The power of typicality applied to magnetic molecules and low-dimensional quantum spin systems

Jürgen Schnack

Department of Physics – University of Bielefeld – Germany

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

APS March Meeting 2020
Denver, Colorado, 3 March 2020

UNIVERSITÄT BIELEFELD
Fakultät für Physik

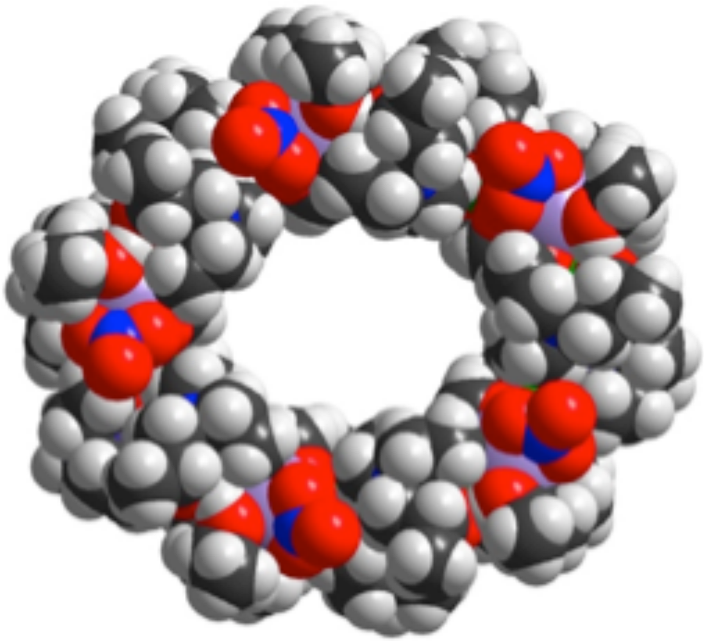
DFG

lrz

We investigate magnetic molecules

J. Schnack, Contemporary Physics **60**, 127-144 (2019)

You have got a molecule!

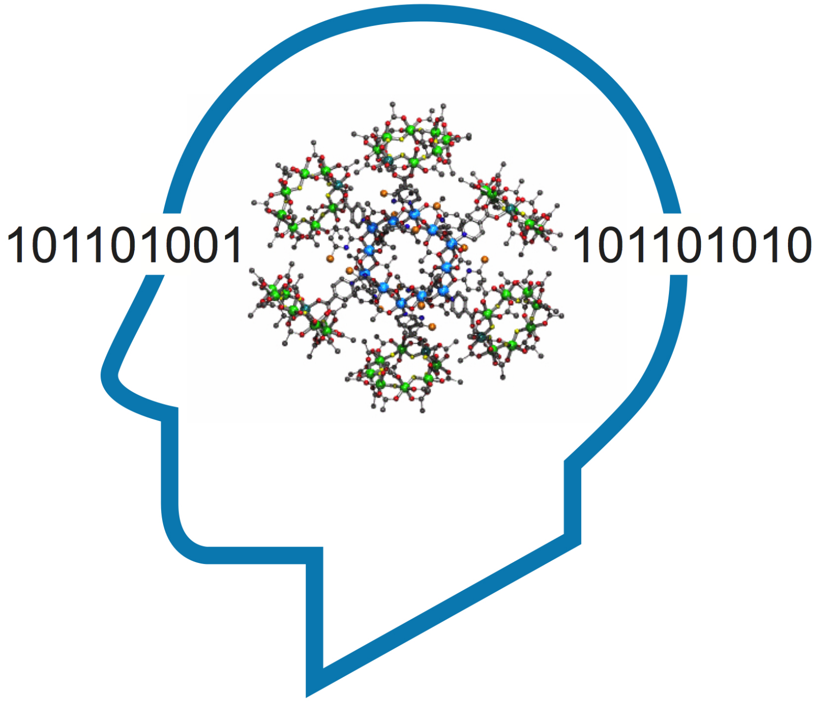


$$S = 60!$$

Congratulations!

Powell group: npj Quantum Materials **3**, 10 (2018)

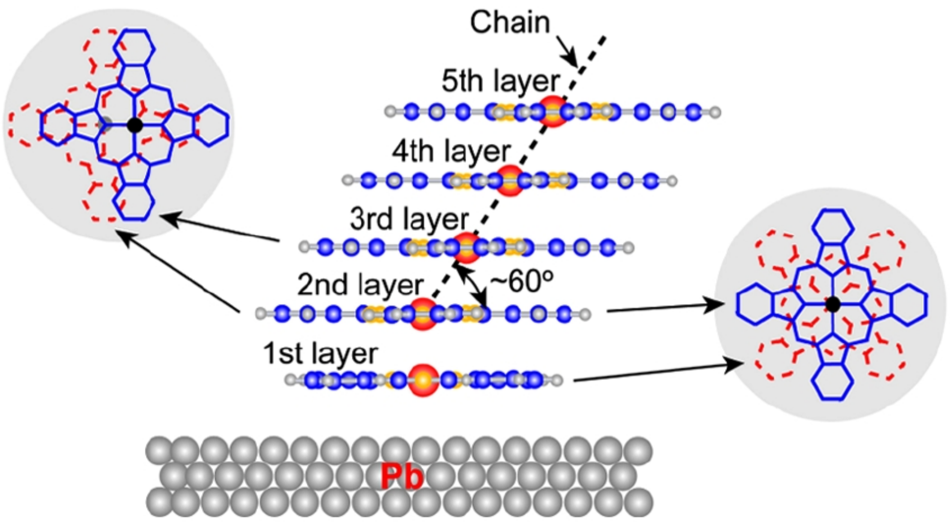
You want to build a quantum computer!



Very smart!

Wernsdorfer group: Phys. Rev. Lett. **119**, 187702 (2017)

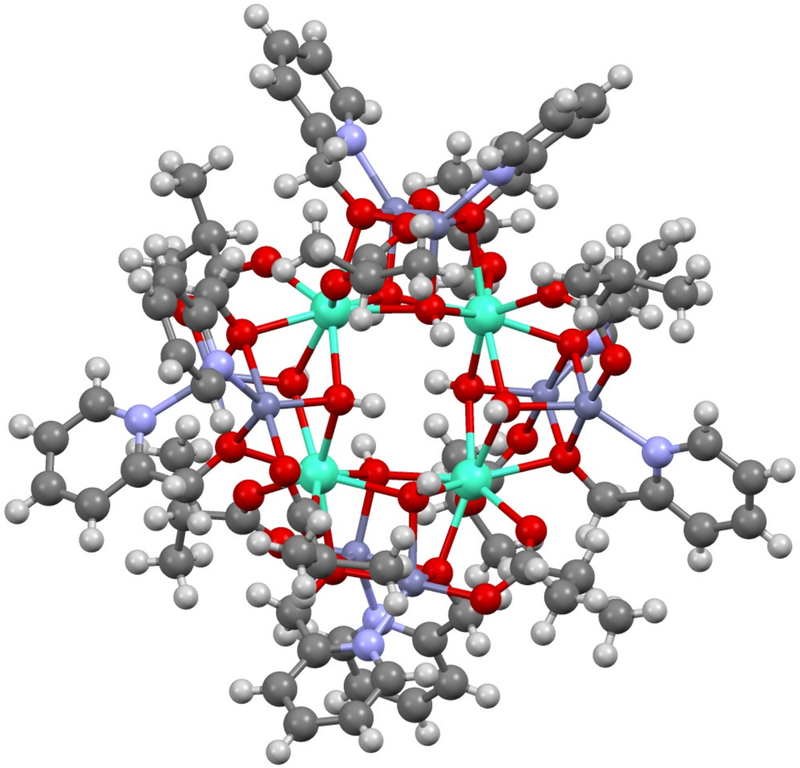
You want to deposit your molecule!



Next generation magnetic storage!

Xue group: Phys. Rev. Lett. **101**, 197208 (2008)

You want molecular magnetocalorics!



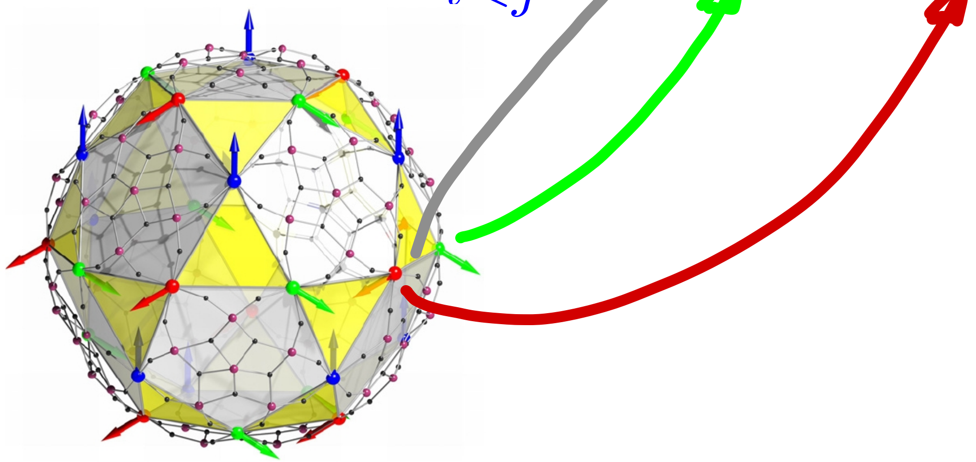
Brilliant!

Brechin group: Angew. Chem. Int. Ed. **51**, 4633 (2012)

You have got an idea about the modeling!

