Anisotropy and Spin-Phonon-Interactions in Molecular Magnets

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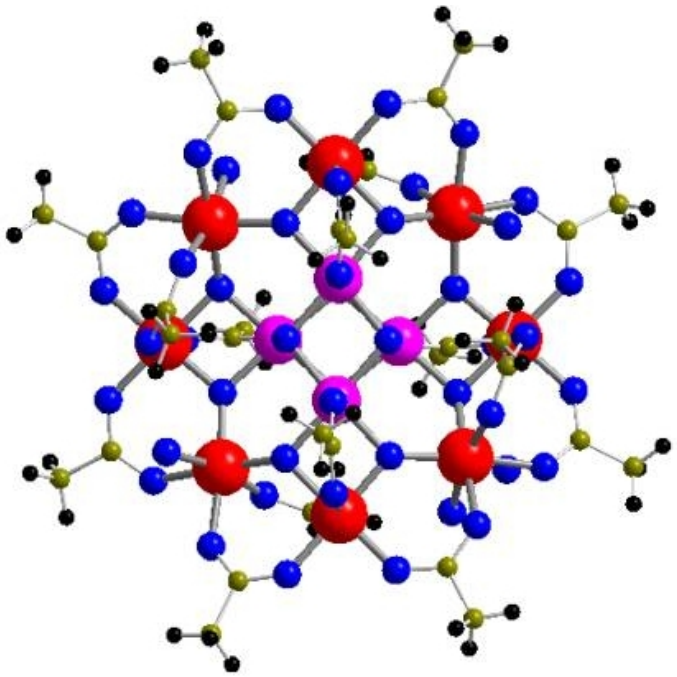
Seminar, The University of Texas at El Paso
Online, 20 November 2020

Beauty of Magnetic Molecules

The beauty of magnetic molecules I

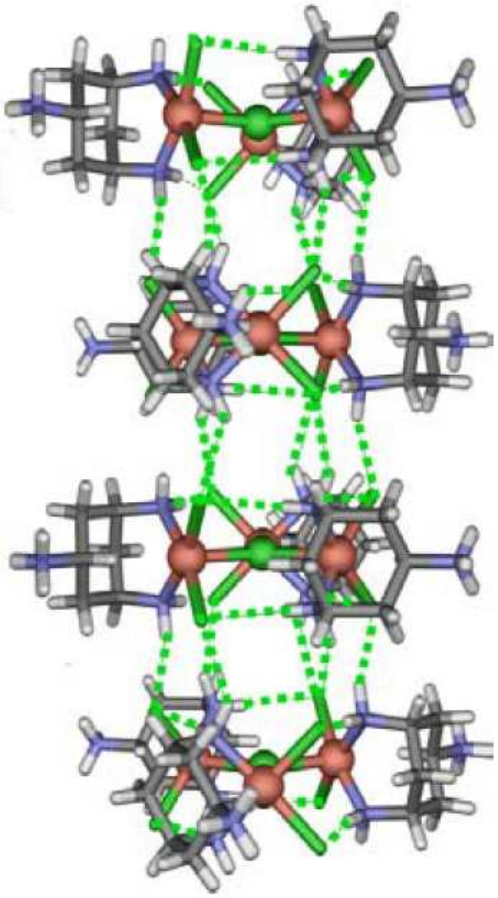


Mn_{12}

- 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;
- 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).

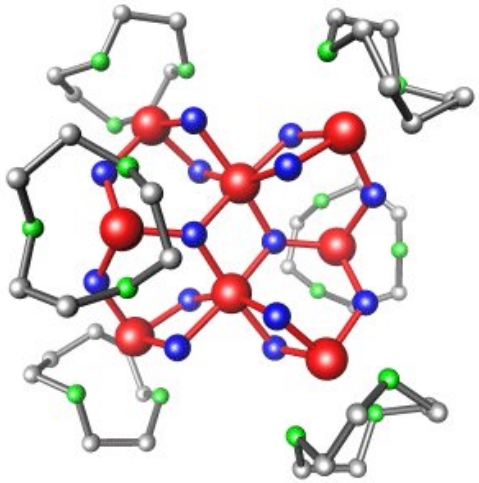
The beauty of magnetic molecules II

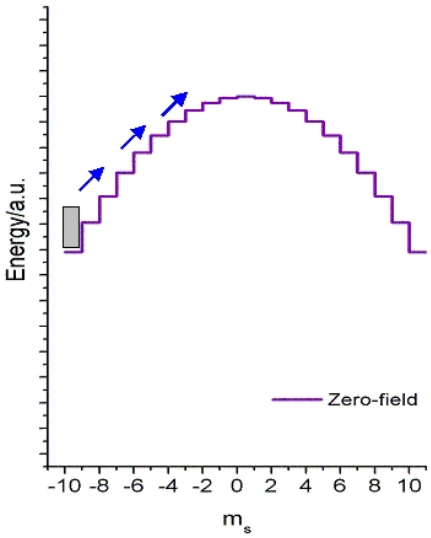


- Dimers (Fe_2), tetrahedra (Cr_4), cubes (Cr_8);
- Rings, especially iron rings (Fe_6, Fe_8, Fe_{10}, . . .);
- Complex structures (Mn_{12}) – drosophila of molecular magnetism;
- “Soccer balls”, more precisely icosidodecahedra (Fe_{30}) and other macro molecules;
- Chain-like and planar structures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

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

1. Beauty of magnetic molecules $\surd$
2. Single-ion anisotropy
3. Bistability and tunneling
4. Spin-phonon interaction
5. SUSY spin-phonon interaction
6. Bonus: Typicality approach

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)

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

Exchange/Anisotropy Zeeman

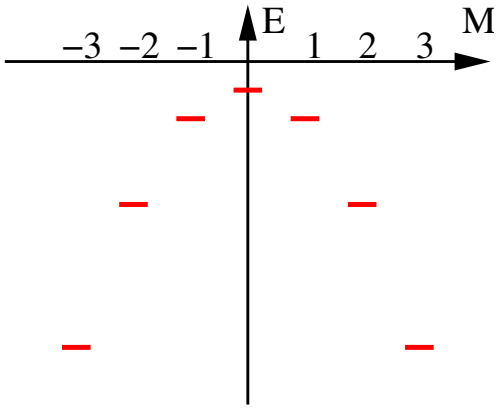
$\mathbf{J}_{ij}$: Heisenberg exchange, anisotropic exchange, and single-ion anisotropy.

