INFLUENCE OF INTERMOLECULAR INTERACTIONS ON MAGNETIC OBSERVABLES

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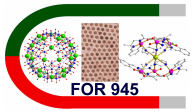
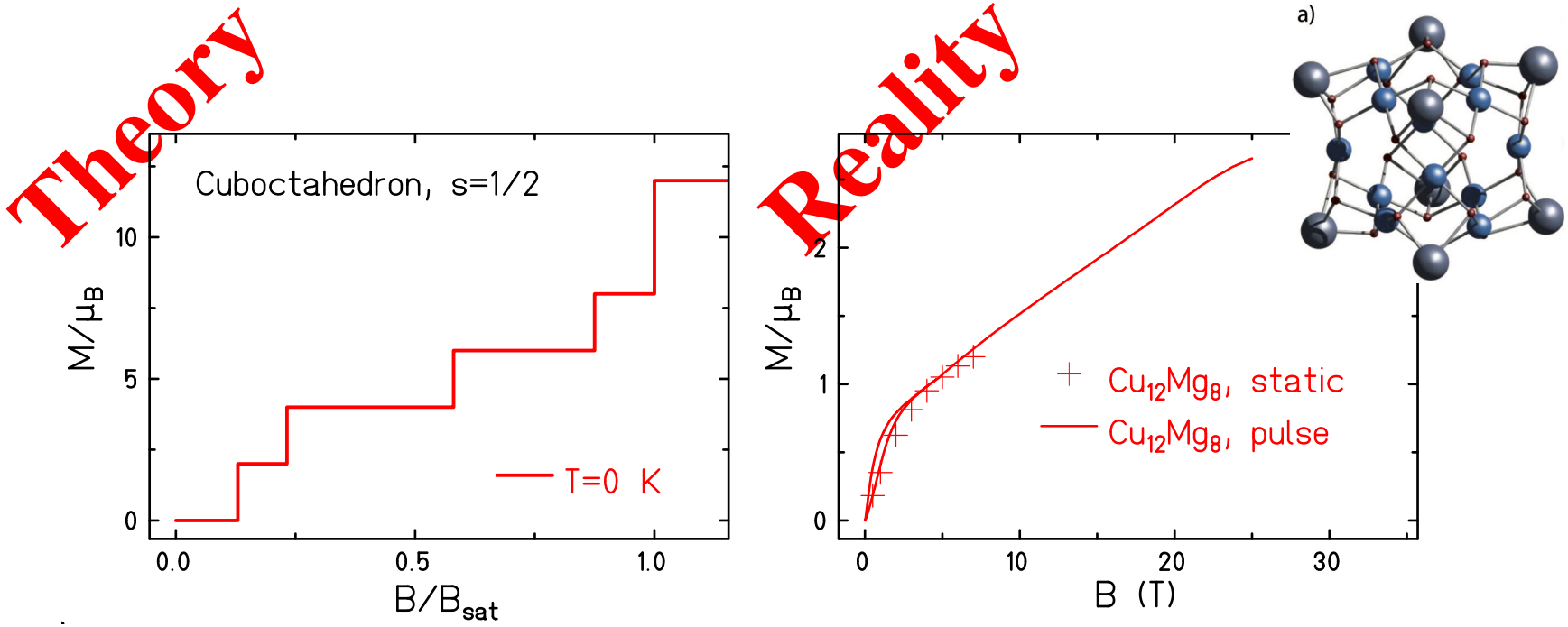


Problem:

How robust are static molecular magnetic observables?

Example: magnetization steps are fingerprints



No magnetization steps! Reasons? Your suggestions?

(1) M. Palacios, E. Pineda, S. Sanz, R. Inglis, M. Pitak, S. Coles, M. Evangelisti, H. Nojiri, C. Heesing, E. Brechin, J. Schnack, R. Winpenny, ChemPhysChem **17**, 55 (2016);
(2) and many more examples.

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. Anisotropic exchange
2. Randomness
3. Some basic theory
4. Intermolecular interactions
5. Interactions with surfaces

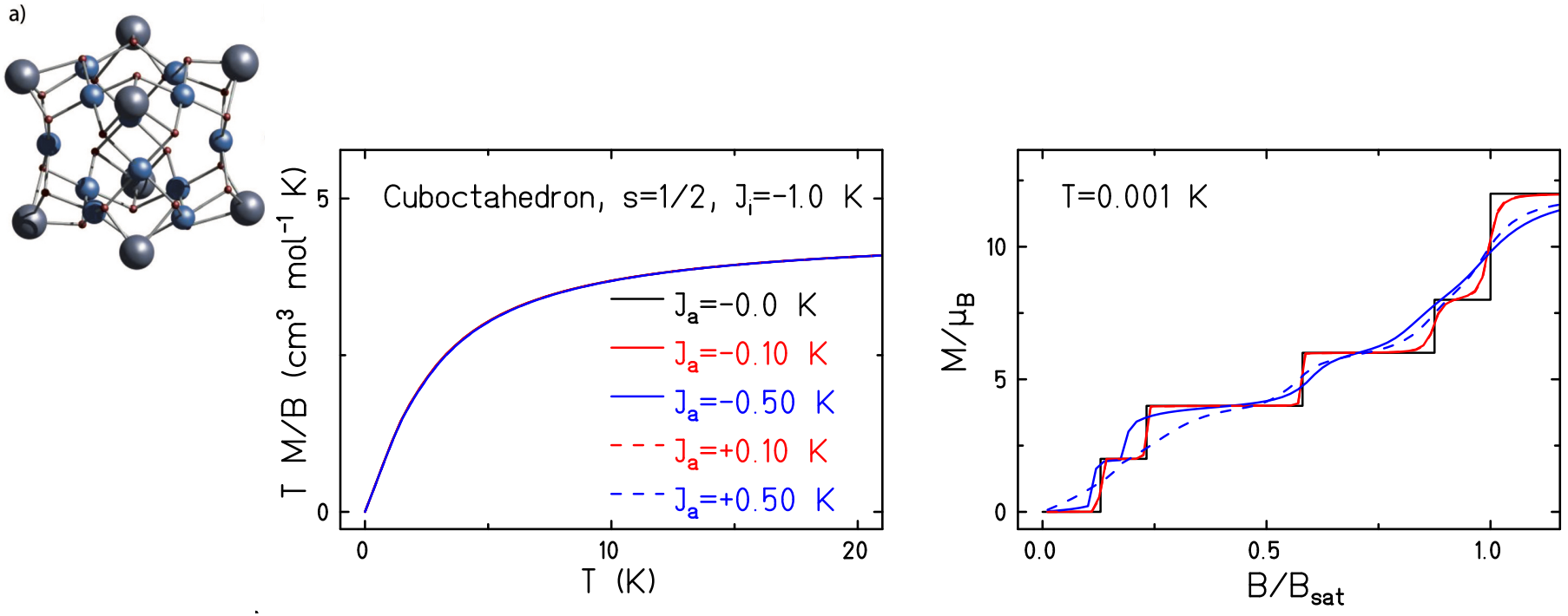
We are the sledgehammer team of matrix diagonalization.
Please send inquiries to jschnack@uni-bielefeld.de!

Anisotropic exchange

$$\underset{\sim}{H} = -2 \sum_{i<j} \underset{\sim}{\vec{s}}_i \cdot \mathbf{J}_{ij} \cdot \underset{\sim}{\vec{s}}_j$$

Matrix $\mathbf{J}_{ij}$ contains isotropic Heisenberg exchange, anisotropic symmetric exchange as well as anisotropic antisymmetric exchange (Dzyaloshinskii-Moriya).

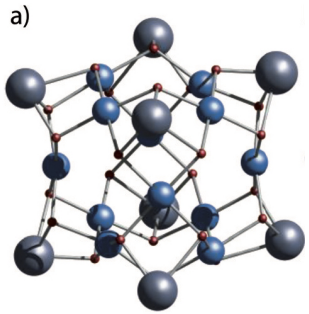
Anisotropic symmetric exchange

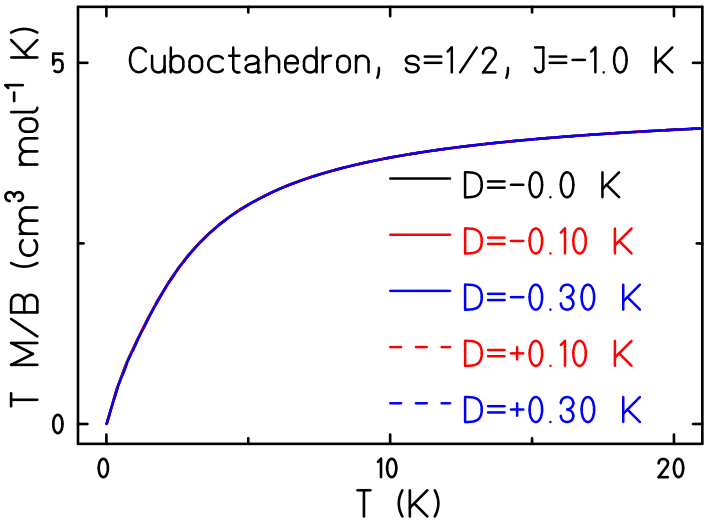


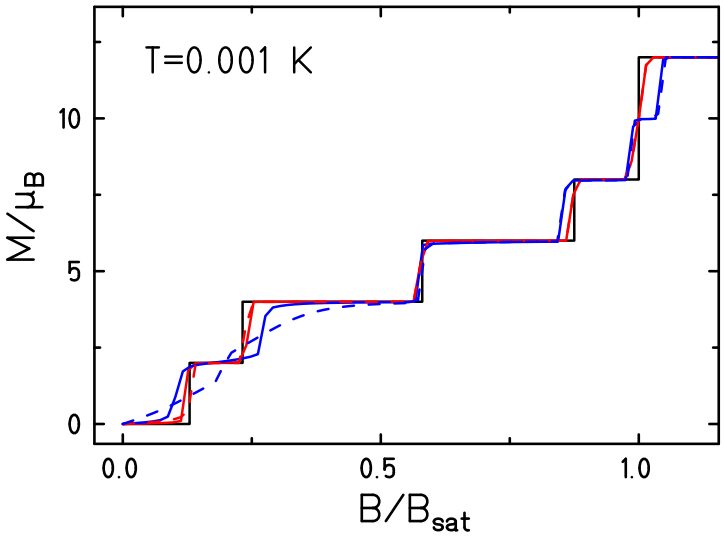
Needs about 50 % of symmetric exchange to wash out magnetization steps.

(1) M. Palacios, E. Pineda, S. Sanz, R. Inglis, M. Pitak, S. Coles, M. Evangelisti, H. Nojiri, C. Heesing, E. Brechin, J. Schnack, R. Winpenny, ChemPhysChem **17**, 55 (2016).

Anisotropic antisymmetric exchange







Needs about 50 % of antisymmetric exchange to wash out magnetization steps.

