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

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~~APS March Meeting 2020~~ Virtual Single Molecule Magnet "March Meeting" session
The internet, 4 March 2020

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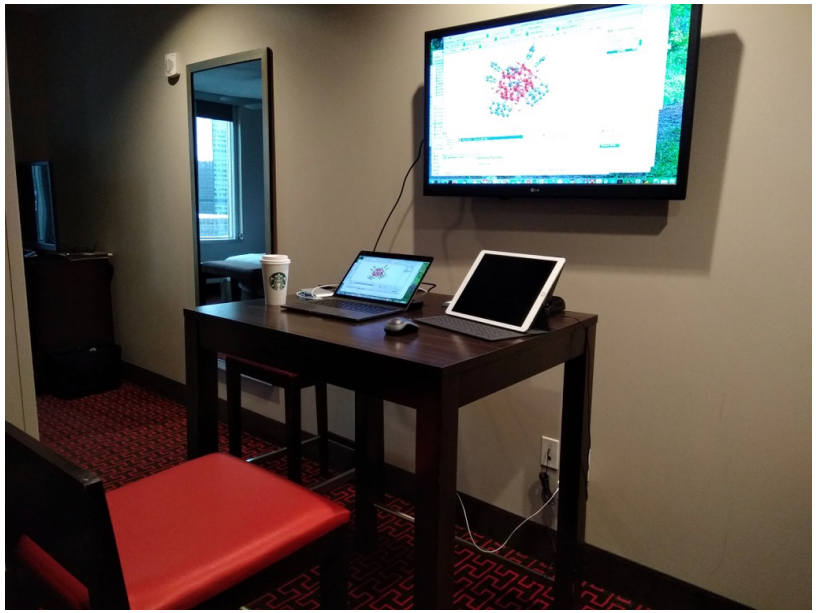
Irz

My new office: 500 15th Street, Denver, CO 80202



We investigate

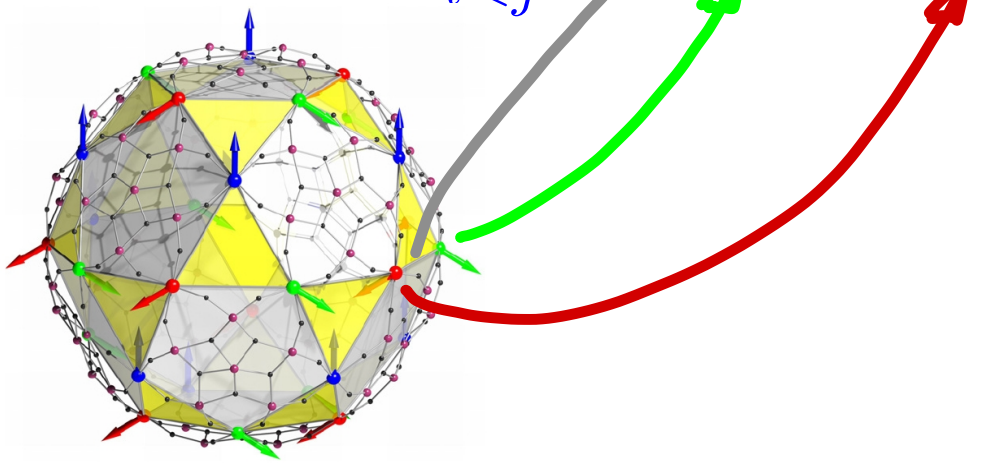
magnetic molecules

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

You have got an idea about the modeling!

Heisenberg Zeeman

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



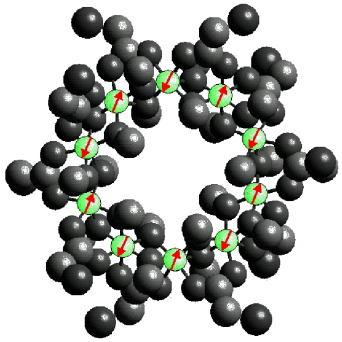
You have to solve the Schrödinger equation!

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

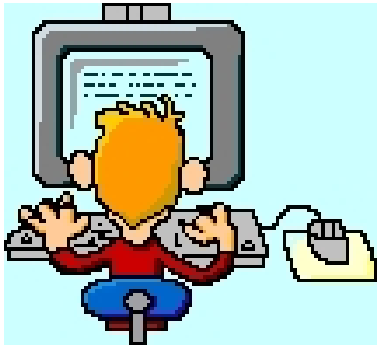
Eigenvalues E_n and eigenvectors $| \, \phi_n \, \rangle$

- 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!



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



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

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: Decoherence of a clock transition
6. 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

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

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

- $|\nu\rangle$ 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

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

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???

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

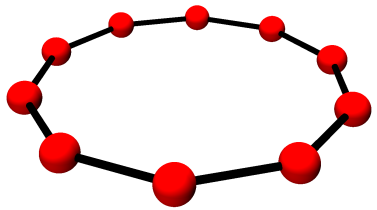
Partition function II: Finite-temperature Lanczos Method

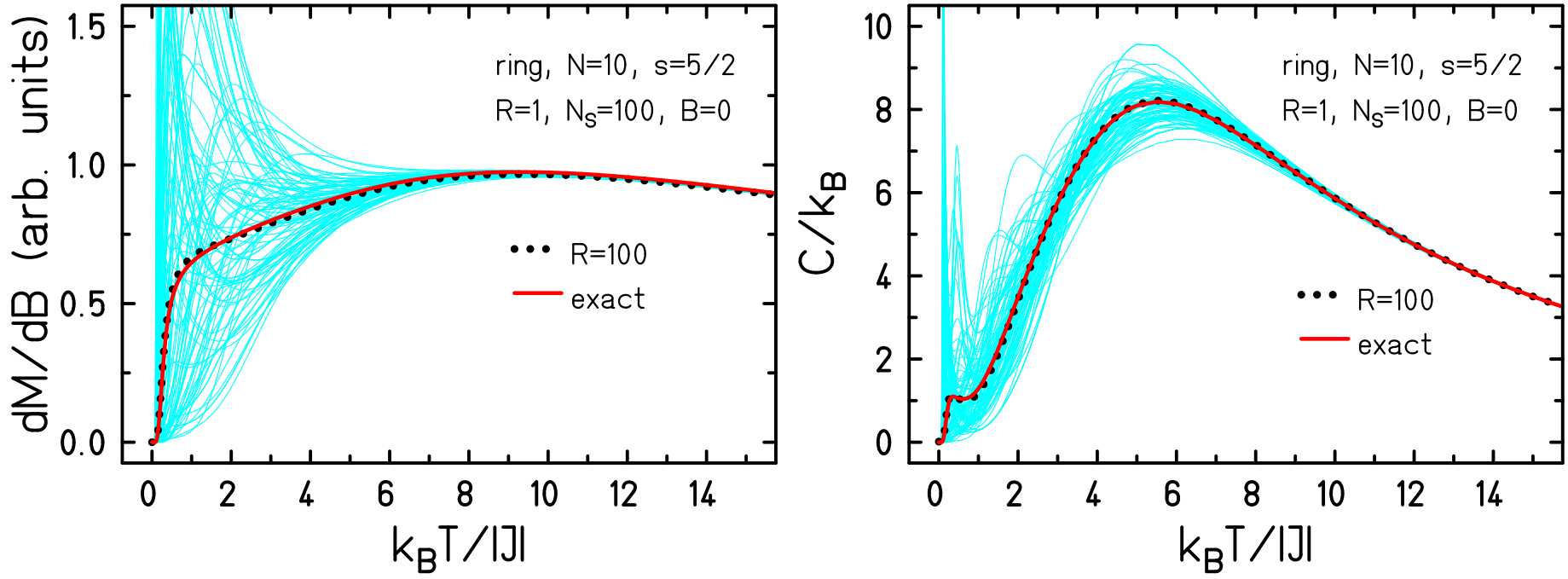
$$Z^{\mathsf{FTLM}}(T,B) \approx \frac{1}{R}\sum_{r=1}^{R}\sum_{n=1}^{N_L} e^{-\beta\epsilon_n^{(r)}} \left|\langle\, n(r)\,|\,r\,\rangle\right|^2$$

