Yes, we can! Advanced quantum methods for the largest magnetic molecules

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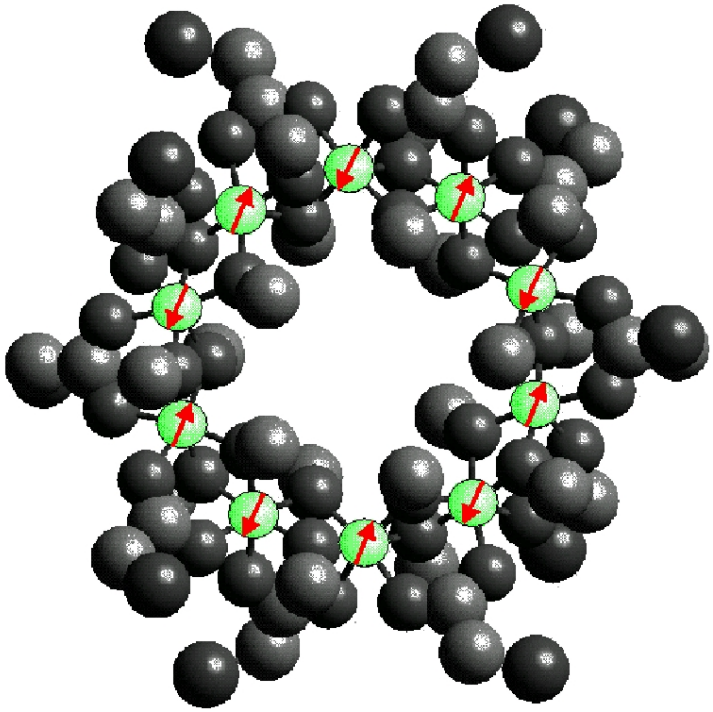
IMR 東北大学金属材料研究所
Institute for Materials Research, Tohoku University

The usual problem

You have got a molecule!

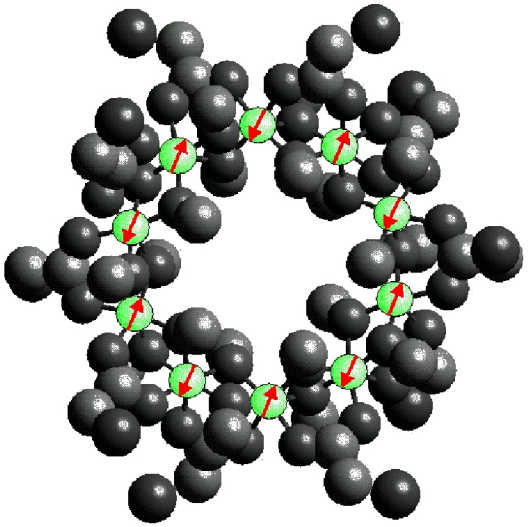


Congratulations!

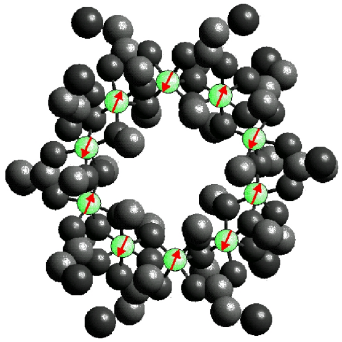
You have got an idea about the modeling!

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

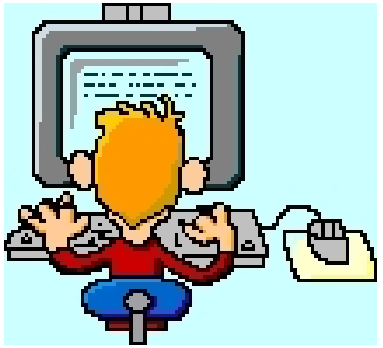
Heisenberg Zeeman



In the end it's always a big matrix!



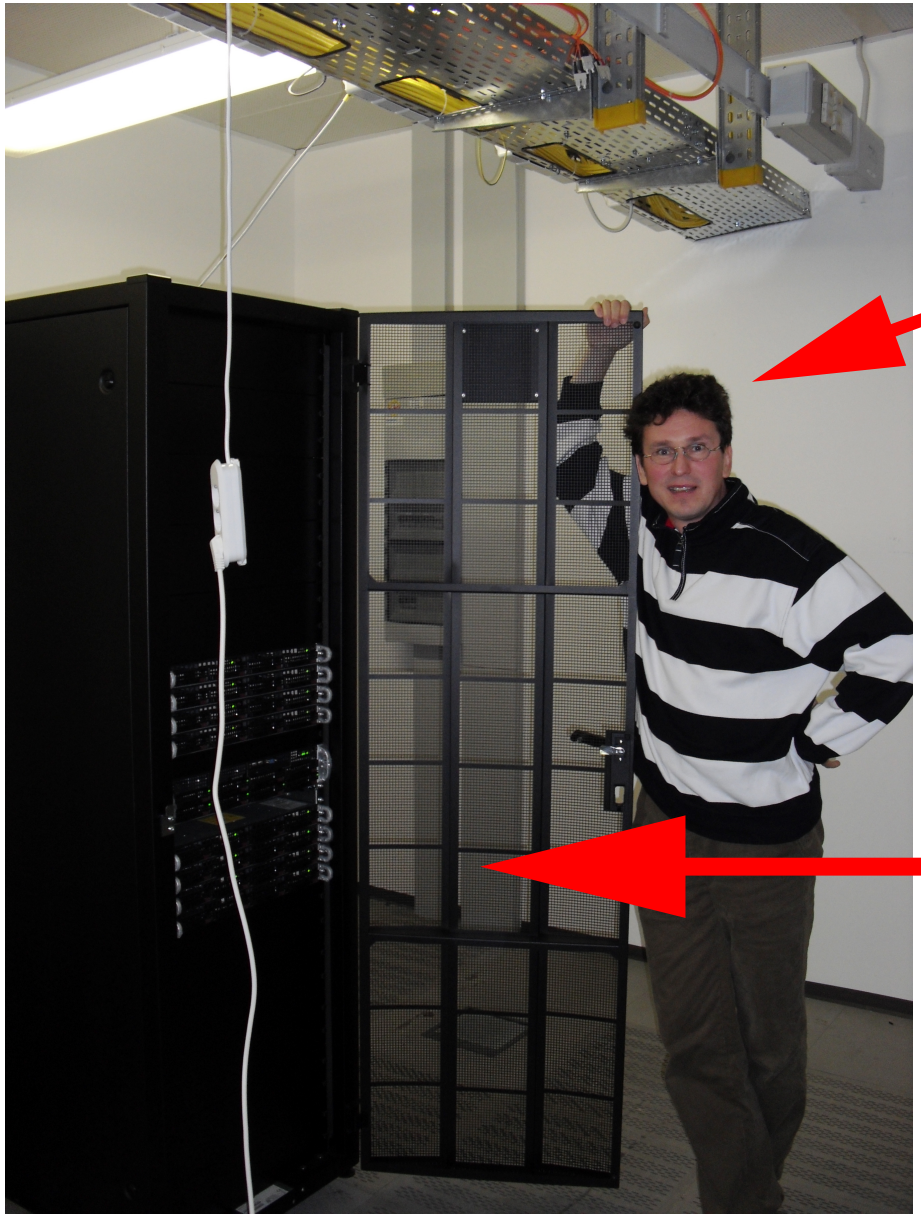
$$\Rightarrow \begin{pmatrix} -27.8 & 3.46 & 0.18 & \cdots \\ 3.46 & -2.35 & -1.7 & \cdots \\ 0.18 & -1.7 & 5.64 & \cdots \\ \vdots & \vdots & \vdots & \cdots \end{pmatrix} \Rightarrow$$



Fe^{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

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

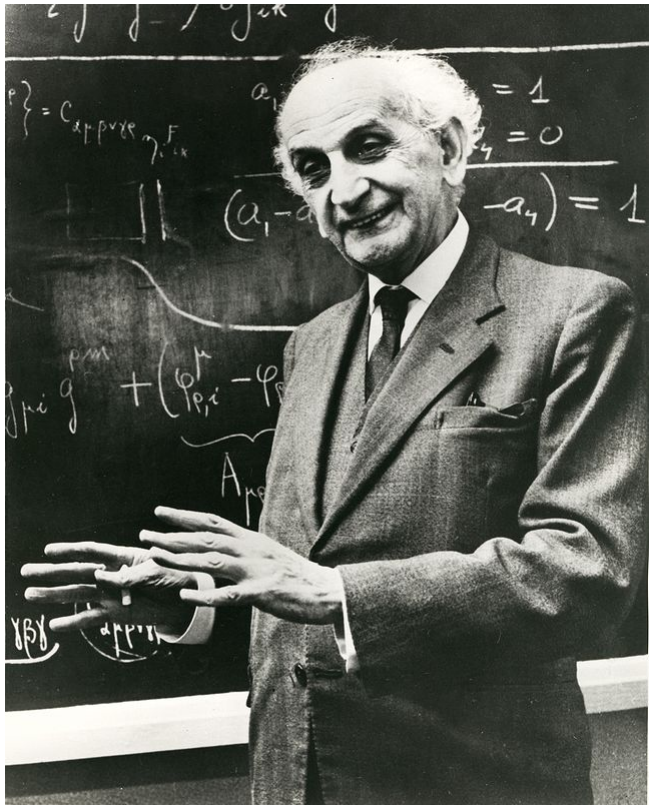
1. Finite-Temperature Lanczos Method
2. Numerical Renormalization Group calculations

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

Finite-Temperature Lanczos Method

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

Lanczos – a Krylov space method



Cornelius Lanczos
(1893-1974)

- You do know exact diagonalization. What about diagonalization in reduced basis sets?!
  Full matrix $\Longrightarrow$ small matrix!
- But which set to choose???
- Idea: generate the basis set with the operator you want to diagonalize:
  $\left\{ |\phi\rangle, \underset{\sim}{H}|\phi\rangle, \underset{\sim}{H}^2|\phi\rangle, \underset{\sim}{H}^3|\phi\rangle, \ldots \right\}$
  Hamiltonian creates its own relevant states!
- But which starting vector to choose???
- Idea: almost any will do!

