Molecular magnetism - a great playground for quantum mechanics

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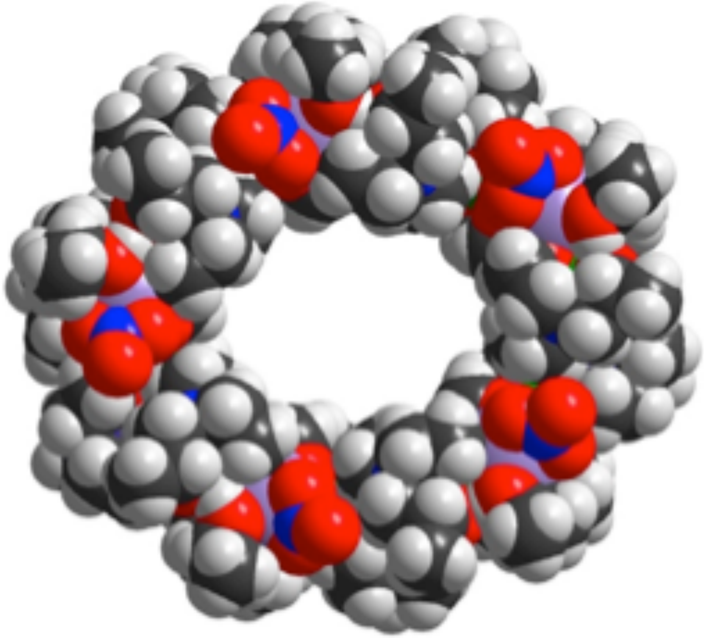
Colloquium, Amherst College, 9 March 2021

We investigate
magnetic molecules.
(Some of you do, too.)

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

You have got a molecule!

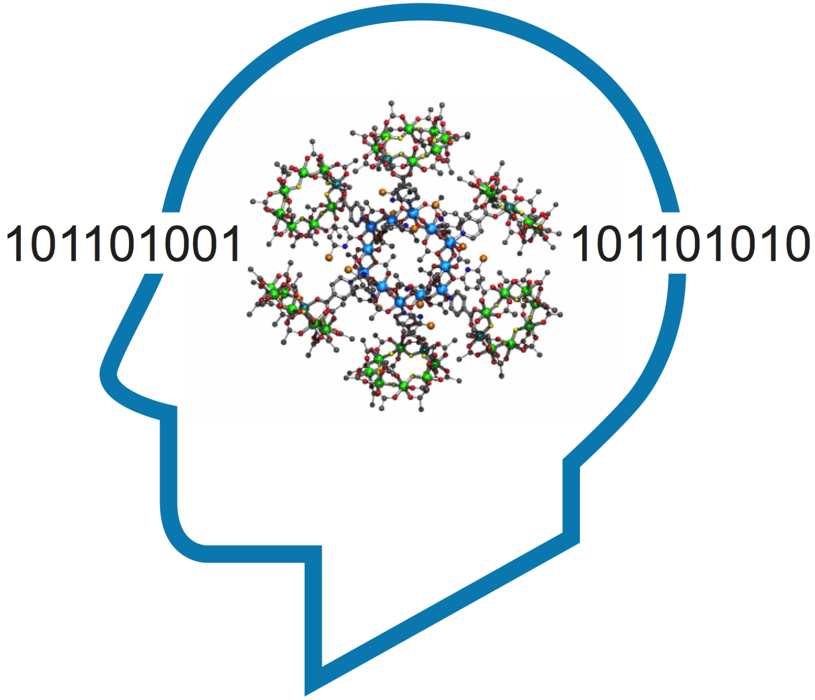


$S = 60!$

Congratulations!

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

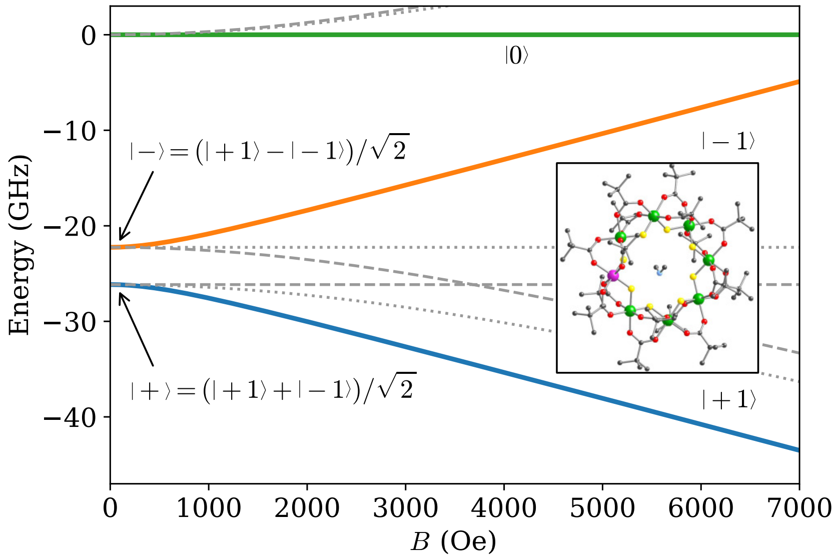
You want to build a quantum computer!



Very smart!

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

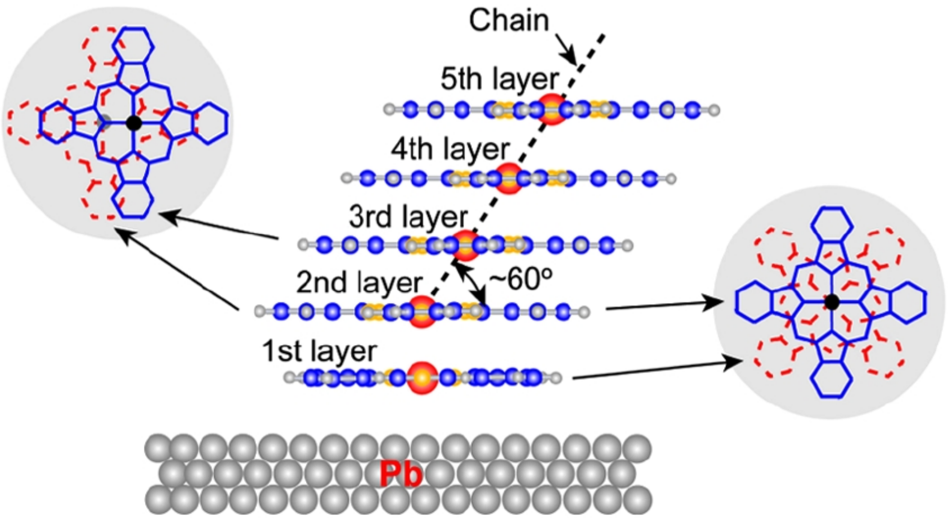
You want to achieve quantum coherence!