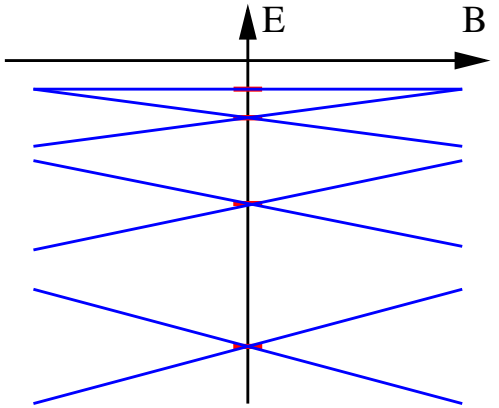
Isotropic Heisenberg Hamiltonian

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

Heisenberg Zeeman

Single-ion anisotropy – single spin I





$$\underset{\sim}{H} = D(\underset{\sim}{s}^z)^2 + g\mu_B B \underset{\sim}{s}^z$$

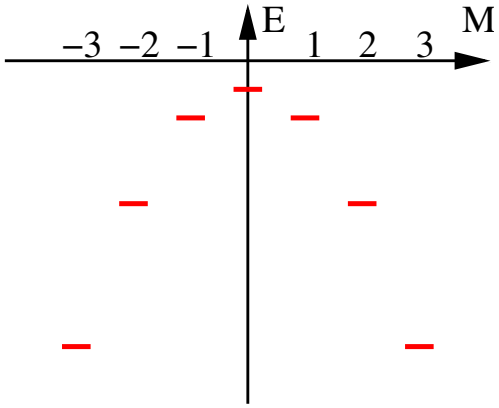
$D < 0$ easy axis, $D > 0$ hard axis;

eigenvectors: $|\, s, m \,\rangle$

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

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

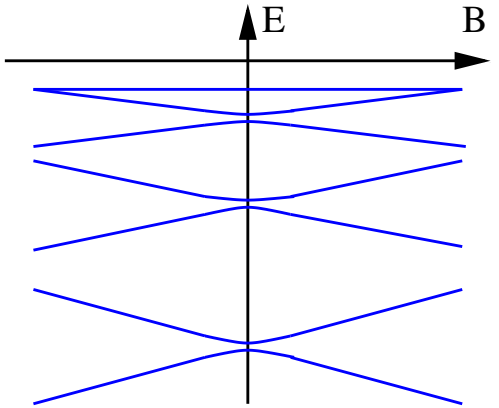
Single-ion anisotropy – single spin II



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

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

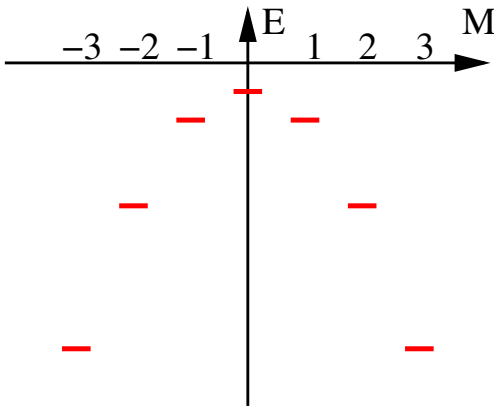
NO LONGER eigenvectors: $|\, s, m \,\rangle$



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)

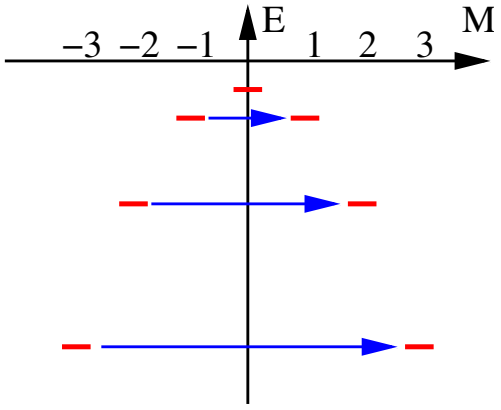
Single-ion anisotropy – single spin III



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

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

What do the spectra and the arrows mean?

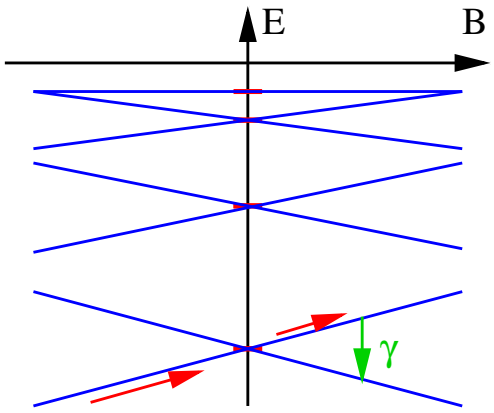


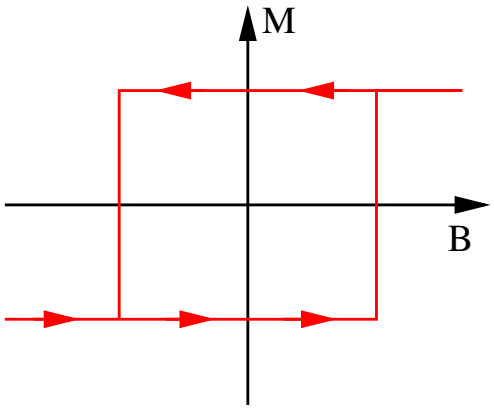
Perturbation picture: spectra show eigenvalues of dominant term $D(\underset{\sim}{s}^z)^2$ with eigenstates $|\, s, m \,\rangle$.

