Toroidal magnetic molecules stripped to their basics

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Seminar Theorie komplexer Systeme
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Imagine . . .

Imagine someone tells you that

toroidal magnetic molecules

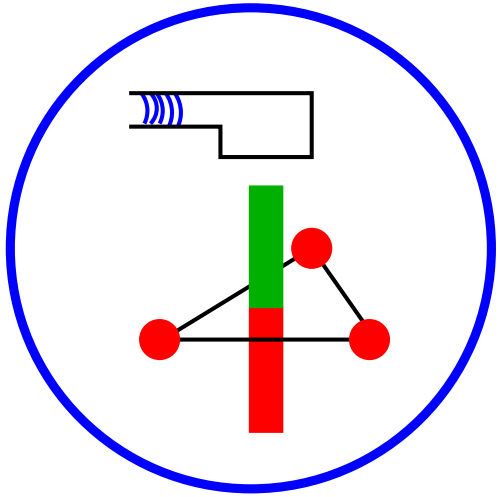
are superb building blocks
of quantum devices.

Would you buy one?

Or would you first check such molecules?

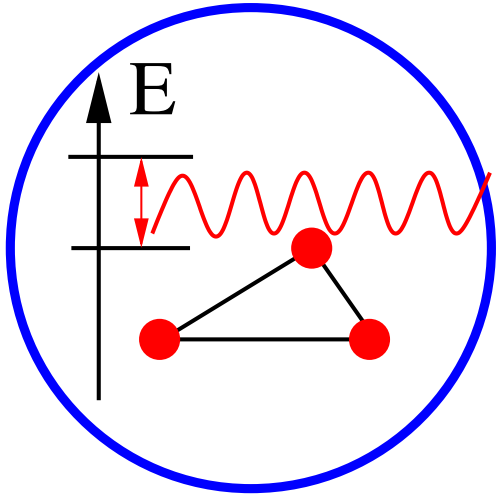
And if, what would you investigate?

Quantum devices – figures of merit



Memory unit

- requires bistability
- problem quantum tunneling



Q-bit

- requires coherence
- problem decoherence

Yes, we can!

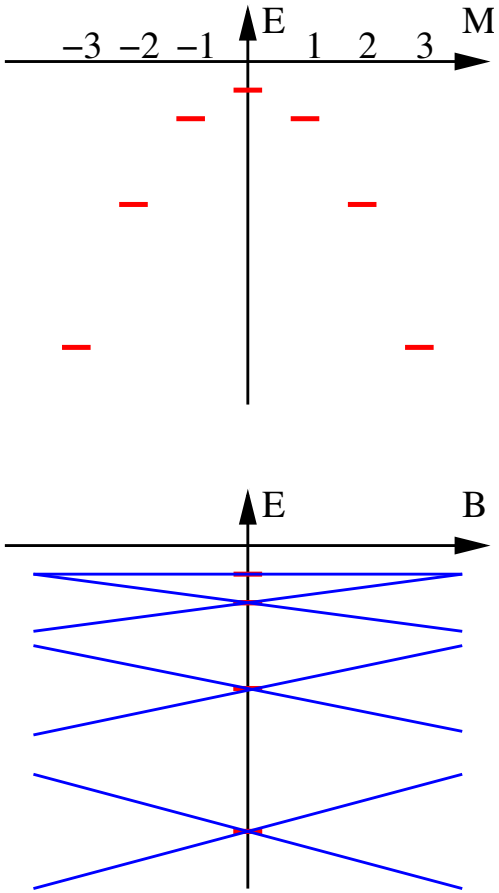
$$\begin{pmatrix} 3 & 42 & 4711 \\ 42 & 0 & 3.14 \\ 4711 & 3.14 & 8 \\ -17 & 007 & 13 \\ 1.8 & 15 & 081 \end{pmatrix}$$

1. Bistability and tunneling
2. Toroidal magnetic molecules
3. Clock transitions and decoherence
4. Bonus program: Some magic

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

Bistability and tunneling

Single-ion anisotropy – single spin I



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

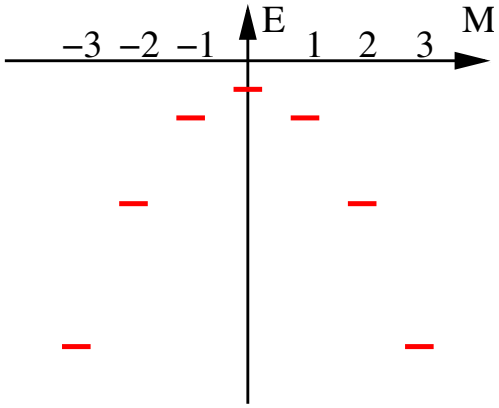
$D < 0$ easy axis, $D > 0$ hard axis;

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 $B = 0$

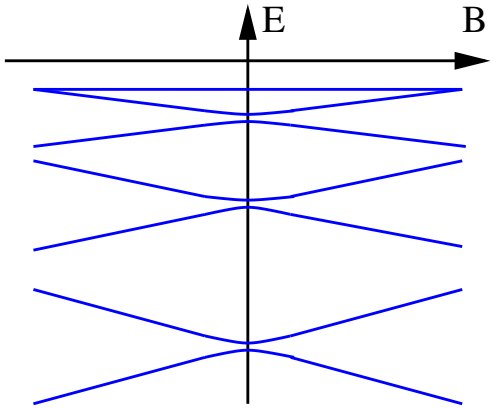
Single-ion anisotropy – single spin II



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

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

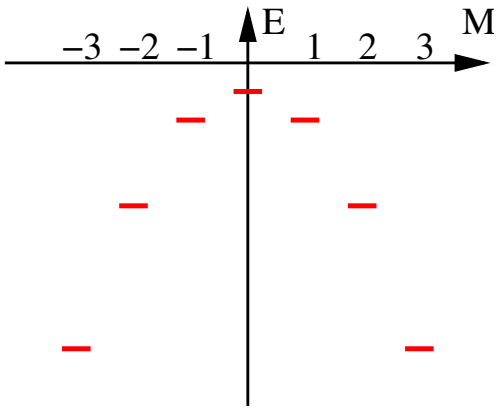
NO LONGER eigenvectors: $|\, s, m \,\rangle$



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 degeneracy)

