Anisotropy and Spin-Phonon-Interactions in Molecular Magnets

Jürgen Schnack
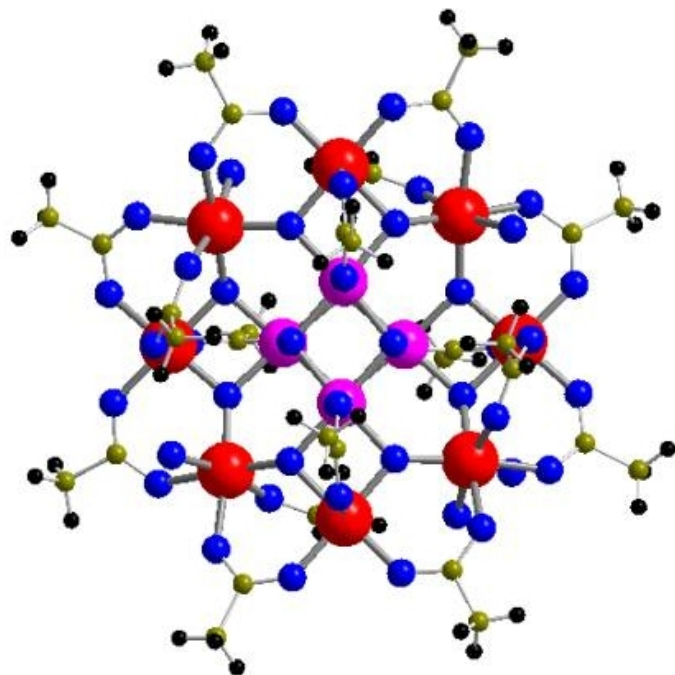
Department of Physics – University of Bielefeld – Germany

http://obelix.physik.uni-bielefeld.de/∼schnack/

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Beauty of Magnetic Molecules

The beauty of magnetic molecules I

Mn$_{12}$

- Inorganic or organic macro molecules, e.g. poly-oxometalates, 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;

- Purely 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.

(1) S. J. Blundell, *Molecular magnets*, Contemp. Phys. **48**, 275 (2007).
(2) J. Schnack, *Large magnetic molecules and what we learn from them*, Contemp. Phys. **60**, 127 (2019).

The beauty of magnetic molecules II
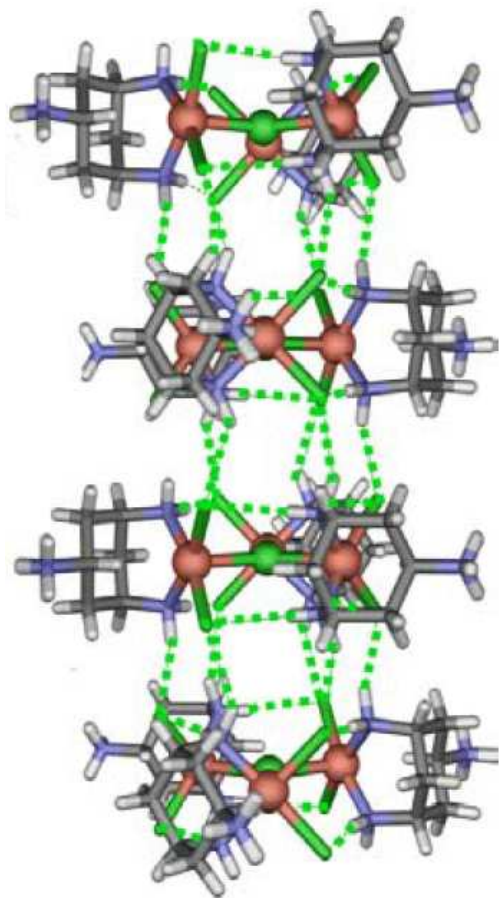
- Dimers (Fe_2), tetrahedra (Cr_4), cubes (Cr_8);

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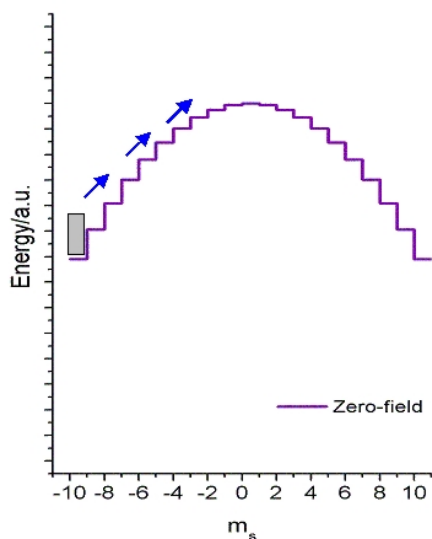
J. Schnack, H. Nojiri, P. Kögerler, G. J. T. Cooper, L. Cronin, Phys. Rev. B 70, 174420 (2004)

The beauty of magnetic molecules III
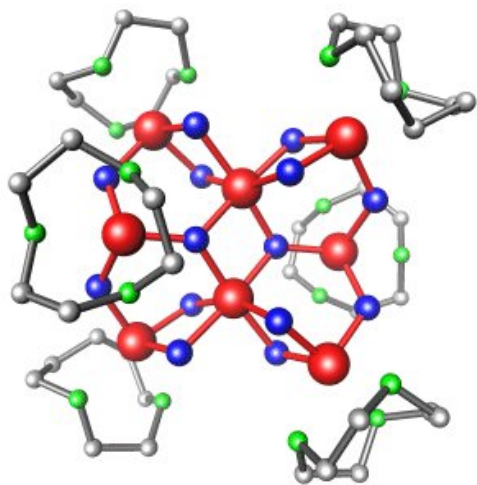
- Single Molecule Magnets (SMM): magnetic molecules with (often) large ground state moment;

- Example: $S = 10$ for Mn_{12} or Fe_8;

- Anisotropy dominates approximate single-spin Hamiltonian:

$$\underset{\sim}{H} = -D\underset{\sim}{S}_z^2 + \underset{\sim}{H}', \qquad \left[\underset{\sim}{S}_z, \underset{\sim}{H}'\right] \neq 0$$

- Single molecule shows: metastable magnetization, hysteresis, ground-state and/or phonon-assisted magnetization tunneling.

- Today's major efforts: improve stability of magnetization; investigate on surfaces.

Yes, we can!