Heisenberg **Zeeman**

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



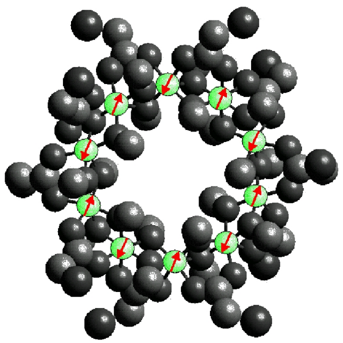
You have to solve the Schrödinger equation!

$$\underset{\sim}{H} \, | \, \phi_n \, \rangle \; = \; E_n \, | \, \phi_n \, \rangle$$

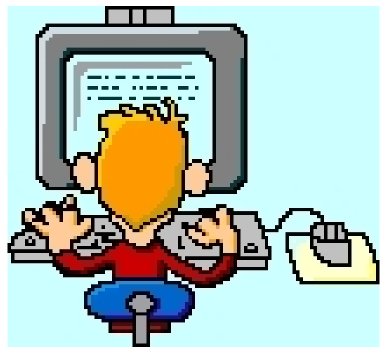
Eigenvalues E_n and eigenvectors $| \, \phi_n \, \rangle$

- 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_{10}^{III}: $N = 10$, $s = 5/2$, $\dim(\mathcal{H}) = (2s+1)^N$

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

Can we evaluate the partition function

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

without diagonalizing the Hamiltonian?

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. Typicality-based estimates
2. Gd_7 and the magnetocaloric effect
3. $Fe_{10}Gd_{10}$ and a quantum critical behavior
4. FTLM for anisotropic spin models
5. Bonus: Kagome lattice antiferromagnet – Is 42 the final answer?

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

Solution I: trace estimators

$$\text{tr}\left(\underset{\sim}{Q}\right) \approx \langle\, r \,|\, \underset{\sim}{Q} \,|\, r \,\rangle$$

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

- $|\, \nu \,\rangle$ 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

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

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

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

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???

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

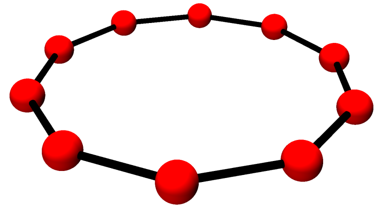
Partition function II: Finite-temperature Lanczos Method

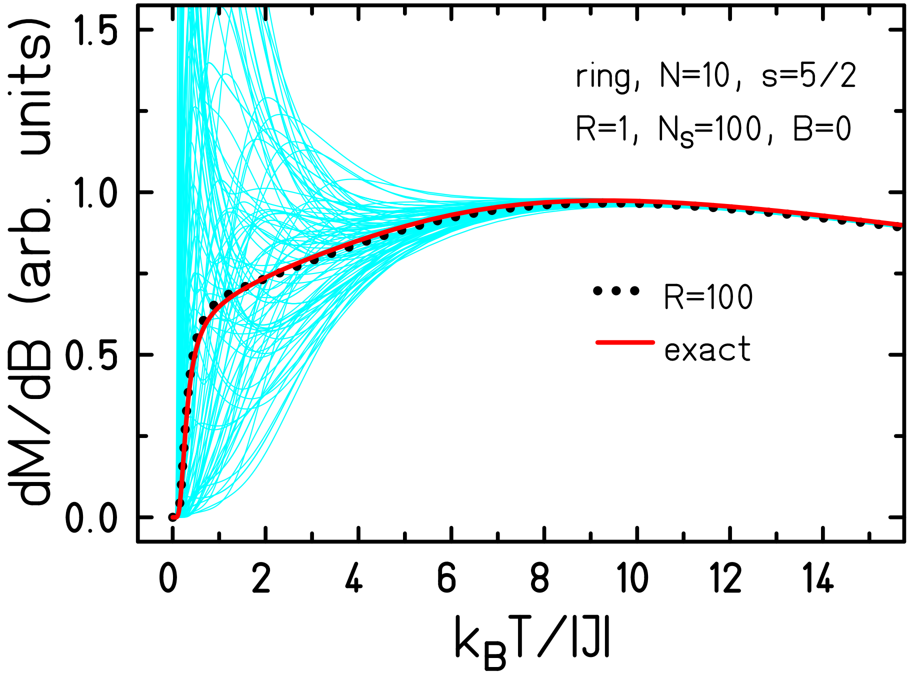
$$Z^{\text{FTLM}}(T,B) \approx \frac{1}{R}\sum_{r=1}^{R}\sum_{n=1}^{N_L} e^{-\beta\epsilon_n^{(r)}} |\langle\, n(r) \,|\, r \,\rangle|^2$$

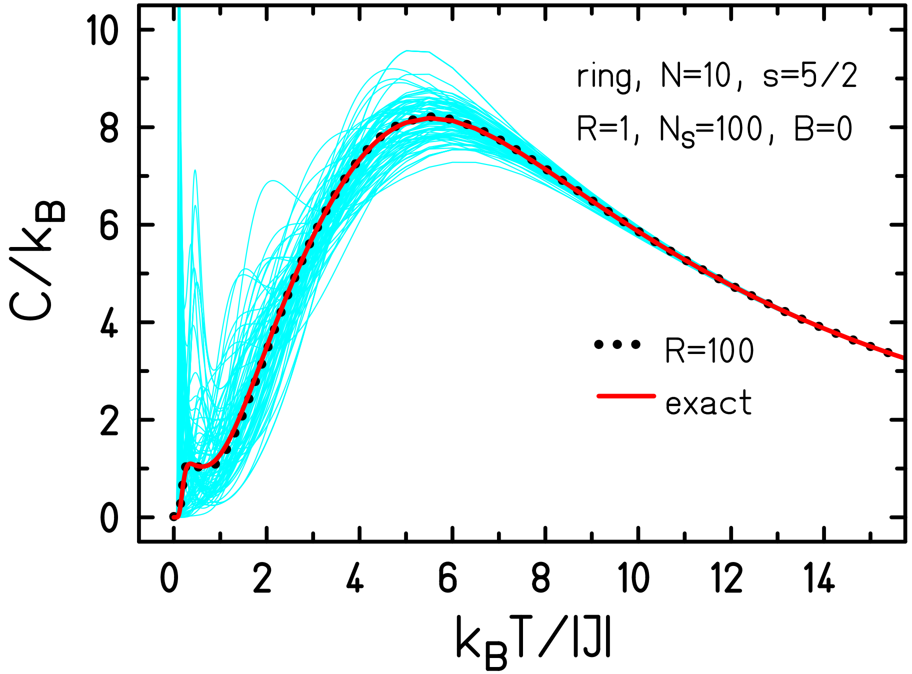
- Averaging over R random vectors is better.
- $|\, n(r) \,\rangle$ n-th Lanczos eigenvector starting from $|\, r \,\rangle$ (Rademacher vectors).
- Partition function replaced by a small sum: $R = 1 \ldots 100, N_L \approx 100$.

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

FTLM 1: ferric wheel





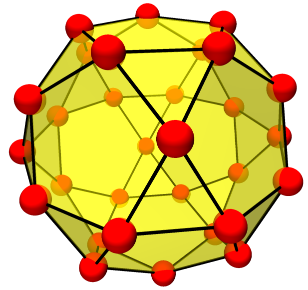


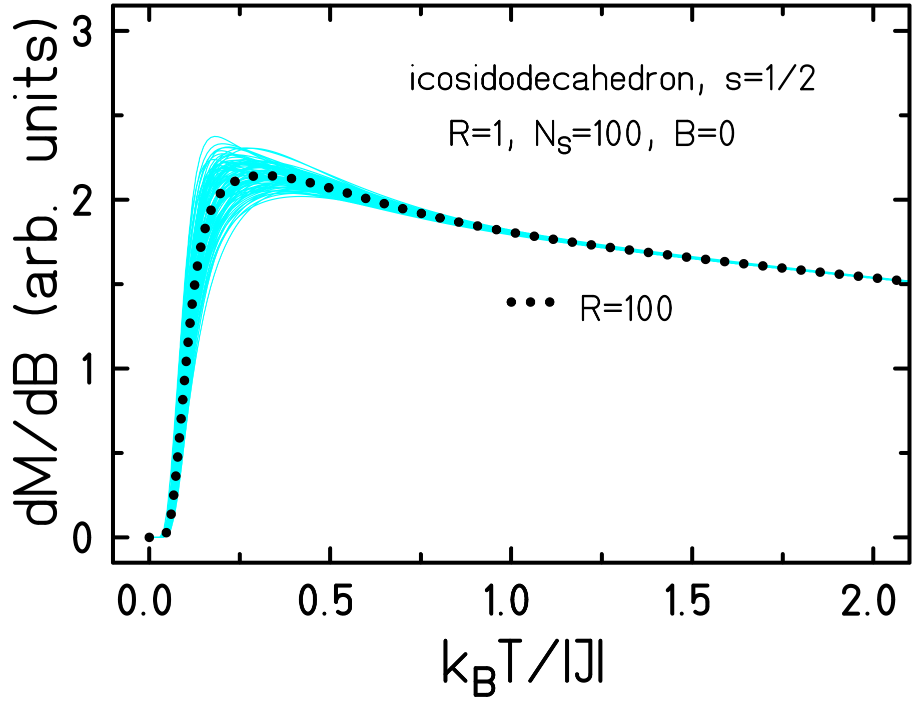
(1) J. Schnack, J. Richter, R. Steinigeweg, Phys. Rev. Research **2**, 013186 (2020).

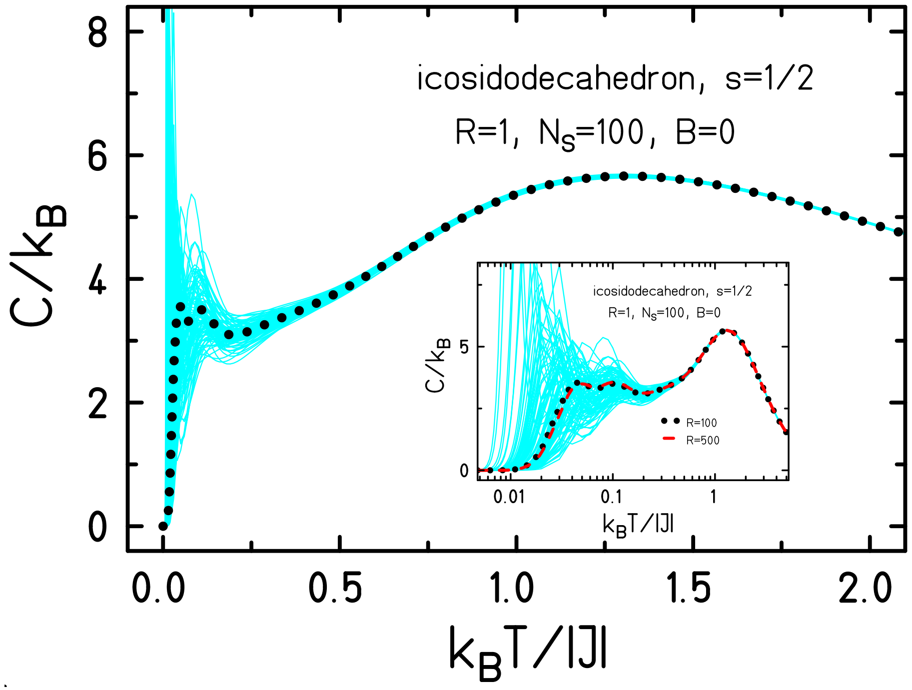
(2) SU(2) & D_2: R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403 (2010).

