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

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Workshop on correlated electronic structure and and spin dynamics
CESSD-2015, Hamburg, 7. 5. 2015

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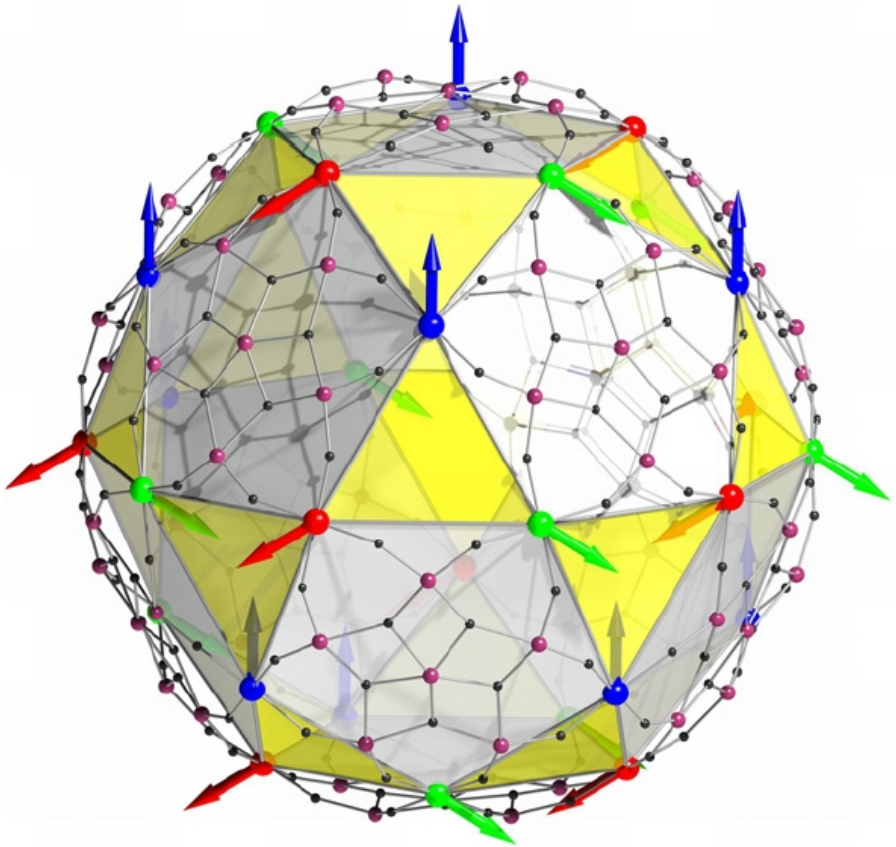
Typical challenges in molecular magnetism

Challenge 1: Highly frustrated molecules

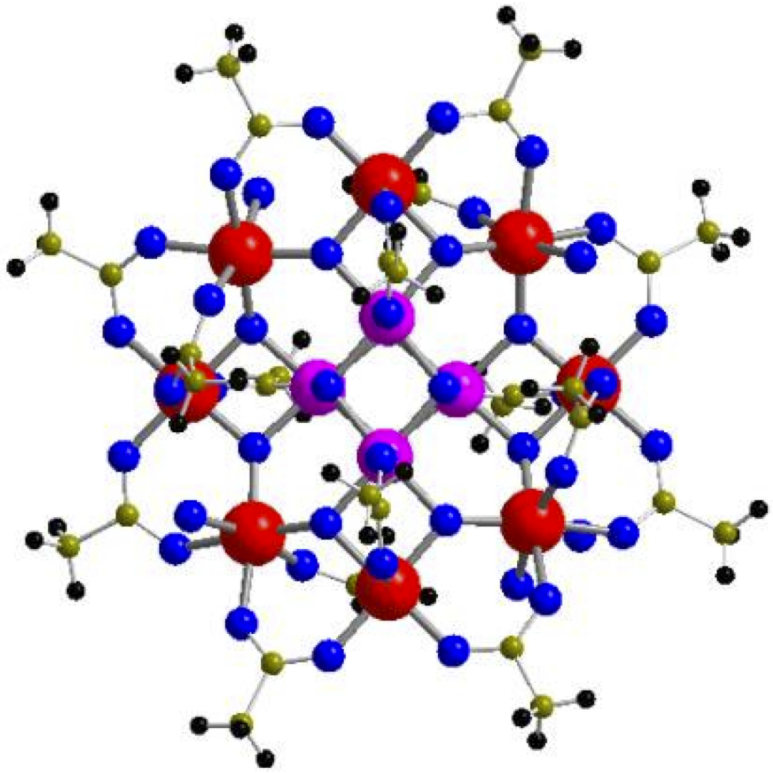


Icosidodecahedron

little brother of the Kagome

A. Müller *et al.*, Chem. Phys. Chem. **2**, 517 (2001)

Challenge 2: Complicated molecules



Molecular magnet

very anisotropic

R. Sessoli *et al.*, J. Am. Chem. Soc. **115**, 1804 (1993)

L. Thomas *et al.*, Nature **383**, 145 (1996)

Challenge 3: This talk

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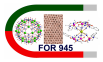
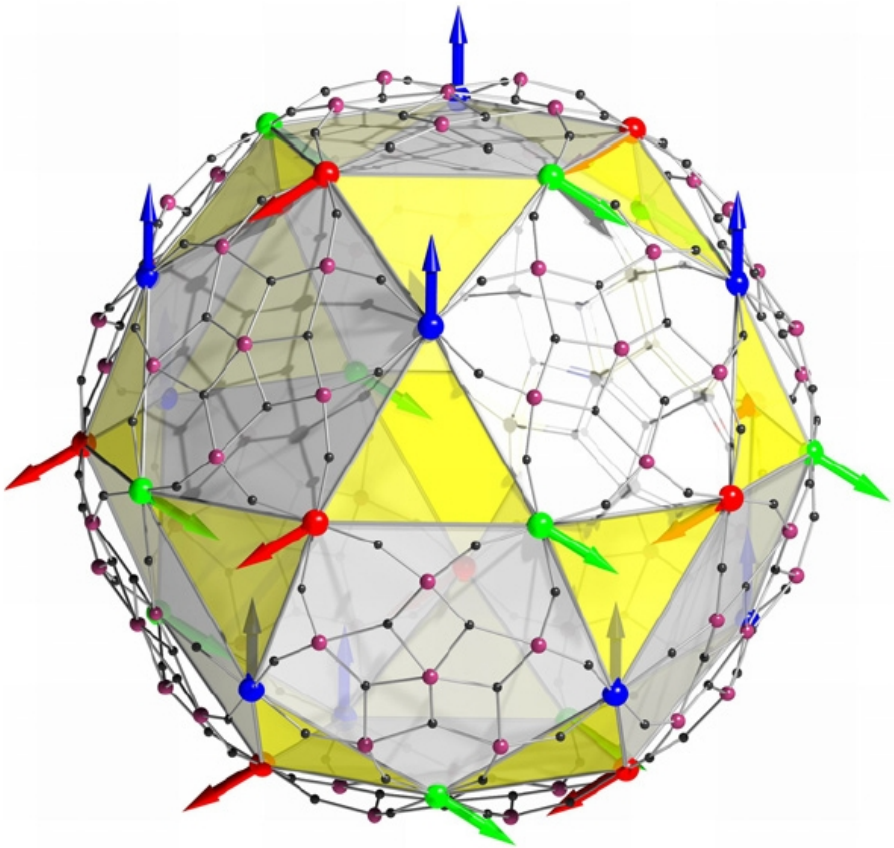


What do these challenges have in common?

60

Highly frustrated molecules



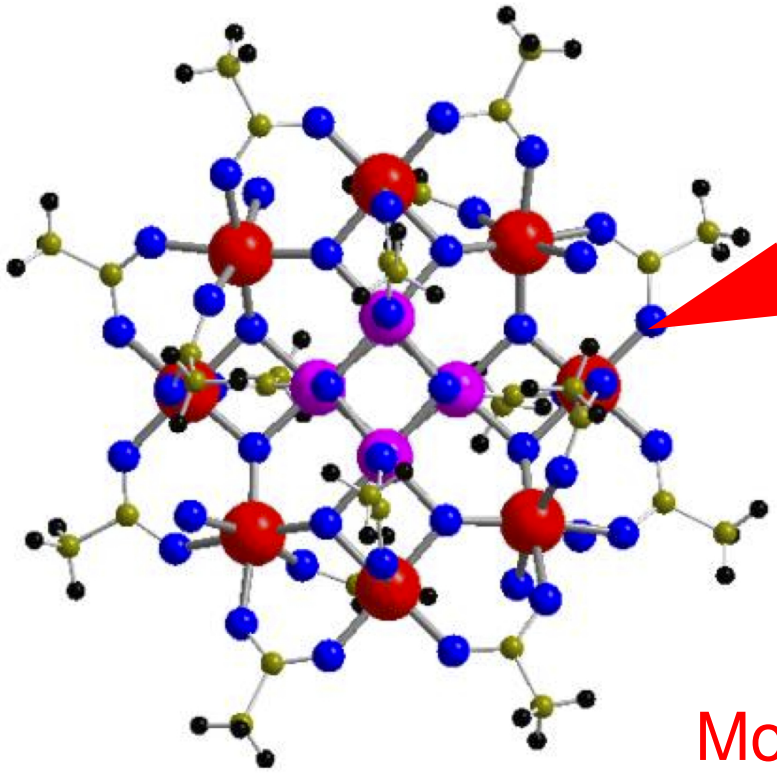
60 edges!

Independent magnons, . . .

J. Schulenburg *et al.*, Rev. Lett. **88**, 167207 (2002)

I. Rousochatzakis *et al.*, Phys. Rev. B **77**, 094420 (2008)

Complicated molecules



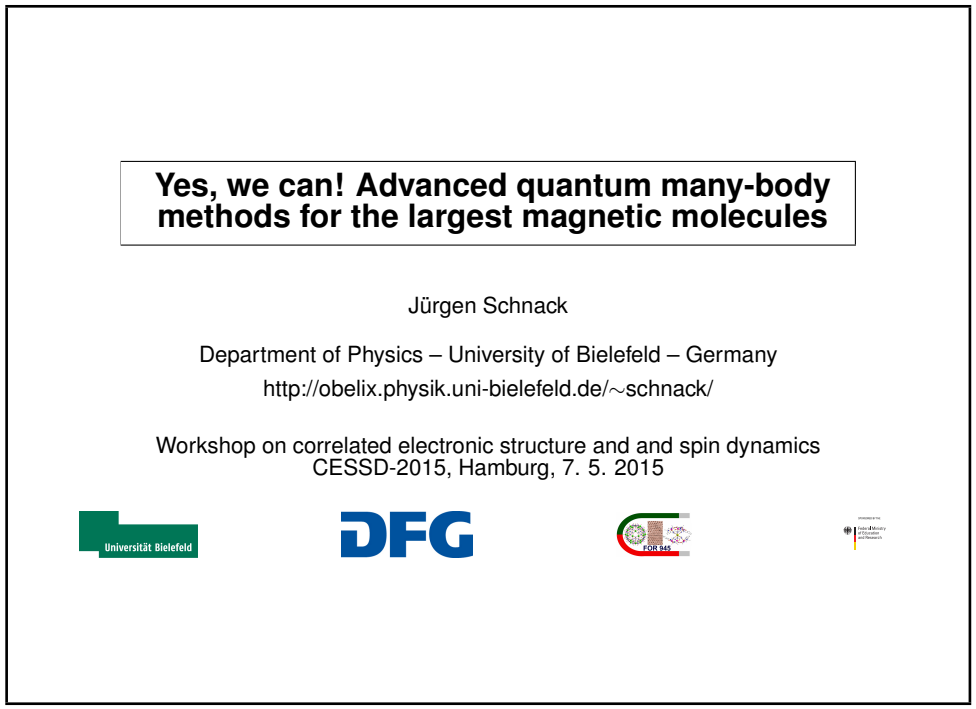
60 parameters for the spin Hamiltonian!