For the full $\underset{\sim}{H}$ 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)

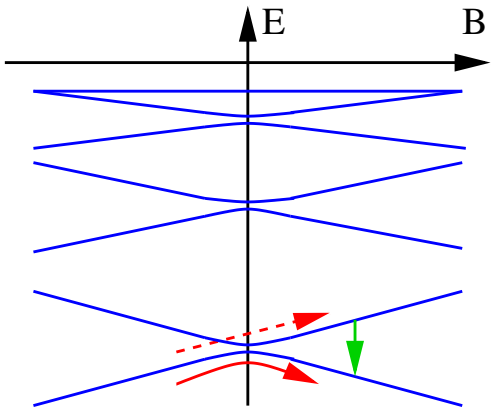
$\underset{\sim}{H} = \sum_i D_i (\underset{\sim}{s}_i^z)^2 + \mu_B B \sum_i g_i \underset{\sim}{s}_i^z + \underset{\sim}{H}_{\text{ferro int}}$

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.

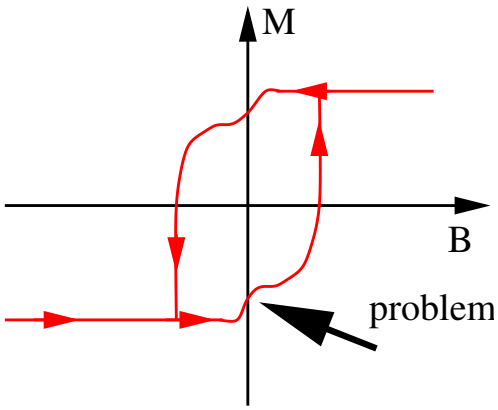
Bistability – general system – NO $\underset{\sim}{S}^z$-symmetry



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

$\mathbf{D}_i$ individual anisotropy tensors

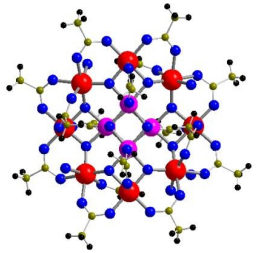
$\Rightarrow$ low-temperature TIME-DEPENDENT hysteresis closes at $B = 0$ – not bistable & bad for storage

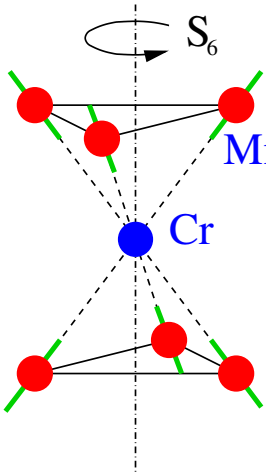


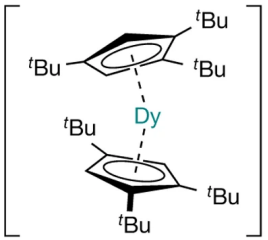
REASON: branching at avoided level crossings;
strong dependence on tunneling gap and $\dot{B}$;

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

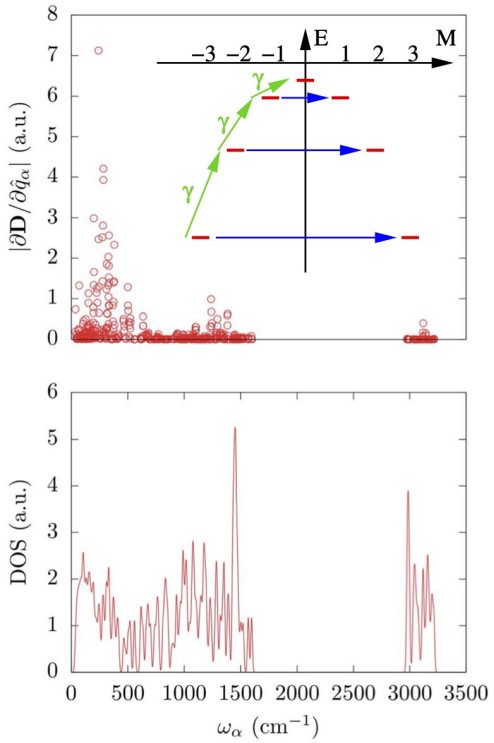


Fig. 2 Top panel: calculated spin-phonon coupling coefficients projected onto the normal modes basis set and displayed as a function of the modes frequency. Bottom panel: DFT calculated density of states for the Γ-point normal modes of vibration.

Calculate structure by means of DFT (1)

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

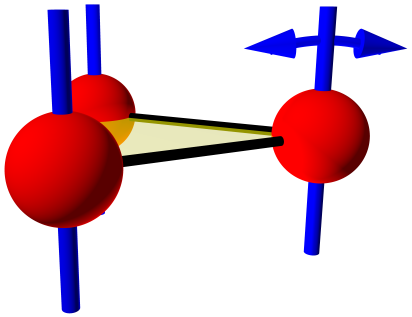
Calculate coupling coefficients from DFT (2,3,4)

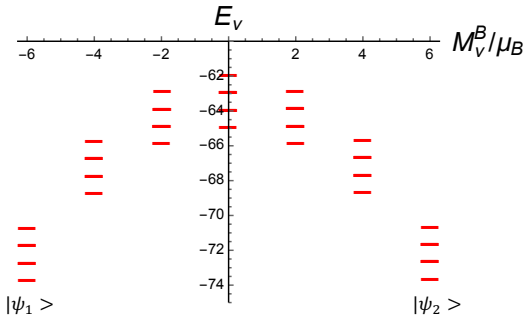
Perturbation picture: set up rate equations for phonon transitions between eigenstates of unperturbed spin Hamiltonian (3,4)

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).