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

FTLM 2: icosidodecahedron



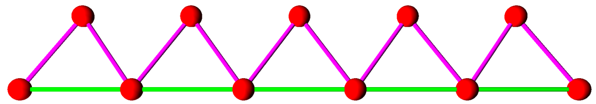


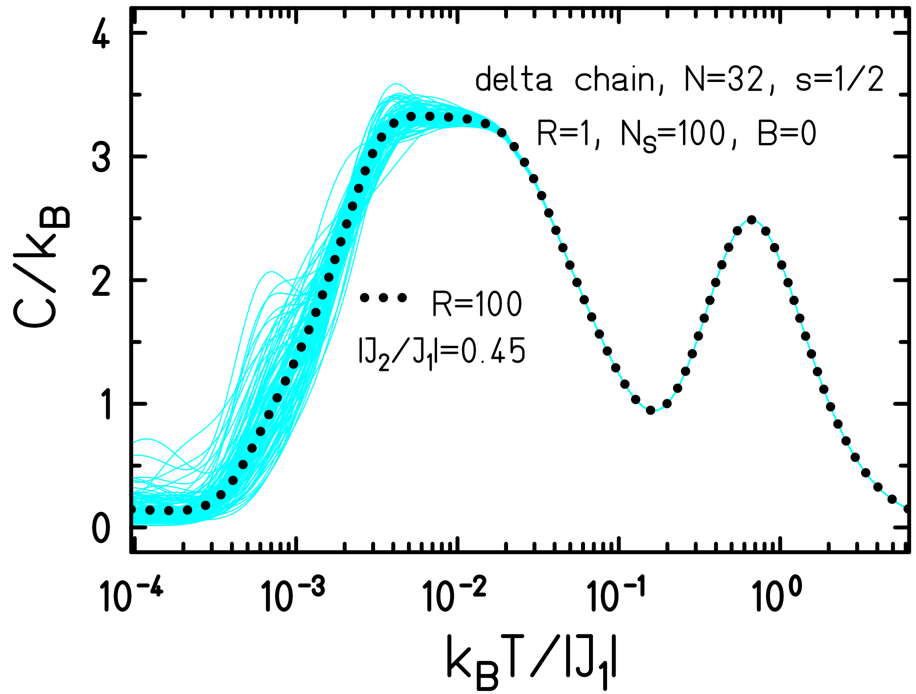


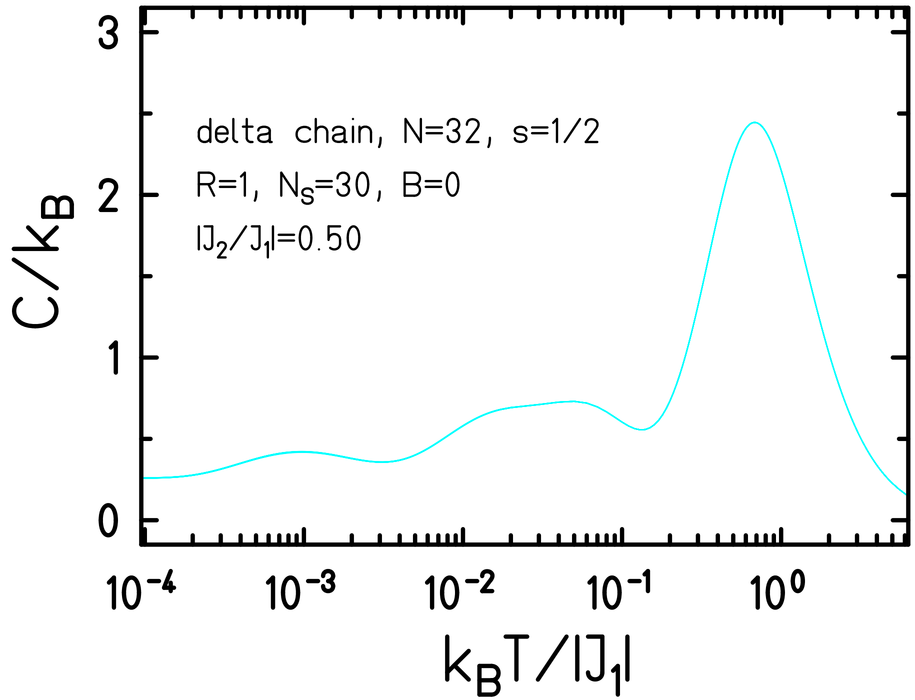
(1) J. Schnack, J. Richter, R. Steinigeweg, Phys. Rev. Research **2**, 013186 (2020).

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

FTLM 3: sawtooth chain







$|J_2/J_1| = 0.45$ – near critical, $|J_2/J_1| = 0.50$ – critical.

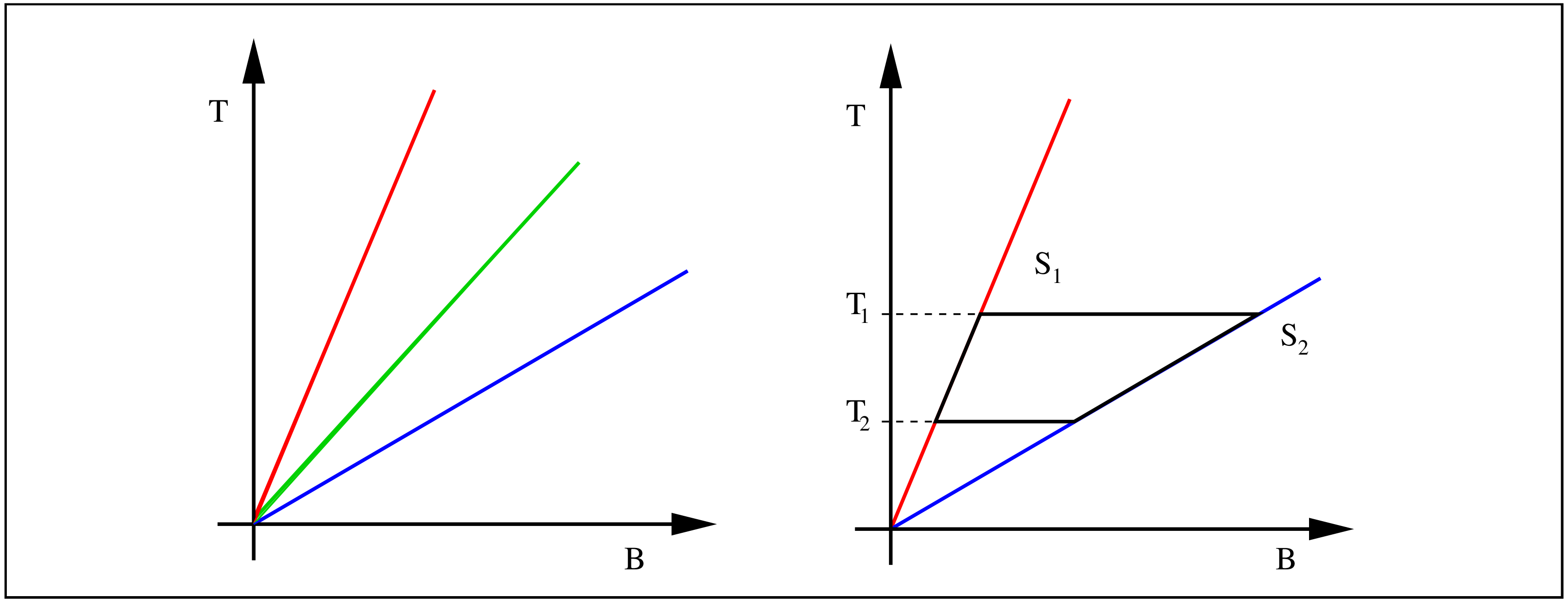
Frustration, technically speaking, works in your favour.

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

(2) J. Schnack, J. Richter, T. Heitmann, J. Richter, R. Steinigeweg, Z. Naturforsch. A (2020) accepted, arXiv:2002.00411

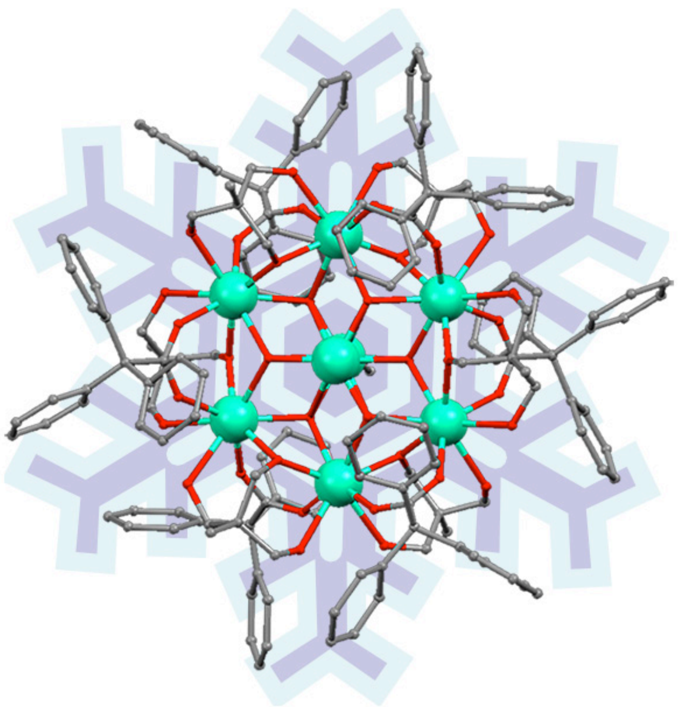
Gd_7 and the magnetocaloric effect

Magnetocaloric effect – Paramagnets



- Ideal paramagnet: $S(T,B) = f(B/T)$, i.e. $S = const \Rightarrow T \propto B$.
- At low T pronounced effects of dipolar interaction prevent further effective cooling.