1. Beauty of magnetic molecules $\sqrt{}$

2. Single-ion anisotropy

3. Bistability and tunneling

4. Spin-phonon interaction

5. SUSY spin-phonon interaction

6. Bonus: Typicality approach

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

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

Single-ion anisotropy

Model Hamiltonian (effective, spin-only, bilinear)

$$\underset{\sim}{H} = \sum_{i,j} \vec{\underset{\sim}{s}}(i) \cdot \mathbf{J}_{ij} \cdot \vec{\underset{\sim}{s}}(j) \quad + \quad \mu_B \vec{B} \cdot \sum_{i}^{N} \mathbf{g}_i \cdot \vec{\underset{\sim}{s}}(i)$$
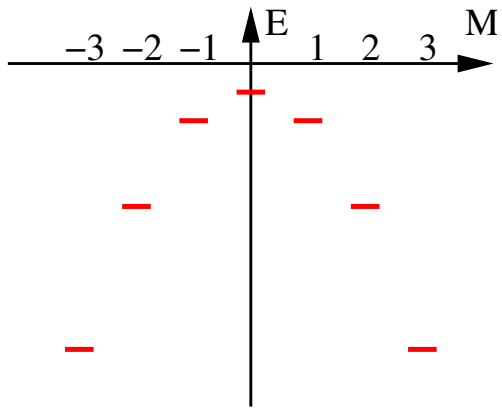
Exchange/Anisotropy   Zeeman

$\mathbf{J}_{ij}$: Heisenberg exchange, anisotropic exchange, and single-ion anisotropy.

Isotropic Heisenberg Hamiltonian

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

Heisenberg   Zeeman

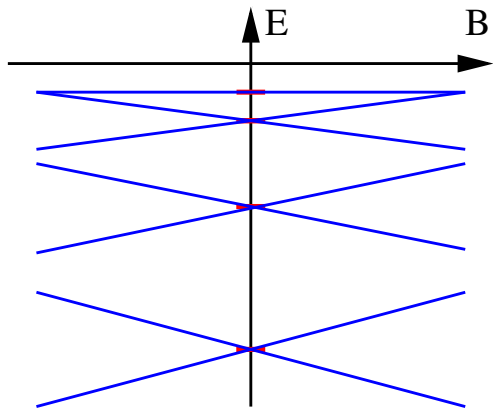# Single-ion anisotropy – single spin I

$$H = D(s^z)^2 + g\mu_B B s^z$$

$D < 0$ easy axis, $D > 0$ hard axis;
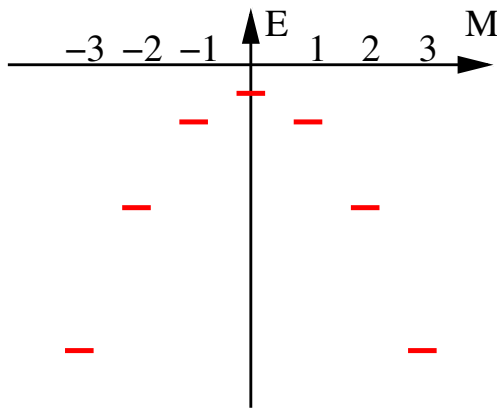
eigenvectors: $|s, m\rangle$

eigenvalues: $E_m = Dm^2 + g\mu_B Bm$, $m = -s, \ldots, s$

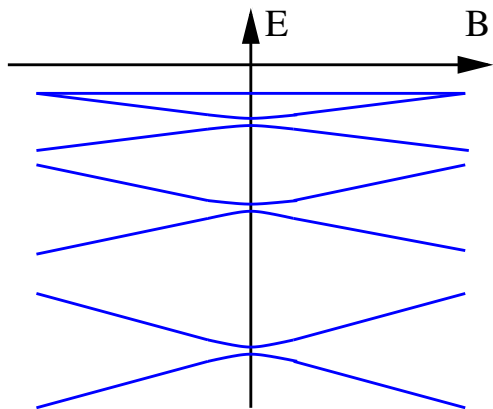IMPORTANT: $[H, s^z] = 0 \Rightarrow$ level crossings at $B = 0$

Single-ion anisotropy – single spin II

$$H = D(\underset{\sim}{s}^z)^2 + E\left\{(\underset{\sim}{s}^x)^2 - (\underset{\sim}{s}^y)^2\right\} + g\mu_B B \underset{\sim}{s}^z$$

$|E| < |D|$ – major axes of the anisotropy tensor;

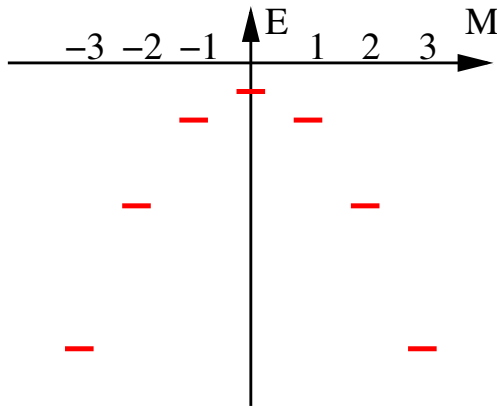NO LONGER eigenvectors: $|\,s,m\,\rangle$

eigenvalues are more complicated functions of $\vec{B} = B\vec{e}_z$: $E_\mu(B)$

IMPORTANT: $[\underset{\sim}{H}, \underset{\sim}{s}^z] \neq 0 \Rightarrow$ avoided level crossings at $B = 0$ for integer spins
(otherwise Kramers degenerecy)

Single-ion anisotropy – single spin III
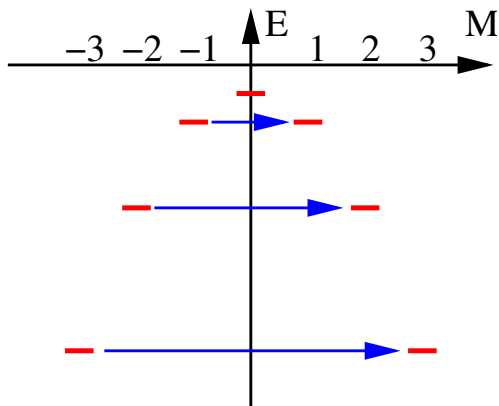
$$H = D(s^z)^2 + E\left\{(s^x)^2 - (s^y)^2\right\} + g\mu_B B s^z$$

$|s, m\rangle - m$ is NOT a good quantum number any longer

What do the spectra and the arrows mean?

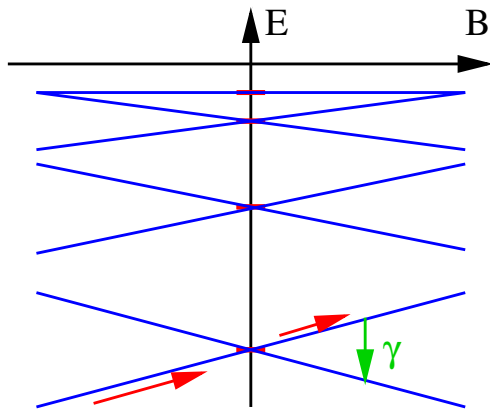Perturbation picture: spectra show eigenvalues of dominant term $D(s^z)^2$ with eigenstates $|s, m\rangle$.