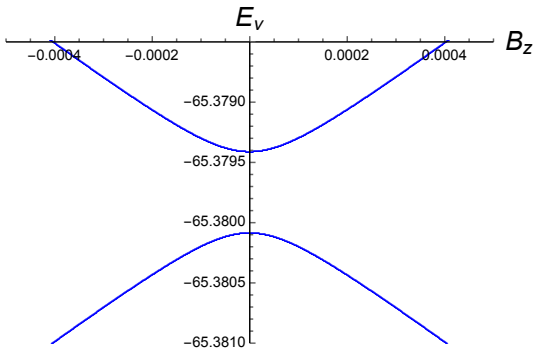
Spin-phonon interaction – Hamiltonian

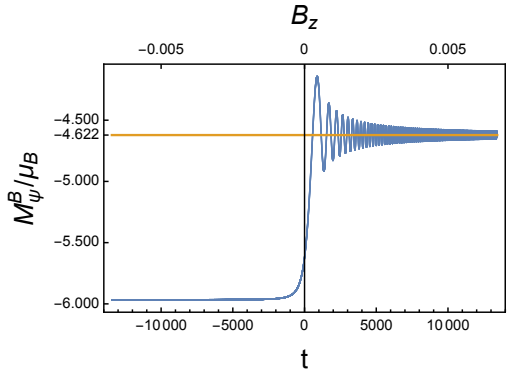
$$
\begin{aligned}
\underset{\sim}{H} &= -2J \left(\vec{\underset{\sim}{s}}_1 \cdot \vec{\underset{\sim}{s}}_2 + \vec{\underset{\sim}{s}}_2 \cdot \vec{\underset{\sim}{s}}_3 + \vec{\underset{\sim}{s}}_3 \cdot \vec{\underset{\sim}{s}}_1 \right) \\
&\quad + \vec{\underset{\sim}{s}}_1 \cdot \mathbf{D}_1(\underset{\sim}{\theta}_1) \cdot \vec{\underset{\sim}{s}}_1 + \vec{\underset{\sim}{s}}_2 \cdot \mathbf{D}_2(\underset{\sim}{\theta}_2) \cdot \vec{\underset{\sim}{s}}_2 + \vec{\underset{\sim}{s}}_3 \cdot \mathbf{D}_3(\underset{\sim}{\theta}_3) \cdot \vec{\underset{\sim}{s}}_3 \\
&\quad + \omega_1 \left(\underset{\sim}{a}_1^\dagger \underset{\sim}{a}_1 + \frac{1}{2} \right) + \omega_2 \left(\underset{\sim}{a}_2^\dagger \underset{\sim}{a}_2 + \frac{1}{2} \right) + \omega_3 \left(\underset{\sim}{a}_3^\dagger \underset{\sim}{a}_3 + \frac{1}{2} \right) \\
&\quad + g\mu_B \cdot \vec{B} \cdot \left(\vec{\underset{\sim}{s}}_1 + \vec{\underset{\sim}{s}}_2 + \vec{\underset{\sim}{s}}_3 \right)
\end{aligned}
$$

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

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

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).

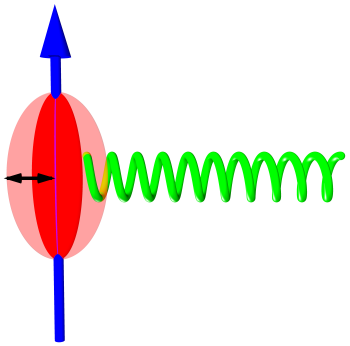
BAD NEWS: It is not enough to cool quantum devices, you have to prevent the coupling to disturbing sources at all.

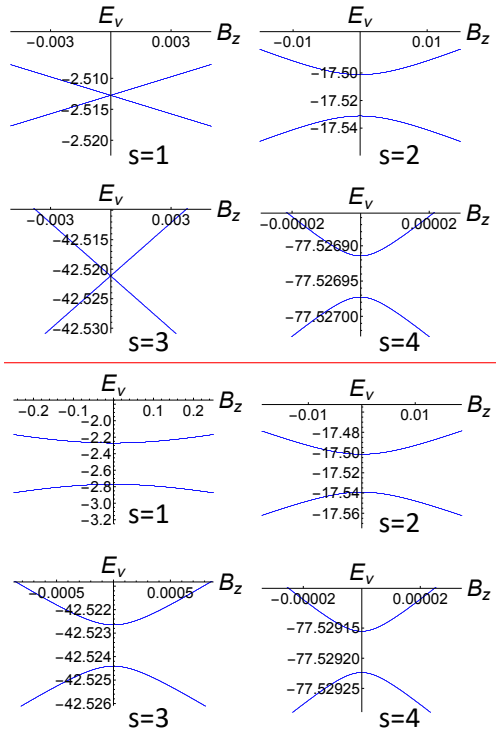
Side remark: result probably already known in field of vibronic coupling.

(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





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

Special phonons that modify only:

L: $E = \alpha\left(\underset{\sim}{a}^\dagger + \underset{\sim}{a}\right)$ or Q: $E = \alpha\left(\underset{\sim}{a}^\dagger + \underset{\sim}{a}\right)^2$

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

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

without diagonalizing the Hamiltonian?