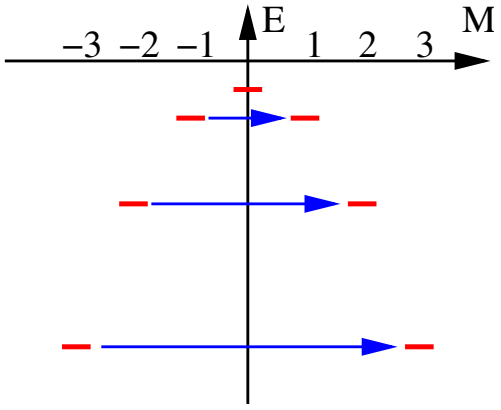
Single-ion anisotropy – single spin III



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

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

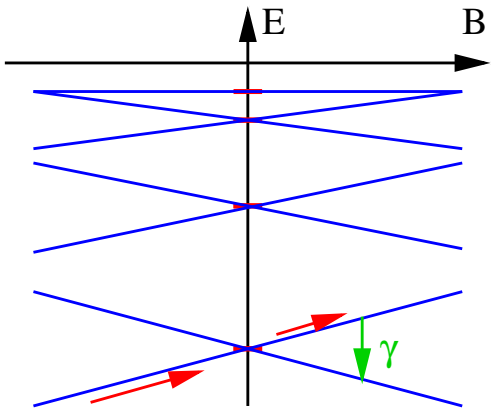
What do the spectra and the arrows mean?

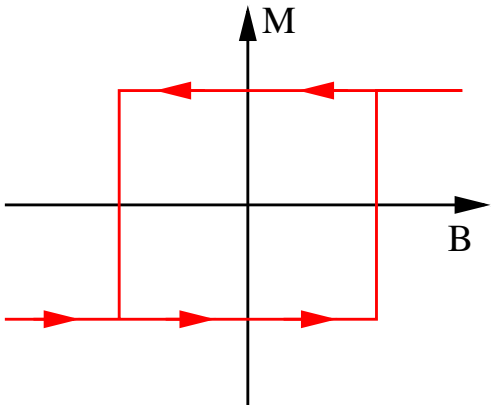


Perturbation picture: spectra show eigenvalues of dominant term $D(\underset{\sim}{s}^z)^2$ with eigenstates $|\, s, m \,\rangle$.

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

Bistability – uniaxial system – $\underset{\sim}{S}^z$-symmetry





Goal: single-molecule magnets (SMM)

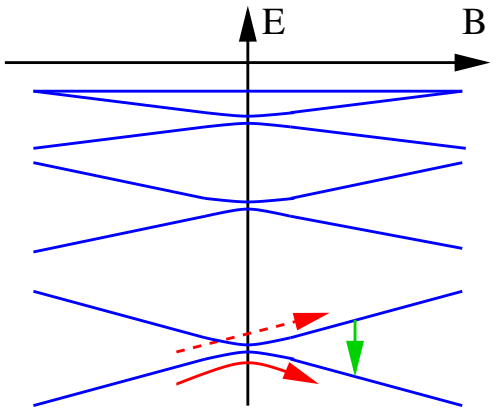
$\underset{\sim}{H} = \sum_i D_i (\underset{\sim}{s}_i^z)^2 + \mu_B B \sum_i g_i \underset{\sim}{s}_i^z + \underset{\sim}{H}_{\text{ferro int}}$

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.

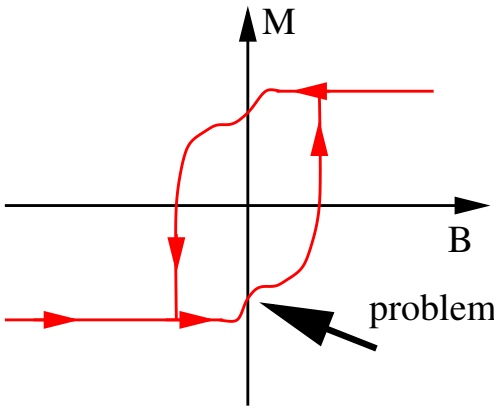
Bistability – general system – NO $\underset{\sim}{S}^z$-symmetry



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

$\mathbf{D}_i$ individual anisotropy tensors

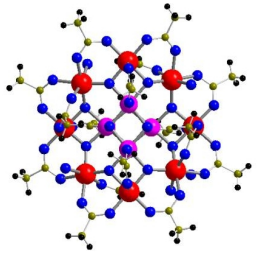
$\Rightarrow$ low-temperature TIME-DEPENDENT hysteresis closes at $B = 0$ – not bistable & bad for storage

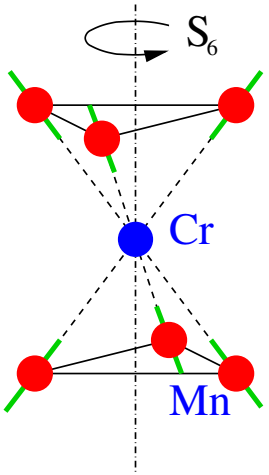


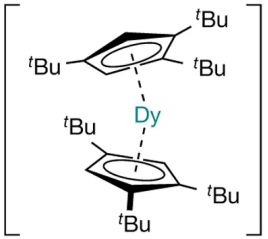
REASON: branching at avoided level crossings;
strong dependence on tunneling gap and $\dot{B}$;

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

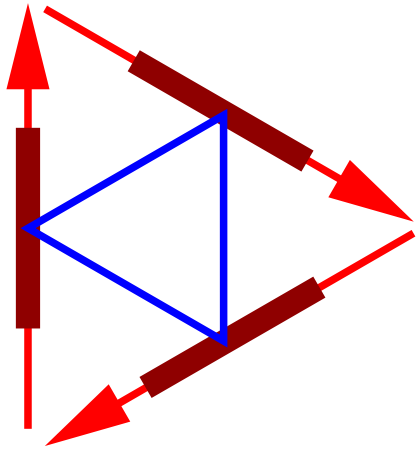
symmetry that does not permit E-terms

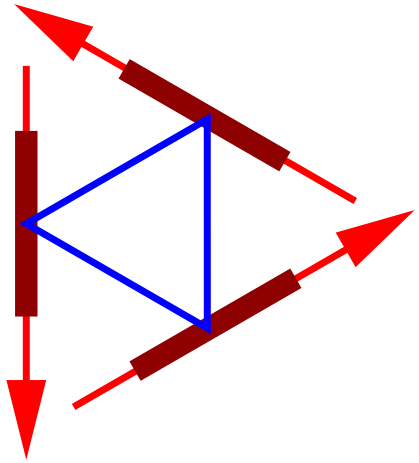
IMPORTANT FOR TODAY: Anisotropy tensors that are not uniaxial cause a tunneling gap for integer total spin (non-Kramers systems)!!!

What about toroidal magnetic molecules?

