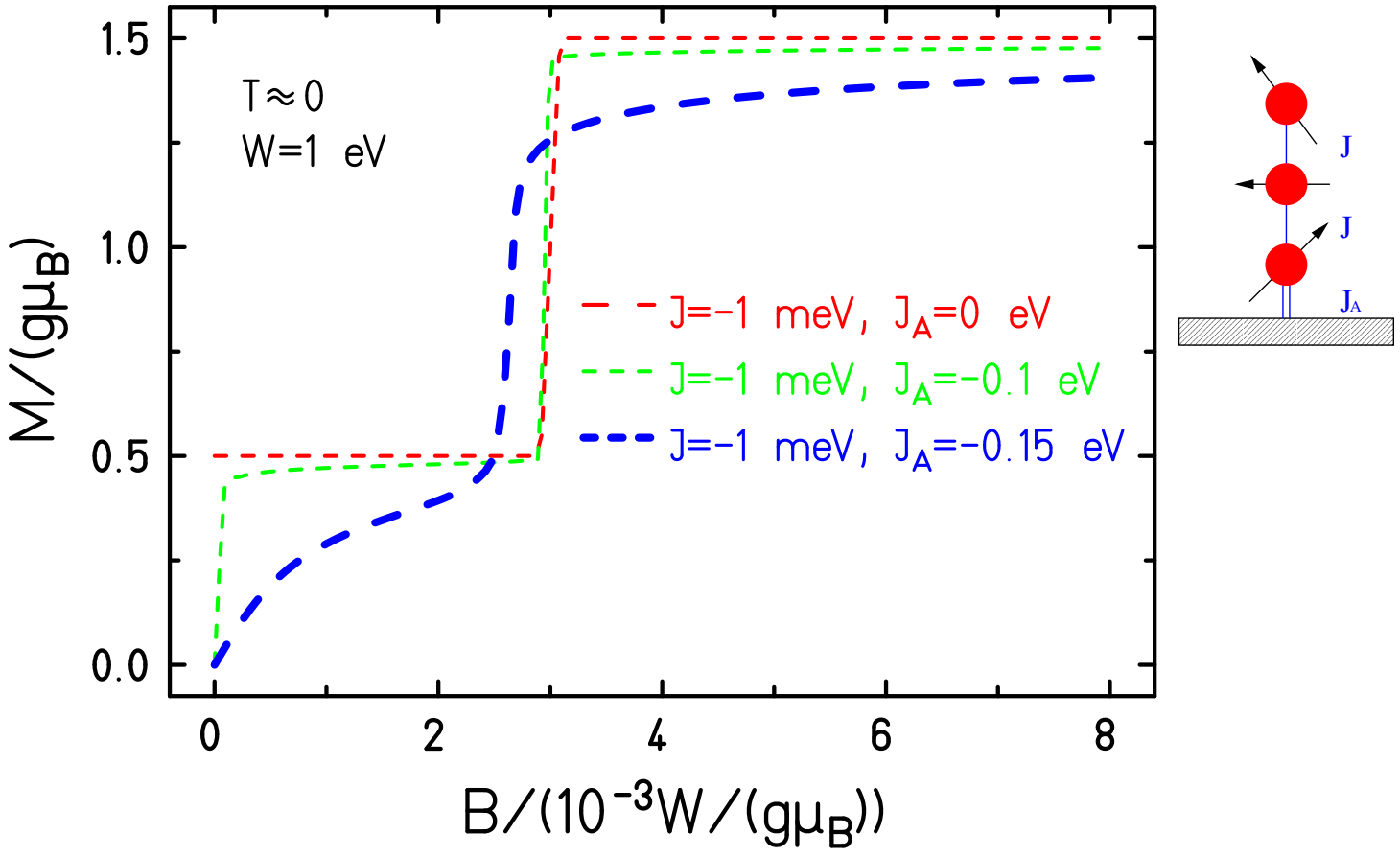
Increasing coupling to the substrate



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