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

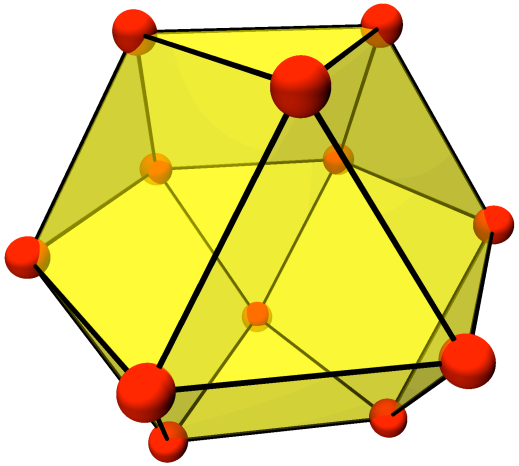
Finite-temperature Lanczos Method I

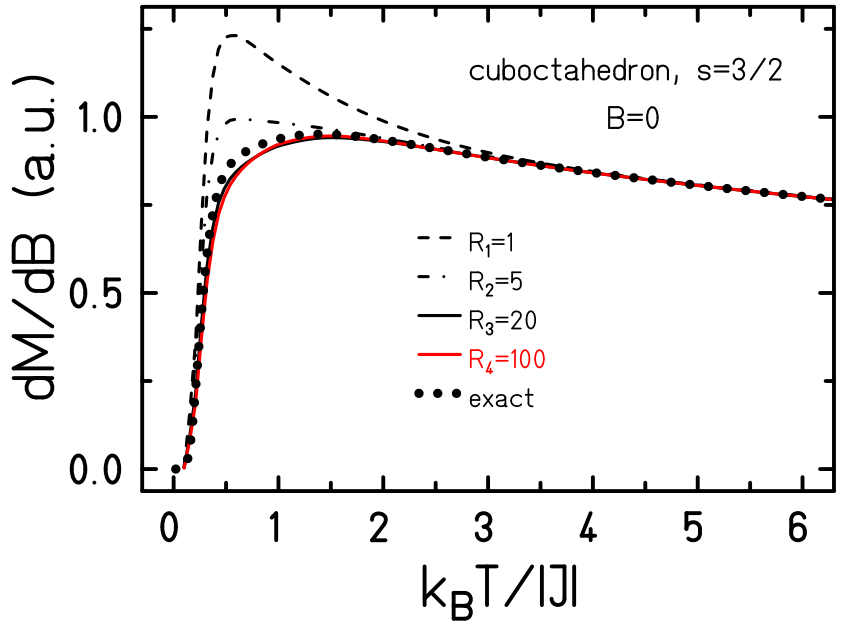
$$
\begin{aligned}
Z(T,B) &= \sum_{\nu} \langle\, \nu \,|\, \exp\left\{-\beta \underset{\sim}{H}\right\} \,|\, \nu \,\rangle \\
\langle\, \nu \,|\, \exp\left\{-\beta \underset{\sim}{H}\right\} \,|\, \nu \,\rangle &\approx \sum_{n} \langle\, \nu \,|\, n(\nu) \,\rangle \exp\left\{-\beta \epsilon_n\right\}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

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

J. Jaklič and P. Prelovšek, Phys. Rev. B **49**, 5065 (1994).

How good is finite-temperature Lanczos?

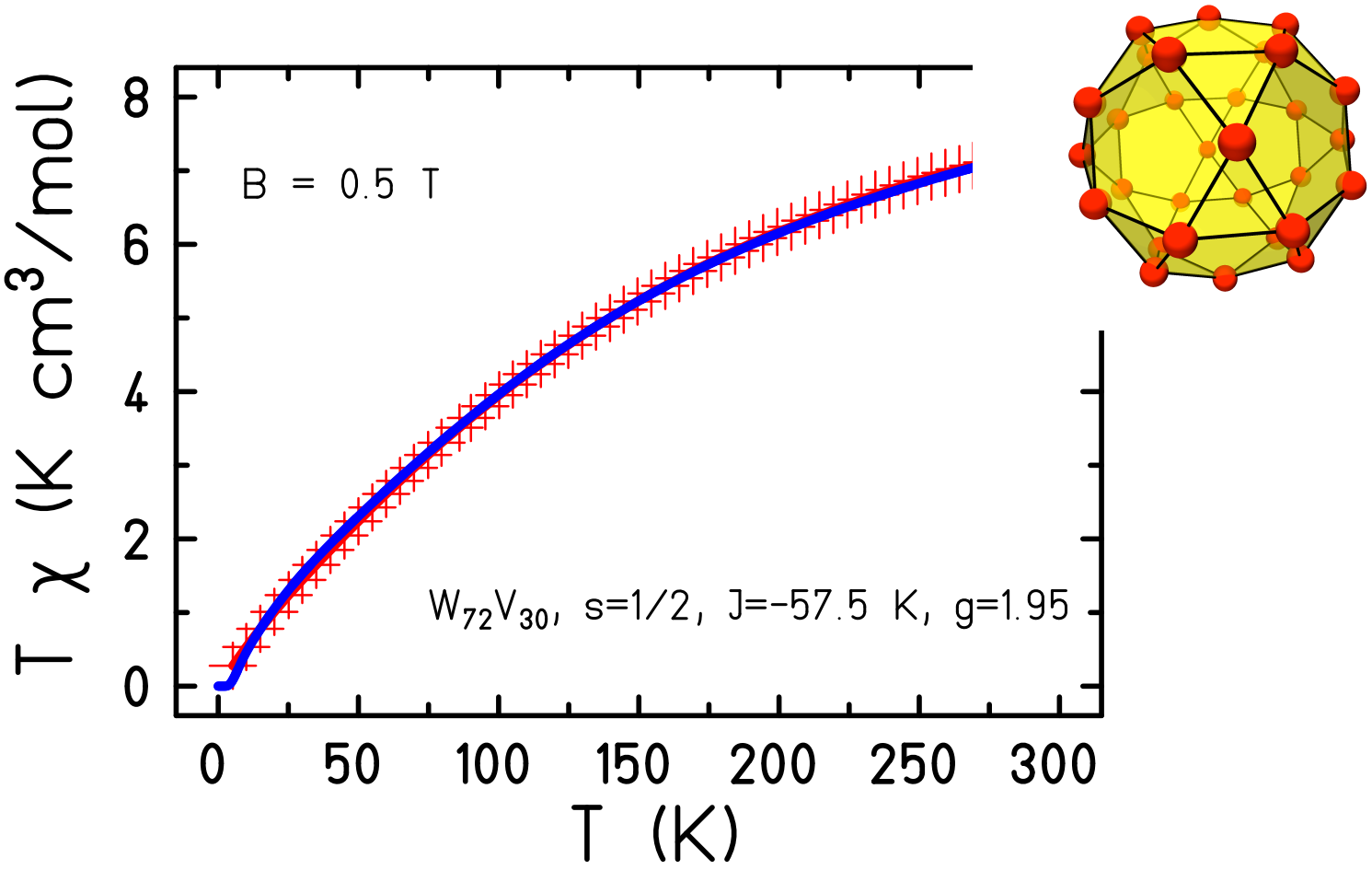




- Works very well: compare frustrated cuboctahedron.
- $N = 12, s = 3/2$: Considered $< 100,000$ states instead of 16,777,216.

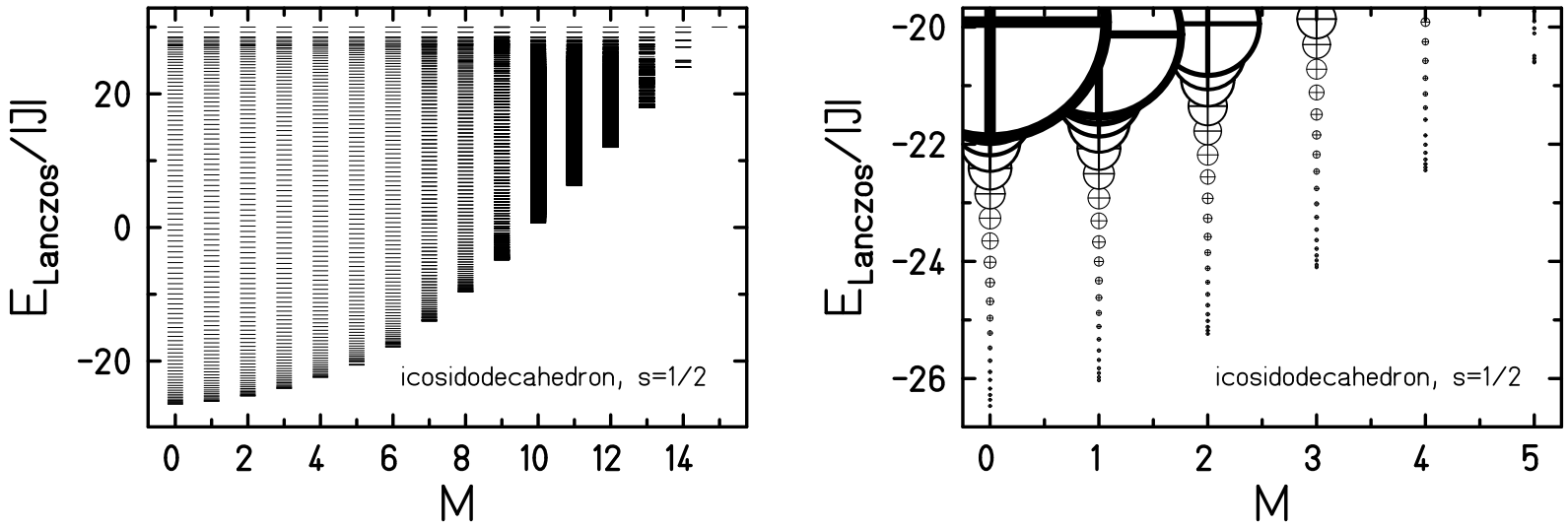
Exact results: R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403-452 (2010).
FTLM: J. Schnack and O. Wendland, Eur. Phys. J. B **78**, 535-541 (2010).

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).