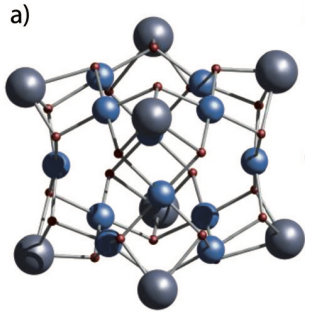
(1) M. Palacios, E. Pineda, S. Sanz, R. Inglis, M. Pitak, S. Coles, M. Evangelisti, H. Nojiri, C. Heesing, E. Brechin, J. Schnack, R. Winpenny, ChemPhysChem **17**, 55 (2016).

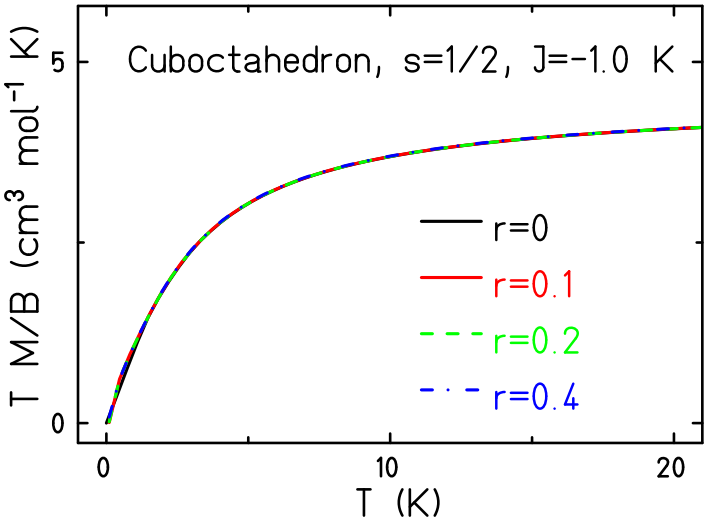
Random exchange

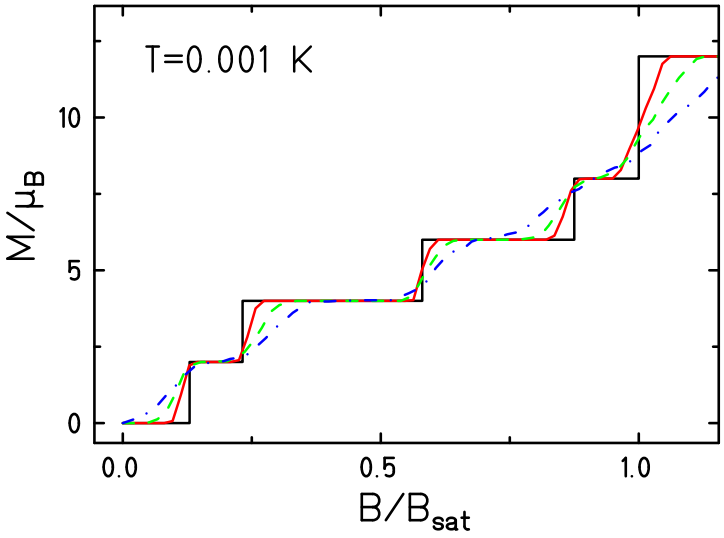
$$\underset{\sim}{H} = -2 \sum_{i<j} \vec{\underset{\sim}{s}}_i J_{ij} \vec{\underset{\sim}{s}}_j$$

$J_{ij} \in [(1-r)J, (1+r)J]$; random for each bond in each molecule,
i.e. each molecule is different ($\rightarrow$ average over many molecules).

Random exchange







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Take home:

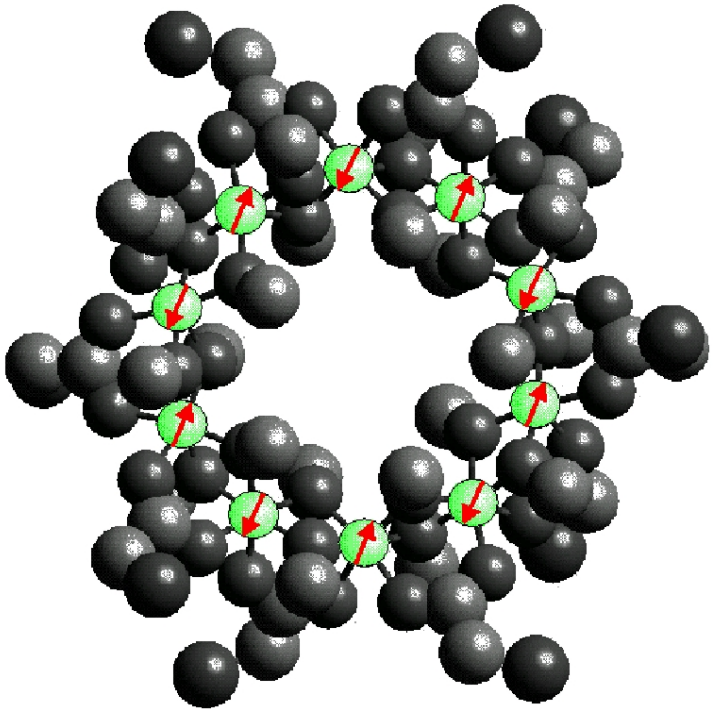
50 % anisotropic interactions or randomness is needed

(. . . to wash out e.g. magnetization steps.)

Before we proceed to intermolecular interactions . . .

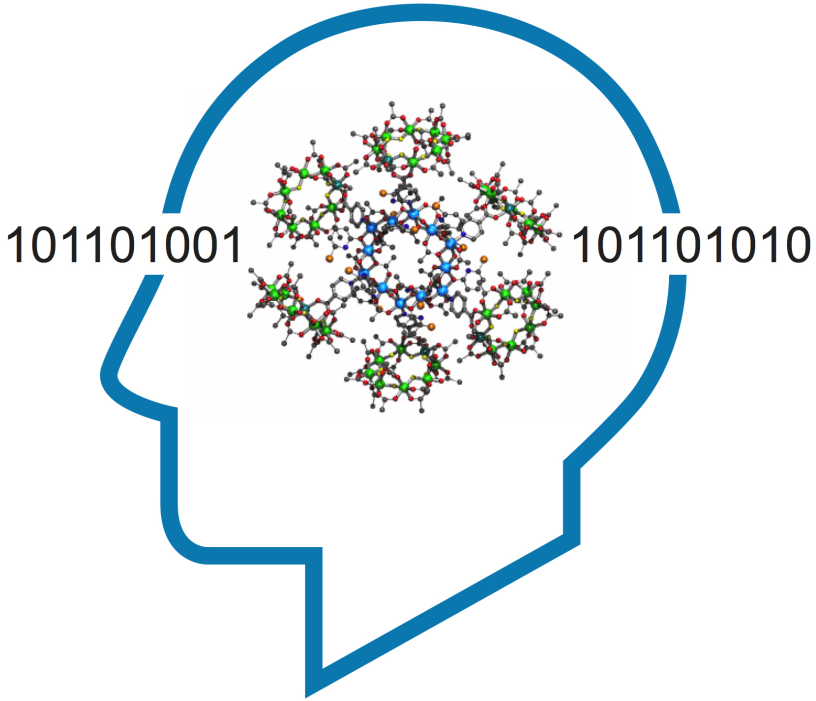
Some basic theory

You have got a molecule!



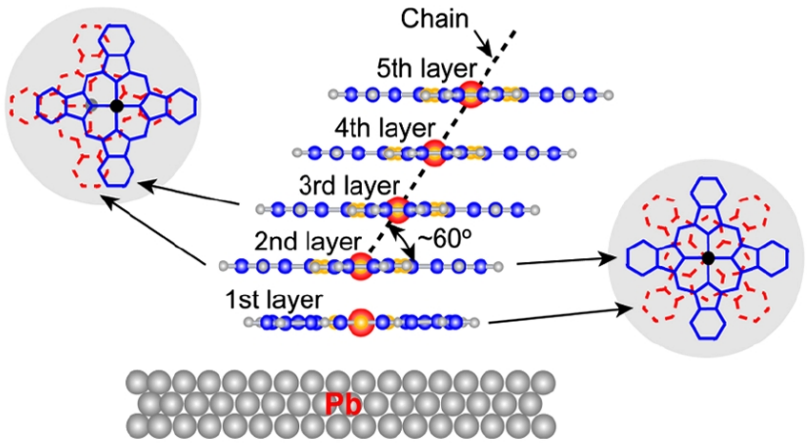
Congratulations!

You want to build a quantum computer!



Very smart!

You want to deposit your molecule!

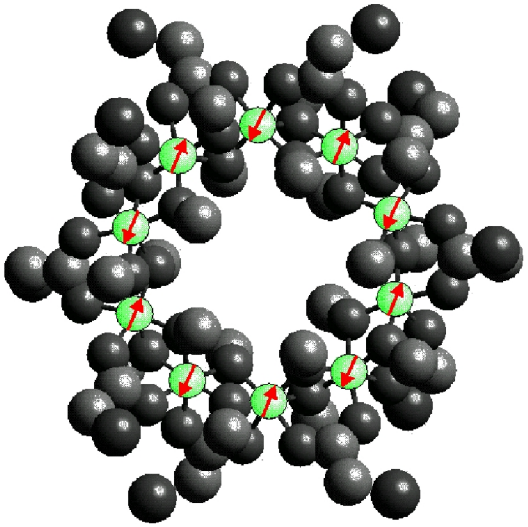


Next generation magnetic storage!

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



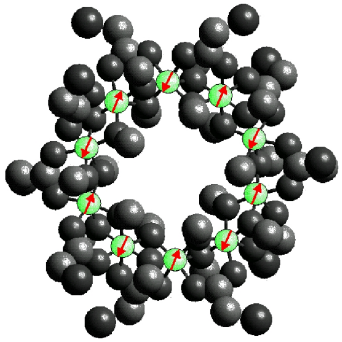
You have to solve the Schrödinger equation!

$$\underset{\sim}{H} \left| \phi_n \right\rangle = E_n \left| \phi_n \right\rangle$$

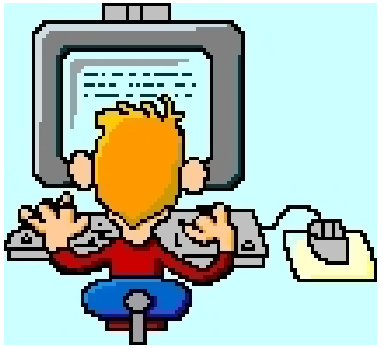
Eigenvalues E_n and eigenvectors $\left| \phi_n \right\rangle$

- needed for spectroscopy (EPR, INS, NMR);
- needed for thermodynamic functions (magnetization, susceptibility, heat capacity);
- needed for time evolution (pulsed EPR, simulate quantum computing, thermalization).

In the end it's always a big matrix!



