Influence of intermolecular interactions on magnetic observables

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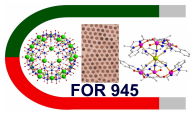
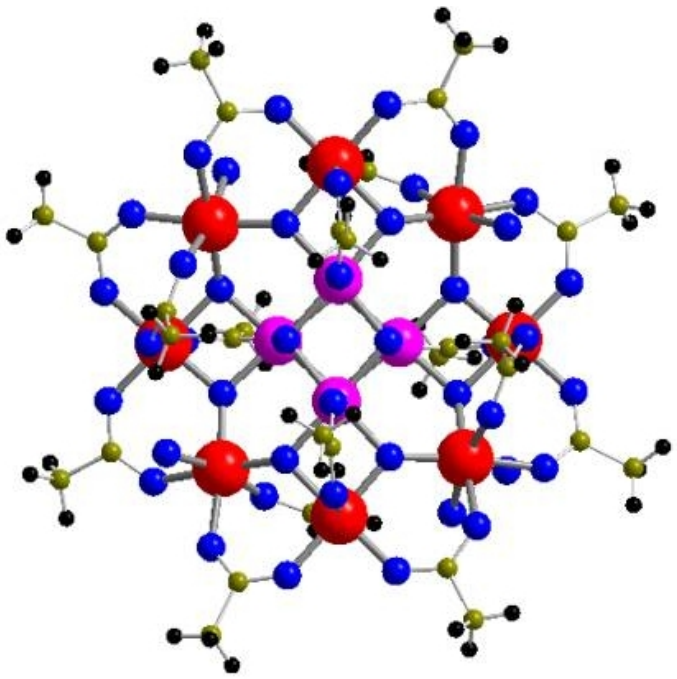


Beauty of Magnetic Molecules

J. Schnack, *Magnetismus im Molekülmaßstab*,
Physik-Journal **16**, 37-42 (2017).

The beauty of magnetic molecules I

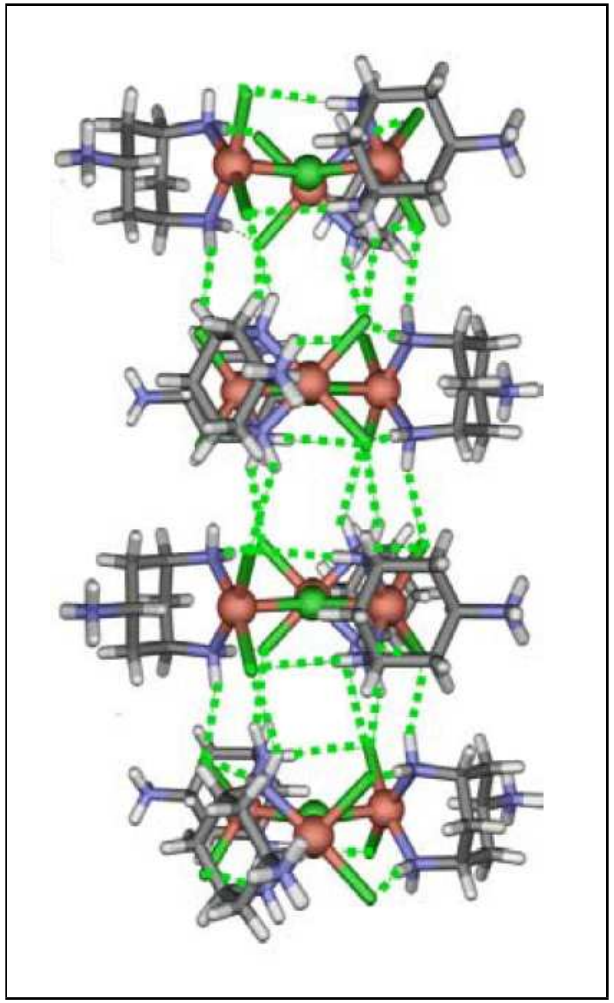


Mn_{12}

- Inorganic or organic macro molecules, e.g. polyoxometalates, where paramagnetic ions such as Iron (Fe), Chromium (Cr), Copper (Cu), Nickel (Ni), Vanadium (V), Manganese (Mn), or rare earth ions are embedded in a host matrix;
- Pure organic magnetic molecules: magnetic coupling between high spin units (e.g. free radicals);
- Single spin quantum number $1/2 \leq s \leq 7/2$;
- Intermolecular interaction relatively small, therefore measurements reflect the thermal behaviour of a single molecule.

Magnetism goes Nano, Ed. Stefan Blügel, Thomas Brückel, and Claus M. Schneider, FZ Jülich, Institute of Solid State Research, Lecture Notes **36** Jülich 2005

The beauty of magnetic molecules II



- Dimers (Fe_2), tetrahedra (Cr_4), cubes (Cr_8);
- Rings, especially iron rings (Fe_6, Fe_8, Fe_{10}, . . .);
- Complex structures (Mn_{12}) – drosophila of molecular magnetism;
- “Soccer balls”, more precisely icosidodecahedra (Fe_{30}) and other macro molecules;
- Chain like and planar structures of interlinked magnetic molecules, e.g. triangular Cu chain:

  J. Schnack, H. Nojiri, P. Kögerler, G. J. T. Cooper, L. Cronin, Phys. Rev. B **70**, 174420 (2004)

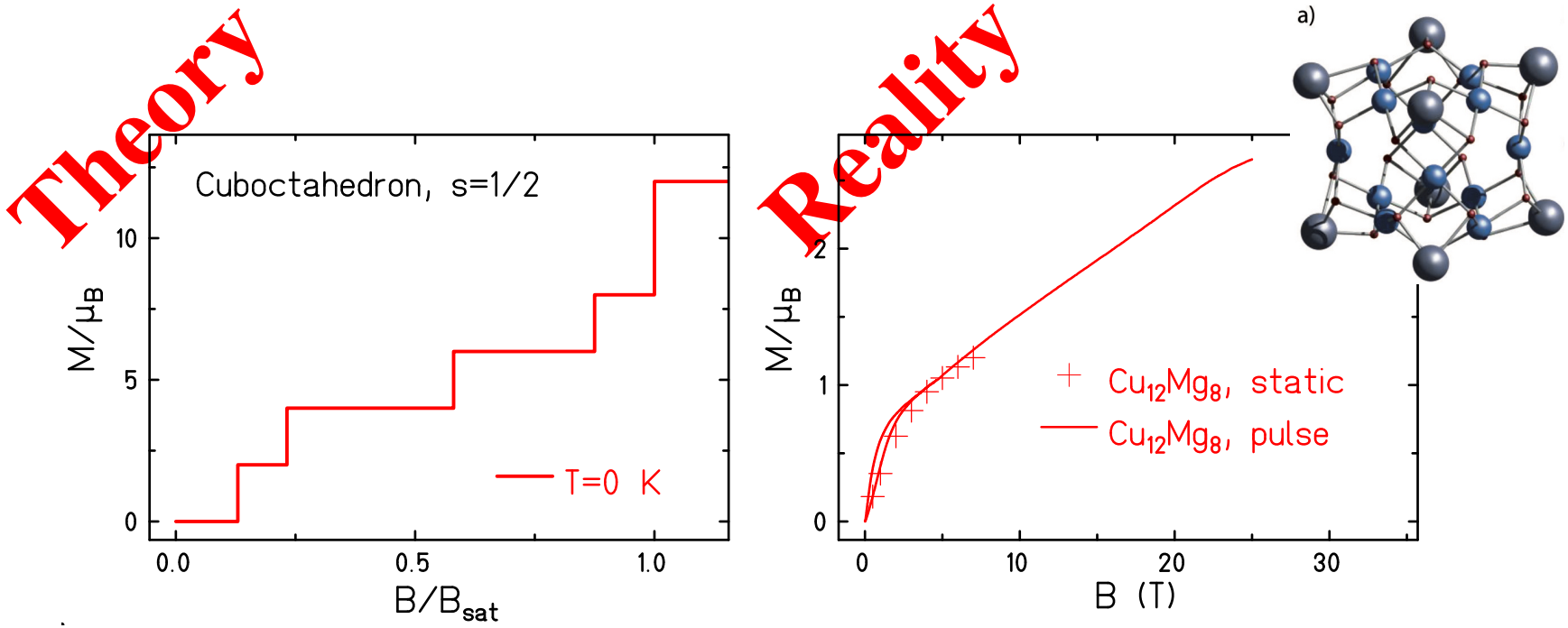
Contents for you today

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

1. Beauty of magnetic molecules $\surd$
2. Intermolecular interactions
3. Deposited molecules
4. AC susceptibility
5. Outlook

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

Example: magnetization steps are fingerprints



No magnetization steps! Reasons? Your suggestions?