Toroidal magnetic molecules

Torodial magnetic molecules I





Toroidal magnetic moment

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

Model Hamiltonian I

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

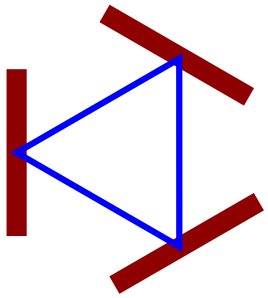
Classical ground states with non-vanishing toroidal moment

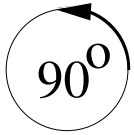
$\Rightarrow$ Leads to two zero-field split quantum ground states.
$\Rightarrow$ Reduced bistability, poor storage unit
(some hope: $\Delta \downarrow$ with S and $D \uparrow$)

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

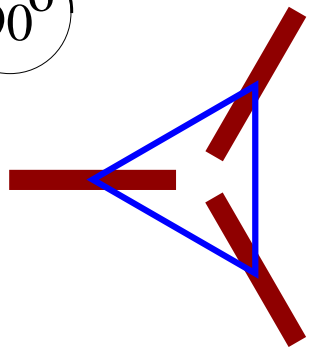
Toroidal magnetic molecules II

(a)





(b)



Model Hamiltonian I

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

Can one distinguish (a) and (b)?

$\Rightarrow$ Collective rotation of the anisotropy axes (and field direction) is a symmetry of the Hamiltonian!

$\Rightarrow$ Spectrum, magnetization not altered, but toroidal moment.

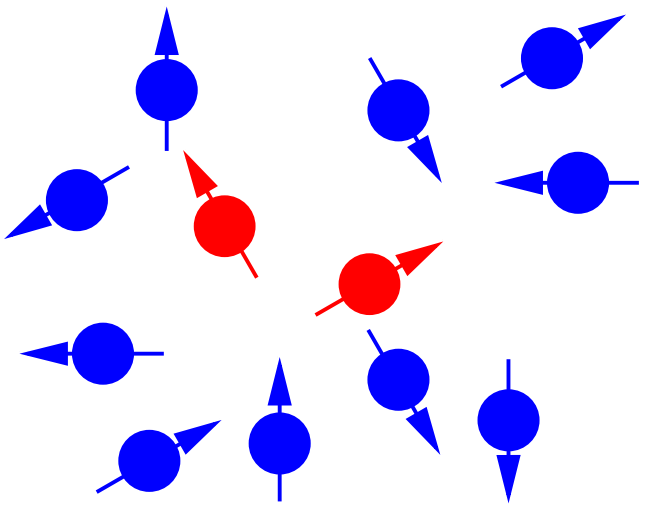
$\Rightarrow$ Concept of toroidal moment does not constitute or explain properties!!!

$\Rightarrow$ Open: Do anisotropic interactions help? Scale!

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

Stability of clock transitions

Context



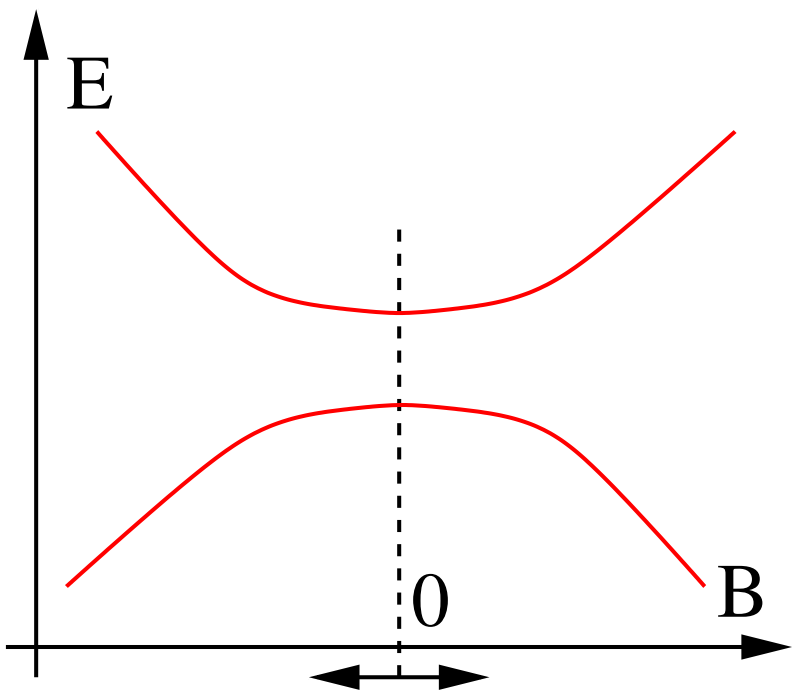
Investigation of decoherence of a subsystem if the combined system (including bath) is evolved via the time-dependent Schrödinger equation.

Employed measure of decoherence: reduced density matrix

$$\underset{\sim}{\rho}_{\text{system}} = \text{Tr}_{\text{bath}}\left(\underset{\sim}{\rho}\right)$$

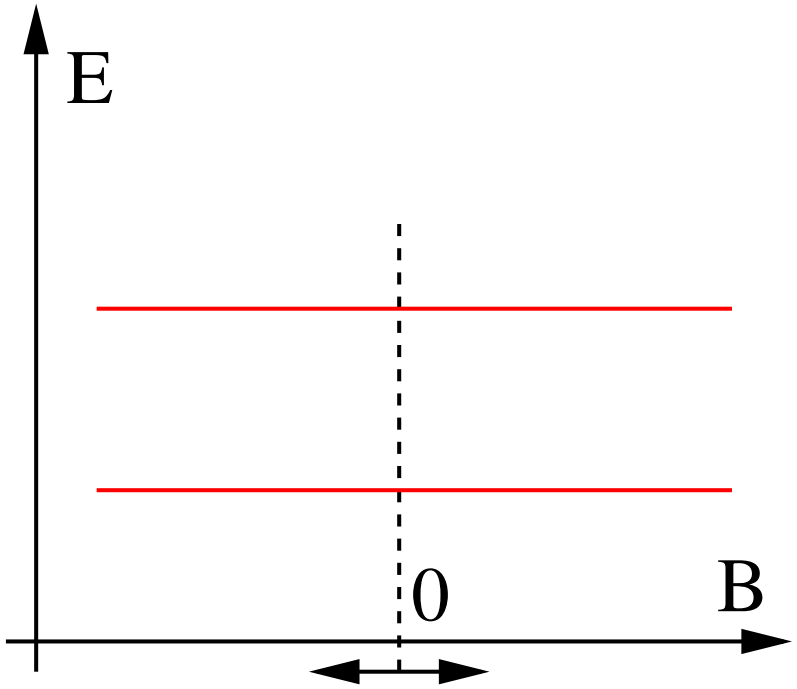
Typicality: unitary-time evolution of pure state approximates dynamics in environment.