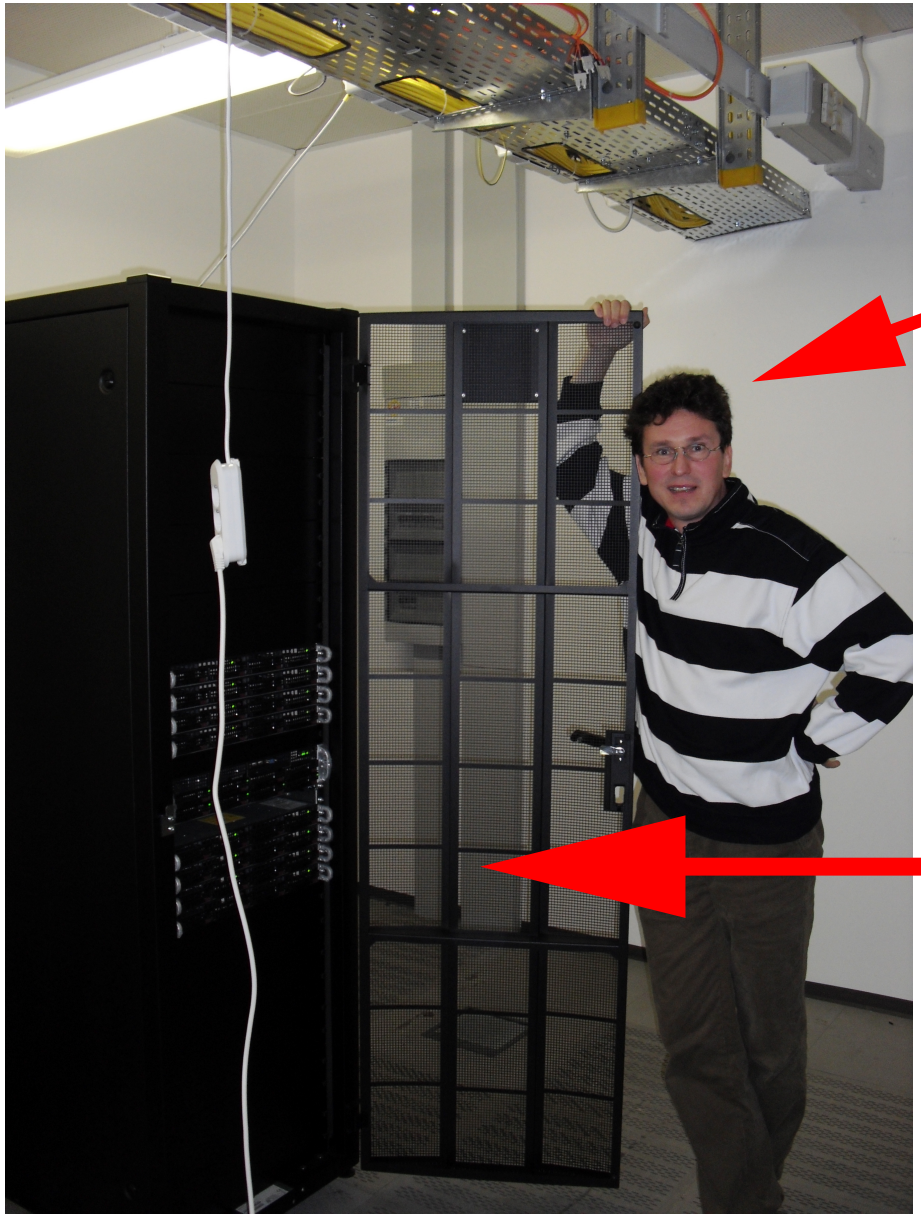
$$\Rightarrow \begin{pmatrix} -27.8 & 3.46 & 0.18 & \cdots \\ 3.46 & -2.35 & -1.7 & \cdots \\ 0.18 & -1.7 & 5.64 & \cdots \\ \vdots & \vdots & \vdots & \cdots \end{pmatrix} \Rightarrow$$



Fe^{III}_{10}: $N = 10, s = 5/2$

Dimension=60,466,176. Maybe too big?

Thank God, we have computers



“Espresso-doped multi-core”

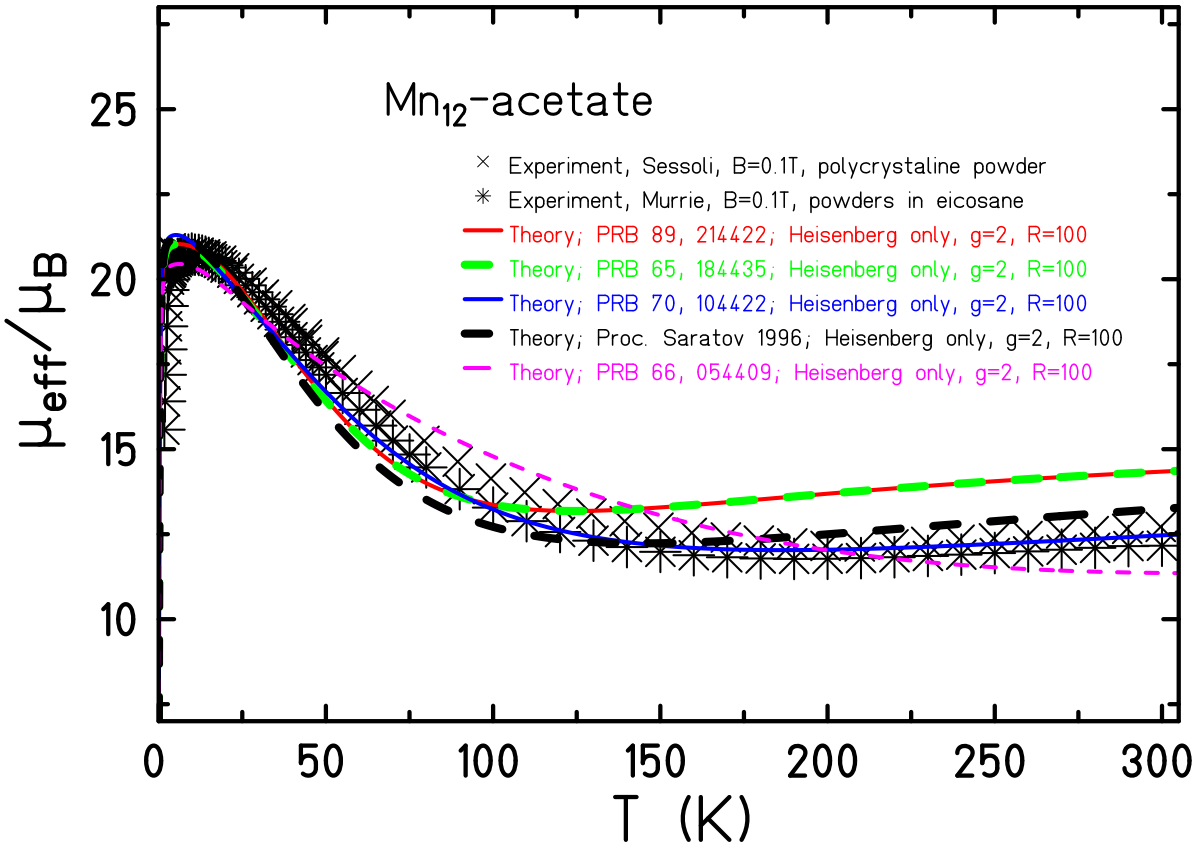
128 cores, 384 GB RAM

. . . but that’s not enough!

Summary: theory methods

- Complete diagonalization: exact; spectra, transitions, observables, time-evolution; Dimension of largest Hilbert space $< 10^5$.
- Finite Temperature Lanczos Method (FTLM): pseudo-spectrum, low-lying levels good, transitions, observables, time-evolution; DoH $< 10^{10}$.
- Quantum Monte Carlo (QMC): observables; bad/no convergence for competing interactions (frustration) due to negative sign problem; otherwise HUGE systems possible.
- Density Matrix Renormalization Theory (DMRG): low-lying target states, correlation functions, short time evolution, maybe thermodynamics; best for 1-d; HUGE systems possible.

Example FTLM: Mn_{12}-acetate with all spins

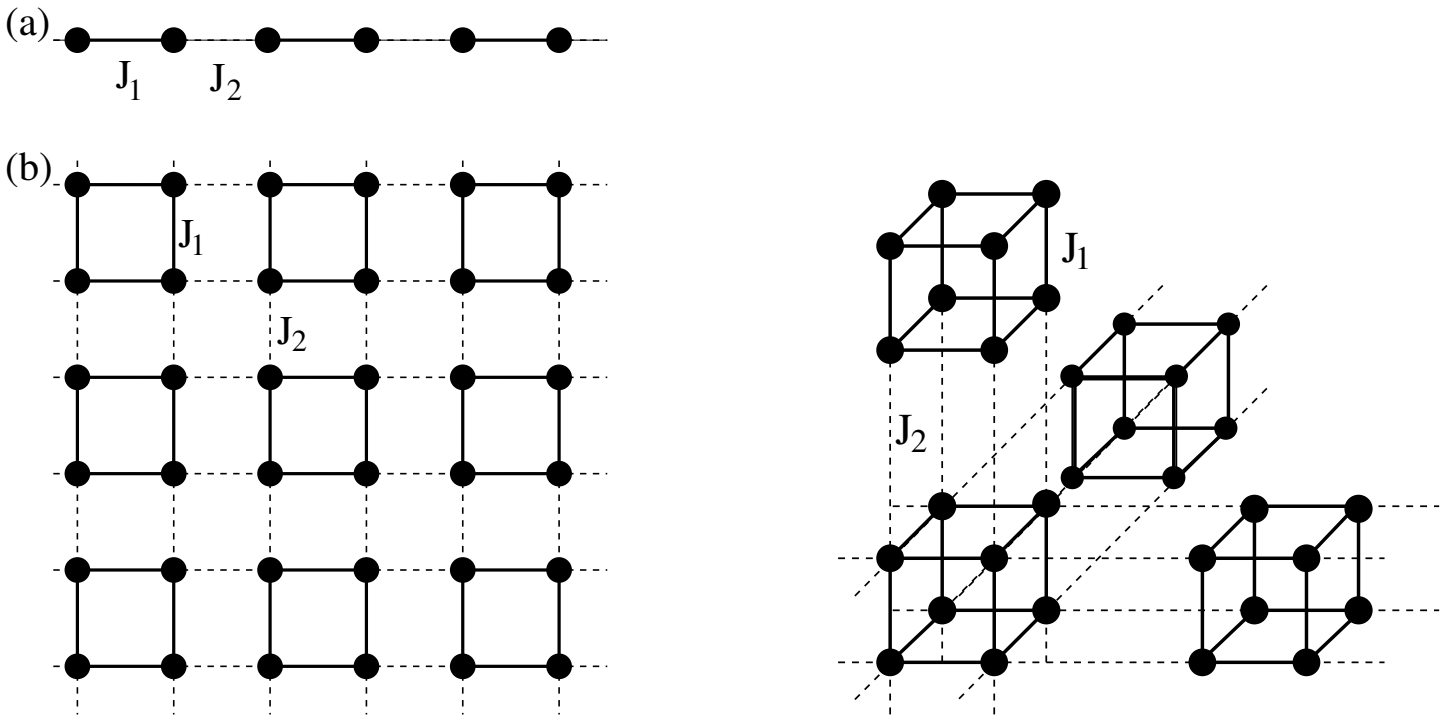


We can check DFT parameter predictions for large molecules (Mn_{12} – 100,000,000)!

