Magnetic molecules – a great playground for quantum magnetism

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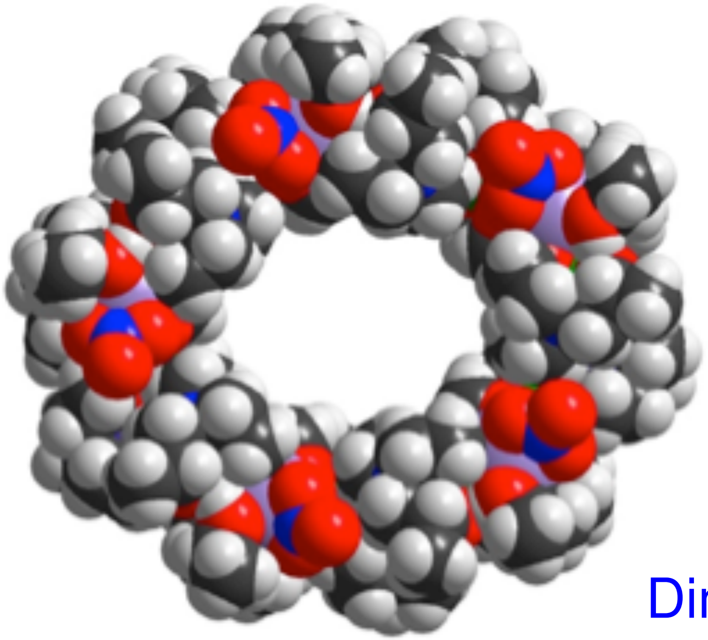
Colloquium Theoretical Physics

Darmstadt, Germany, 3 February 2026

Beauty of Magnetic Molecules

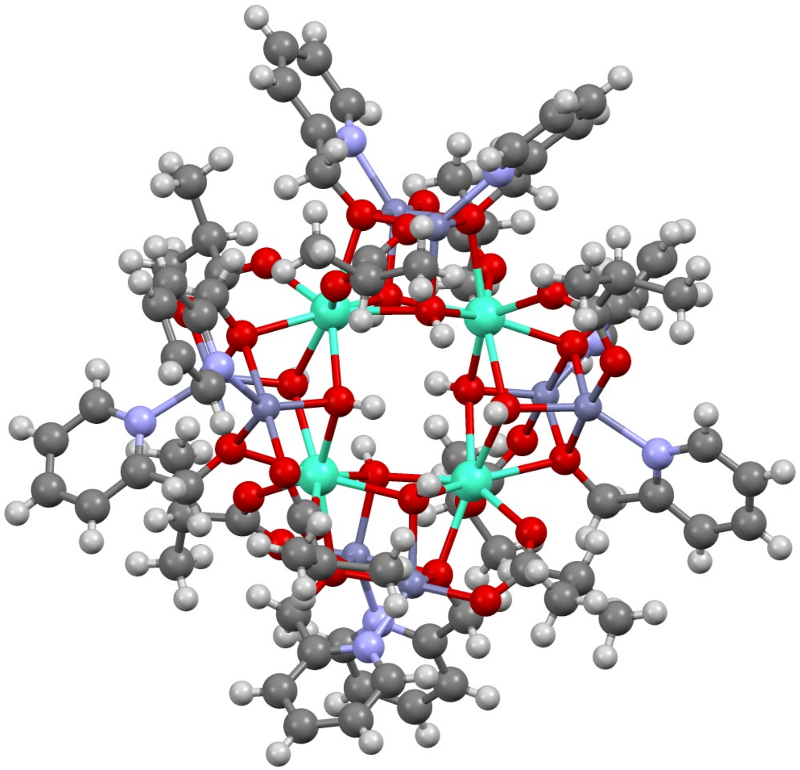
$Fe_{10}Gd_{10}$ with $S = 60$ and close to a quantum phase transition!



Dimension of Hilbert space 64,925,062,108,545,024!

npj Quantum Materials **3**, 10 (2018)

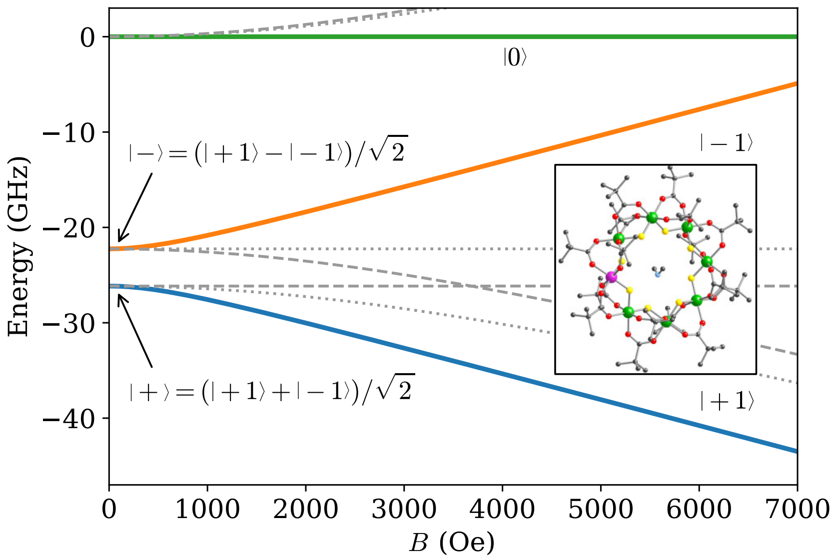
You want molecular magnetocalorics!



Cool!

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

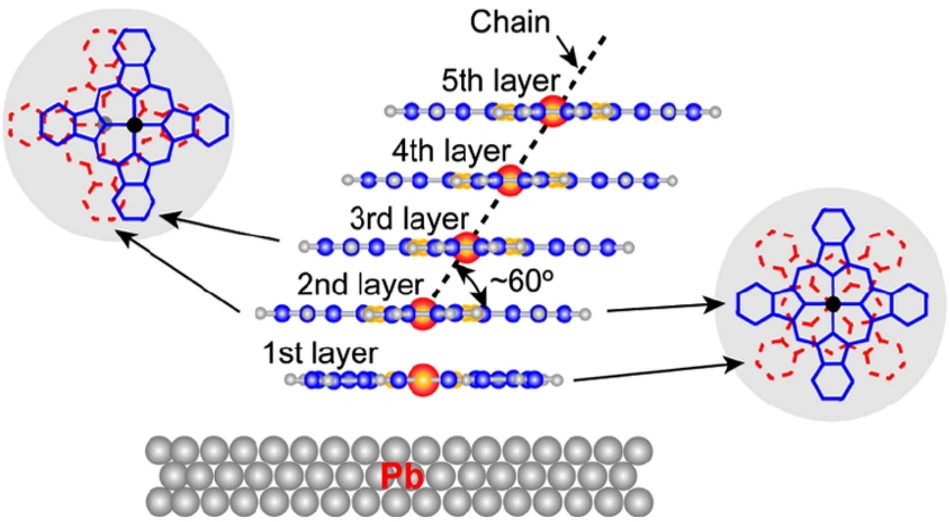
You want to achieve quantum coherence!



Desperately needed!

Friedman group: Phys. Rev. Research **2**, 032037(R) (2020)

You want to deposit your molecule!



Next generation magnetic storage!

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

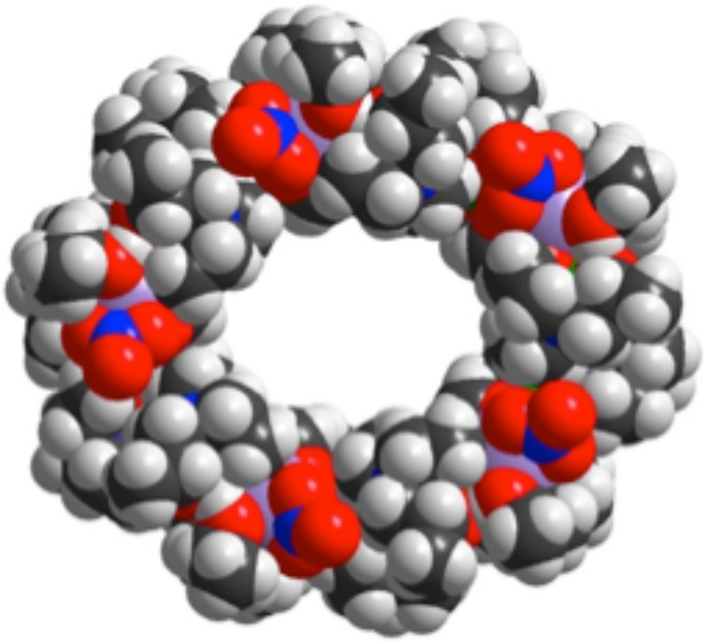
Yes, we can!

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

1. Quantum magnetism
2. Molecular magnetocalorics
3. Bistability, tunneling, and stability
4. Toroidal magnetic molecules
5. FTLM for very anisotropic spin systems

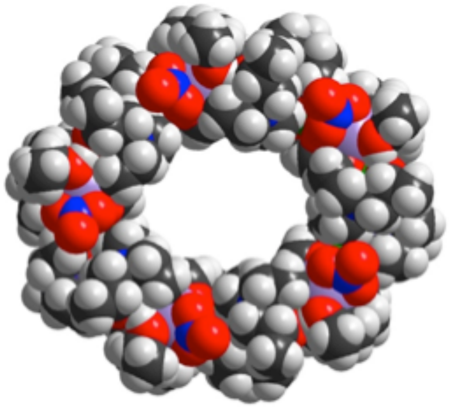
We are the sledgehammer team of matrix diagonalization.
Please send inquiries to jschnack@uni-bielefeld.de!