Concept of clock transitions

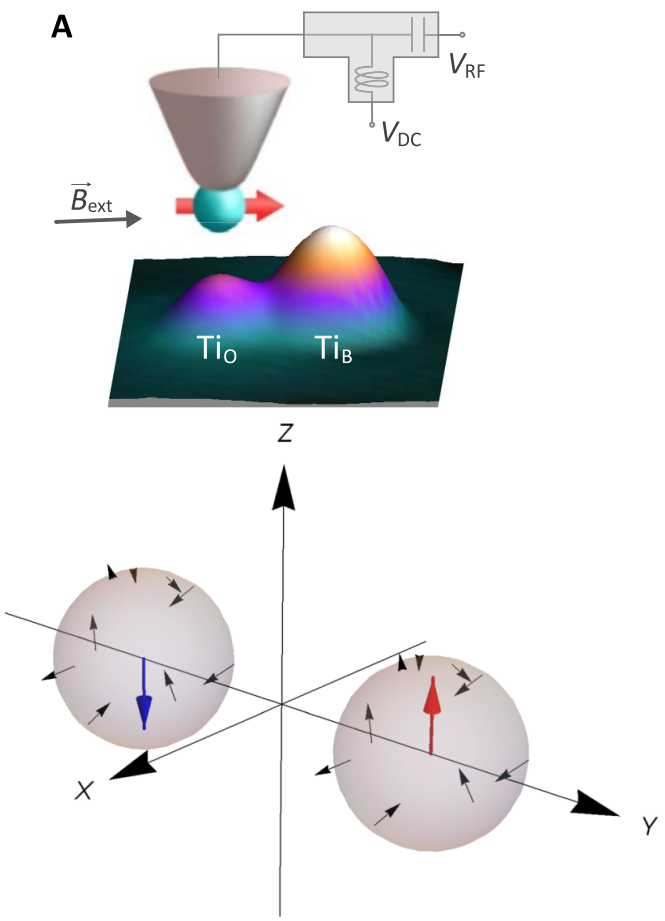


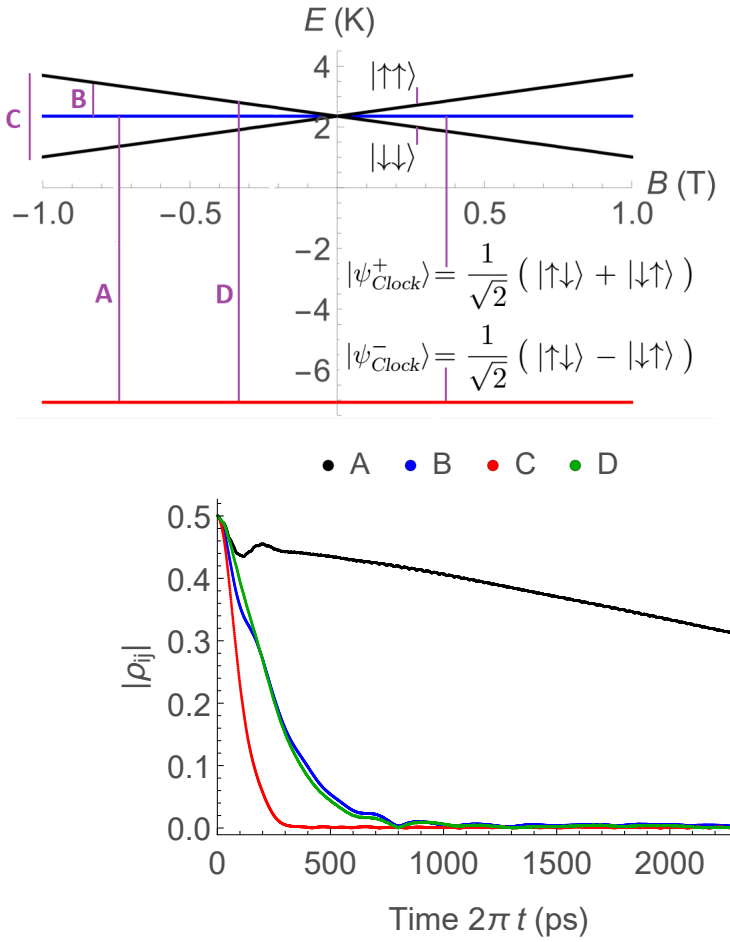
Fluctuations of B produce little effect on dynamics of superposition since ΔE of clock transition is independent of field at $B = 0$, at least to some order of a Taylor expansion.

Perfect clock transitions



Fluctuations produce very small effect on superposition since ΔE of transition is *totally* independent of field.

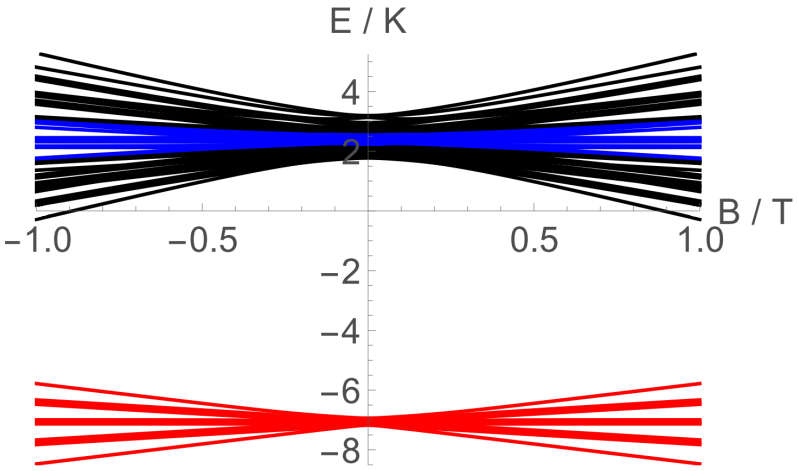




P. Vorndamme, J. Schnack, Phys. Rev. B 101, 075101 (2020)

Y. Bae, K. Yang, P. Willke, T. Choi, A. J. Heinrich, and C. P. Lutz, Sci. Adv. 4, eaau4159 (2018)

Decoherence of clock transitions III

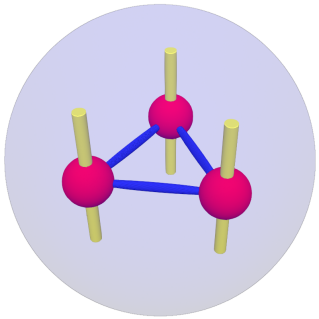


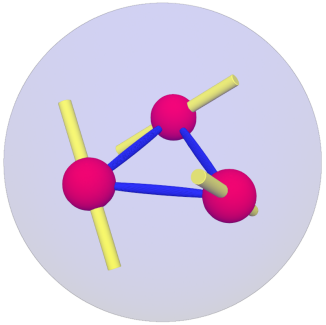
Single-particle/mean-field picture only valid for small couplings to a few bath spins.