(1) O. Hanebaum, J. Schnack, Phys. Rev. B **92**, 064424 (2015).)

Intermolecular interactions

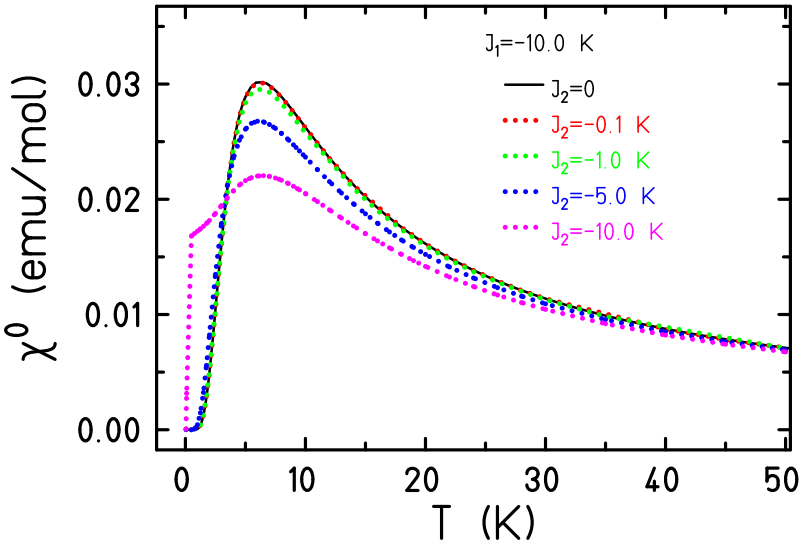
Intermolecular interactions – systems

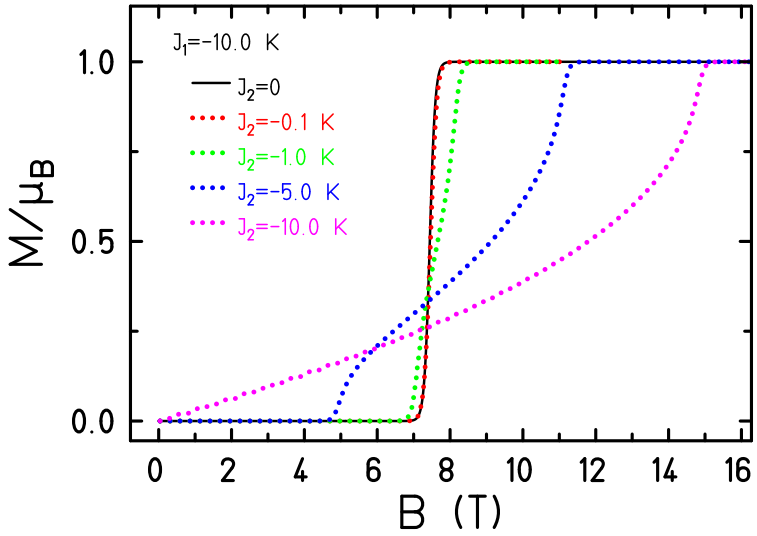


QMC investigation: Dimers in 1-d, squares in 2-d, cubes in 3-d.
All interactions antiferromagnetic, all spins $s = 1/2$. $N = 100 \ldots 1000$. PBC.

(1) J. Schnack, Phys. Rev. B **93**, 054421 (2016).

Intermolecular interactions – 1-d

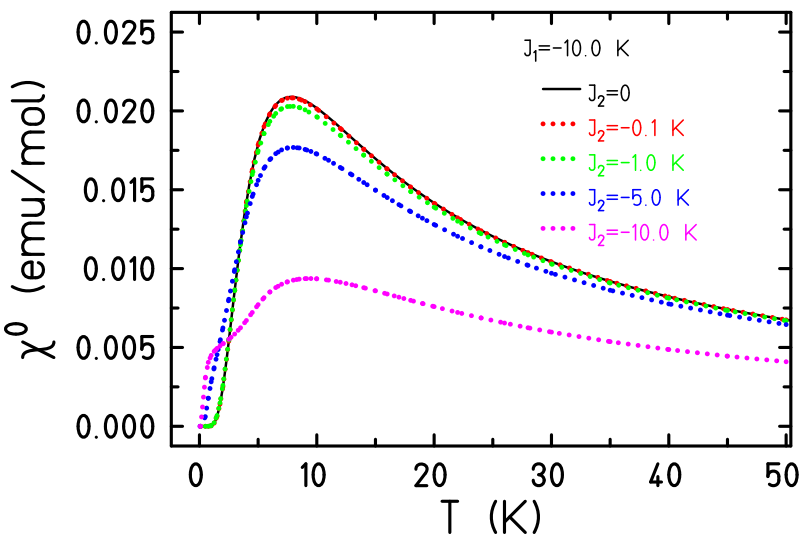


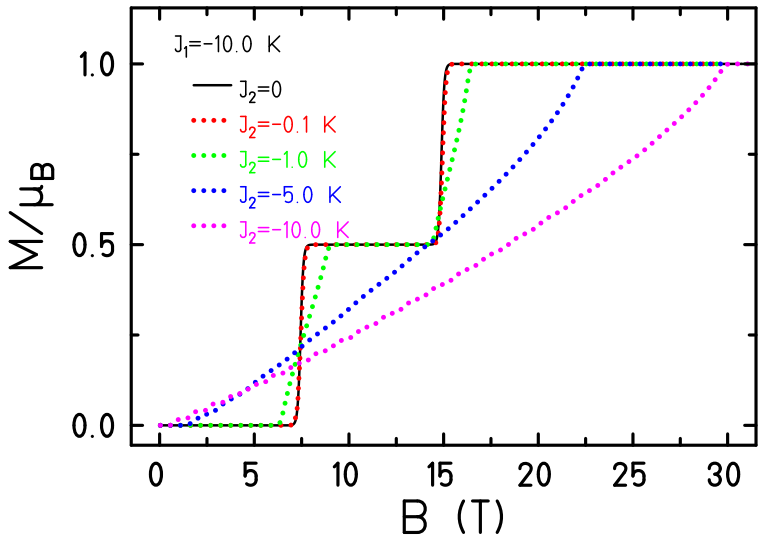


Gradually af dimers turn into gapless af chain.
Even at 50 % gap still large.

(1) J. Schnack, Phys. Rev. B **93**, 054421 (2016).

Intermolecular interactions – 2-d

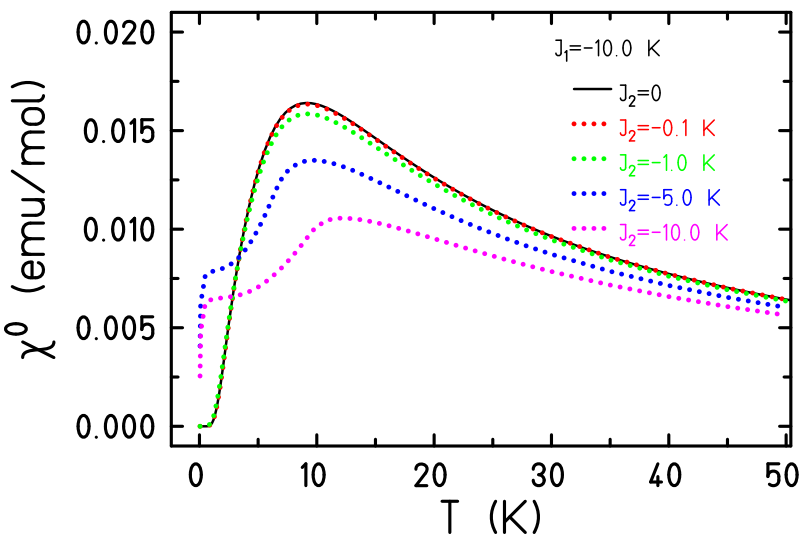


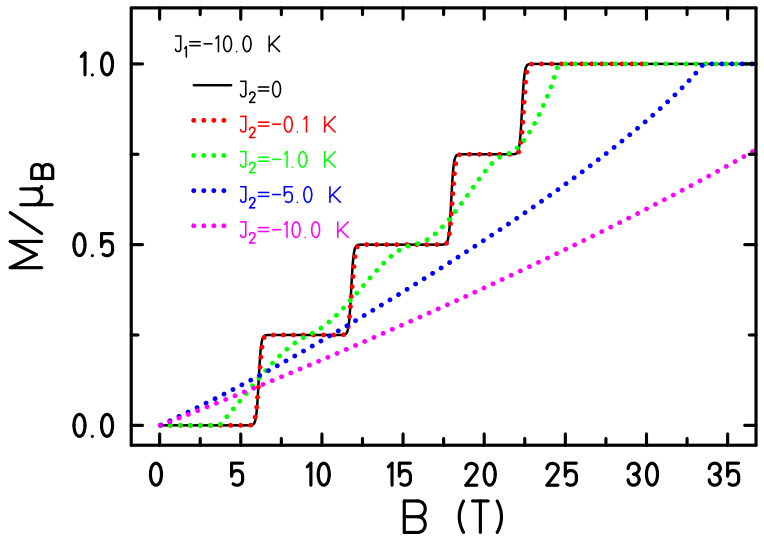


The two magnetization steps vanish more rapidly with intermolecular interactions in 2-d.

(1) J. Schnack, Phys. Rev. B **93**, 054421 (2016).

Intermolecular interactions – 3-d





In 3-d 10 % intermolecular interactions sufficient to wash out magnetization steps.

(1) J. Schnack, Phys. Rev. B **93**, 054421 (2016).