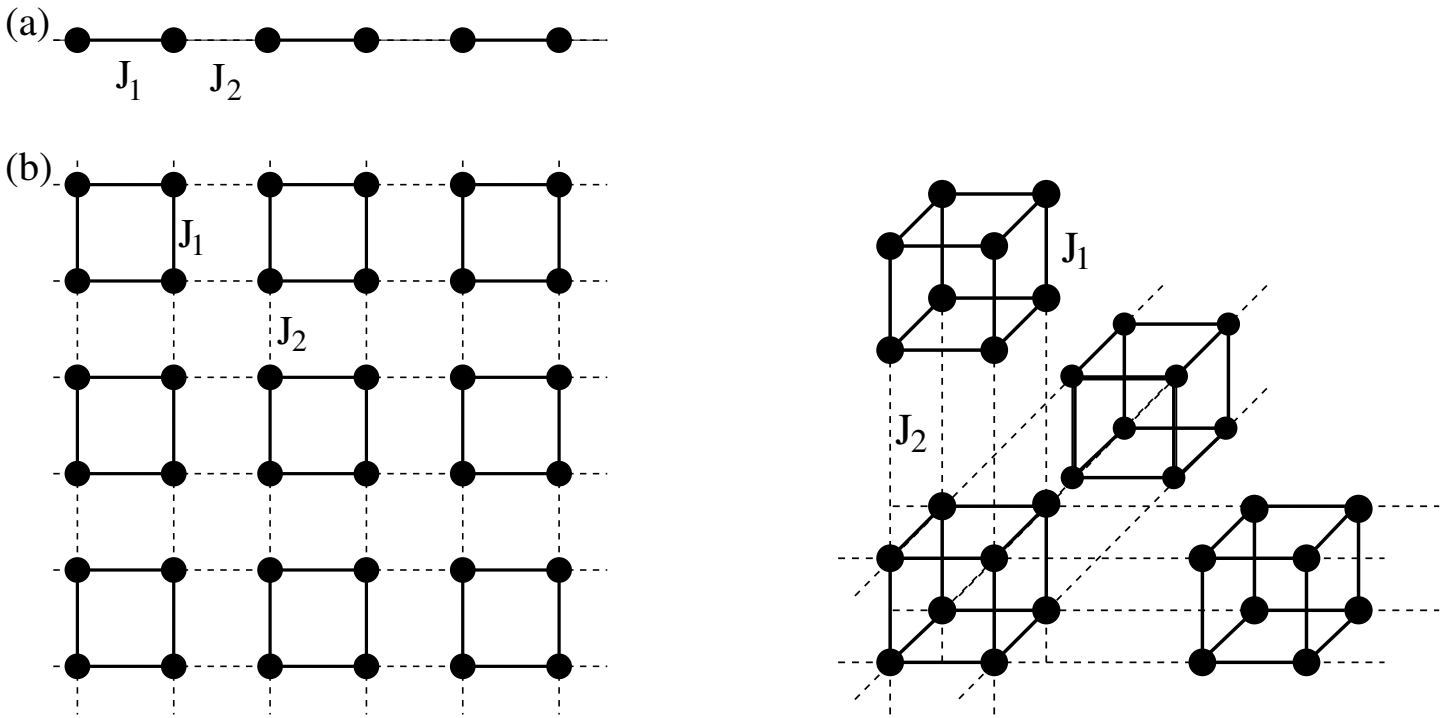
(1) M. Palacios, E. Pineda, S. Sanz, R. Inglis, M. Pitak, S. Coles, M. Evangelisti, H. Nojiri, C. Heesing, E. Brechin, J. Schnack, R. Winpenny, ChemPhysChem **17**, 55 (2016);
(2) and many more examples.

Summary: theory methods for correlated spins/electrons

- 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.
- Numerical Renormalization Group (NRG): impurity problems (Kondo, Anderson), thermodynamics of small systems coupled to conduction electrons.

Intermolecular interactions

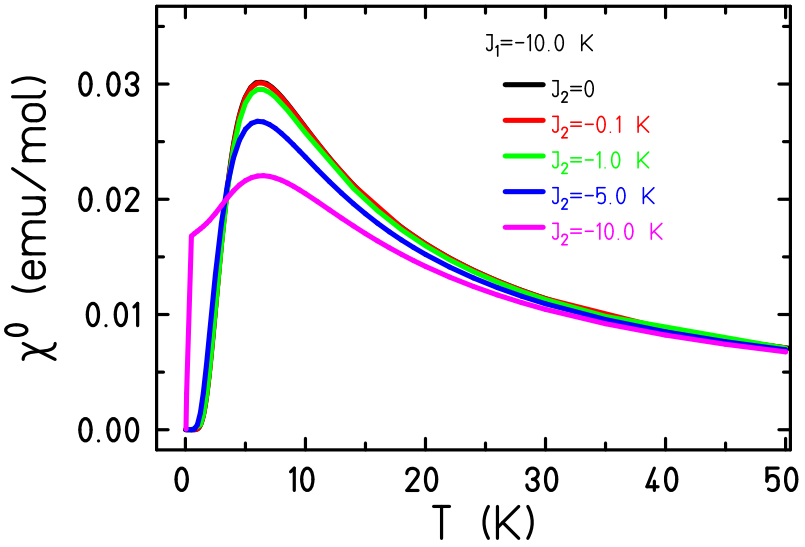
Intermolecular interactions – systems

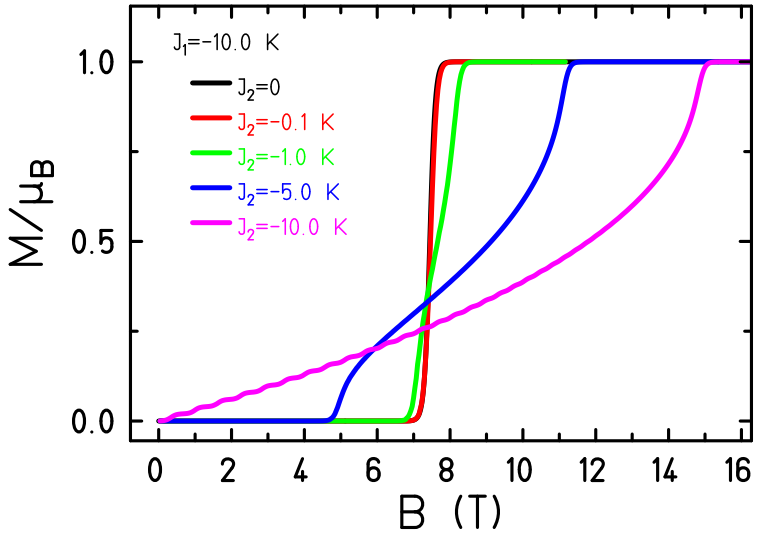


QMC investigation: Dimers in 1-d, squares in 2-d, cubes in 3-d.
All interactions antiferromagnetic, all spins $s = 1/2$. $N = 100 \ldots 1000$. PBC.

