Advanced many-body quantum methods for magnetic molecules

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Symposium, DFG Research Unit FOR 945
16-17 January 2015 – Bielefeld University, Germany

Universität Bielefeld

DFG

FOR 945

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Many thanks to Thorsten!

In case you don’t know . . .

In case you don’t know . . .

Publications

1. T. Glaser, M. Heidemeier, E. Krickemeyer, H. Bögge, A. Stammler, R. Fröhlich, E. Bill, J. Schnack, **Inorg. Chem. 48 (2009) 607-620**
2. Thorsten Glaser, Maik Heidemeier, Hubert Theil, Anja Stammler, Hartmut Bögge and Jürgen Schnack, **Dalton Trans. 39 (2010) 192-199**
3. Erich Krickemeyer, Veronika Hoeke, Anja Stammler, Hartmut Bögge, Jürgen Schnack, and Thorsten Glaser, **Z. Naturforsch. 65b (2010) 295-303**
4. Veronika Hoeke, Klaus Gieb, Paul Müller, Liviu Ungur, Liviu F. Chibotaru, Maik Heidemeier, Erich Krickemeyer, Anja Stammler, Hartmut Bögge, Christian Schröder, Jürgen Schnack, Thorsten Glaser, **Chem. Sci. 3 (2012) 2868**
5. Veronika Hoeke, Maik Heidemeier, Erich Krickemeyer, Anja Stammler, Hartmut Bögge, Jürgen Schnack, Thorsten Glaser, **Dalton. Trans. 41 (2012) 12942-12959**
6. Veronika Hoeke, Maik Heidemeier, Erich Krickemeyer, Anja Stammler, Hartmut Bögge, Jürgen Schnack, Andrei Postnikov, Thorsten Glaser, **Inorg. Chem. 51 (2012) 10929-10954**
7. Veronika Hoeke, Erich Krickemeyer, Maik Heidemeier, Hubert Theil, Anja Stammler, Hartmut Bögge, Thomas Weyhermüller, Jürgen Schnack, Thorsten Glaser, **Eur. J. Inorg. Chem. (2013) 4398-4409**
8. A. Merca, J. Schnack, J. van Slageren, T. Glaser, H. Bögge, V. Hoeke, M. Läge, A. Müller, B. Krebs, **Journal of Cluster Science 24 (2013) 979**
9. V. Hoeke, A. Stammler, H. Bögge, J. Schnack, T. Glaser, **Inorg. Chem. 53 (2014) 257**
10. Chandan Mukherjee, V. Hoeke, A. Stammler, H. Bögge, J. Schnack, T. Glaser, **Dalton Trans. 43 (2014) 9690-9703**
11. T. Glaser, V. Hoeke, K. Gieb, J. Schnack, Chr. Schröder, P. Müller, **Coord. Chem. Rev. (2015)** in print

Contents for you today

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

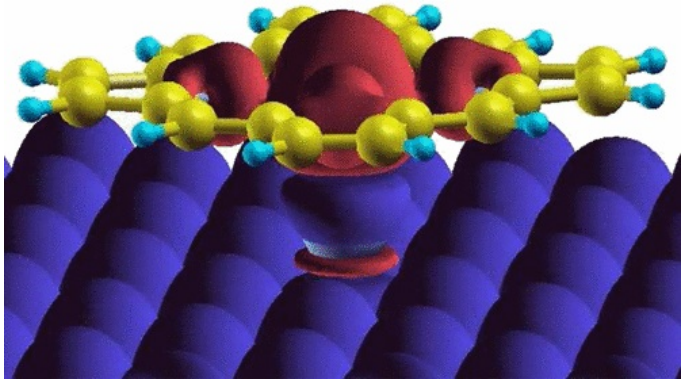
1. Numerical Renormalization Group
2. Finite-Temperature Lanczos
3. Magnetocalorics

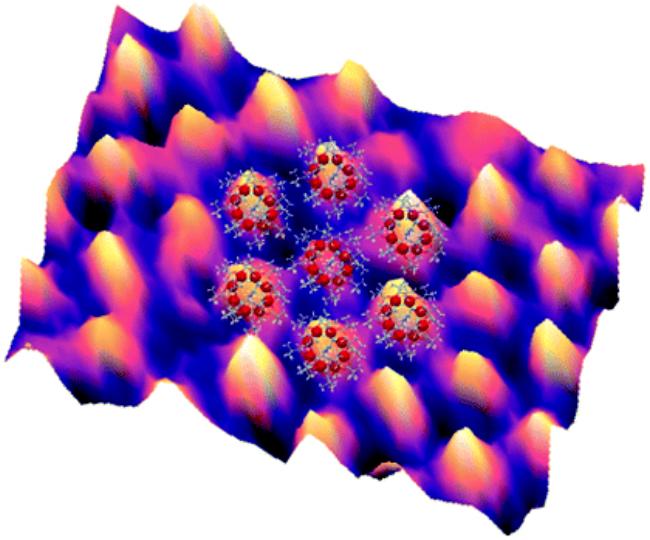
We are the sledgehammer team of matrix diagonalization.
Please send inquiries to jschnack@uni-bielefeld.de!

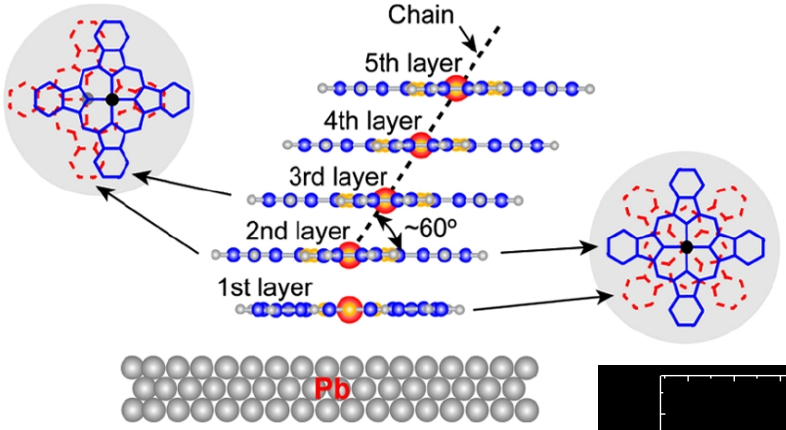
Numerical Renormalization Group calculations

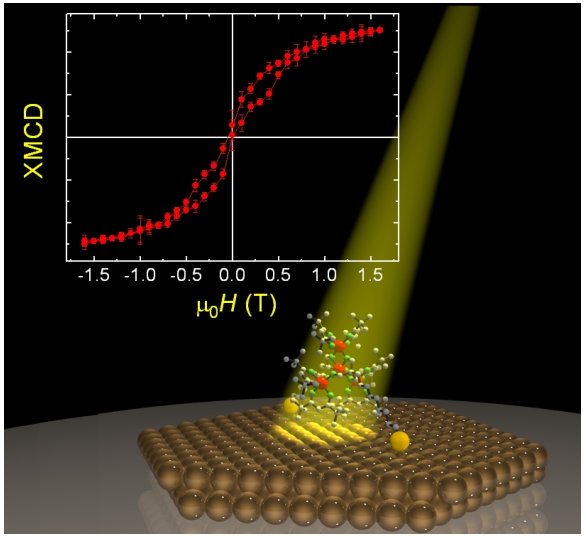
(Good for deposited molecules.)

You want to deposite a molecule



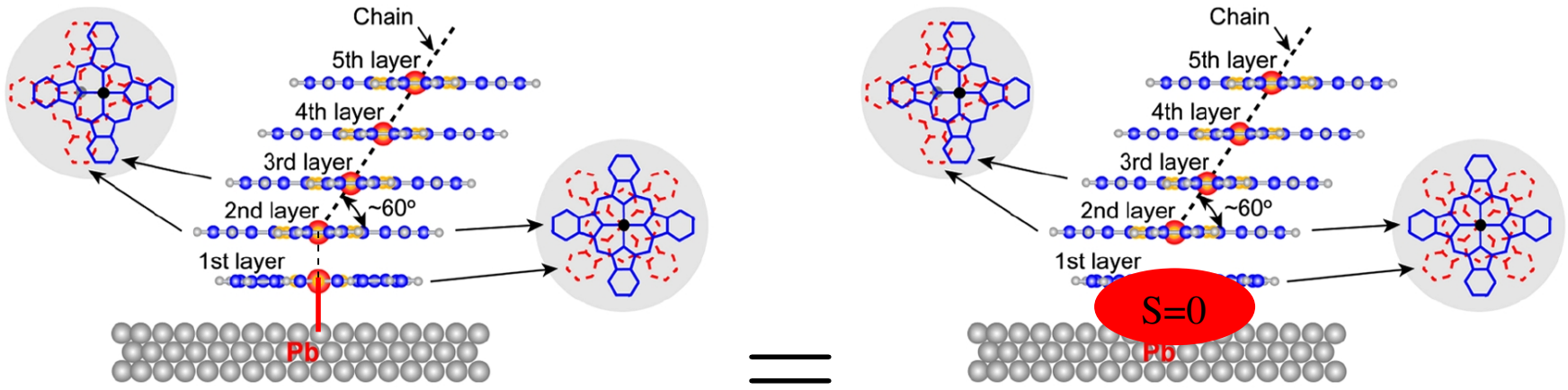






M. Bernien *et al.*, Phys. Rev. Lett. **102**, 047202 (2009); A. Ghirri*et al.*, ACS Nano, **5**, 7090-7099 (2011); X. Chen *et al.*, Phys. Rev. Lett. **101**, 197208 (2008); M. Mannini *et al.*, Nature Materials **8**, 194 - 197 (2009).

Physical example (ICMM 2010)

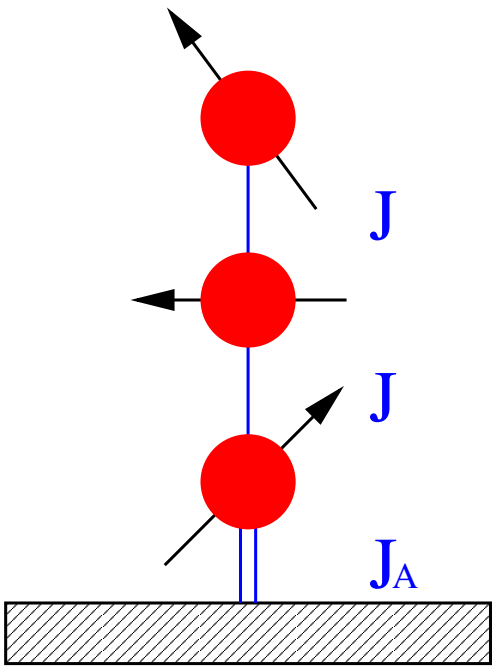


Stack of deposited Cobalt phthalocyanine (CoPc) molecules;
Co^{2+} with spin $s = 1/2$.