- 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



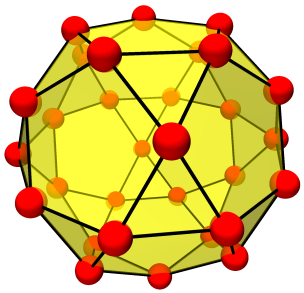


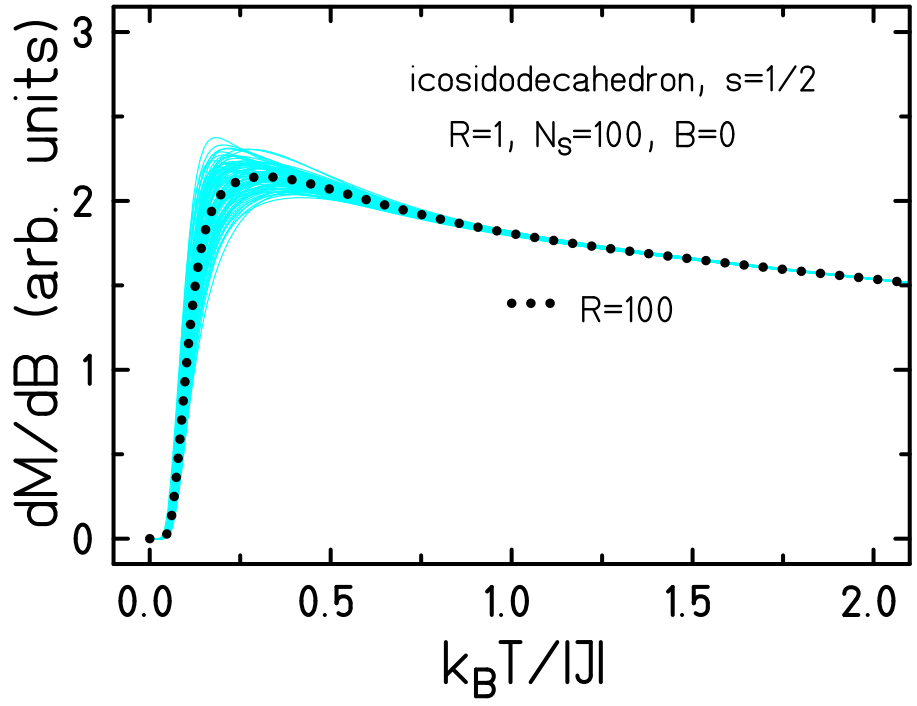
(1) J. Schnack, J. Richter, R. Steinigeweg, Phys. Rev. Research **2**, 013186 (2020).

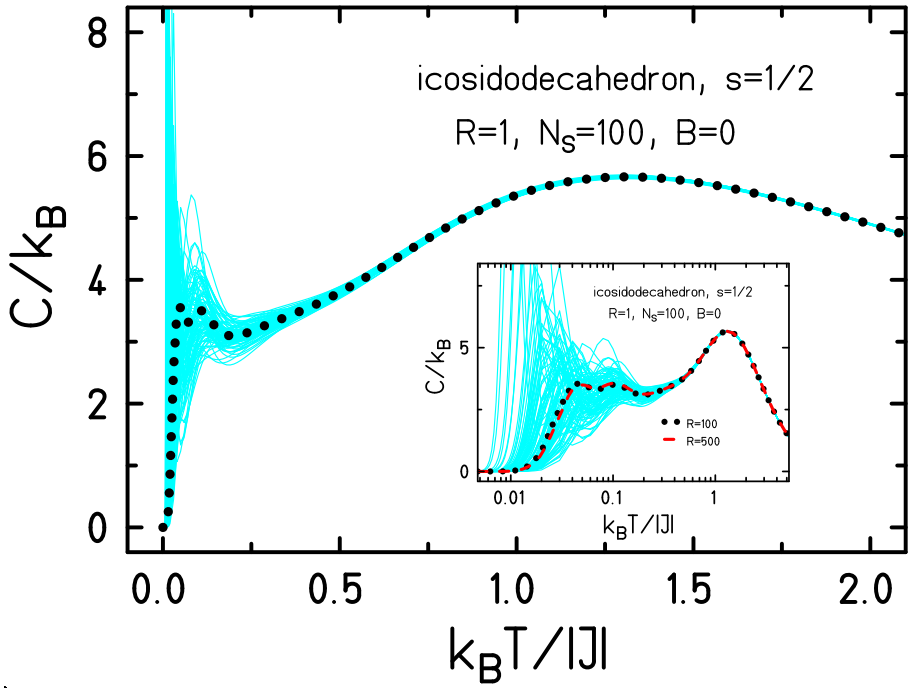
(2) SU(2) & D_2: R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403 (2010).

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

FTLM 2: icosidodecahedron







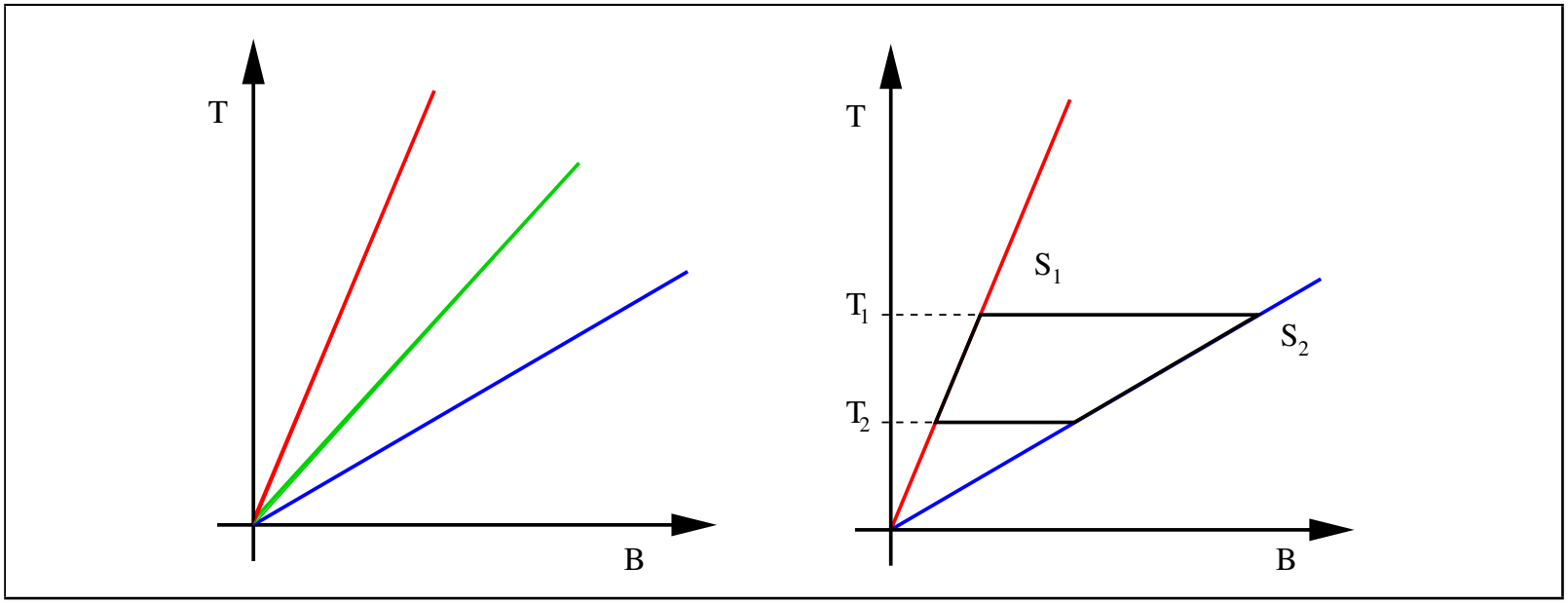
(1) J. Schnack, J. Richter, R. Steinigeweg, Phys. Rev. Research **2**, 013186 (2020).