For the full H these states are NOT stationary and thus time-evolve (tunnel) into $|s, -m\rangle$ after some time.
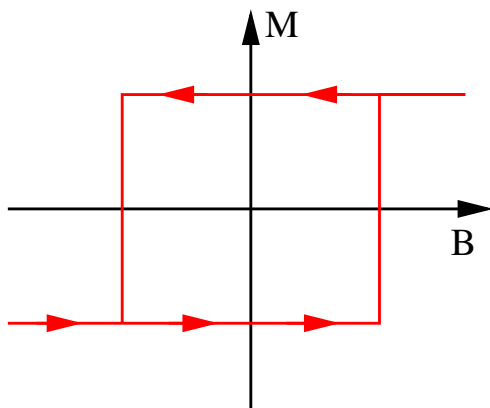
Bistability and tunneling

Bistability – uniaxial system – $\underset{\sim}{S}^z$-symmetry

Goal: single-molecule magnets (SMM)

$$\underset{\sim}{H} = \sum_i D_i (\underset{\sim}{s}_i^z)^2 + \mu_B B \sum_i g_i \underset{\sim}{s}_i^z + \underset{\sim}{H}_{\text{ferro int}}$$

IMPORTANT: $[\underset{\sim}{H}, \underset{\sim}{S}^z] = 0 \Rightarrow$ level crossings at $B = 0$

$\Rightarrow$ **low-temperature TIME-DEPENDENT hysteresis**

Side remark: For macroscopic systems in the ferromagnetic phase the relaxation time is HUGE, that's why we don't experience it.

Bistability – general system – NO $\underset{\sim}{S}^z$-symmetry

$$\underset{\sim}{H} = \sum_i \vec{\underset{\sim}{s}}_i \cdot \mathbf{D}_i \cdot \vec{\underset{\sim}{s}}_i + \mu_B B \sum_i g_i \underset{\sim}{s}_i^z + \underset{\sim}{H}_{\text{ferro int}}$$

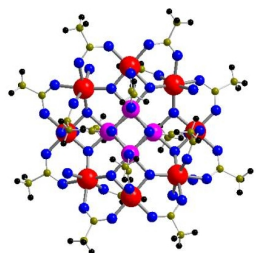$\mathbf{D}_i$ individual anisotropy tensors

$\Rightarrow$ low-temperature TIME-DEPENDENT hysteresis closes at $B = 0$ – not bistable & bad for storage

REASON: branching at avoided level crossings; strong dependence on tunneling gap and $\dot{B}$;

slow change of $B \Rightarrow$ system follows ground state, compare Landau-Zener-Stückelberg or slow/fast train at switch
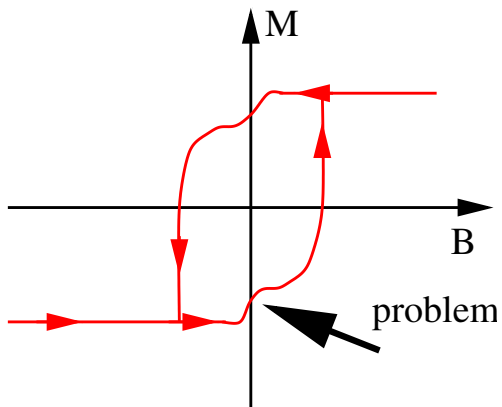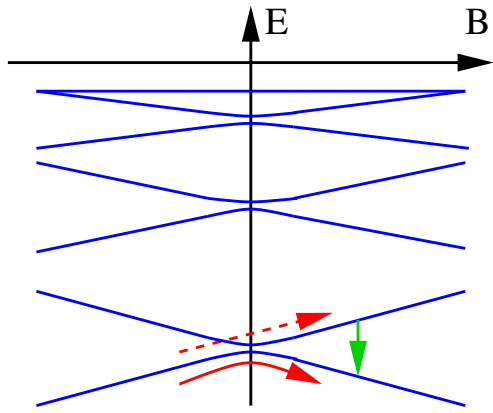
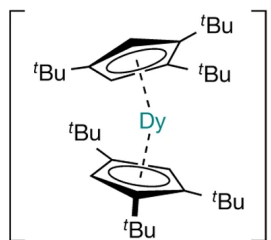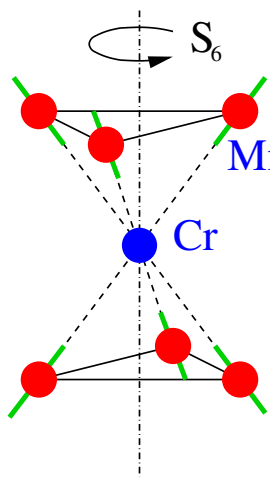# Bistability – state of the art

Today's major goals:

ferromagnetic spin-spin interaction

uniaxial anisotropy tensors

symmetry that does not permit E-terms

PERSISTENT PROBLEM: phonons

Nick Chilton, Thorsten Glaser, Jeff Long, Alessandro Lunghi, Mark Murrie, Frank Neese, Stefano Sanvito, Roberta Sessoli, Richard Winpenny, Yan-Zhen Zheng, ...

Spin-phonon interaction

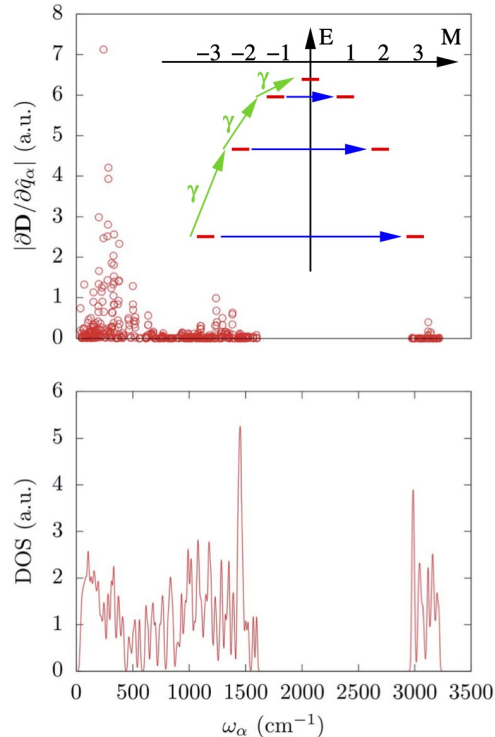# Spin-phonon interaction – DFT view of the problem

Fig. 2 Top panel: calculated spin-phonon coupling coefficients projected onto the normal modes basis set and displayed as a function of the modes frequency. Bottom panel: DFT calculated density of states for the Γ-point normal modes of vibration.

Calculate structure by means of DFT (1)

Calculate phonon density of states by means of DFT + molecular dynamics (2,3,4)

Calculate coupling coefficients from DFT (2,3,4)

Perturbation picture: set up rate equations for phonon transitions between eigenstates of unperturbed spin Hamiltonian (3,4)

ADVANTAGE: many realistic phonons

(1) A. V. Postnikov, J. Kortus, and M. R. Pederson, physica status solidi (b) **243**, 2533 (2006).
(2) M. R. Pederson, N. Bernstein, and J. Kortus, Phys. Rev. Lett. **89**, 097202 (2002).
(3) A. Lunghi and S. Sanvito, Science Advances **5**, eaax7163 (2019).
(4) A. Albino, S. Benci, L. Tesi, M. Atzori, R. Torre, S. Sanvito, R. Sessoli, and A. Lunghi, Inorg. Chem. **58**, 10260 (2019); $\Rightarrow$ figure.