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!)



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

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

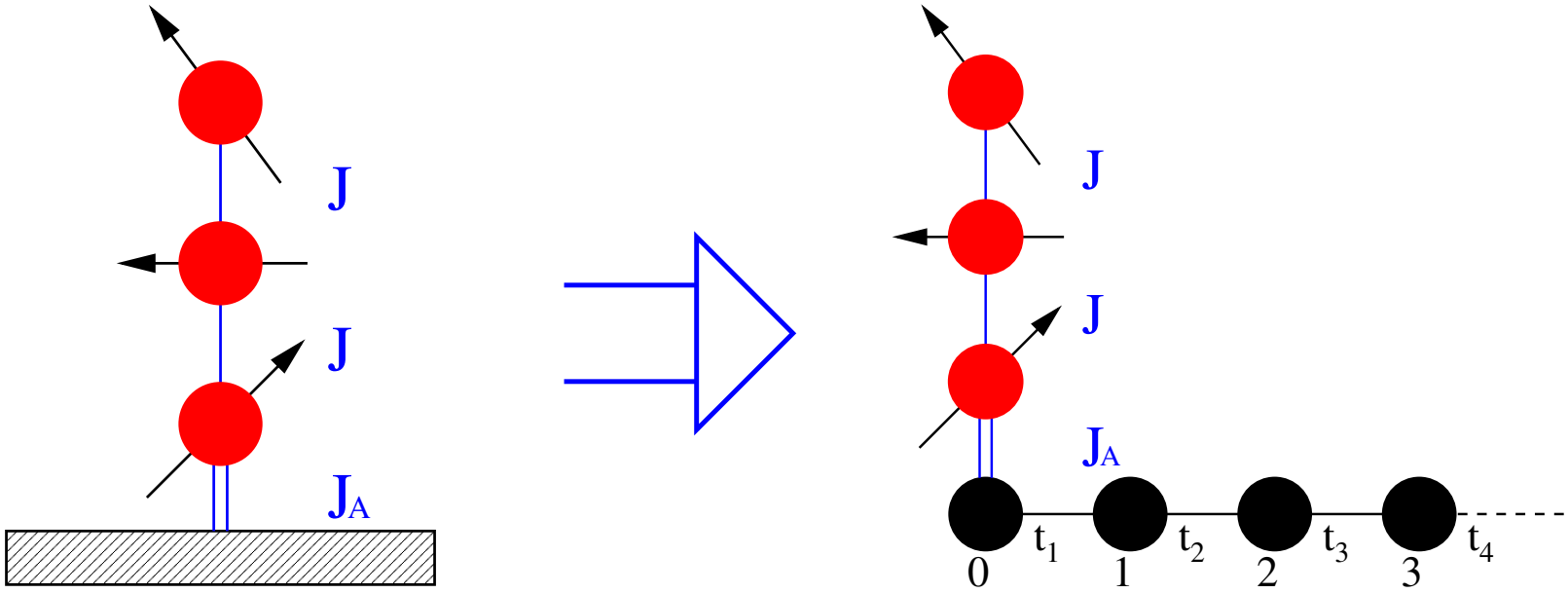
  $\underset{\sim}{H}_{\text{coupling}} = -2 J_A \underset{\sim}{\boldsymbol{S}} \cdot \underset{\sim}{\boldsymbol{s}}_0$, $\underset{\sim}{\boldsymbol{s}}_0$ – spin density at contact

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

- NRG ≡ 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



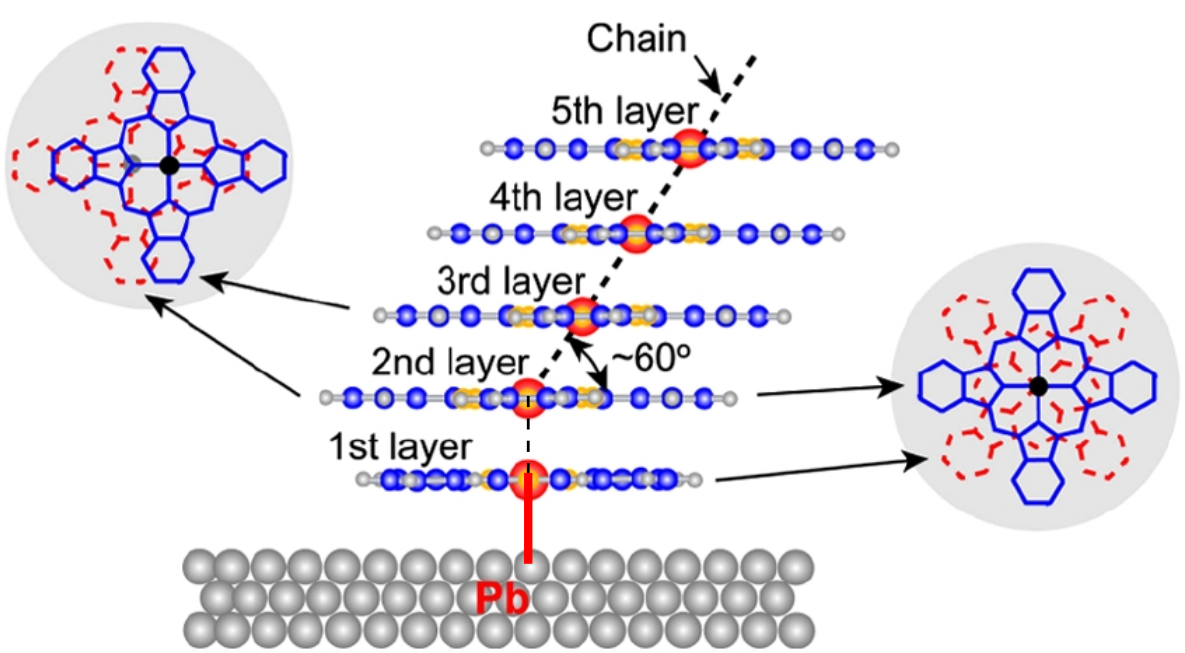
Metallic surface is replaced by semi-infinite Hubbard chain;

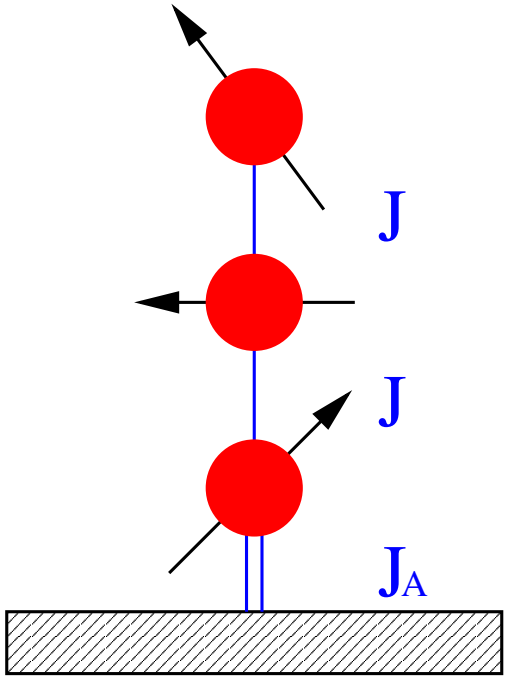
Parameters of the chain: hopping matrix elements and on-site energies;

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

Truncation of basis set when matrices grow too big.