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

Gd_7 and

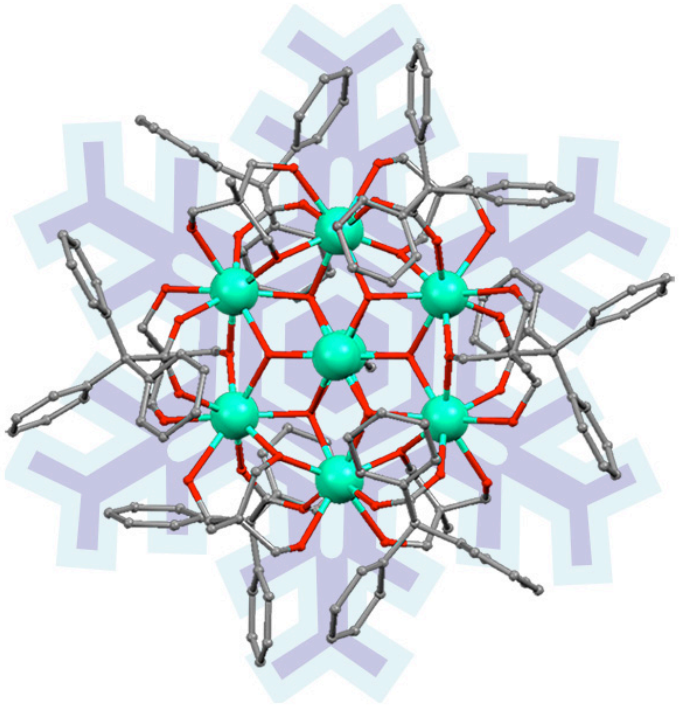
the magnetocaloric effect

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

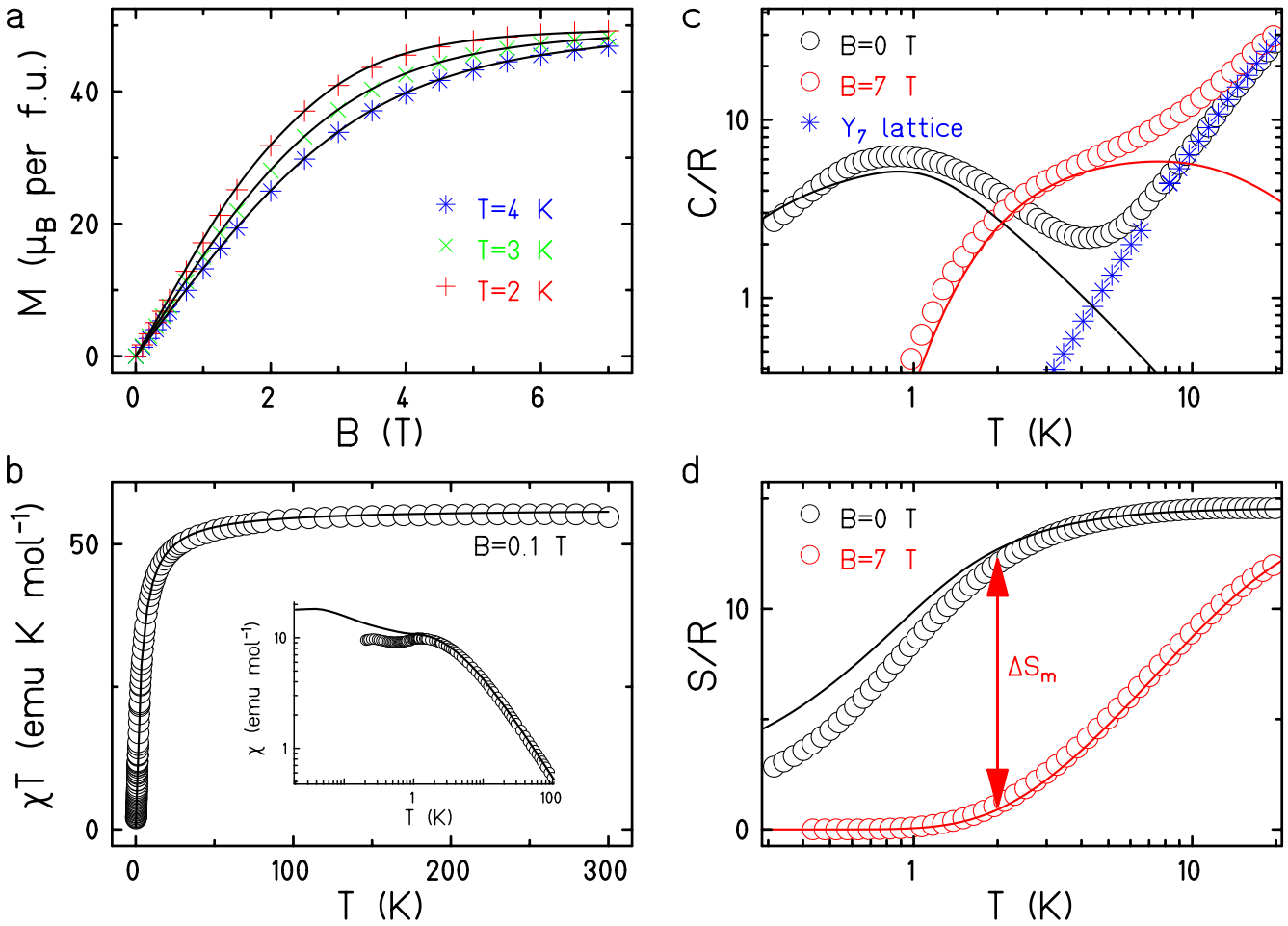


- Often magnetocaloric observables not directly measured, but inferred from Maxwell's relations.
- First real cooling experiment with a molecule.
- $\underset{\sim}{H} = -2 \sum_{i<j} J_{ij}\, \underset{\sim}{\vec{s}}_i \cdot \underset{\sim}{\vec{s}}_j + g\,\mu_B\, B \sum_i^N \underset{\sim}{s}_i^z$

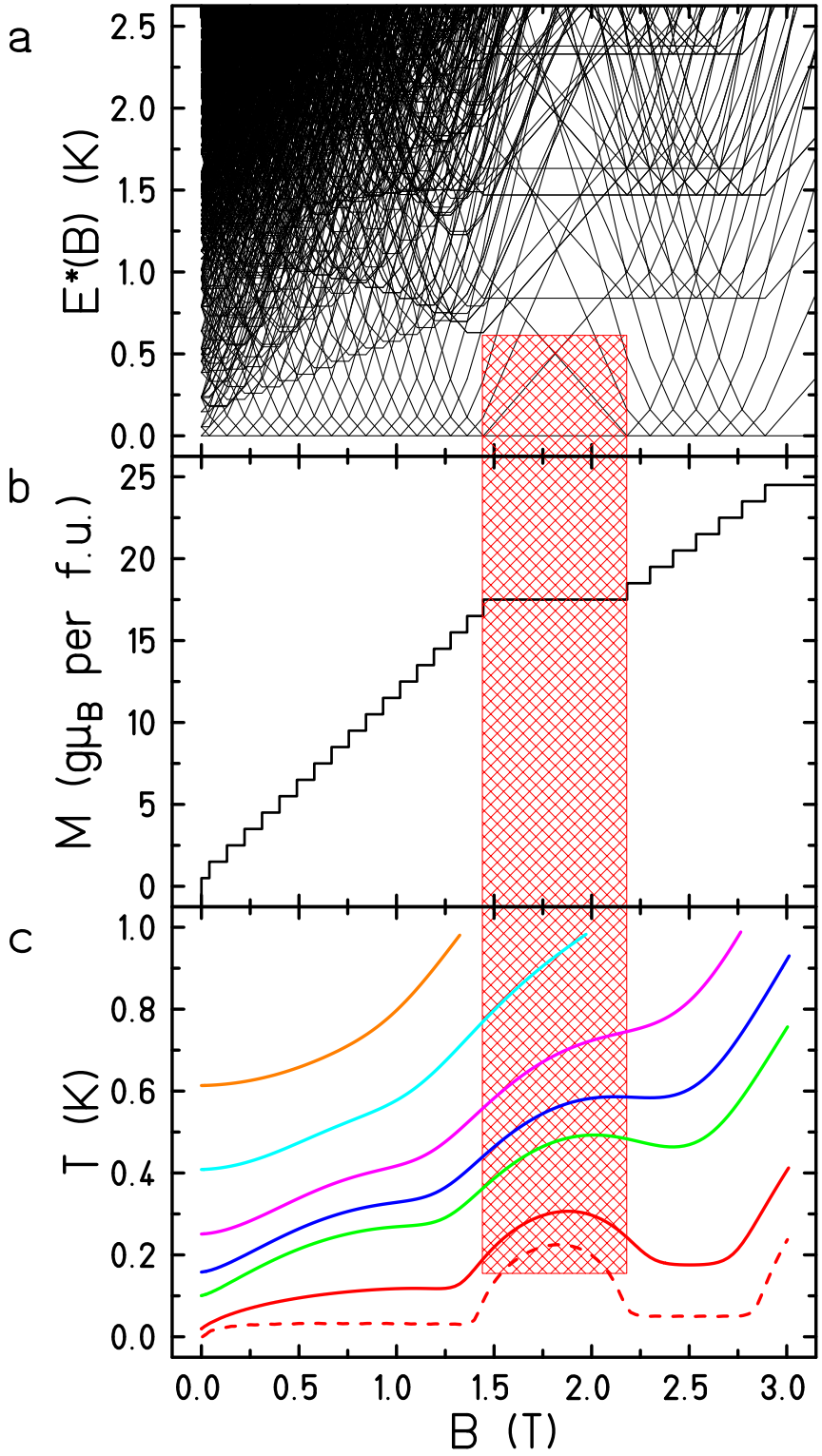
  $J_1 = -0.090(5)$ K, $J_2 = -0.080(5)$ K and $g = 2.02$.
- Very good agreement down to the lowest temperatures.