Gd$_7$ – Basics

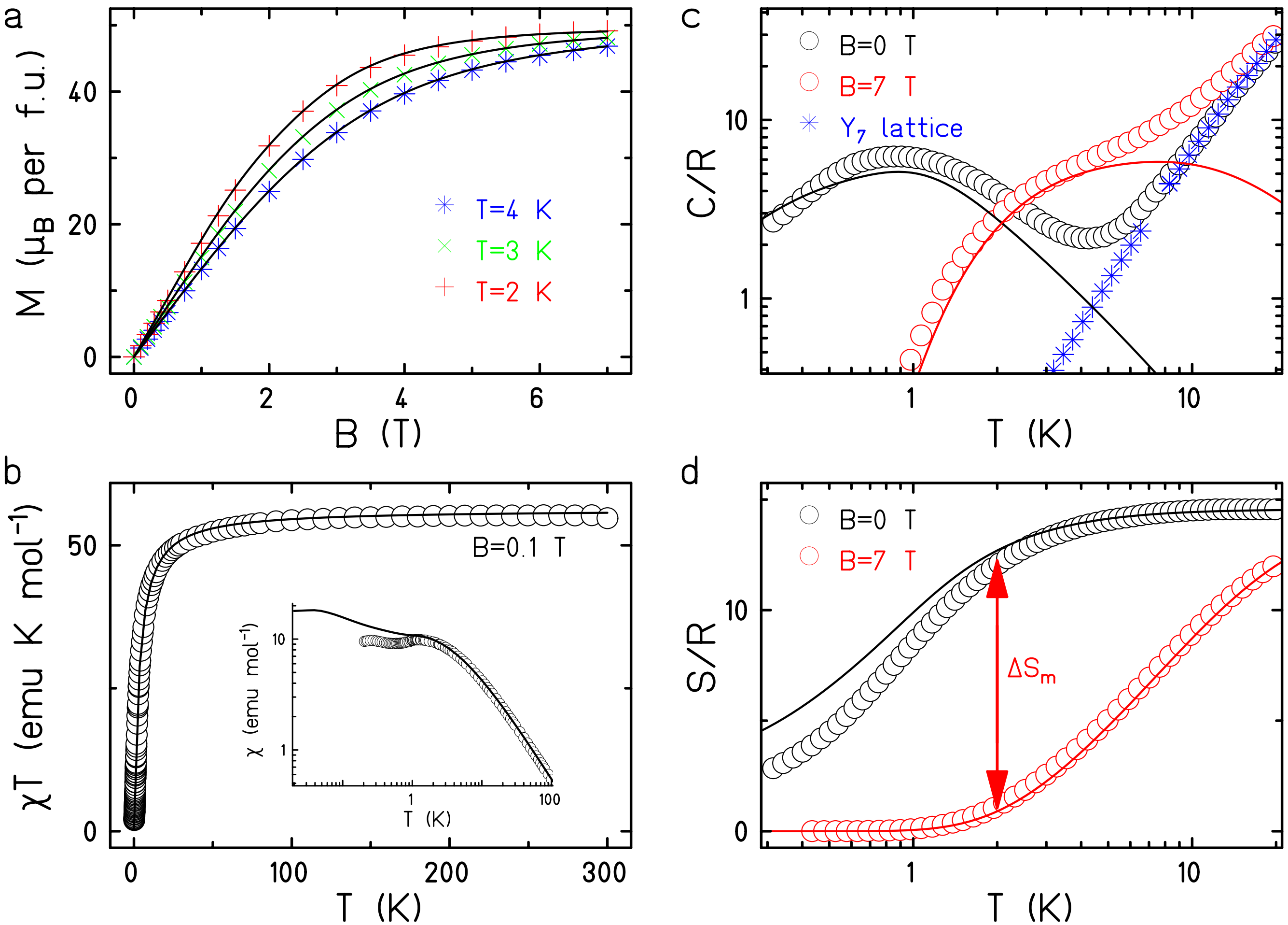


- Often magnetocaloric observables not directly measured, but inferred from Maxwell's relations.
- First real cooling experiment with a molecule.
- $\underset{\sim}{H} = -2 \sum_{i<j} J_{ij} \,\vec{\underset{\sim}{s}}_i \cdot \vec{\underset{\sim}{s}}_j + g\,\mu_B\,B \sum_i^N \underset{\sim}{s}_i^z$

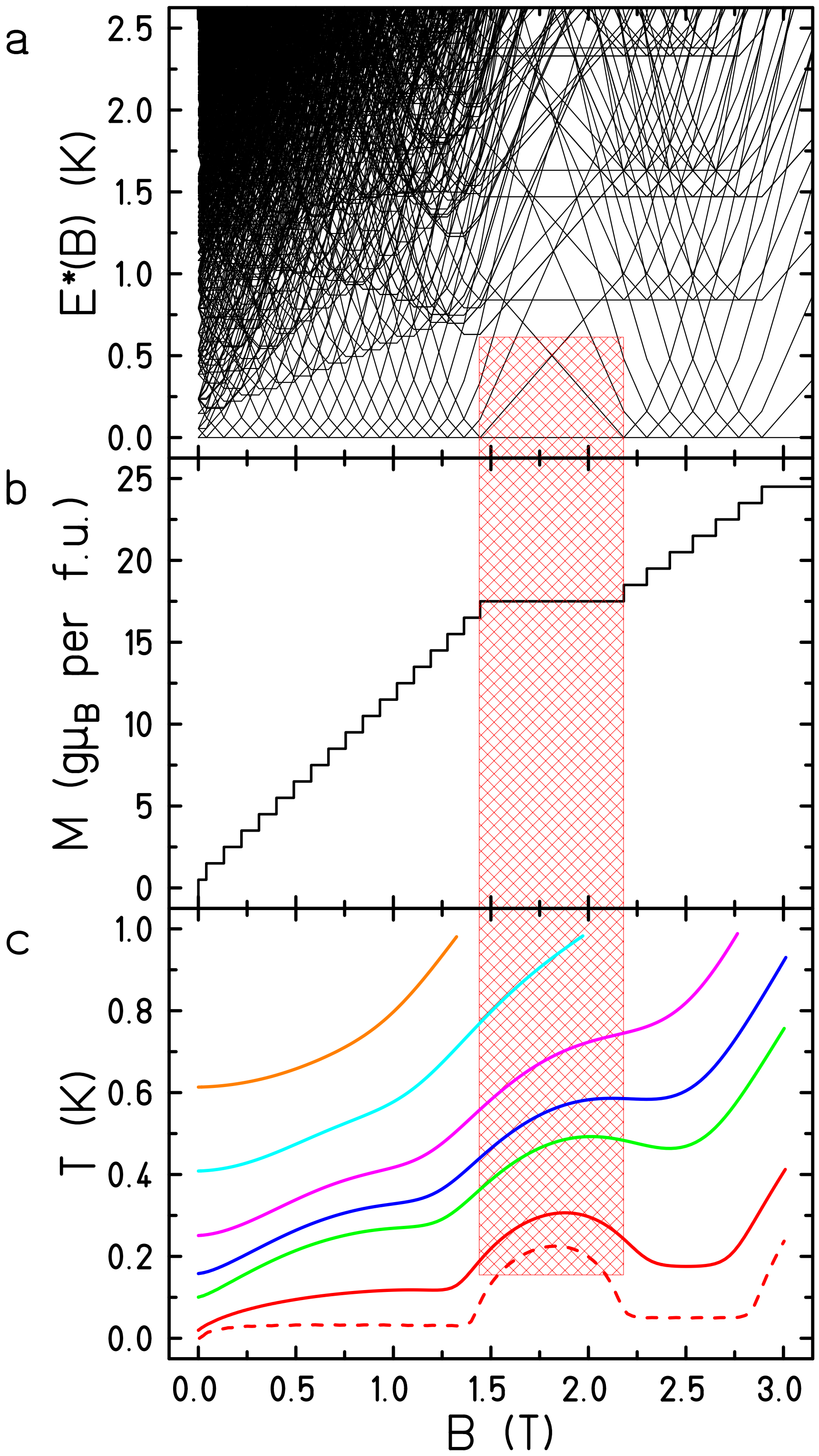
  $J_1 = -0.090(5)$ K, $J_2 = -0.080(5)$ K and $g = 2.02$.
- Very good agreement down to the lowest temperatures.

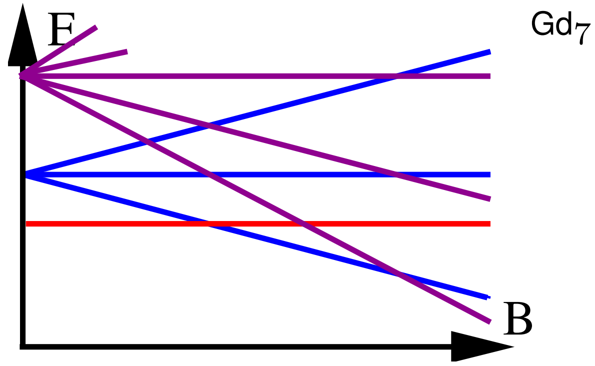
J. W. Sharples, D. Collison, E. J. L. McInnes, J. Schnack, E. Palacios, M. Evangelisti, Nat. Commun. **5**, 5321 (2014).