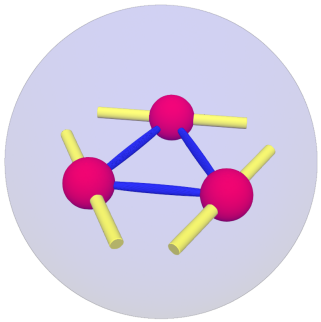
Initial product state entangles in the course of time. Eigenstates of the full Hamiltonian loose clock property.

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

Clock transitions with toroidal magnetic molecules







Model Hamiltonian II

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

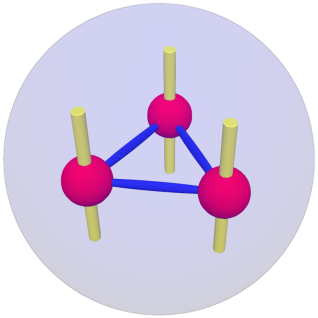
Dipolar interactions with and among $8\ldots10$ bath spins.

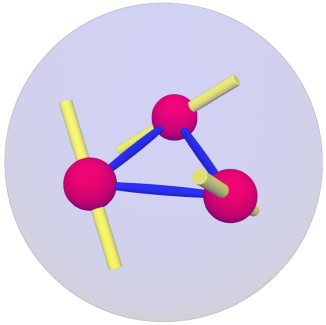
Investigation as function of tilt angle

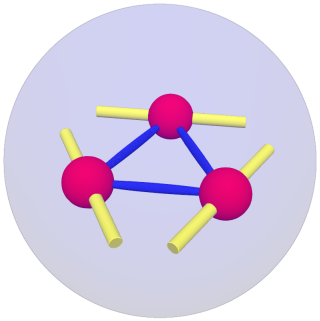
- various clock transitions of the spectrum,
- various arrangements of the decohering bath.

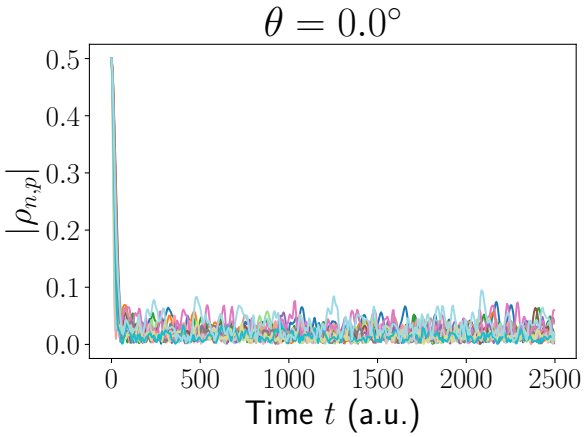
K. Irländer, J. Schnack, arXiv:2211.07281.

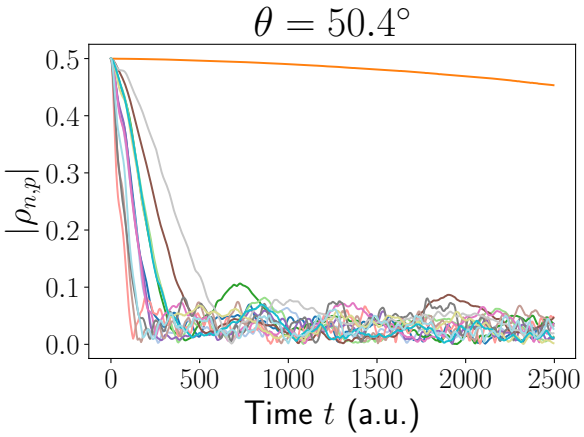
Clock transitions with toroidal magnetic molecules