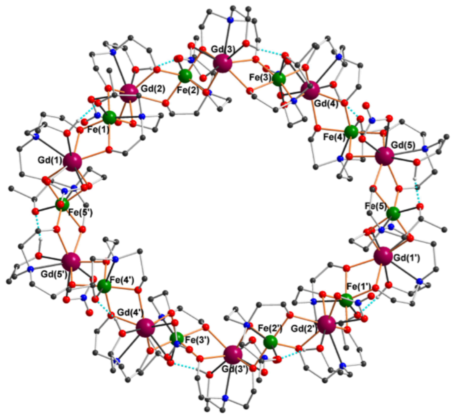
Quantum Magnetism

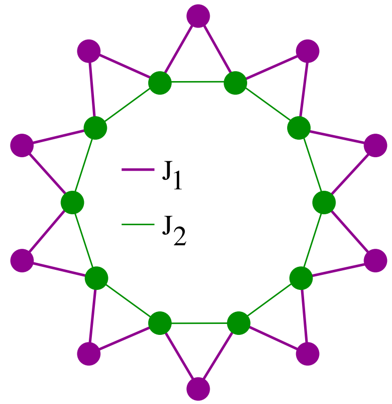


$Gd_{10}Fe_{10}$ – one example for quantum magnetism

Reduction + modelling.







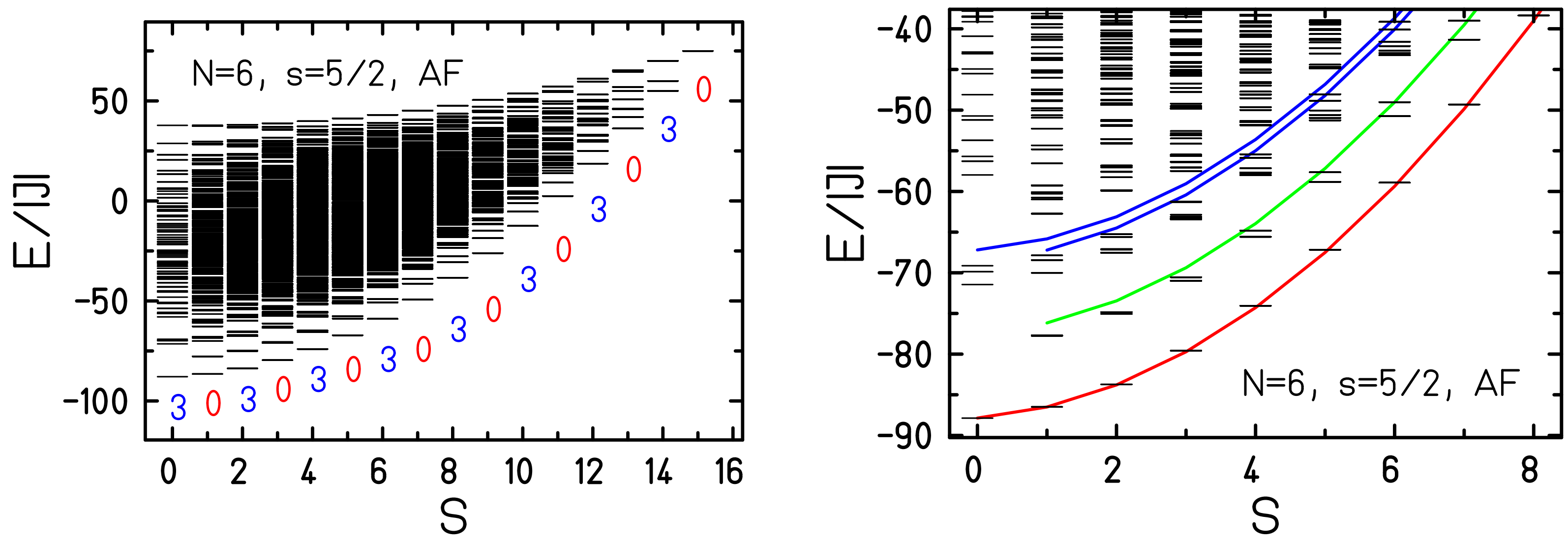
green: Fe ($s = 5/2$), purple: Gd ($s = 7/2$)

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

The effective model also depends on what you measure!

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

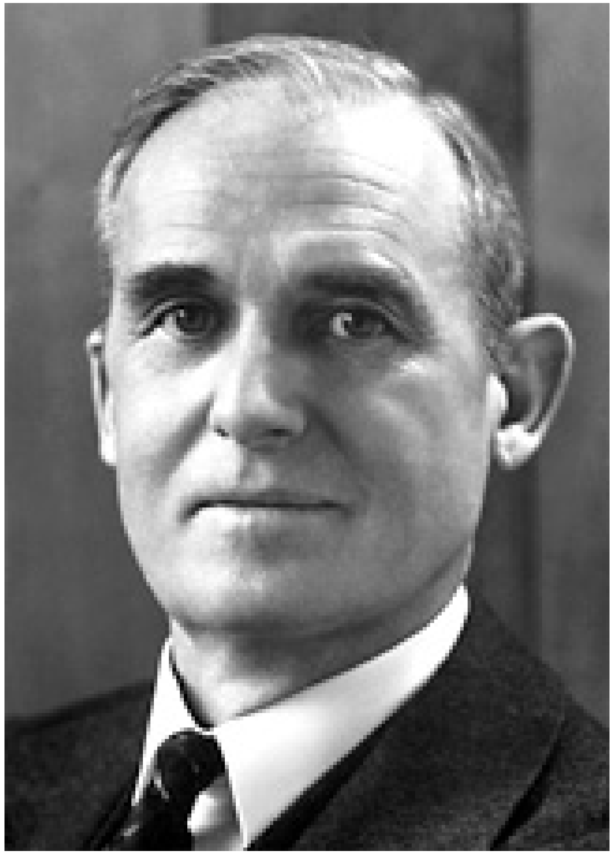
Example: Heisenberg model for spin rings



1. finite-dimensional Hilbert space, product basis;
2. Hamiltonian matrix, symmetries, e.g., $SU(2)$ and point groups;
3. exact diagonalization, canonical ensemble, equilibrium thermodynamics;
4. time-dependent problems.

The magnetocaloric effect

Sub-Kelvin cooling: Nobel prize 1949



The Nobel Prize in Chemistry 1949 was awarded to William F. Giauque *for his contributions in the field of chemical thermodynamics, particularly concerning the behaviour of substances at extremely low temperatures*.

Sub-Kelvin cooling: Nobel prize 1949

768 LETTERS TO THE EDITOR

Attainment of Temperatures Below 1° Absolute by Demagnetization of $Gd_2(SO_4)_3 \cdot 8H_2O$

We have recently carried out some preliminary experiments on the adiabatic demagnetization of $Gd_2(SO_4)_3 \cdot 8H_2O$ at the temperatures of liquid helium. As previously predicted by one of us, a large fractional lowering of the absolute temperature was obtained.

An iron-free solenoid producing a field of about 8000 gauss was used for all the measurements. The amount of $Gd_2(SO_4)_3 \cdot 8H_2O$ was 61 g. The observations were checked by many repetitions of the cooling. The temperatures were measured by means of the inductance of a coil surrounding the gadolinium sulfate. The coil was immersed in liquid helium and isolated from the gadolinium by means of an evacuated space. The thermometer was in excellent agreement with the temperature of liquid helium as indicated by its vapor pressure down to 1.5°K.

On March 19, starting at a temperature of about 3.4°K, the material cooled to 0.53°K. On April 8, starting at about 2°, a temperature of 0.34°K was reached. On April 9, starting at about 1.5°, a temperature of 0.25°K was attained.

It is apparent that it will be possible to obtain much lower temperatures, especially when successive demagnetizations are utilized.

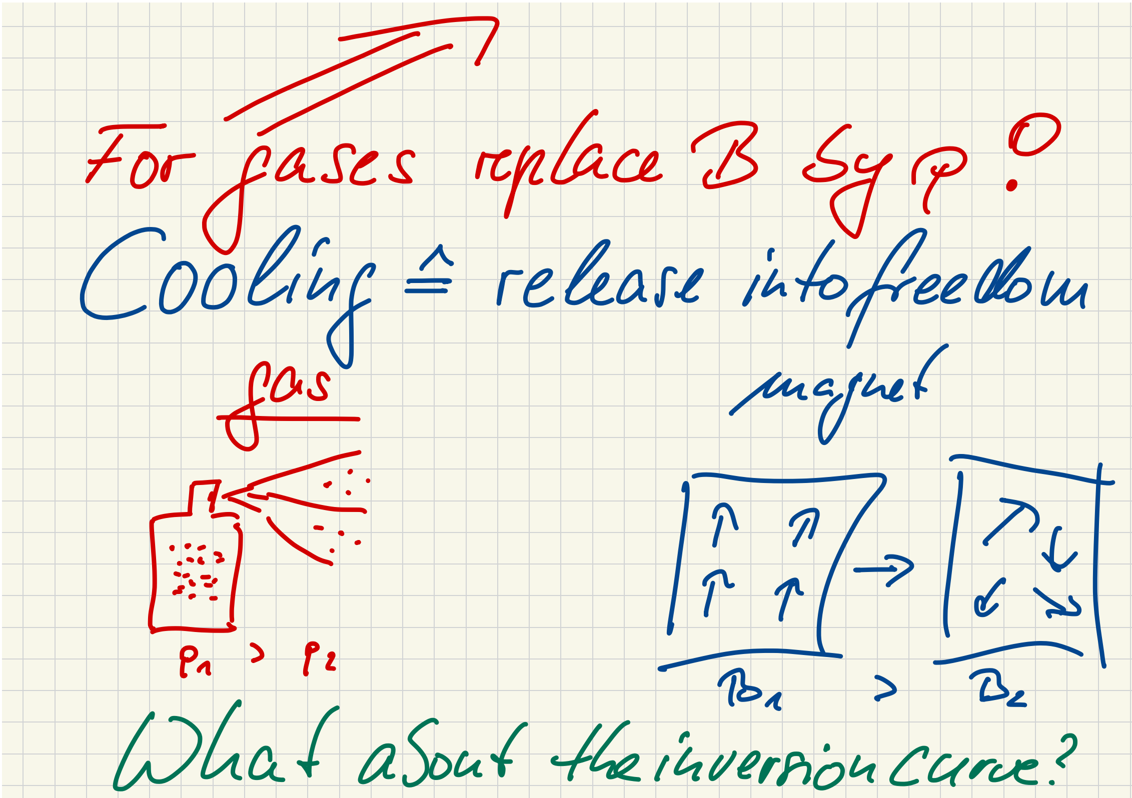
W. F. Giauque
D. P. MacDougall

Department of Chemistry,
University of California,
Berkeley, California,
April 12, 1933.