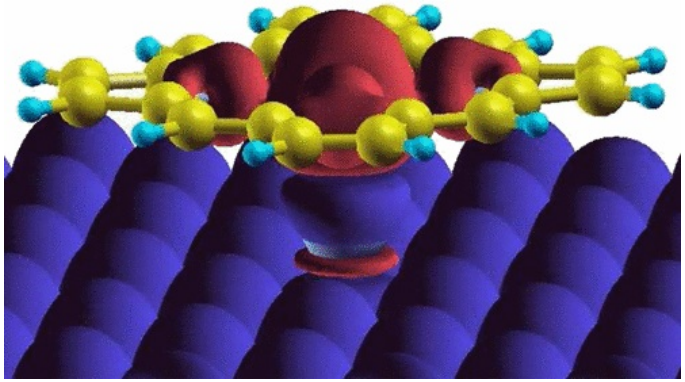
Take home:

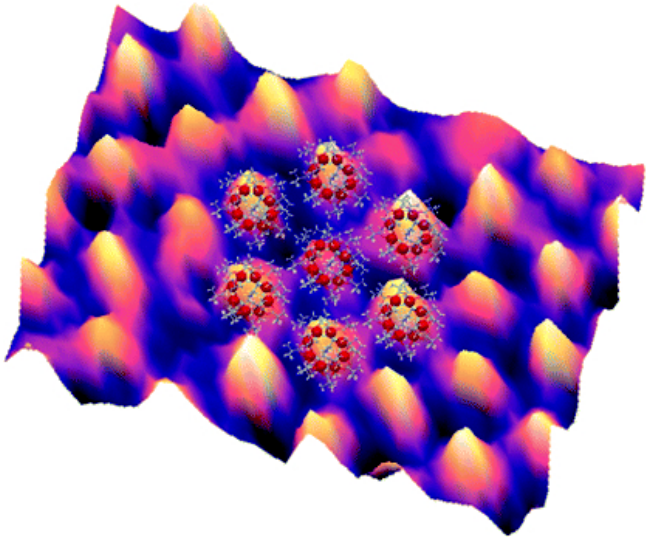
10 % intermolecular interactions in 3-d is enough

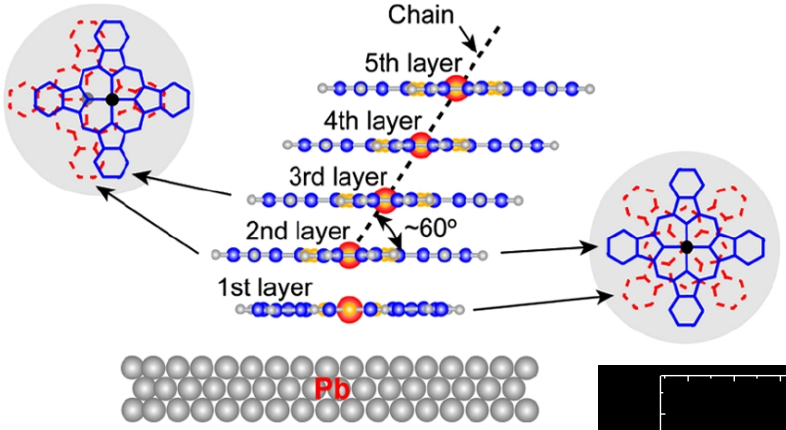
(. . . to spoil static molecular magnetic observables.)

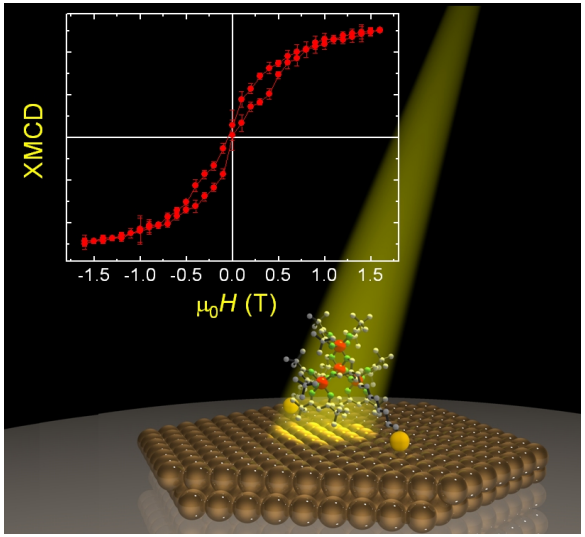
Interactions with surfaces

You want to deposite a molecule



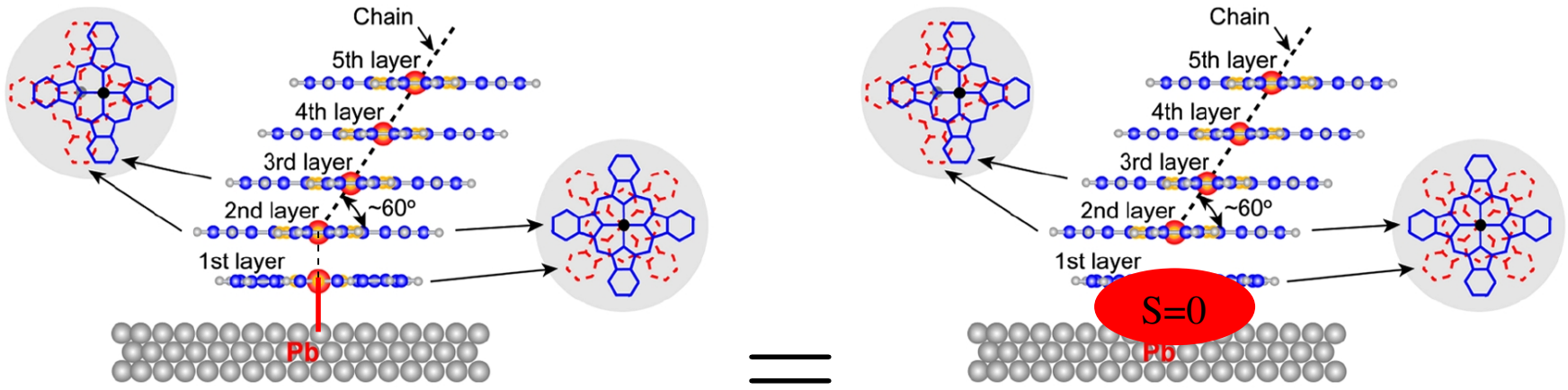






M. Bernien *et al.*, Phys. Rev. Lett. **102**, 047202 (2009); A. Ghirri*et al.*, ACS Nano, **5**, 7090-7099 (2011); X. Chen *et al.*, Phys. Rev. Lett. **101**, 197208 (2008); M. Mannini *et al.*, Nature Materials **8**, 194 - 197 (2009).

Physical example (ICMM 2010)

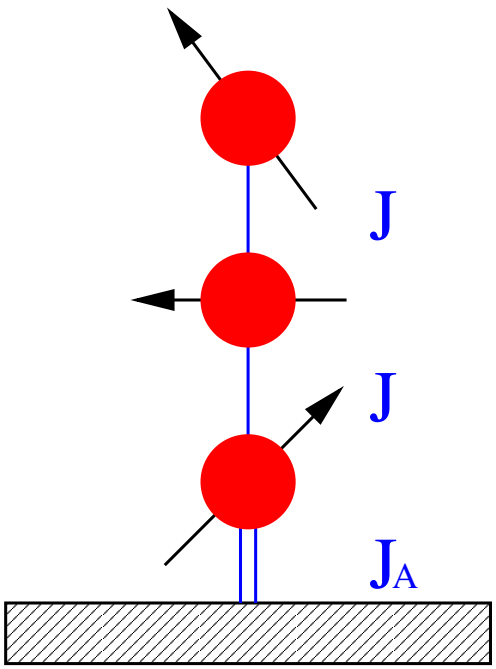


Stack of deposited Cobalt phthalocyanine (CoPc) molecules;
Co^{2+} with spin $s = 1/2$.

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!)



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

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

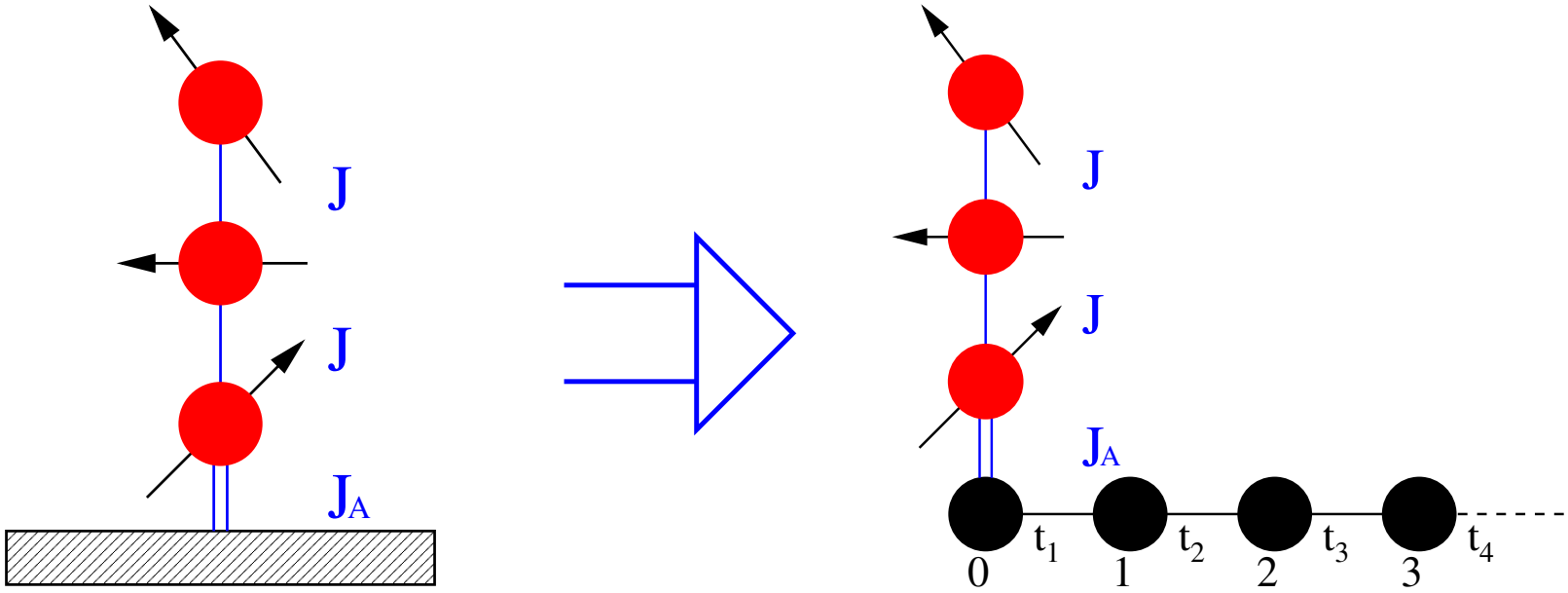
  $\underset{\sim}{H}_{\text{coupling}} = -2 J_A \underset{\sim}{\boldsymbol{S}} \cdot \underset{\sim}{\boldsymbol{s}}_0 \quad , \quad \underset{\sim}{\boldsymbol{s}}_0$ – spin density at contact