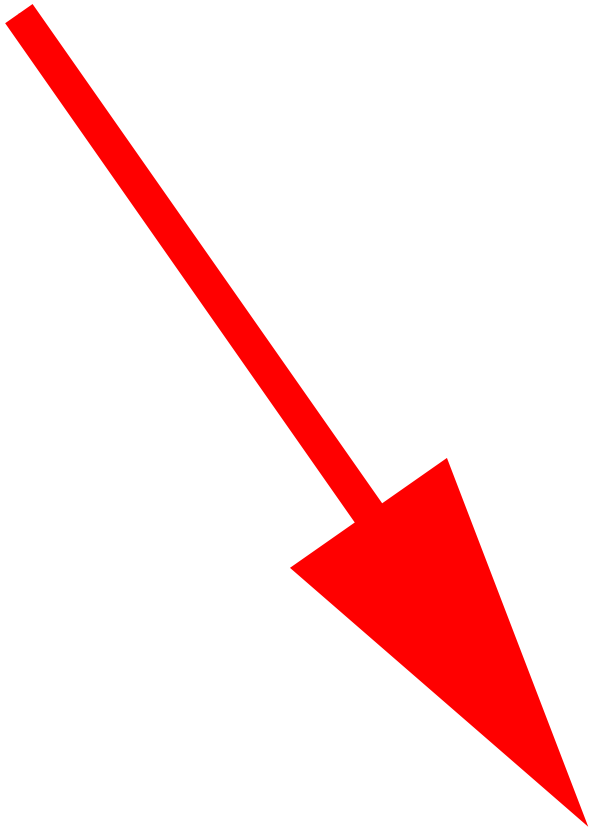
Most complete DFT parameterization ever!

V. V. Mazurenko *et al.*, Phys. Rev. B **89**, 214422 (2014)

This talk

Already 5 minutes gone
and still 60 slides to show!





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. Complete diagonalization (SU(2) & point group)
2. Finite-Temperature Lanczos
3. NRG for deposited molecules

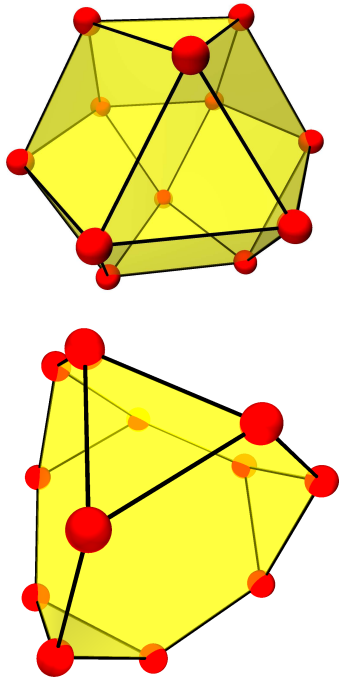
We are the sledgehammer team of matrix diagonalization.
Please send inquiries to jschnack@uni-bielefeld.de!

Complete diagonalization: SU(2) & point group symmetry

Quantum chemists need to be much smarter since they have smaller computers!

(1) D. Gatteschi and L. Pardi, Gazz. Chim. Ital. **123**, 231 (1993).
(2) J. J. Borras-Almenar, J. M. Clemente-Juan, E. Coronado, and B. S. Tsukerblat, Inorg. Chem. **38**, 6081 (1999).
(3) B. S. Tsukerblat, *Group theory in chemistry and spectroscopy: a simple guide to advanced usage*, 2nd ed. (Dover Publications, Mineola, New York, 2006).

Irreducible Tensor Operator approach



Spin rotational symmetry SU(2):

- $\underset{\sim}{H} = -2\sum_{i<j} J_{ij}\ \vec{\underset{\sim}{s}}_i \cdot \vec{\underset{\sim}{s}}_j + g\mu_B \vec{\underset{\sim}{S}} \cdot \vec{B}$;
- Physicists employ: $\left[\underset{\sim}{H}, \underset{\sim}{S}_z\right] = 0$;
- Chemists employ: $\left[\underset{\sim}{H}, \vec{\underset{\sim}{S}}^2\right] = 0$, $\left[\underset{\sim}{H}, \underset{\sim}{S}_z\right] = 0$;

  Irreducible Tensor Operator (ITO) approach;
  Free program MAGPACK (2) available.

(1) D. Gatteschi and L. Pardi, Gazz. Chim. Ital. **123**, 231 (1993).
(2) J. J. Borras-Almenar, J. M. Clemente-Juan, E. Coronado, and B. S. Tsukerblat, Inorg. Chem. **38**, 6081 (1999).
(3) B. S. Tsukerblat, *Group theory in chemistry and spectroscopy: a simple guide to advanced usage*, 2nd ed. (Dover Publications, Mineola, New York, 2006).

Idea of Irreducible Tensor Operator approach

$$
\begin{aligned}
\underset{\sim}{H}_{\text{Heisenberg}} &= -2\sum_{i<j} J_{ij}\ \underset{\sim}{\vec{s}}_i \cdot \underset{\sim}{\vec{s}}_j \\
&= 2\sqrt{3}\sum_{i<j} J_{ij}\ \underset{\sim}{T}^{(0)}(\{k_i\},\{\overline{k}_i\}|k_i = k_j = 1)
\end{aligned}
$$

- Express spin operators and functions thereof as ITOs;
- Use vector coupling basis $|\,\alpha\ S\ M\,\rangle$ and recursive recoupling (Wigner-Eckart);
- Never ever write down the wave function with CG coefficients!

(1) Gatteschi, Tsukerblat, Coronado, Waldmann, ...
(2) R. Schnalle, Ph.D. thesis, Osnabrück University (2009)

Point Group Symmetry

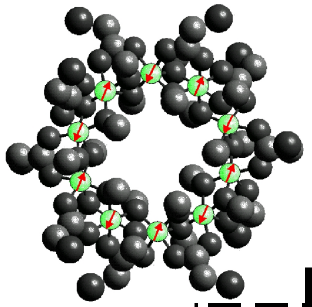
$$|\,\alpha'\,S\,M\,\Gamma\,\rangle = \mathcal{P}^{(\Gamma)}\,|\,\alpha\,S\,M\,\rangle = \left(\frac{l_\Gamma}{h}\sum_R \left(\chi^{(\Gamma)}(R)\right)^*\,\underset{\sim}{G}(R)\right)\,|\,\alpha\,S\,M\,\rangle$$

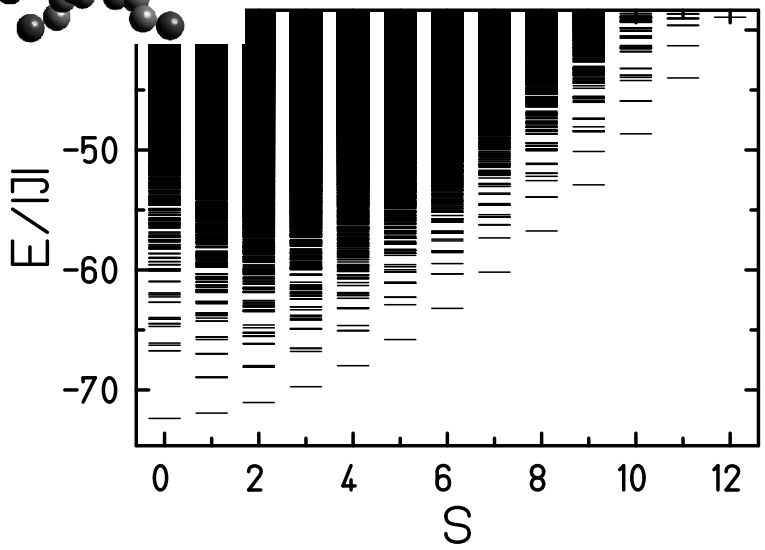
Method:

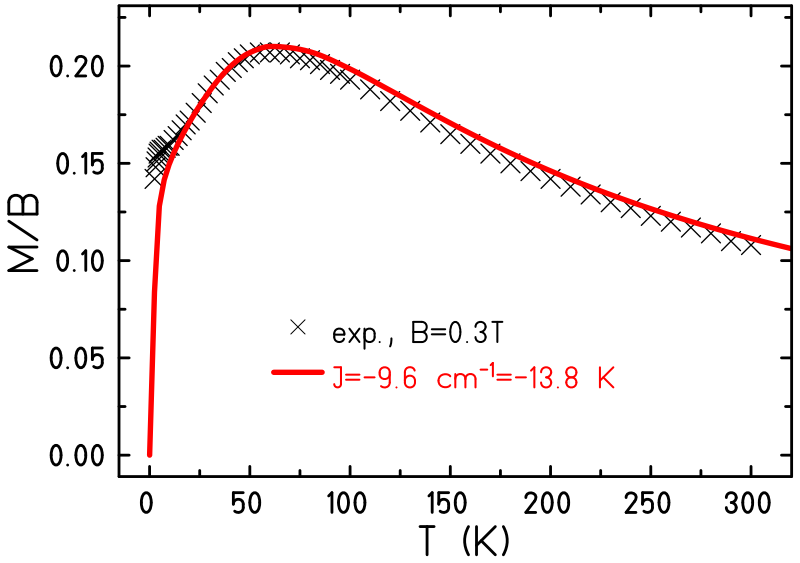
- Projection onto irreducible representations Γ of the point group (1,2);
- No free program, things are a bit complicated (3,4).

(1) M. Tinkham, *Group Theory and Quantum Mechanics*, Dover.
(2) D. Gatteschi and L. Pardi, Gazz. Chim. Ital. **123**, 231 (1993).
(3) O. Waldmann, Phys. Rev. B **61**, 6138 (2000).
(4) R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403-452 (2010) $\Leftarrow$ contains EVERYTHING.

Example: Fe_{10} – SU(2) & D_2

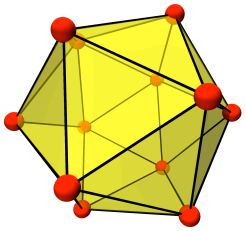




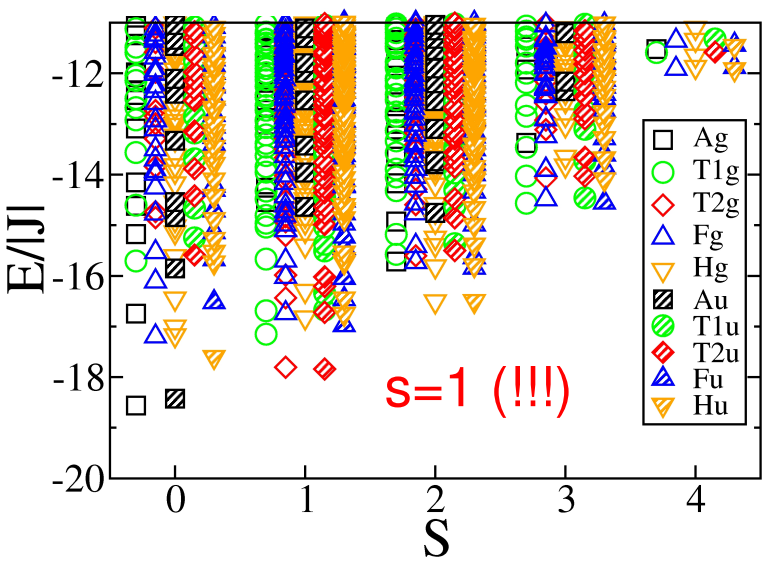


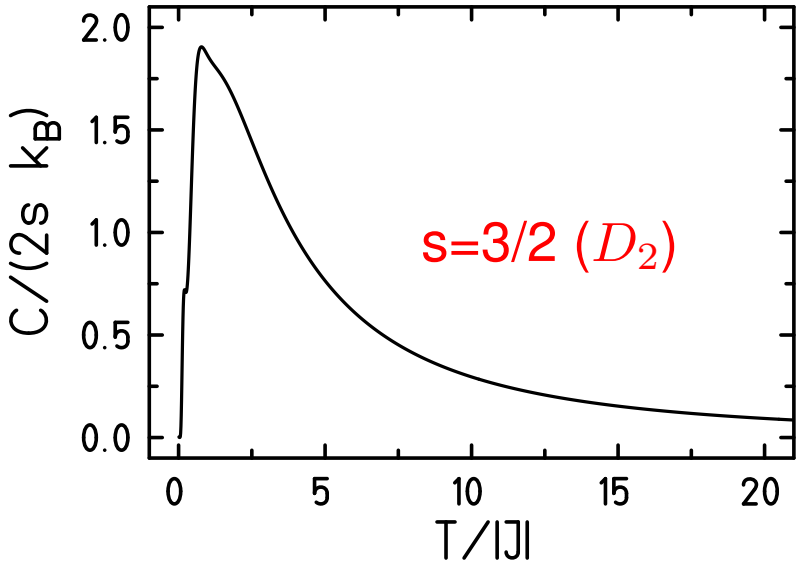
Spin ring, $N = 10$, $s = 5/2$, Hilbert space dimension 60,466,176; symmetry D_2 (1).

(1) R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403-452 (2010).
(2) C. Delfs *et al.*, Inorg. Chem. **32**, 3099 (1993).



Example: Icosahedron – SU(2) & I_h





Icosahedron, $s = 3/2$, Hilbert space dimension 16,777,216; symmetry I_h;
Evaluation of recoupling coefficients for $s = 3/2$ in I_h **practically impossible** (1).

(1) R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403-452 (2010).

World-leading, but . . .

This world-leading method was developed in Osnabrück, unfortunately . . .

World-leading, but . . .