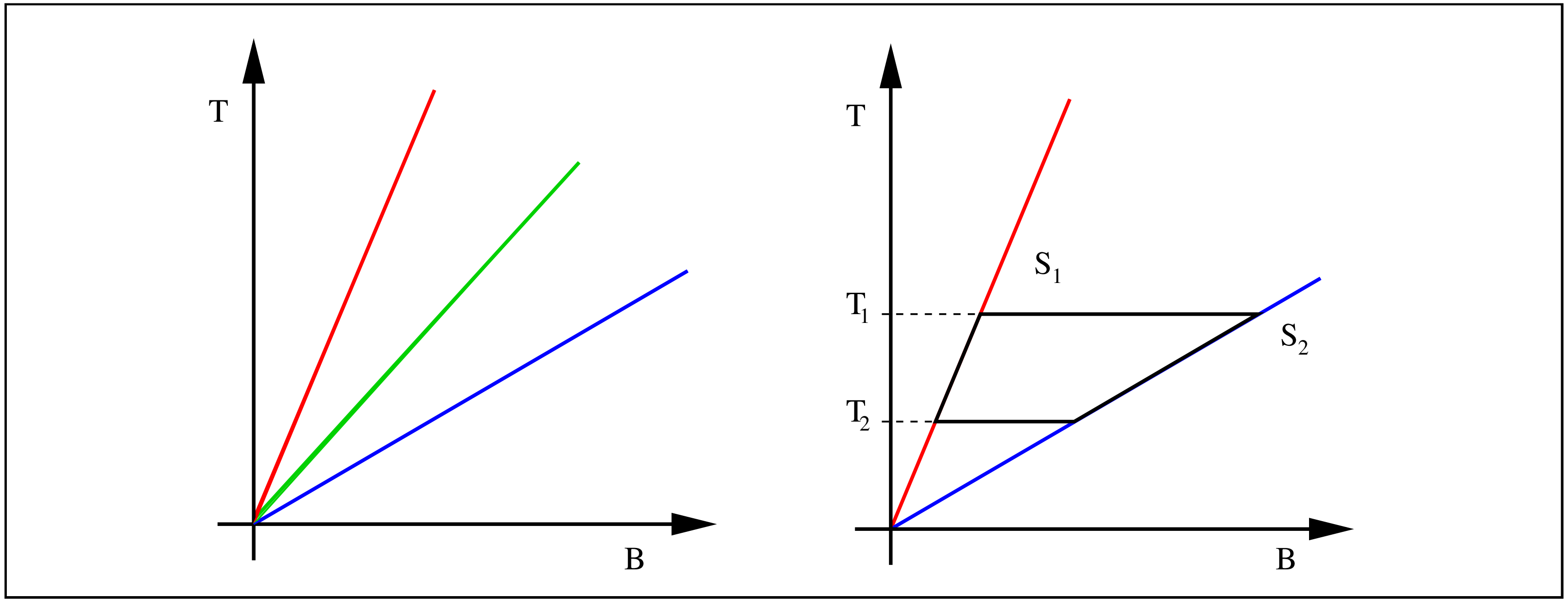
W. F. Giauque and D. MacDougall, Phys. Rev. **43**, 768 (1933).

Magnetocaloric effect – cooling rate (⇒ Wu)

$$\left(\frac{\partial T}{\partial B}\right)_S = -\frac{T}{C}\left(\frac{\partial S}{\partial B}\right)_T$$



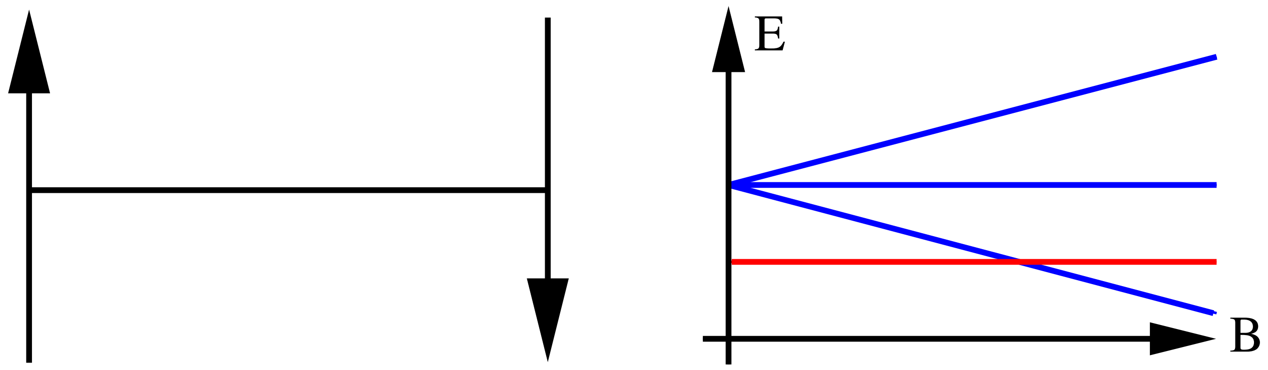
Magnetocaloric effect – Paramagnets



- Ideal paramagnet: $S(T,B) = f(B/T)$, i.e. $S = const \Rightarrow T \propto B$.

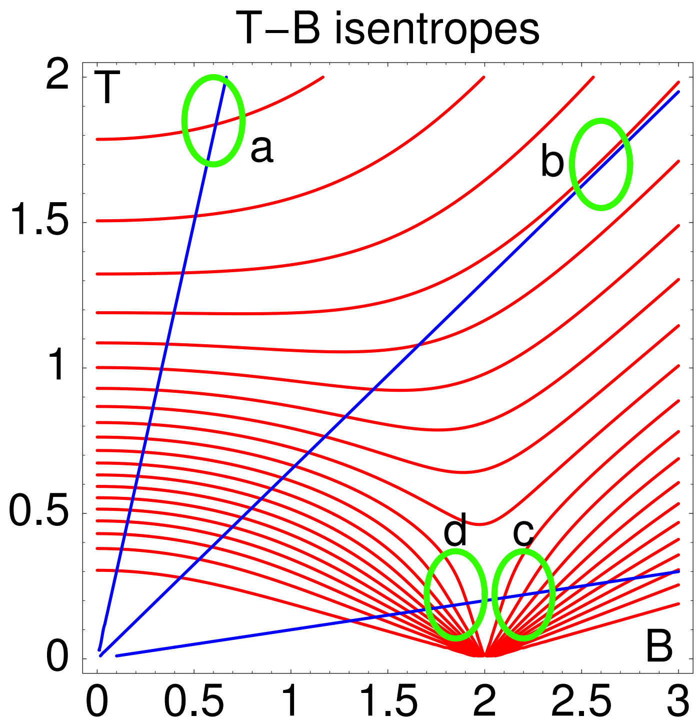
- At low T pronounced effects of dipolar interaction prevent further effective cooling.

Magnetocaloric effect – af $s = 1/2$ dimer



- Singlet-triplet level crossing causes a peak of S at $T \approx 0$ as function of B.
- $M(T = 0, B)$ and $S(T = 0, B)$ not analytic as function of B.
- $M(T = 0, B)$ jumps at B_c; $\quad S(T = 0, B_c) = k_B \ln 2$, otherwise zero.

Magnetocaloric effect – af $s = 1/2$ dimer



blue lines: ideal paramagnet, red curves: af dimer

Magnetocaloric effect:

(a) reduced,

(b) the same,

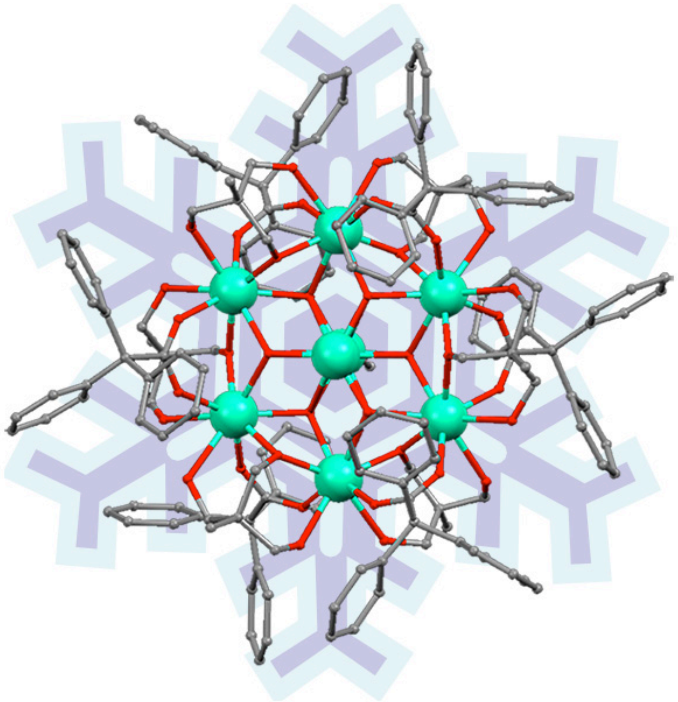
(c) enhanced,

(d) opposite

when compared to an ideal paramagnet.