Gd$_7$ – experiment & theory



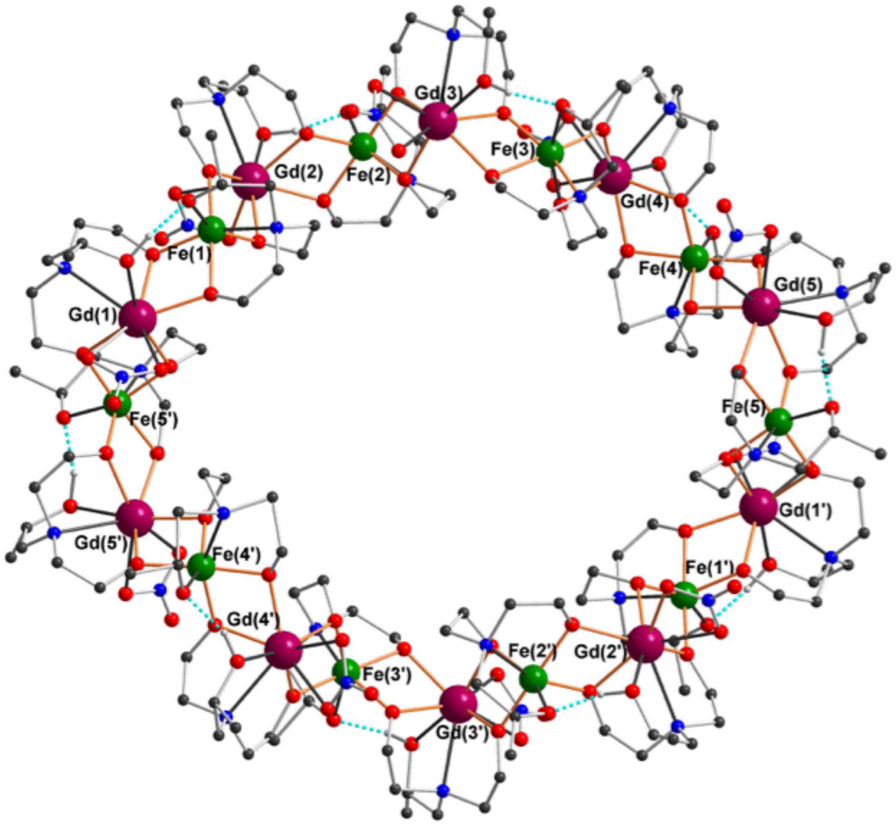
J. W. Sharples, D. Collison, E. J. L. McInnes, J. Schnack, E. Palacios, M. Evangelisti, Nat. Commun. **5**, 5321 (2014).

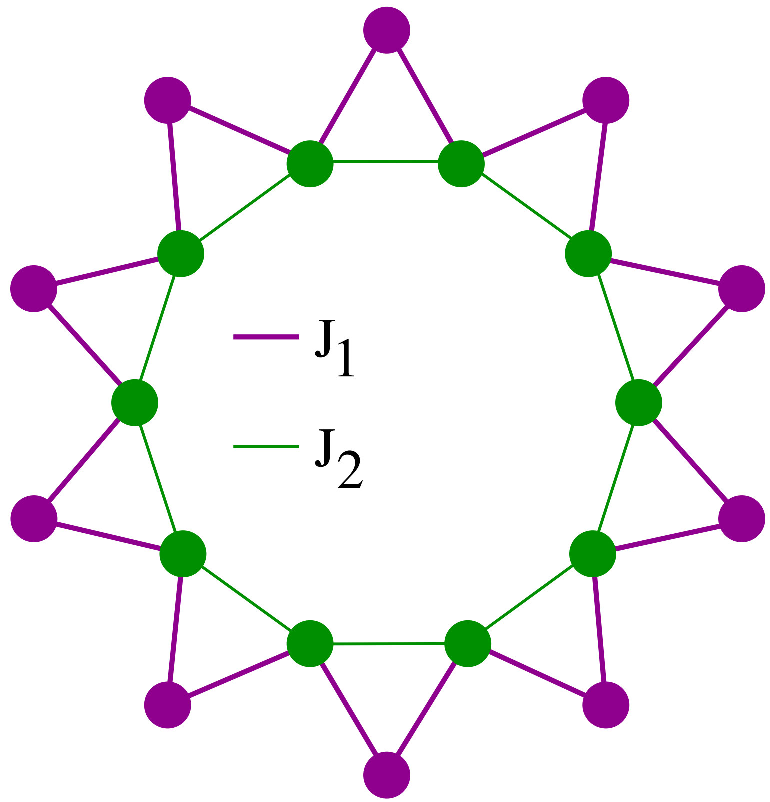

a
b
c
E*(B) (K)
M (gμB per f.u.)
T (K)
B (T)
0.0 0.5 1.0 1.5 2.0 2.5
0 5 10 15 20 25
0.0 0.2 0.4 0.6 0.8 1.0
0.0 0.5 1.0 1.5 2.0 2.5 3.0


E
B
Gd7

$Fe_{10}Gd_{10}$ and quantum critical behavior

$Gd_{10}Fe_{10}$ – structure = delta chain

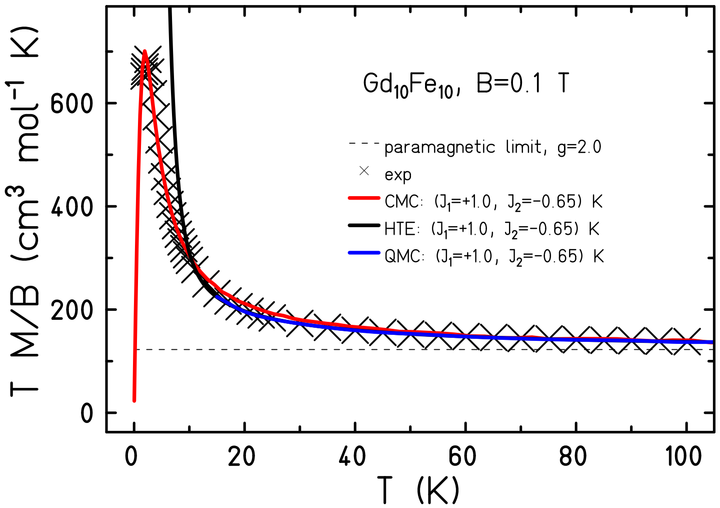


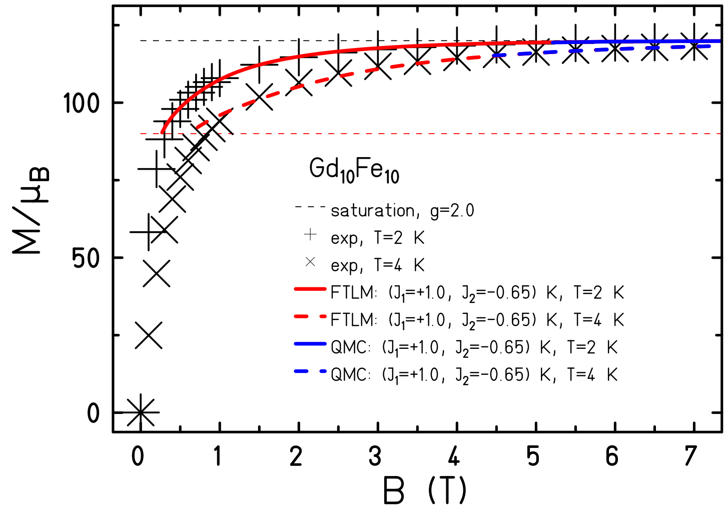


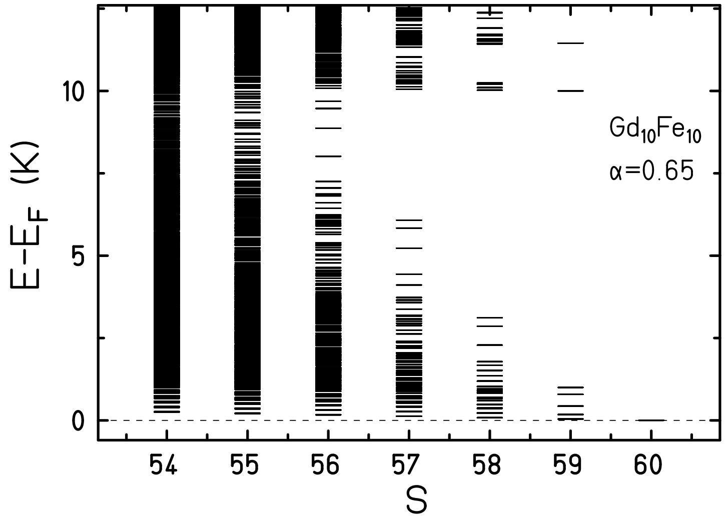
purple: Gd ($s = 7/2$), green: Fe ($s = 5/2$)