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

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

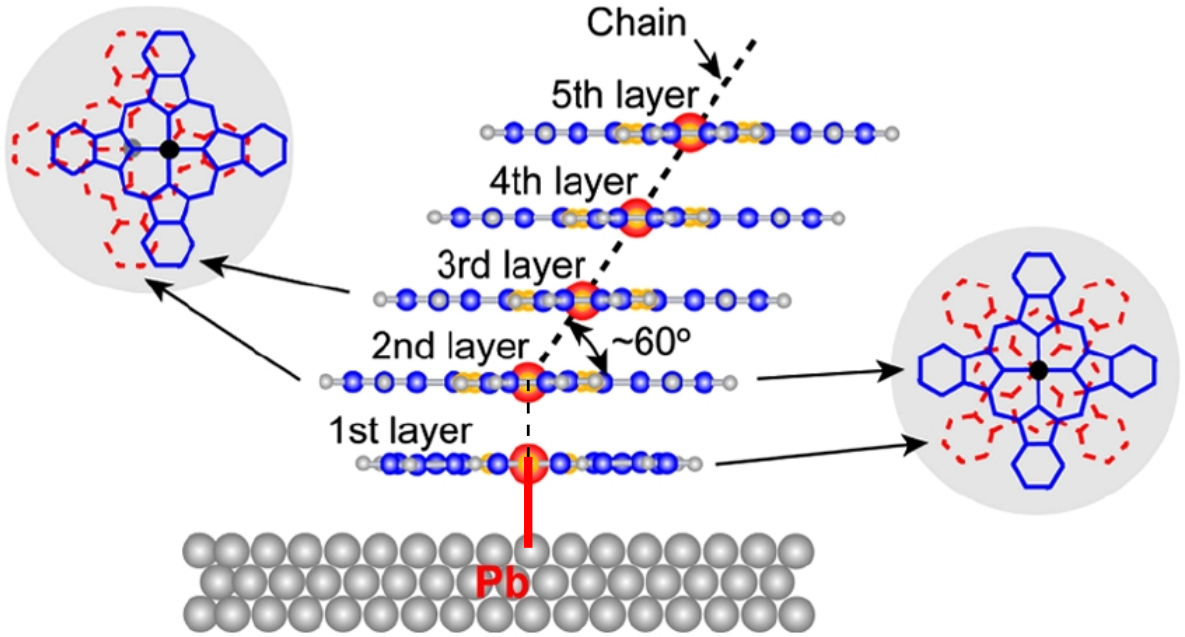
(1) K. G. Wilson, Rev. Mod. Phys. **47**, 773 (1975)
(2) M. Höck, J. Schnack, Phys. Rev. B **87**, 184408 (2013)
(3) *Impurity* is a technical term in this context and not an insult to chemists.

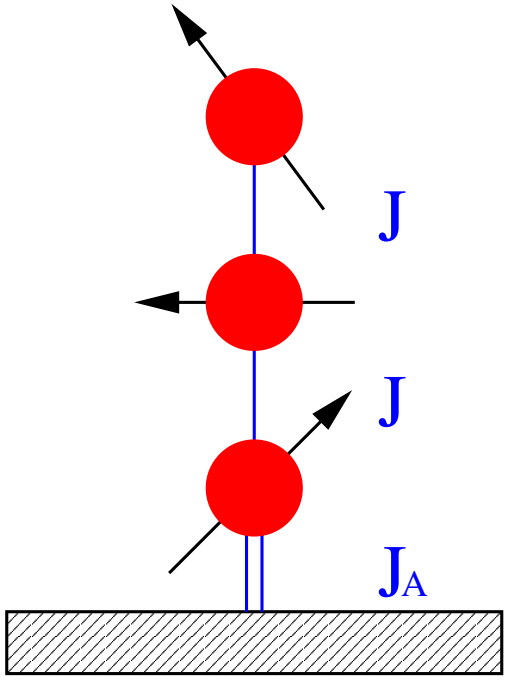
NRG in a cartoon



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.