Case (d) does not occur for a paramagnet.

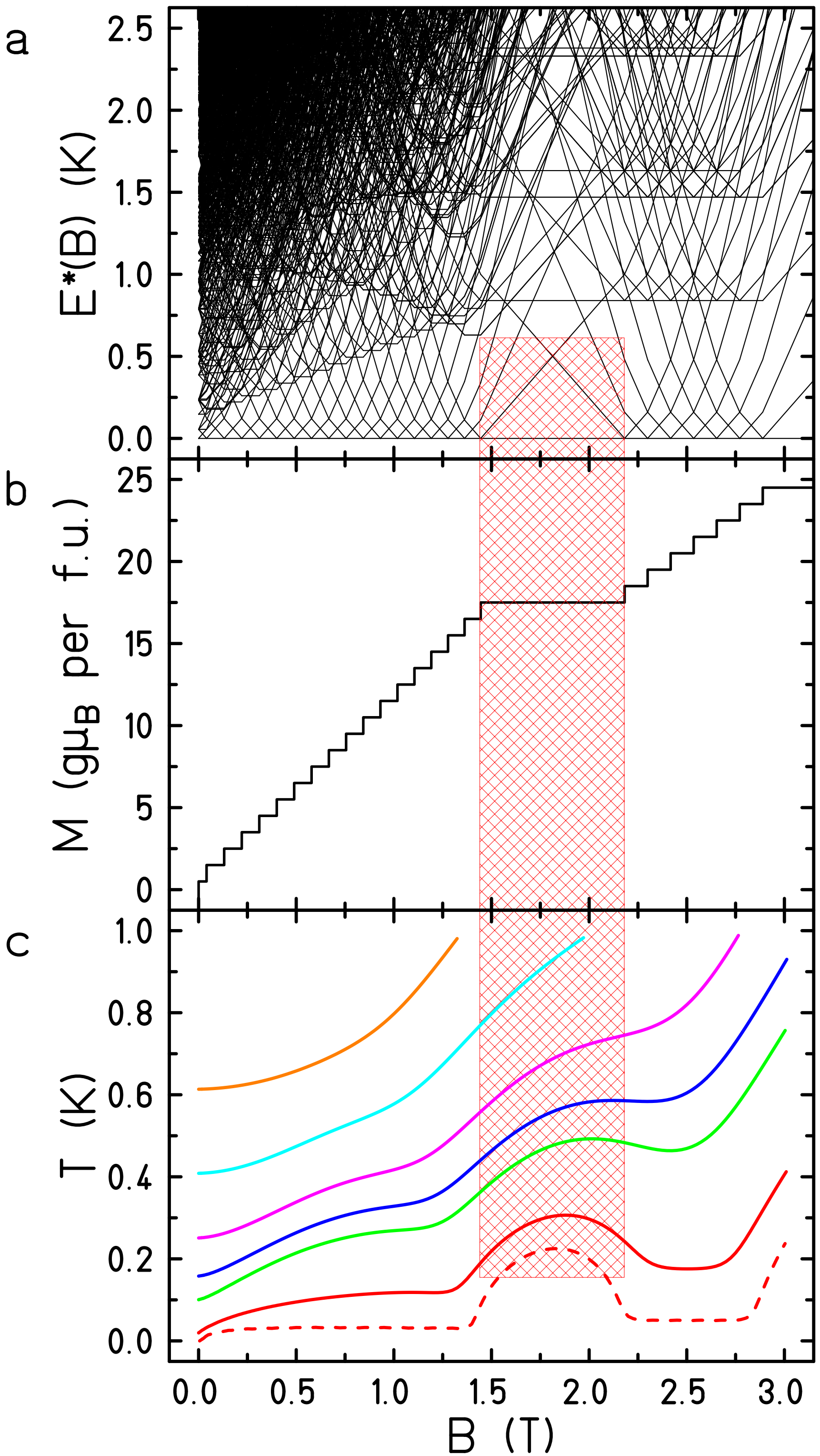
Gd$_7$ – Basics

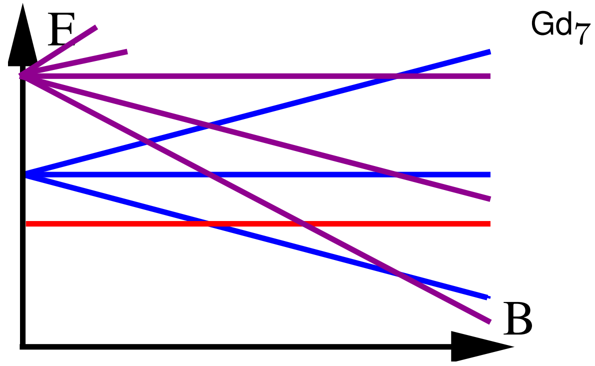


- Often magnetocaloric observables not directly measured, but inferred from Maxwell's relations.
- First real cooling experiment with a molecule.
- $\underset{\sim}{H} = -2\sum_{i<j} J_{ij}\, \vec{\underset{\sim}{s}}_i \cdot \vec{\underset{\sim}{s}}_j + g\,\mu_B\, B \sum_i^N \underset{\sim}{s}_i^z$

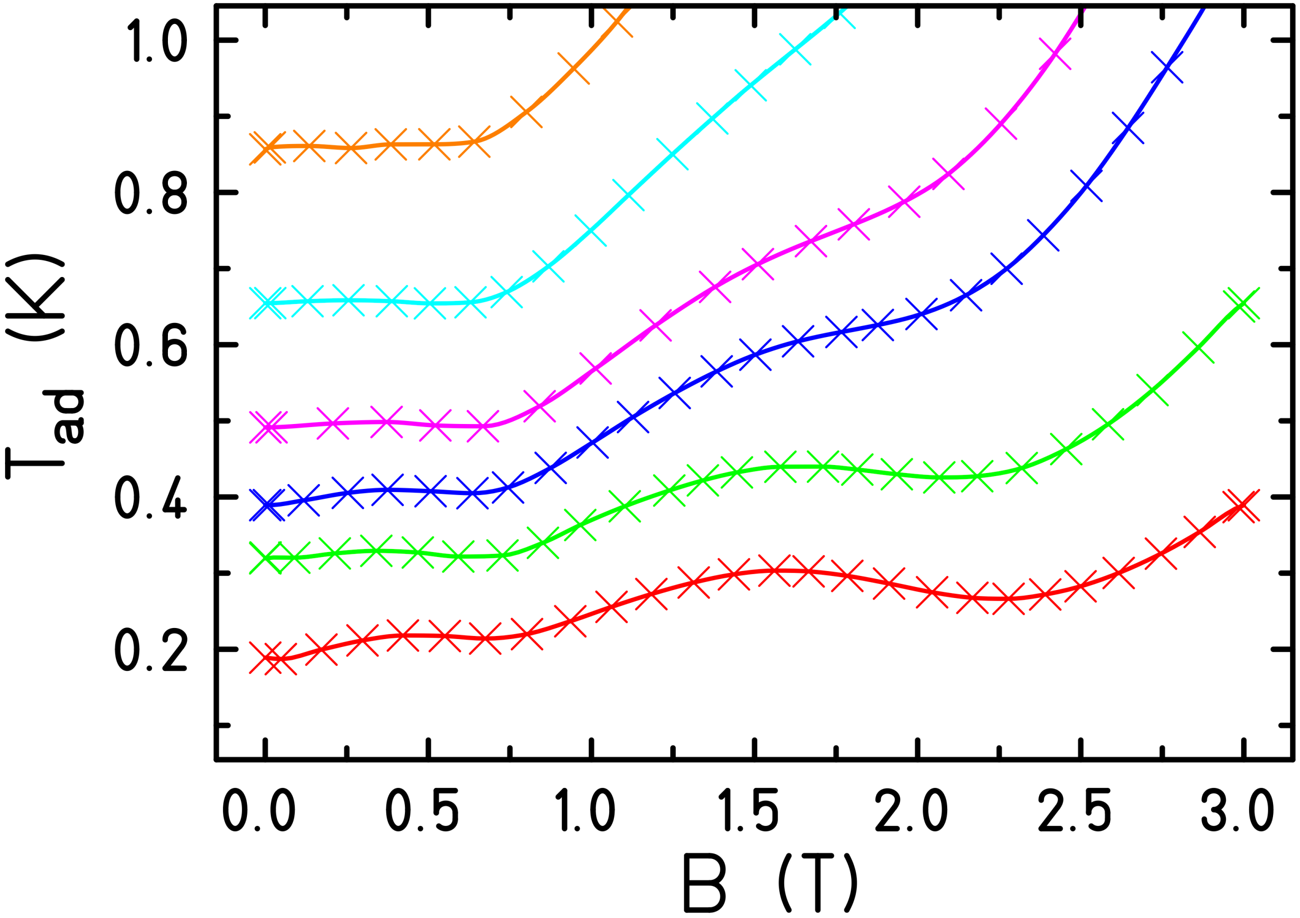
  $J_1 = -0.090(5)$ K, $J_2 = -0.080(5)$ K and $g = 2.02$.
- Very good agreement down to the lowest temperatures.