. . . too late!
There are more powerful and easy to program methods.

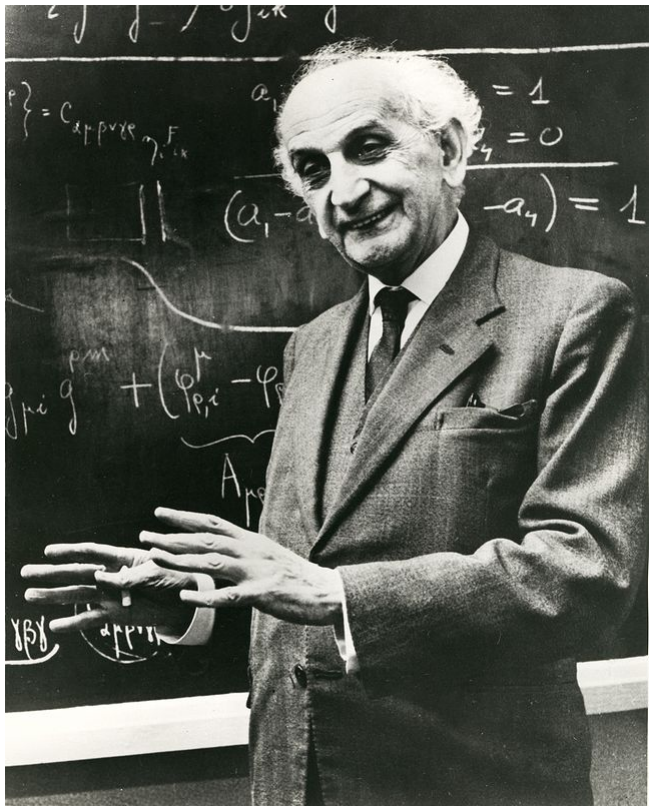
Nevertheless, matrix theory goes on . . .

. . . at the Hessische Landesbank!

Finite-temperature Lanczos Method

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

Lanczos – a Krylov space method



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

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

Finite-temperature Lanczos Method I

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

- $|\, n(\nu)\,\rangle$ 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).

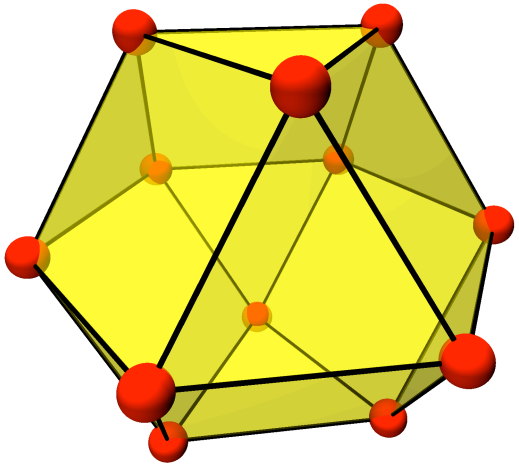
Finite-temperature Lanczos Method II

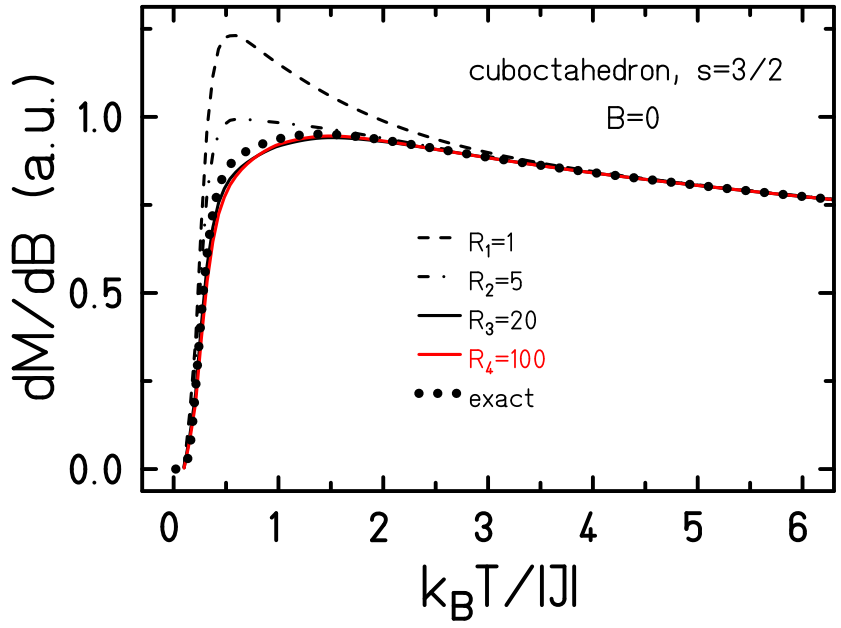
$$Z(T,B) \approx \sum_{\Gamma} \frac{\dim(\mathcal{H}(\Gamma))}{R_\Gamma} \sum_{\nu=1}^{R_\Gamma} \sum_{n=1}^{N_L} \exp\{-\beta\epsilon_n\} \left|\langle\, n(\nu,\Gamma) \,|\, \nu,\Gamma \,\rangle\right|^2$$

- Approximation better if symmetries taken into account.
- Γ denotes the used irreducible representations.

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

How good is finite-temperature Lanczos?

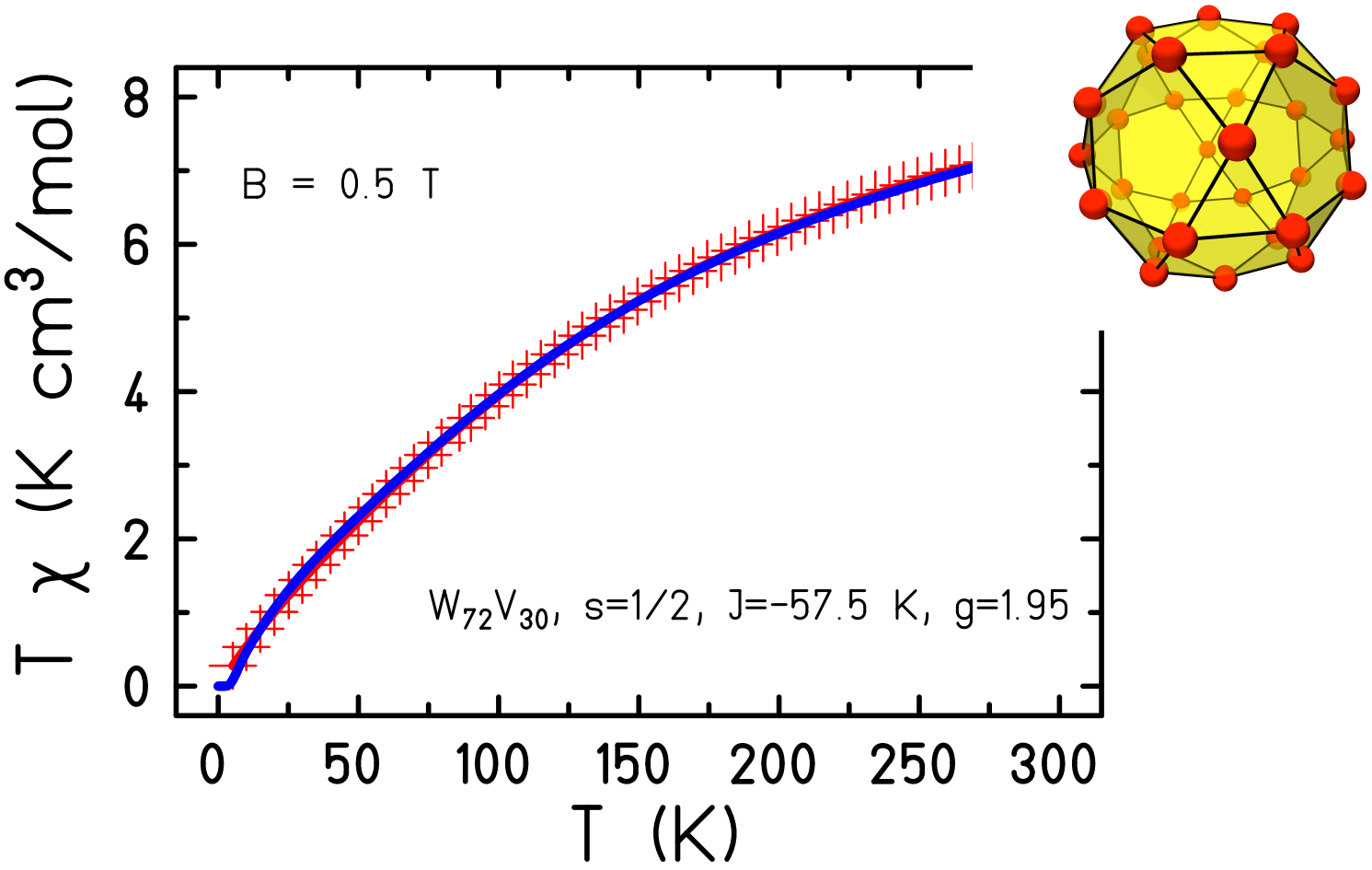




- Works very well: compare frustrated cuboctahedron.
- $N = 12, s = 3/2$: Considered $< 100,000$ states instead of 16,777,216.

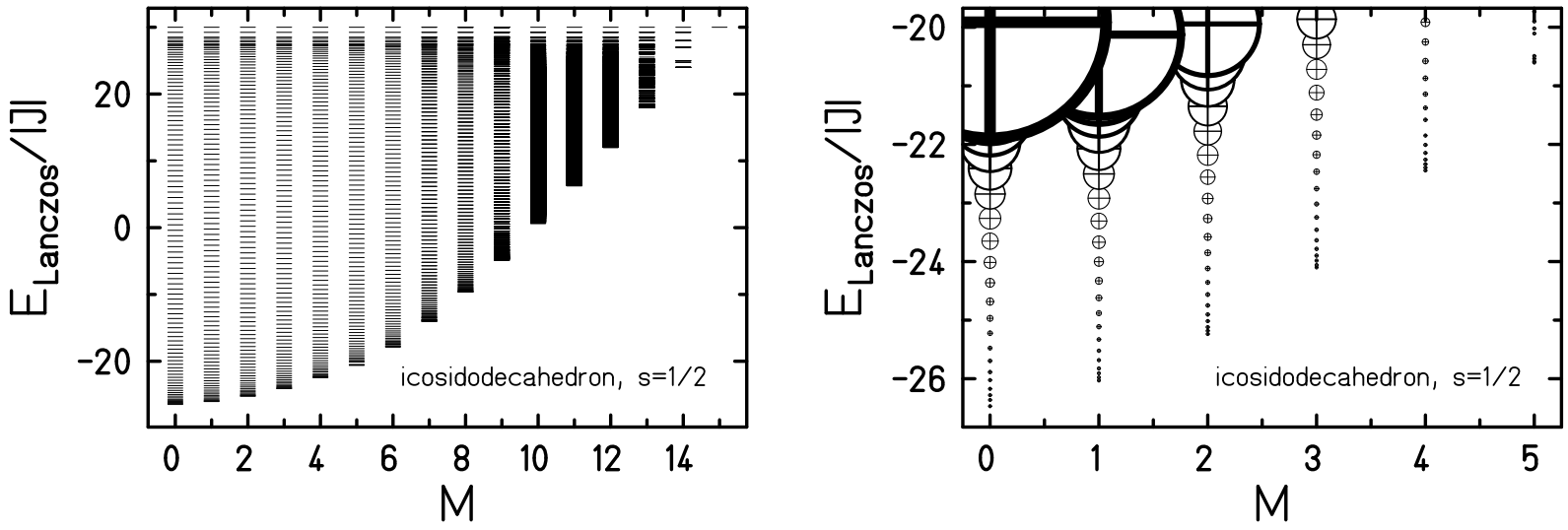
Exact results: R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403-452 (2010).
FTLM: J. Schnack and O. Wendland, Eur. Phys. J. B **78**, 535-541 (2010).

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.

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

Finite-temperature Lanczos Method III

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

- Problem: for anisotropic Hamiltonians no symmetry left
  $\rightarrow$ accuracy drops (esp. for high T).
- Simple traces such as Tr $\left(\underset{\sim}{S}^z\right) = 0$ tend to be wrong for R not very big.