Desperately needed!

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

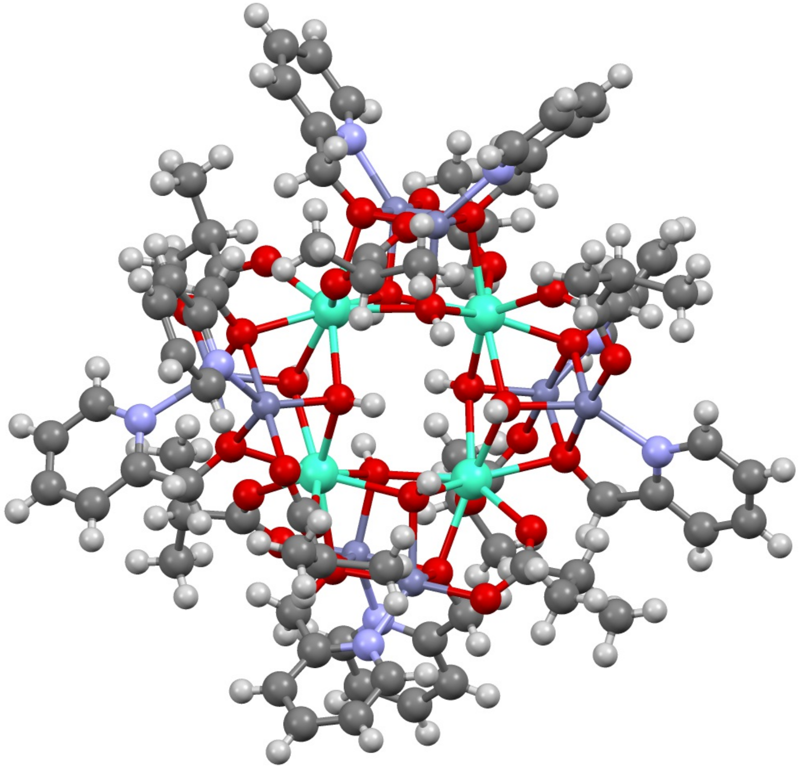
You want to deposit your molecule!



Next generation magnetic storage!

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

You want molecular magnetocalorics!

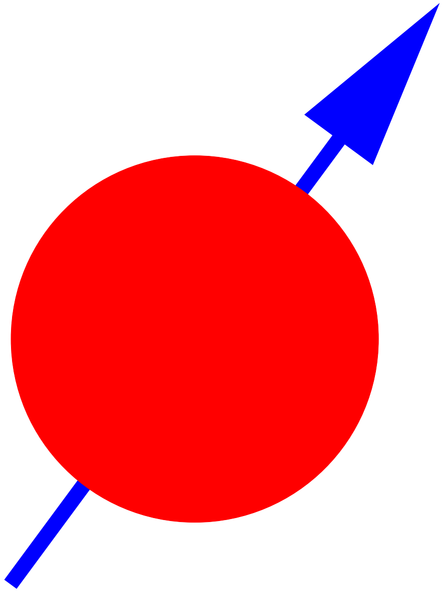


Cool!

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

How do we get there?

Today’s approach to quantum magnetism

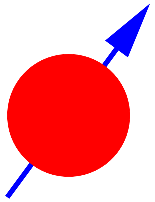


- **1 spin** – storage and calorics
- **2 spins** – decoherence and clock transitions
- **3 spins** – frustration
- **Many spins** – a universe opens up
- **Mag**(net)**ic** calculations

One spin

(One spin can do a lot!)

One spin – basic quantum mechanics



spins defined through commutator relations

$\left[\underset{\sim}{s}^{x}, \underset{\sim}{s}^{y}\right] = i\,\hbar\,\underset{\sim}{s}^{z}$, and cyclic permutations thereof

eigenvalue equations

$$\begin{aligned} \underset{\sim}{\vec{s}}^{2} \mid sm\,\rangle &= \hbar^{2} s(s+1) \mid sm\,\rangle \\ \underset{\sim}{s}^{z} \mid sm\,\rangle &= \hbar m \mid sm\,\rangle\ ,\ m = -s, -s+1, \dots, s-1, s \end{aligned}$$

magnetic moment (simple, but common version)

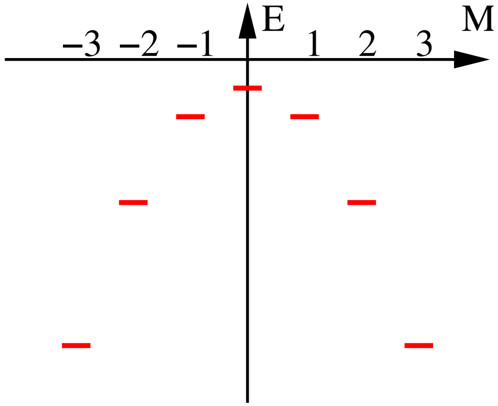
Theorists like $\hbar = 1$!

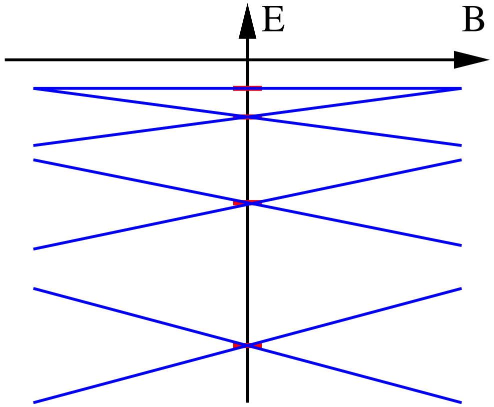
$$\underset{\sim}{\vec{\mu}} = -g\mu_B \underset{\sim}{\vec{s}}$$

"–", because electron carries negative charge.

$$\underset{\sim}{H}_{\text{Zeeman}} = -\underset{\sim}{\vec{\mu}} \cdot \vec{B} = g\mu_B \underset{\sim}{\vec{s}} \cdot \vec{B}$$