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

Intermolecular interactions – 1-d

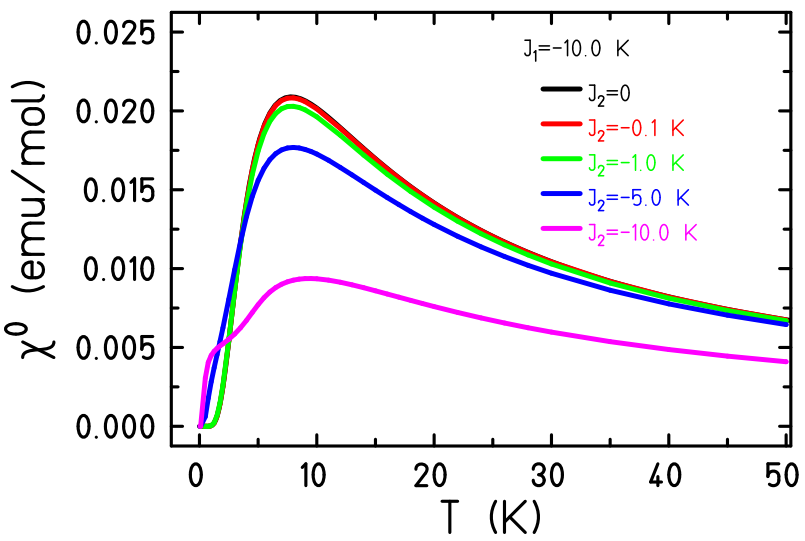


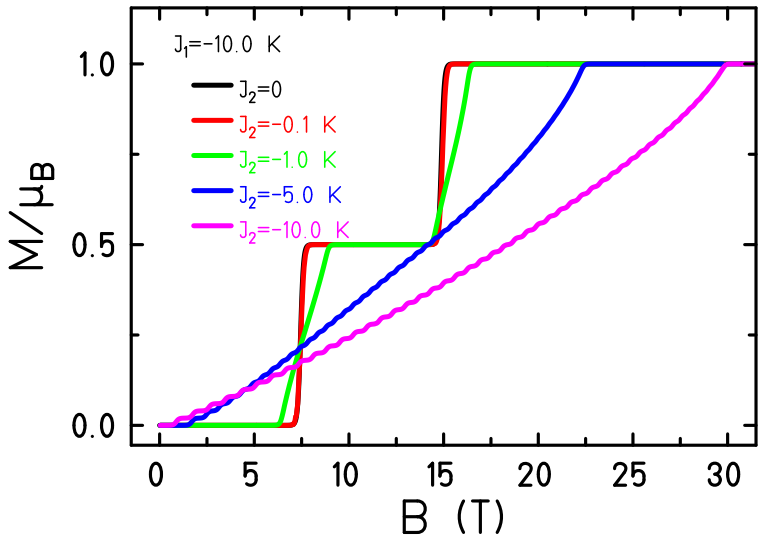


Gradually af dimers turn into gapless af chain.
Even at 50 % gap still large.

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

Intermolecular interactions – 2-d

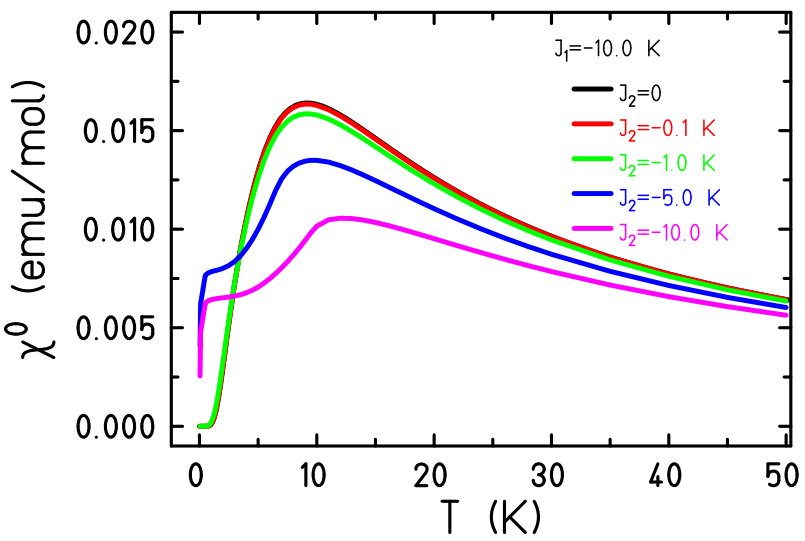


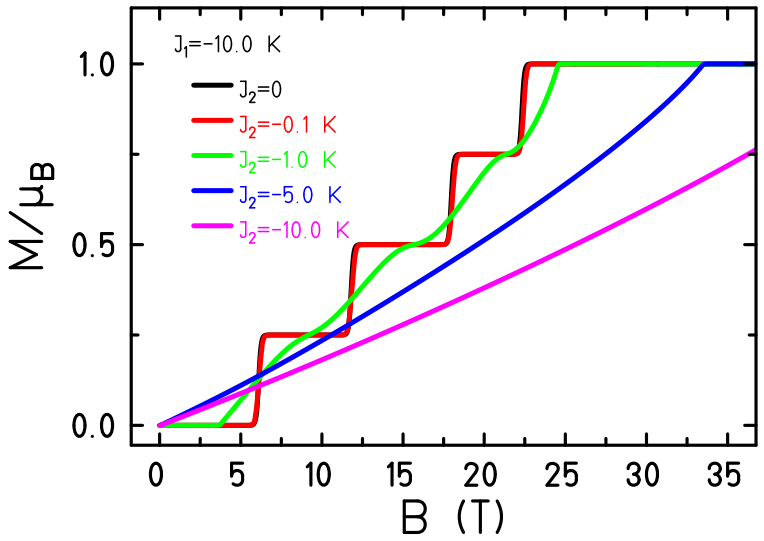


The two magnetization steps vanish more rapidly with intermolecular interactions in 2-d.

(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

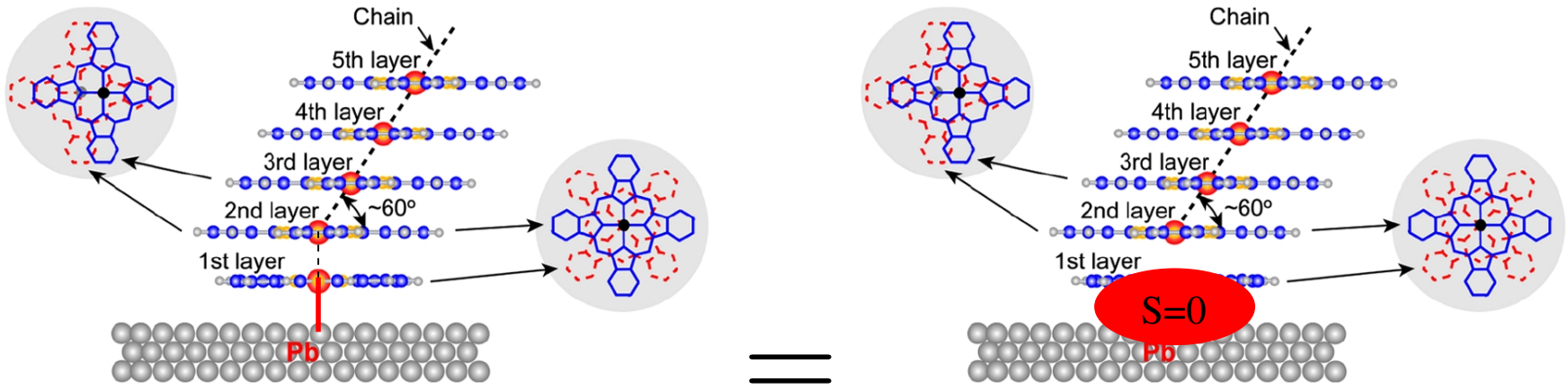
. . . to spoil static molecular magnetic observables.

(Less is needed to spoil the dynamics.)

Numerical Renormalization Group calculations

(Good for deposited molecules.)