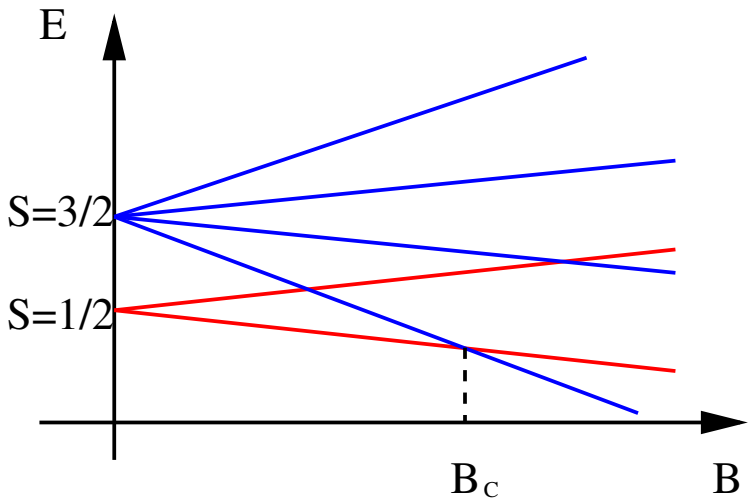
Once more: deposited chain

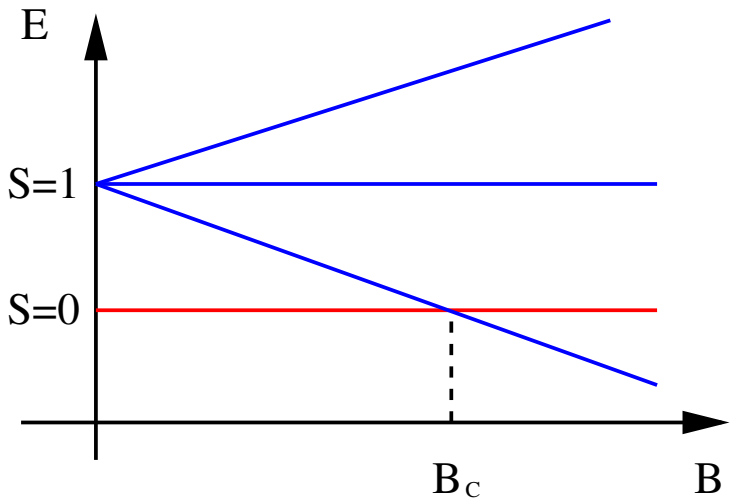




X. Chen *et al.*, Phys. Rev. Lett. **101**, 197208 (2008).

Energy levels of limiting cases for deposited trimer

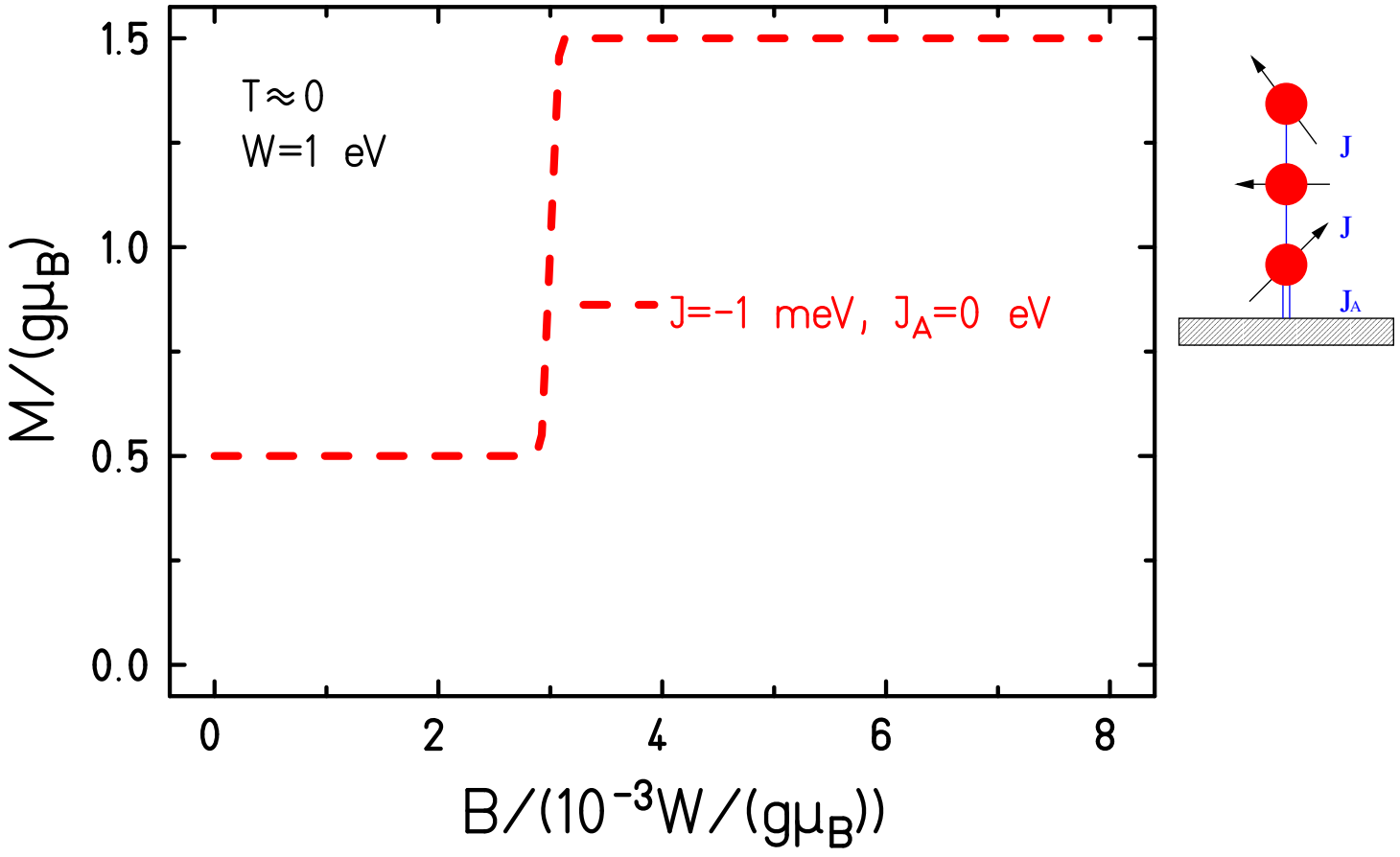




- energy levels of a trimer
- energy levels of a dimer

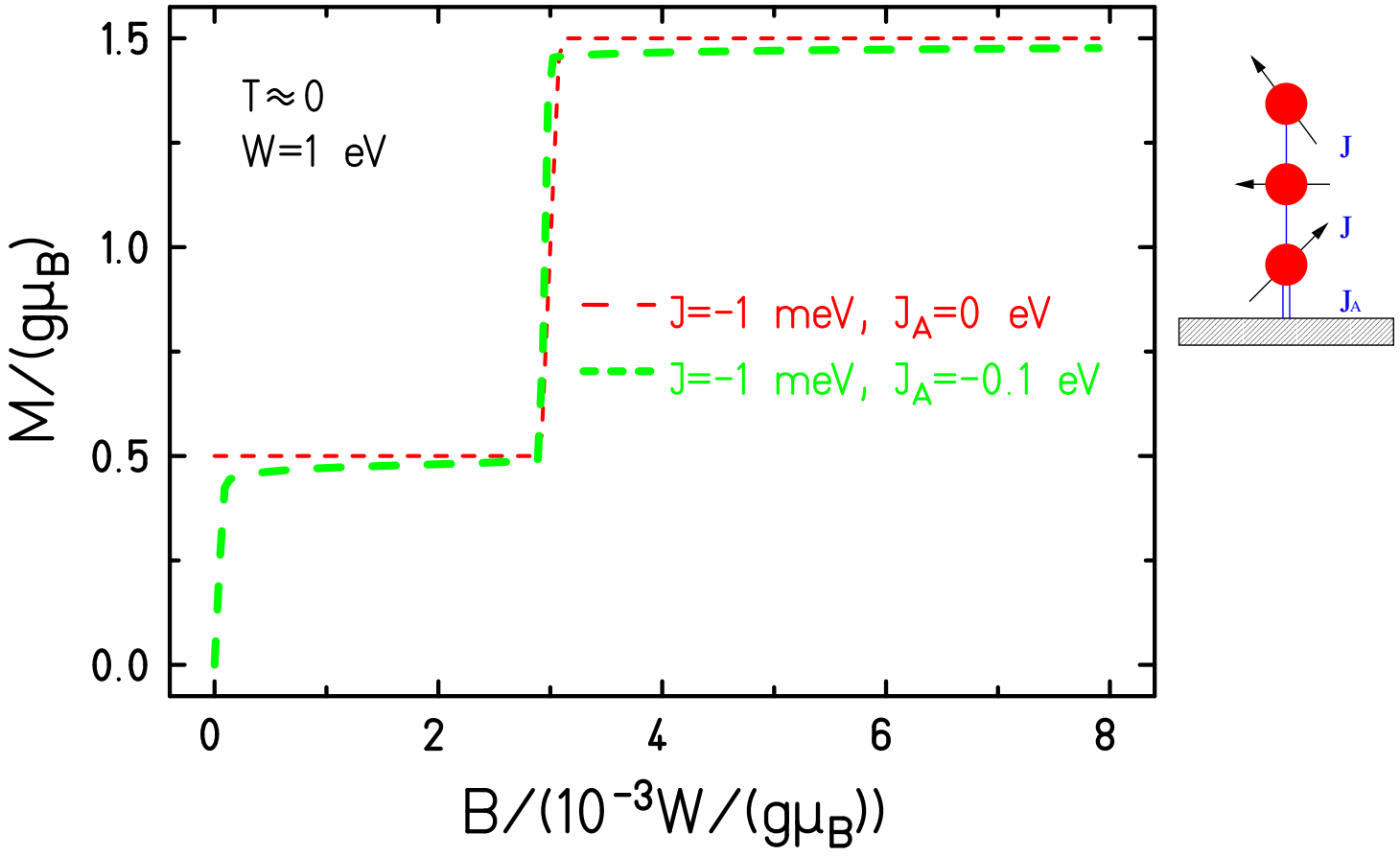
Magnetization curves different; could be seen in XMCD.
NRG calculates observables also between limiting cases
and can thus tell under which circumstances a limiting case applies.

Increasing coupling to the substrate



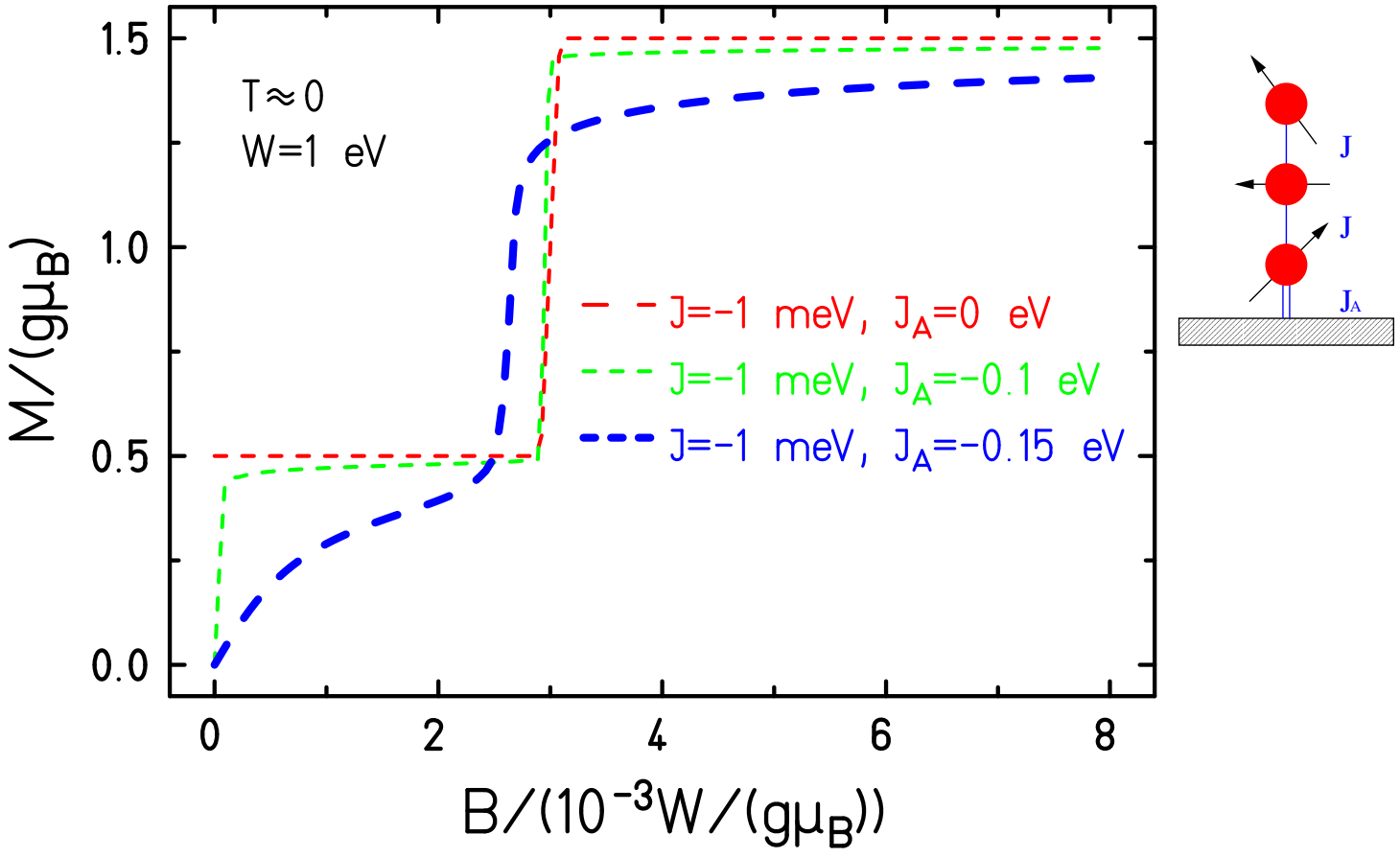
H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