Spin-phonon interaction – our question

Can phonons induce a tunnel splitting?
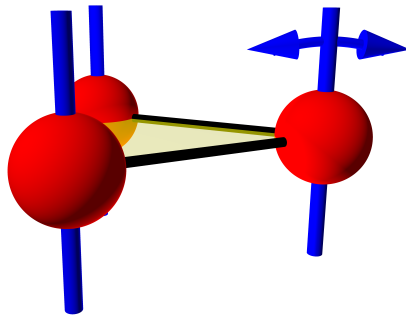
Know that non-collinear easy axes produce tunnel splitting

Set up special phonon modes that tilt easy axes in plane with C_3 axis out of uniaxial alignment
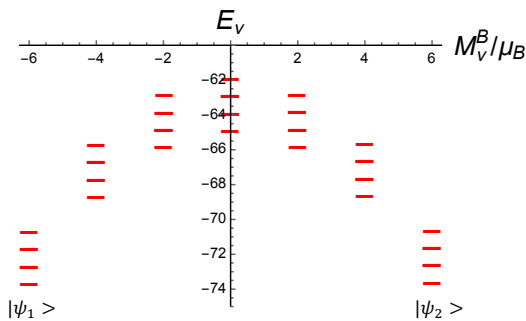
ADVANTAGE: quantum many-body solution for spins and phonons

$\Rightarrow$ correlated spin-phonon states:

$$\Psi_\nu = \sum c^\nu_{m_1, m_2, m_3, n_1, n_2, n_3} \left| m_1, m_2, m_3, n_1, n_2, n_3 \right\rangle$$

(1) K. Irländer and J. Schnack, Phys. Rev. B **102**, 054407 (2020).

Spin-phonon interaction – Hamiltonian

$$
\underset{\sim}{H} = -2J \left(\underset{\sim 1}{\vec{s}} \cdot \underset{\sim 2}{\vec{s}} + \underset{\sim 2}{\vec{s}} \cdot \underset{\sim 3}{\vec{s}} + \underset{\sim 3}{\vec{s}} \cdot \underset{\sim 1}{\vec{s}} \right)
$$

$$
+ \underset{\sim 1}{\vec{s}} \cdot \mathbf{D}_1(\underset{\sim}{\theta}_1) \cdot \underset{\sim 1}{\vec{s}} + \underset{\sim 2}{\vec{s}} \cdot \mathbf{D}_2(\underset{\sim}{\theta}_2) \cdot \underset{\sim 2}{\vec{s}} + \underset{\sim 3}{\vec{s}} \cdot \mathbf{D}_3(\underset{\sim}{\theta}_3) \cdot \underset{\sim 3}{\vec{s}}
$$

$$
+ \omega_1 \left(\underset{\sim 1}{a^\dagger} \underset{\sim 1}{a} + \frac{1}{2} \right) + \omega_2 \left(\underset{\sim 2}{a^\dagger} \underset{\sim 2}{a} + \frac{1}{2} \right) + \omega_3 \left(\underset{\sim 3}{a^\dagger} \underset{\sim 3}{a} + \frac{1}{2} \right)
$$

$$
+ g\mu_B \cdot \vec{B} \cdot \left(\underset{\sim 1}{\vec{s}} + \underset{\sim 2}{\vec{s}} + \underset{\sim 3}{\vec{s}} \right)
$$

$$
\mathbf{D}_i(\underset{\sim}{\theta}_i) = D\, \vec{e}_i(\underset{\sim}{\theta}_i, \phi_i) \otimes \vec{e}_i(\underset{\sim}{\theta}_i, \phi_i)
$$

$$
\underset{\sim}{\theta}_i = \theta_{i,0} + \alpha \left(\underset{\sim i}{a^\dagger} + \underset{\sim i}{a} \right) , \qquad \theta_{i,0} = 0
$$

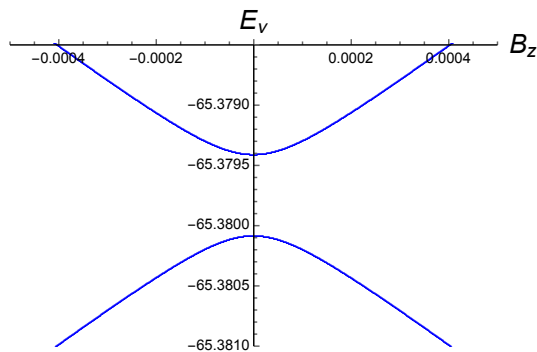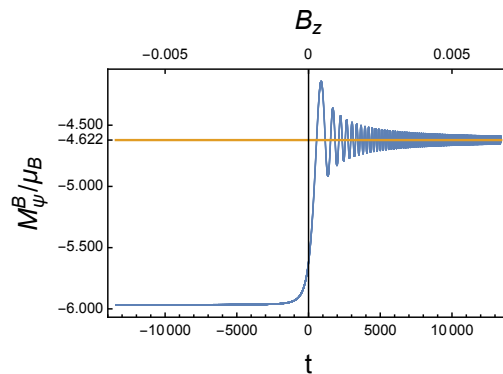# Spin-phonon interaction – our result

Can phonons induce a tunnel splitting?

$\Rightarrow$ Yes, they can!

Ground state, practically, does not contain any phonons, nevertheless tunneling occurs. Coupling to zero-point motion suffices (2).
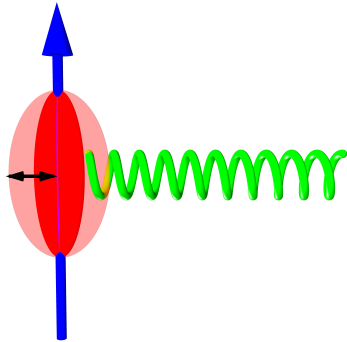

BAD NEWS: It is not enough to cool quantum devices, you have to prevent the coupling to disturbing sources at all.

Side remark: result probably already known in field of vibronic coupling.

(1) K. Irländer and J. Schnack, Phys. Rev. B **102**, 054407 (2020).
(2) F. Ortu *et al.*, Dalton Trans. **48**, 8541 (2019).

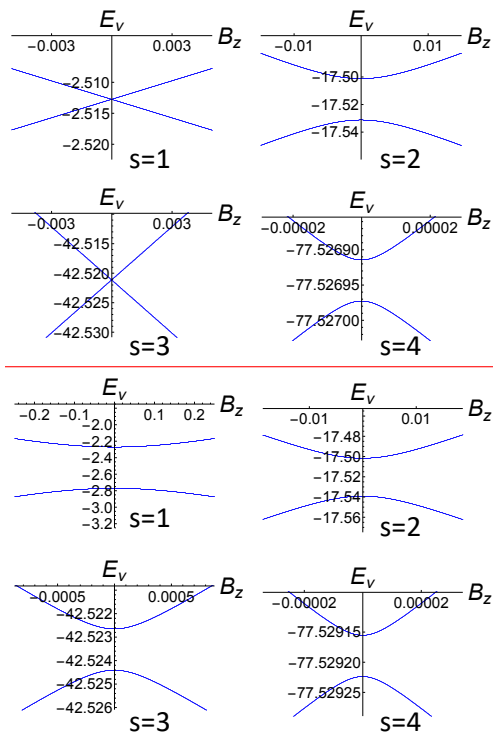# Supersymmetric spin-phonon interaction

Supersymmetric spin-phonon interaction

$$H = D(s^z)^2 + E\left\{(s^x)^2 - (s^y)^2\right\} + g\mu_B B\,s^z + H_{\text{HO}}$$

Special phonons that modify only:

L: $E = \alpha\left(a^\dagger + a\right)$ or   **Q:** $E = \alpha\left(a^\dagger + a\right)^2$

L: tunneling gap for even s, no gap for odd s.
This is not Kramers, but related to another symmetry.
Q: tunneling gap for all s.