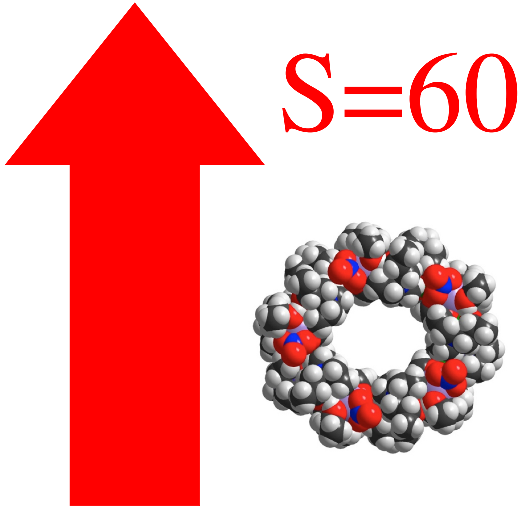
We will see: J_1 ferro, J_2 antiferro

A. Baniodeh *et al., npj Quantum Materials* ***3****, 10 (2018)*

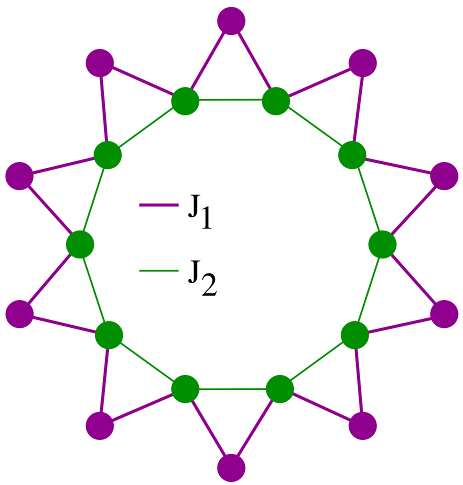


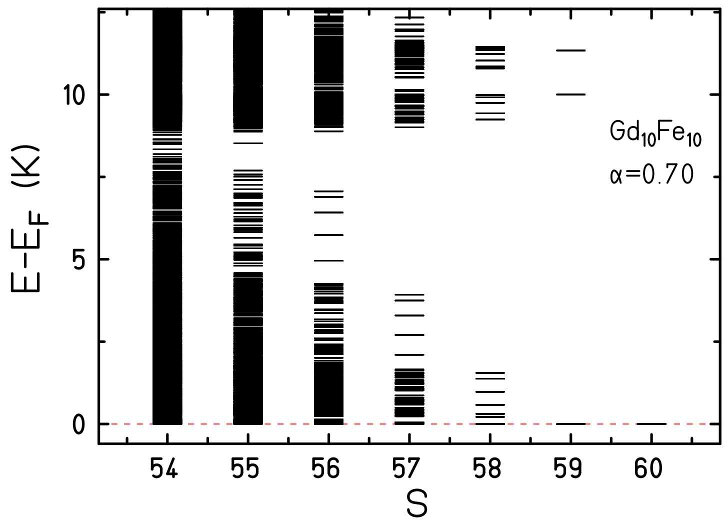


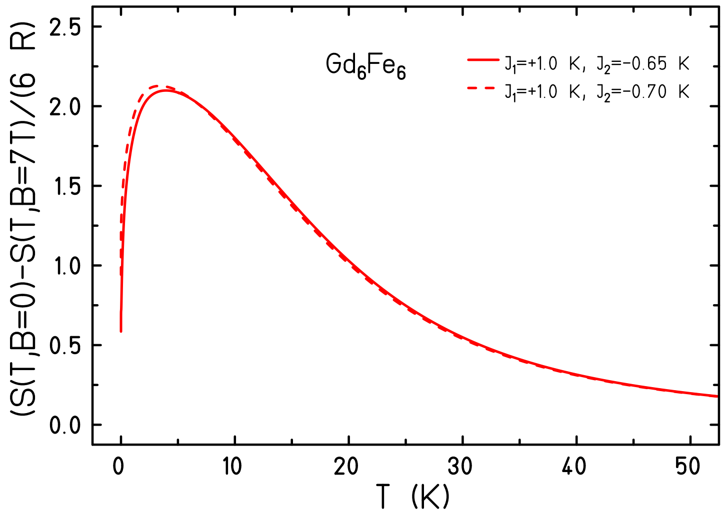


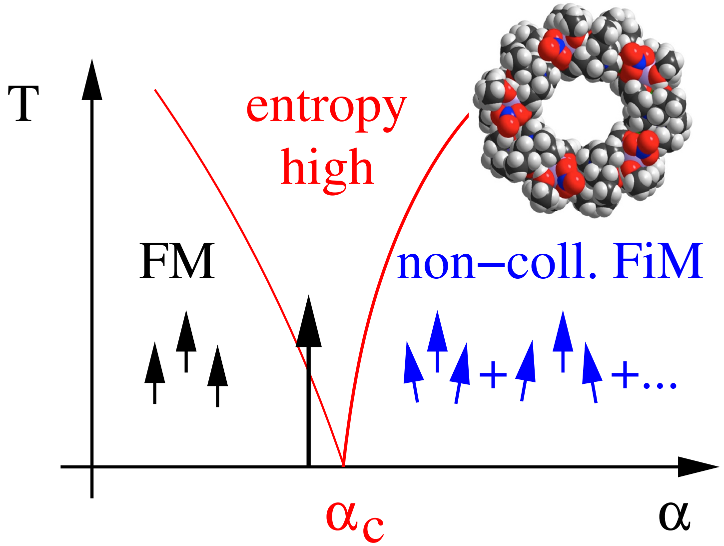


A. Baniodeh *et al., npj Quantum Materials* ***3****, 10 (2018)*









A. Baniodeh *et al.*, *npj Quantum Materials* ***3**, 10 (2018)*

Single Molecule Magnets

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)

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

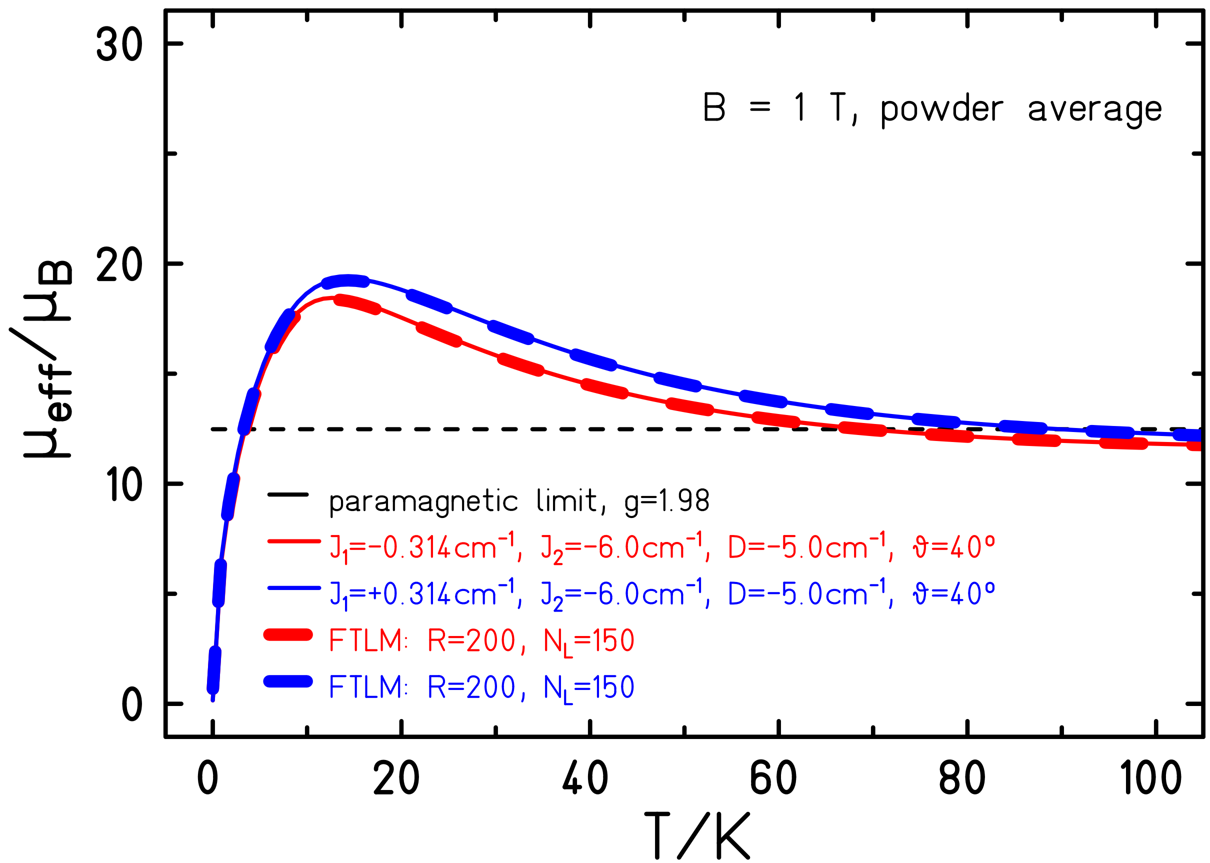
Use Lanczos energy eigenvector $|\, n(\nu)\,\rangle$ and time-reversed counterpart $|\, \tilde{n}(\nu)\,\rangle$

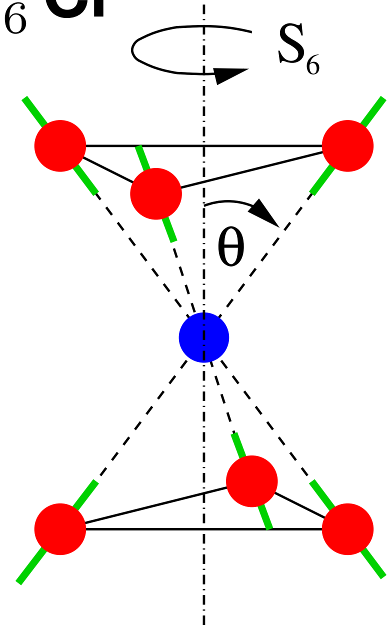
$$|\, n(\nu)\,\rangle = \sum_{\vec{m}} c_{\vec{m}}\, |\, \vec{m}\,\rangle \qquad , \qquad |\, \tilde{n}(\nu)\,\rangle = \sum_{\vec{m}} c^{*}_{\vec{m}}\, |\, -\vec{m}\,\rangle$$