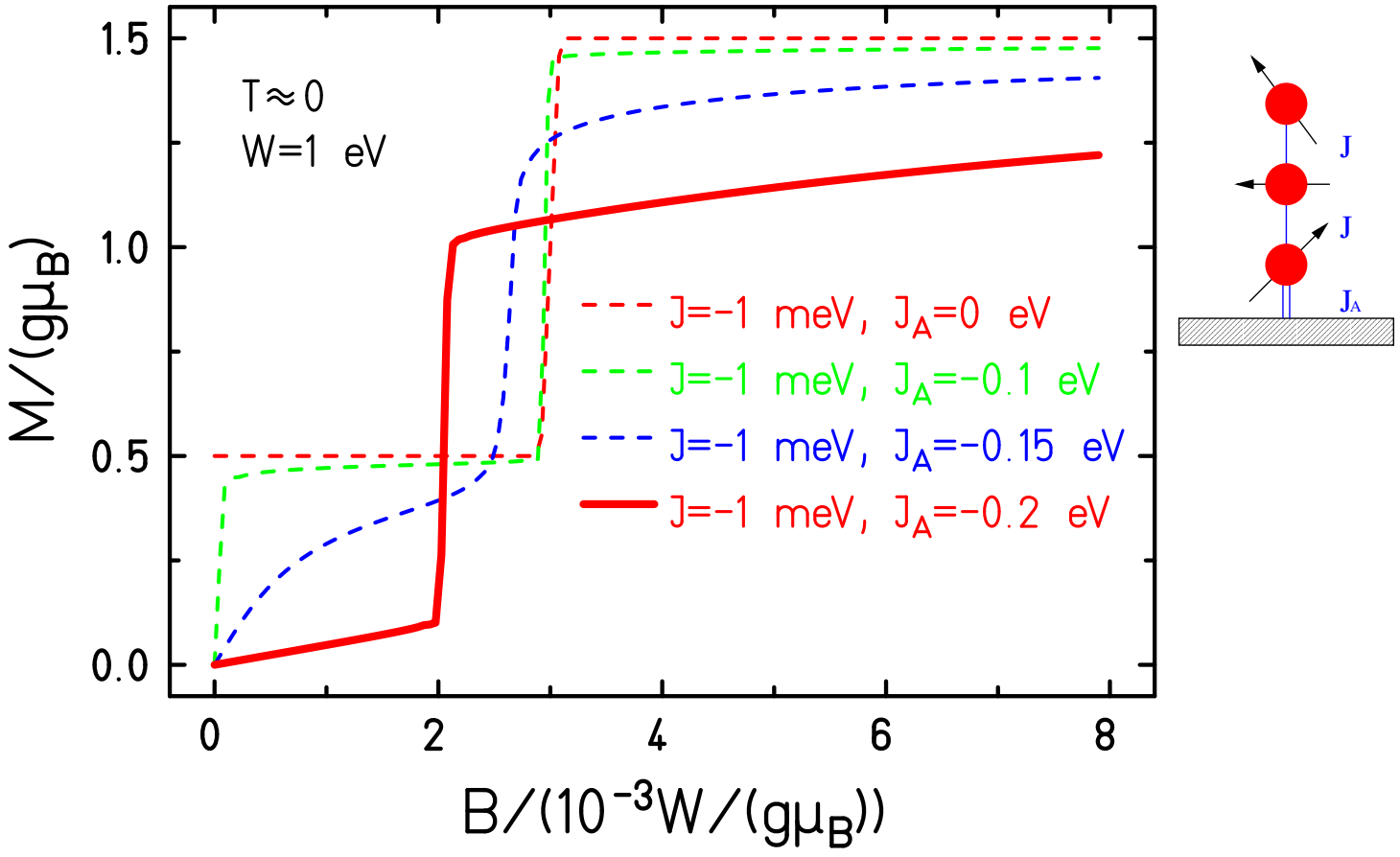
Increasing coupling to the substrate