RESULT: very interesting behavior; there are some phonons that do not produce a tunneling gap thanks to the way they couple.

(1) K. Irländer, H.-J. Schmidt, J. Schnack, Supersymmetric spin-phonon coupling prevents odd integer spins from quantum tunneling, arXiv:2006.16575

Typicality approach to molecular magnetism

Can we evaluate the partition function

$$Z(T,B) \;=\; \mathsf{tr}\left(\exp\left[-\beta \underset{\sim}{H}\right]\right)$$

without diagonalizing the Hamiltonian?

Solution I: trace estimators

$$\text{tr}\left(\underset{\sim}{Q}\right) \approx \langle r | \underset{\sim}{Q} | r \rangle = \sum_\nu \langle \nu | \underset{\sim}{Q} | \nu \rangle + \sum_{\nu \neq \mu} r_\nu r_\mu \langle \nu | \underset{\sim}{Q} | \mu \rangle$$

$$| r \rangle = \sum_\nu r_\nu | \nu \rangle, \quad r_\nu = \pm 1$$

- $| \nu \rangle$ some orthonormal basis of your choice; not the eigenbasis of $\underset{\sim}{Q}$, since we don't know it.

- $r_\nu = \pm 1$ random, equally distributed. Rademacher vectors.

- Amazingly accurate, bigger (Hilbert space dimension) is better.

M. Hutchinson, Communications in Statistics - Simulation and Computation **18**, 1059 (1989).

Solution II: Krylov space representation

$$\exp\left[-\beta \underset{\sim}{H}\right] \approx \underset{\sim}{1} - \beta \underset{\sim}{H} + \frac{\beta^2}{2!}\underset{\sim}{H}^2 - \cdots \frac{\beta^{N_L-1}}{(N_L-1)!}\underset{\sim}{H}^{N_L-1}$$

applied to a state $|\,r\,\rangle$ yields a superposition of

$$\underset{\sim}{1}\,|\,r\,\rangle, \quad \underset{\sim}{H}\,|\,r\,\rangle, \quad \underset{\sim}{H}^2\,|\,r\,\rangle, \quad \ldots \underset{\sim}{H}^{N_L-1}\,|\,r\,\rangle\,.$$

These (linearly independent) vectors span a small space of dimension N_L; it is called Krylov space.

Let's diagonalize $\underset{\sim}{H}$ in this space!

Partition function I: simple approximation

$$Z(T,B) \approx \langle\, r \,|\, e^{-\beta \underset{\sim}{H}} \,|\, r \,\rangle \approx \sum_{n=1}^{N_L} e^{-\beta \epsilon_n^{(r)}} |\langle\, n(r) \,|\, r \,\rangle|^2$$

$$O^{\mathrm{r}}(T,B) \approx \frac{\langle\, r \,|\, \underset{\sim}{Q} e^{-\beta \underset{\sim}{H}} \,|\, r \,\rangle}{\langle\, r \,|\, e^{-\beta \underset{\sim}{H}} \,|\, r \,\rangle}$$

- Wow!!!

- One can replace a trace involving an intractable operator by an expectation value with respect to just ONE random vector evaluated by means of a Krylov space representation???

- Typicality = any random vector will do

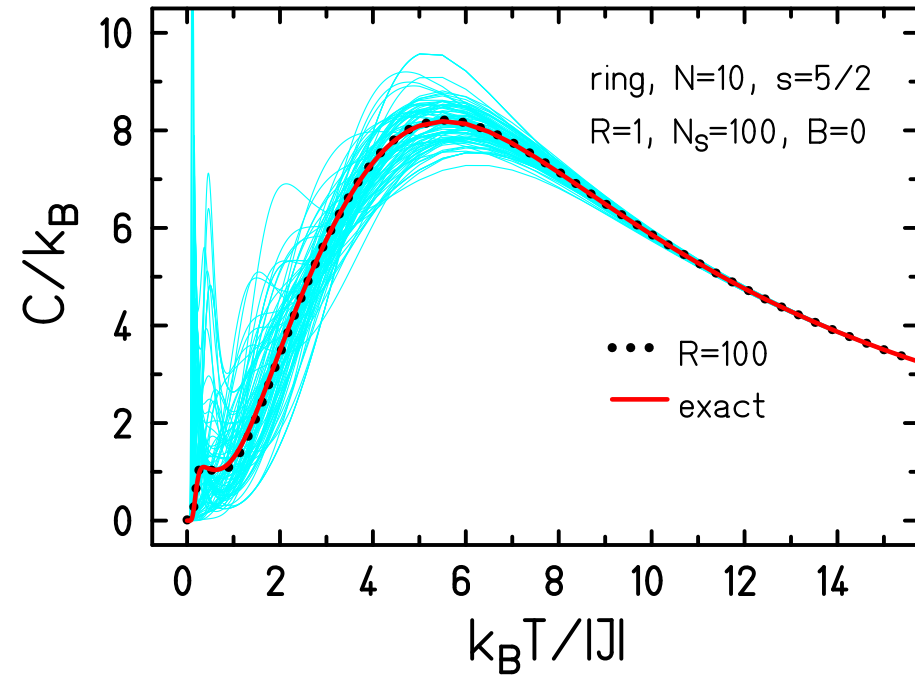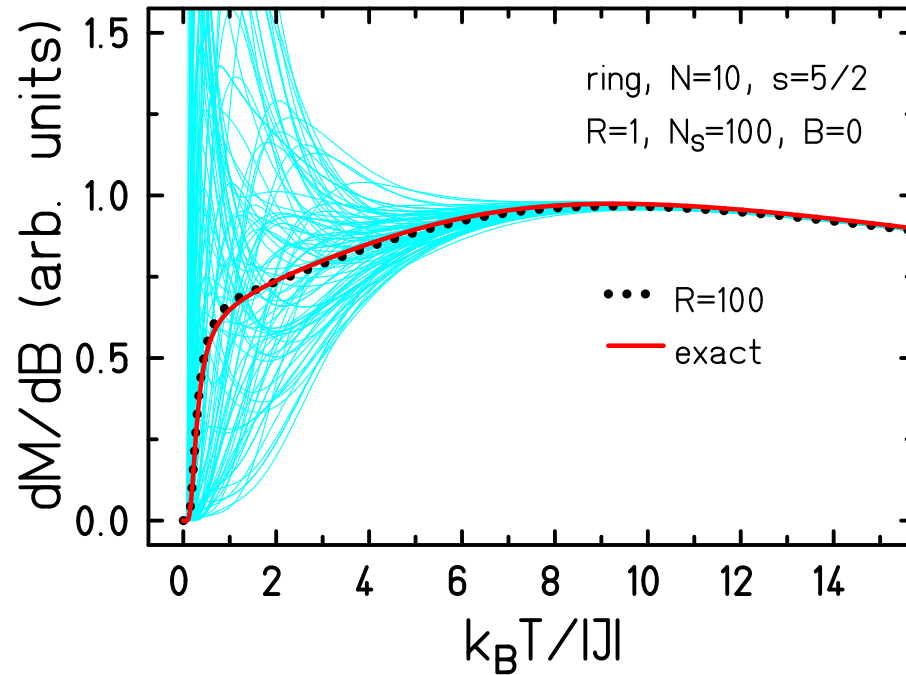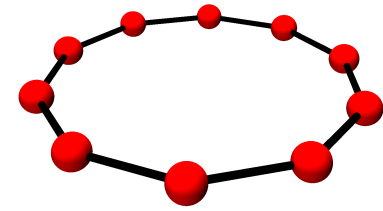J. Jaklic and P. Prelovsek, Phys. Rev. B **49**, 5065 (1994).