- 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: $Mn_6^{III}Cr^{III}$





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

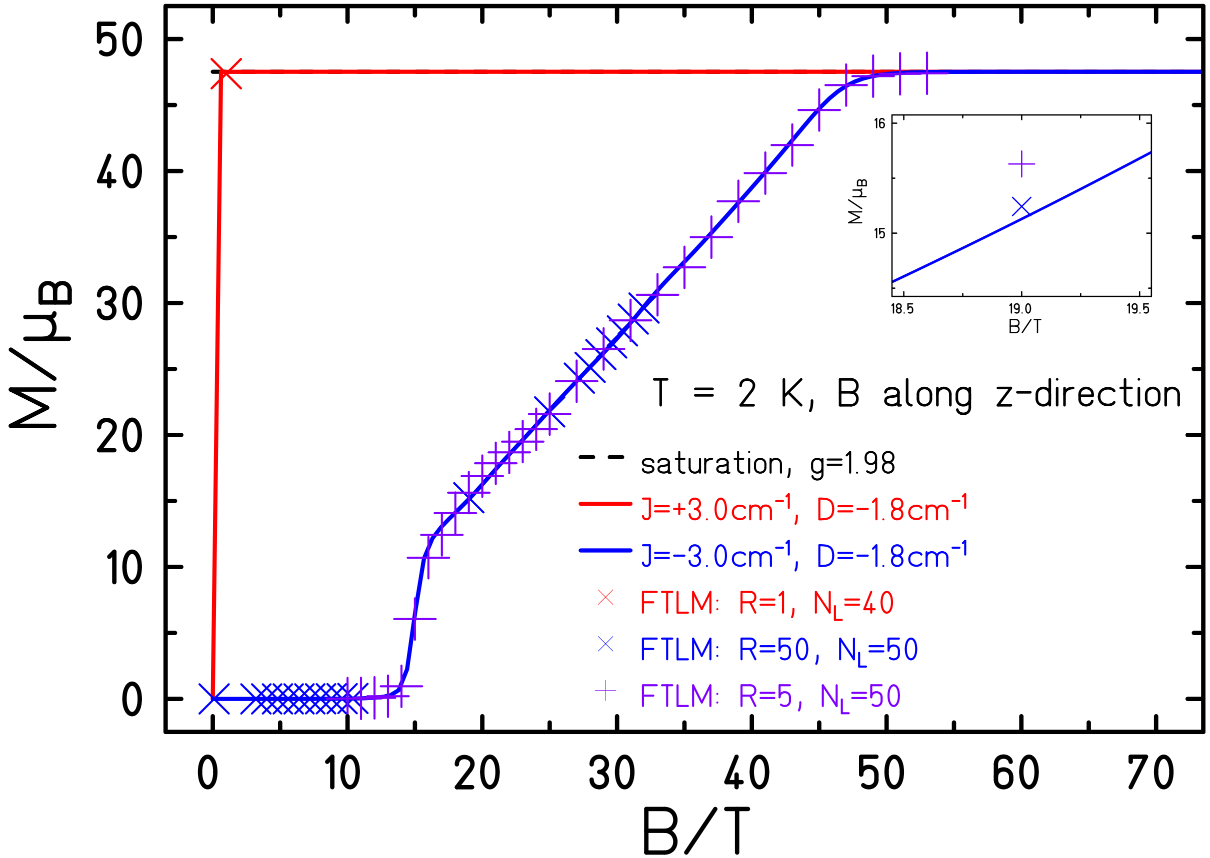
dim$(\mathcal{H}) = 62,500$

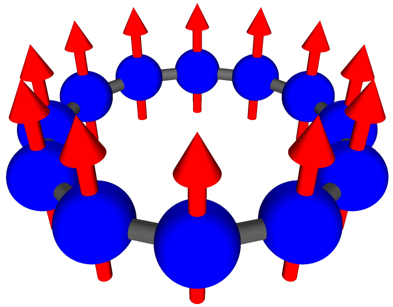
non-collinear easy axes

Hours compared to days, notebook compared to supercomputer!

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

A fictitious Mn^{III}_{12} – M_z vs B_z





$s = 2$

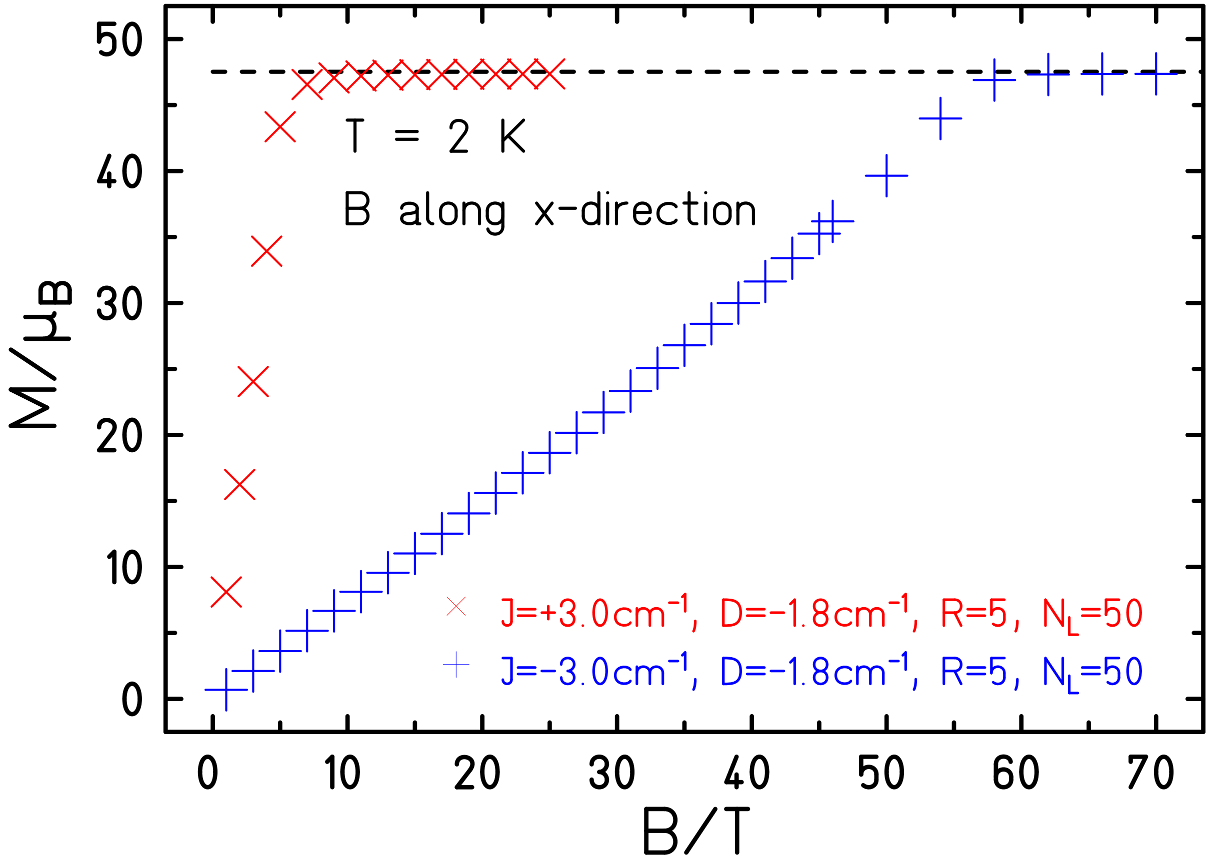
dim$(\mathcal{H}) = 244,140,625$

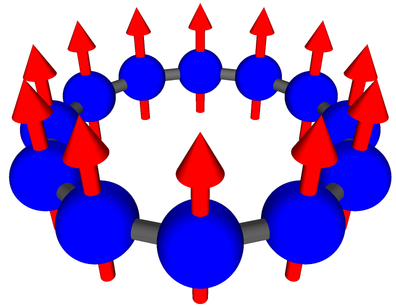
collinear easy axes

A few days compared to *impossible*!

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

A fictitious Mn^{III}_{12} – M_x vs B_x

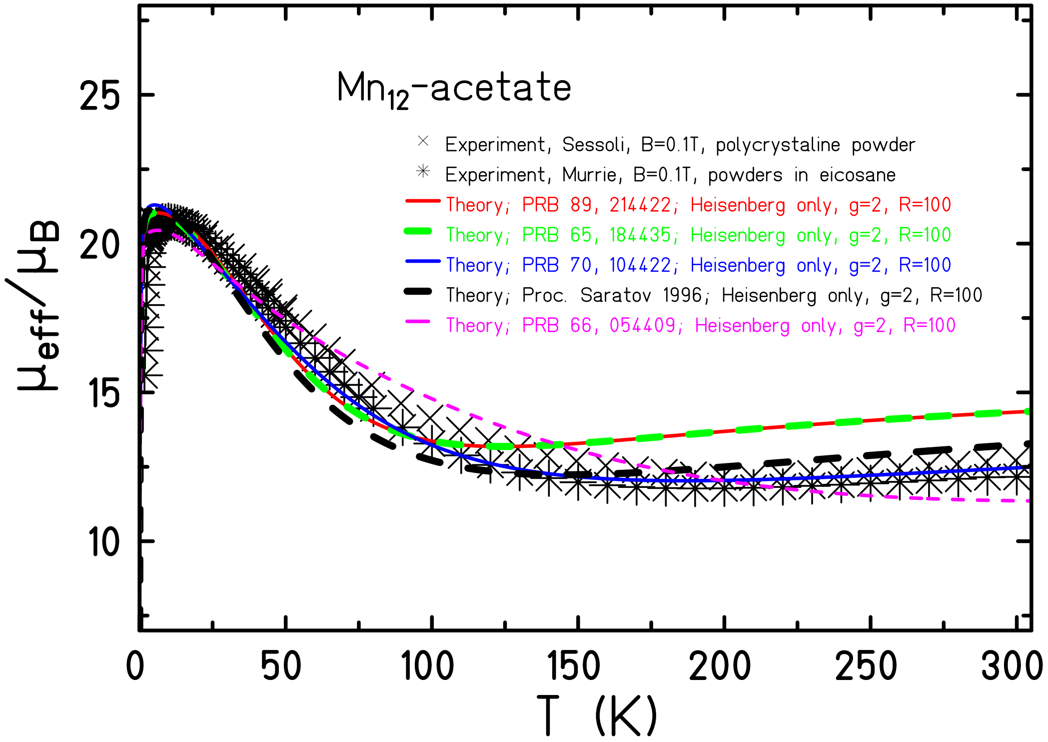




No other method can deliver these curves!

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!