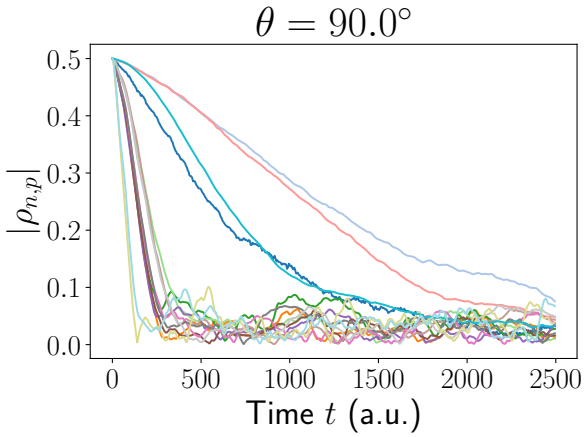






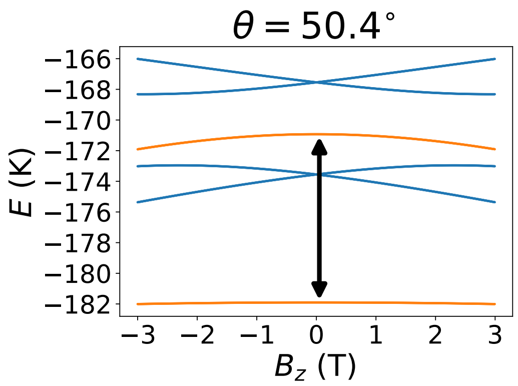


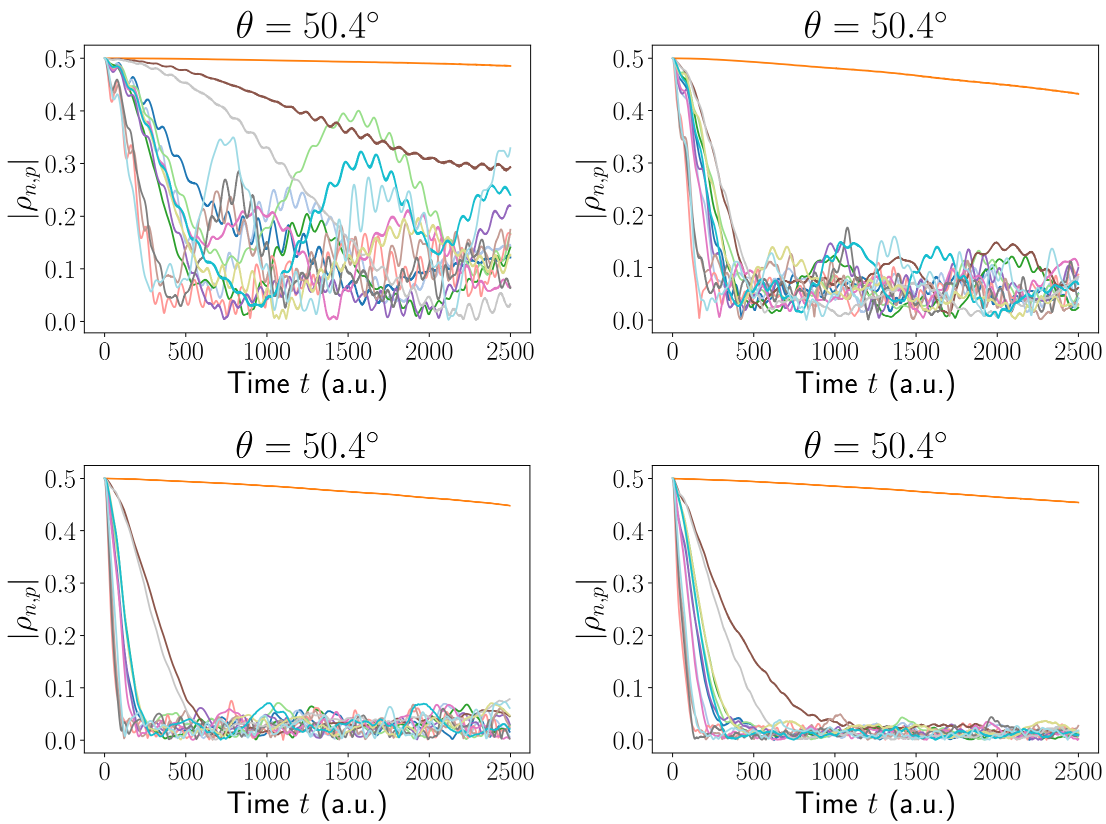




K. Irländer, J. Schnack, arXiv:2211.07281.

Clock transitions with toroidal magnetic molecules

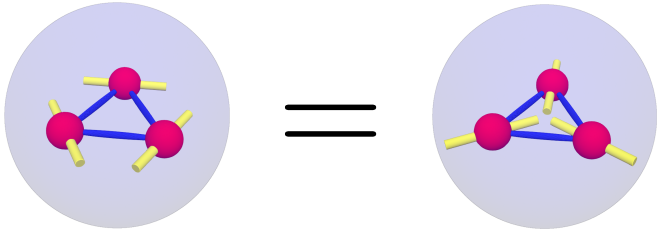


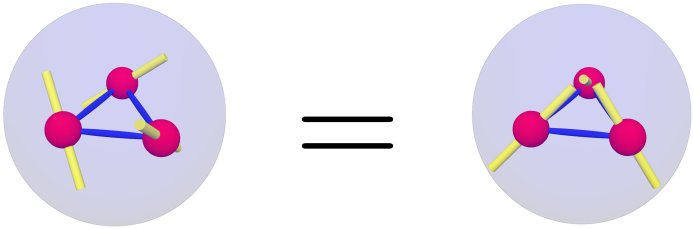


Decoherence as function of size of the bath (4, 6, 8, 10).

K. Irländer, J. Schnack, arXiv:2211.07281.

Clock transitions with toroidal magnetic molecules





Decoherence of toroidal magnetic molecules

- Toroidal structure irrelevant.
- Canted, near orthogonal anisotropy axes often optimal.
- Dipolar interaction between system spins does not alter the picture.

K. Irländer, J. Schnack, arXiv:2211.07281.

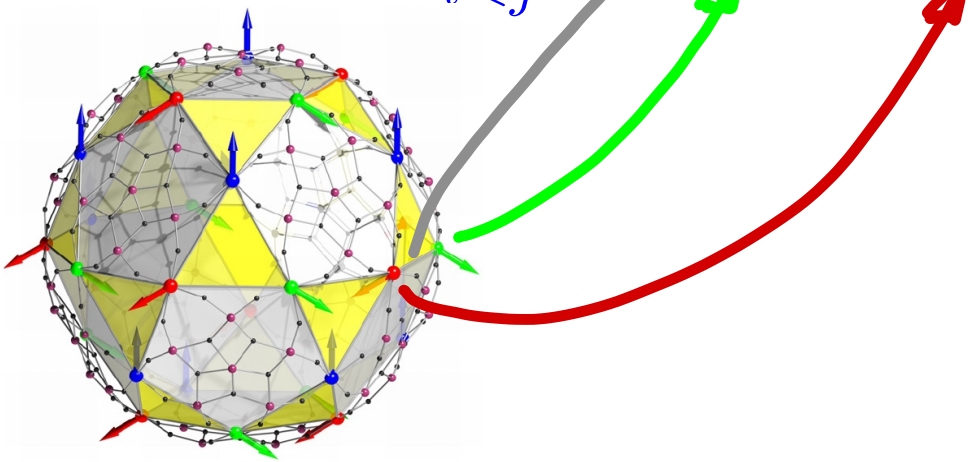
no time left – no magic

Typicality approach to molecular magnetism

You have got an idea about the modeling!

Heisenberg Zeeman

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



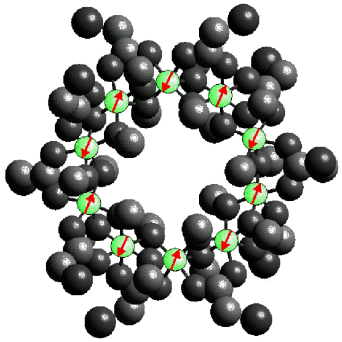
You have to solve the Schrödinger equation!

$$\underset{\sim}{H} \left| \phi_n \right\rangle = E_n \left| \phi_n \right\rangle$$

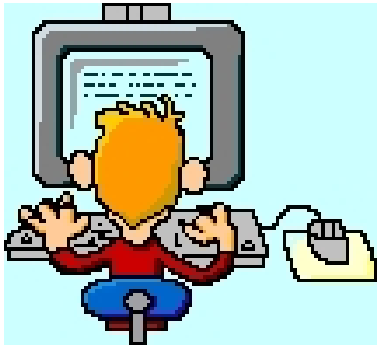
Eigenvalues E_n and eigenvectors $\left| \phi_n \right\rangle$

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

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

Can we evaluate the partition function

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

without diagonalizing the Hamiltonian?

Yes, with magic!