Increasing coupling to the substrate



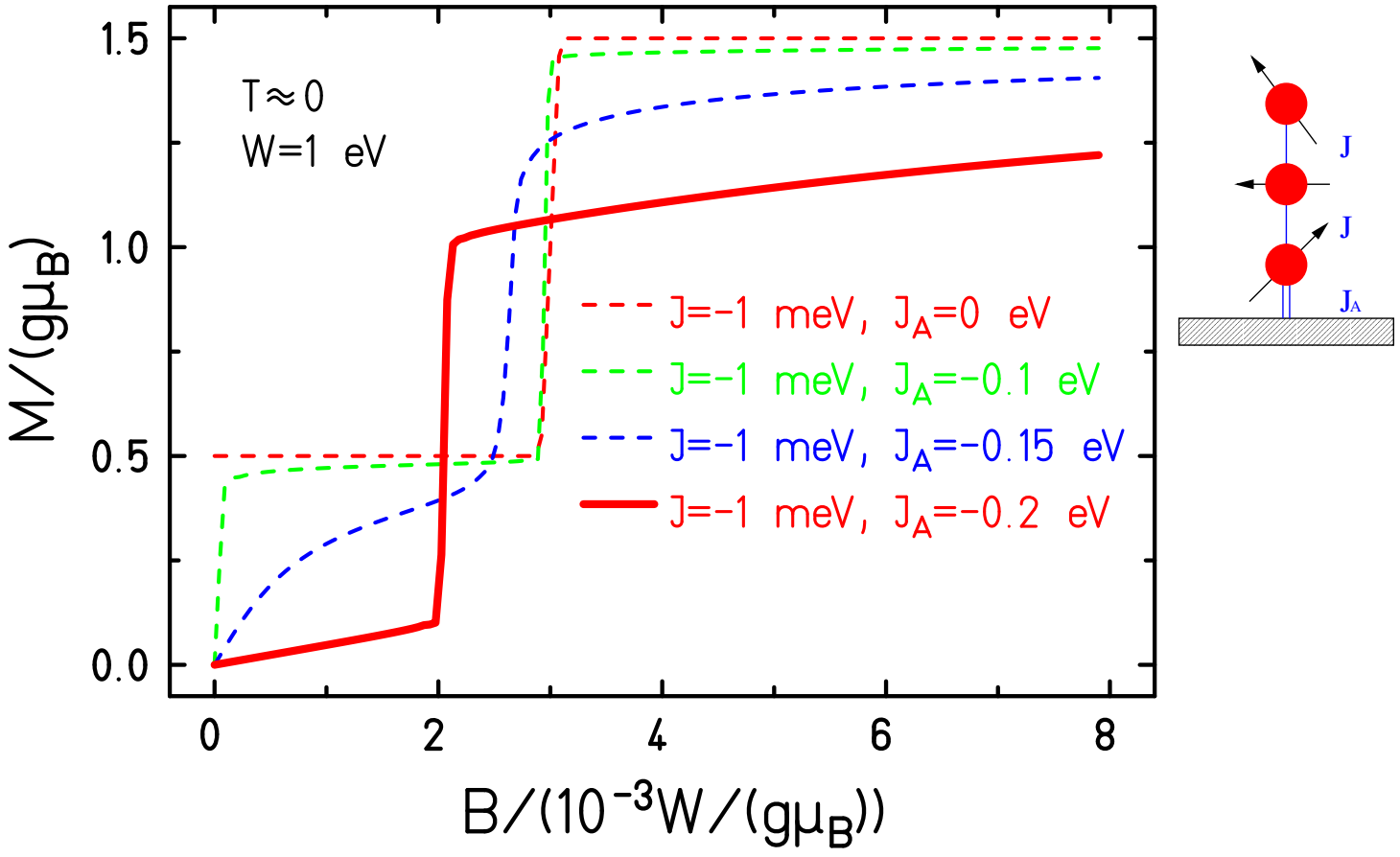
H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

Increasing coupling to the substrate



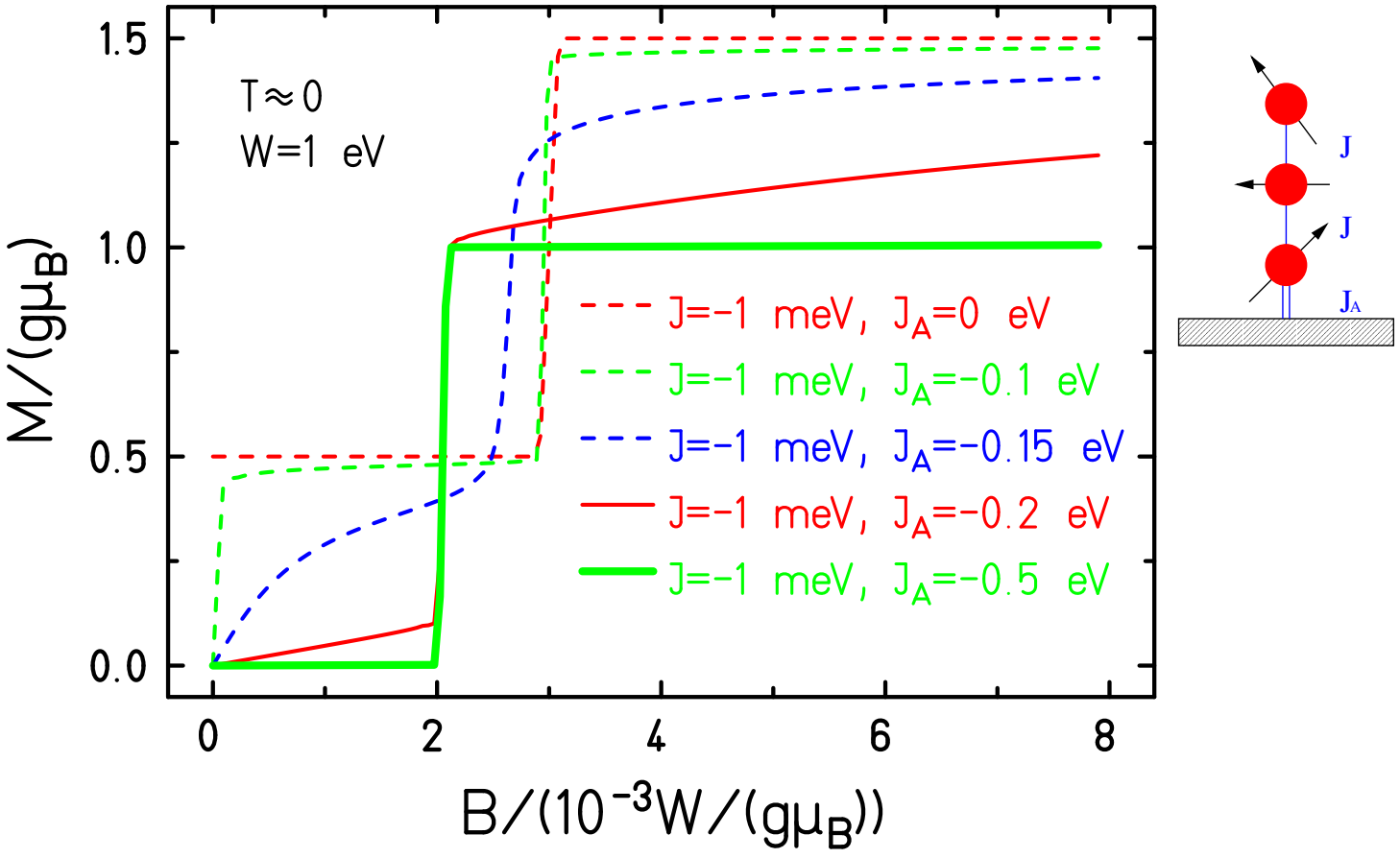
H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

Increasing coupling to the substrate



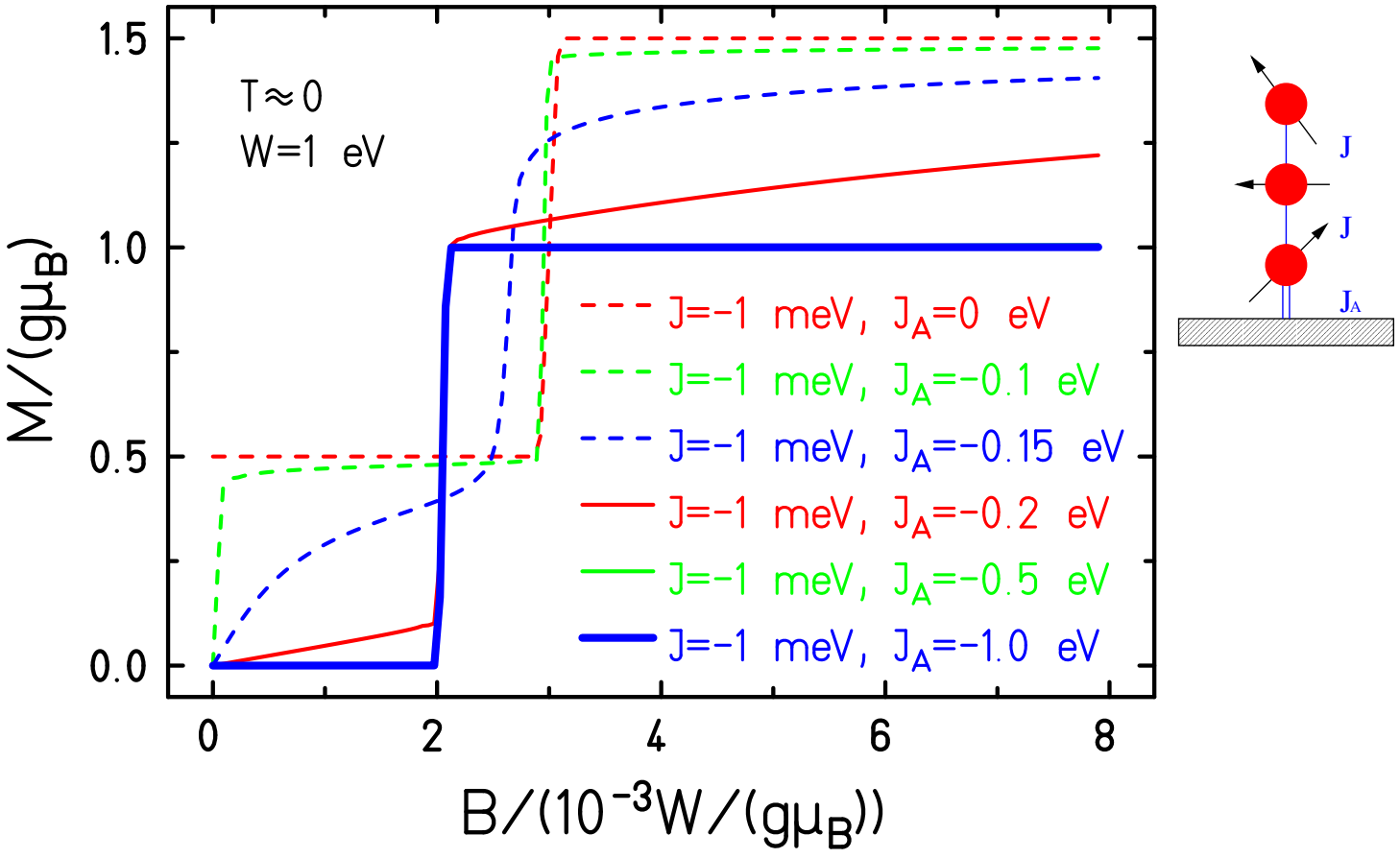
H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