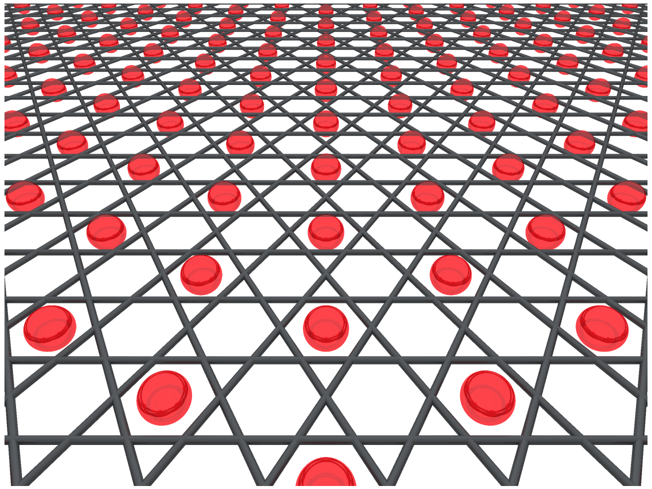
O. Hanebaum, J. Schnack, Phys. Rev. B **92** (2015) 064424

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

The kagome lattice antiferromagnet

Is 42 the final answer?

Kagome lattice antiferromagnet – scientific problems

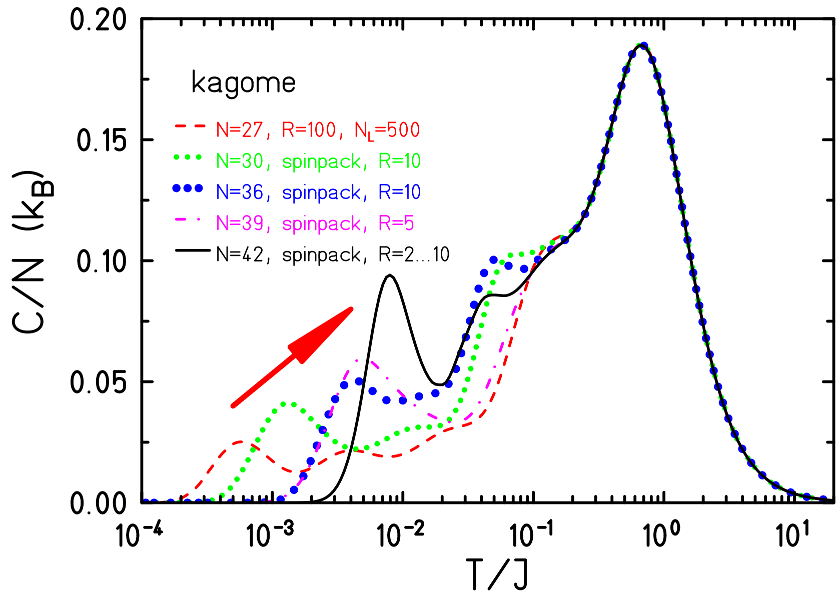


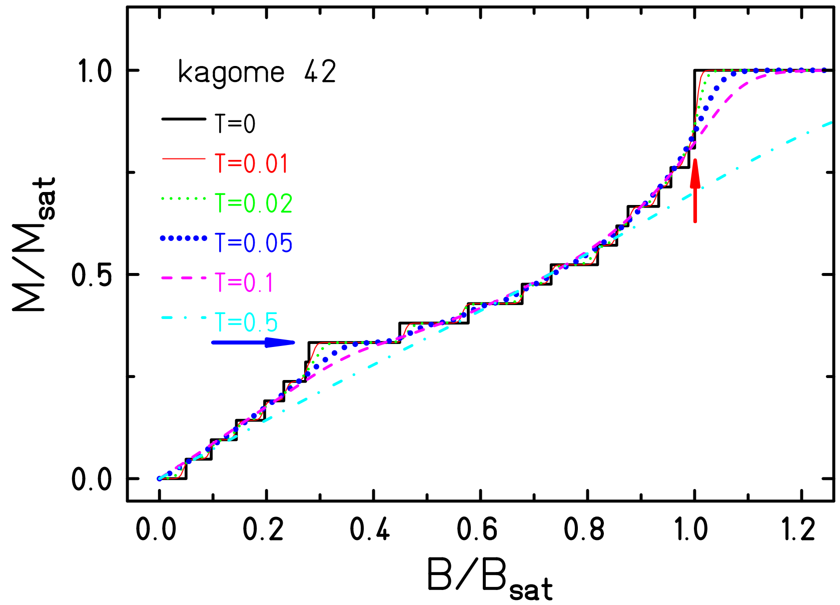
- Thermodynamic functions, in particular heat capacity and susceptibility (1)
- "Condensation" of low-lying singlets below the first triplet?
- Magnetization jump to saturation
- Thermal stability of magnetization plateaus, e.g. at $\mathcal{M}_{\text{sat}}/3$.
- Notoriously enigmatic (2)!

(1) J. Schnack, J. Schulenburg, J. Richter, Phys. Rev. B **98**, 094423 (2018)

(2) A.M. Läuchli, J. Sudan, R. Moessner, Phys. Rev. B **100**, 155142 (2019)

Kagome 42 – magnetic properties

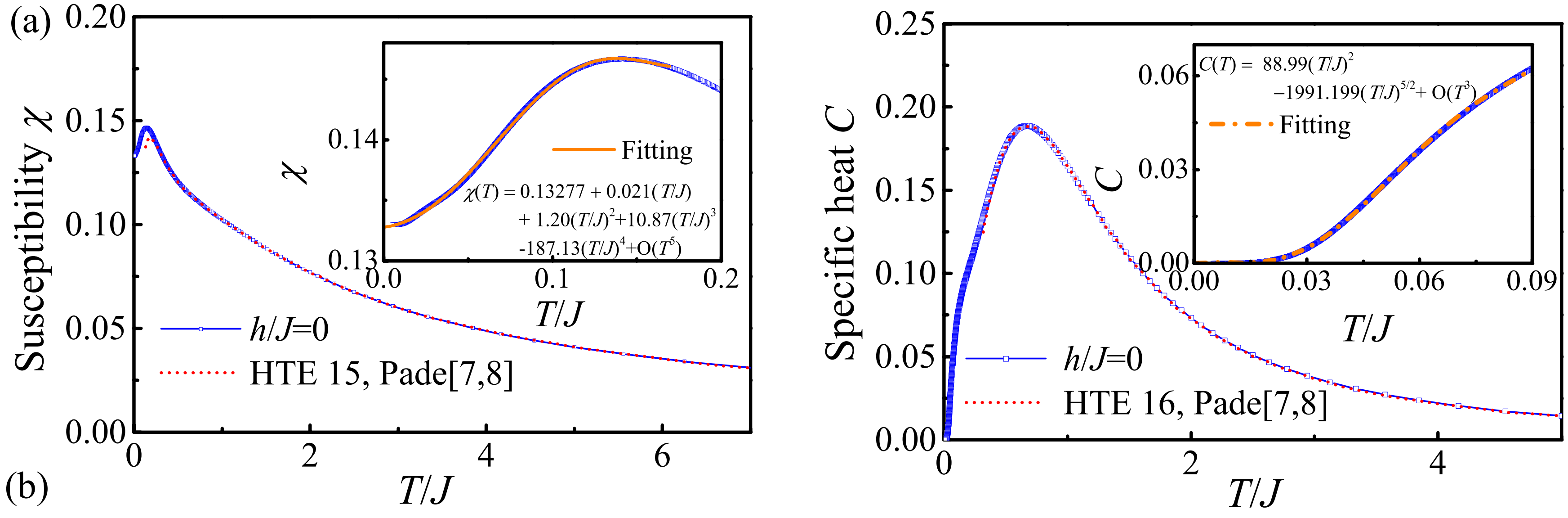




- Low-T peak moves to higher T with increasing N.
- Density of low-lying singlets seems to move to higher excitation energies!

J. Schnack, J. Schulenburg, J. Richter, Phys. Rev. B **98**, 094423 (2018)

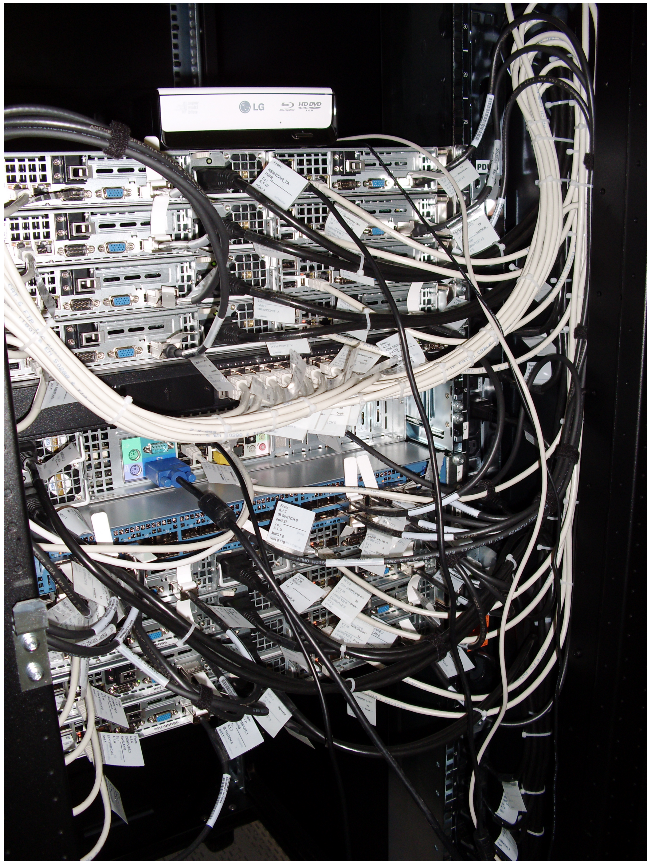
Kagome – tensor network calculations



- Tensor network calculations for the infinite system (1).

(1) Xi Chen, Shi-Ju Ran, Tao Liu, Cheng Peng, Yi-Zhen Huang, Gang Su, Science Bulletin **63**, 1545 (2018).

Summary



- Magnetic molecules for storage, q-bits, MCE, and since they are nice.
- Molecules taught us about frustrated systems.
- Isentropes for interacting systems are much richer than for paramagnets. Good for applications away from $(T = 0, B = 0)$.
- Quantum phase transitions may allow barocaloric applications.
- ED, HTE, CMC, QMC, FTLM, DMRG, DDMRG, thDMRG for magnetic molecules.

Many thanks to my collaborators

- 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, 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.

Molecular Magnetism Web

www.molmag.de

Highlights. Tutorials. Who is who. Conferences.