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

Finite-temperature Lanczos Method IV

Employ very general symmetry (time-reversal invariance)

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

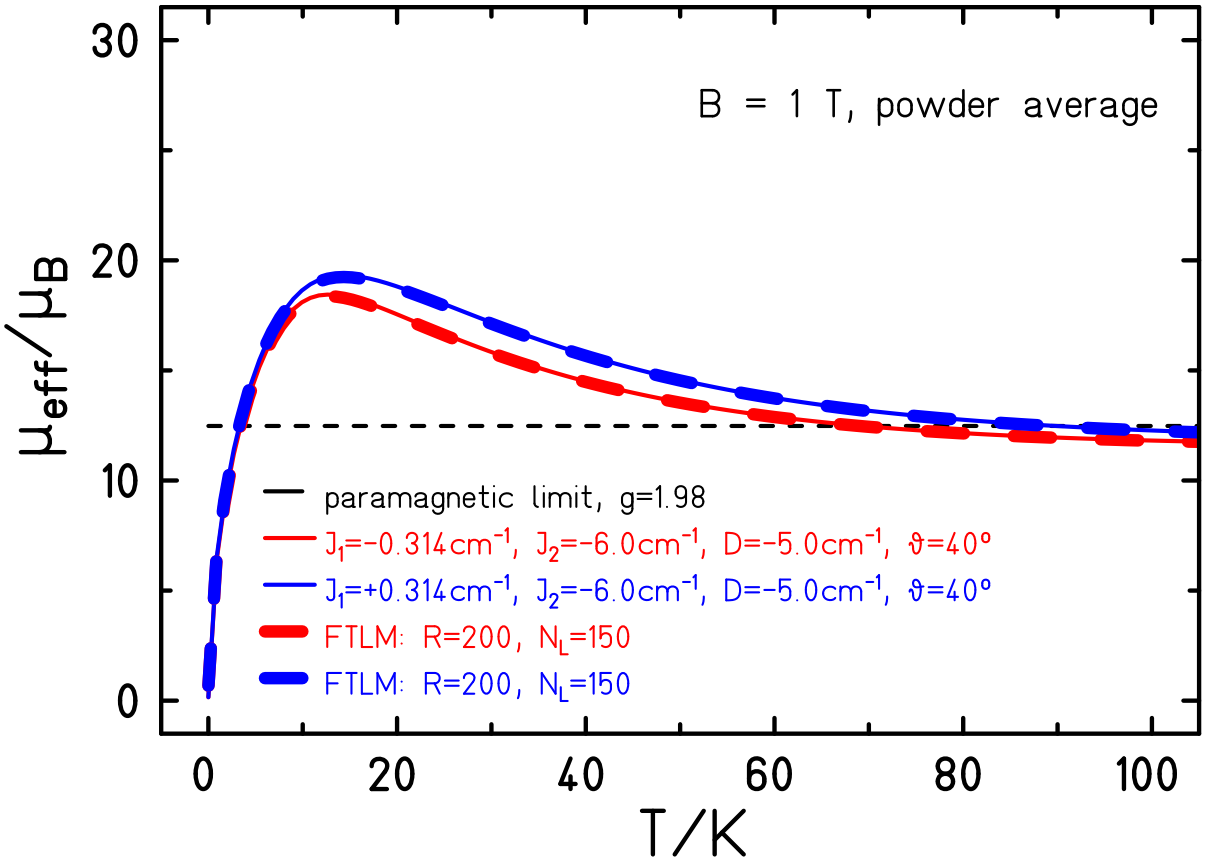
Use Lanczos energy eigenvector $|\,n(\nu)\,\rangle$ and time-reversed counterpart $|\,\tilde{n}(\nu)\,\rangle$

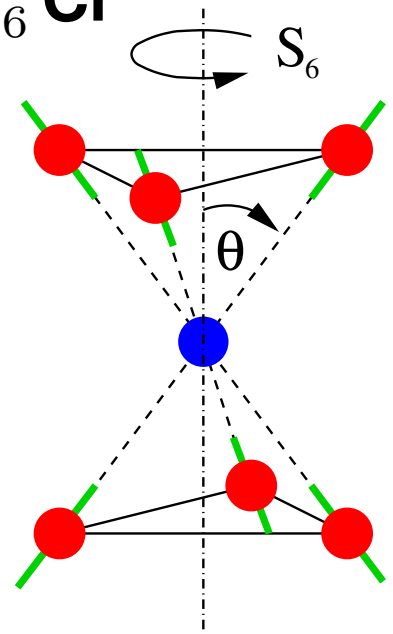
$$|\,n(\nu)\,\rangle = \sum_{\vec{m}} c_{\vec{m}}\,|\,\vec{m}\,\rangle \quad uad, \quad |\,\tilde{n}(\nu)\,\rangle = \sum_{\vec{m}} c^*_{\vec{m}}\,|\,-\vec{m}\,\rangle$$