Solution I: trace estimators

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

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

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

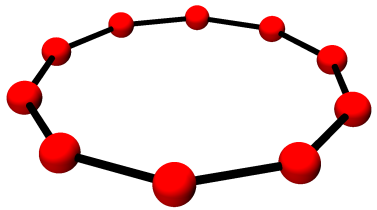
Partition function II: Finite-temperature Lanczos Method

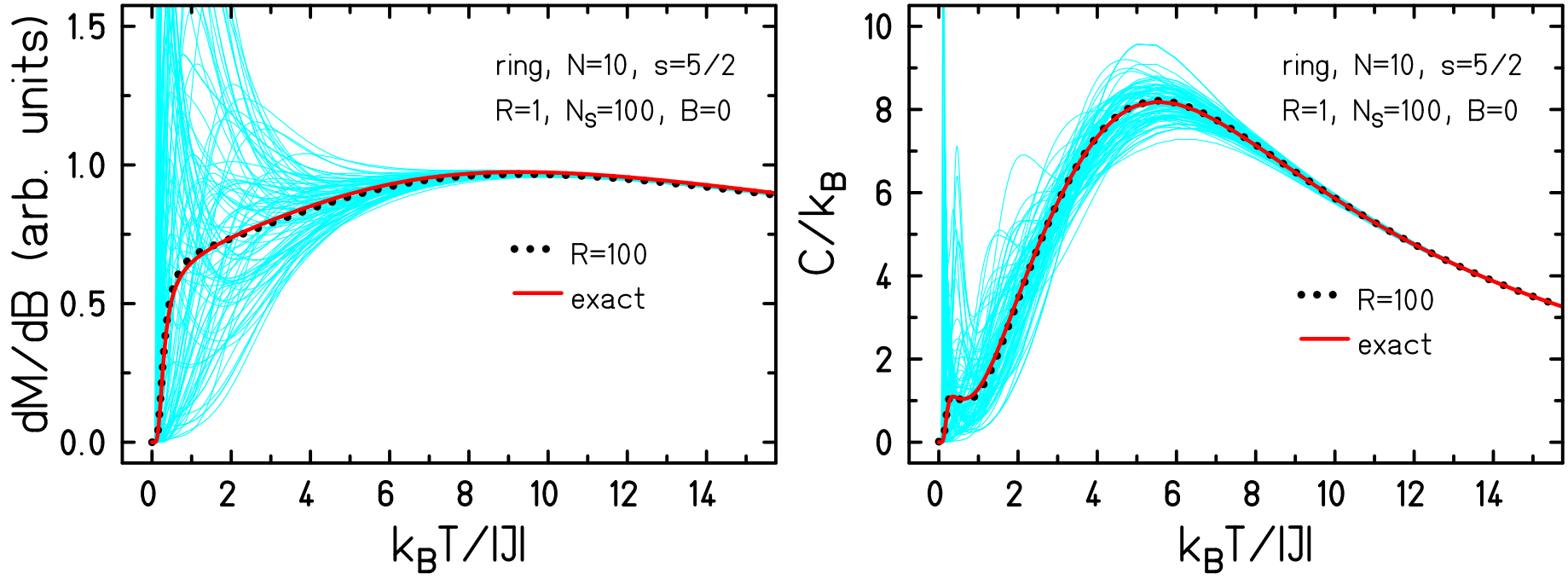
$$Z^{\mathsf{FTLM}}(T,B) \approx \frac{1}{R}\sum_{r=1}^{R}\sum_{n=1}^{N_L} e^{-\beta\epsilon_n^{(r)}} \left|\langle\, n(r)\,|\,r\,\rangle\right|^2$$

- 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: $R = 1\ldots 100, N_L \approx 100$.