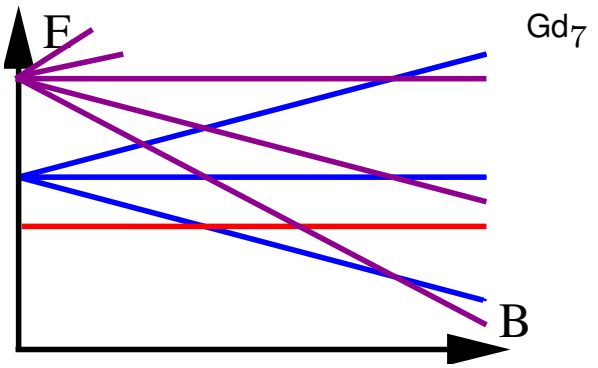
J. W. Sharples, D. Collison, E. J. L. McInnes, J. Schnack, E. Palacios, M. Evangelisti, Nat. Commun. **5**, 5321 (2014).

Gd$_7$ – experiment & theory



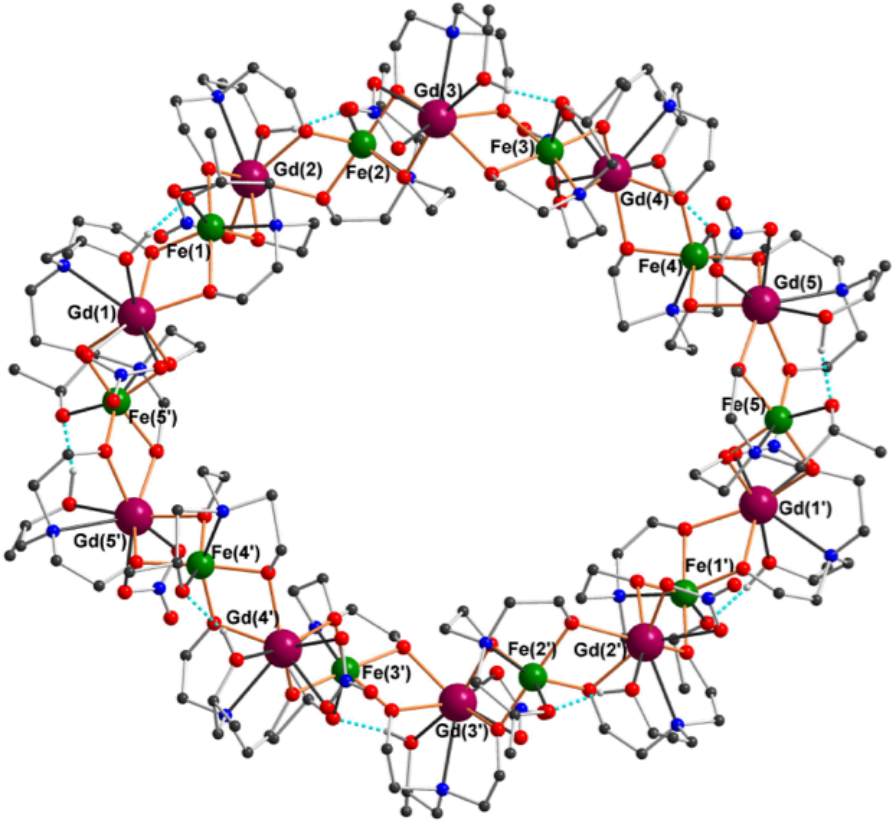
J. W. Sharples, D. Collison, E. J. L. McInnes, J. Schnack, E. Palacios, M. Evangelisti, Nat. Commun. **5**, 5321 (2014).

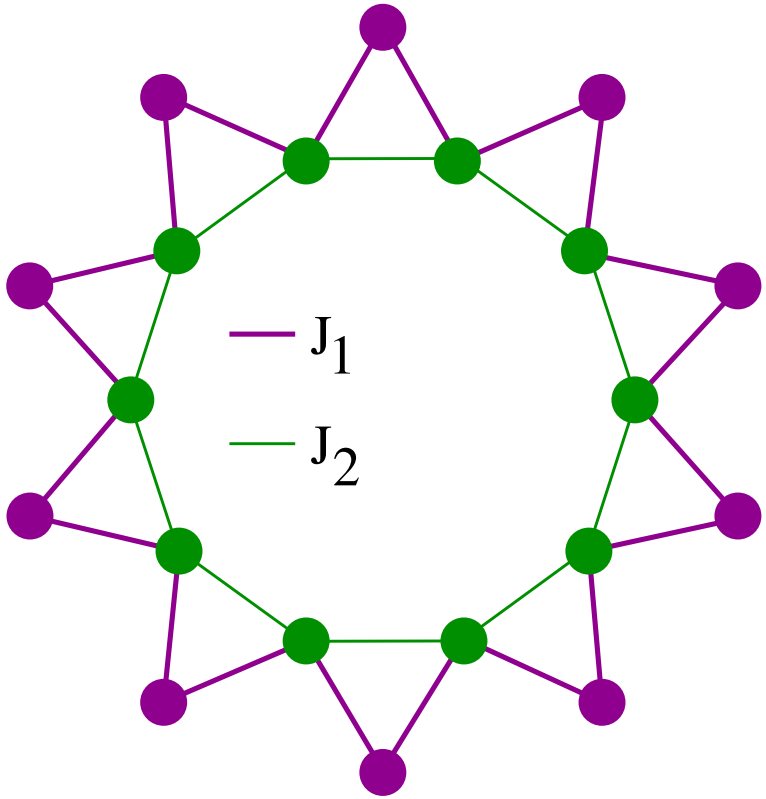

a
b
c
E*(B) (K)
M (gμB per f.u.)
T (K)
B (T)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
5
10
15
20
25
0.2
0.4
0.6
0.8