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





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

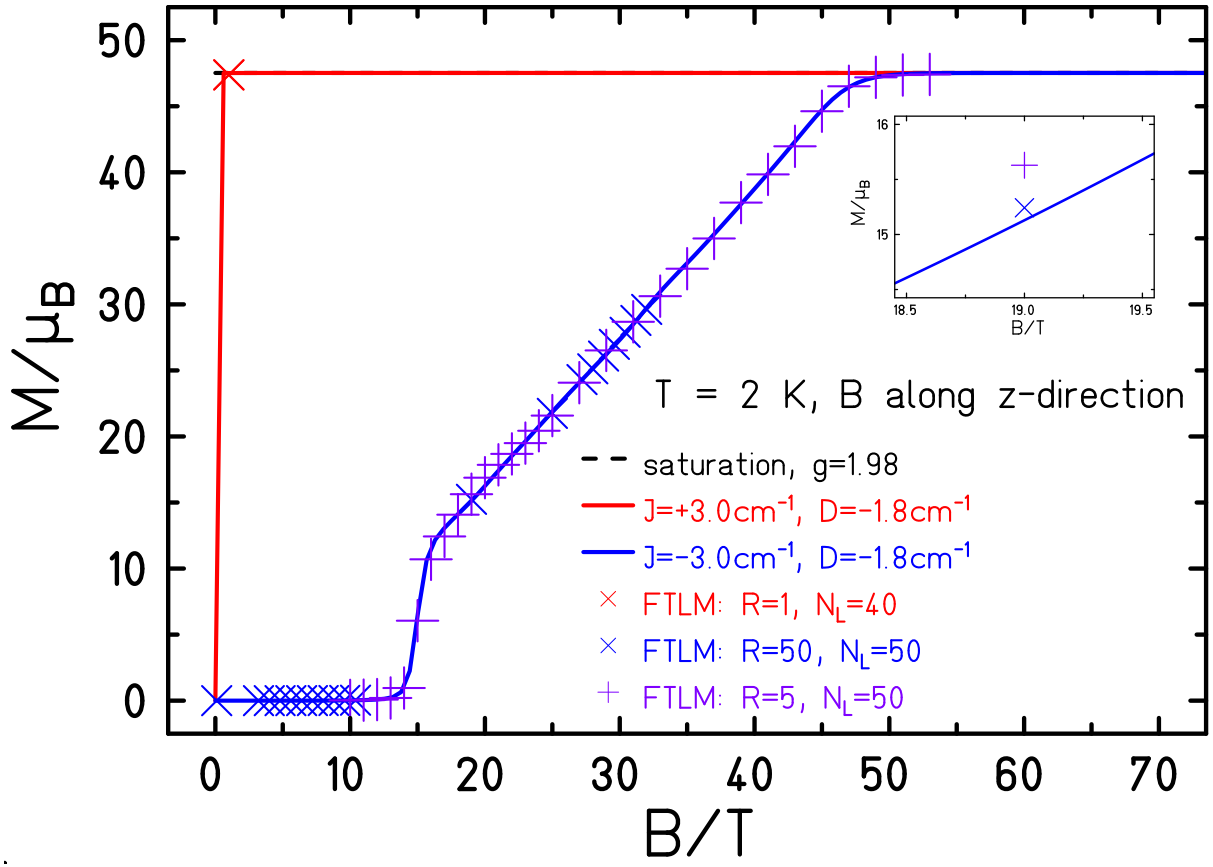
$\dim(\mathcal{H}) = 62,500$

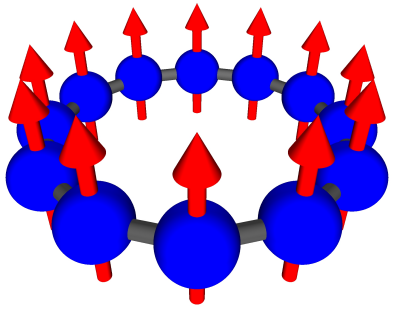
non-collinear easy axes

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





$s = 2$

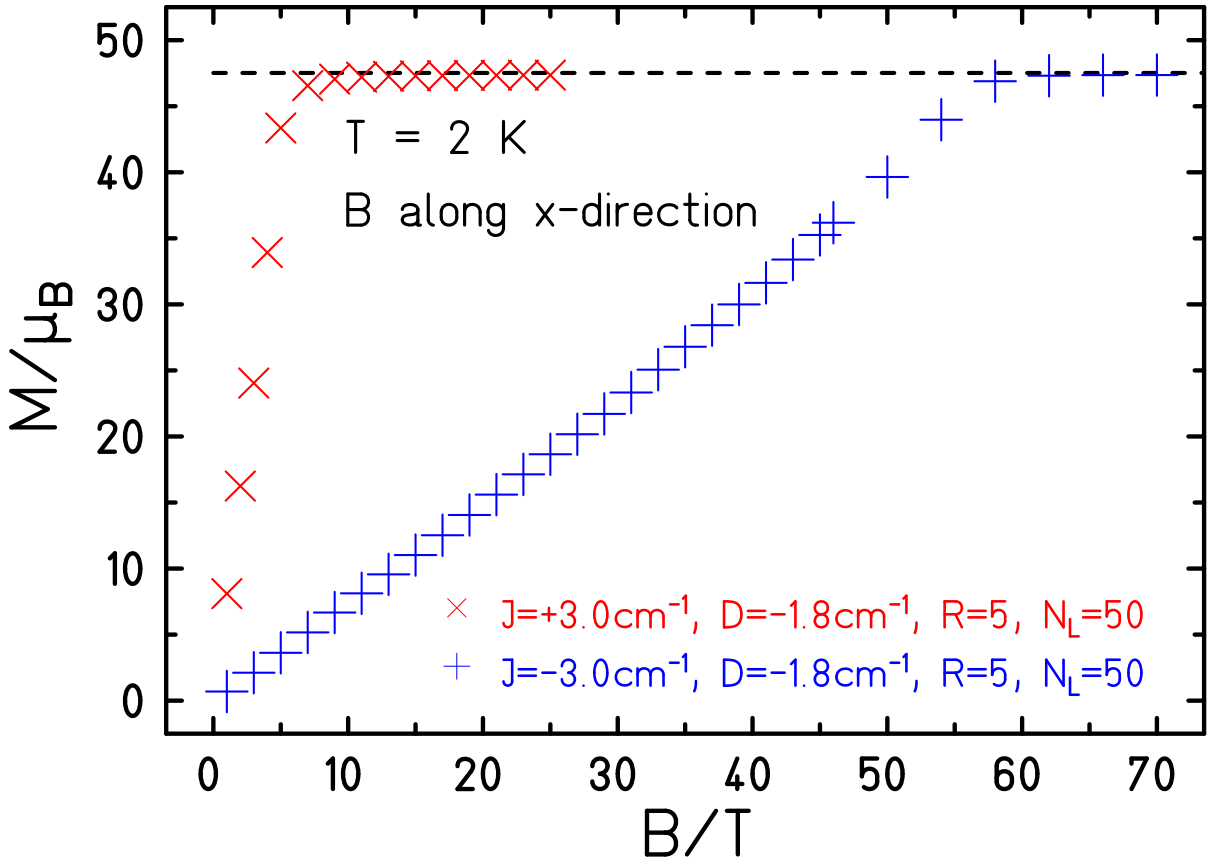
$\dim(\mathcal{H}) = 244,140,625$

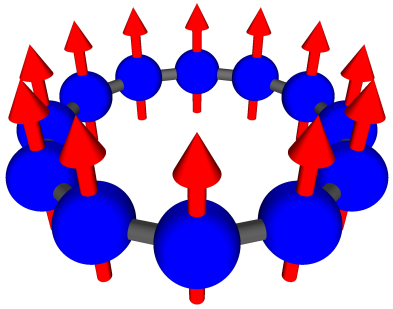
collinear easy axes

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

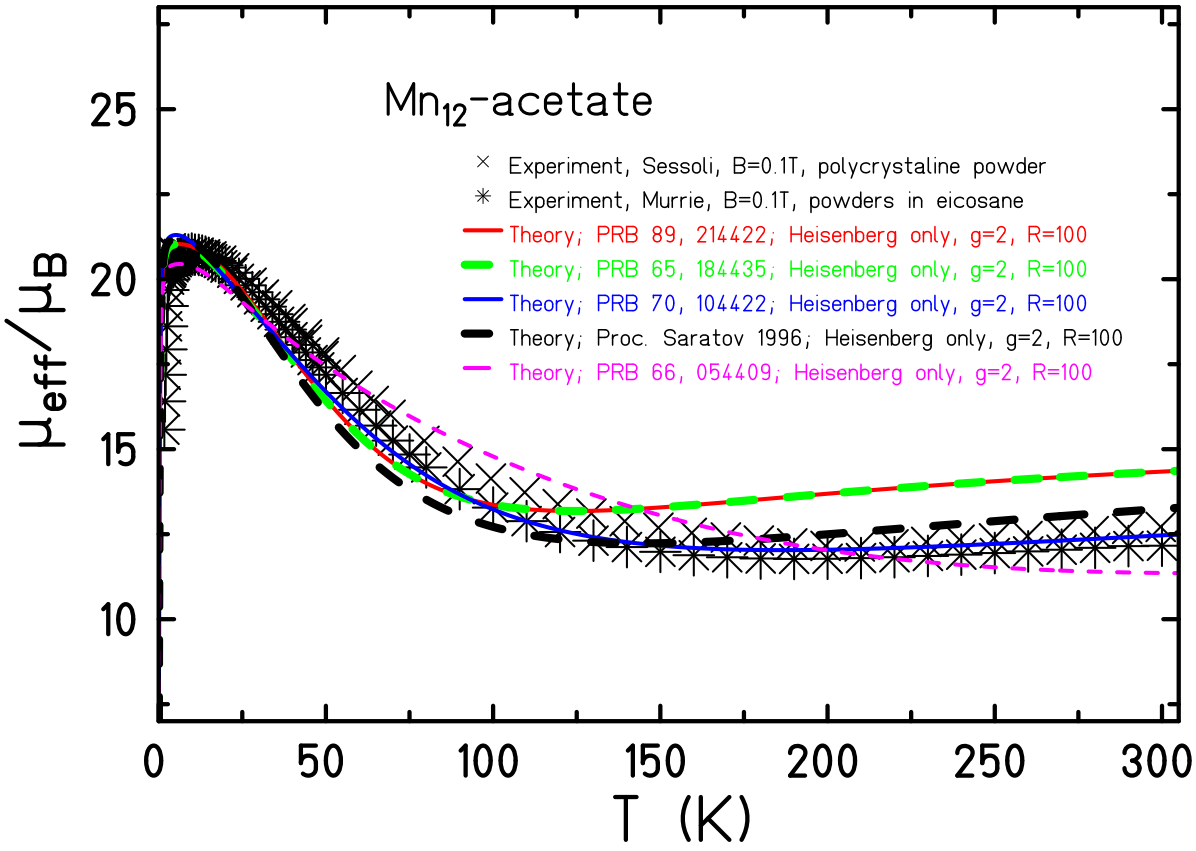




No other method can deliver these curves!

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

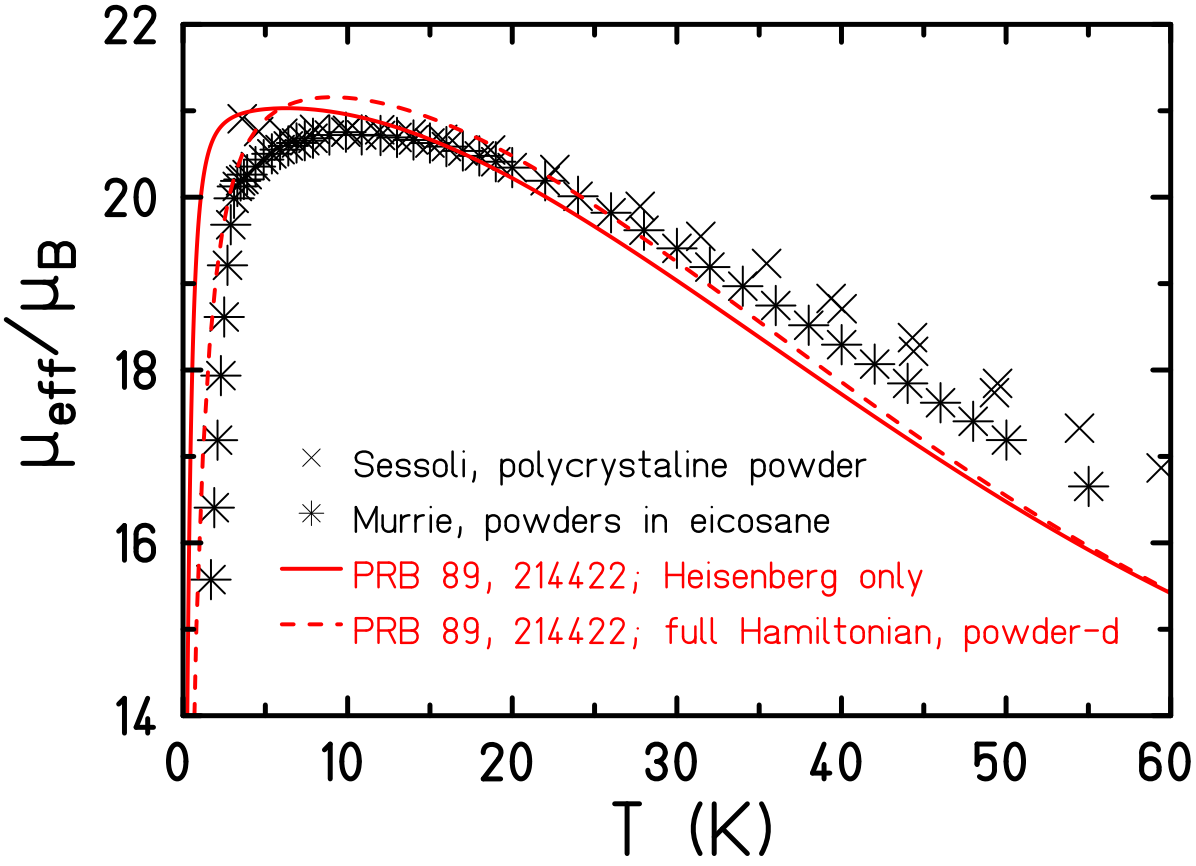
Effective magnetic moment of Mn_{12}-acetate



We can check DFT parameter predictions for large molecules!

O. Hanebaum, J. Schnack, work in progress

Effective magnetic moment of Mn_{12}-acetate



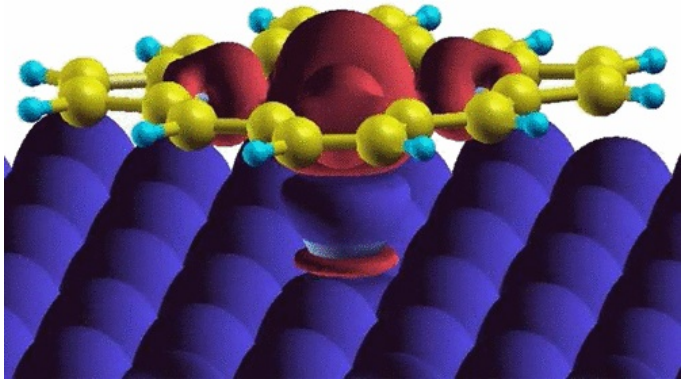
We can check DFT parameter predictions for large molecules!

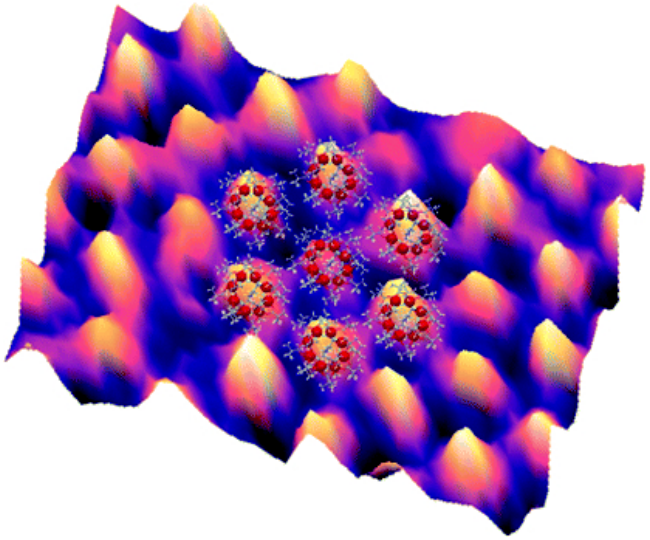
O. Hanebaum, J. Schnack, work in progress

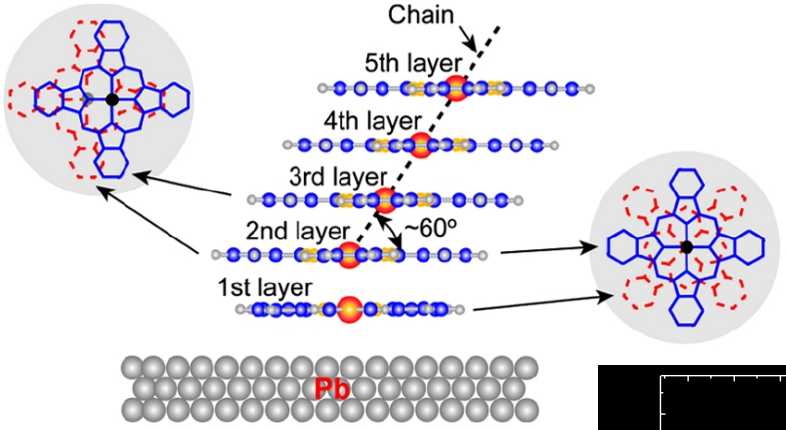
Numerical Renormalization Group calculations

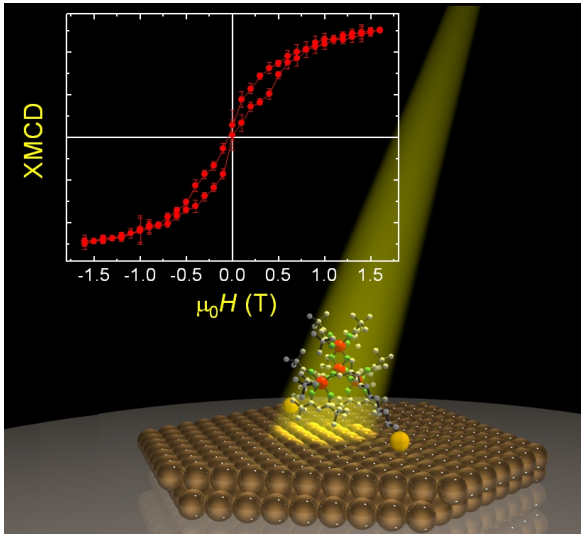
(Good for deposited molecules.)

You want to deposite a molecule



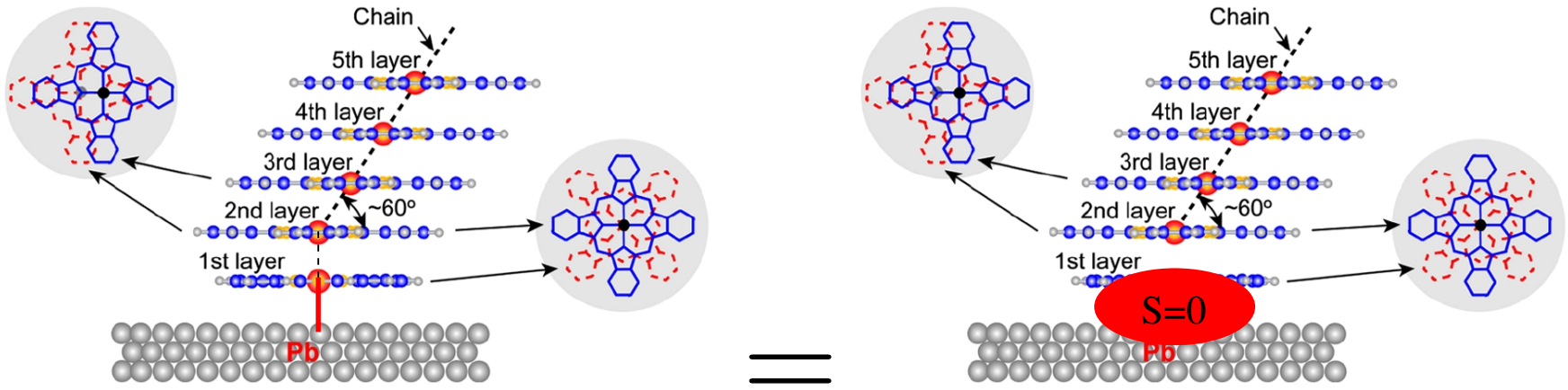






M. Bernien *et al.*, Phys. Rev. Lett. **102**, 047202 (2009); A. Ghirri*et al.*, ACS Nano, **5**, 7090-7099 (2011); X. Chen *et al.*, Phys. Rev. Lett. **101**, 197208 (2008); M. Mannini *et al.*, Nature Materials **8**, 194 - 197 (2009).