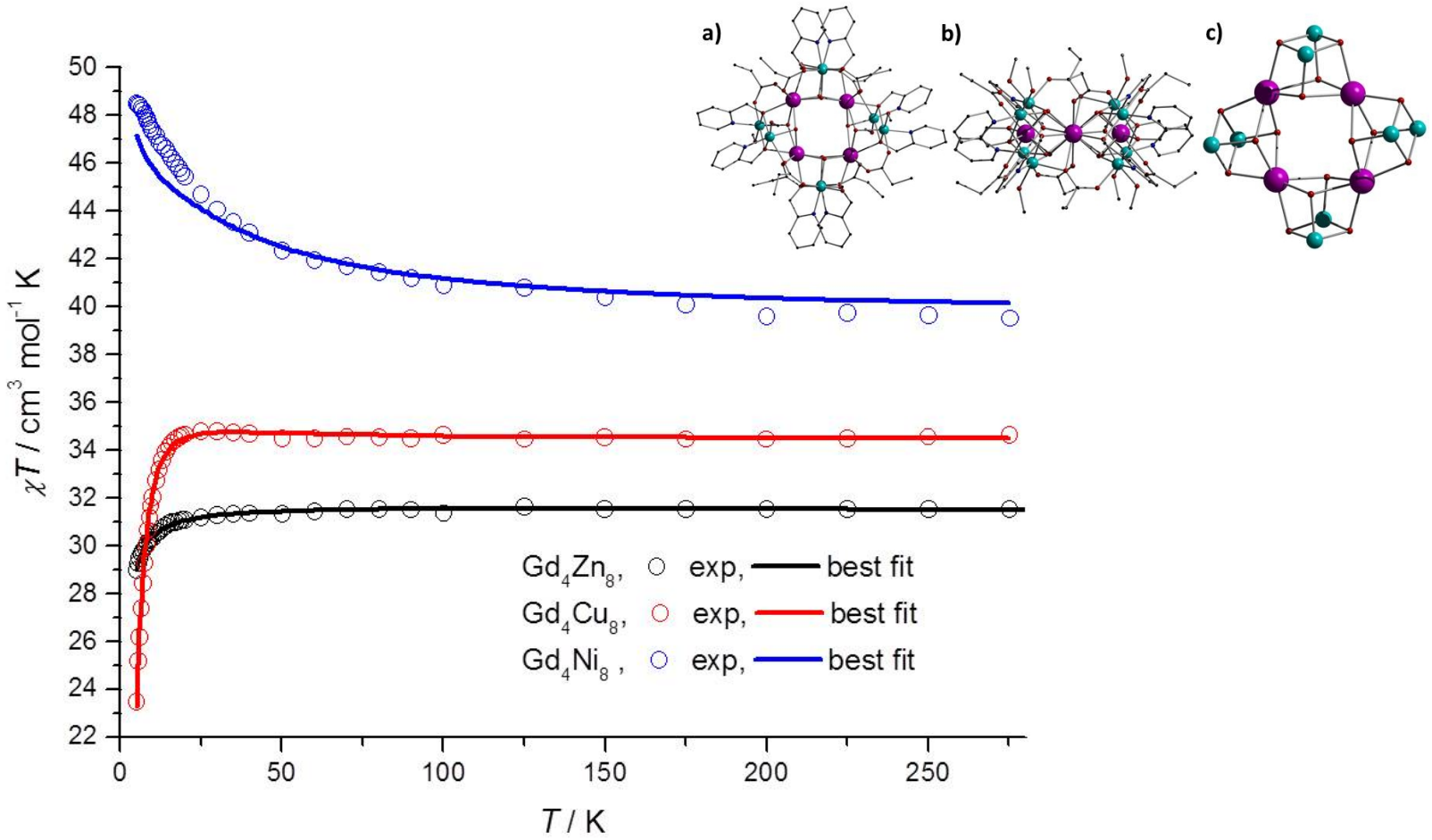
Icosidodecahedron $s = 1/2$



- The true spectrum will be much denser. This is miraculously compensated for by the weights. (Exact at low T, coarse grained at high T.)

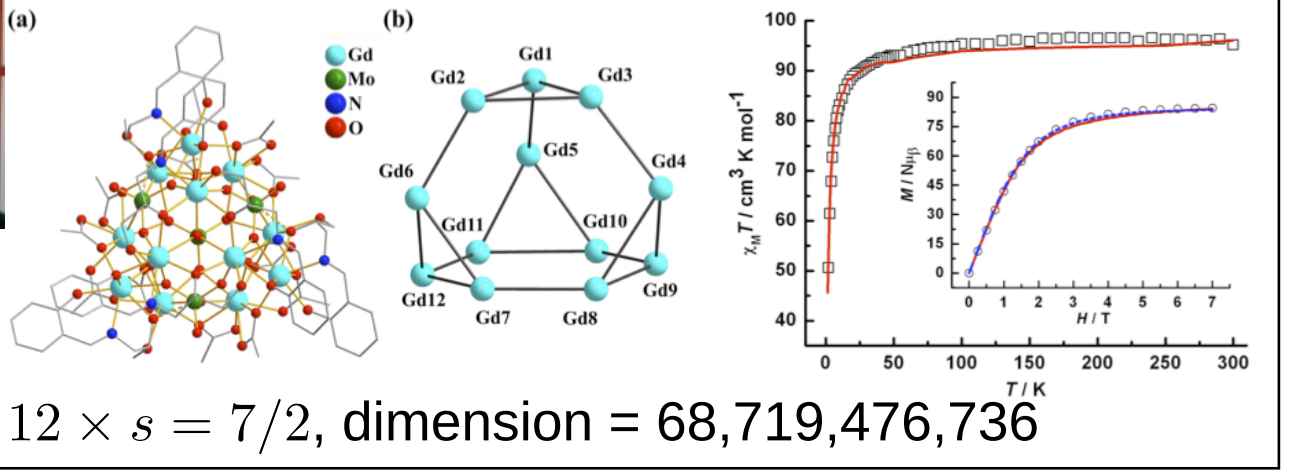
$$Z(T,B) \approx \frac{\dim(\mathcal{H})}{R} \sum_{\nu=1}^{R} \sum_{n=1}^{N_L} \exp\{-\beta\epsilon_n\} \left| \langle\, n(\nu,\Gamma) \,|\, \nu,\Gamma \,\rangle \right|^2$$

Gd_4M_8 – Susceptibility



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

Recent developments



$12 \times s = 7/2$, dimension = 68,719,476,736

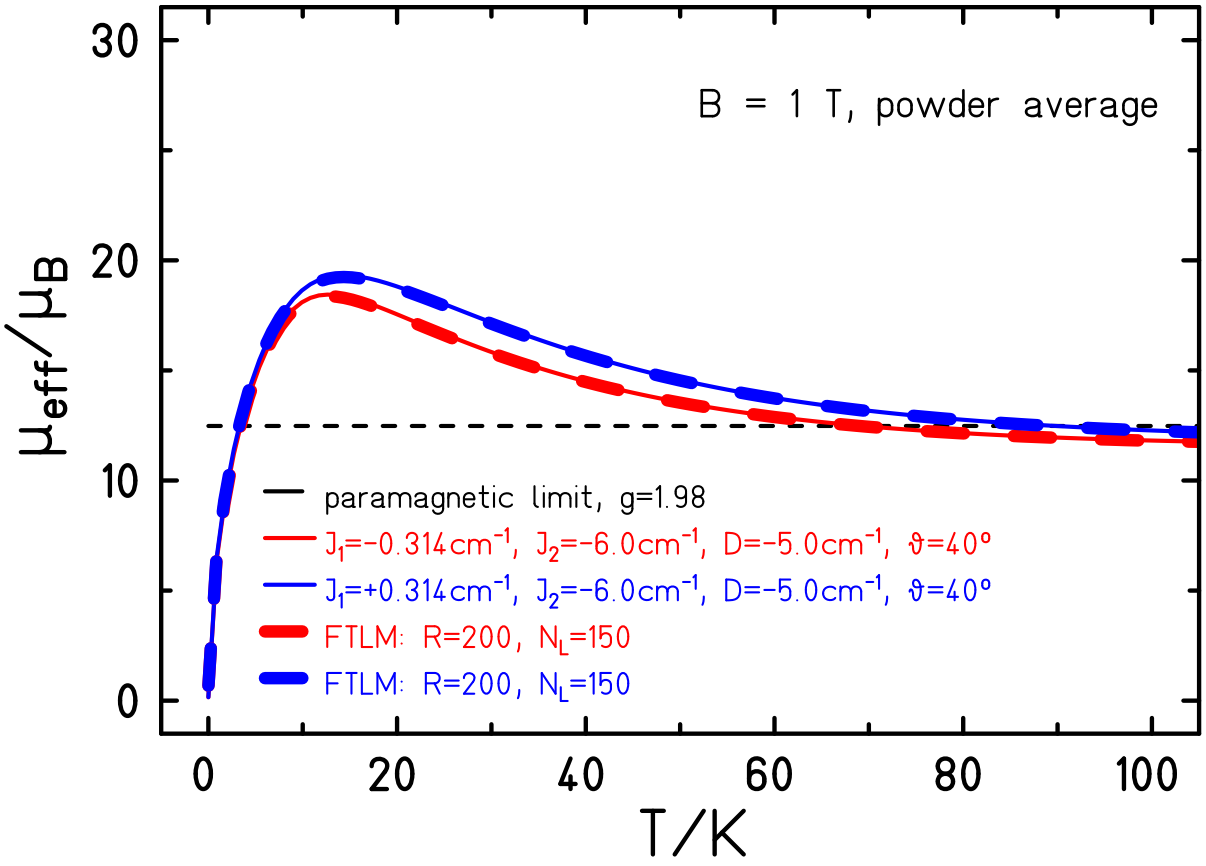
- Goal: magnetic properties of anisotropic systems;
- Oliver Hanebaum: single-ion anisotropy;
- Christian Heesing: Dzyaloshinskii-Moriya & anisotropic exchange.