E
B
Gd7

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

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

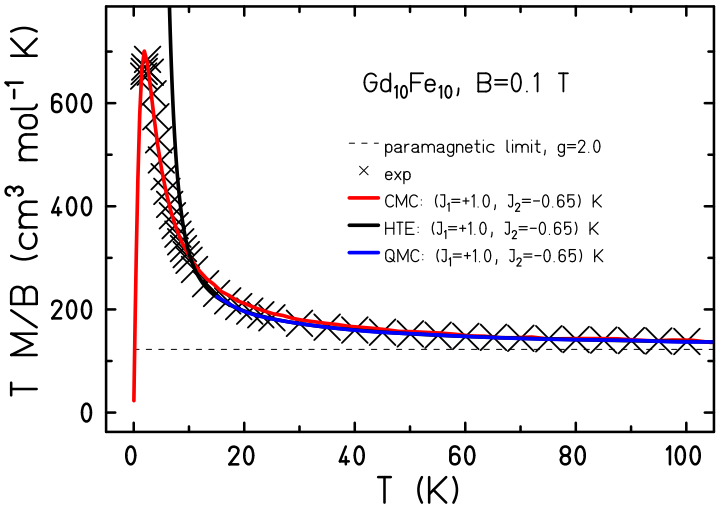


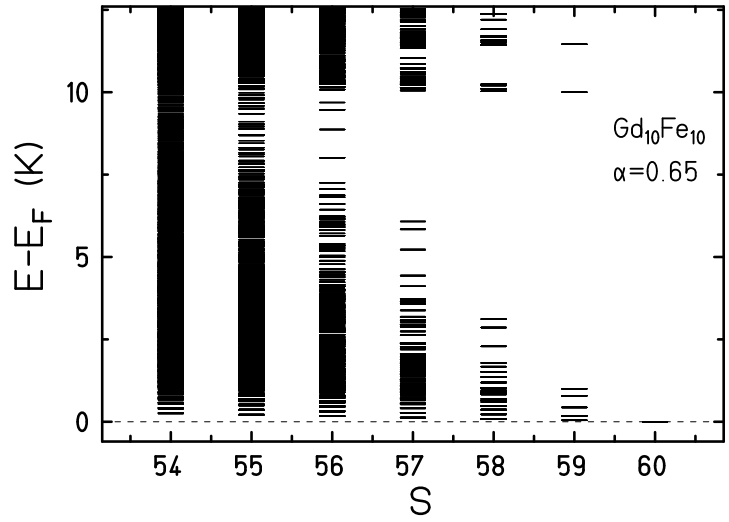


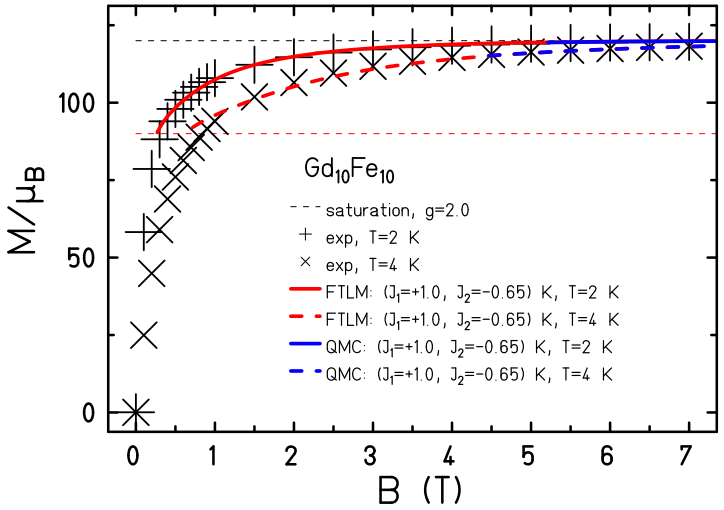
purple: Gd ($s = 7/2$), green: Fe ($s = 5/2$)

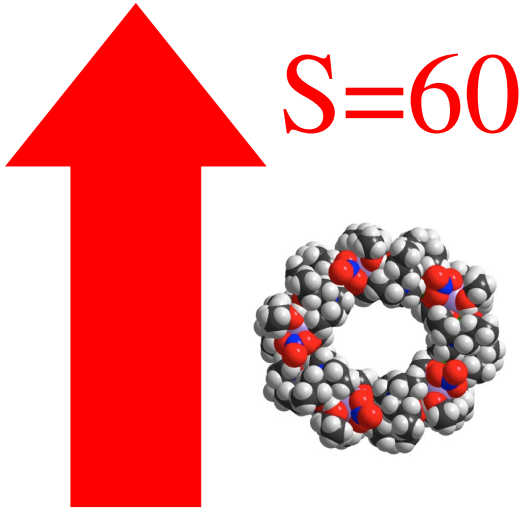
We will see: J_1 ferro, J_2 antiferro

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

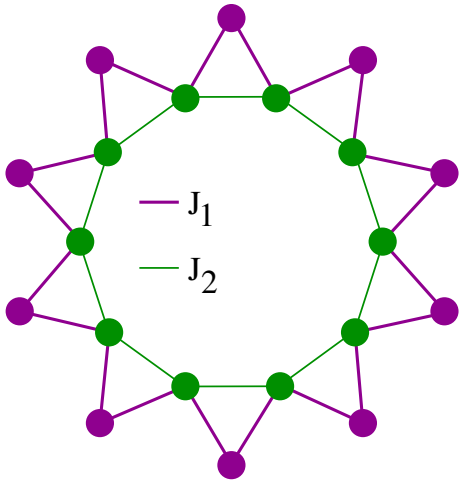


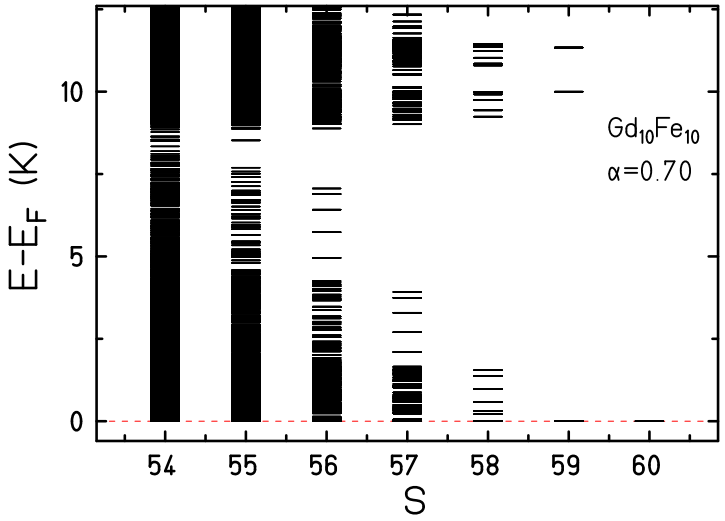


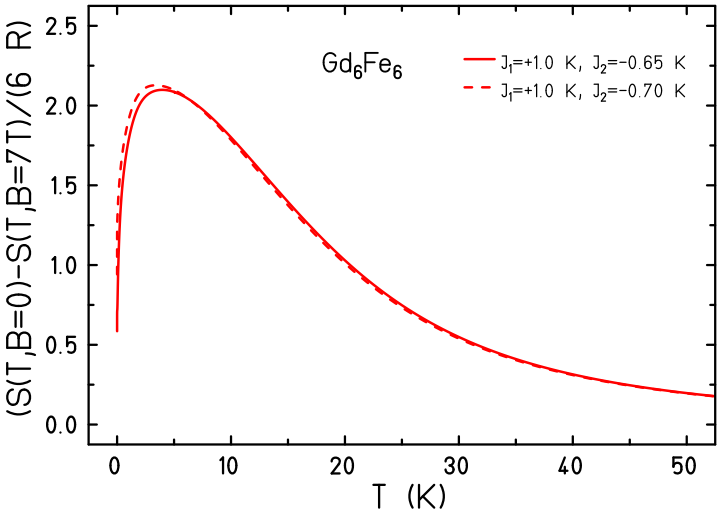


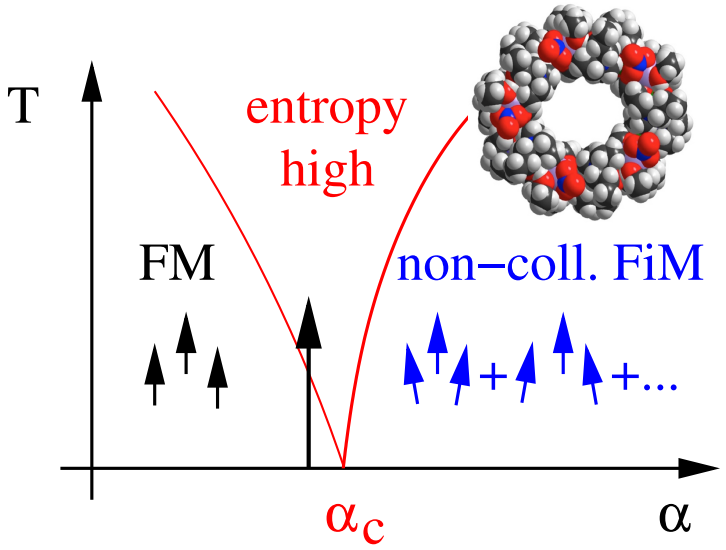


A. Baniodeh *et al., npj Quantum Materials* ***3****, 10 (2018)*









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)