Physical example (ICMM 2010)

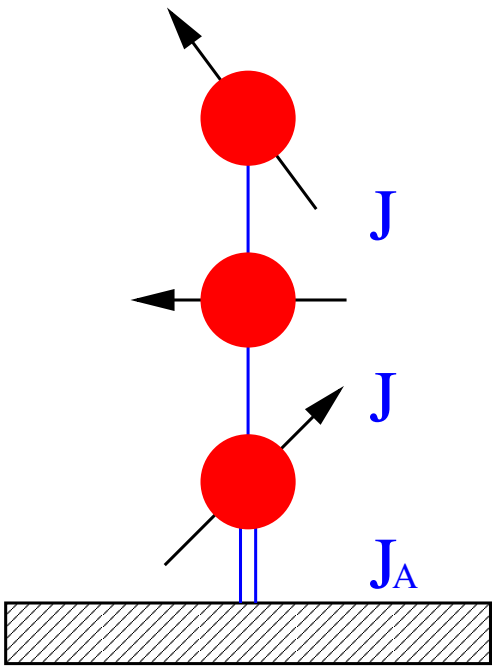


Stack of deposited Cobalt phthalocyanine (CoPc) molecules;
Co^{2+} with spin $s = 1/2$.

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!)



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

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

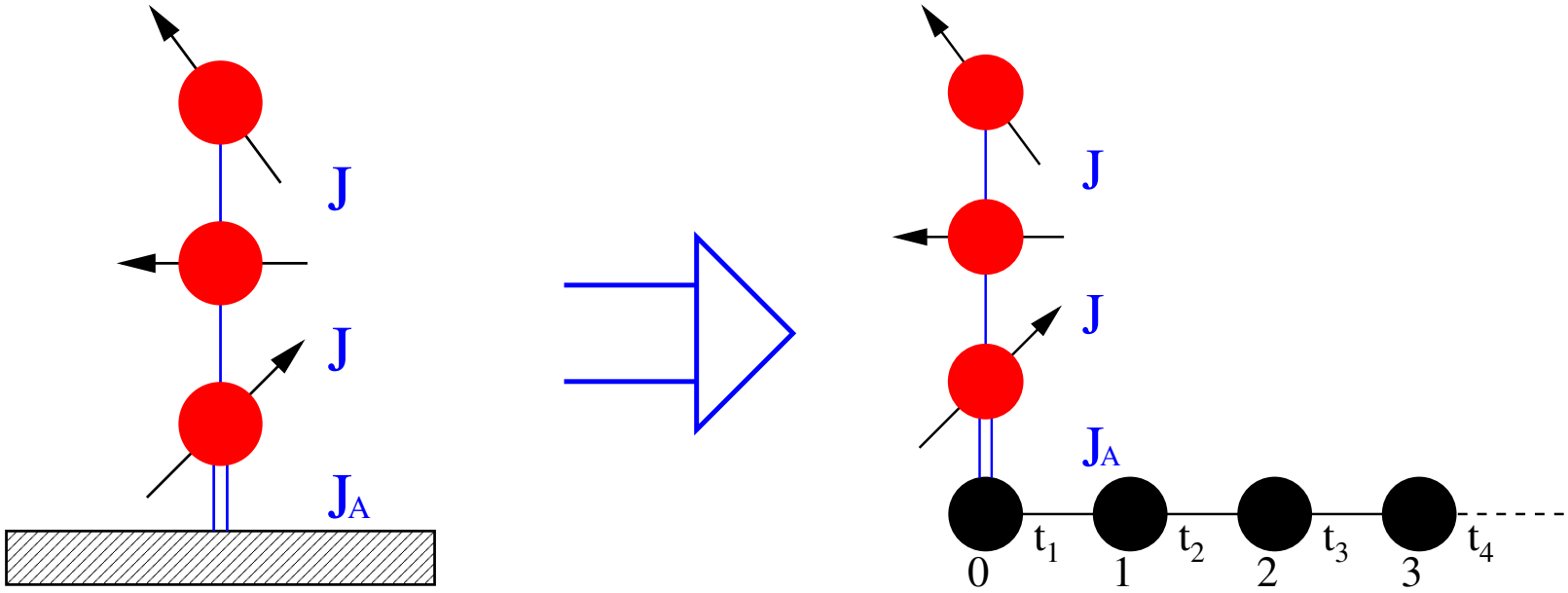
  $\underset{\sim}{H}_{\text{coupling}} = -2 J_A \underset{\sim}{\boldsymbol{S}} \cdot \underset{\sim}{\boldsymbol{s}}_0 \quad , \quad \underset{\sim}{\boldsymbol{s}}_0$ – spin density at contact

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

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

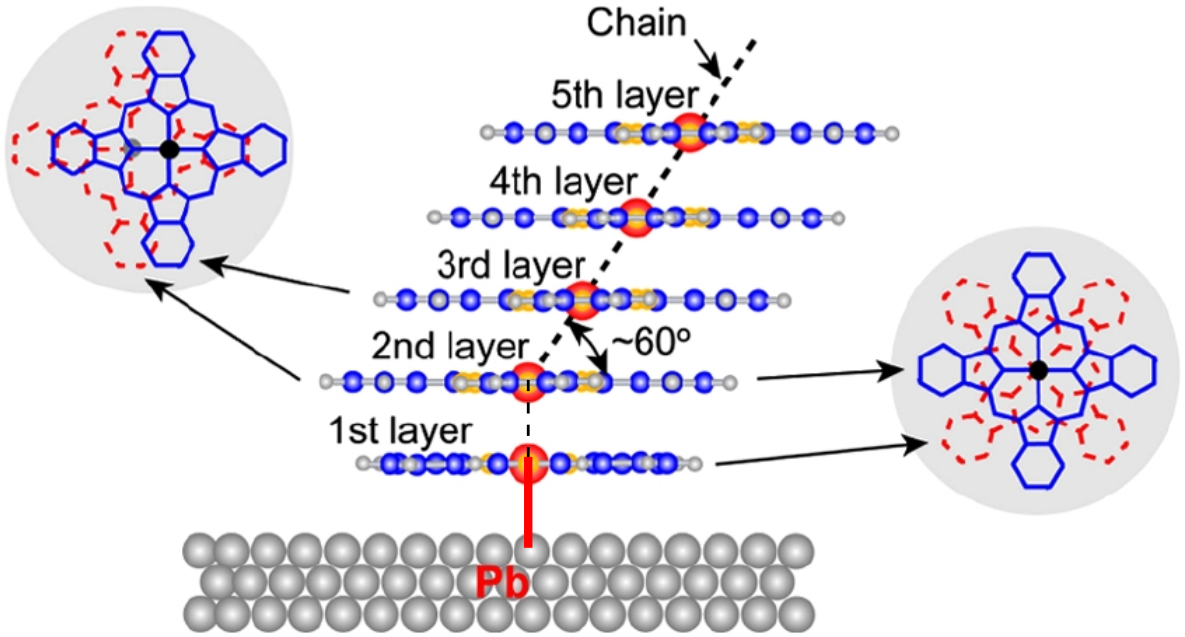
(1) K. G. Wilson, Rev. Mod. Phys. **47**, 773 (1975)
(2) M. Höck, J. Schnack, Phys. Rev. B **87**, 184408 (2013)
(3) *Impurity* is a technical term in this context and not an insult to chemists.

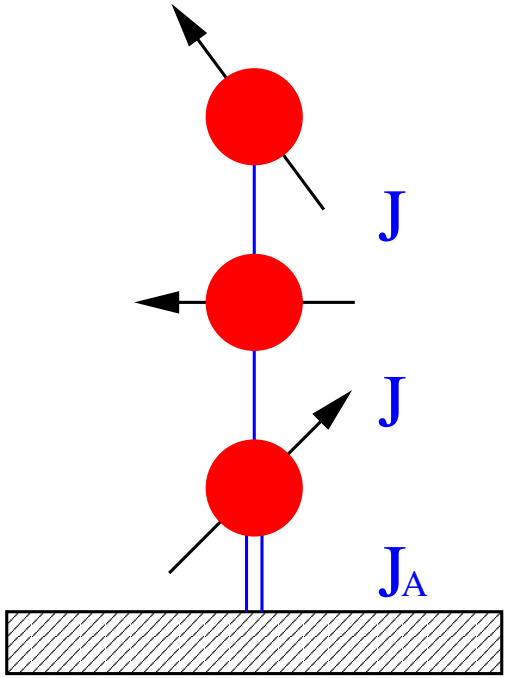
NRG in a cartoon



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.