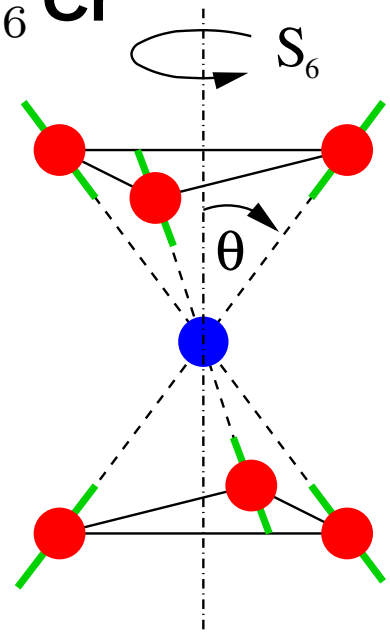
Hamiltonian with single-ion anisotropy

$$\underset{\sim}{H}(\vec{B}) \;=\; -2\sum_{i<j} J_{ij}\;\underset{\sim}{\vec{s}}_i \cdot \underset{\sim}{\vec{s}}_j \;+\sum_i d_i \left(\vec{e}_i \cdot \underset{\sim}{\vec{s}}_i\right)^2 + \;\mu_B\,\vec{B}\cdot\sum_i^N g_i \underset{\sim}{\vec{s}}_i$$

- $\left[\underset{\sim}{H}, \underset{\sim}{\vec{S}}^2\right] \neq 0$, $\left[\underset{\sim}{H}, \underset{\sim}{\vec{S}}_z\right] \neq 0$; $\Rightarrow$ MAGPACK does not work!
- You have to diagonalize $\underset{\sim}{H}(\vec{B})$ for every field (direction and strength)!
- Orientational average for powder samples.

Glaser-type molecules: $Mn_6^{III}Cr^{III}$





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

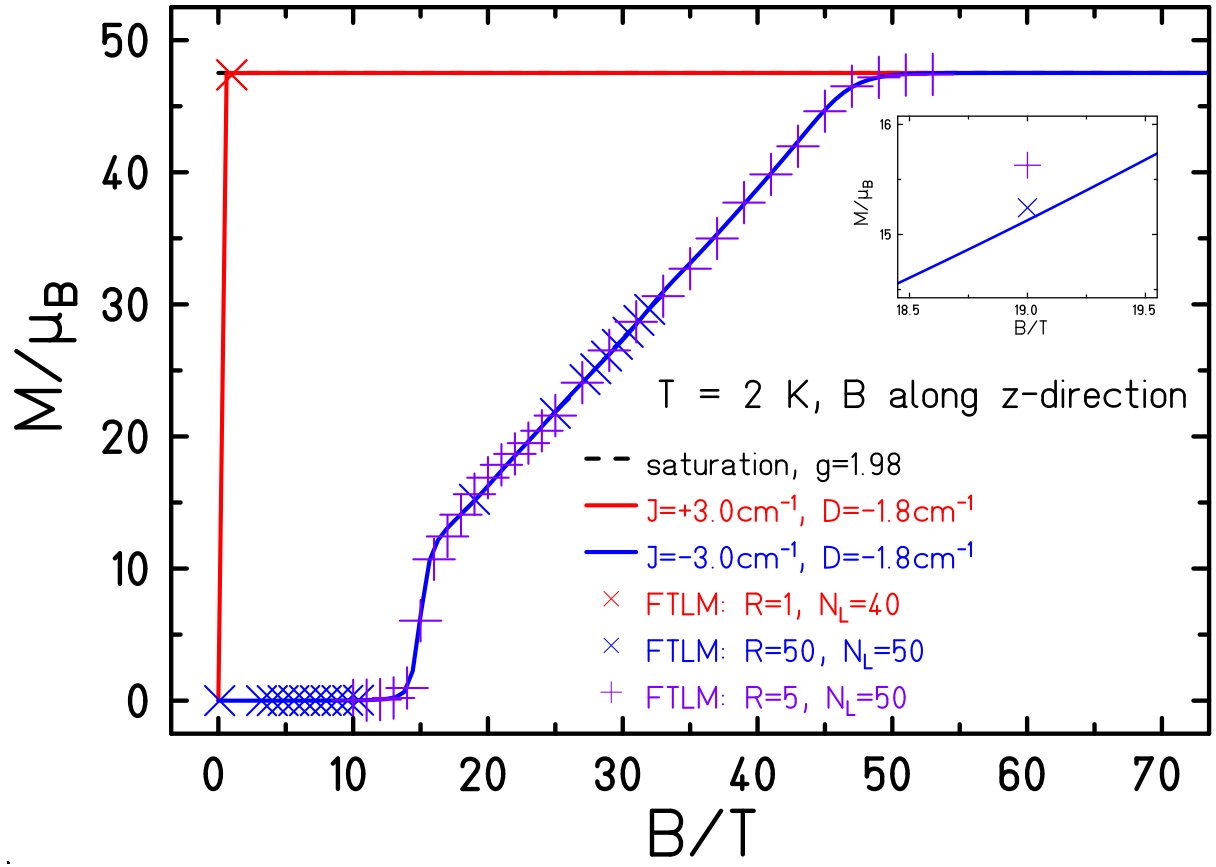
$\dim(\mathcal{H}) = 62,500$

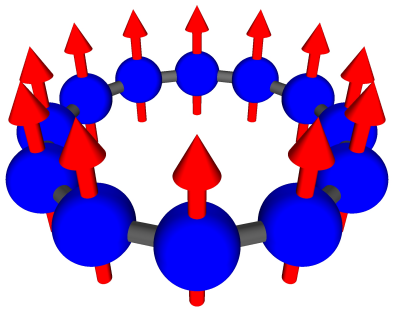
non-collinear easy axes

Hours compared to days, notebook compared to supercomputer!

O. Hanebaum, J. Schnack, submitted; arXiv:1405.3068.

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





$s = 2$

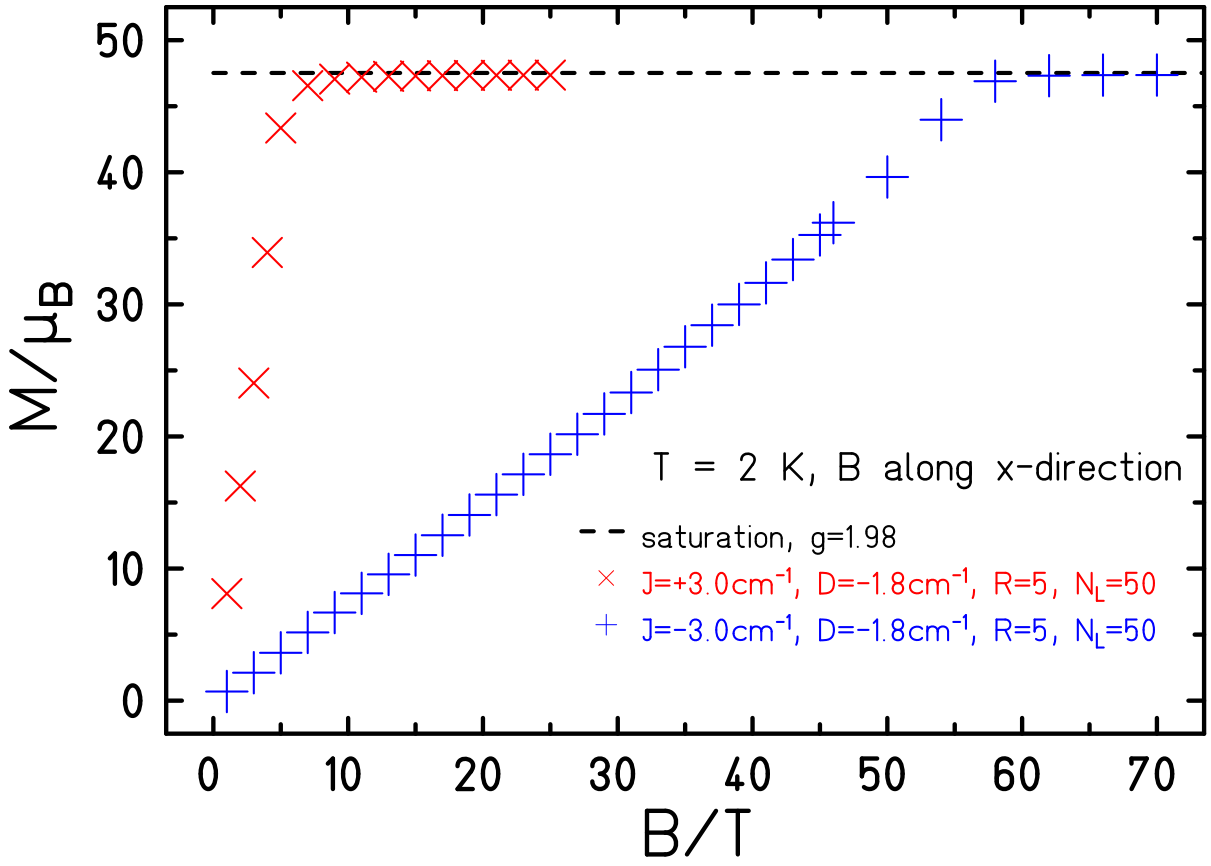
$\dim(\mathcal{H}) = 244,140,625$

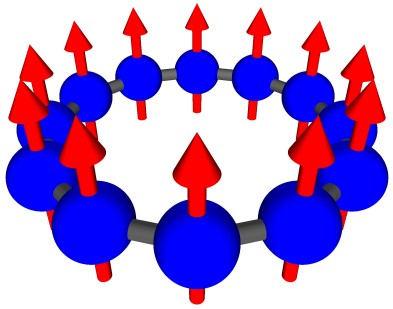
collinear easy axes

A few days compared to *impossible*!