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


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

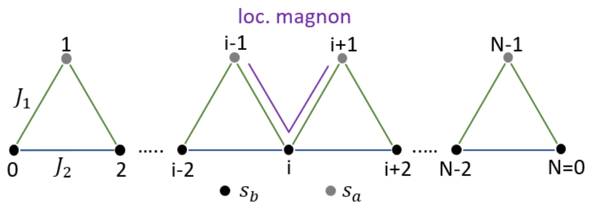

E
B
Gd7

Gd$_7$ – Experimental cooling

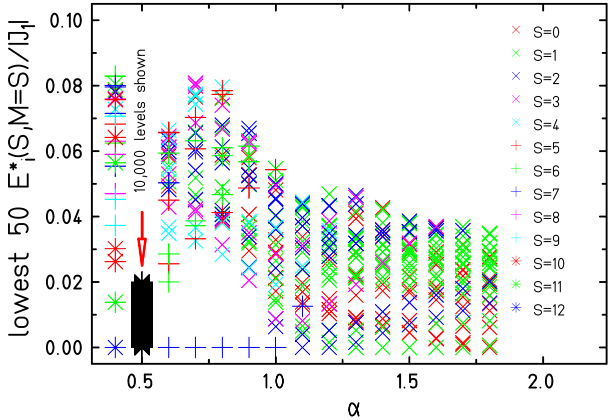


J. W. Sharples, D. Collison, E. J. L. McInnes, J. Schnack, E. Palacios, M. Evangelisti, Nat. Commun. **5**, 5321 (2014).

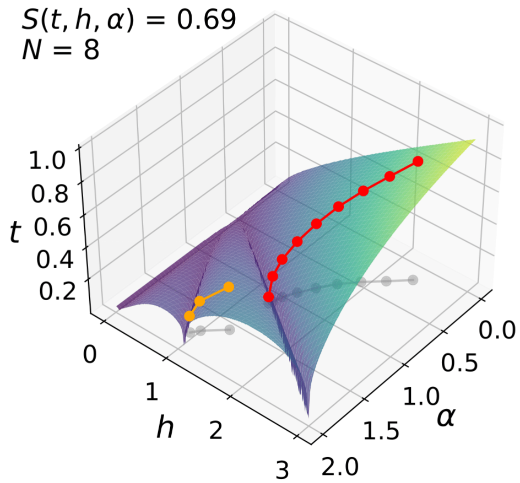
Frustration, quantum phase transition, and barocalorics



frustrated structure



quantum phase transition



magneto- and barocaloric

$\alpha = |J_2/J_1|$ $t = k_B T/|J_1|, h = g\mu_B B/|J_1|$

Magneto- and barocalorics allow to heat and cool via changes of magnetic field and pressure: Entropy $S = S(T, \vec{B}, \alpha)$

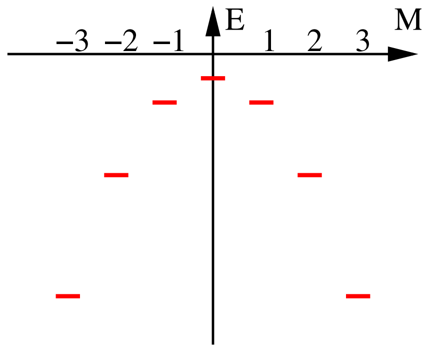
N. Reichert, H. Schlüter, T. Heitmann, J. Richter, R. Rausch, and J. Schnack, Z. Naturforsch. A **79**, 283 (2024).

Bistability, tunneling, and stability against field fluctuations

Single-molecule magnets – SMM

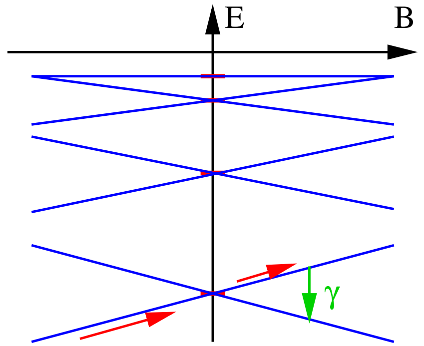
Single-molecule toroidics – SMT

Single-ion anisotropy and bistability I – good SMM



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

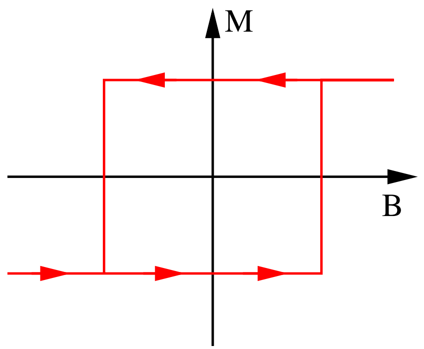
$D_i < 0$ collinear easy axes



eigenvectors: $|\, M, \alpha\,\rangle$

low-lying eigenvalues: $E_M = DM^2 + g\mu_B BM$

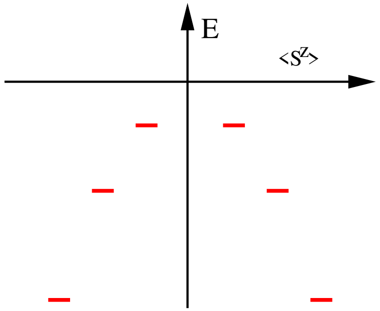
(strong exchange limit)



IMPORTANT: $[\underset{\sim}{H}, \underset{\sim}{S}^z] = 0$ since all D tensors aligned!!!

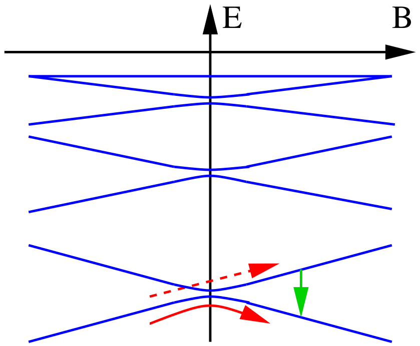
$\Rightarrow$ level crossings at $B = 0$
$\Rightarrow$ good hysteresis

Single-ion anisotropy and bistability II – bad/no SMM



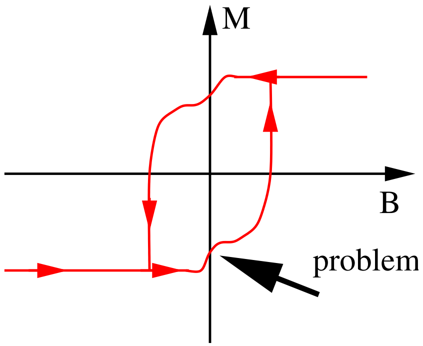
$$\underset{\sim}{H} = \sum_i \vec{\underset{\sim}{s}}_i \cdot \mathbf{D}_i \cdot \vec{\underset{\sim}{s}}_i + \mu_B B \sum_i g_i \underset{\sim}{s}_i^z + \underset{\sim}{H}_{\text{ferro int}}$$

$\mathbf{D}_i$ individual non-collinear anisotropy tensors



NO LONGER eigenvectors: $|\, M, \alpha \,\rangle$

low-lying eigenvalues only approx. parabola (if at all)

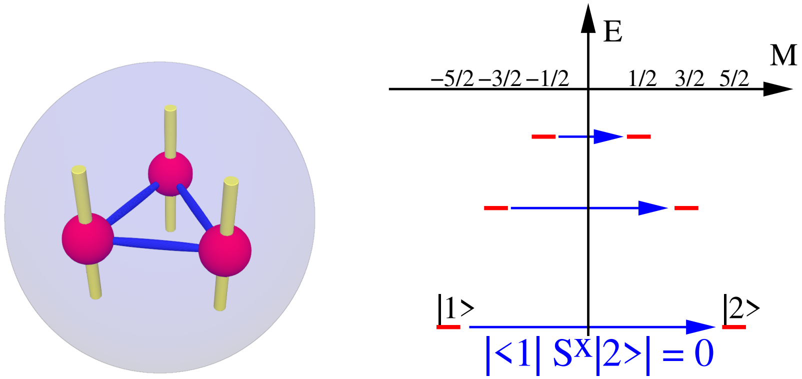


IMPORTANT: $[\underset{\sim}{H}, \underset{\sim}{S}^z] \neq 0$

$\Rightarrow$ avoided level crossings at $B = 0$ for integer spins

$\Rightarrow$ poor/no hysteresis – not bistable & bad for storage

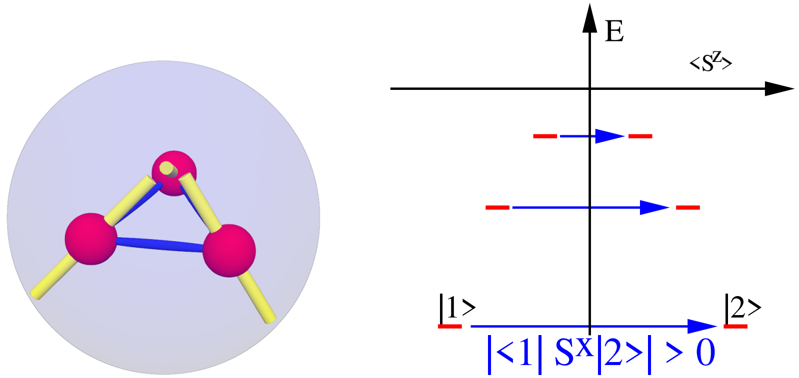
Single-ion anisotropy and bistability III – stability