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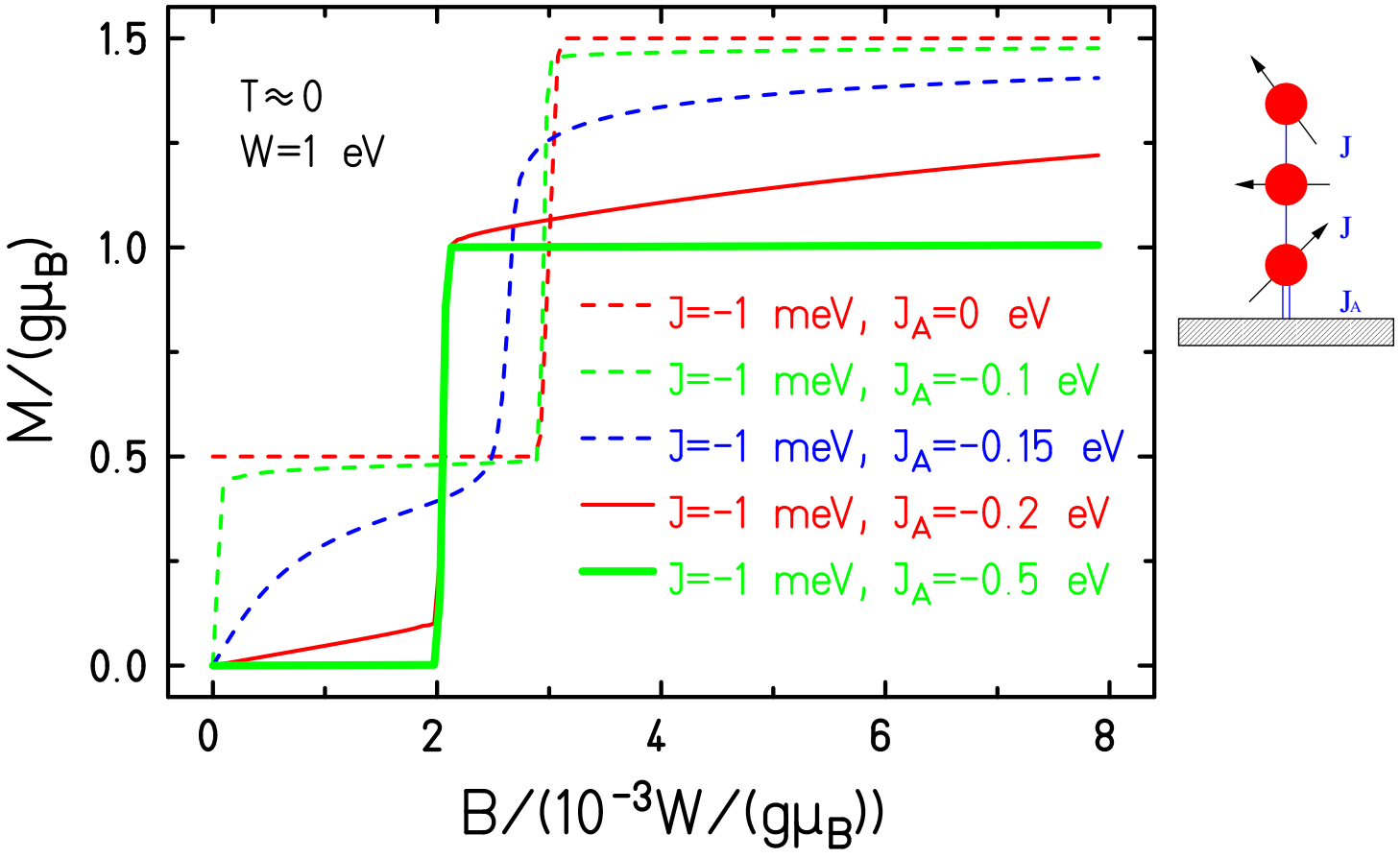