Physical example (ICMM 2010)

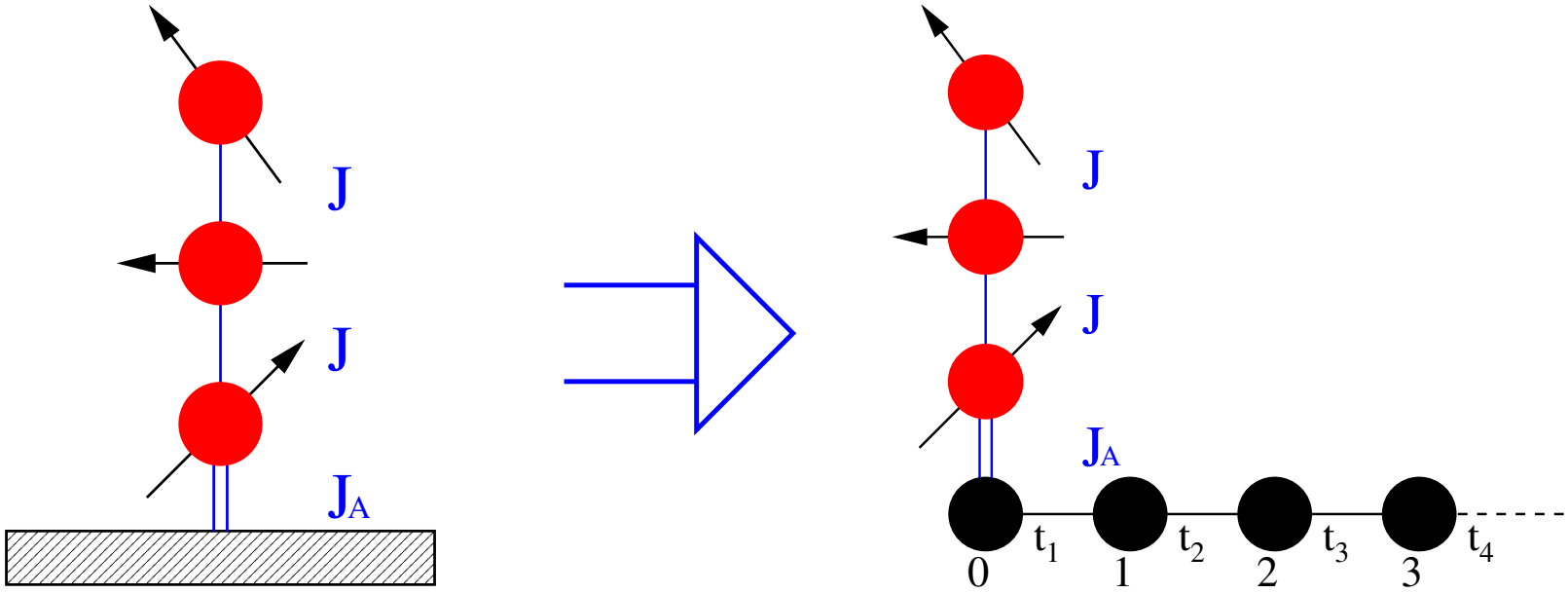


Stack of deposited Cobalt phthalocyanine (CoPc) molecules;
Co^{2+} with spin $s = 1/2$.

Under which circumstances is the picture of total screening correct?

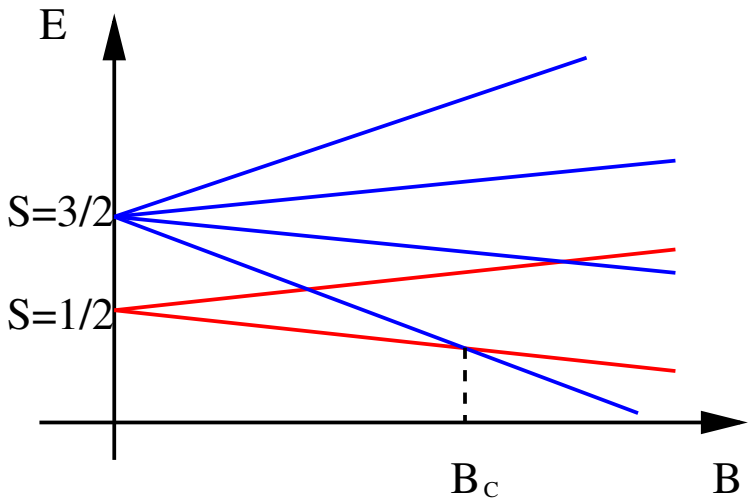
X. Chen *et al.*, Phys. Rev. Lett. **101**, 197208 (2008).

NRG in a cartoon

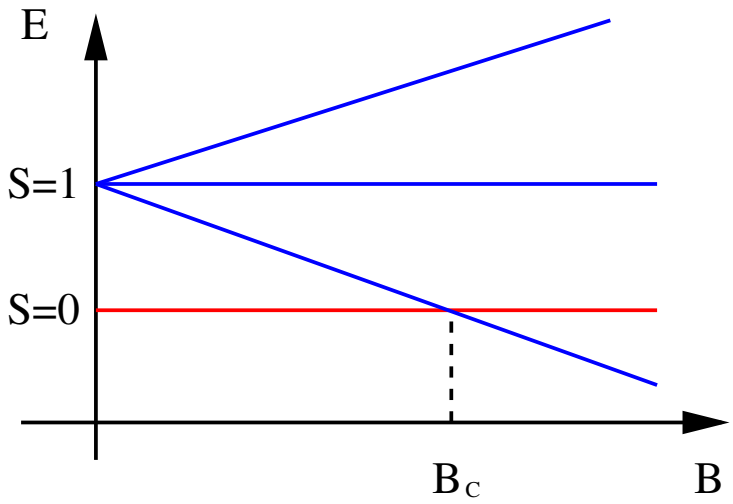


Metallic surface is replaced by semi-infinite Hubbard chain;
Parameters of the chain: hopping matrix elements and on-site energies;
Stepwise enlargement of the chain ($t_1 > t_2 > t_3 \ldots$);
Truncation of basis set when matrices grow too big.