Increasing coupling to the substrate



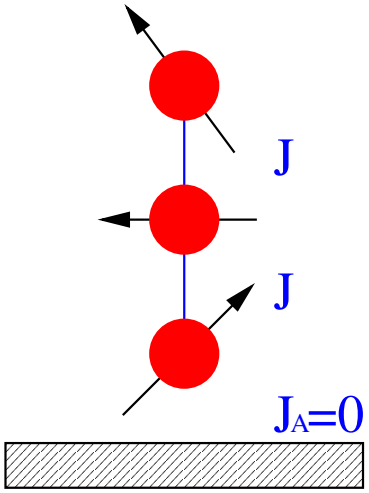
H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

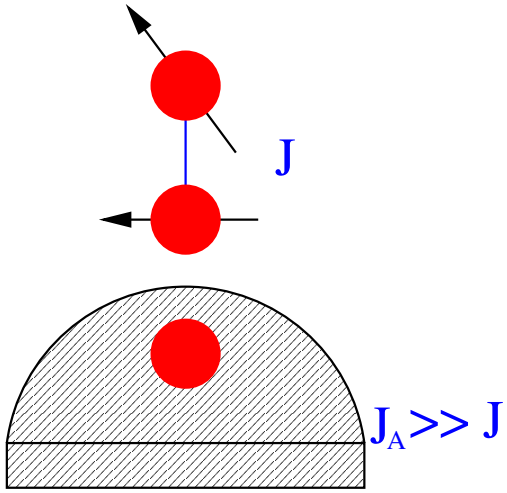
Increasing coupling to the substrate



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

Weak vs. strong coupling





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

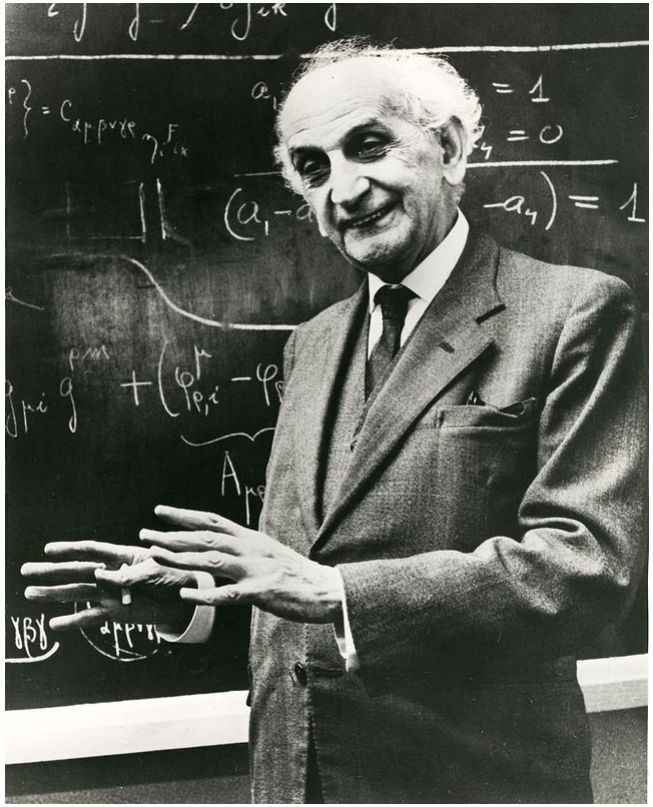
- strong coupling limit: effective remainder (dimer)
- $|J_A| \gtrapprox 0.5W$

Inbetween: no simple characterization + further sequential screening possible

Finite-Temperature Lanczos Method

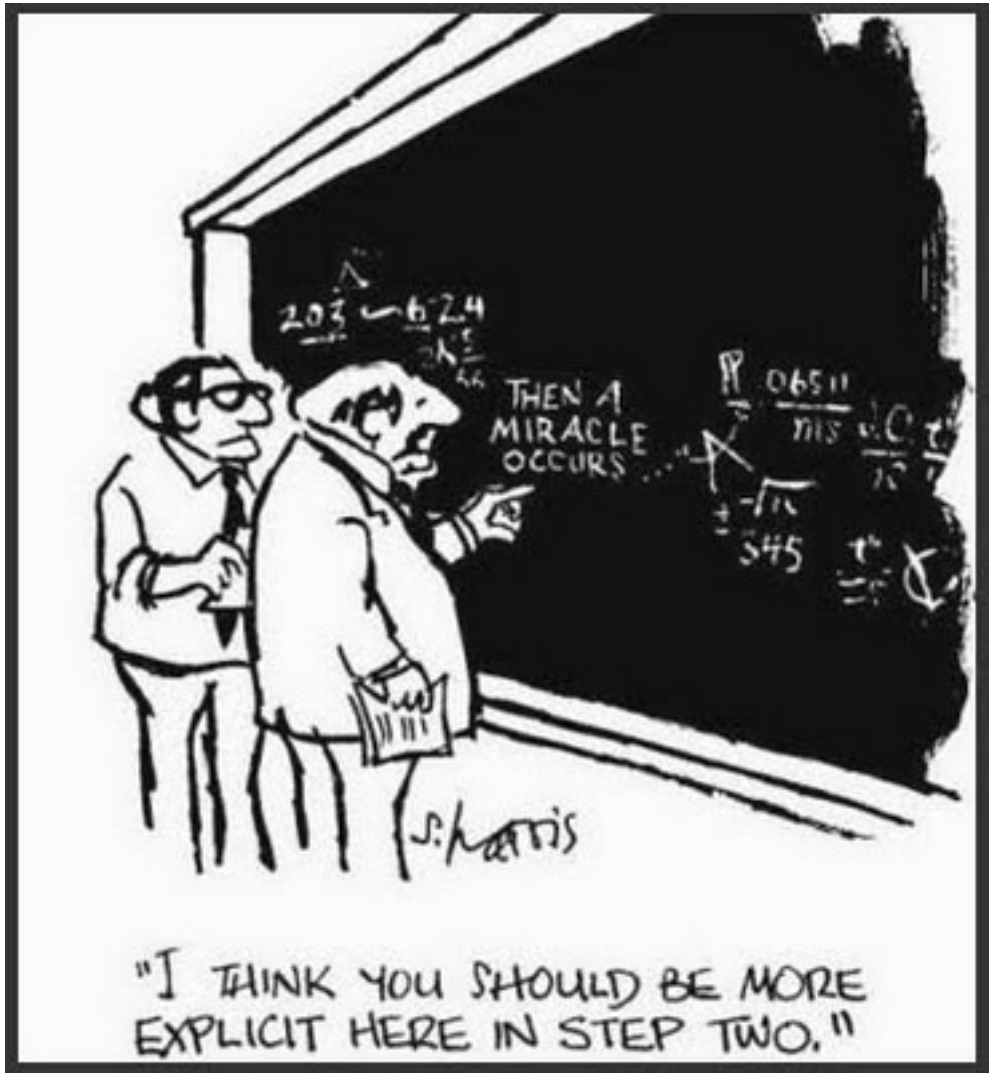
(Good for dimensions up to 10^{10}.)

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).