O. Hanebaum, J. Schnack, submitted; arXiv:1405.3068.

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



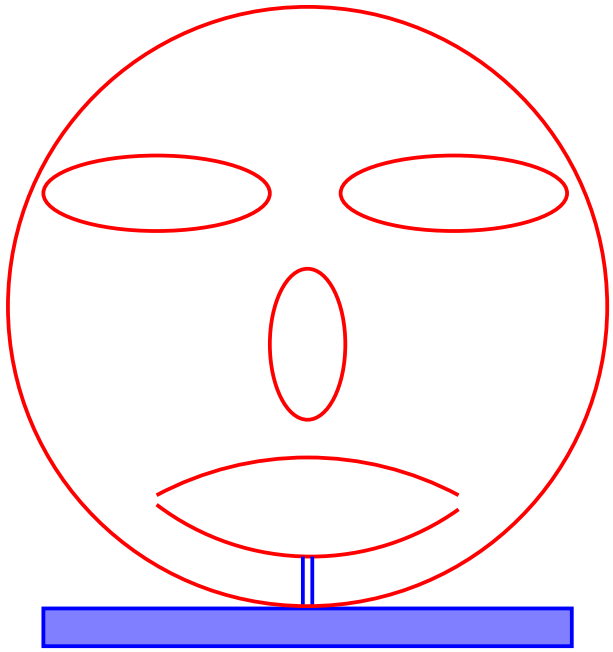


No other method can deliver these curves!

O. Hanebaum, J. Schnack, submitted; arXiv:1405.3068.

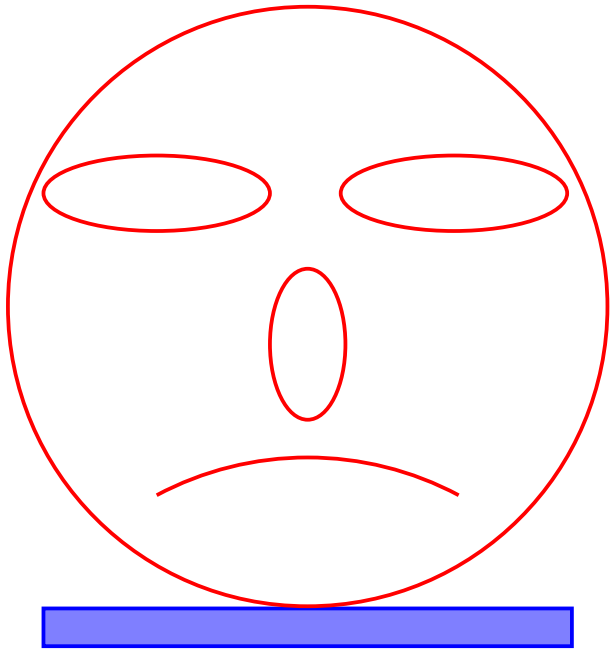
The advanced problem

You deposite a molecule I



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

You deposite a molecule II

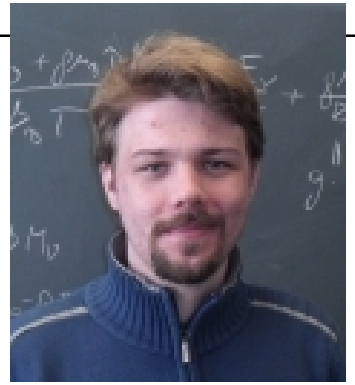


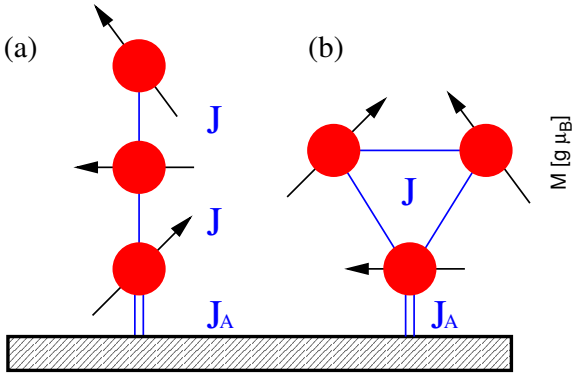
Kondo screening may improve or worsen the magnetic properties;
How does the exchange coupling to the metal influence the magnetic properties?
How to calculate such things?

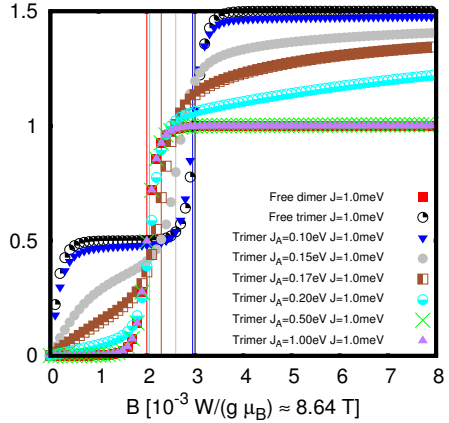
Numerical Renormalization Group calculations

(Good for deposited molecules.)

Numerical Renormalization Group (Wilson)

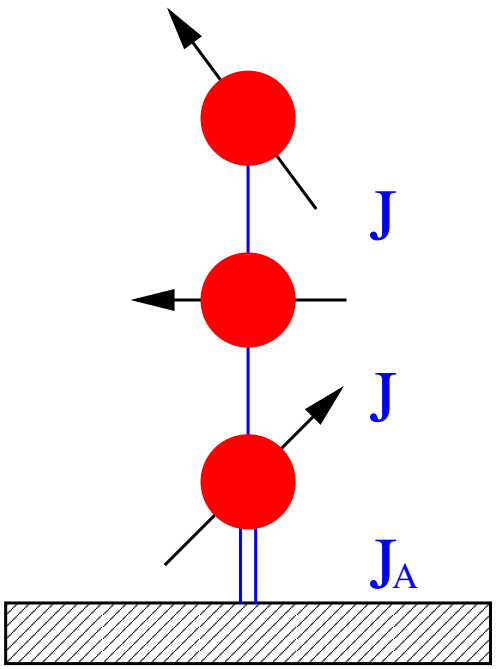






- Magnetic properties of deposited spin systems;
- Martin Höck (until 07/2013): anisotropic single spins (PRB **87**, 184408 (2013));
- Henning-Timm Langwald: deposited Heisenberg systems.

NRG – minimal model



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

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

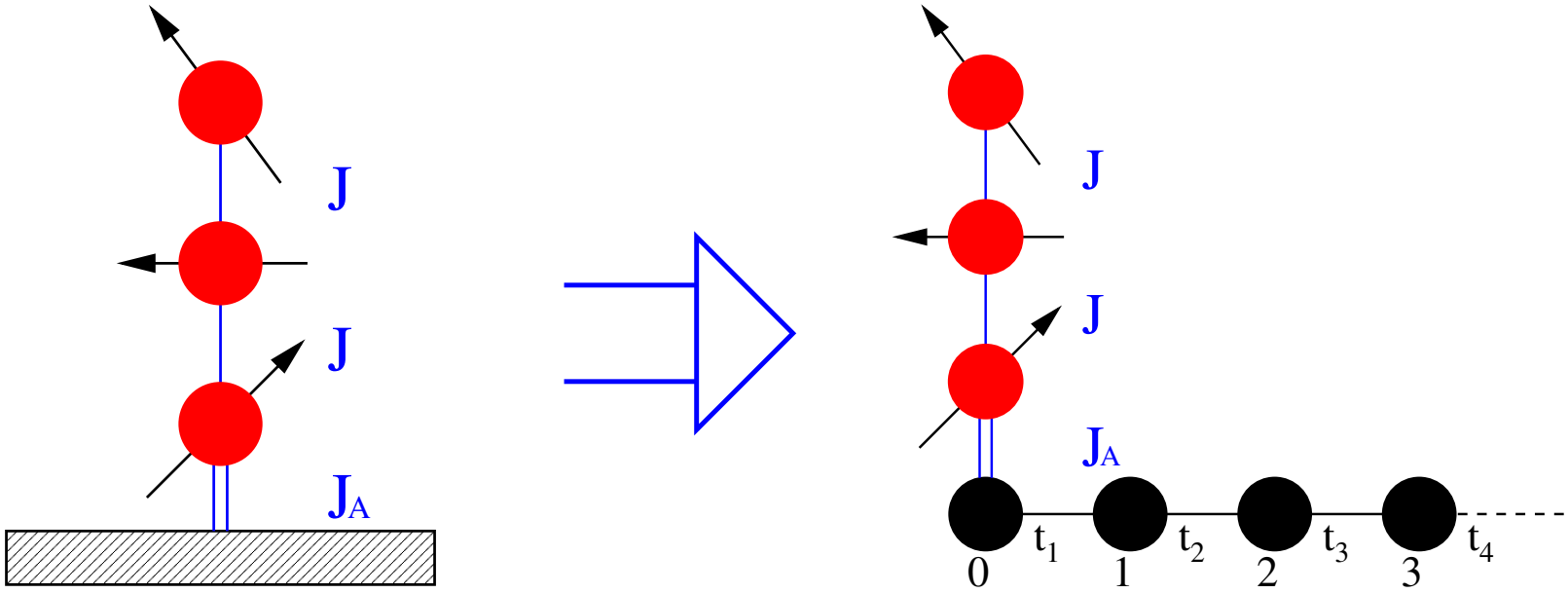
  $\underset{\sim}{H}_{\text{coupling}} = -2 J_A \underset{\sim}{\boldsymbol{S}} \cdot \underset{\sim}{\boldsymbol{s}}_0$; $\underset{\sim}{\boldsymbol{s}}_0$ – spin density at contact;