One spin – single-ion anisotropy





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

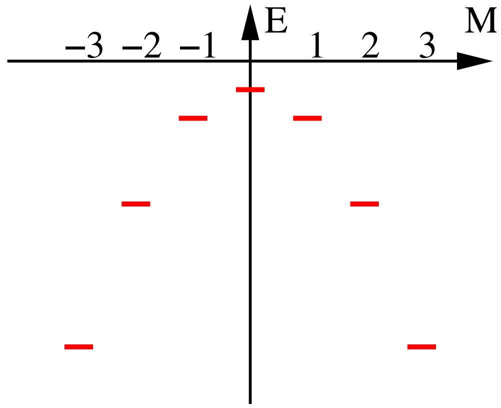
$D < 0$ easy axis, $D > 0$ hard axis;

eigenvectors: $|\, sm \,\rangle$

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

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

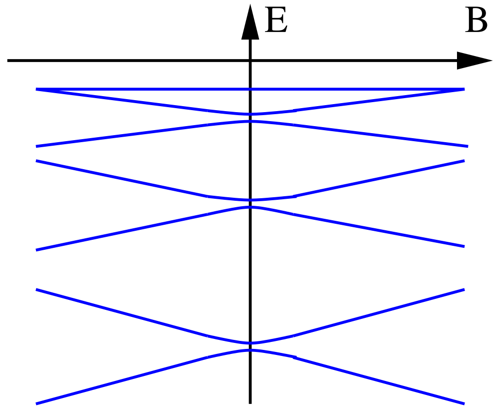
One spin – single-ion anisotropy



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

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

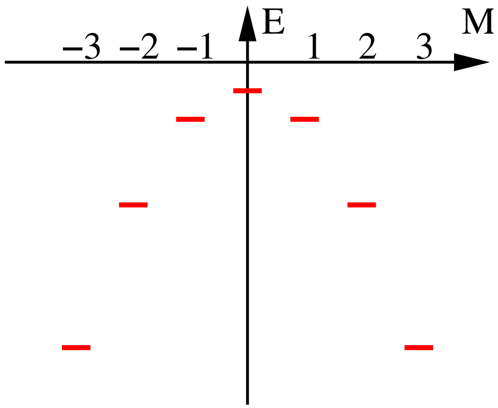
NO LONGER eigenvectors: $|\, sm\, \rangle$



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)

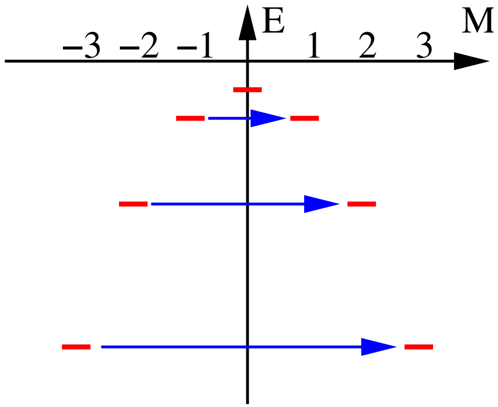
One spin – single-ion anisotropy



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

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

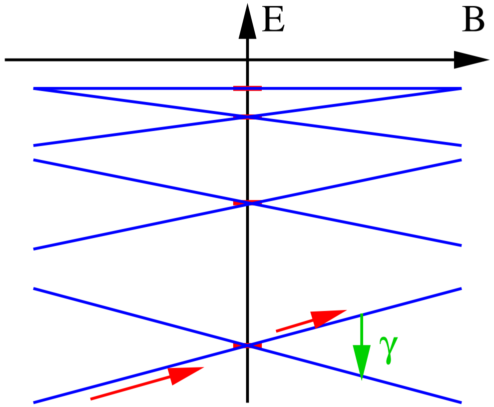
What do the spectra and the arrows mean?

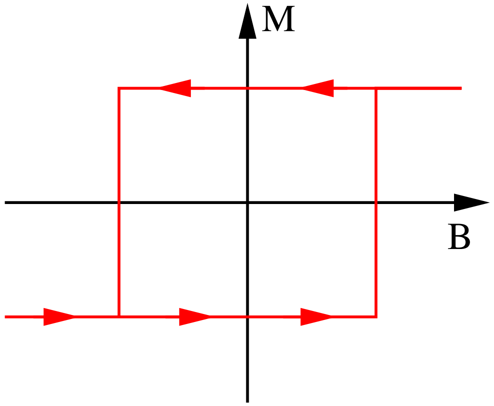


Perturbation picture: spectra show eigenvalues of dominant term $D(\underset{\sim}{s}^z)^2$ with eigenstates $|\, sm \,\rangle$.

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

One spin – bistability





Goal: single-molecule magnets (SMM)

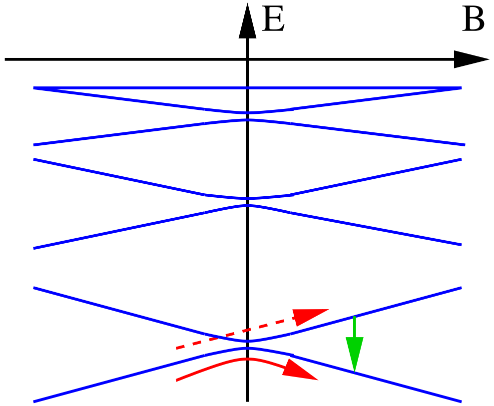
$$\underset{\sim}{H} = D(\underset{\sim}{s}^z)^2 + g\mu_B B \underset{\sim}{s}^z$$

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

$\Rightarrow$ low-temperature TIME-DEPENDENT hysteresis

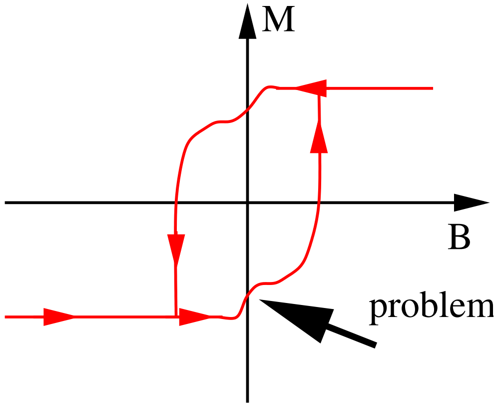
Side remark: For macroscopic systems in the ferromagnetic phase the relaxation time is HUGE, that's why we don't experience it.