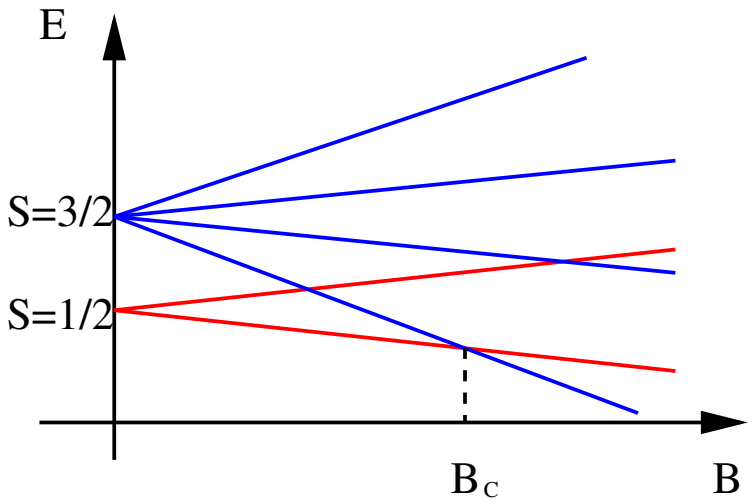
Once more: deposited chain



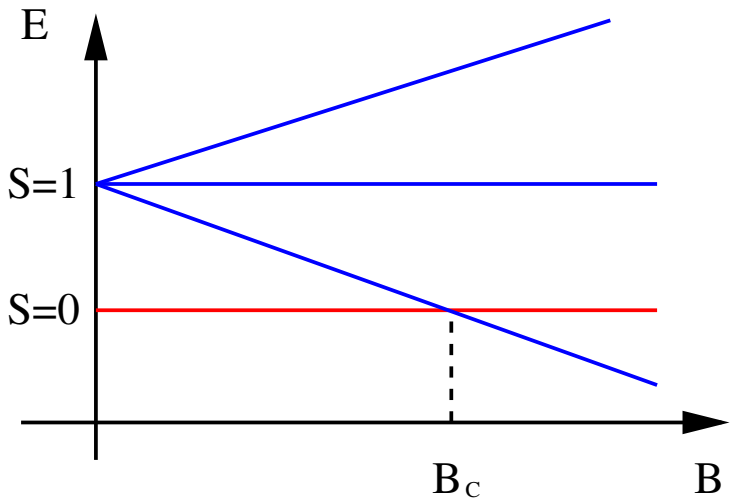


X. Chen *et al.*, Phys. Rev. Lett. **101**, 197208 (2008).

Energy levels of limiting cases for deposited trimer



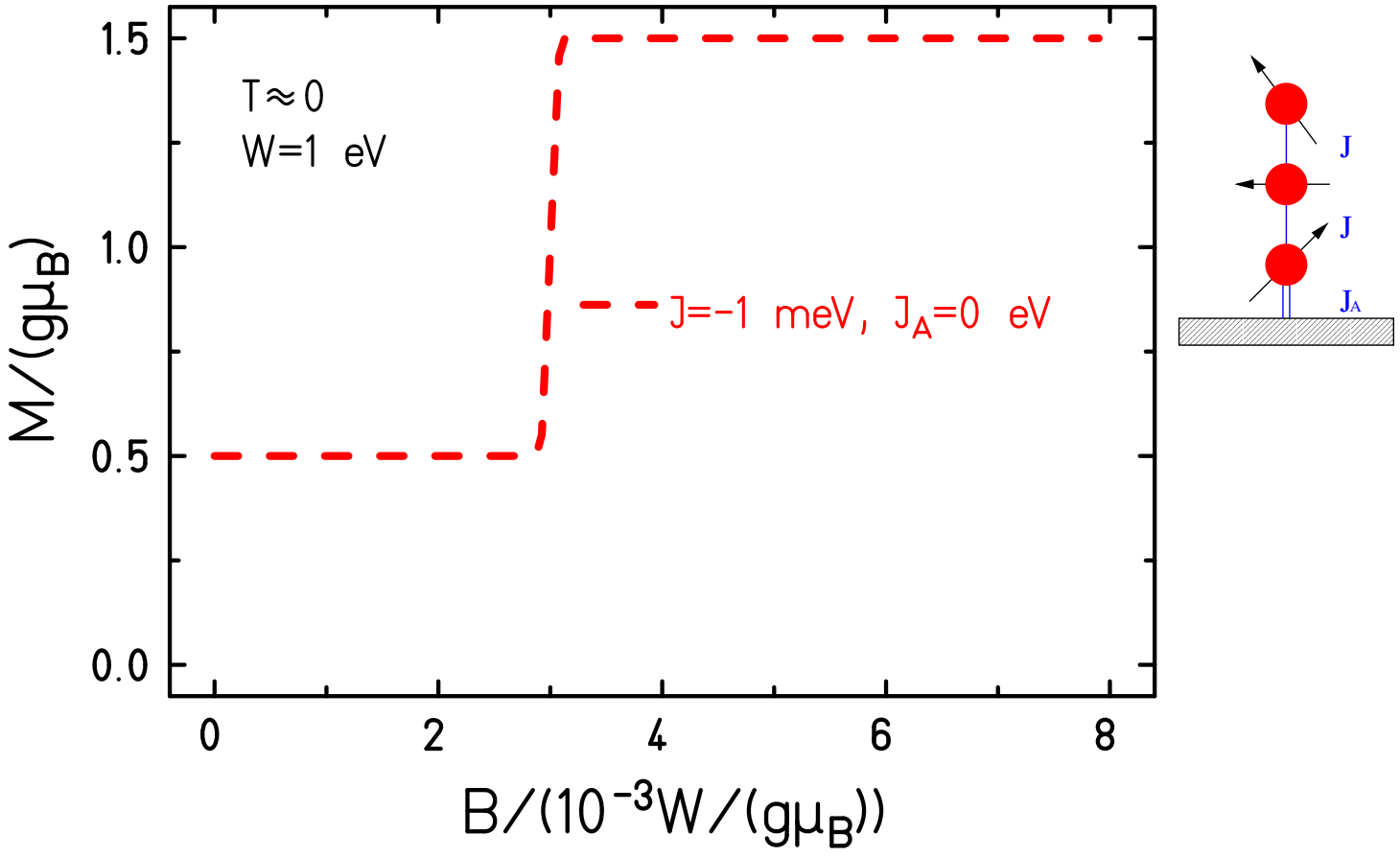
- energy levels of a trimer



- energy levels of a dimer

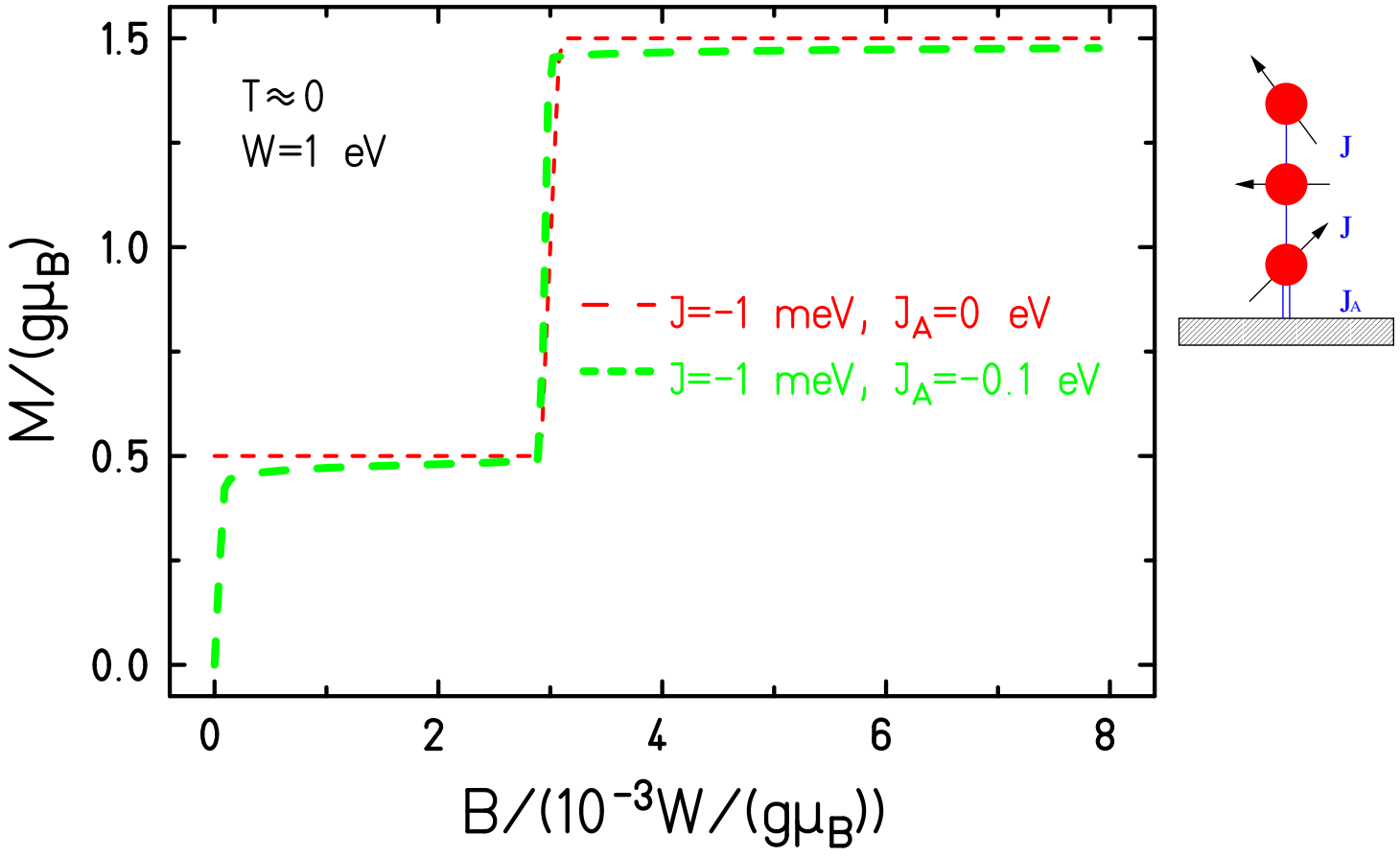
Magnetization curves different; could be seen in XMCD.
NRG calculates observables also between limiting cases
and can thus tell under which circumstances a limiting case applies.

Increasing coupling to the substrate



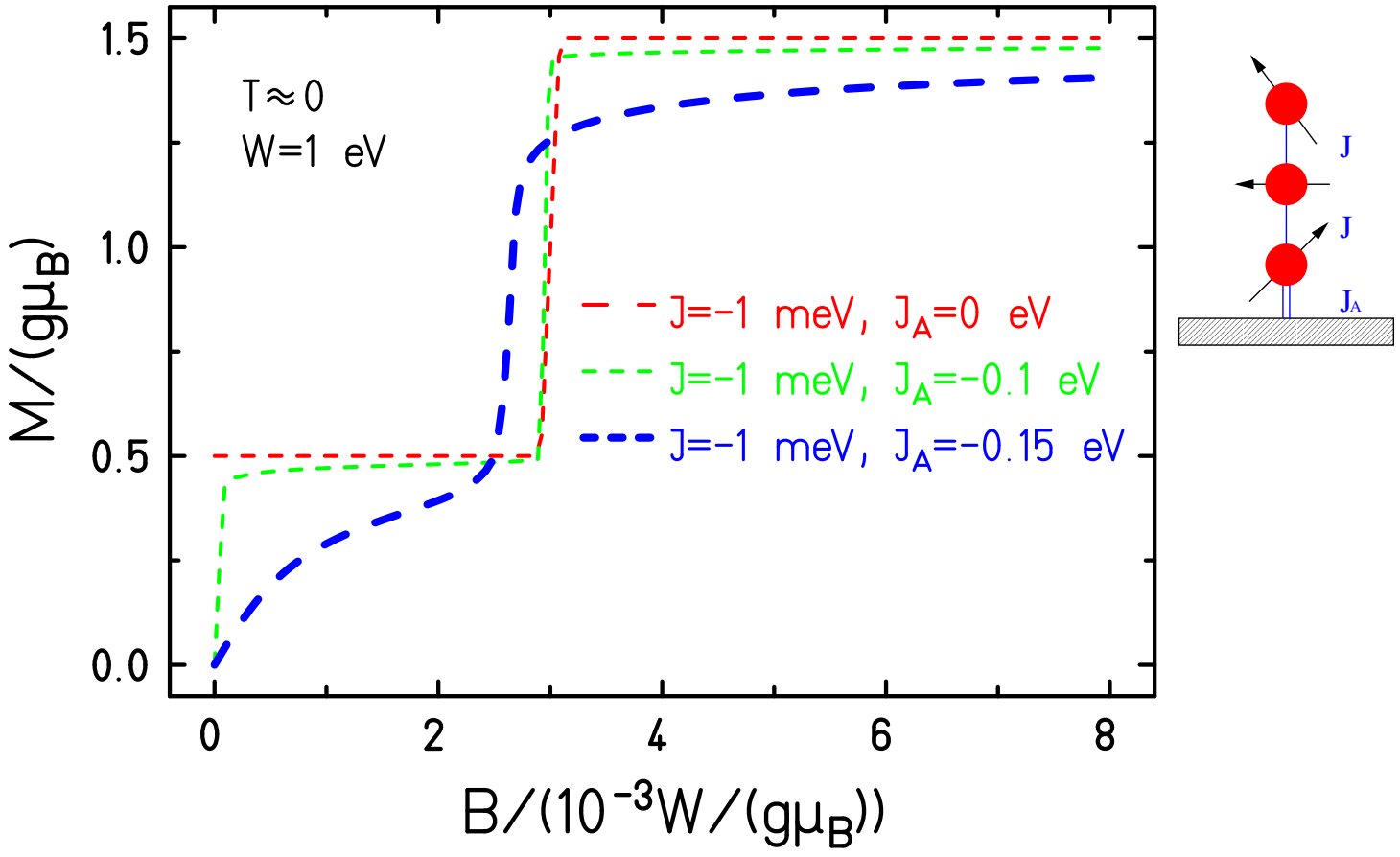
H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

Increasing coupling to the substrate



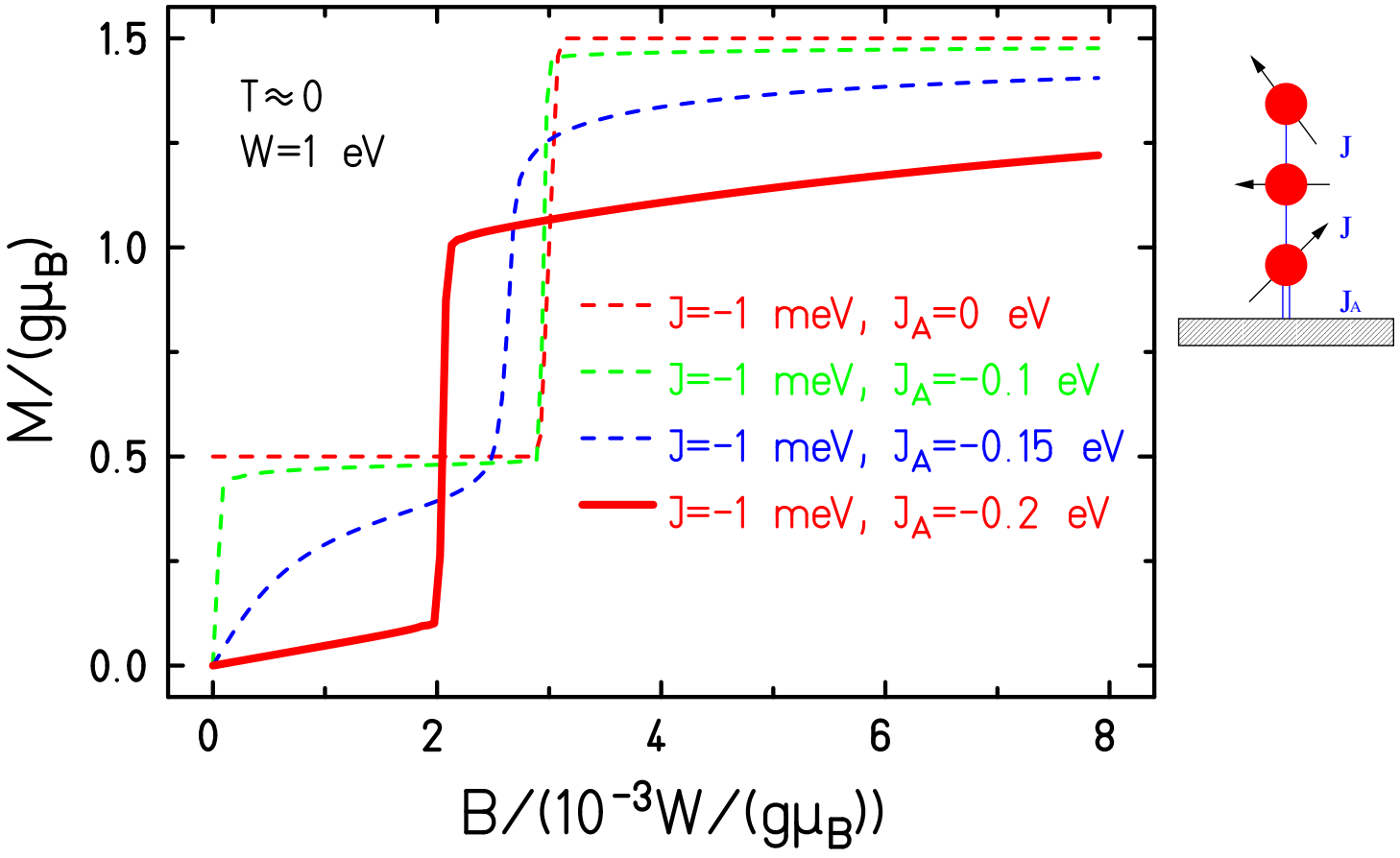
H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