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

FTLM 1: ferric wheel



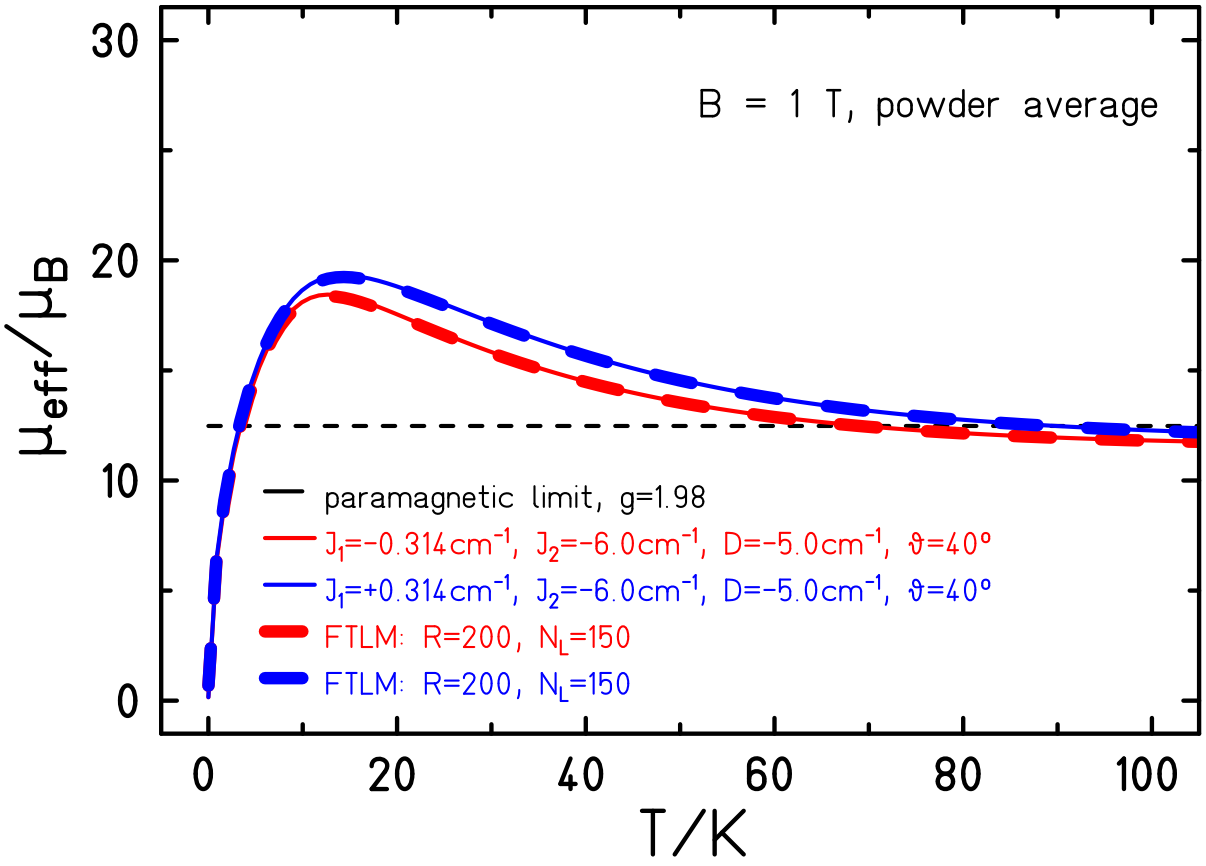


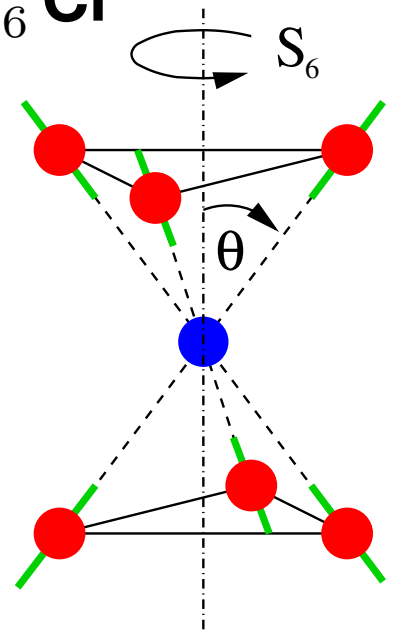
(1) J. Schnack, J. Richter, R. Steinigeweg, Phys. Rev. Research **2**, 013186 (2020).