Energy levels of limiting cases for deposited trimer



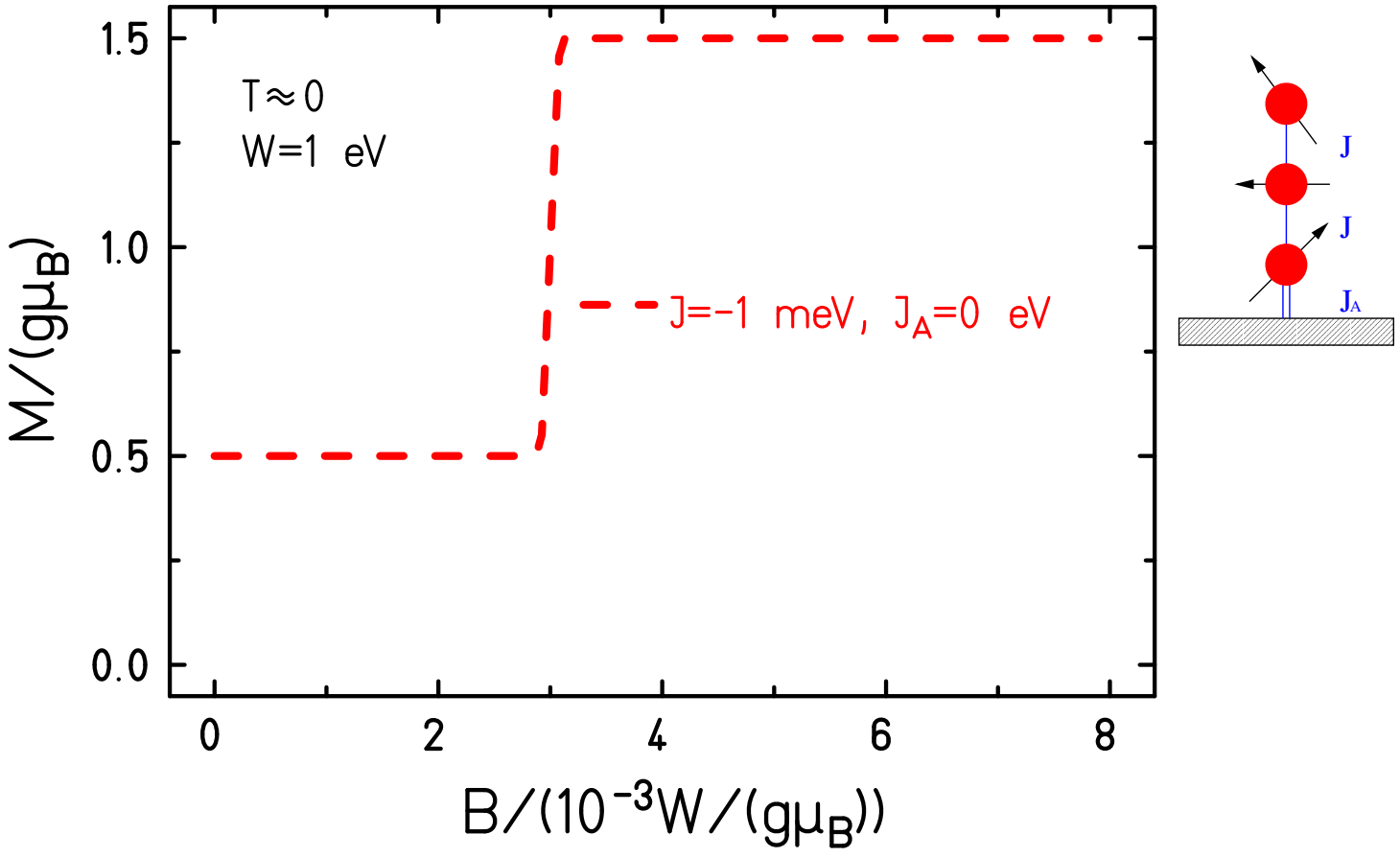
- energy levels of a trimer



- energy levels of a dimer

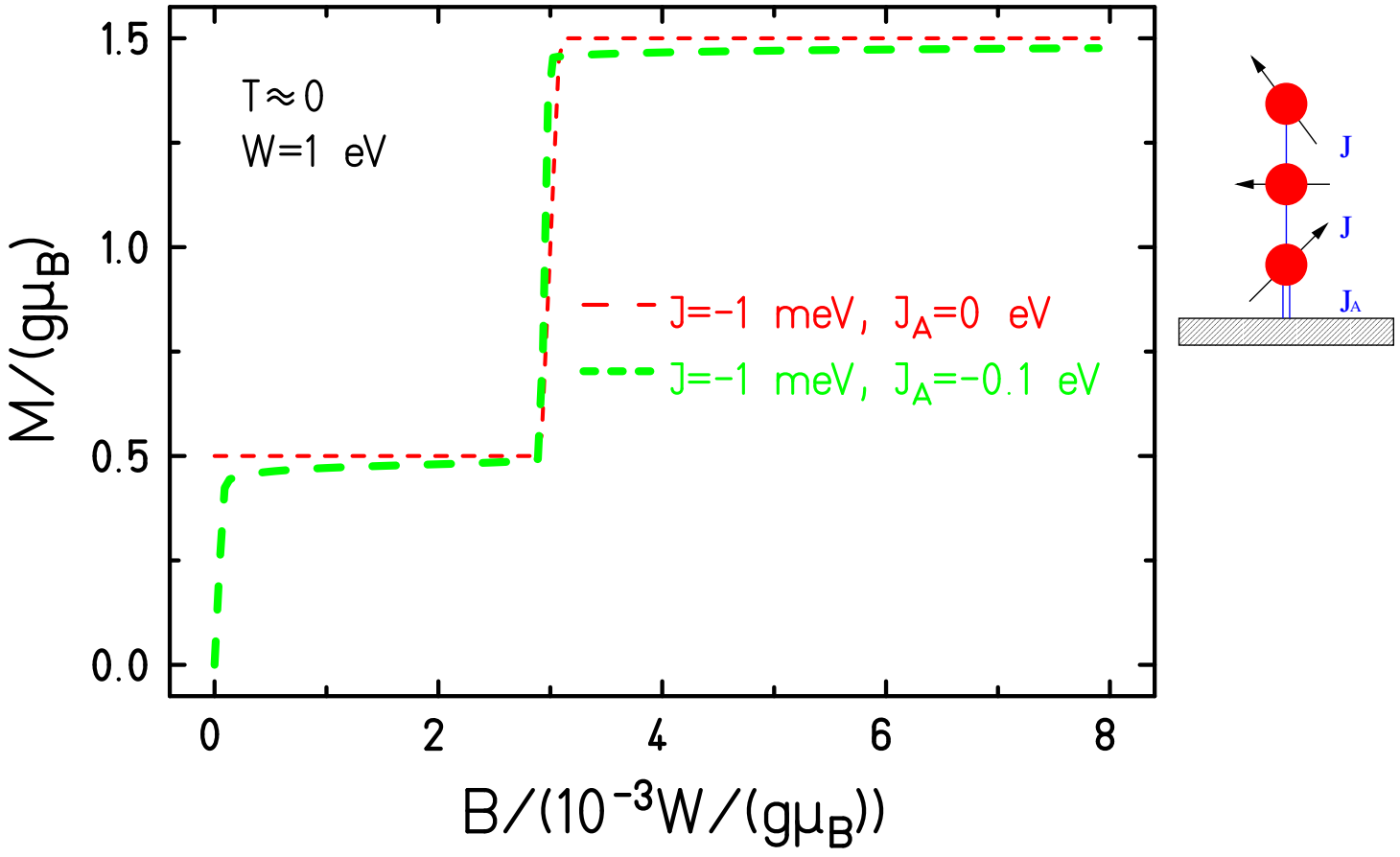
Magnetization curves different; could be seen in XMCD.
NRG calculates observables also between limiting cases
and can thus tell under which circumstances a limiting case applies.

Increasing coupling to the substrate



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

Increasing coupling to the substrate



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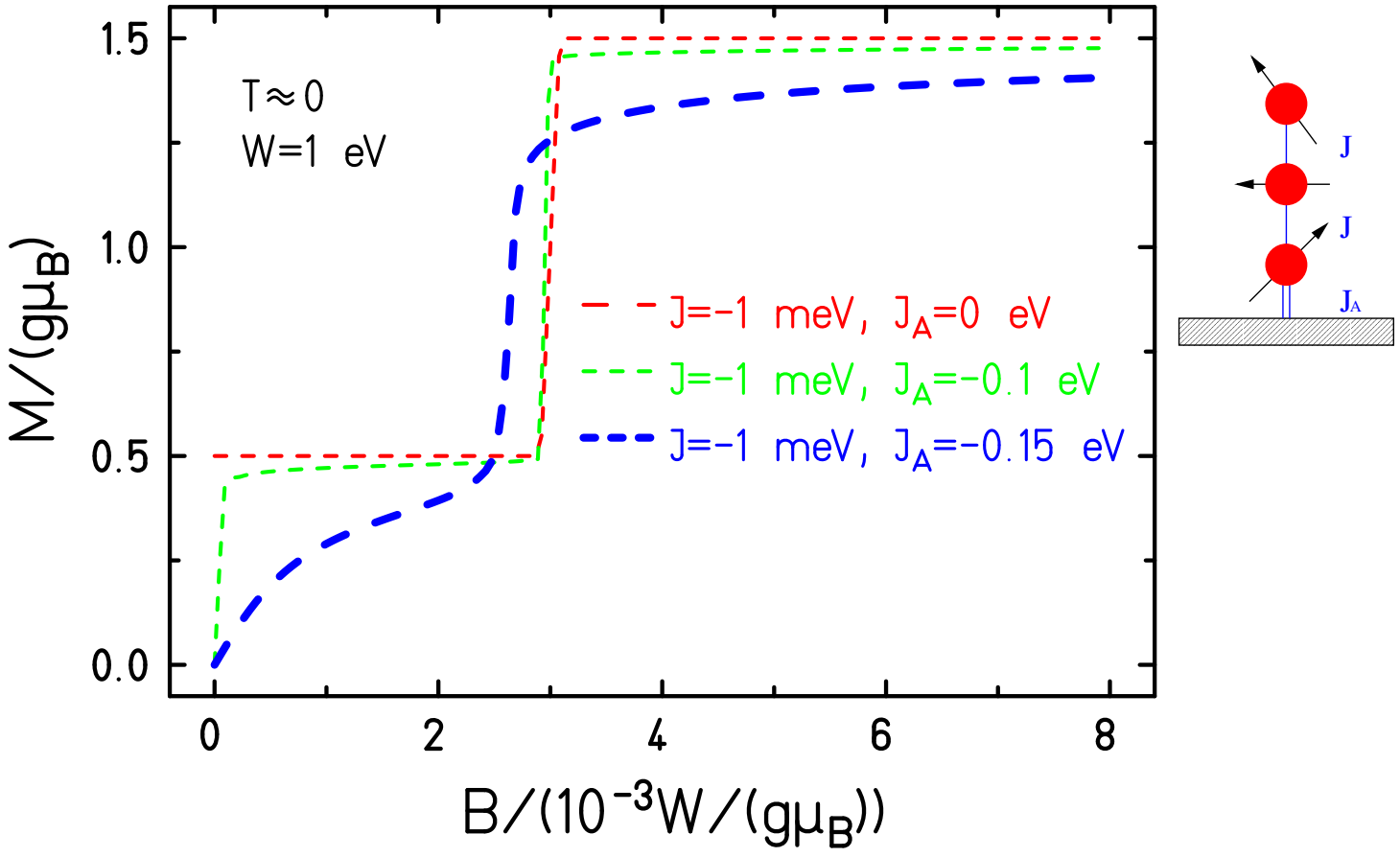