One spin – bistability



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

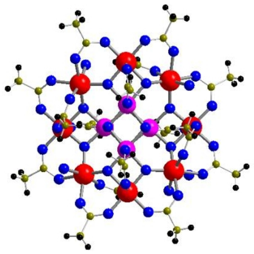
$\Rightarrow$ low-temperature TIME-DEPENDENT hysteresis closes at $B = 0$ – not bistable & bad for storage

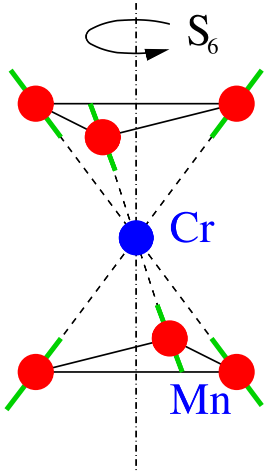


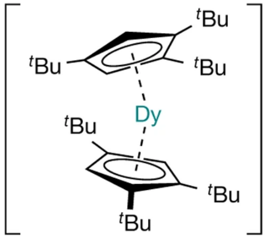
REASON: branching at avoided level crossings; strong dependence on tunneling gap and $\dot{B}$;

slow change of $B \Rightarrow$ system follows ground state,
compare **Landau-Zener-Stückelberg**
or slow/fast train at switch

One spin, e.g. ground state spin of molecule – outlook







Today’s major goals:

ferromagnetic spin-spin interaction

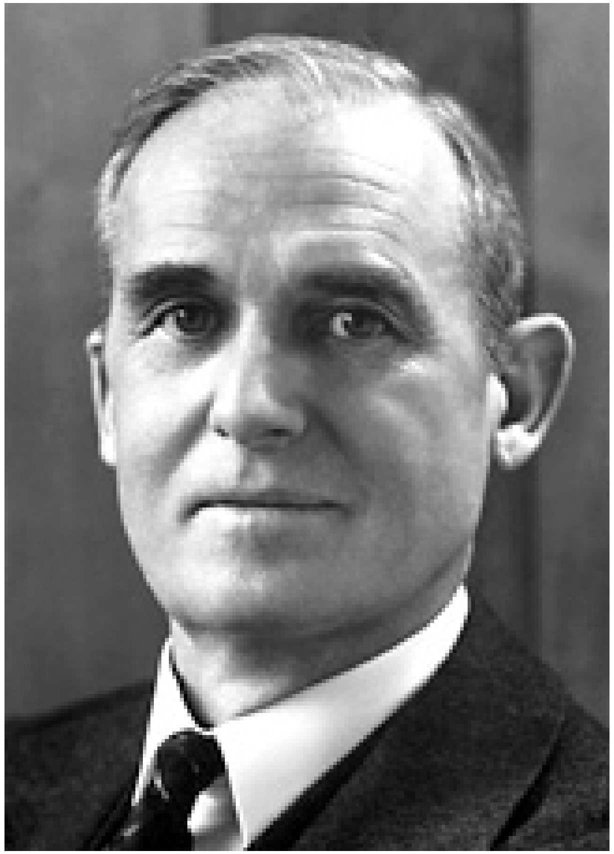
uniaxial anisotropy tensors

symmetry that does not permit E-terms

PERSISTENT PROBLEM: phonons

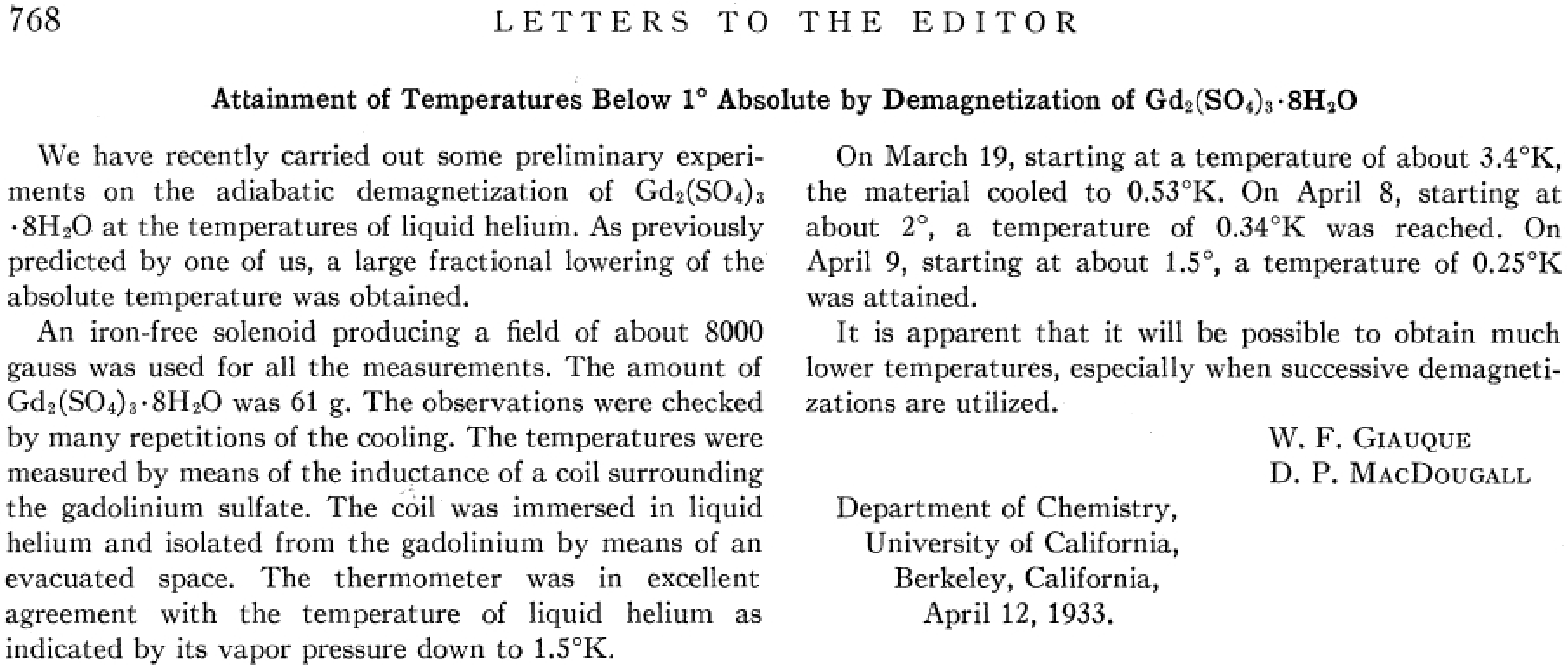
Nick Chilton, Thorsten Glaser, Jeff Long, Alessandro Lunghi, Mark Murrie, Frank Neese, Stefano Sanvito, Roberta Sessoli, Richard Winpenny, Yan-Zhen Zheng, . . .

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



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.