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

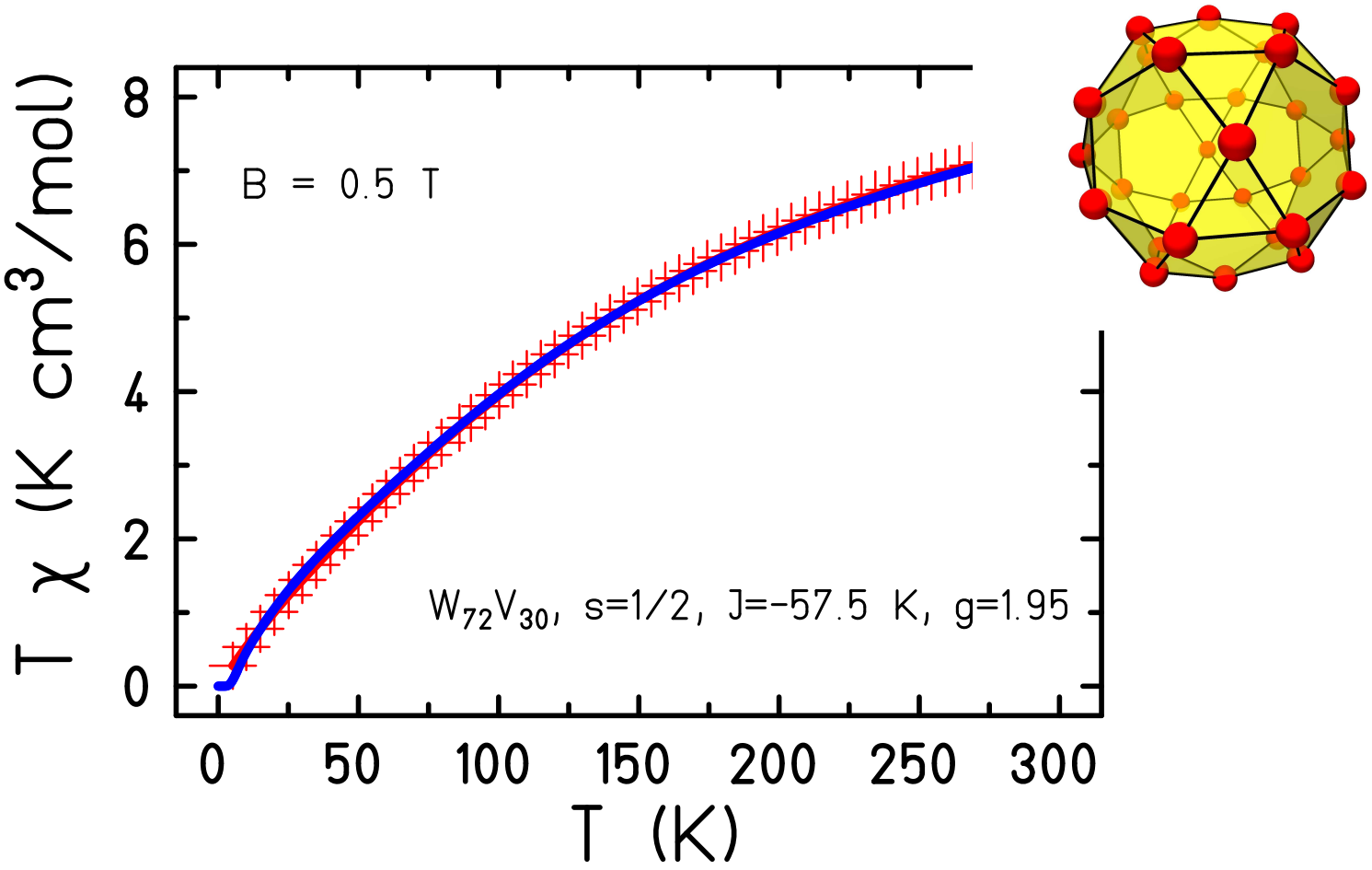
Finite-temperature Lanczos Method I

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

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

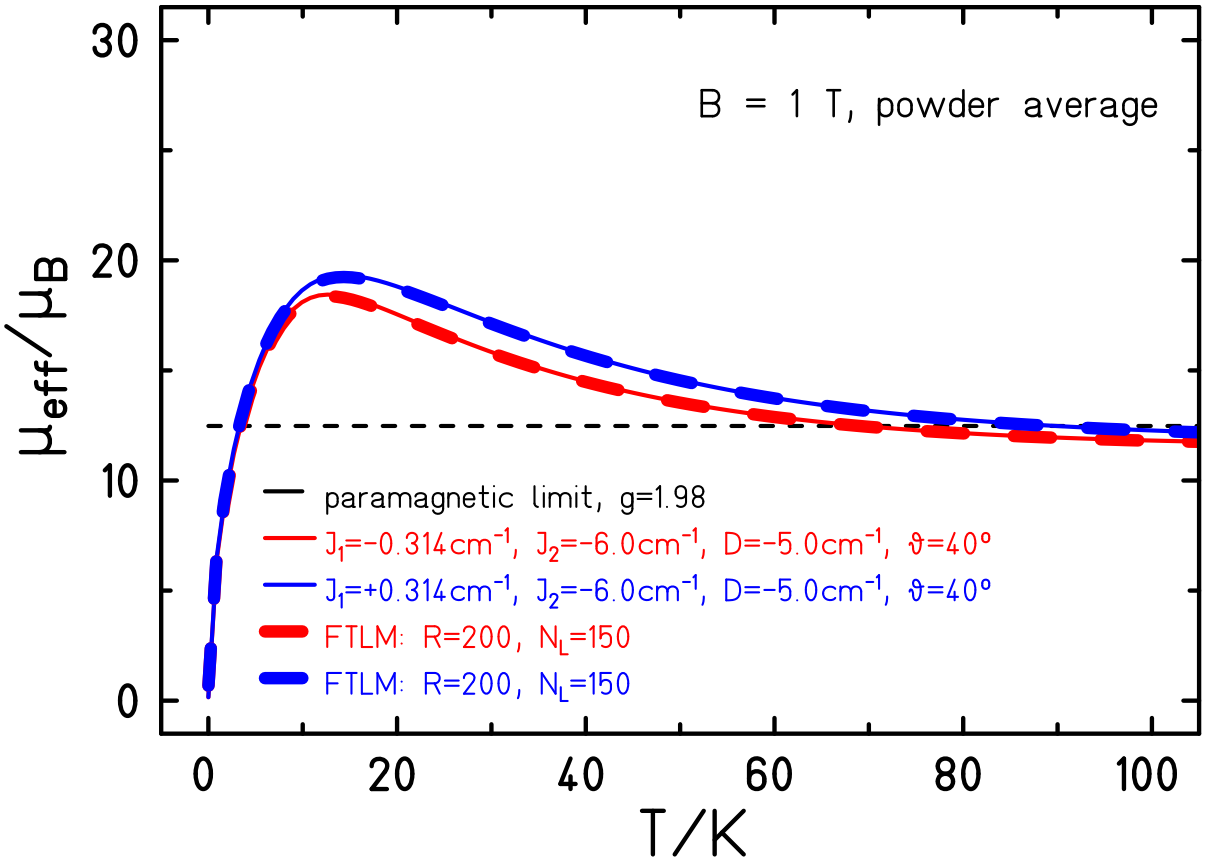
J. Jaklic and P. Prelovsek, Phys. Rev. B **49**, 5065 (1994).