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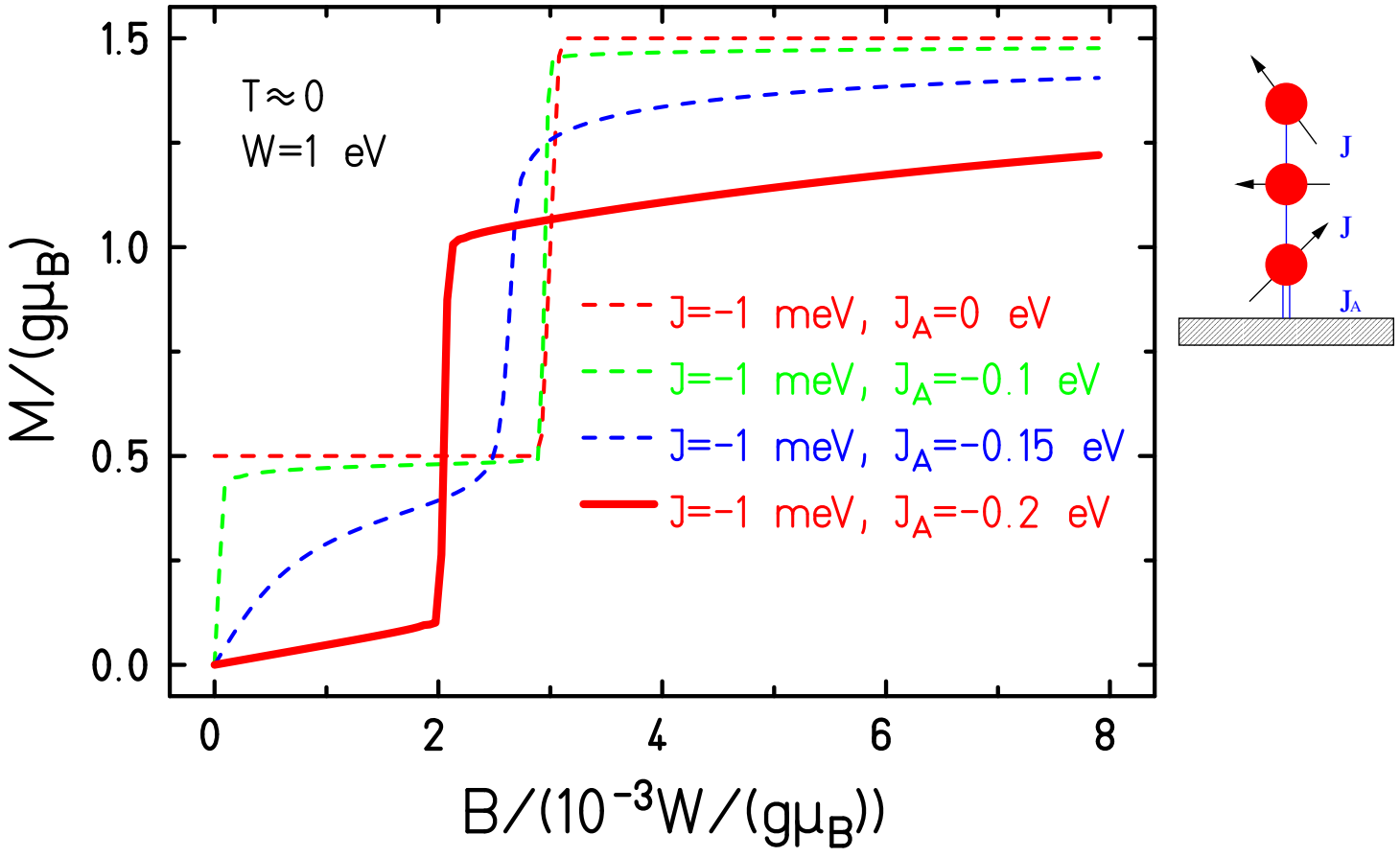

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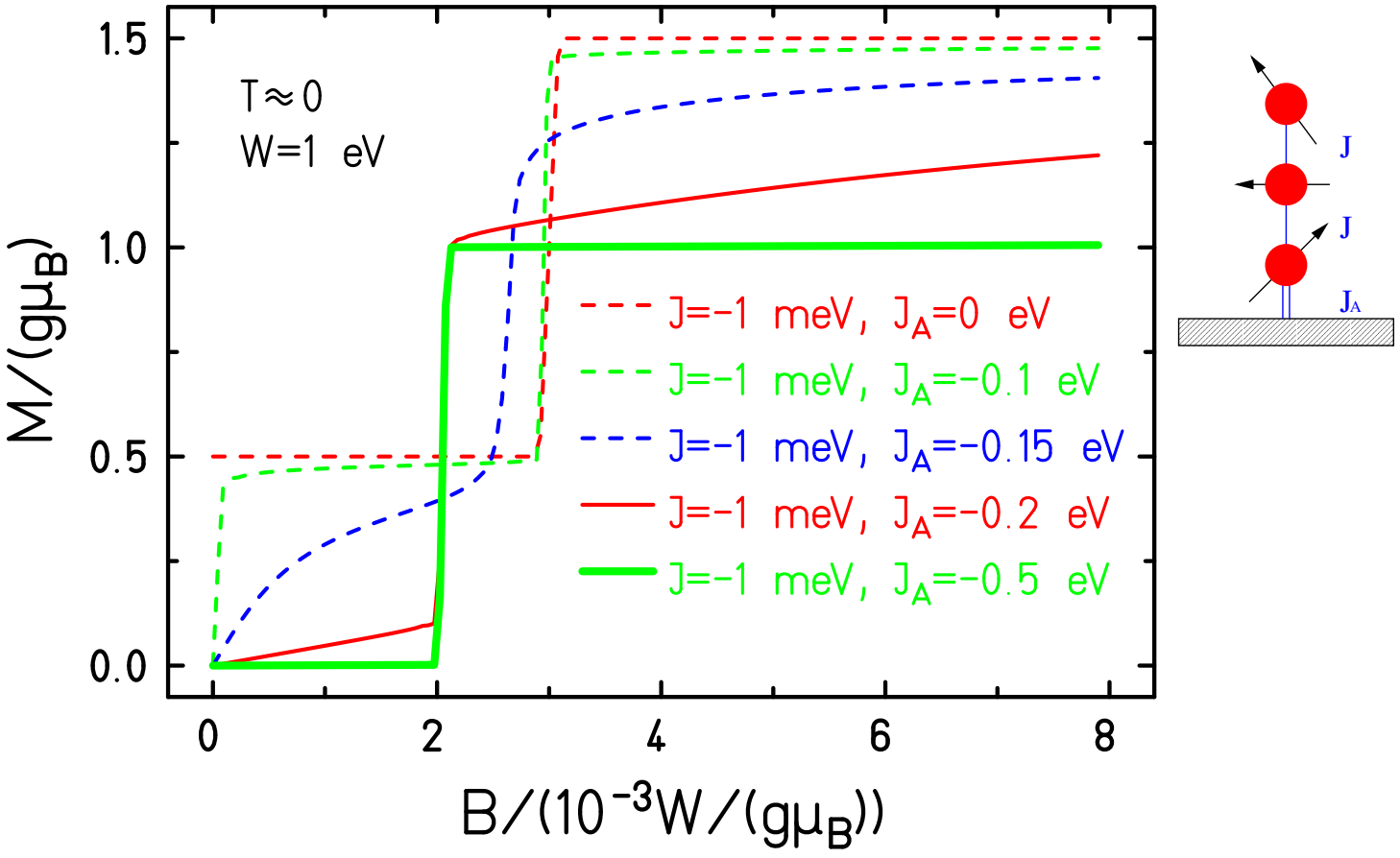
Increasing coupling to the substrate