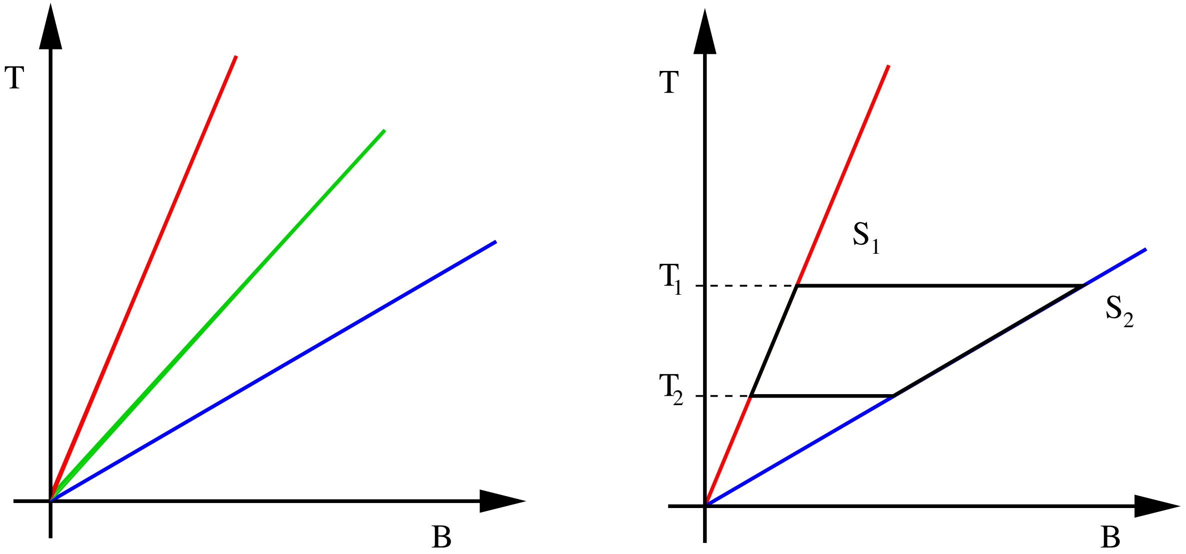
It is apparent that it will be possible to obtain much lower temperatures, especially when successive demagnetizations are utilized.

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).

One spin – magnetocalorics

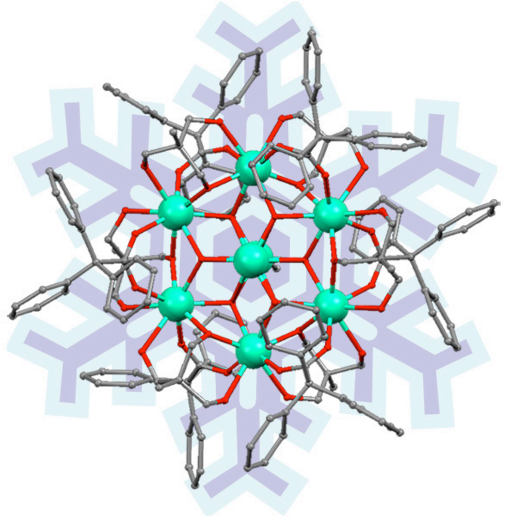


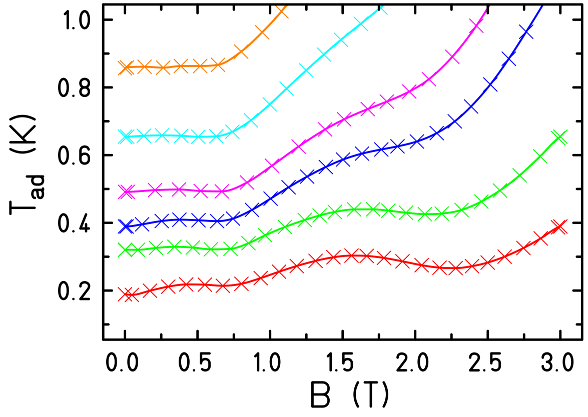
- $\underset{\sim}{H} = g \mu_B \underset{\sim}{s}^z B$,   paramagnet = independent spins = ideal gas of magnetism.

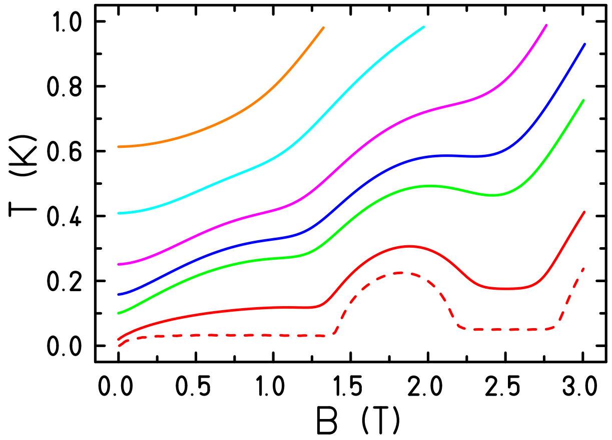
- Ideal paramagnet: $S(T, B) = f(B/T)$, i.e. $S = const \Rightarrow T \propto B$.

- Often, at low T dipolar interaction between spins prevents further cooling.

One spin – magnetocalorics – outlook







- Often magnetocaloric observables not directly measured, but inferred from Maxwell's relations.

- Gd_7: real cooling experiment with a molecule.

- Goal: development of new coolants – isentrope design.

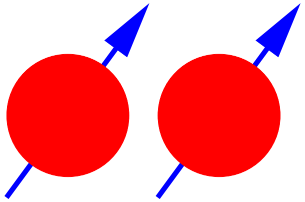
J. W. Sharples, D. Collison, E. J. L. McInnes, J. Schnack, E. Palacios, M. Evangelisti, Nat. Commun. **5**, 5321 (2014).

This was the warmup!

Two spins

(Two spins can do more!)