Increasing coupling to the substrate



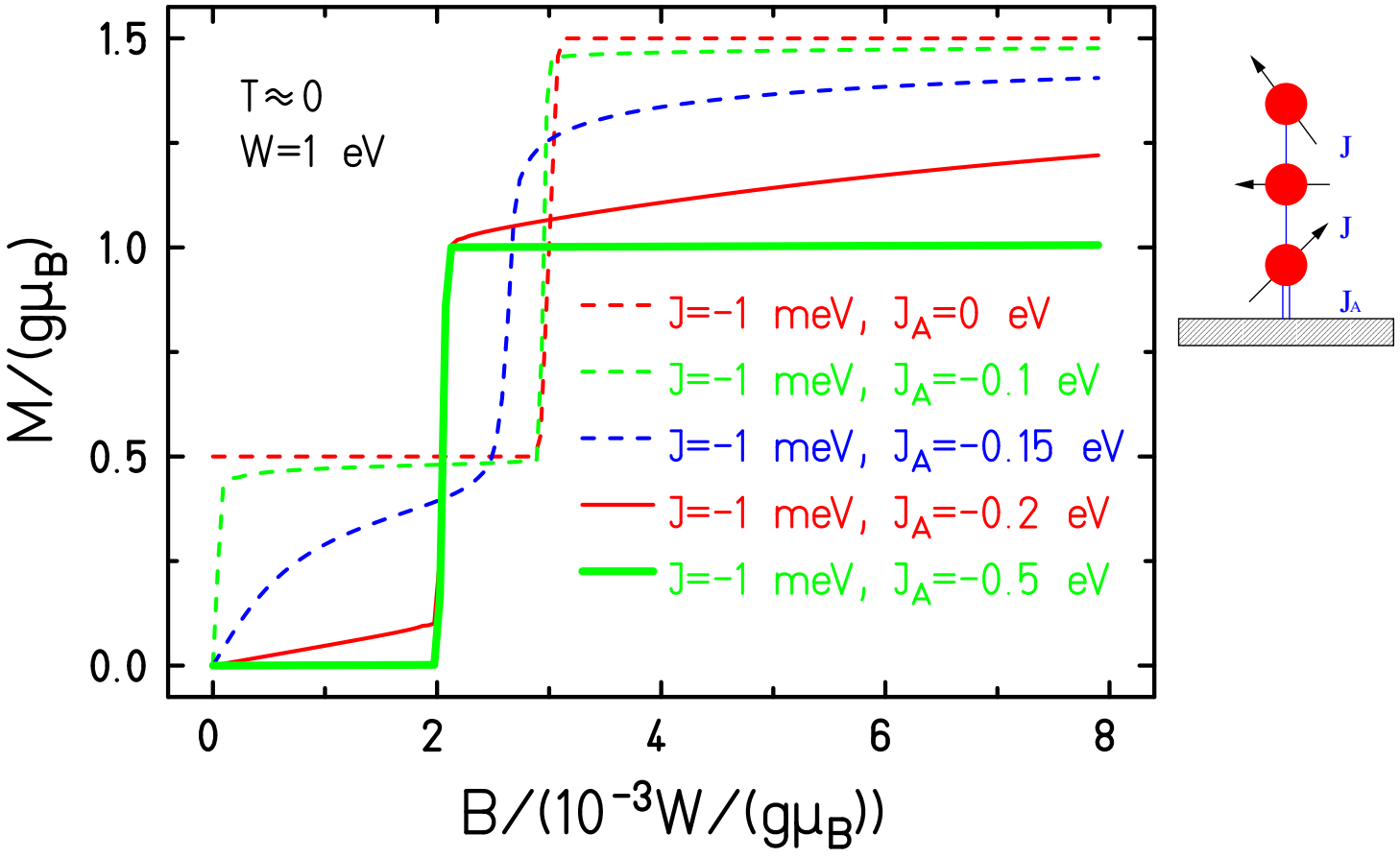
H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

Increasing coupling to the substrate



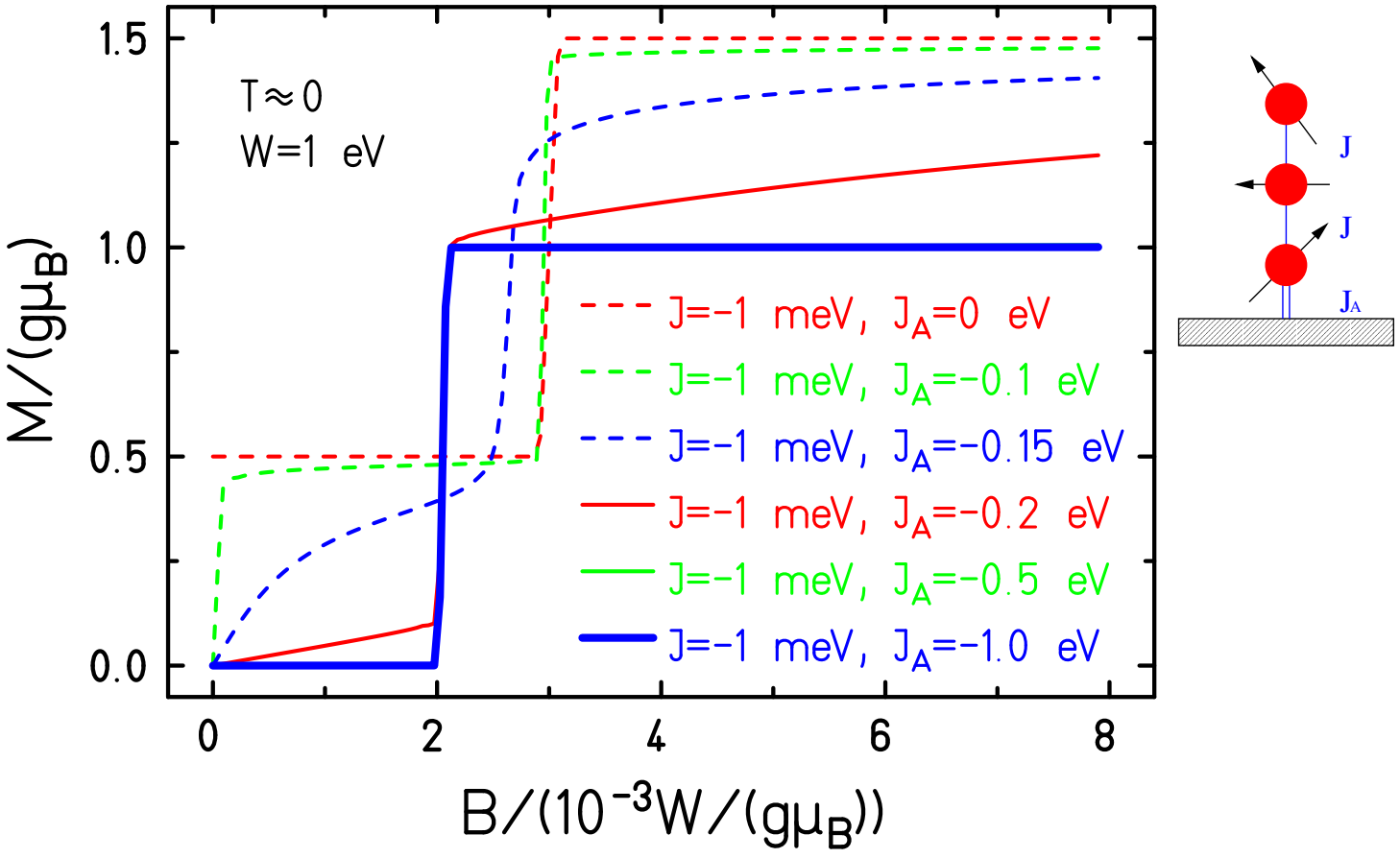
H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

Increasing coupling to the substrate



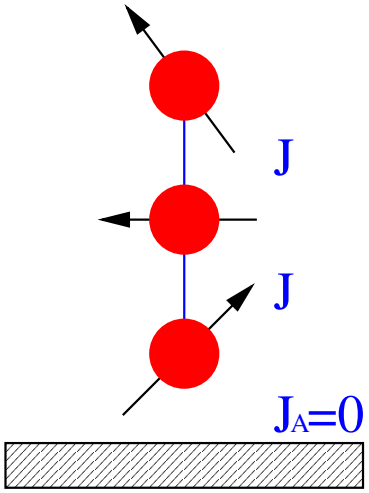
H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

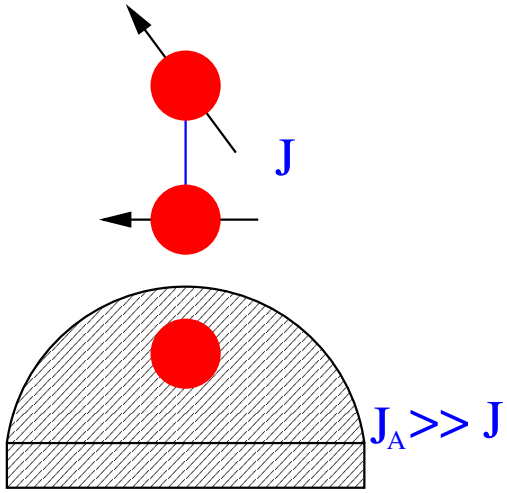
Increasing coupling to the substrate



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

Weak vs. strong coupling



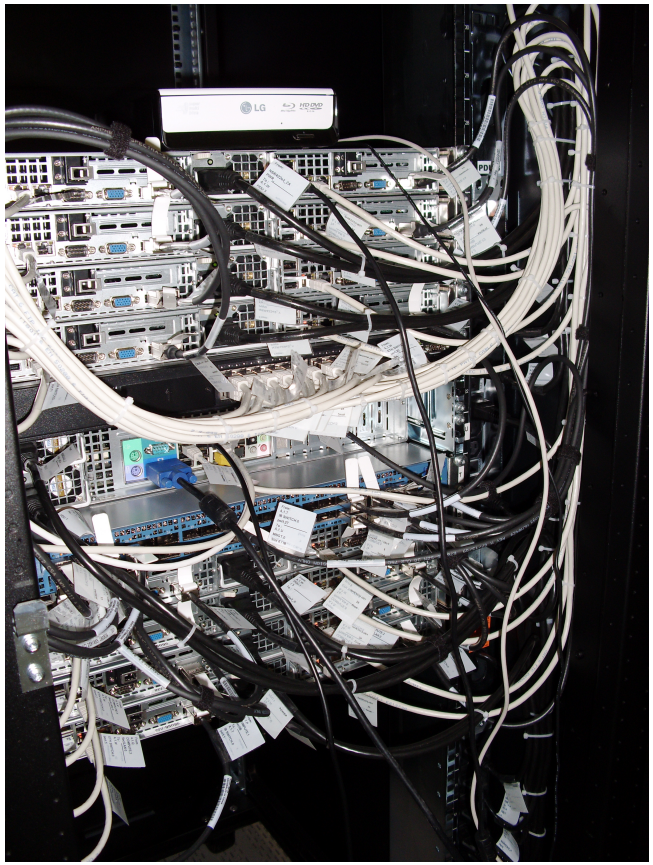


- weak coupling limit: unperturbed molecule (trimer)
- $|J_A| \lessapprox 0.1W$

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

Inbetween: no simple characterization + further sequential screening possible

Summary



- Exact diagonalization is great but limited.
- Finite-Temperature Lanczos is a good approximate method for Hilbert space dimensions smaller than 10^{10}. The accuracy is amazing!
- FTLM works for anisotropic spin systems.
- Magnetic molecules for storage, q-bits, MCE, and since they are nice.

Many thanks to my collaborators worldwide

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Thank you very much for your attention.

The end.

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