Partition function II: Finite-temperature Lanczos Method

$$Z^{\mathsf{FTLM}}(T,B) \quad \approx \quad \frac{1}{R}\sum_{r=1}^{R}\sum_{n=1}^{N_L} e^{-\beta\epsilon_n^{(r)}}|\langle\, n(r)\,|\,r\,\rangle|^2$$

- Averaging over R random vectors is better.

- $|\,n(r)\,\rangle$ n-th Lanczos eigenvector starting from $|\,r\,\rangle$ (Rademacher vectors).

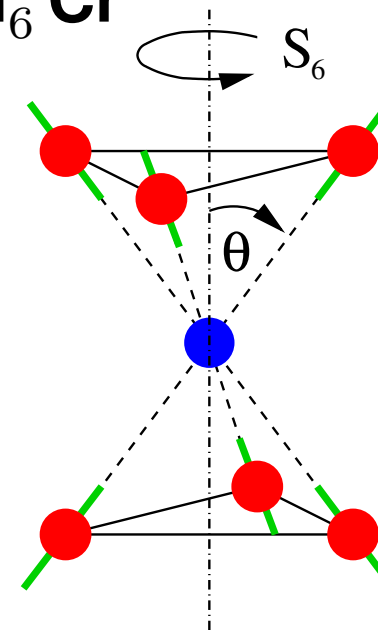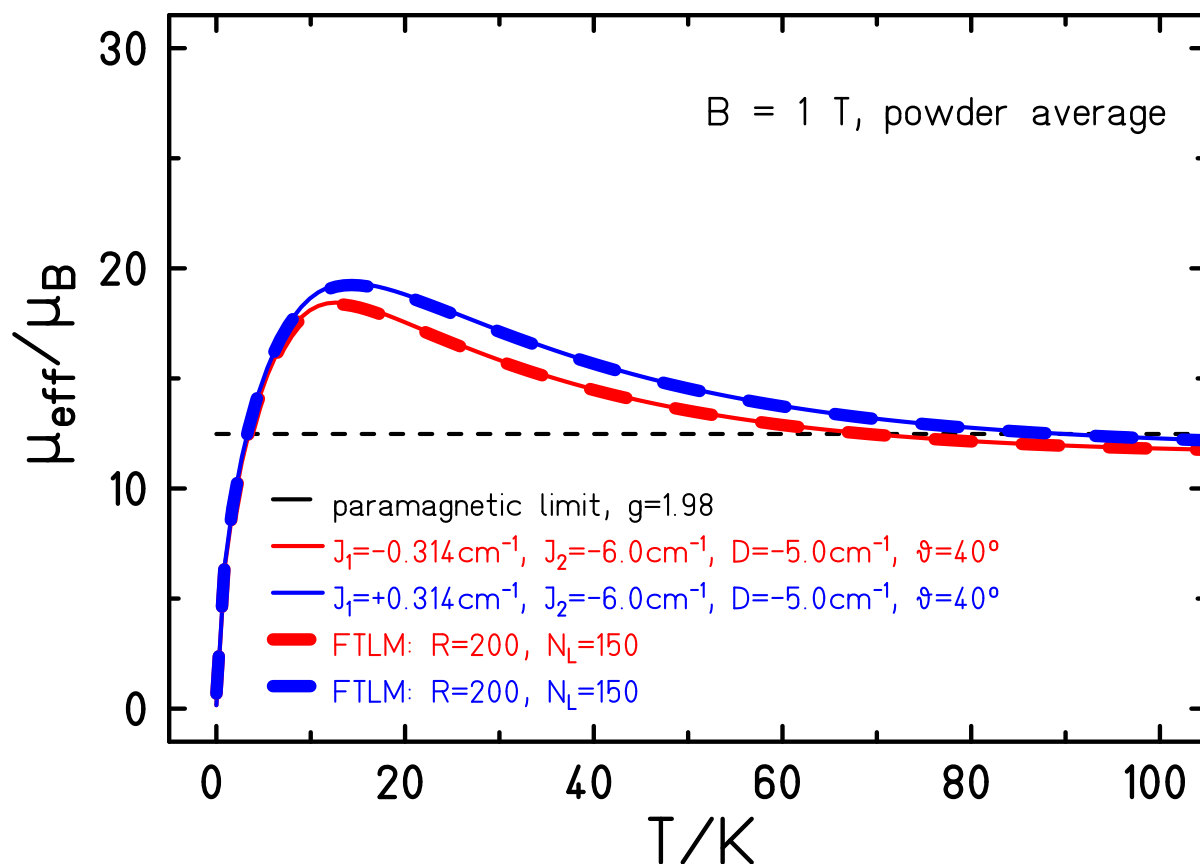- Partition function replaced by a small sum: $R = 1\ldots100, N_L \approx 100$.

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

FTLM 1: ferric wheel

Left plot: dM/dB (arb. units) vs $k_B T/|J|$ — ring, N=10, s=5/2, R=1, N_S=100, B=0; R=100 (dotted), exact (red).

Right plot: C/k_B vs $k_B T/|J|$ — ring, N=10, s=5/2, R=1, N_S=100, B=0; R=100 (dotted), exact (red).

(1) J. Schnack, J. Richter, R. Steinigeweg, Phys. Rev. Research **2**, 013186 (2020).

(2) SU(2) & D_2: R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403 (2010).