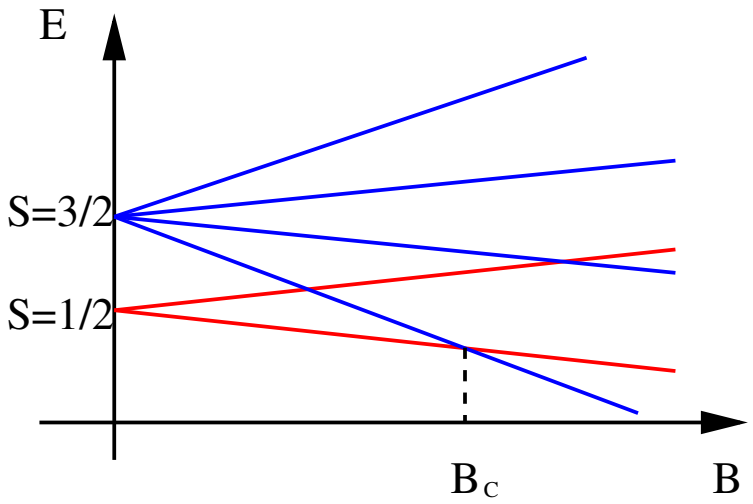
Once more: deposited chain



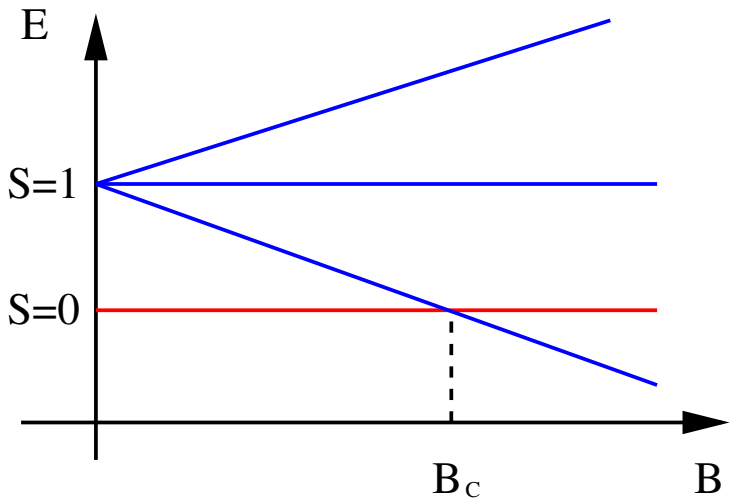


X. Chen *et al.*, Phys. Rev. Lett. **101**, 197208 (2008).

Energy levels of limiting cases for deposited trimer



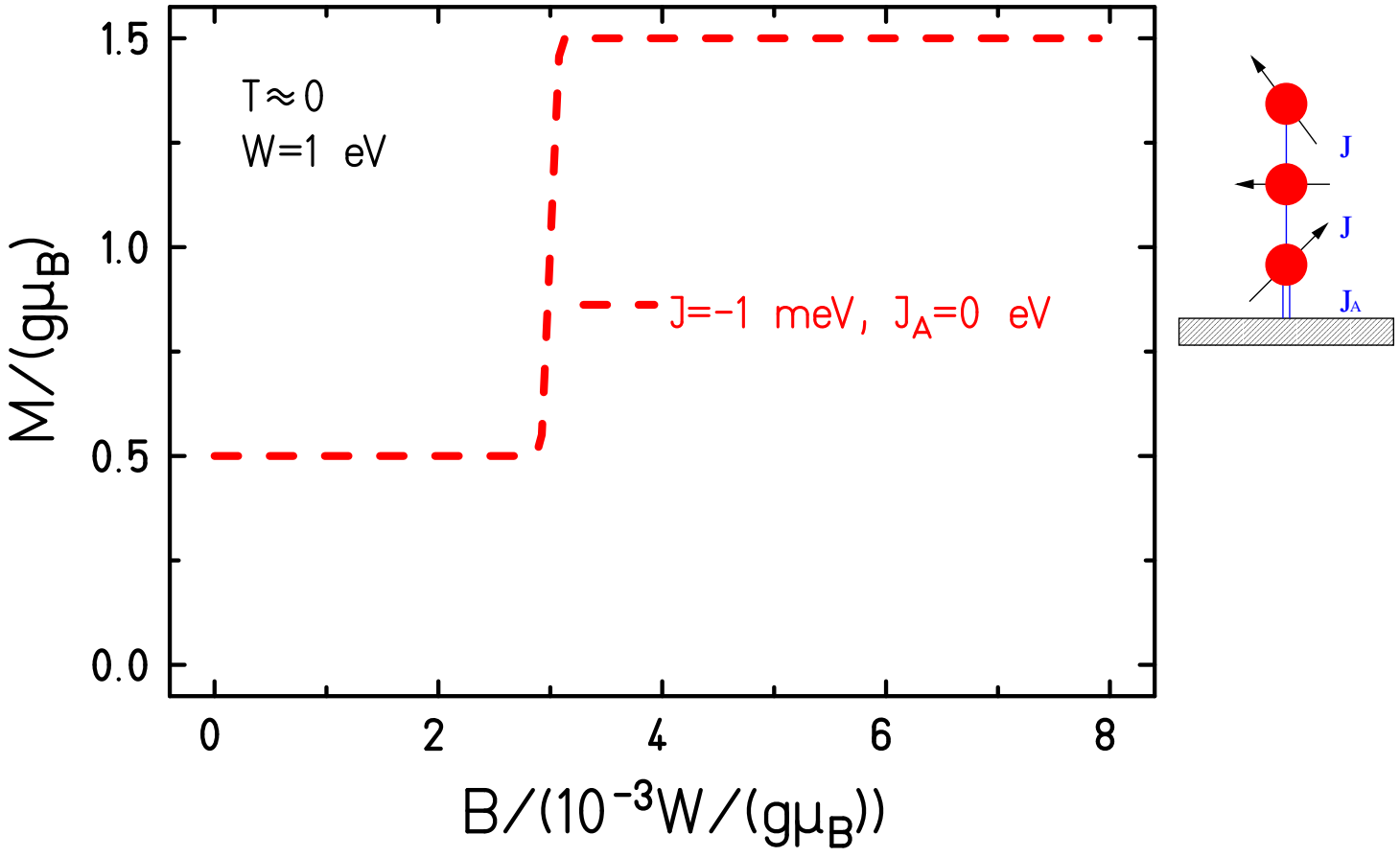
- energy levels of a trimer



- energy levels of a dimer

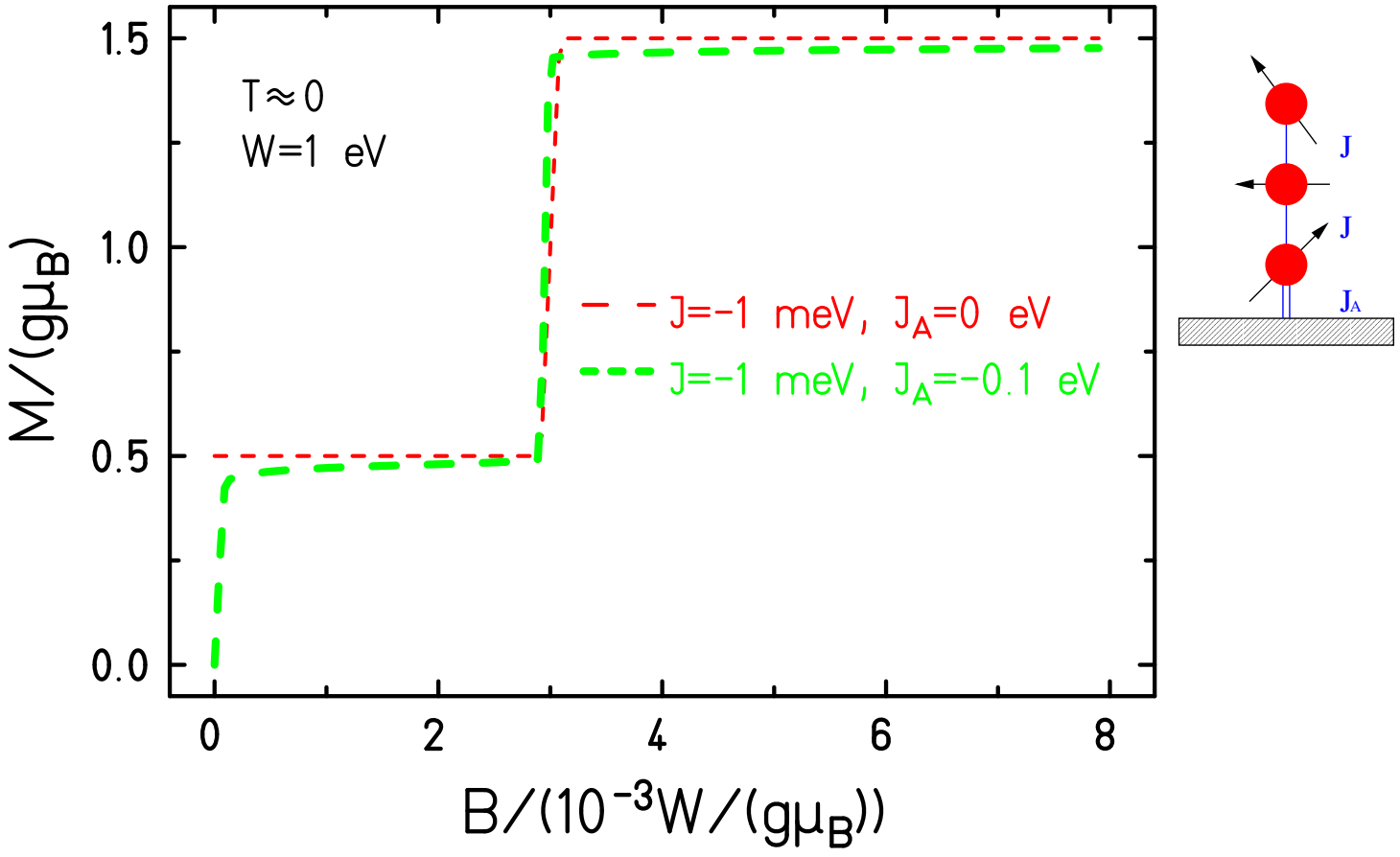
Magnetization curves different; could be seen in XMCD.
NRG calculates observables also between limiting cases
and can thus tell under which circumstances a limiting case applies.

Increasing coupling to the substrate



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

Increasing coupling to the substrate



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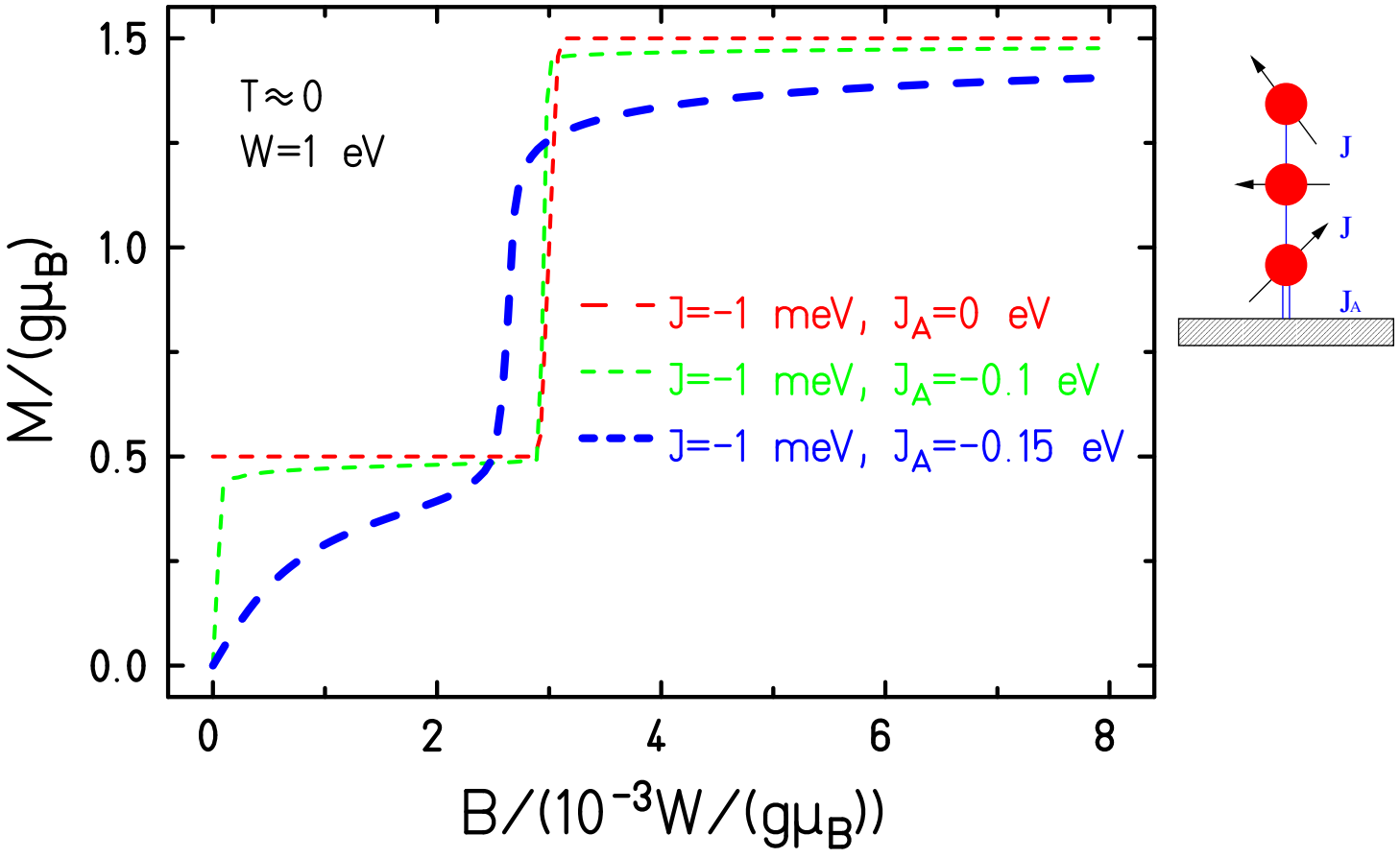

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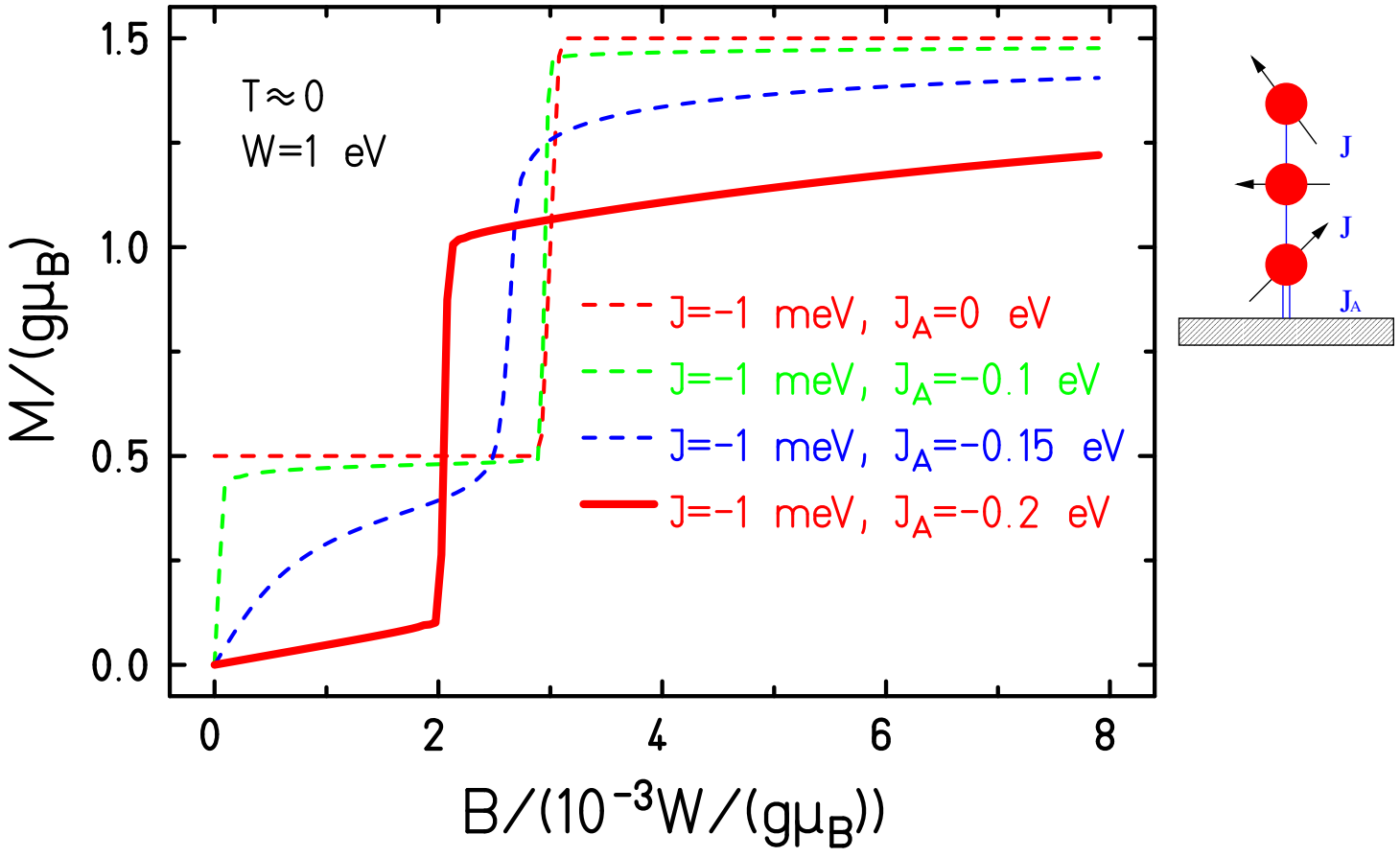