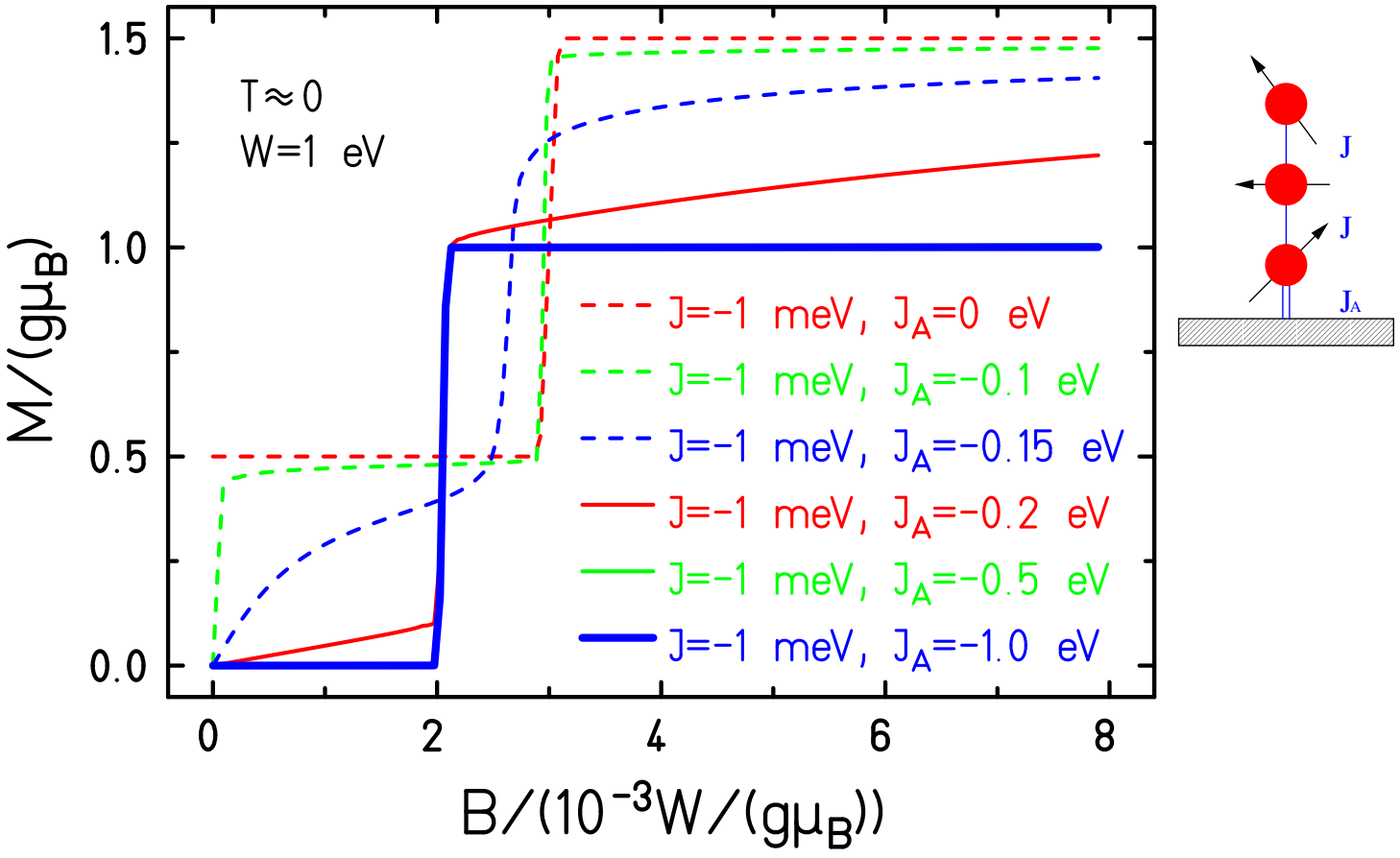
Increasing coupling to the substrate