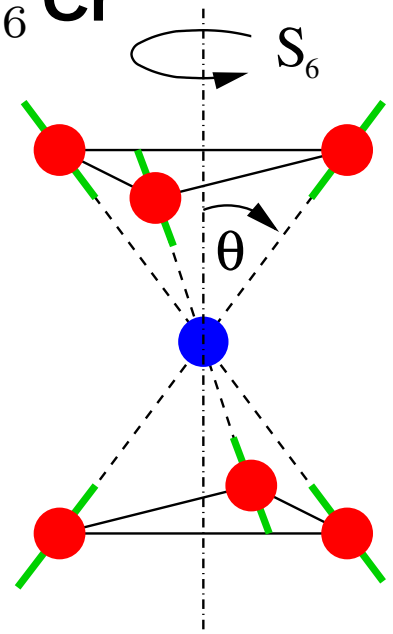
Icosidodecahedron $s = 1/2$



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: $Mn^{III}_6Cr^{III}$





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

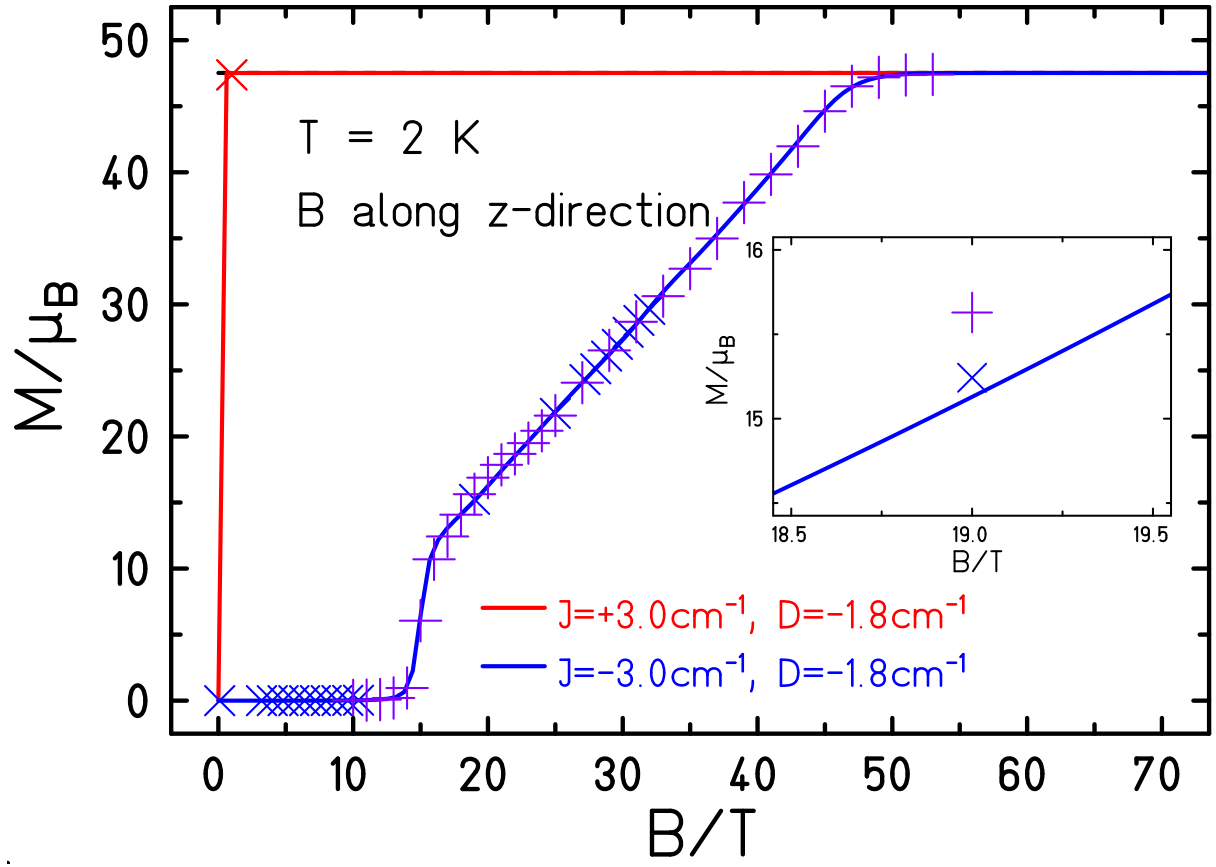
$\dim(\mathcal{H}) = 62,500$

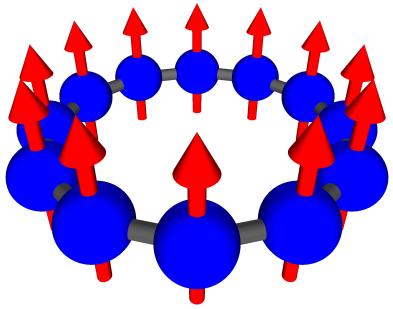
non-collinear easy axes

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





$s = 2$

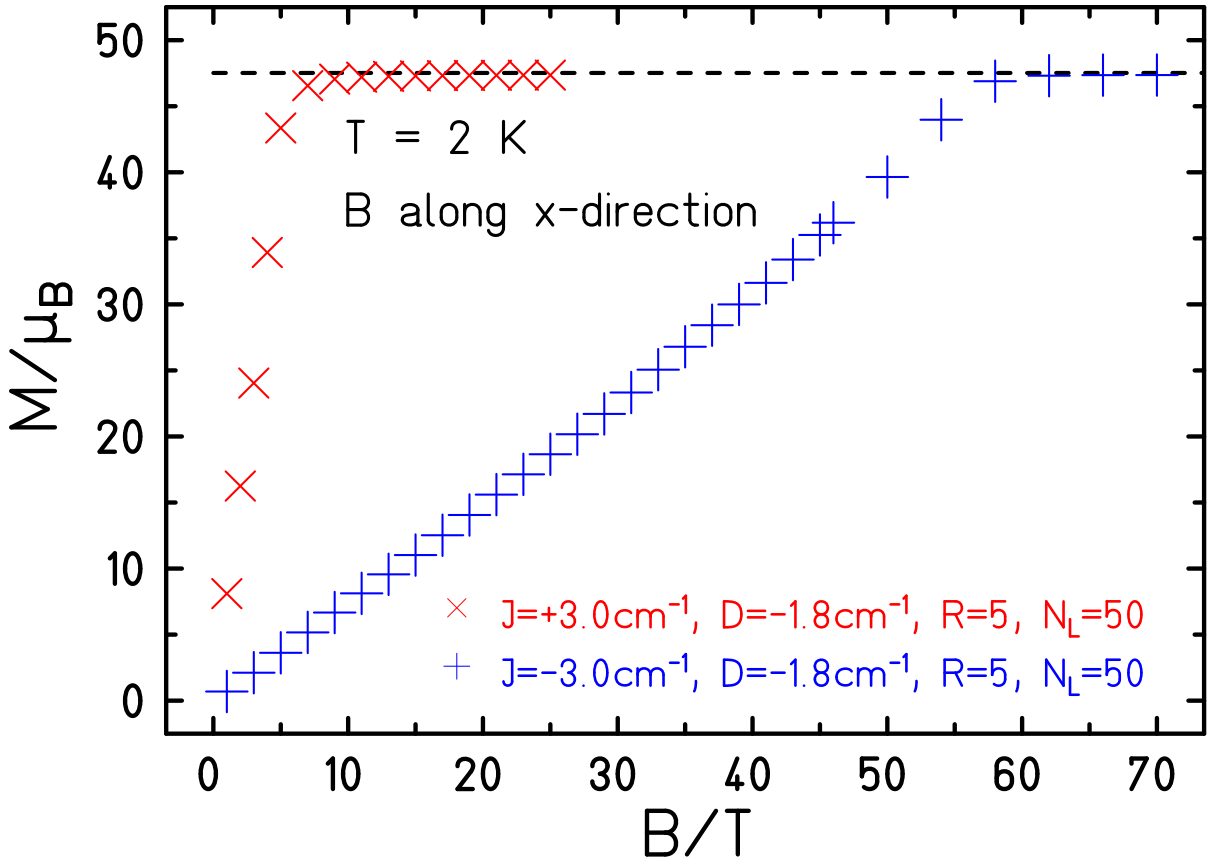
$\dim(\mathcal{H}) = 244,140,625$

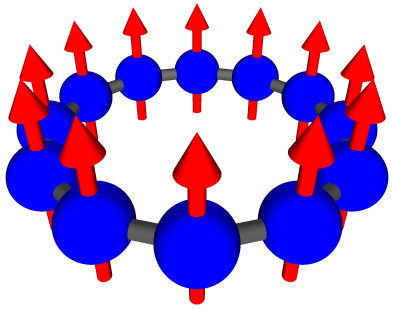
collinear easy axes

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

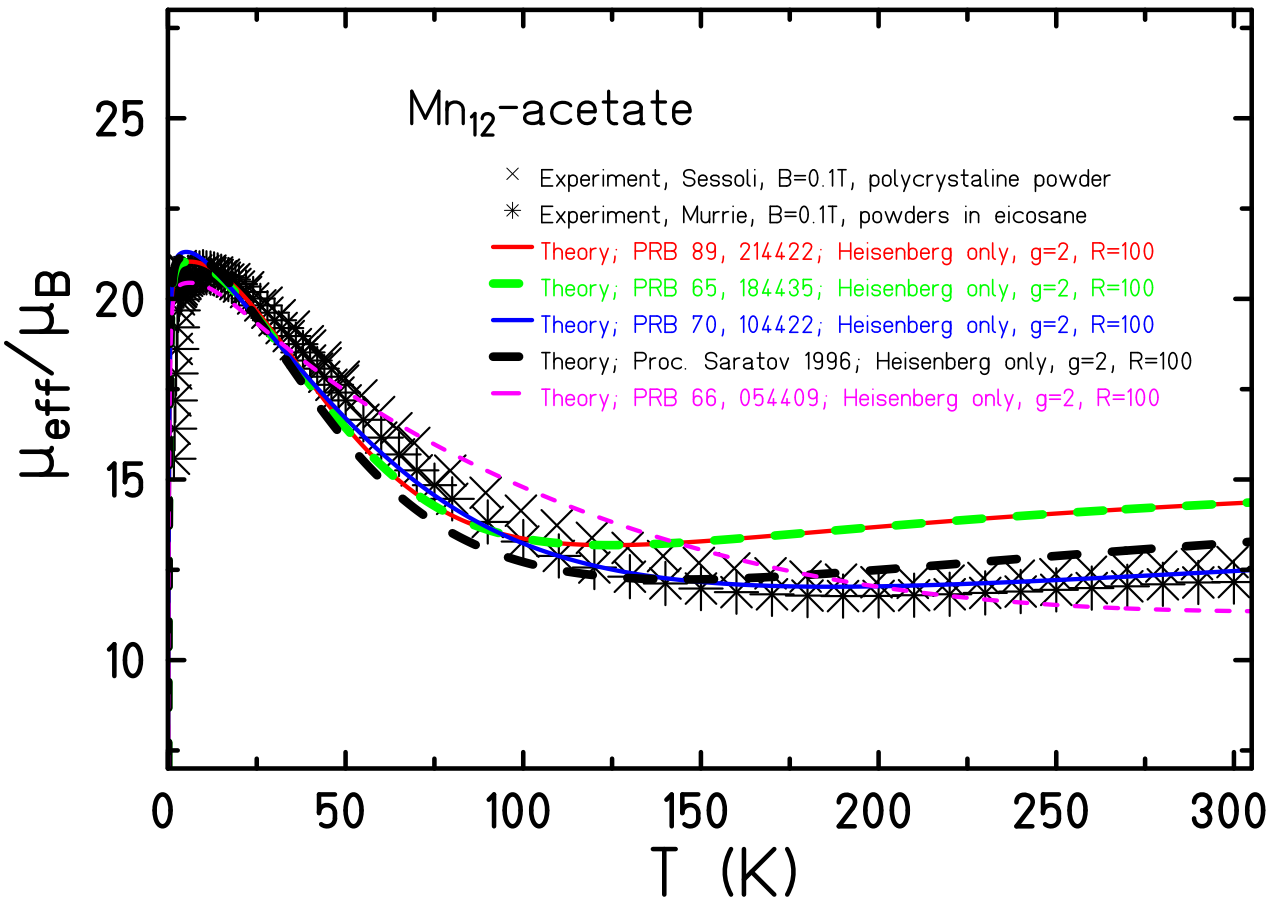




No other method can deliver these curves!

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

Mn_{12}–acetate

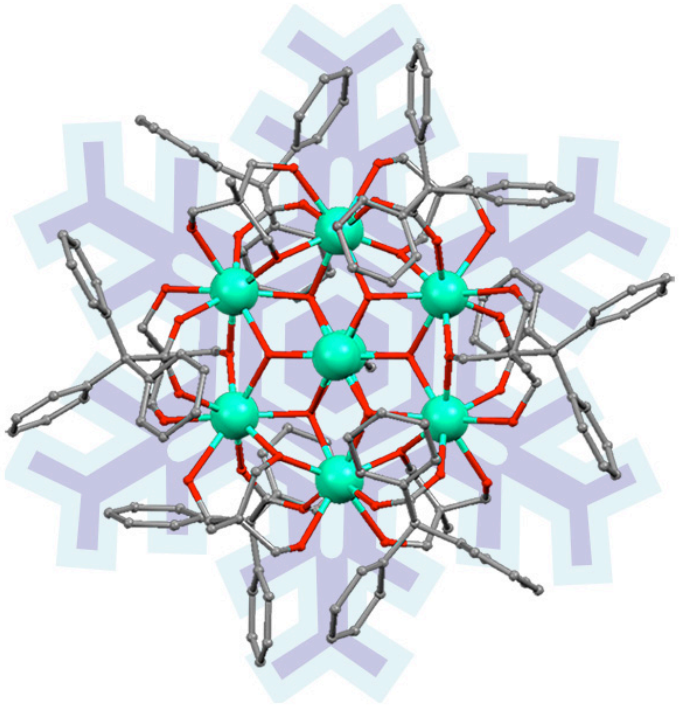


We can check DFT parametrizations for large molecules.

O. Hanebaum, J. Schnack, work in progress

Enhanced magnetocaloric effect

Gd$_7$ – Basics

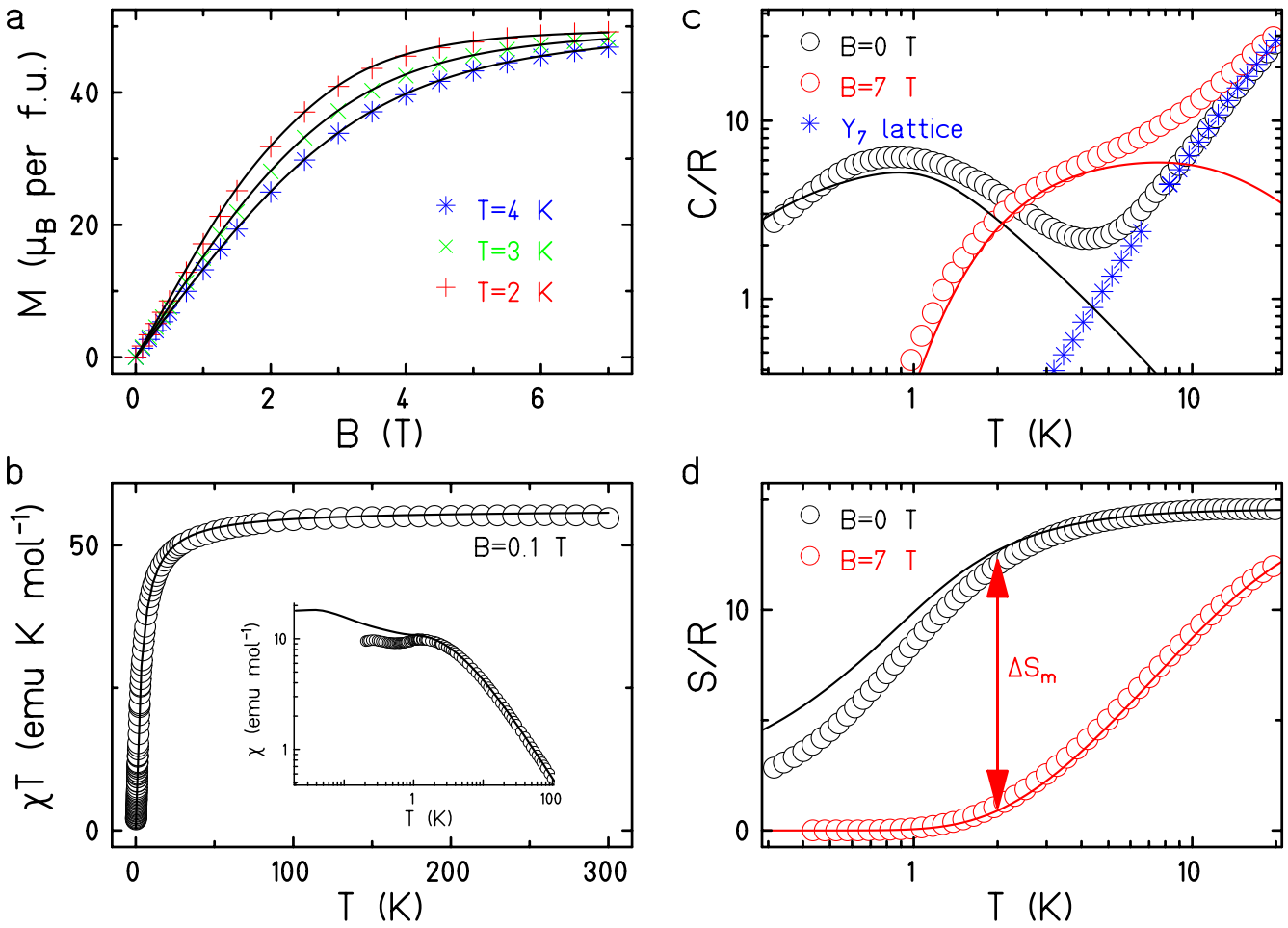


- Often magnetocaloric observables not directly measured, but inferred from Maxwell's relations.
- First real cooling experiment with a molecule.
- $\underset{\sim}{H} = -2 \sum_{i<j} J_{ij}\, \underset{\sim}{\vec{s}}_i \cdot \underset{\sim}{\vec{s}}_j + g\,\mu_B\, B \sum_i^N \underset{\sim}{s}_i^z$