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



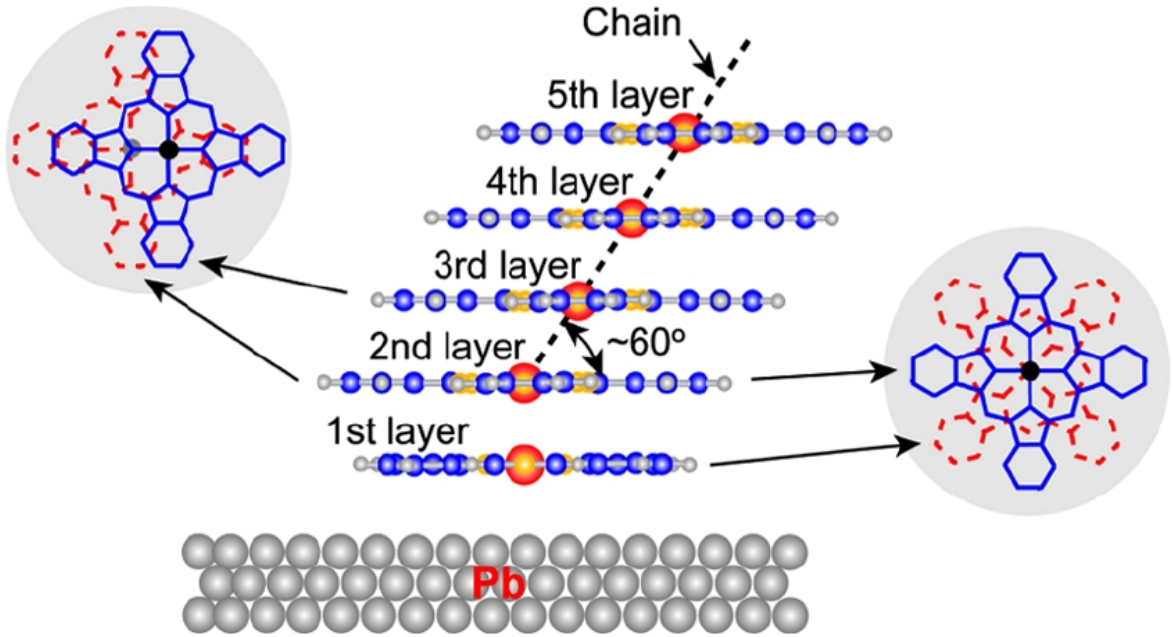
Metallic surface is replaced by semi-infinite Hubbard chain;

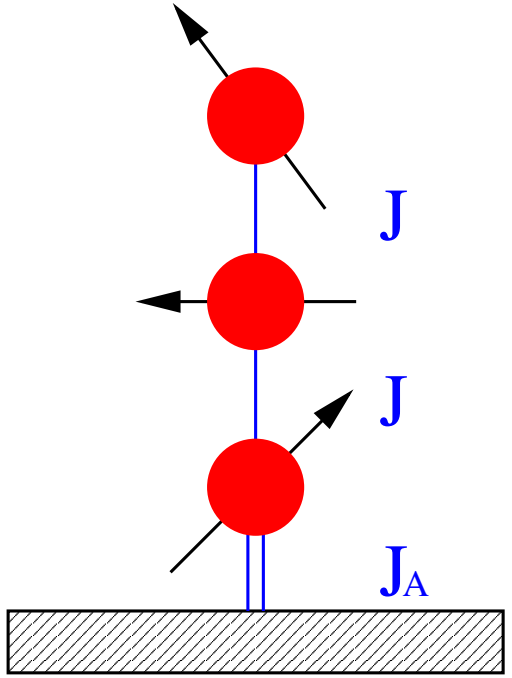
Parameters of the chain: hopping matrix elements and on-site energies;

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

Truncation of basis set when necessary.

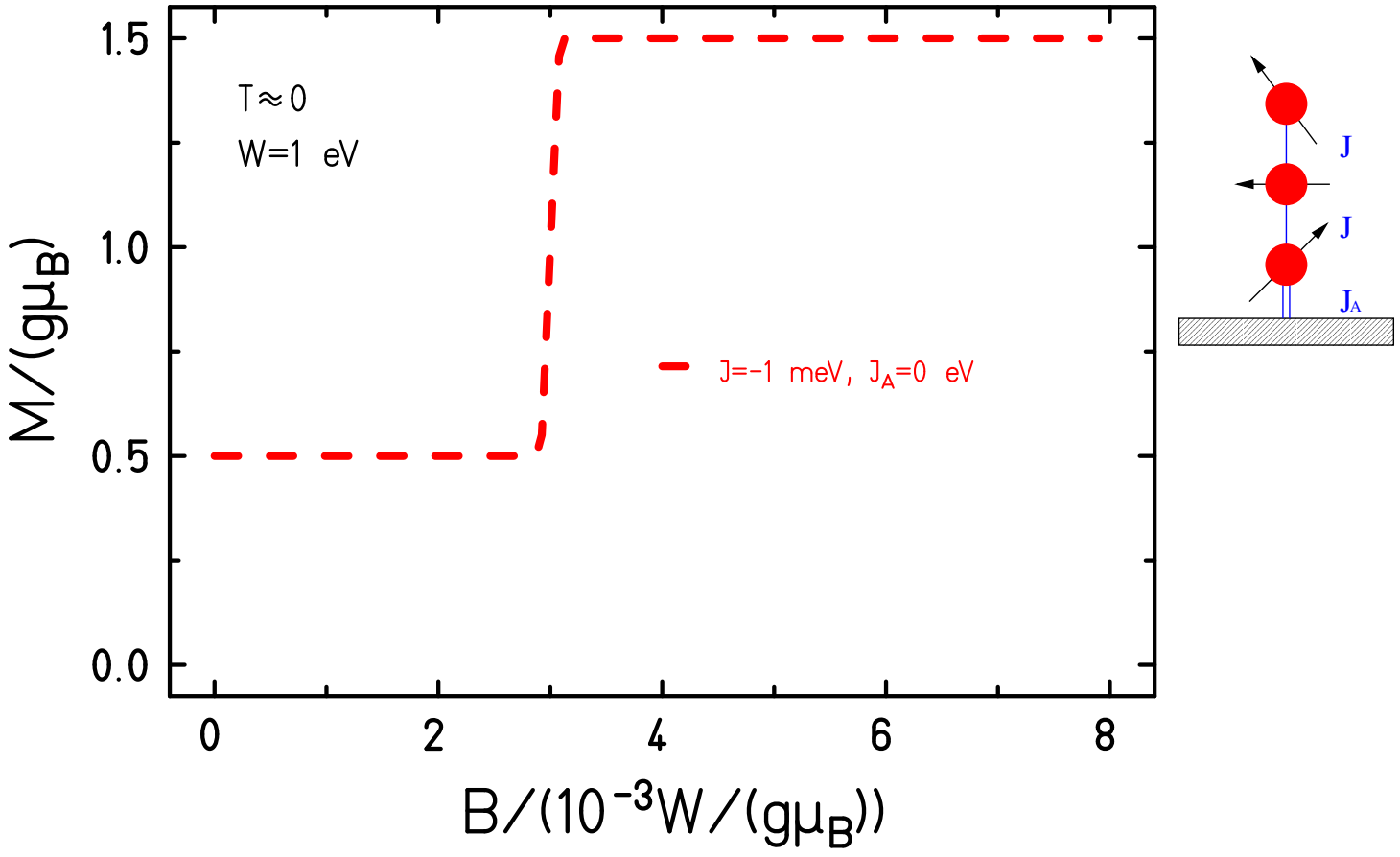
Physical example





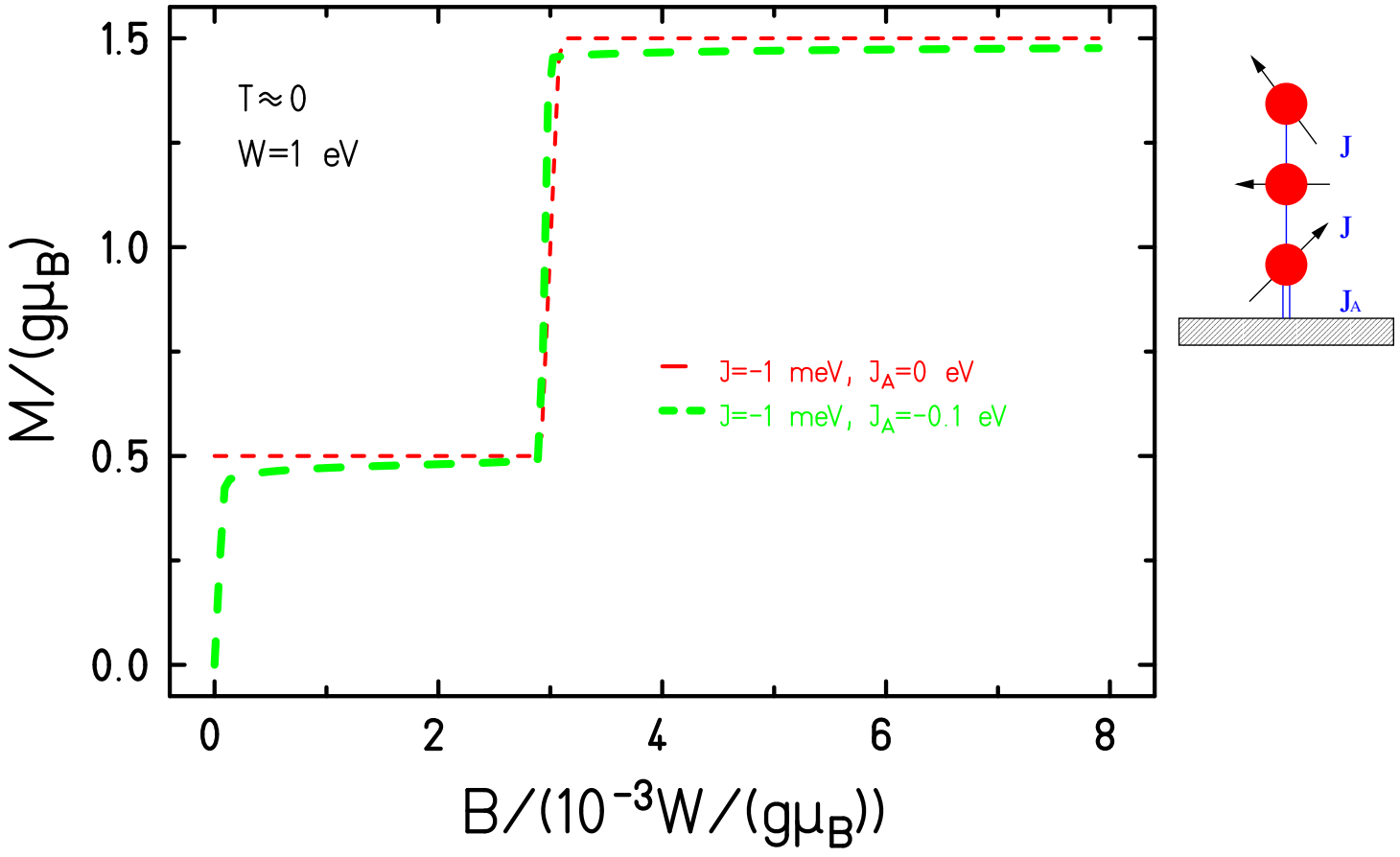
X. Chen *et al.*, Phys. Rev. Lett. **101**, 197208 (2008).