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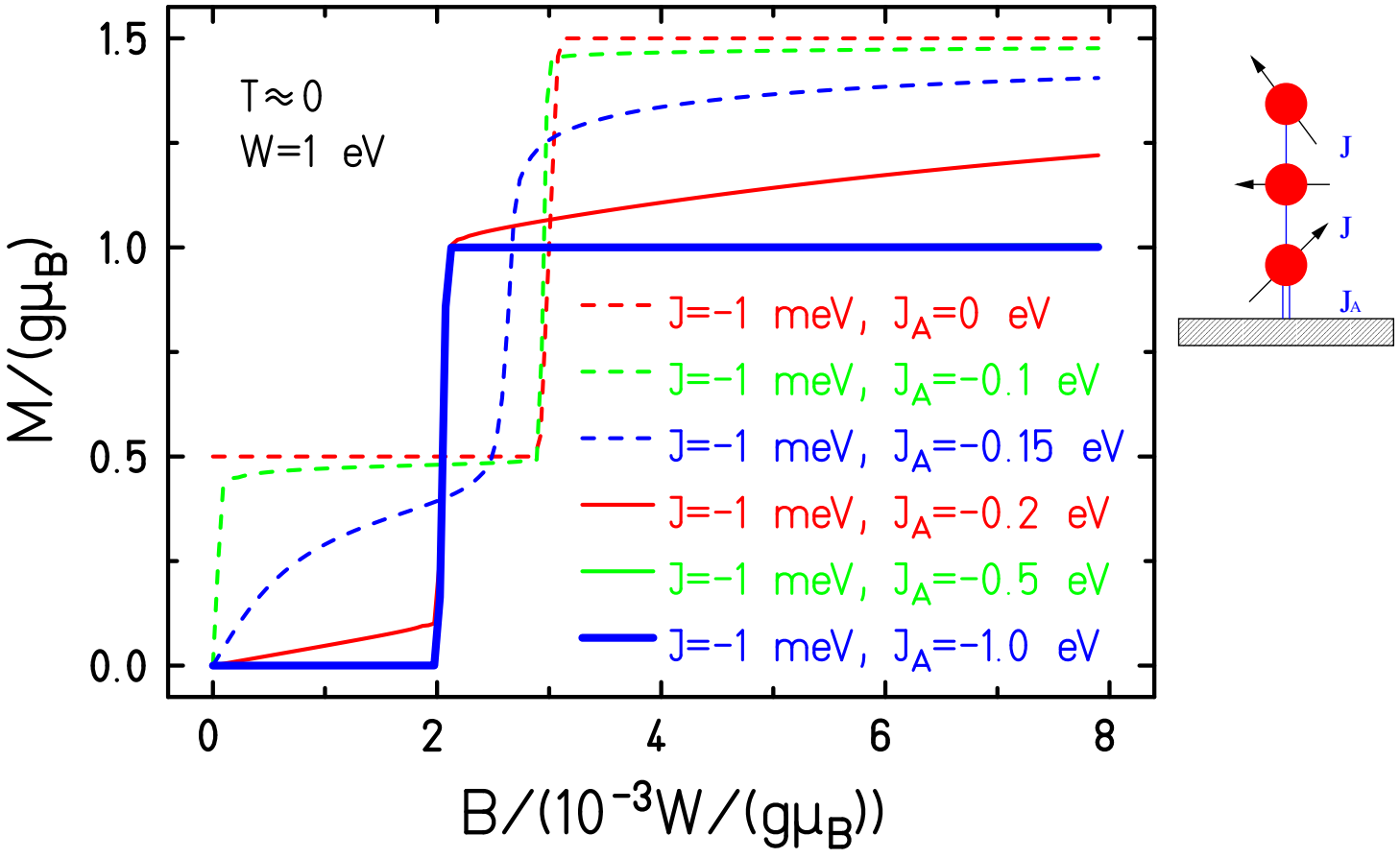
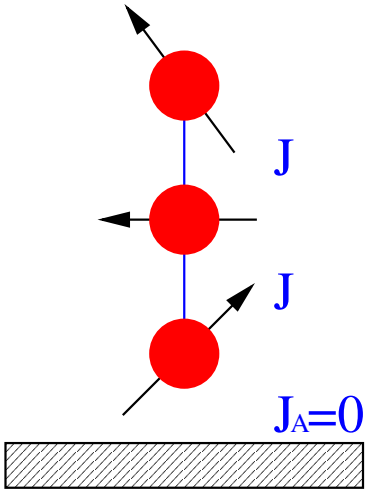
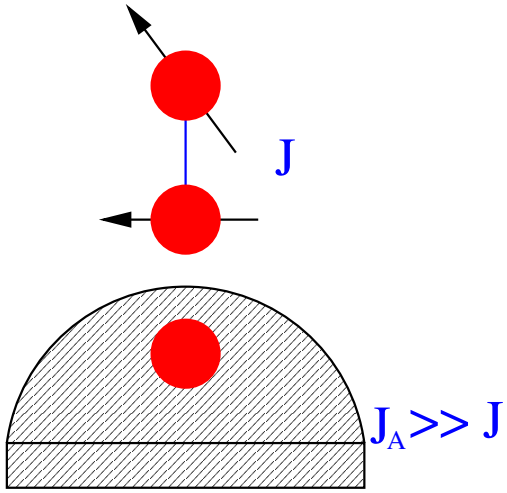


H.-T. Langwald and J. Schnack, submitted; arXiv:1312.0864.

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

AC susceptibility

Why is AC susceptibility complicated?

AC susceptibility I

$$\frac{d}{dt}\underset{\sim}{\rho}(t) = -i\left[\underset{\sim}{H}(t),\underset{\sim}{\rho}(t)\right] - \lambda\left(\left[\underset{\sim}{X},\underset{\sim}{R}\underset{\sim}{\rho}(t)\right] + \left[\underset{\sim}{X},\underset{\sim}{R}\underset{\sim}{\rho}(t)\right]^{\dagger}\right) ,$$

$$\langle k|\underset{\sim}{R}|n\rangle = \frac{I(E_k - E_n) - I(E_n - E_k)}{e^{\beta(E_k - E_n)} - 1}\langle k|\underset{\sim}{X}|n\rangle ,$$

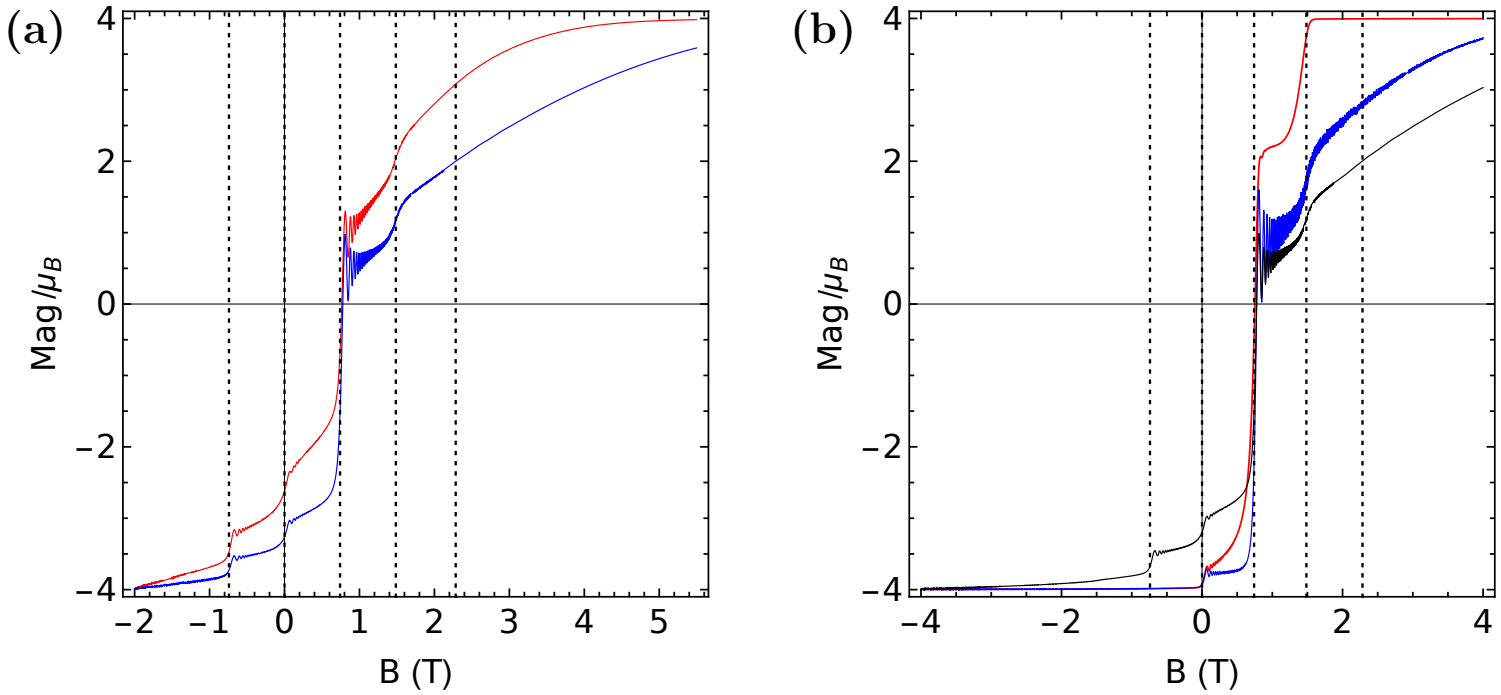
$$I(E_k - E_n) = I_0 \cdot (E_k - E_n) ,$$