Two spins – basic quantum mechanics



interaction – Heisenberg Hamiltonian (isotropic)

$$\underset{\sim}{H}_{\text{Heisenberg}} = -2J_{12}\,\underset{\sim}{\vec{s}}_1 \cdot \underset{\sim}{\vec{s}}_2 \ , \qquad \underset{\sim}{H}_{\text{Zeeman}} = g\,\mu_B\,B \sum_i^N \underset{\sim}{s}_i^z$$

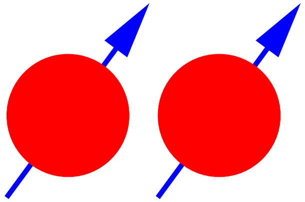
symmetries (+ possible point group symmetries), total spin: $\underset{\sim}{\vec{S}} = \sum_i^N \underset{\sim}{\vec{s}}_i$

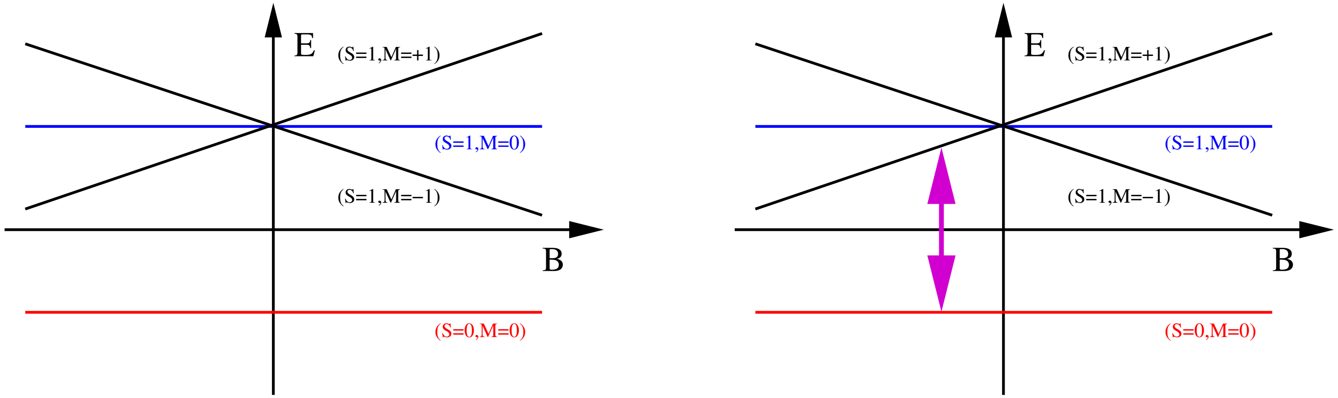
$$\left[\underset{\sim}{H}_{\text{Heisenberg}} + \underset{\sim}{H}_{\text{Zeeman}}, \underset{\sim}{\vec{S}}^2\right] = \left[\underset{\sim}{H}_{\text{Heisenberg}} + \underset{\sim}{H}_{\text{Zeeman}}, \underset{\sim}{S}^z\right] = 0$$

dipolar interaction: ⇒ symmetries lost

$$\underset{\sim}{H}_{\text{dipolar}} = \frac{\mu_0 \mu_B^2}{4\pi\, r_{12}^3}\left(\underset{\sim}{\vec{s}}_1 \cdot \underset{\sim}{\vec{s}}_2 - 3(\underset{\sim}{\vec{s}}_1 \cdot \vec{e}_{12})(\underset{\sim}{\vec{s}}_2 \cdot \vec{e}_{12})\right) \ , \quad \vec{e}_{12} = \vec{r}_{12}/r_{12}$$

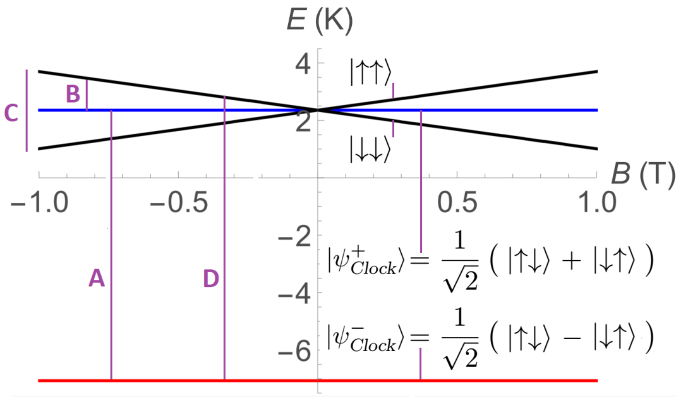
Two spins – Heisenberg dimer $s_1 = s_2 = \frac{1}{2}$

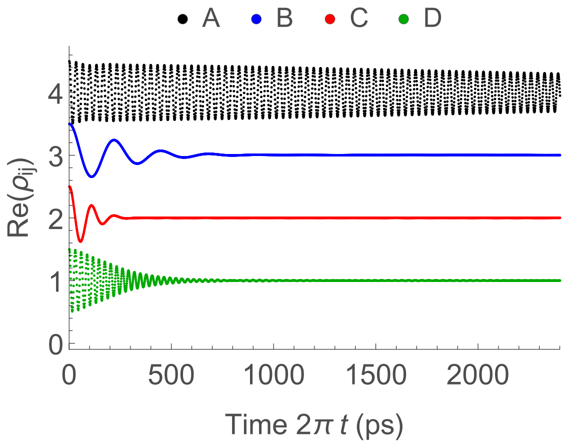


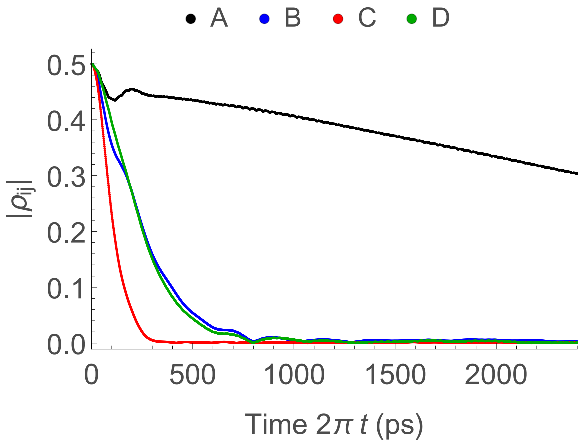


- Product basis $\{\,|\,m_1 = \pm 1/2, m_2 = \pm 1/2\,\rangle\}$ = $\{\,|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle\}$
- Energy eigenstates (stationary):
  $|\,S=0, M=0\,\rangle = \frac{1}{\sqrt{2}}(\,|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle),\ |\,S=1, M=0\,\rangle = \frac{1}{\sqrt{2}}(\,|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle),$
  $|\,S=1, M=1\,\rangle = |\uparrow\uparrow\rangle,\ |\,S=1, M=-1\,\rangle = |\downarrow\downarrow\rangle$
- A superposition would oscillate for ever! ⇒ Quantum coherence!

Two spins – Heisenberg dimer decoheres in environment

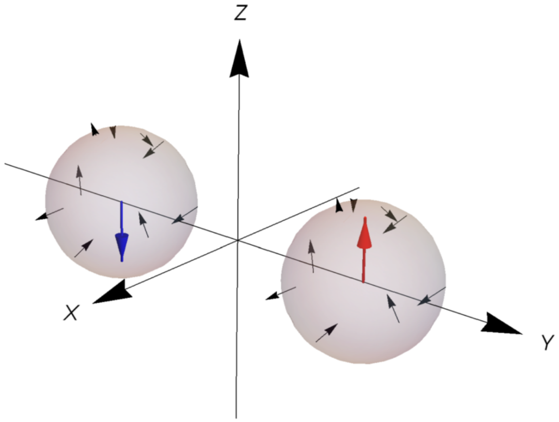






Solve time-dependent Schrödinger equation for full system.