Increasing coupling to the substrate



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

Increasing coupling to the substrate



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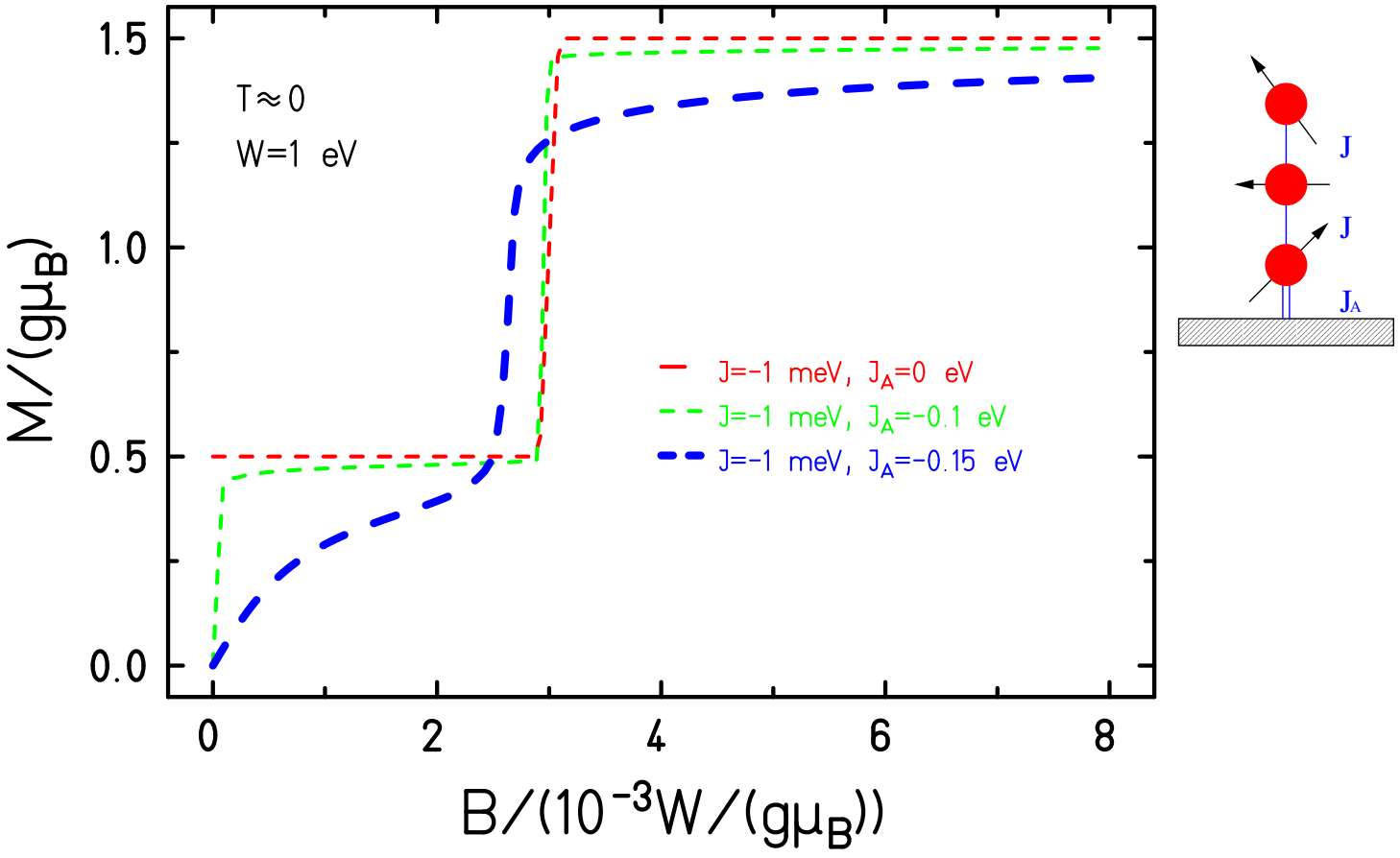
Increasing coupling to the substrate



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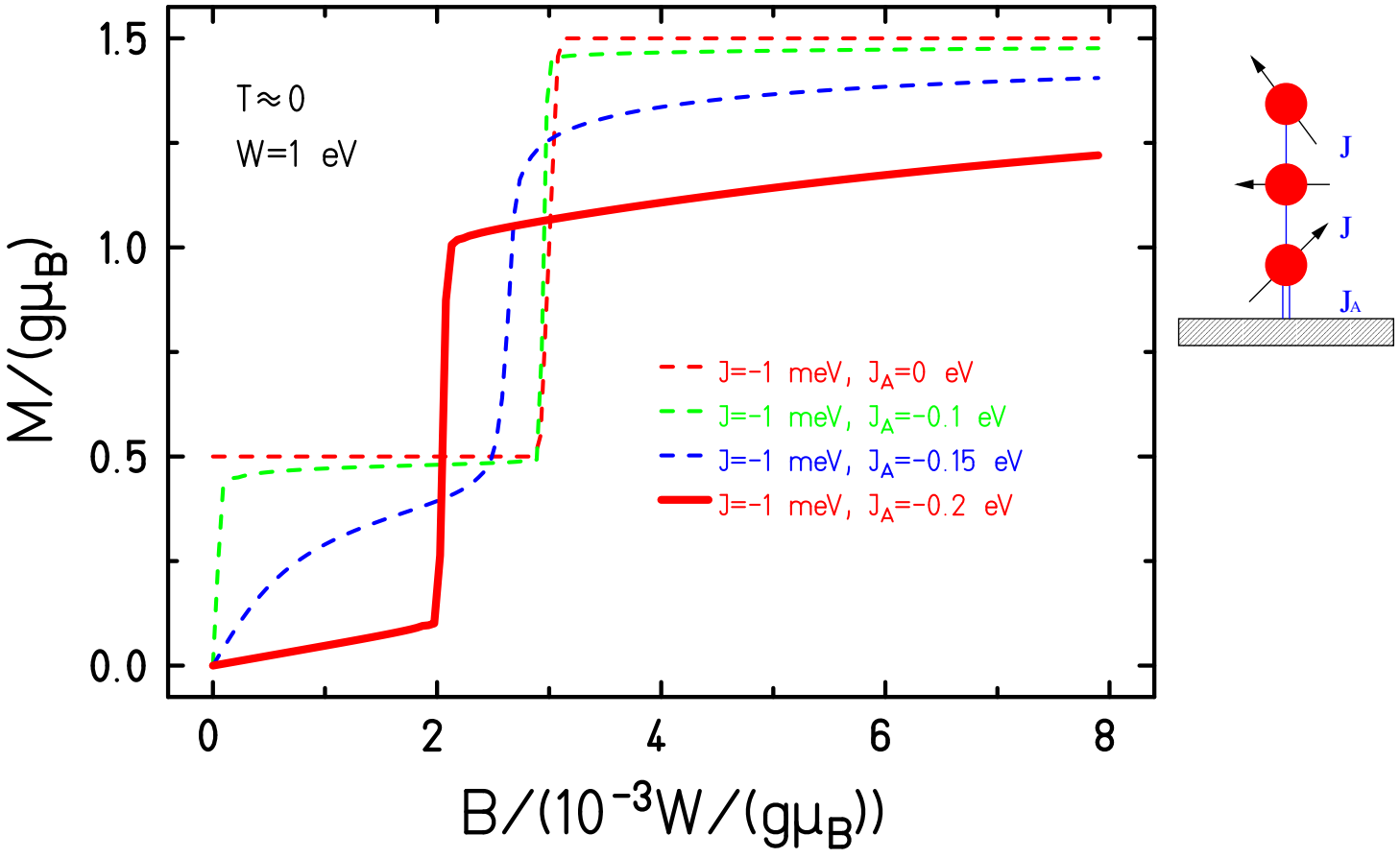
Increasing coupling to the substrate