(3) SU(2) & C_N: T. Heitmann, J. Schnack, Phys. Rev. B **99**, 134405 (2019)

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

B = 1 T, powder average

— paramagnetic limit, g=1.98
— J_1=-0.314cm^{-1}, J_2=-6.0cm^{-1}, D=-5.0cm^{-1}, ϑ=40°
— J_1=+0.314cm^{-1}, J_2=-6.0cm^{-1}, D=-5.0cm^{-1}, ϑ=40°
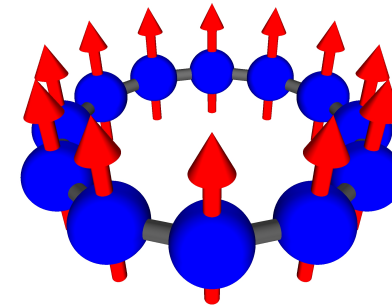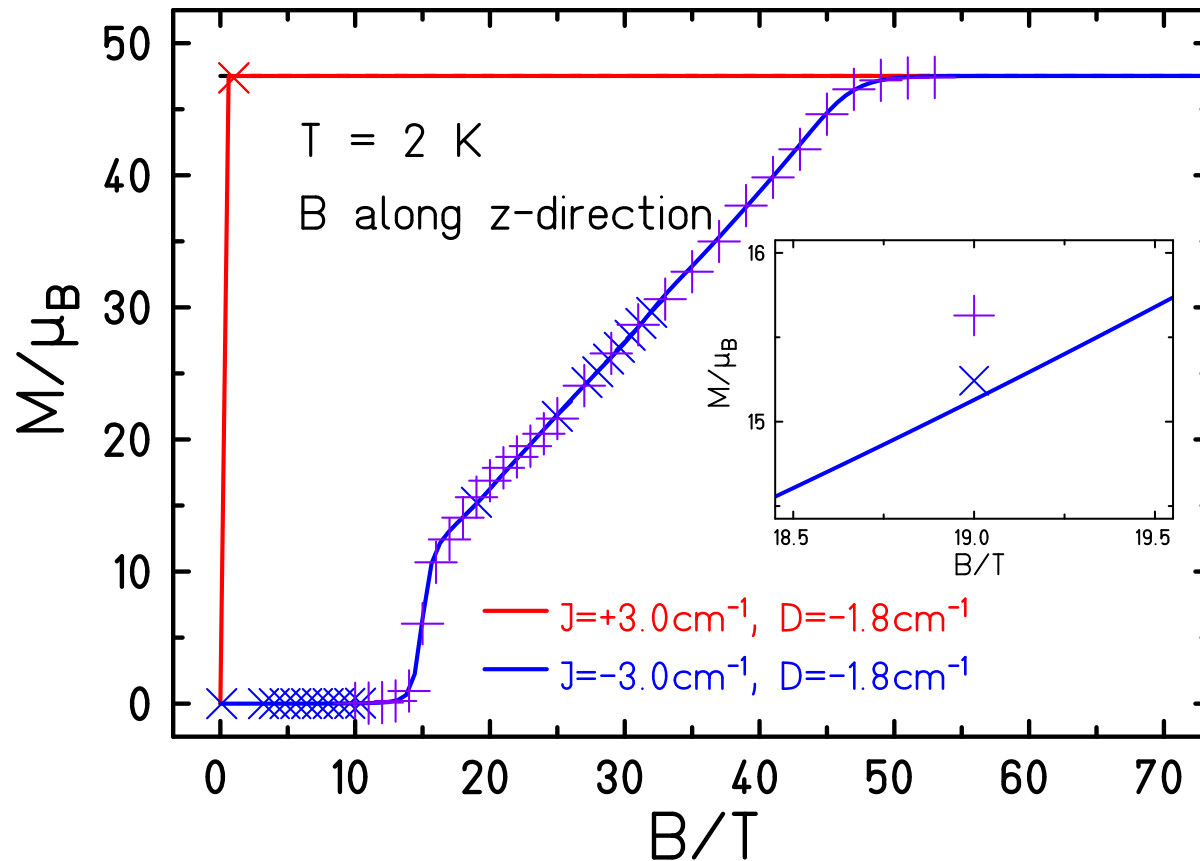— FTLM: R=200, N_L=150
— FTLM: R=200, N_L=150

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

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

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

T = 2 K

B along z-direction

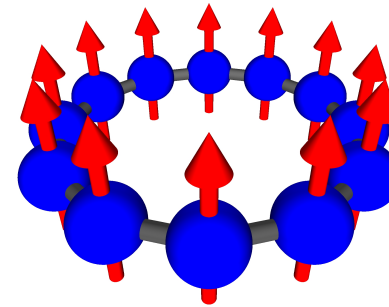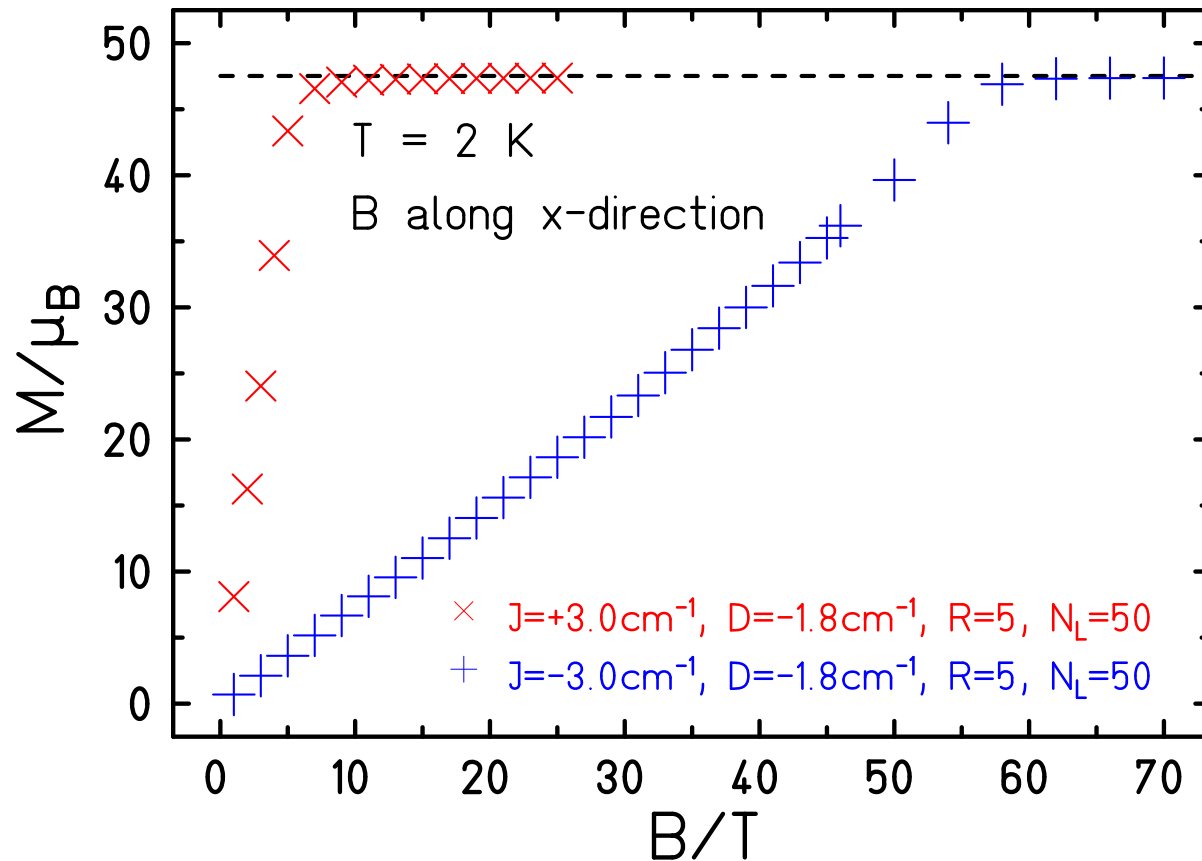J=+3.0cm^{-1}, D=-1.8cm^{-1}
J=-3.0cm^{-1}, D=-1.8cm^{-1}

$s = 2$

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

collinear easy axes

A few days compared to *impossible*!