Scenario A is a (perfect) **clock transition**.



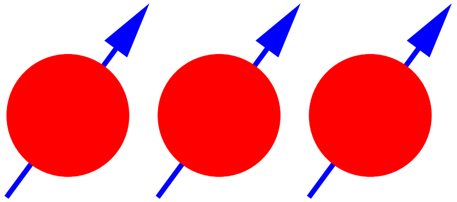
P. Vorndamme, J. Schnack, Phys. Rev. B **101**, 075101 (2020)

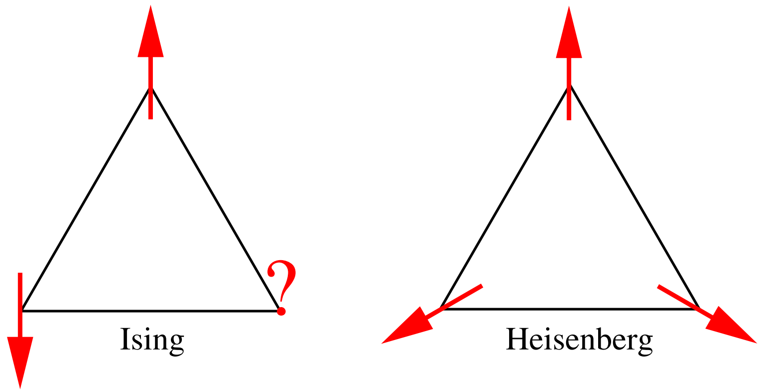
Y. Bae *et al.*, Science Advances **4**, eaau4159 (2018)

Three spins

(Triangles add new features!)

Three spins – triangles and frustration



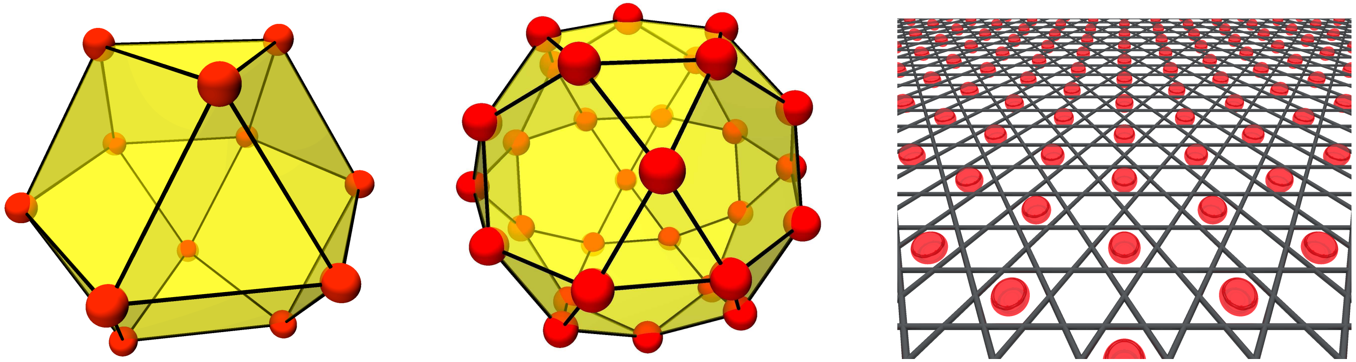


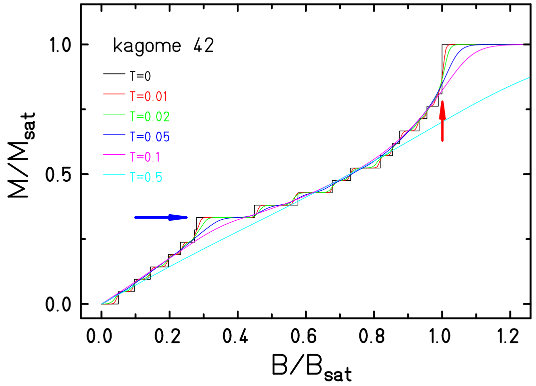
- $\underset{\sim}{H} = -2 \sum_{i<j} J_{ij}\, \underset{\sim}{\vec{s}}_i \cdot \underset{\sim}{\vec{s}}_j$, $J_{ij} < 0$ – antiferromagnetic coupling

- Ferromagnets are useful, but boring; antiferromagnets are mind-boggling!

- Example: $J_{ij} = J < 0$;
  $s_1 = s_2 = s_3 = \frac{1}{2}$ $\rightarrow$ ground state $S = \frac{1}{2}$ fourfold degenerate.
  $s_1 = s_2 = s_3 = 1$ $\rightarrow$ ground state $S = 0$ non-degenerate.
  $s_1 = s_2 = s_3 = \frac{3}{2}$ $\rightarrow$ ground state $S = \frac{1}{2}$ fourfold degenerate . . .

Three spins – triangles and frustration





- Antiferromagnetic frustrated molecules and lattices may exhibit fascinating properties: unusual magnetization curves, plateaus and jumps, magnon crystallization, strange ground states , e.g. spin liquids, spin ice, . . .

A.P. Ramirez, MRS Bull. **30**, 447 (2005).
J. Schnack, Dalton Trans. **39**, 4677 (2010).
S.T. Bramwell, M.J.P. Gingras, Science **294**, 1495 (2001).
C. Castelnovo, R. Moessner, S.L. Sondhi, Nature **451**, 42 (2008).
J. Schnack, J. Schulenburg, J. Richter, Phys. Rev. B **98**, 094423 (2018).

For physicists:

Past “three” comes “many”.

(Interesting collective behavior possible.)

How to calculate big systems?

(Typicality approach to magnetism)

Partition function

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

$$\underset{\sim}{H}\,|\,\nu\,\rangle = E_\nu\,|\,\nu\,\rangle\ , \qquad \beta = \frac{1}{k_B T}$$

Questionnaire 1: Why do we diagonalize Hamiltonians?

Questionnaire 2: How big matrices can we diagonalize?

Poll 1

Why do we diagonalize Hamiltonians, i.e. determine eigenvalues and eigenstates?

1. They are needed for spectroscopy (EPR, INS, NMR).
2. They are needed for thermodynamic functions (partition function, magnetization, heat capacity).
3. They are handy to calculate the time evolution (pulsed EPR, simulate quantum computing, thermalization).
4. My professor wants to keep us busy.