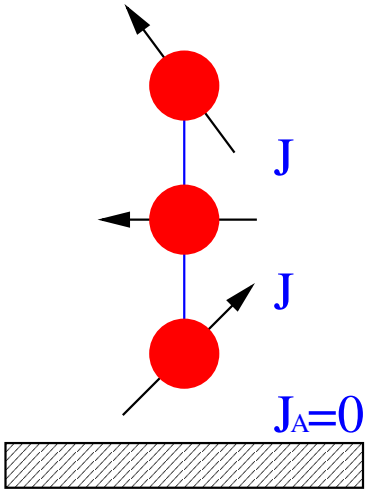
H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

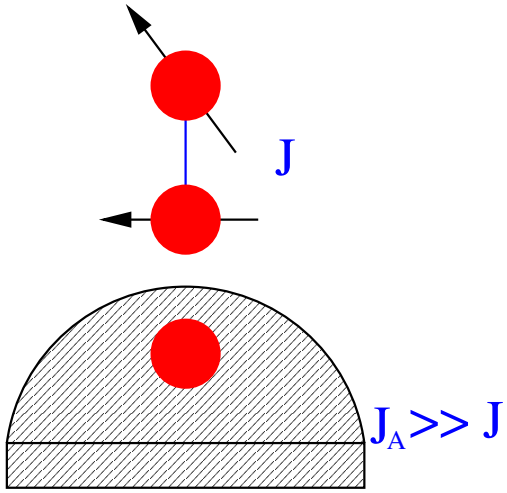
Increasing coupling to the substrate



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

Weak vs. strong coupling



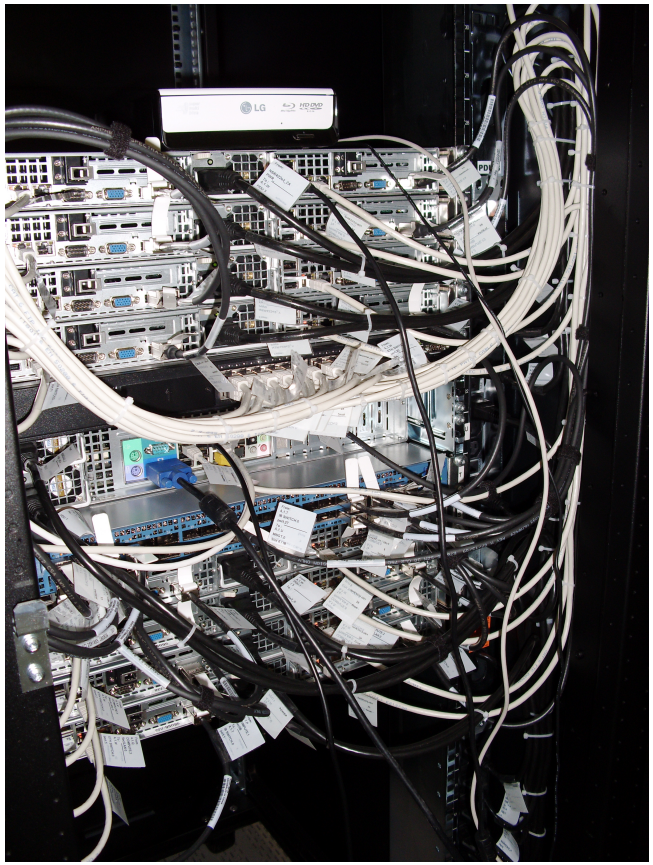


- weak coupling limit: unperturbed molecule (trimer)
- $|J_A| \lessapprox 0.1W$

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

Inbetween: no simple characterization + further sequential screening possible

Summary



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

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

Many thanks to my collaborators worldwide

- T. Glaser, Chr. Heesing, M. Höck, N.B. Ivanov, S. Leiding, A. Müller, R. Schnalle, Chr. Schröder, J. Ummethum, O. Wendland (Bielefeld)
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Thank you very much for your attention.

The end.

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