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

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

$$O^{\mathrm{r}}(T,B) \approx \frac{\langle r | \underset{\sim}{Q} e^{-\beta \underset{\sim}{H}} | r \rangle}{\langle r | e^{-\beta \underset{\sim}{H}} | r \rangle} = \frac{\langle r | e^{-\beta \underset{\sim}{H}/2} \underset{\sim}{Q} e^{-\beta \underset{\sim}{H}/2} | r \rangle}{\langle r | e^{-\beta \underset{\sim}{H}/2} e^{-\beta \underset{\sim}{H}/2} | r \rangle}$$

- 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: $|r\rangle \equiv (T = \infty)$

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

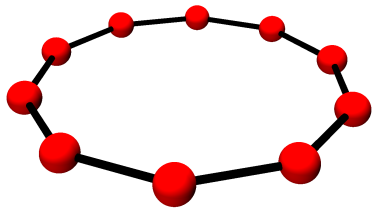
Partition function II: Finite-temperature Lanczos Method

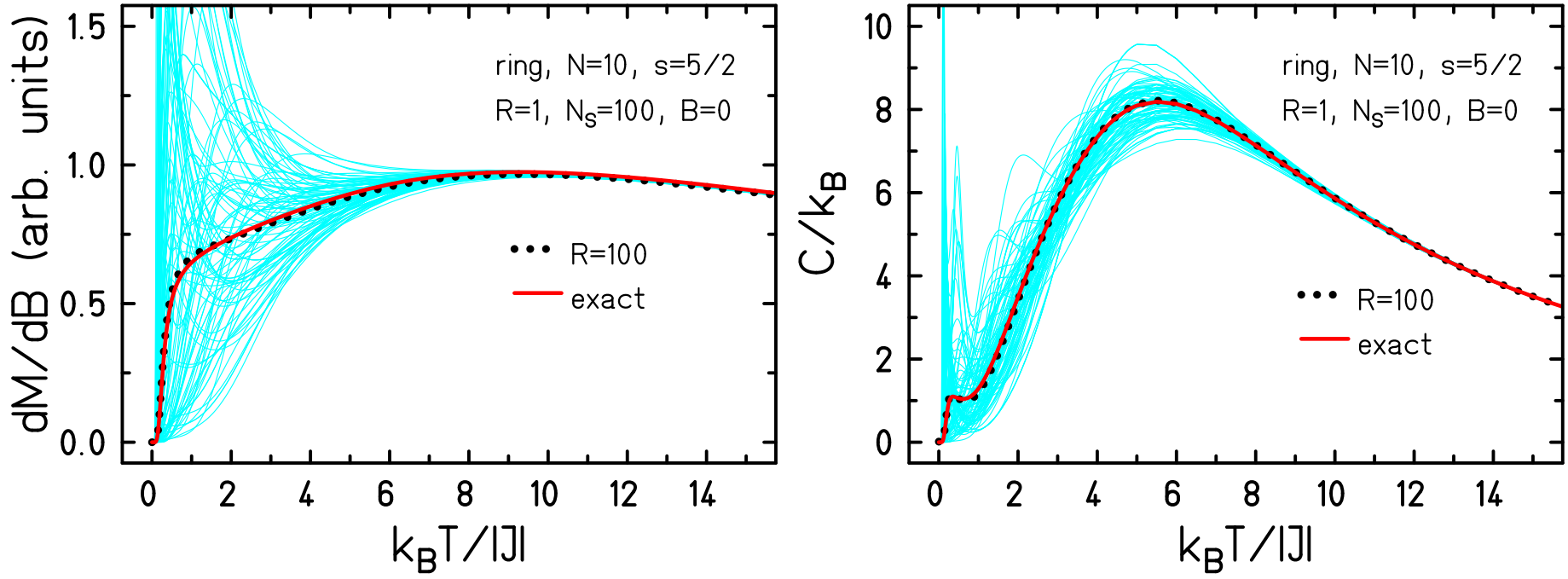
$$Z^{\mathrm{FTLM}}(T,B) \approx \frac{1}{R}\sum_{r=1}^{R}\sum_{n=1}^{N_L} e^{-\beta\epsilon_n^{(r)}} |\langle\, n(r)\,|\,r\,\rangle|^2$$

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

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

FTLM 1: ferric wheel



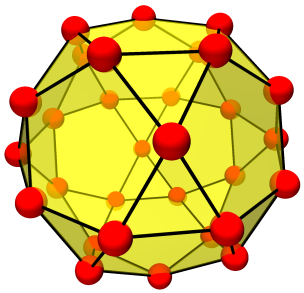


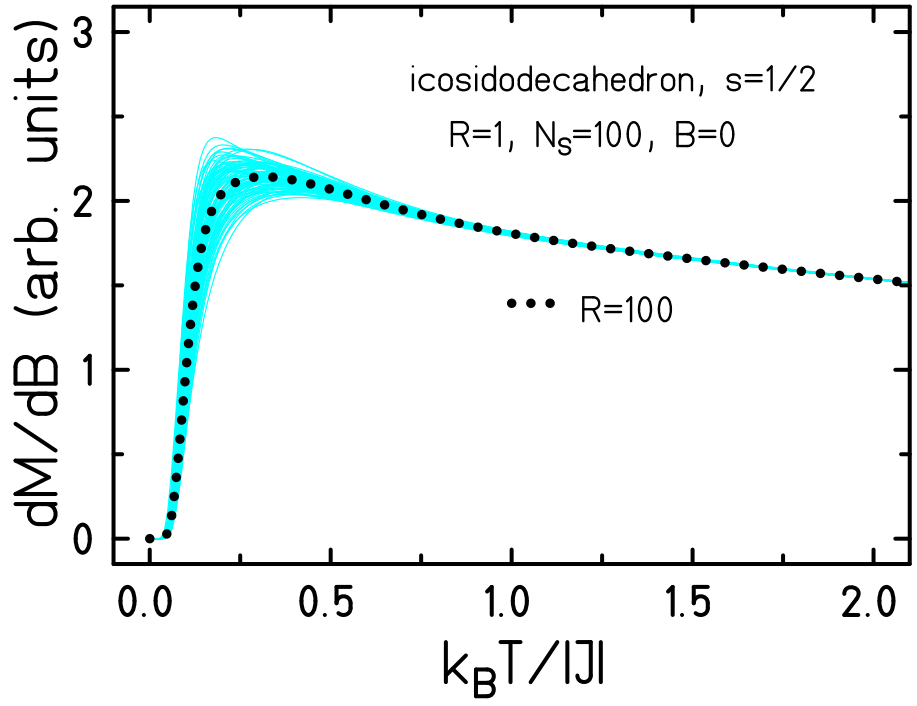
(1) J. Schnack, J. Richter, R. Steinigeweg, Phys. Rev. Research **2**, 013186 (2020).