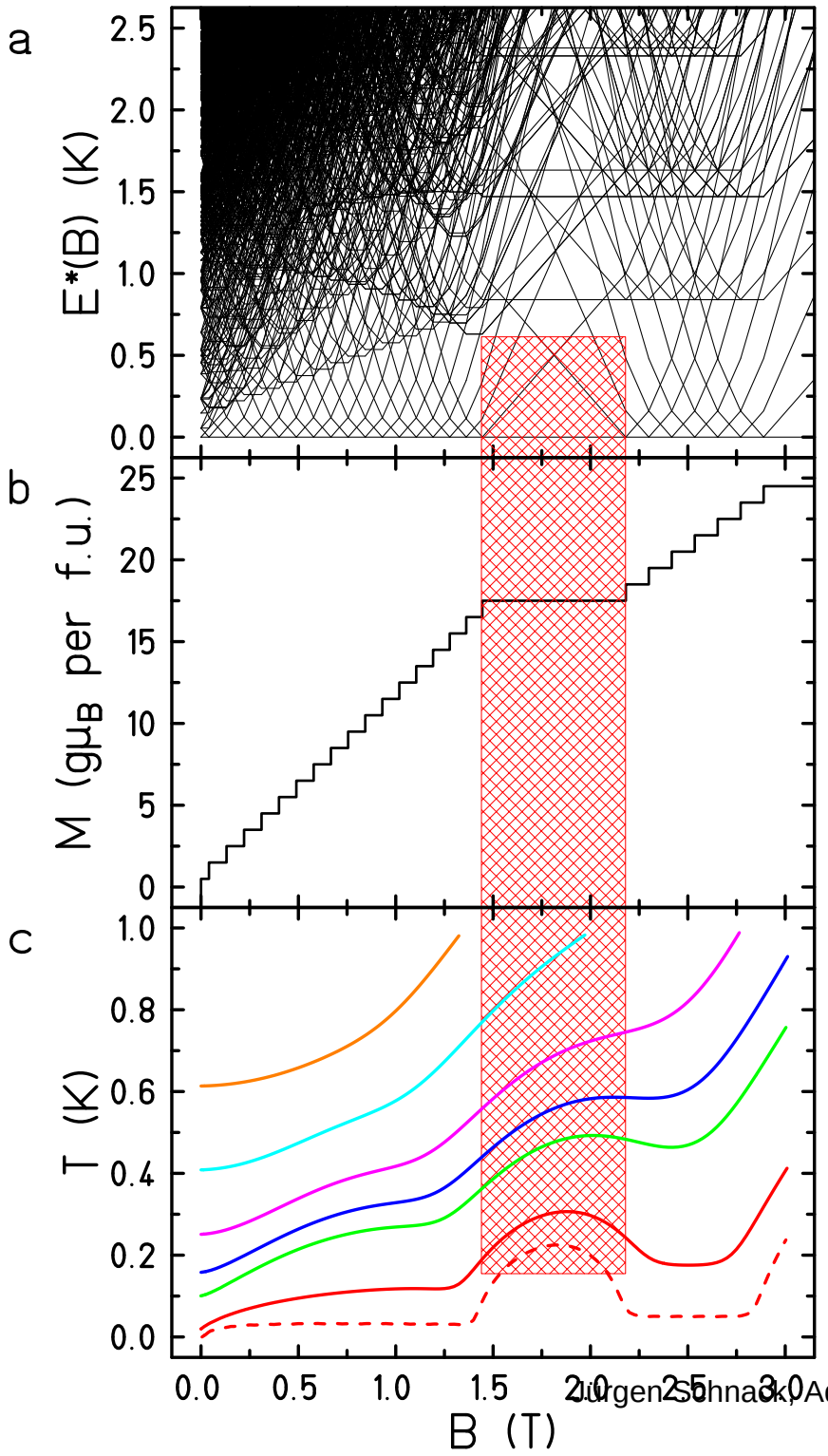
  $J_1 = -0.090(5)$ K, $J_2 = -0.080(5)$ K and $g = 2.02$.
- Very good agreement down to the lowest temperatures.

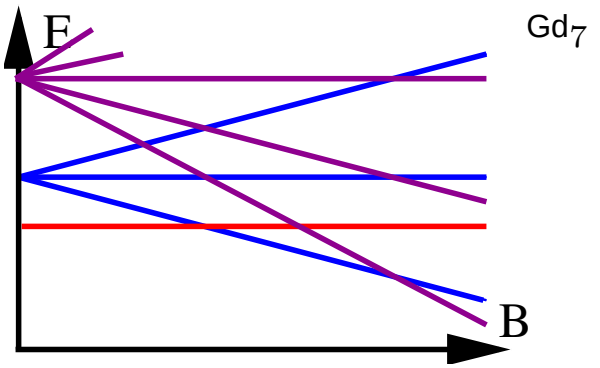
J. W. Sharples, D. Collison, E. J. L. McInnes, J. Schnack, E. Palacios, M. Evangelisti, Nat. Commun. **5**, 5321 (2014).

Gd$_7$ – experiment & theory

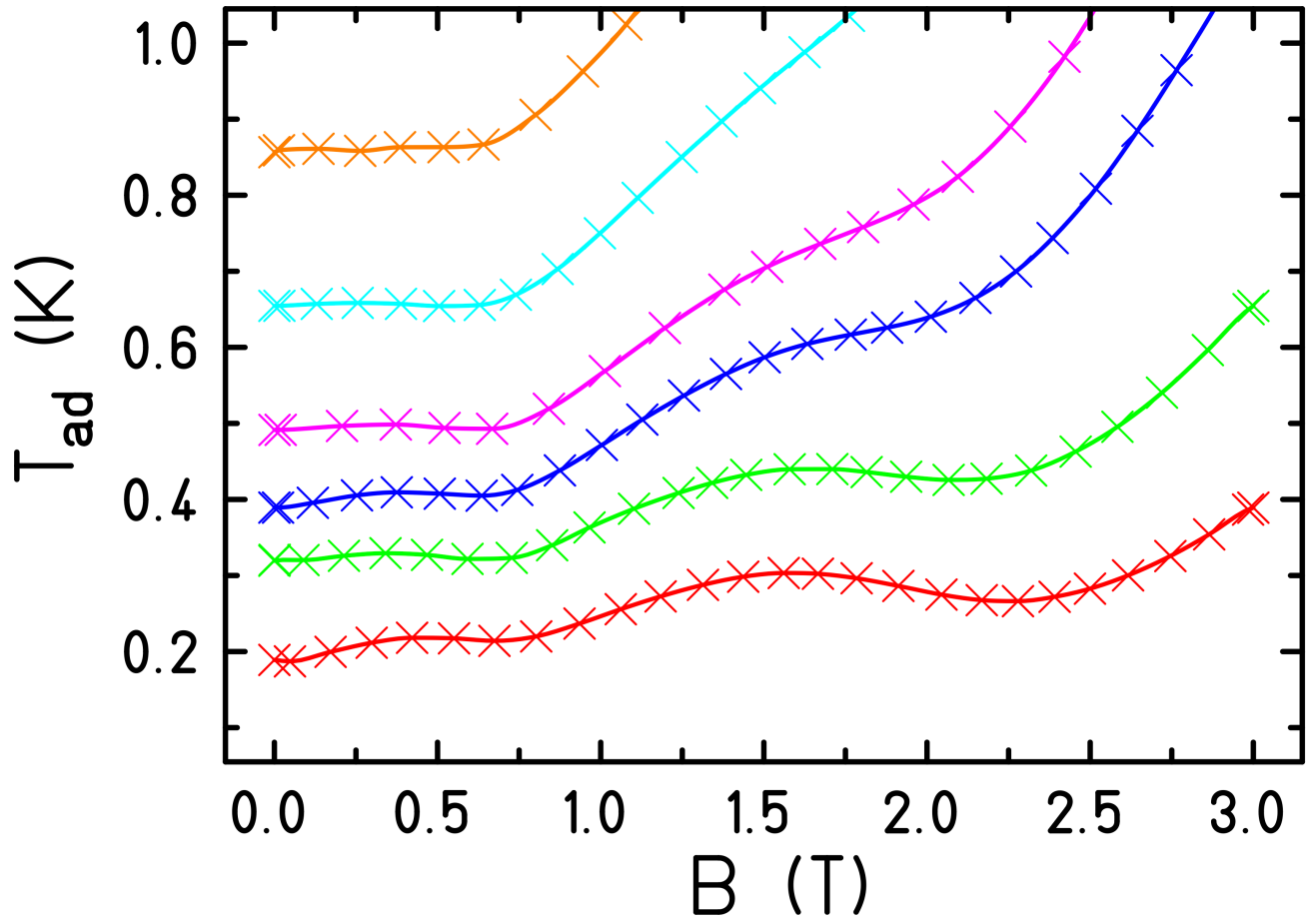


J. W. Sharples, D. Collison, E. J. L. McInnes, J. Schnack, E. Palacios, M. Evangelisti, Nat. Commun. **5**, 5321 (2014).


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


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).

Here is what I could have talked 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

Please ask, if you are interested.

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)
- K. Bärwinkel, H.-J. Schmidt, M. Neumann (Osnabrück)
- M. Luban (Ames Lab, USA); P. Kögerler (Aachen, Jülich, Ames); R.E.P. Winpenny, E.J.L. McInnes (Man U, UK); L. Cronin, M. Murrie (Glasgow, UK); E. Brechin (Edinburgh, UK); H. Nojiri (Sendai, Japan); A. Postnikov (Metz, France); M. Evangelisti (Zaragosa, Spain)
- 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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Highlights. Tutorials. Who is who. Conferences.