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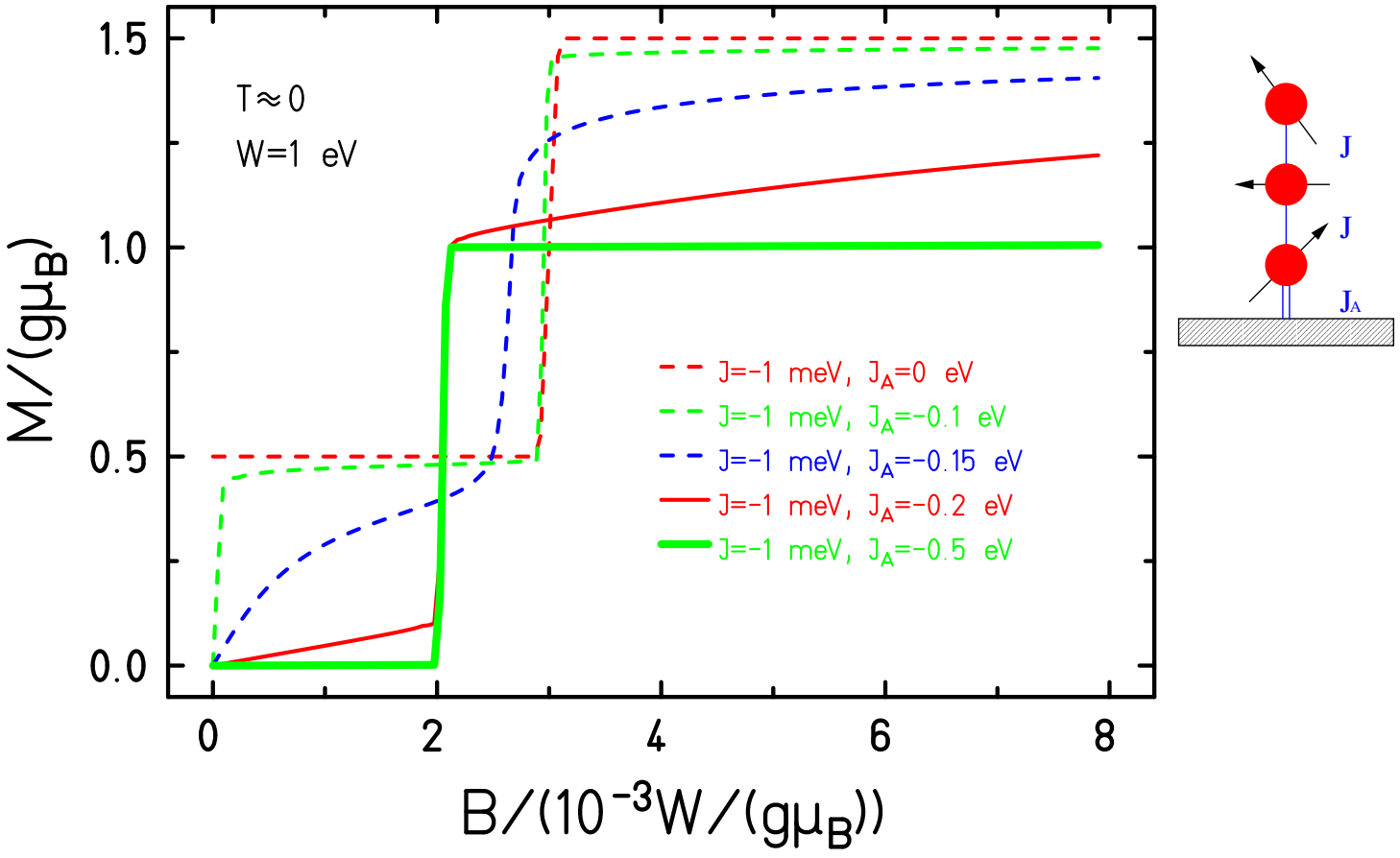
Increasing coupling to the substrate



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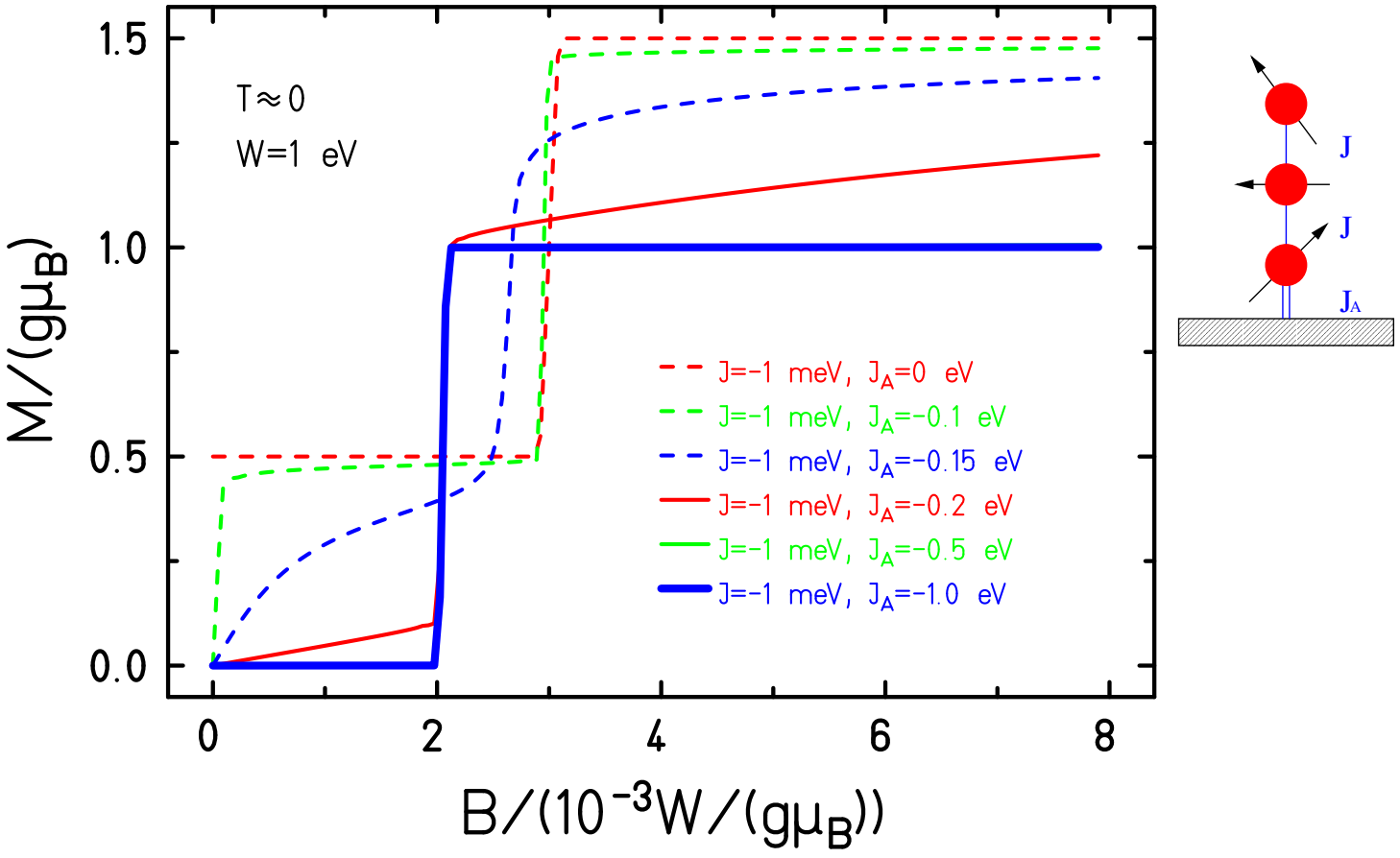
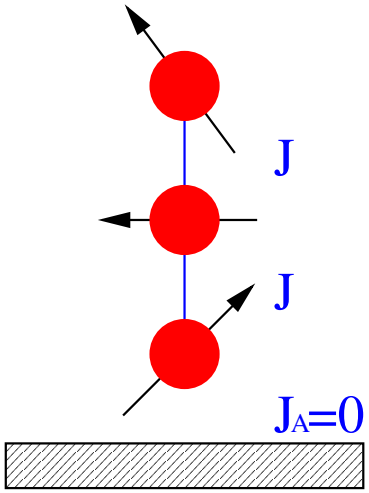
Increasing coupling to the substrate

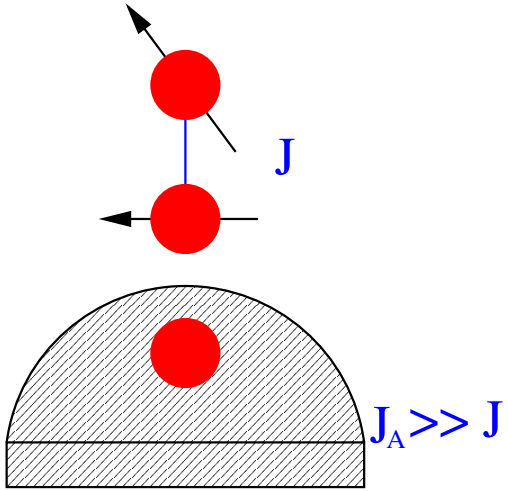


H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

Weak vs. strong coupling



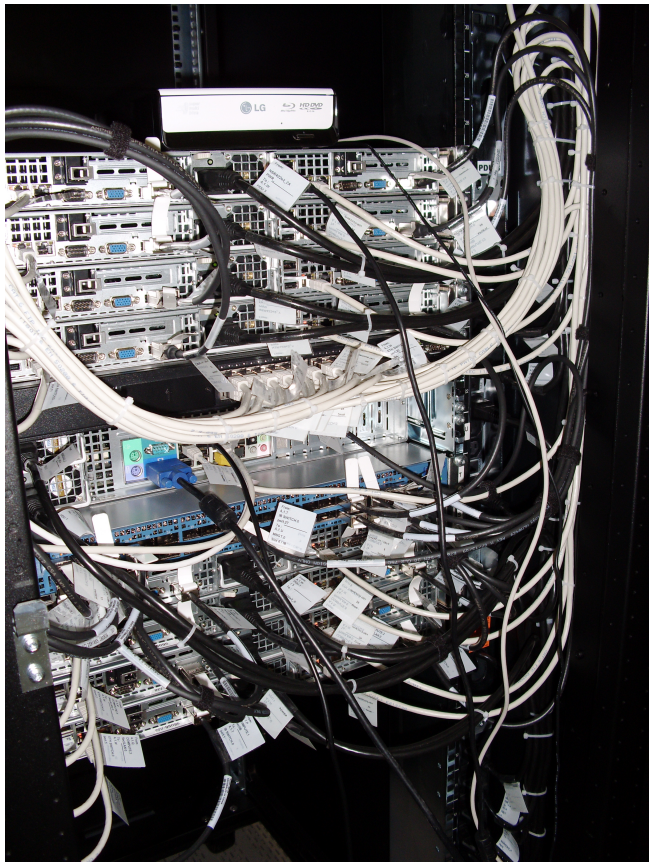
- weak coupling limit: unperturbed trimer
- $|J_A| \lessapprox 0.1W$
- no impact of the substrate



- strong coupling limit: effective dimer
- $|J_A| \gtrapprox 0.5W$
- partial screening; effective remainder

Inbetween: no simple characterization

Summary



- Exact diagonalization is great but limited.
- Finite-Temperature Lanczos is a good approximate method for Hilbert space dimensions smaller than 10^{10}.
- Magnetic molecules change their properties on metallic surfaces.
- Question: appropriate model? NRG deals with molecules that are exchange-coupled to the substrate.

Many thanks to my collaborators worldwide

- M. Czopnik, T. Glaser, O. Hanebaum, Chr. Heesing, N.B. Ivanov, F. Kaiser, H.-T. Langwald, A. Müller, Chr. Schröder (Bielefeld)
- K. Bärwinkel, H.-J. Schmidt, M. Neumann (Osnabrück)
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The end.

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