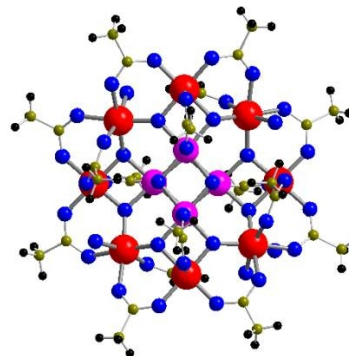O. Hanebaum, J. Schnack, Eur. Phys. J. B **87**, 194 (2014)

A fictitious $\mathbf{Mn}_{12}^{\mathrm{III}} - M_x$ **vs** B_x

$T = 2\,\mathrm{K}$

B along x-direction

× $J=+3.0\,\mathrm{cm}^{-1}$, $D=-1.8\,\mathrm{cm}^{-1}$, R=5, N_L=50

+ $J=-3.0\,\mathrm{cm}^{-1}$, $D=-1.8\,\mathrm{cm}^{-1}$, R=5, N_L=50

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
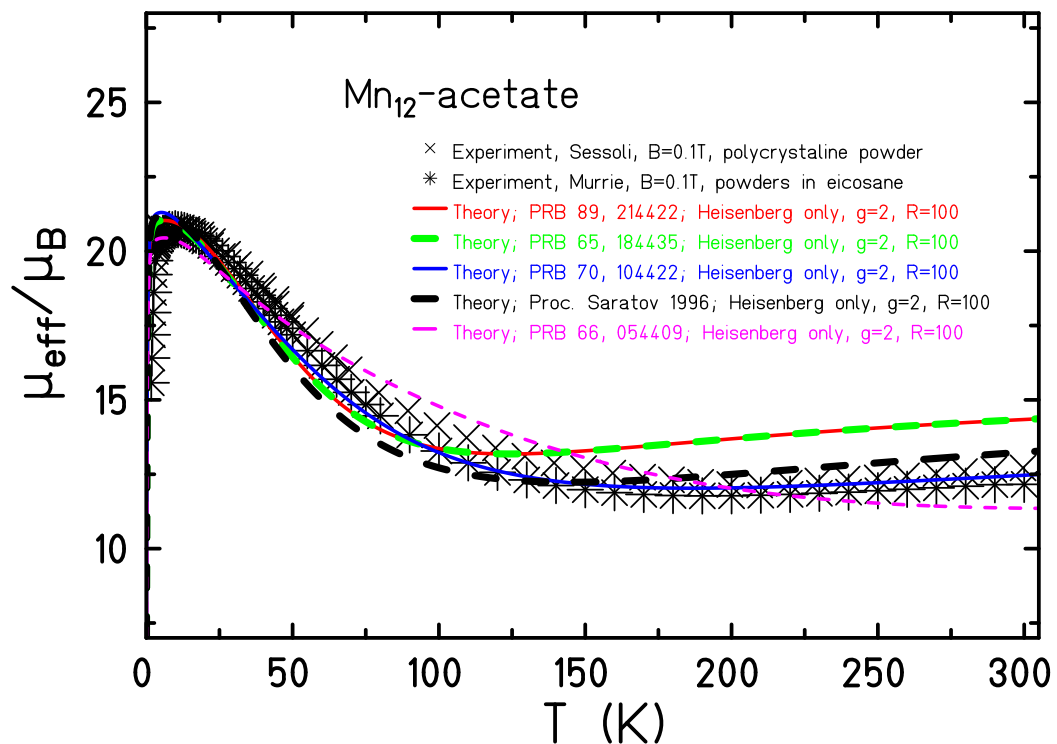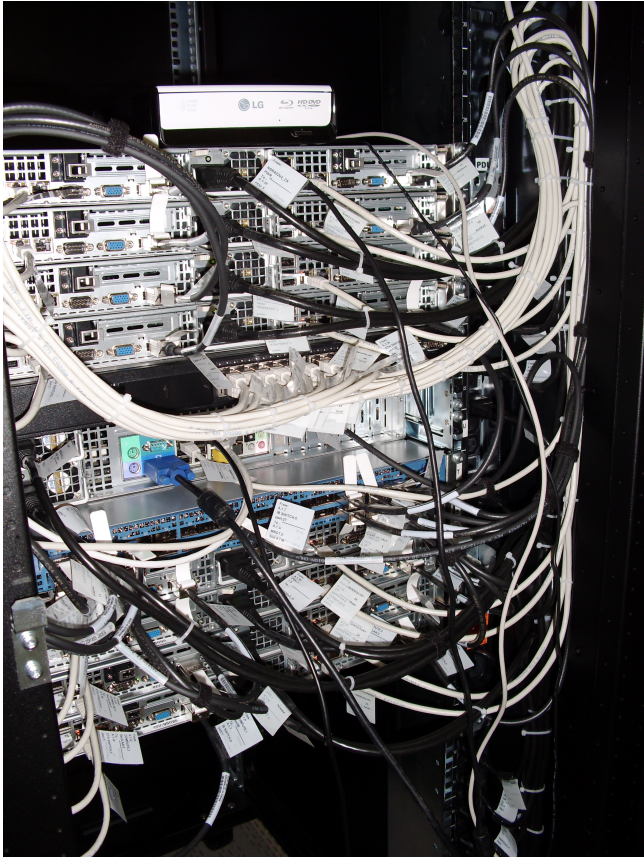

We can check DFT parameter predictions for large molecules! Normally!

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

$\Rightarrow$ S. Ghassemi Tabrizi, A. V. Arbuznikov, and M. Kaupp, J. Phys. Chem. A **120**, 6864 (2016).

Summary

- **Magnetic molecules for storage, q-bits, MCE, and since they are nice.**

- SMM challenges: quantum tunneling and phonons

- **Magnetism is much richer and more complicated than shown here. Talk focused on 3d ions with weak spin-orbit interaction.**

- Trend: lanthanide ions such as Dy with strange symmetries

- **ED, HTE, CMC, QMC, <u>FTLM</u>, DMRG, DDMRG, thDMRG, DFT for magnetic molecules.**

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Thank you very much for your attention.

The end.

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