Collinear easy axes:

⇒ No tunneling gap

⇒ No transition matrix elements



Non-collinear easy axes:

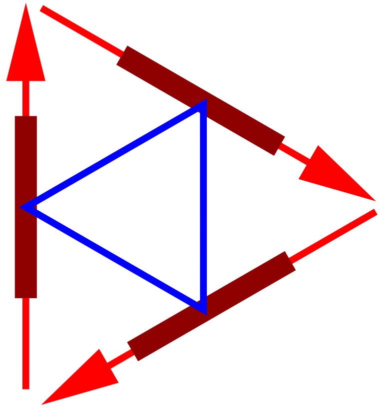
⇒ Tunneling gap for integer spin

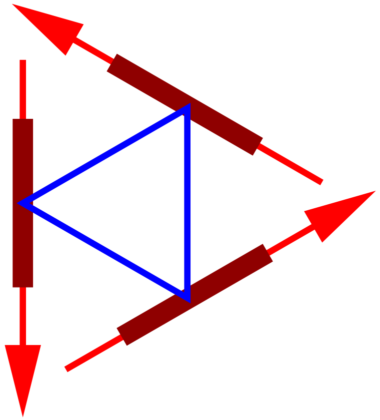
⇒ (large) Transition matrix elements (1)

(1) K.-A. Lippert, C. Mukherjee, J.-P. Broschinski, Y. Lippert, S. Walleck, A. Stammler, H. Bögge, J. Schnack, and T. Glaser, Inorg. Chem. **56**, 15119 (2017).

Toroidal magnetic molecules

Torodial magnetic molecules I





Model Hamiltonian

$$\underset{\sim}{H} = -2 \sum_{i<j} J_{ij} \underset{\sim}{\vec{s}}_i \cdot \underset{\sim}{\vec{s}}_j + D \sum_i \left(\underset{\sim}{\vec{s}}_i \cdot \vec{e}_i^{\,3} \right)^2 + \mu_B \, g \, \vec{B} \cdot \sum_i \underset{\sim}{\vec{s}}_i$$

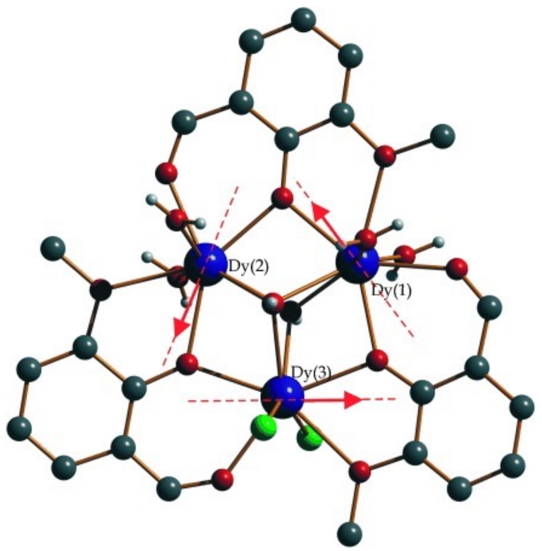
Toroidal magnetic moment

$$\underset{\sim}{\vec{\tau}} = \sum_i \vec{r}_i \times \underset{\sim}{\vec{s}}_i$$

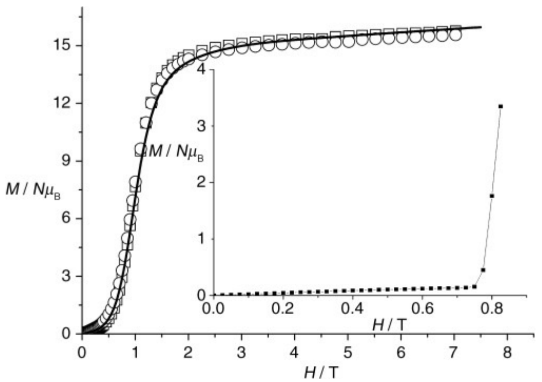
Classical ground states with vanishing moment, but non-vanishing toroidal moment possible (easy axes $D < 0$ & weak exchange $|J_{ij}| \ll |D|$).

J. Tang, I. Hewitt, N. T. Madhu, G. Chastanet, W. Wernsdorfer, C. E. Anson, C. Benelli, R. Sessoli, and A. K. Powell, Angew. Chem. Int. Ed. **45**, 1729 (2006).
A. Soncini and L. F. Chibotaru, Phys. Rev. B **77**, 220406 (2008).
D. Pister, K. Irländer, D. Westerbeck, and J. Schnack, Phys. Rev. Research **4**, 033221 (2022).

Torodial magnetic molecules II – Example 1



The Origin of Nonmagnetic Kramers Doublets in the Ground State of Dysprosium Triangles: Evidence for a Toroidal Magnetic Moment (1)



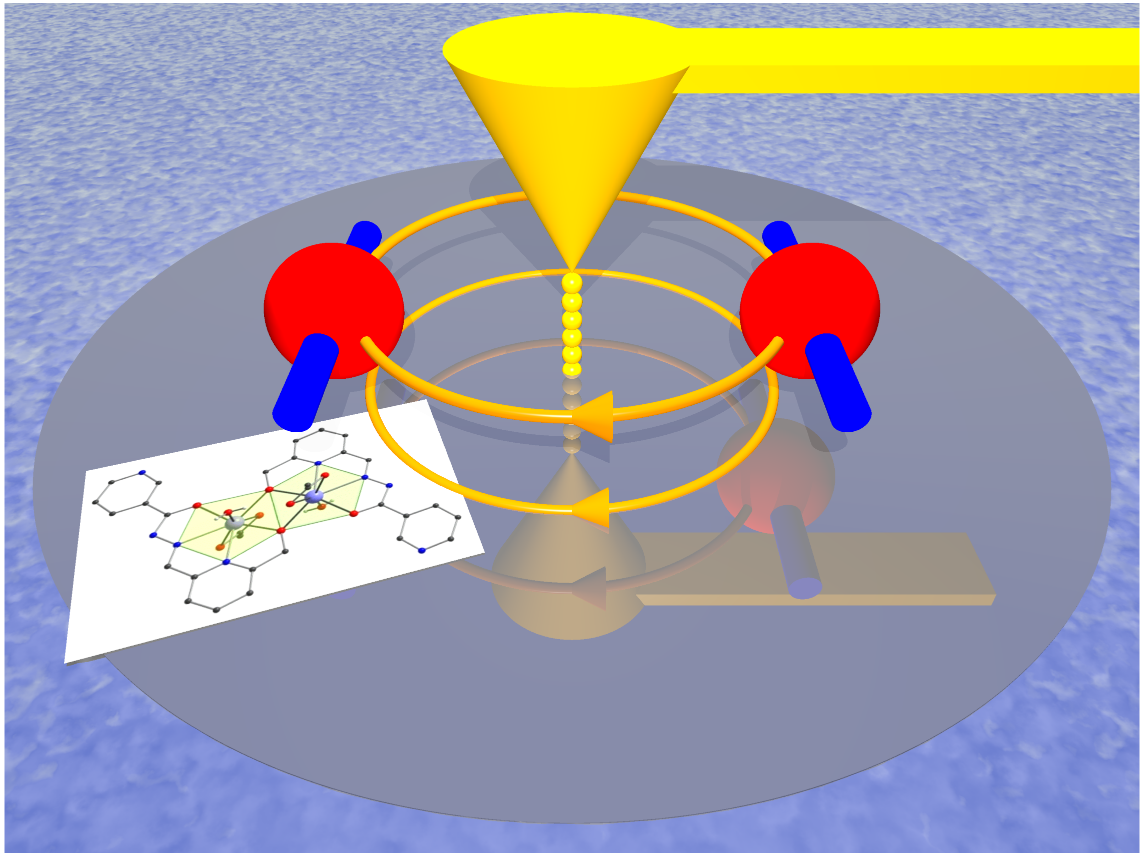
Kramers doublet – two states

Toroidal magnetic moment – left/right rotating

Vanishing moment reduces crosstalk!

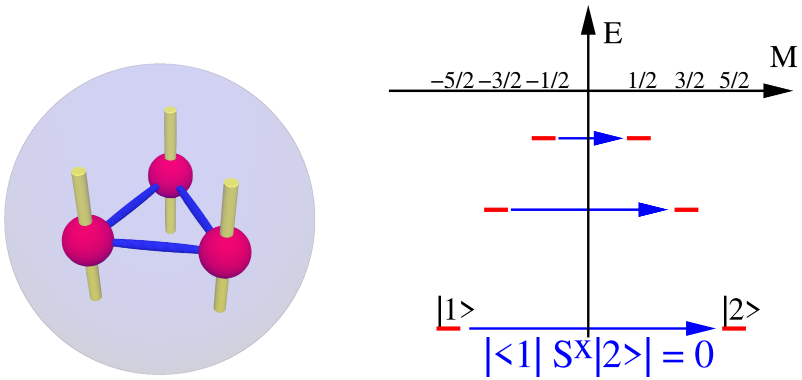
(1) L. F. Chibotaru, L. Ungur, and A. Soncini, Angew. Chem. Int. Ed. **47**, 4126 (2008).

Torodial magnetic molecules IV – switching???