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

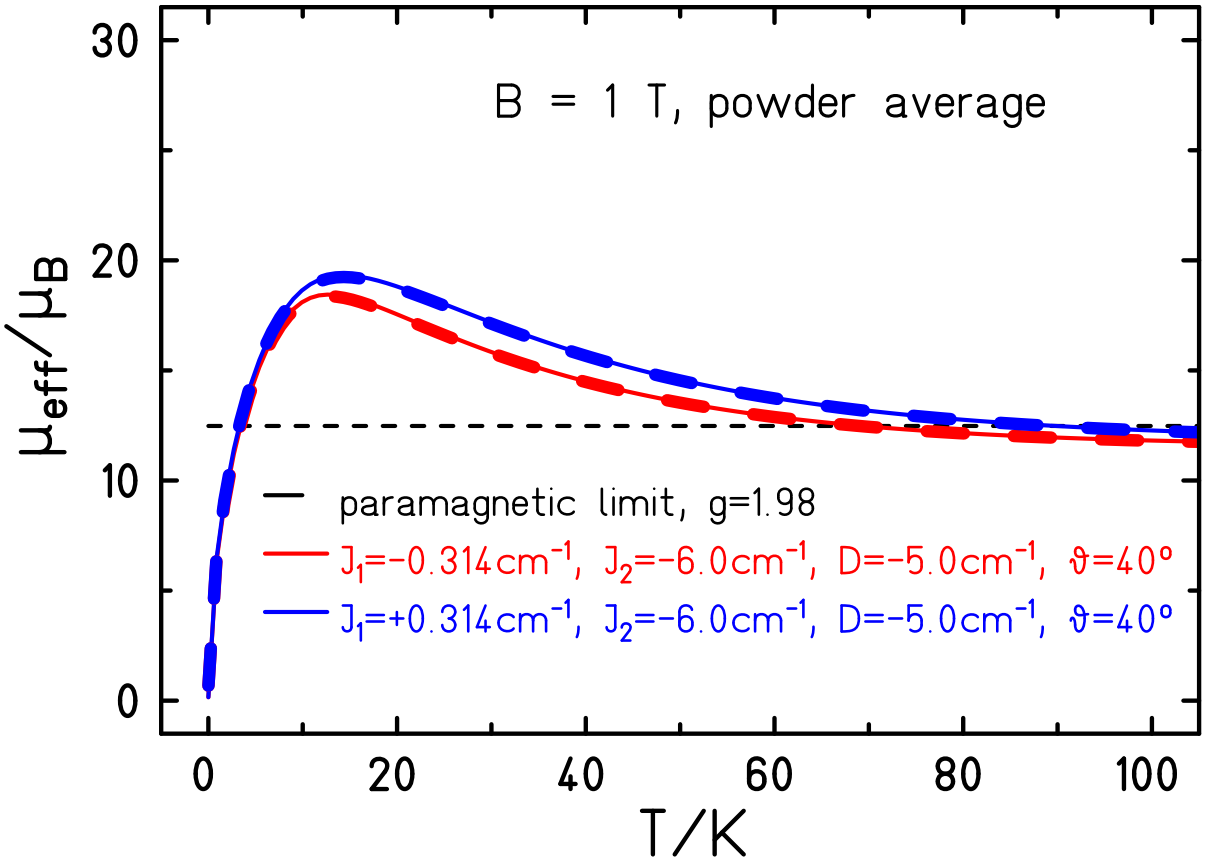
Use Lanczos energy eigenvector $|\,n(\nu)\,\rangle$ and time-reversed counterpart $|\,\tilde{n}(\nu)\,\rangle$

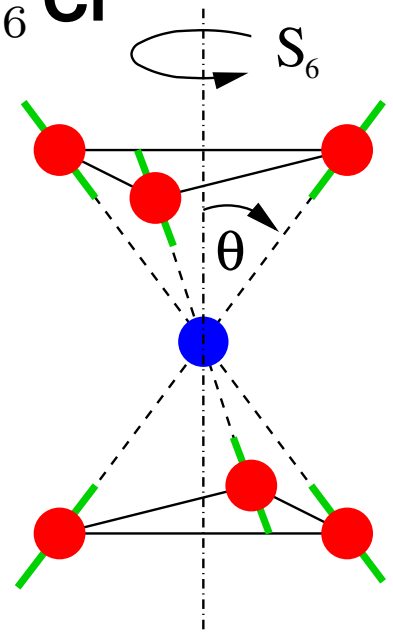
$$|\,n(\nu)\,\rangle = \sum_{\vec{m}} c_{\vec{m}}\,|\,\vec{m}\,\rangle \qquad , \qquad |\,\tilde{n}(\nu)\,\rangle = \sum_{\vec{m}} c^*_{\vec{m}}\,|\,-\vec{m}\,\rangle$$