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





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

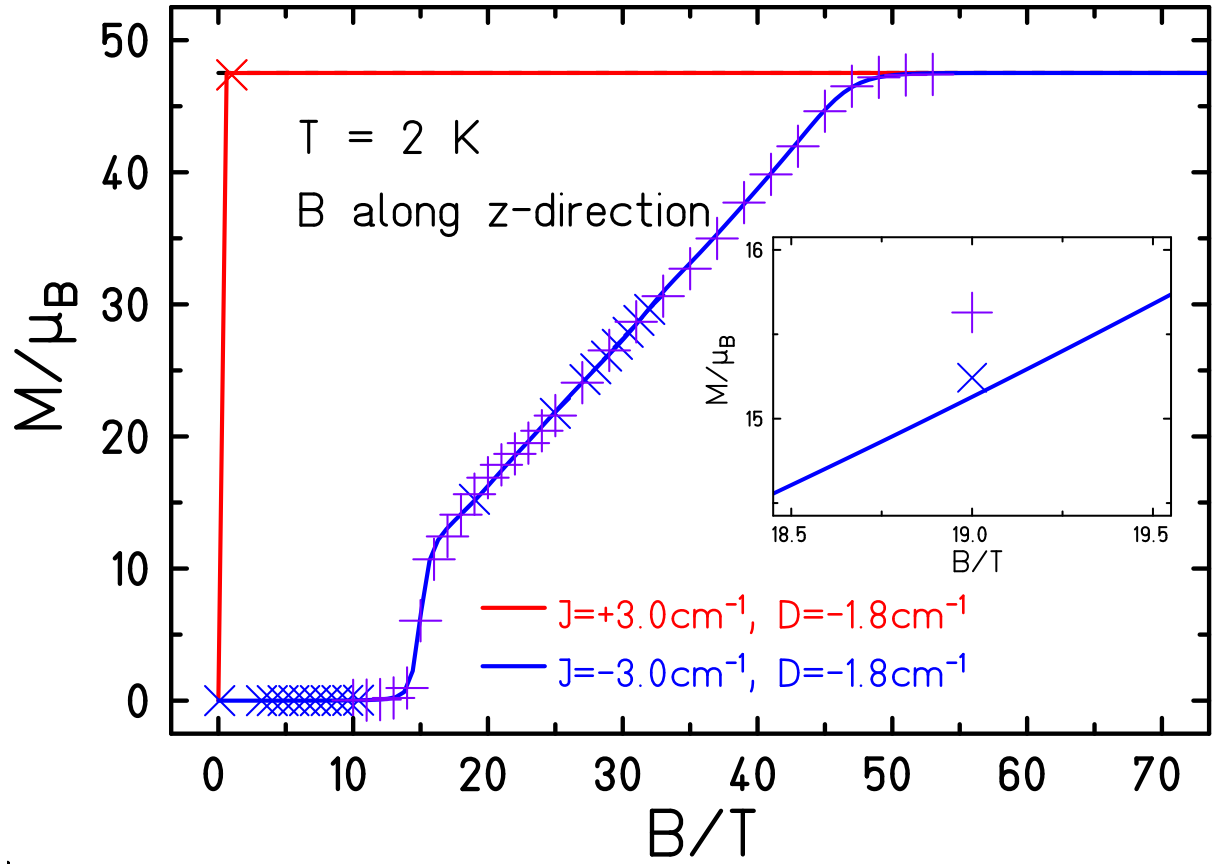
$\dim(\mathcal{H}) = 62,500$

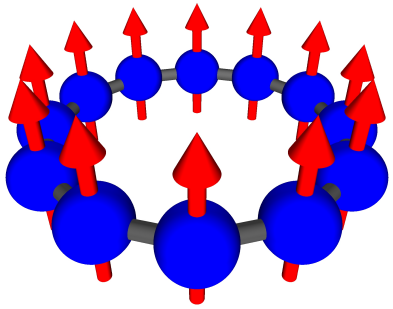
non-collinear easy axes

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





$s = 2$

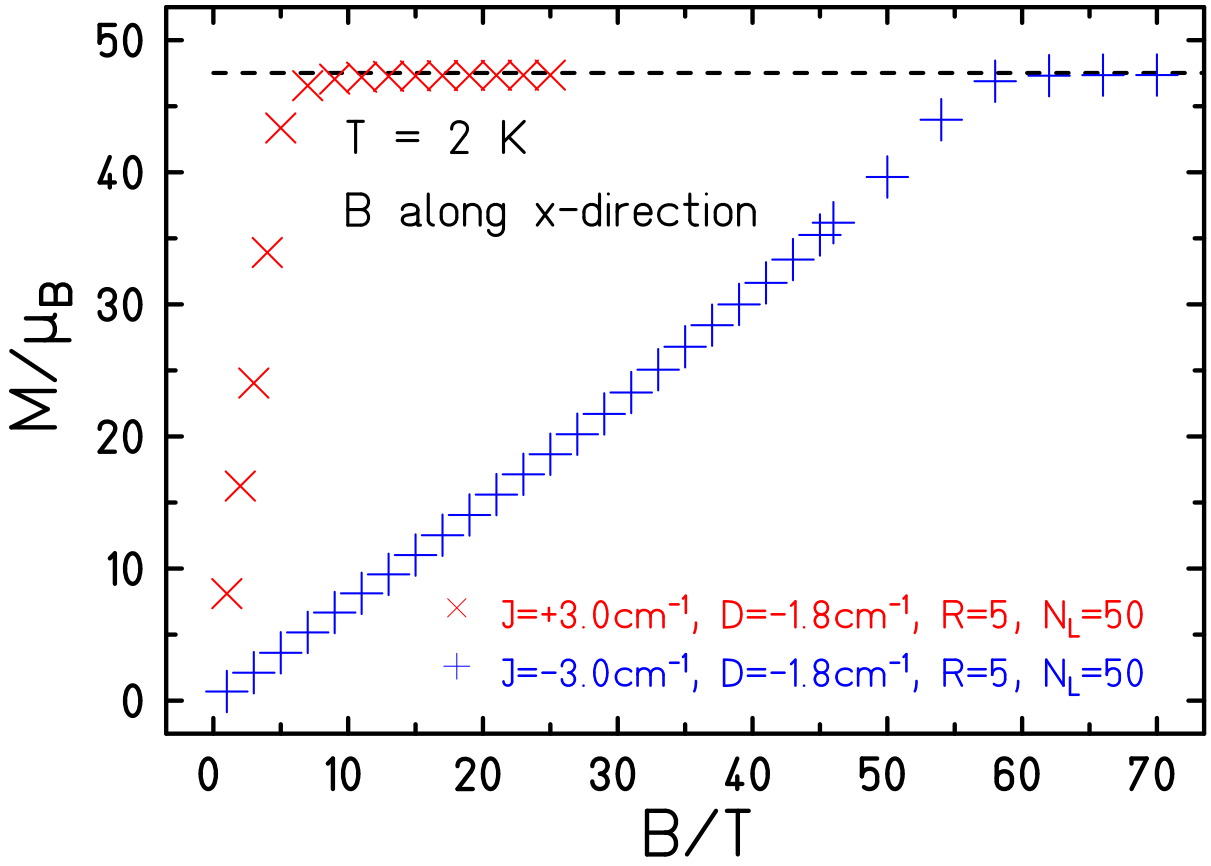
$\dim(\mathcal{H}) = 244,140,625$

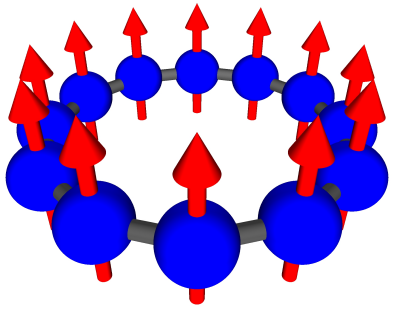
collinear easy axes

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

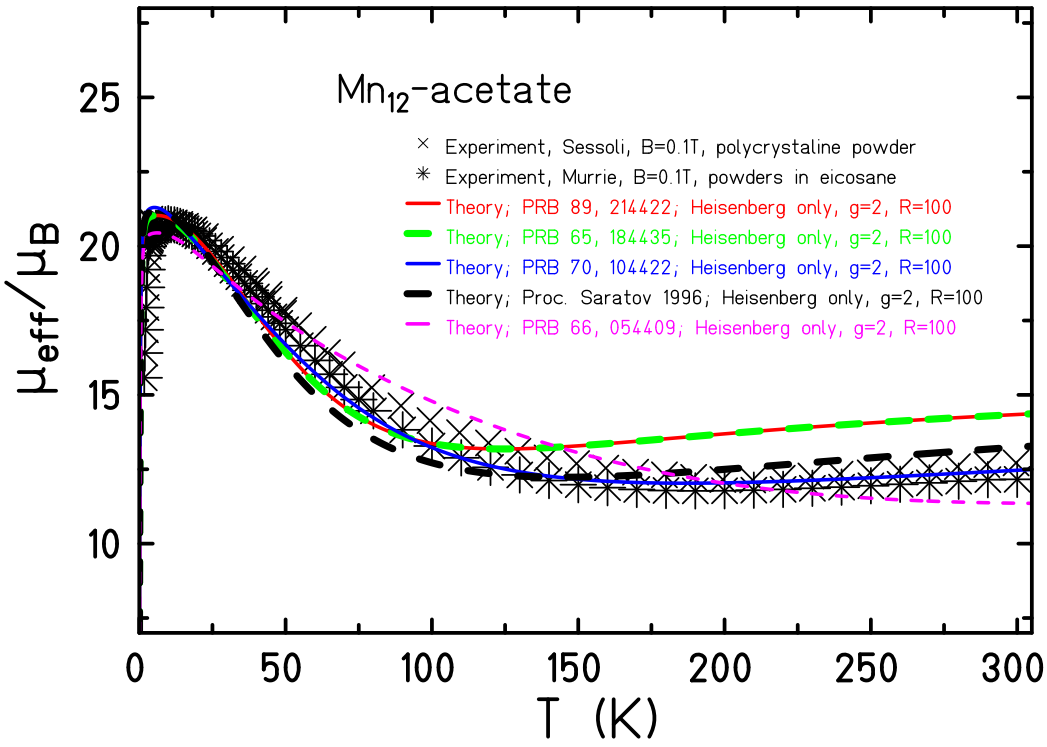


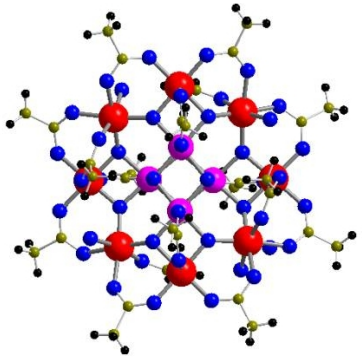


No other method can deliver these curves!

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

Effective magnetic moment of Mn_{12}-acetate



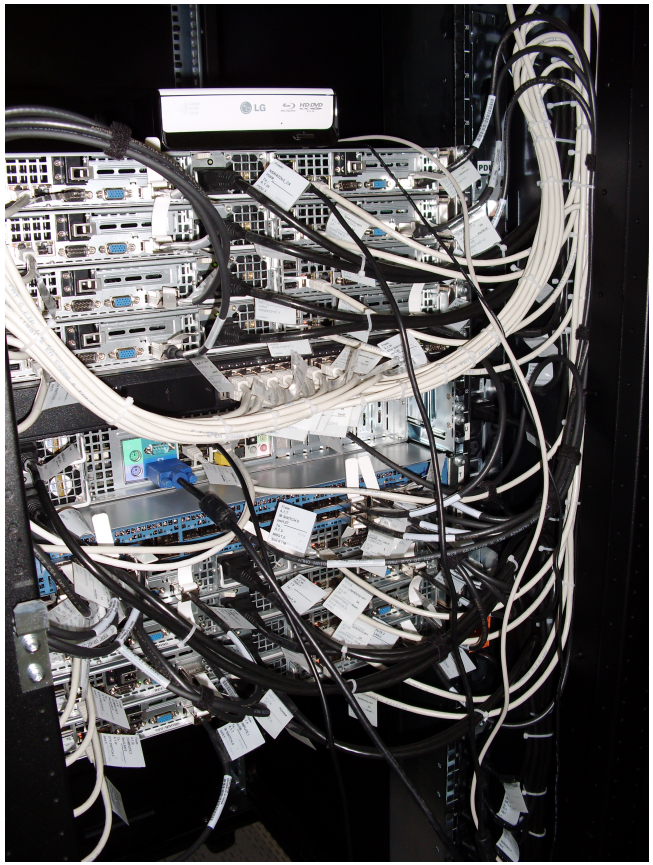


We can check DFT parameter predictions for large molecules! Normally!

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

⇒ 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, FTLM, DMRG, DDMRG, thDMRG, DFT for magnetic molecules.

Many thanks to my collaborators