D. Pister, K. Irländer, D. Westerbeck, and J. Schnack, Phys. Rev. Research **4**, 033221 (2022).

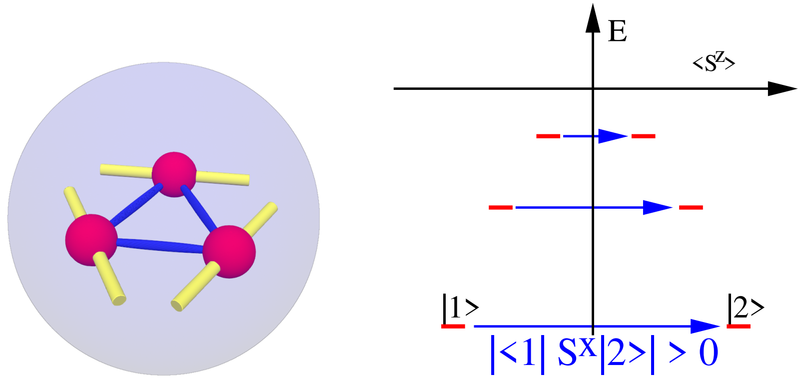
Single-ion anisotropy and bistability IV – stability



Collinear easy axes:

⇒ No tunneling gap

⇒ No transition matrix elements



Non-collinear easy axes:

⇒ Tunneling gap for integer spin

⇒ (large) Transition matrix elements

Toroidal moments are here!

Typicality approach to molecular magnetism

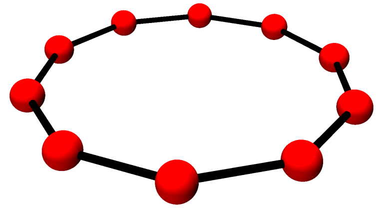
Finite-temperature Lanczos method in one slide

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

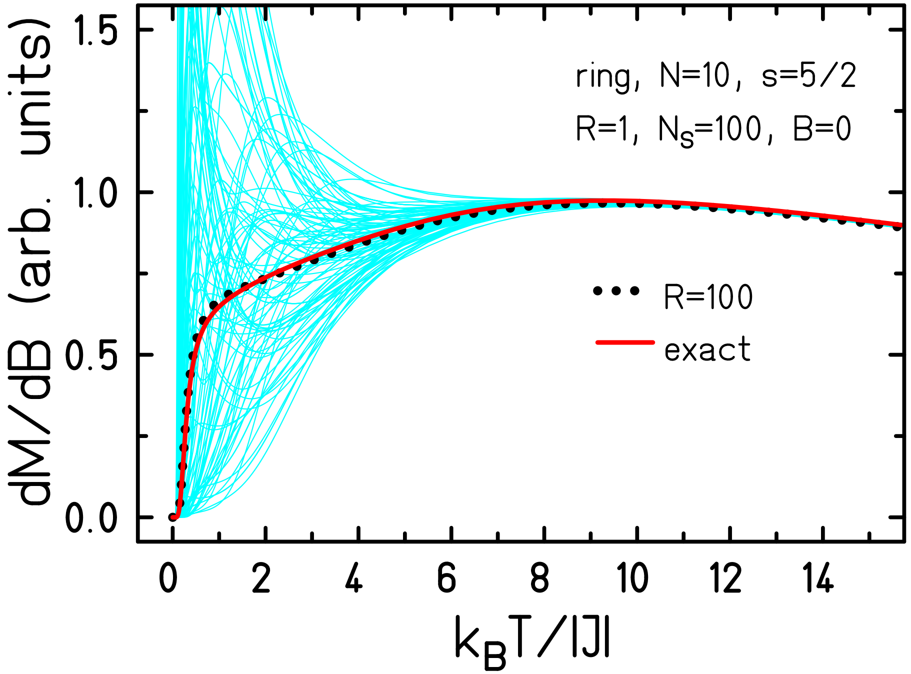
$$O^{\mathrm{r}}(T,B) \approx \frac{\langle\, r \,|\, \underset{\sim}{O} e^{-\beta \underset{\sim}{H}} \,|\, r \,\rangle}{\langle\, r \,|\, e^{-\beta \underset{\sim}{H}} \,|\, r \,\rangle}$$

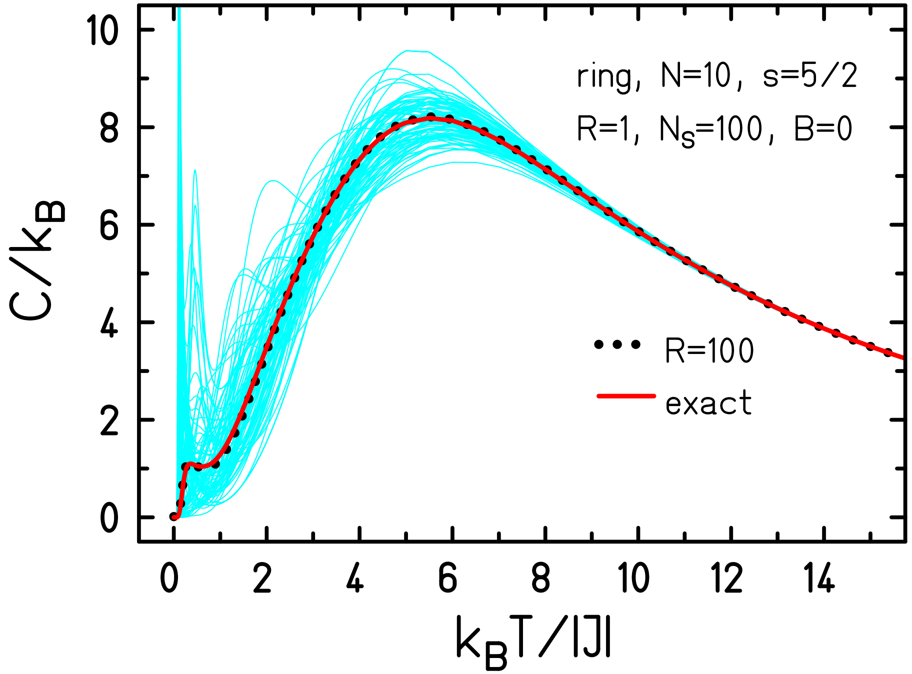
- $|\, r \,\rangle$ is a random vector. Any random vector will do: $|\, r \,\rangle \equiv (T = \infty)$
- $e^{-\beta \underset{\sim}{H}} = \sum_{n=1}^{N_L} \,|\, n(r) \,\rangle e^{-\beta \epsilon_n^{(r)}} \langle\, n(r) \,|$ is the spectral representation in the Krylov space of dimension N_L grown from seed $|\, r \,\rangle$.

(1) J. Jaklic and P. Prelovsek, Phys. Rev. B **49**, 5065 (1994).
(2) J. Schnack, J. Richter, R. Steinigeweg, Phys. Rev. Research **2**, 013186 (2020).



FTLM 1: ferric wheel





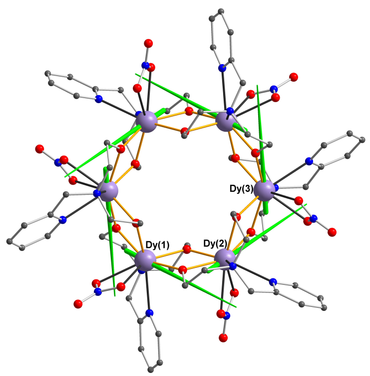
(1) J. Schnack, J. Richter, R. Steinigeweg, Phys. Rev. Research **2**, 013186 (2020).

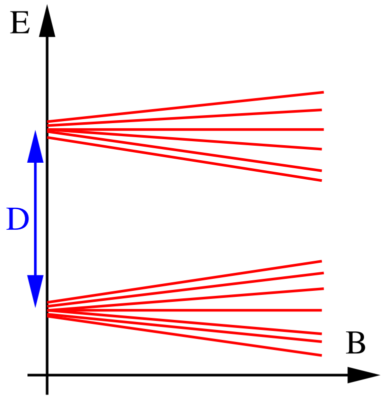
(2) SU(2) & D_2: R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403 (2010).

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

Effective model for Dy$_6$

$$\underset{\sim}{H} = \sum_{k<\ell} \underset{\sim}{\vec{j}}_k \cdot \mathbf{J}_{k\ell} \cdot \underset{\sim}{\vec{j}}_\ell + \sum_k \underset{\sim}{\vec{j}}_k \cdot \mathbf{D}_k \cdot \underset{\sim}{\vec{j}}_k + \mu_B \vec{B} \cdot \sum_k g_k \underset{\sim}{\vec{j}}_k$$