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





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

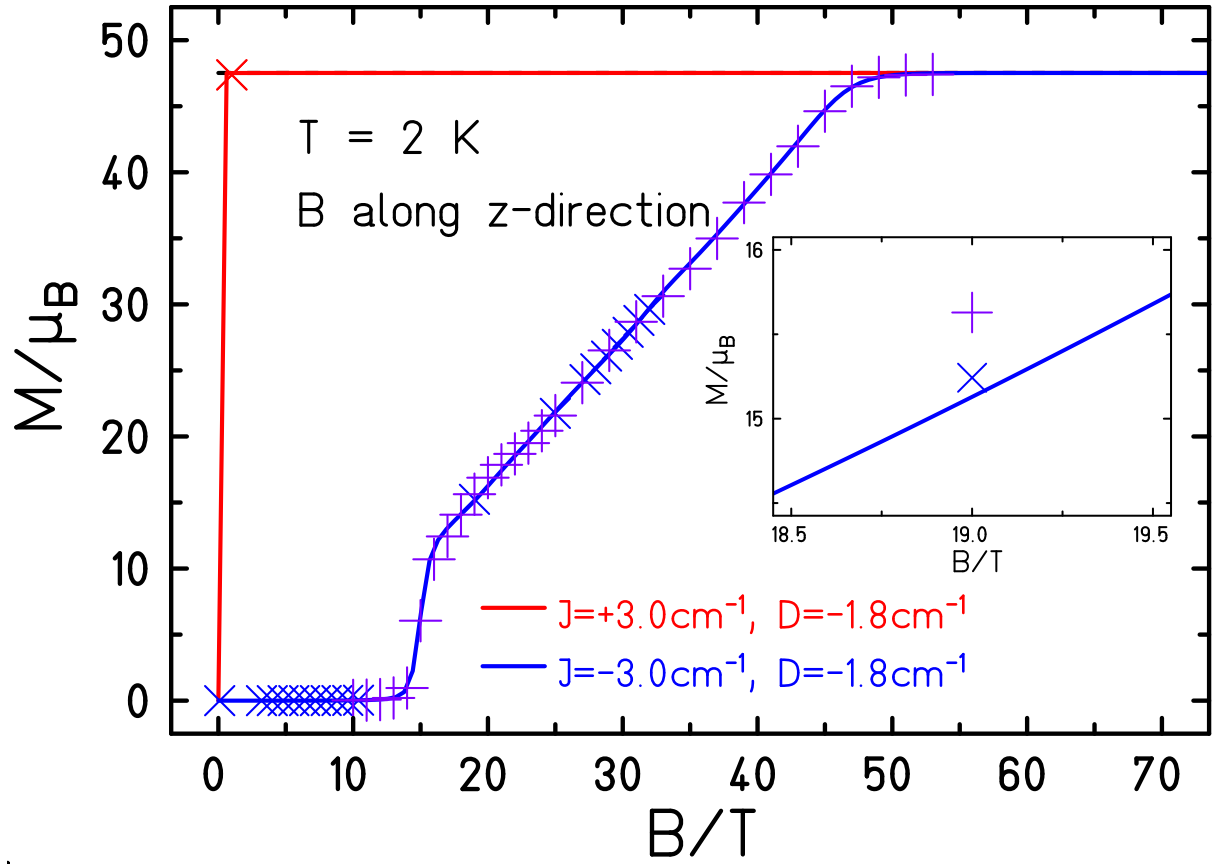
$\dim(\mathcal{H}) = 62,500$

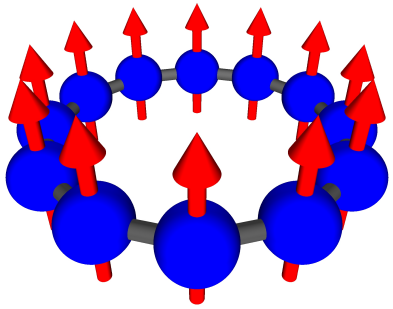
non-collinear easy axes

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





$s = 2$

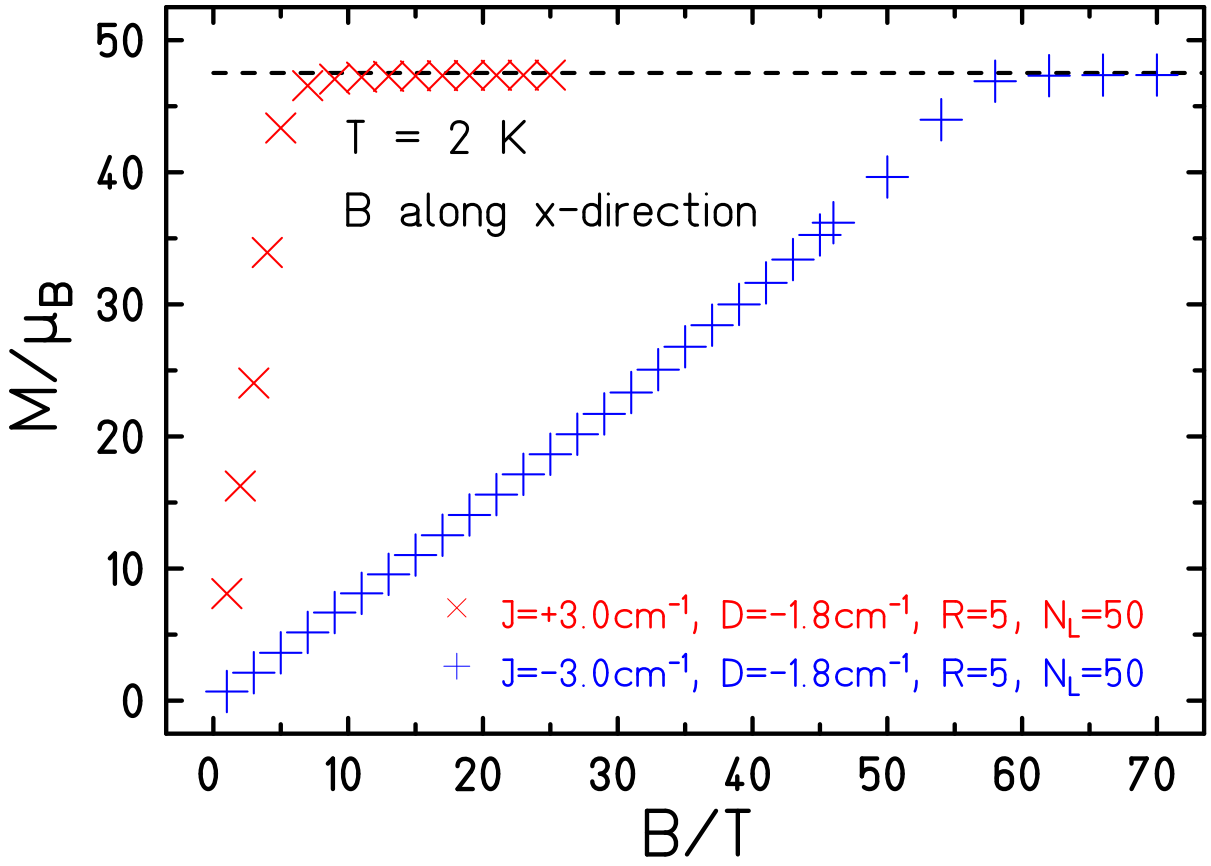
$\dim(\mathcal{H}) = 244,140,625$

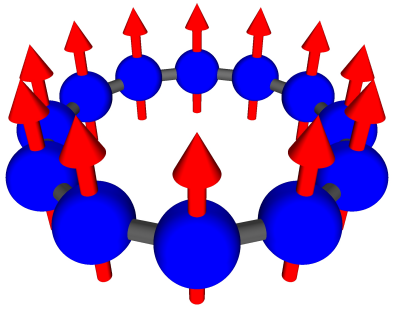
collinear easy axes

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

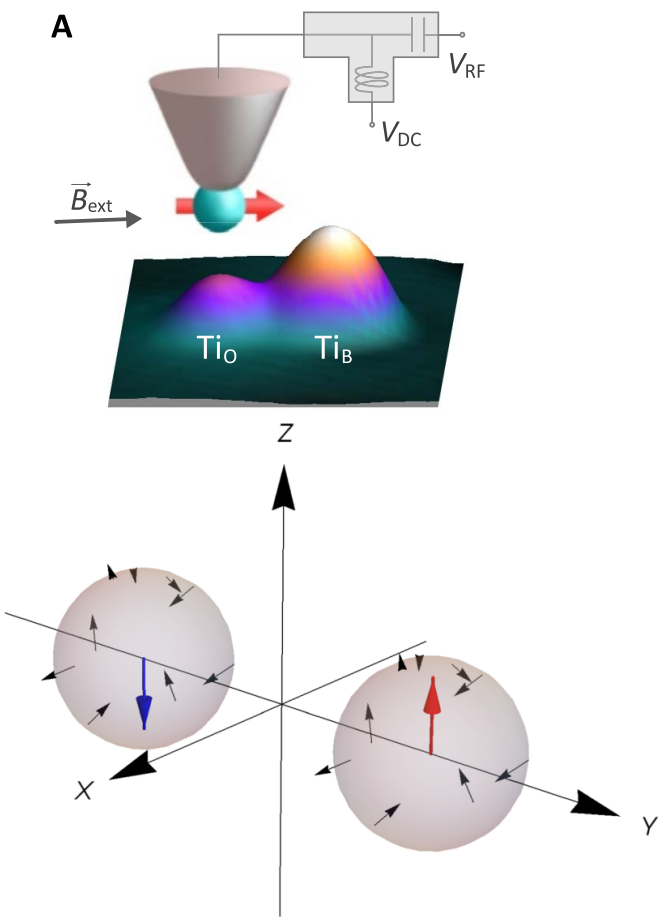


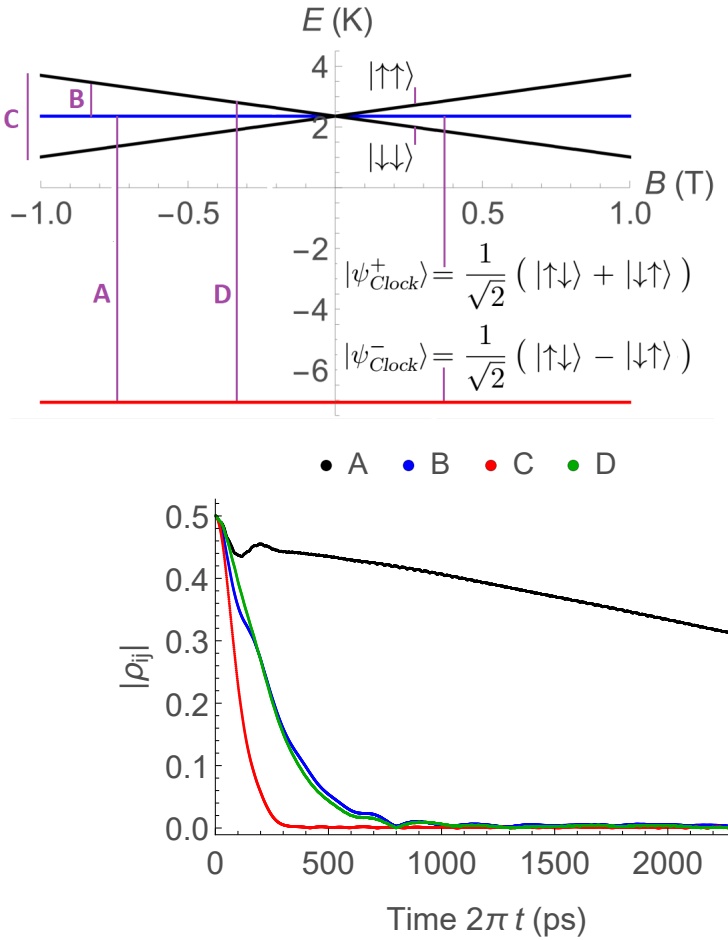


No other method can deliver these curves!

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

Decoherence of a clock transition



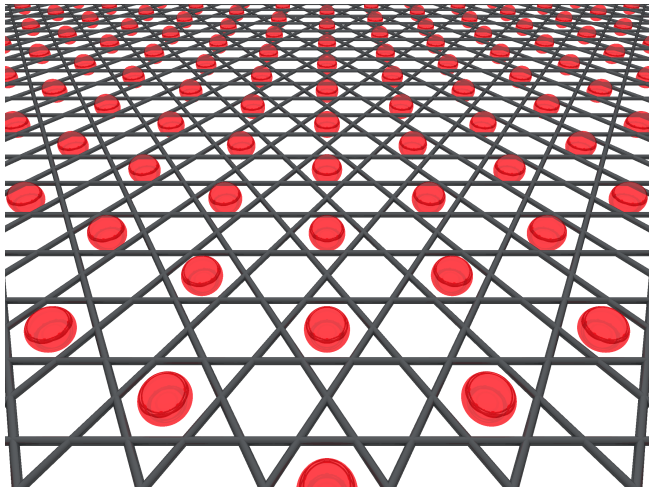


P. Vorndamme, J. Schnack, Phys. Rev. B 101, 075101 (2020)

The kagome lattice antiferromagnet

Is 42 the final answer?