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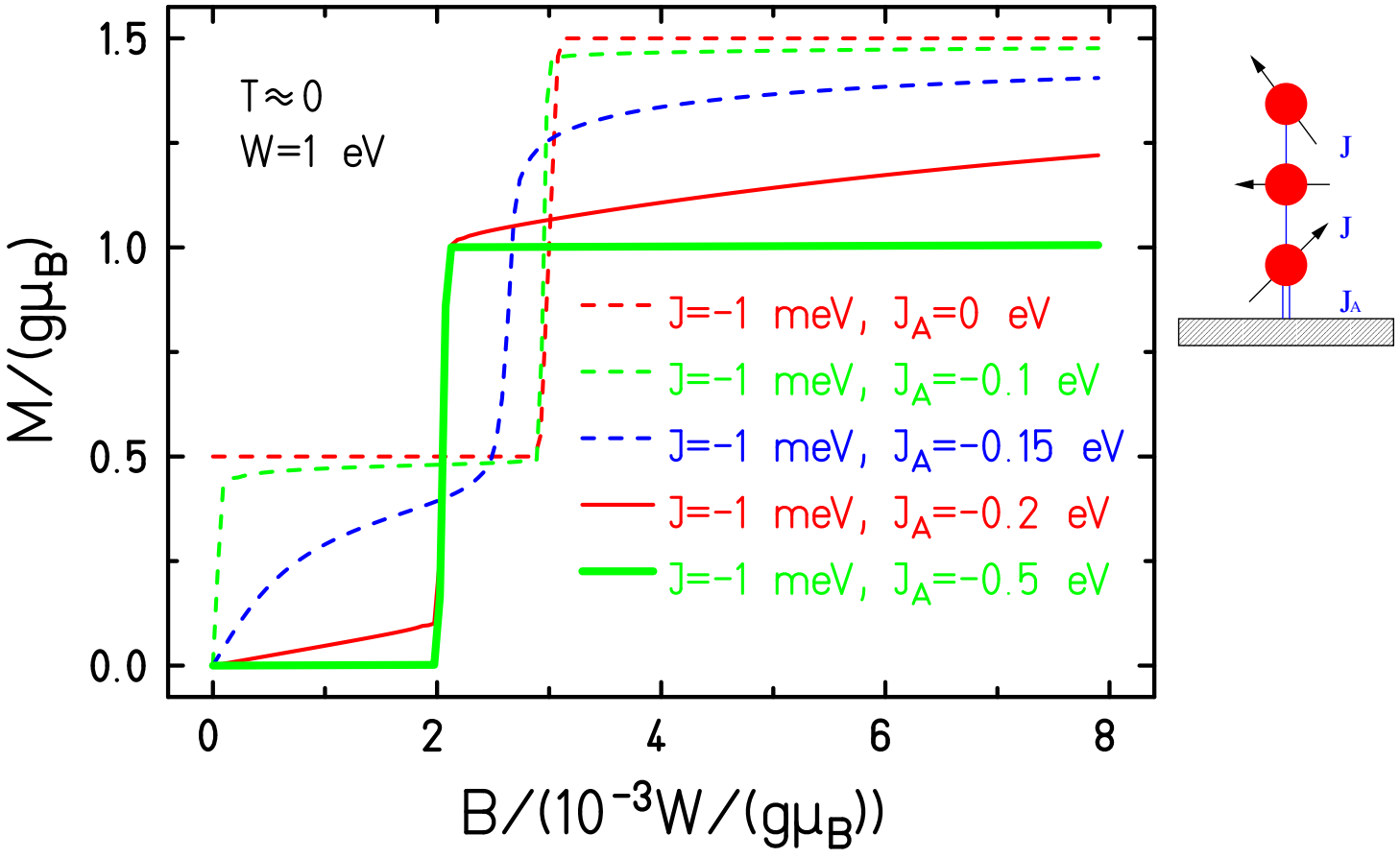

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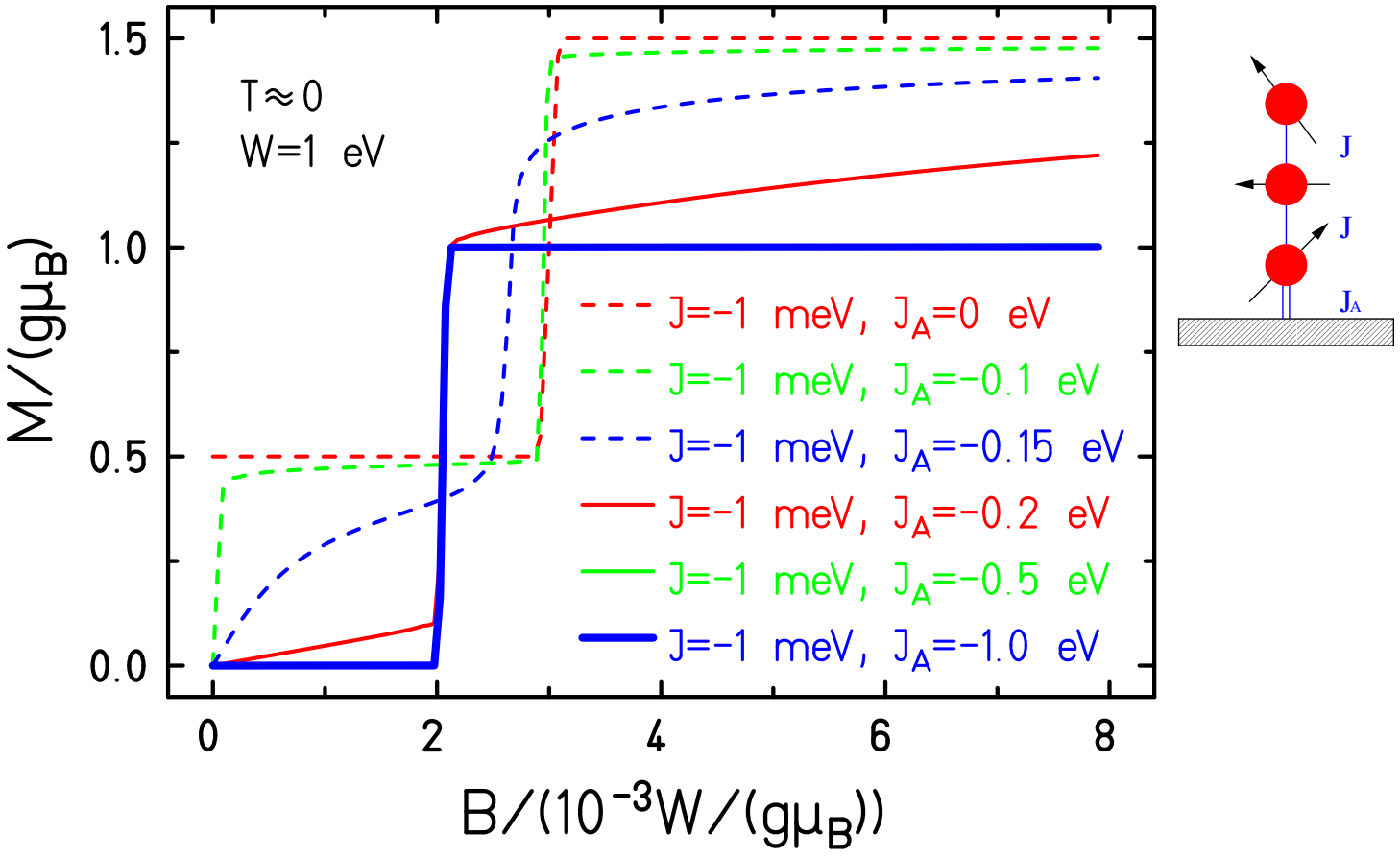
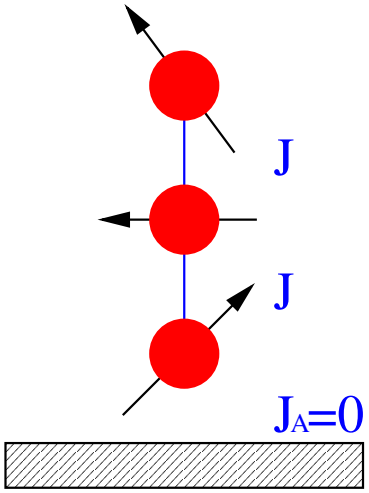
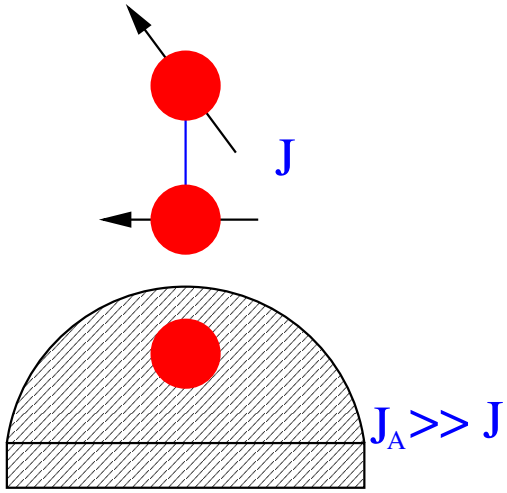


H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

Weak vs. strong coupling



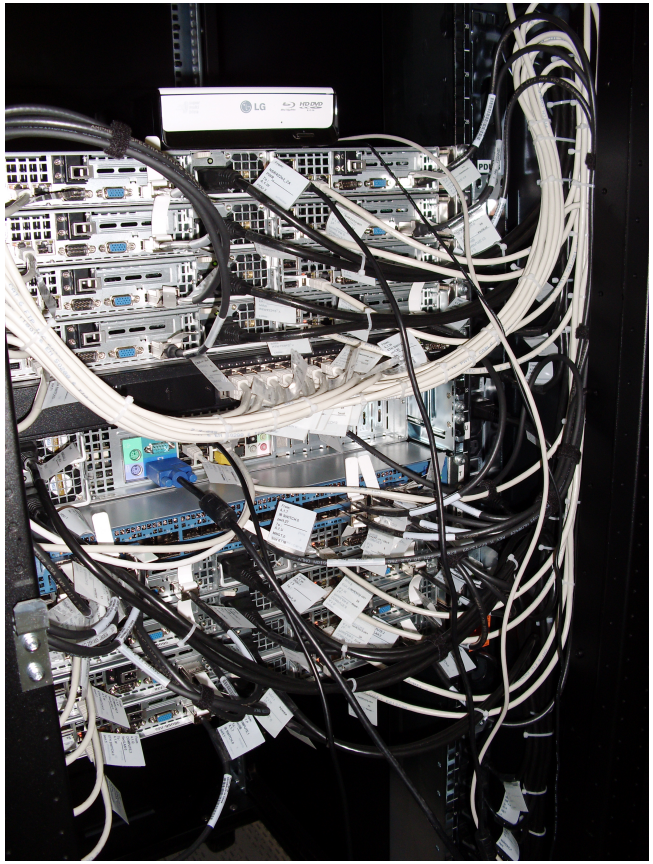


- weak coupling limit: unperturbed molecule (trimer)
- $|J_A| \lessapprox 0.1W$

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

Inbetween: no simple characterization + further sequential screening possible

Summary



- 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}.
- In 3-d intermolecular interactions of 10 % strength wash out magnetization features. To spoil controlled time-evolution much less is needed.
- NRG delivers local observables, such as magnetization, which can be compared with XMCD results.

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Thank you very much for your attention.

The end.

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