(multiple answers allowed)

Poll 2

How big (complex hermitean) matrices can we diagonalize on a (super-) computer?

1. 3 x 3
2. 10,000 x 10,000
3. 100,000 x 100,000
4. 1,000,000 x 1,000,000

(multiple answers allowed)

Can we evaluate the partition function

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

without diagonalizing the Hamiltonian?

Yes, with magic!

Solution I: trace estimators

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

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

- $|\, \nu \,\rangle$ 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 $\mid r \,\rangle$ yields a superposition of

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

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

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

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

- 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).

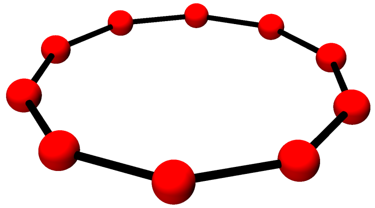
Partition function II: Finite-temperature Lanczos Method

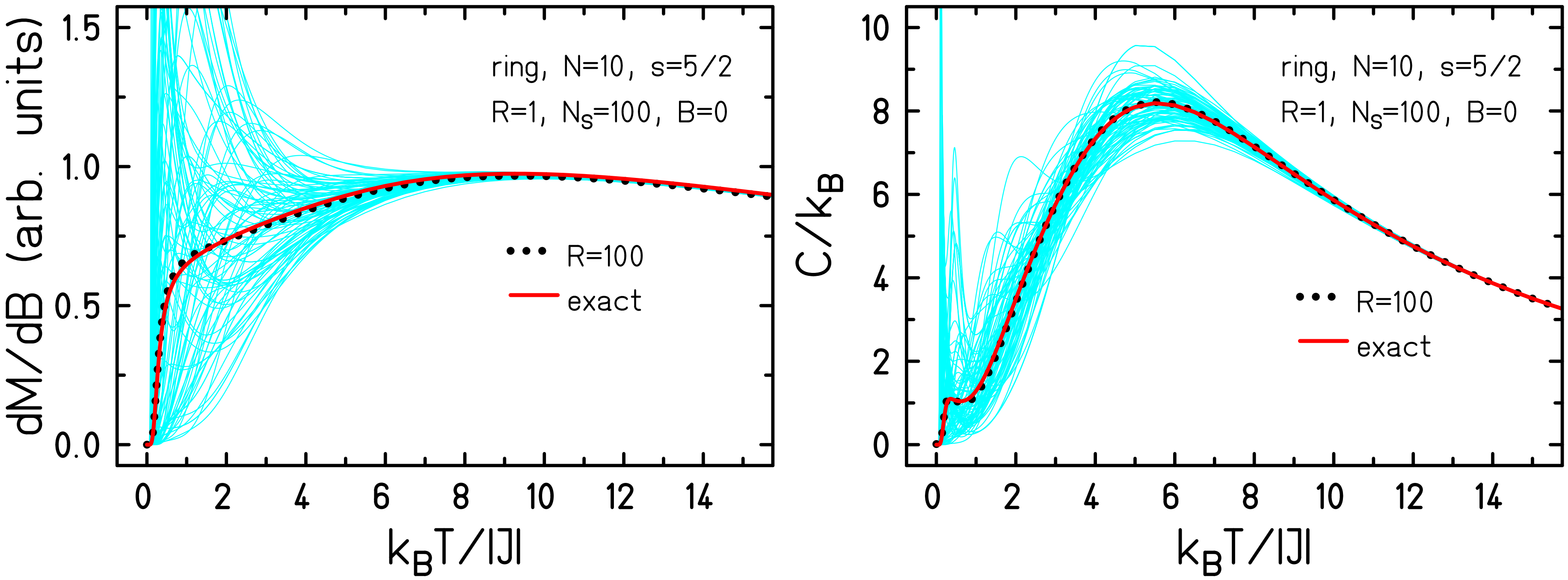
$$Z^{\text{FTLM}}(T,B) \quad \approx \quad \frac{1}{R}\sum_{r=1}^{R}\sum_{n=1}^{N_L} e^{-\beta\epsilon_n^{(r)}} |\langle\, n(r)\,|\,r\,\rangle|^2$$

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

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

Magic typicality for the ferric wheel





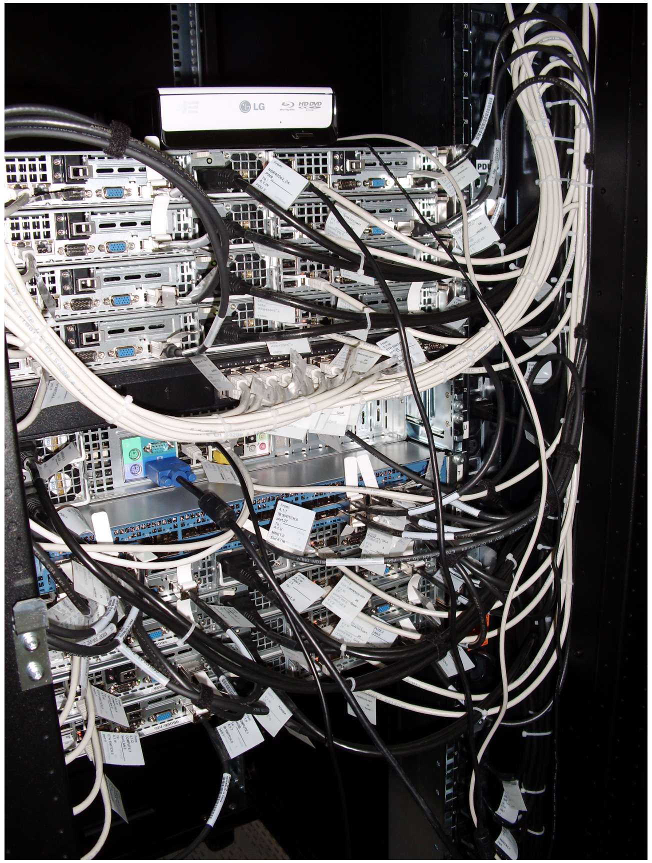
Accuracy: J. Schnack, J. Richter, R. Steinigeweg, Phys. Rev. Research **2**, 013186 (2020).

SU(2) & D$_2$: R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403 (2010).

SU(2) & C$_N$: T. Heitmann, J. Schnack, Phys. Rev. B **99**, 134405 (2019)

Ferric wheel: K.L. Taft *et al., J. Am. Chem. Soc.* ***116****, 823 (1994)*

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 $(T=0, B=0)$.
- Coherence and thermalization under investigation.
- 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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