Kagome lattice antiferromagnet – scientific problems

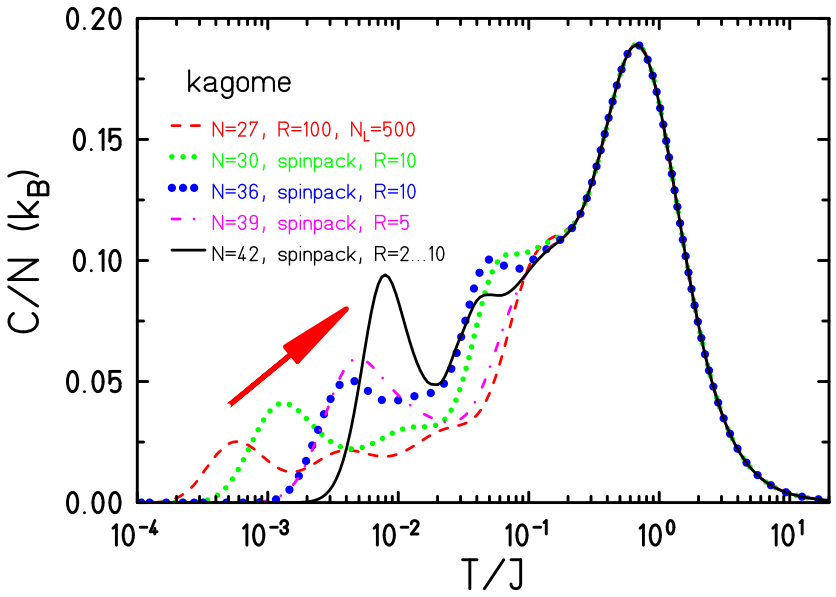


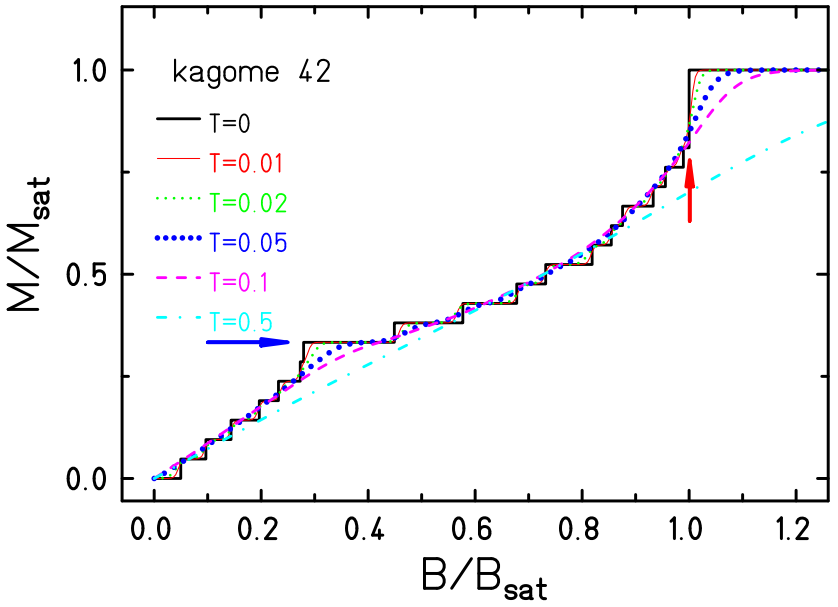
- Thermodynamic functions, in particular heat capacity and susceptibility (1)
- "Condensation" of low-lying singlets below the first triplet?
- Magnetization jump to saturation
- Thermal stability of magnetization plateaus, e.g. at $\mathcal{M}_{\text{sat}}/3$.
- Notoriously enigmatic (2)!

(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

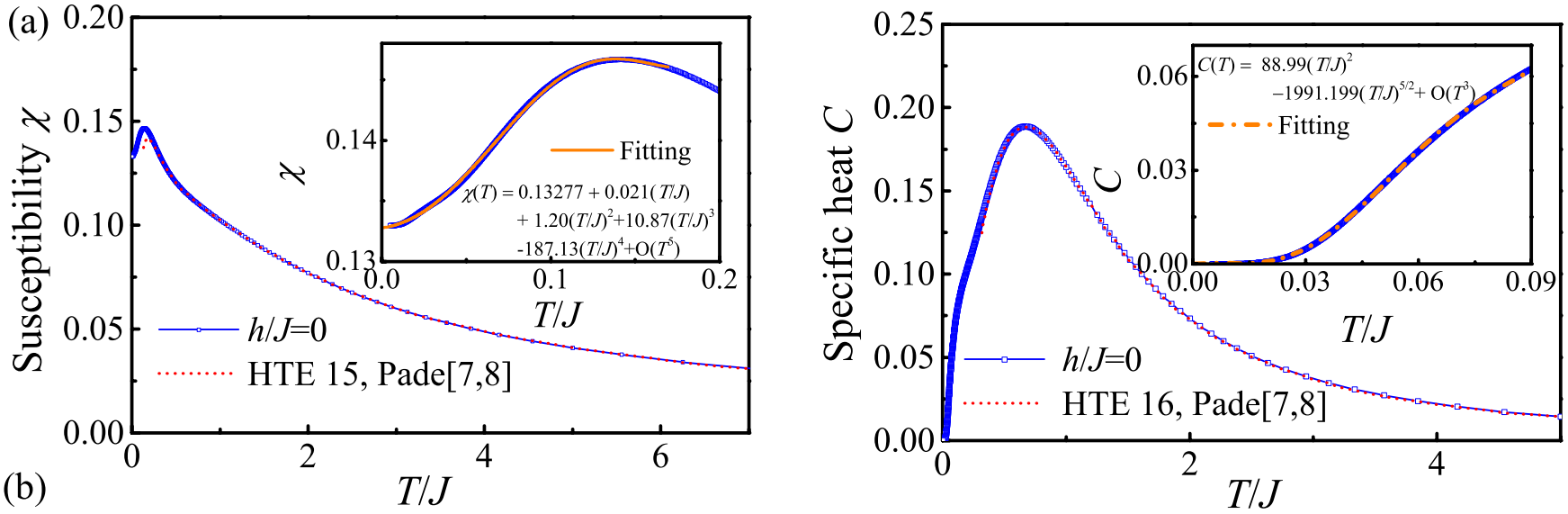




- Low-T peak moves to higher T with increasing N.
- Density of low-lying singlets seems to move to higher excitation energies!

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

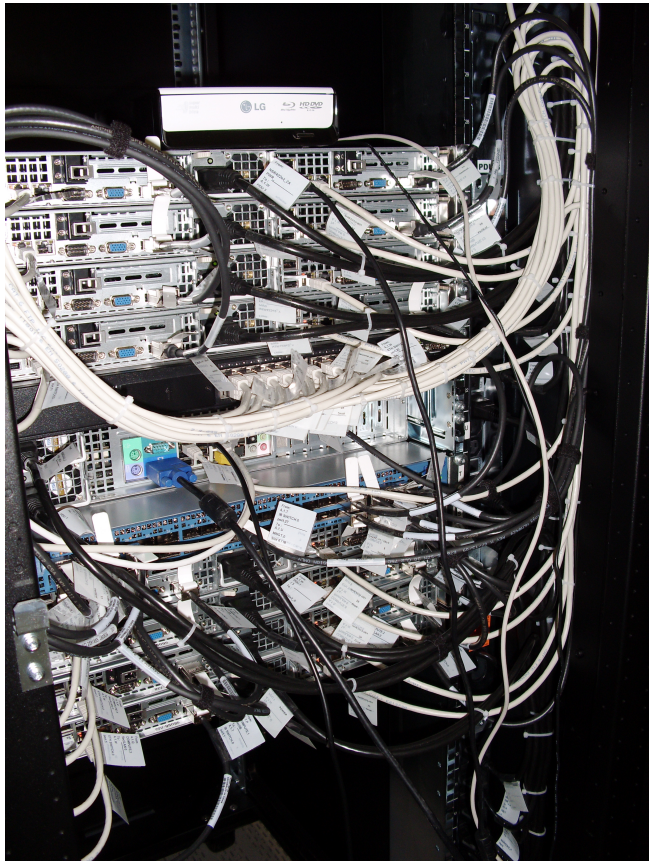
Kagome – tensor network calculations



- 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.

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Thank you very much for your attention.

The end.

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