- C. Beckmann, M. Czopnik, T. Glaser, O. Hanebaum, Chr. Heesing, M. Höck, K. Irländer, N.B. Ivanov, H.-T. Langwald, A. Müller, H. Schlüter, R. Schnalle, Chr. Schröder, J. Ummethum, P. Vorndamme (Bielefeld)
- K. Bärwinkel, T. Heitmann, R. Heveling, H.-J. Schmidt, R. Steinigeweg (Osnabrück)
- M. Luban (Ames Lab); P. Kögerler (Aachen, Jülich, Ames); D. Collison, R.E.P. Winpenny, E.J.L. McInnes, F. Tuna (Man U); L. Cronin, M. Murrie (Glasgow); E. Brechin (Edinburgh); H. Nojiri (Sendai, Japan); A. Postnikov (Metz); M. Evangelisti (Zaragosa); A. Honecker (U Cergy-Pontoise); E. Garlatti, S. Carretta, G. Amoretti, P. Santini (Parma); A. Tennant (ORNL); Gopalan Rajaraman (Mumbai); M. Affronte (Modena)
- J. Richter, J. Schulenburg (Magdeburg); B. Lake (HMI Berlin); B. Büchner, V. Kataev, H.-H. Klauß (Dresden); A. Powell, W. Wernsdorfer (Karlsruhe); J. Wosnitza (Dresden-Rossendorf); J. van Slageren (Stuttgart); R. Klingeler (Heidelberg); O. Waldmann (Freiburg)

Thank you very much for your attention.

The end.

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Highlights. Tutorials. Who is who. Conferences.