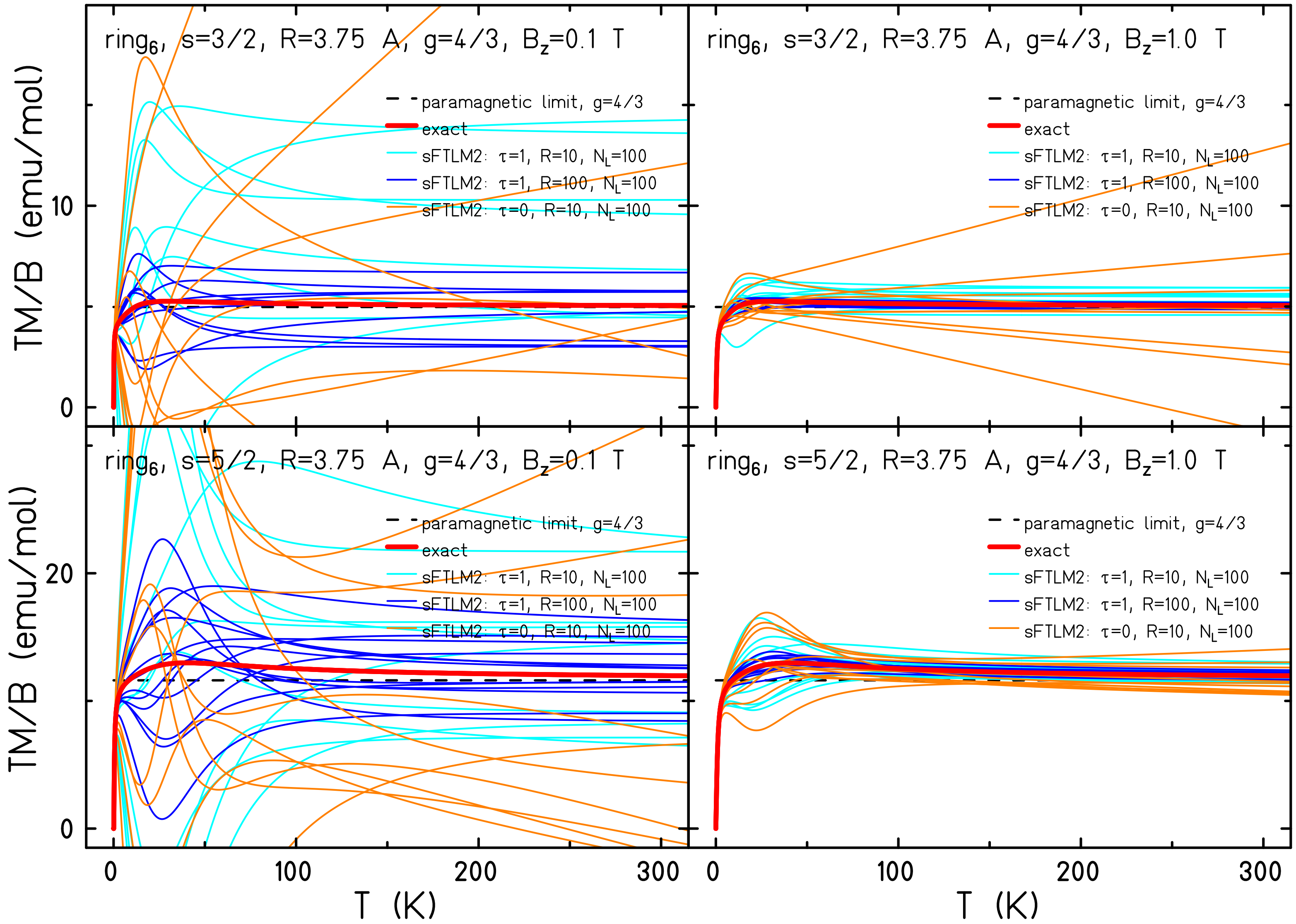




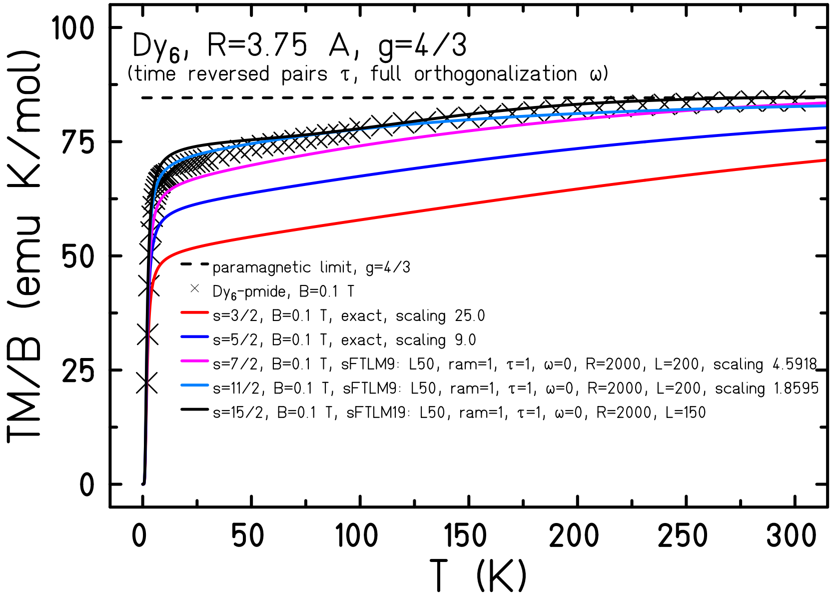
- Very strong alternating easy axes with $D \approx -20$ K. $J \approx -0.02$ K and (stronger) dipolar interaction.
- Hamiltonian has no symmetries!
- dim$\mathcal{H} = 16,777,216 \quad \Rightarrow \quad$ FTLM!

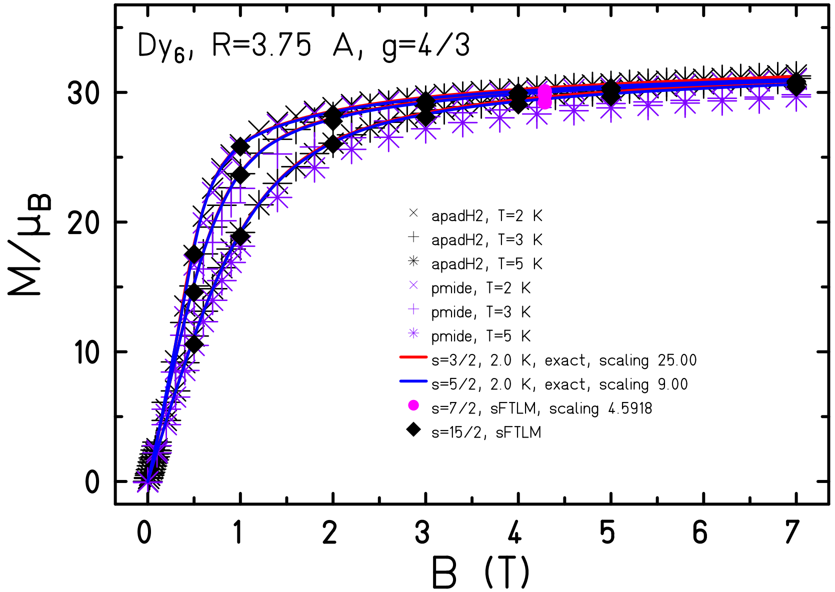
Warning! Method is approximate and holds only for small enough B since spin and orbital angular momentum have got different g_k.

Problem III – FTLM converges badly for anisotropic models



Dy_6 – results





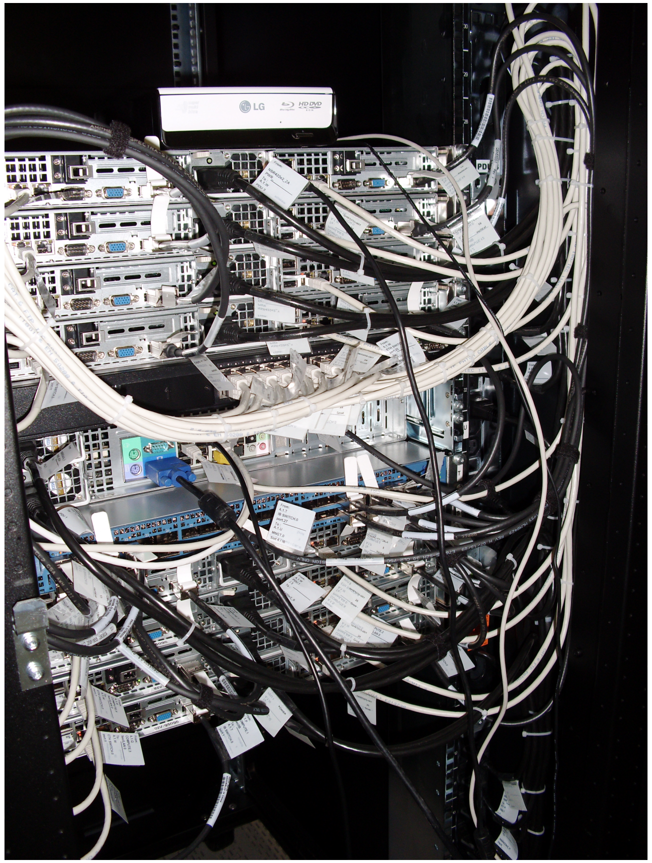
1. Use pairs of time-reversed random vectors (1)

2. Use symmetric version of FTLM (2):

$$\mathrm{Tr}\left(\underset{\sim}{Q} e^{-\beta \underset{\sim}{H}}\right) = \mathrm{Tr}\left(e^{-\beta \underset{\sim}{H}/2} \underset{\sim}{Q} e^{-\beta \underset{\sim}{H}/2}\right) \approx \langle\, r \,|\, e^{-\beta \underset{\sim}{H}/2} \underset{\sim}{Q} e^{-\beta \underset{\sim}{H}/2} \,|\, r \,\rangle \neq \langle\, r \,|\, e^{-\beta \underset{\sim}{H}} \underset{\sim}{Q} \,|\, r \,\rangle$$

(1) O. Hanebaum, J. Schnack, Eur. Phys. J. B **87**, 194 (2014).
(2) M. Aichhorn, M. Daghofer, H. G. Evertz, and W. von der Linden, Phys. Rev. B **67**, 161103(R) (2003).
(3) D. Westerbeck, Ph.D. thesis, Bielefeld University (2025).

Summary



- Magnetic molecules are rich quantum spin systems.
- Magnetic molecules allow to study quantum phenomena for finite-size systems.
- Numerical methods such as sFTLM or thDMRG can be used for and are challenged by magnetic molecules.

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