$$\underset{\sim}{X}_1 = \underset{\sim}{S}_x , \ldots$$

Lindblad, Markov, but transitions $\underset{\sim}{X}$ physically motivated (selection rules), combined unitary time-evolution and relaxation

(1) T. Kawakami, H. Nitta, M. Takahata, M. Shoji, Y. Kitagawa, M. Nakano, M. Okumura, and K. Yamaguchi, Polyhedron **28**, 2092 (2009).

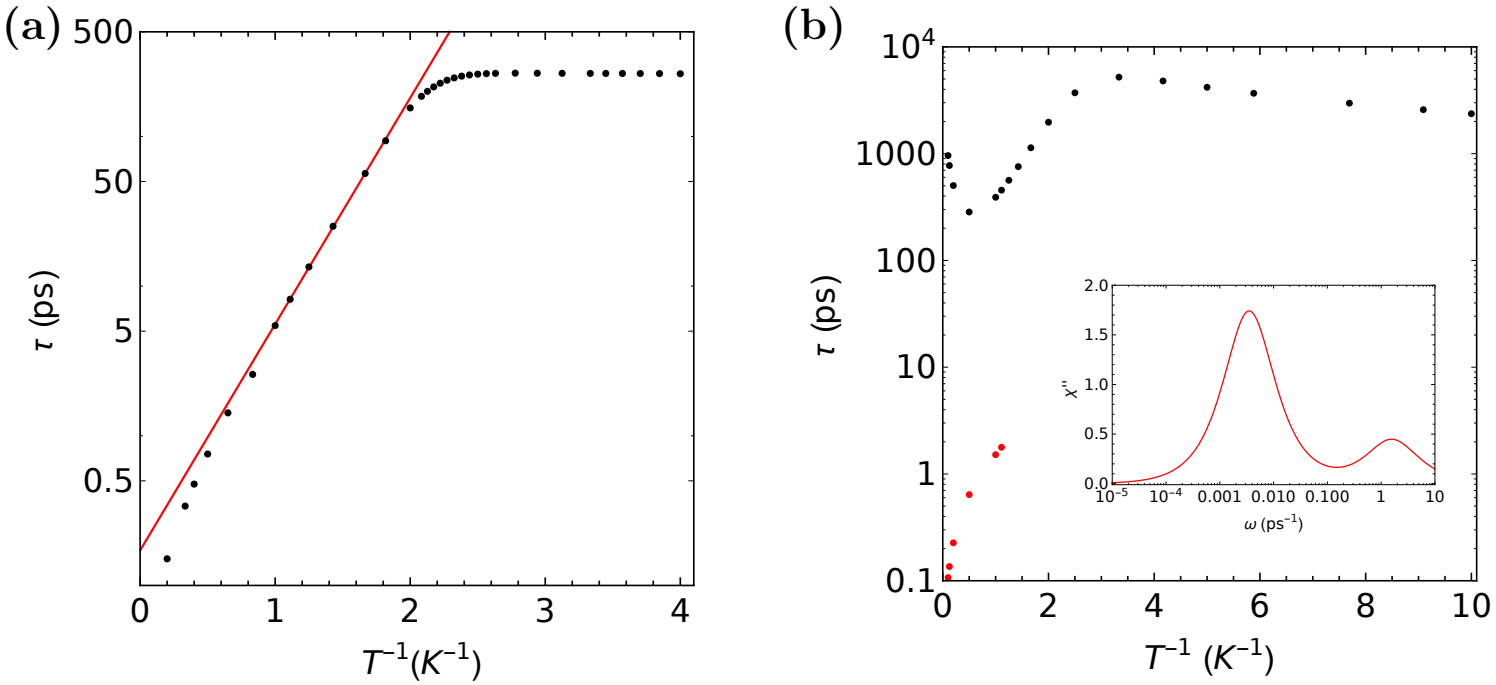
AC susceptibility II



Magnetization dynamics using various transition operators and couplings to the bath ($S = 2$, $D = -1$ K, $E = 0.1$ K, $g = 2$).

(1) C. Beckmann and J. Schnack, J. Magn. Magn. Mater. **437**, 7 (2017).

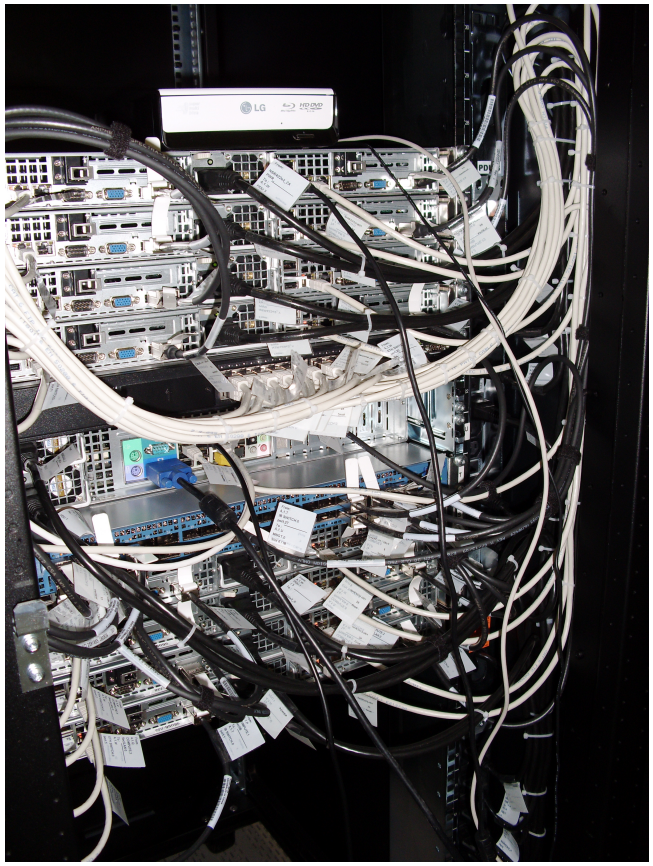
AC susceptibility III



Relaxation times derived from AC simulations for two transition operators ($S = 2$, $D = -1$ K, $E = 0.1$ K, $g = 2$).

(1) C. Beckmann and J. Schnack, J. Magn. Magn. Mater. **437**, 7 (2017).

Outlook



- We may learn something about spin-bath interactions via simulations of AC susceptibility.
- More general interesting question: how does thermodynamics emerges from a unitary time evolution (of a few spins)?
- Also related: how do small quantum heat engines (of a few spins) work under realistic conditions?
- New molecules are ahead: $S = 60$ ground state close to a quantum critical point (publication soon).

Many thanks to my collaborators worldwide

- C. Beckmann, M. Czopnik, T. Glaser, O. Hanebaum, Chr. Heesing, M. Höck, N.B. Ivanov, H.-T. Langwald, A. Müller, R. Schnalle, Chr. Schröder, J. Ummethum (Bielefeld)
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Thank you very much for your attention.

The end.

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