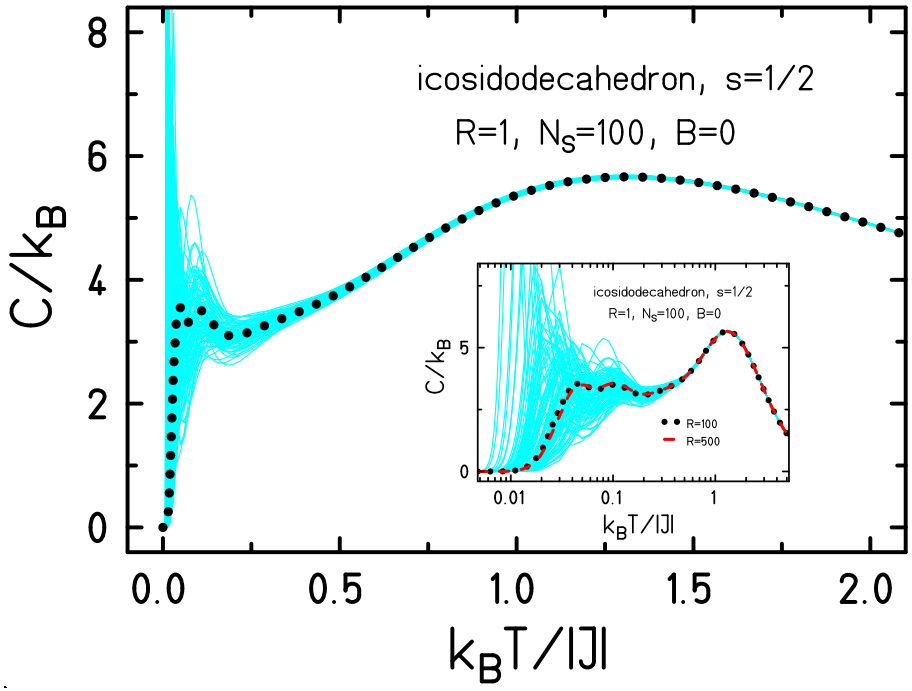
(2) SU(2) & D_2: R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403 (2010).

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

FTLM 2: icosidodecahedron



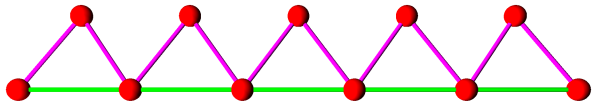


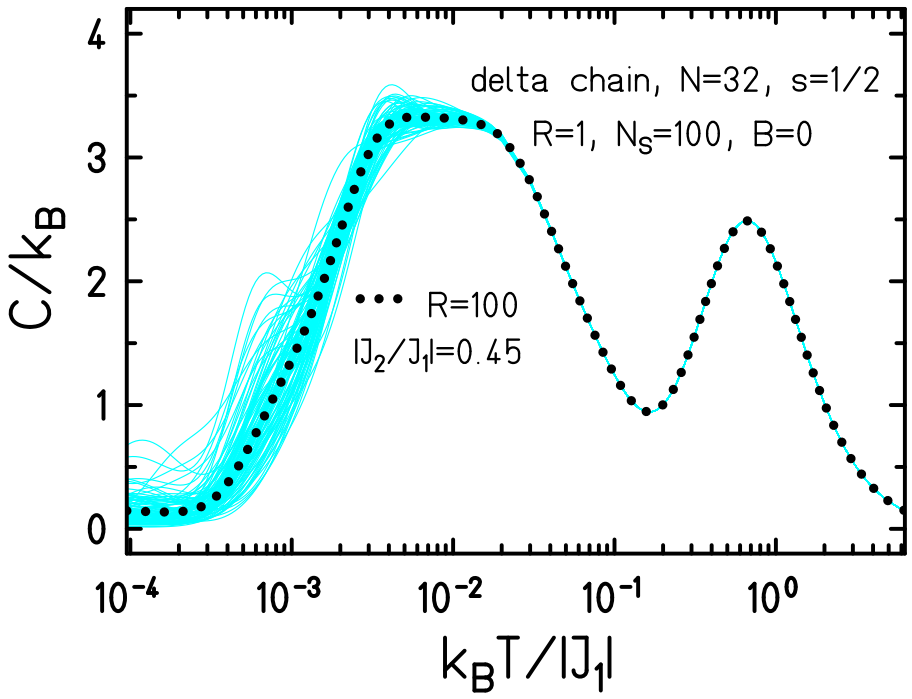


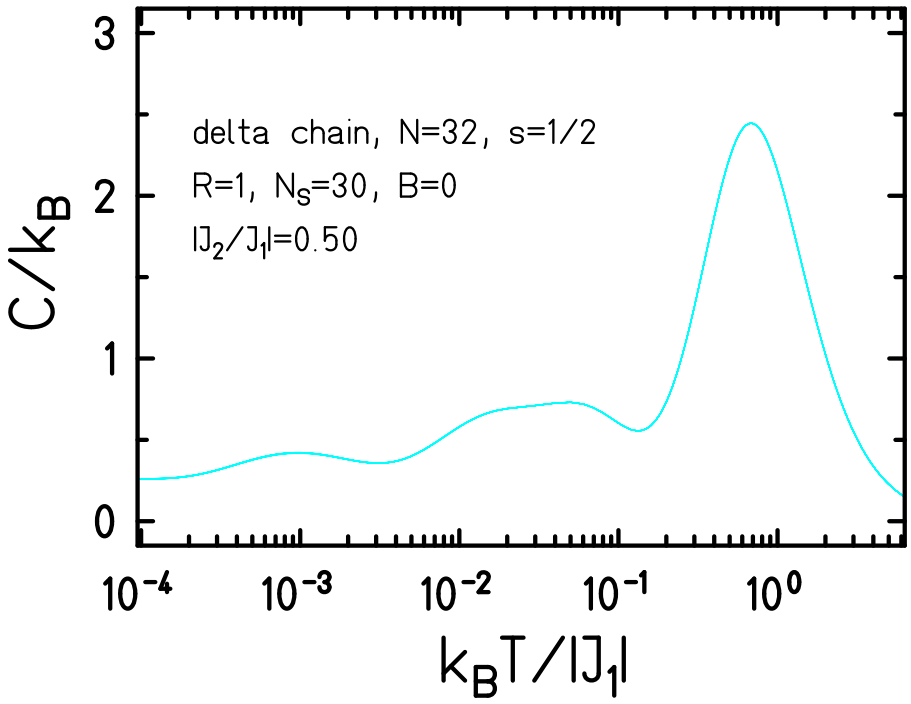
(1) J. Schnack, J. Richter, R. Steinigeweg, Phys. Rev. Research **2**, 013186 (2020).

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

FTLM 3: sawtooth chain







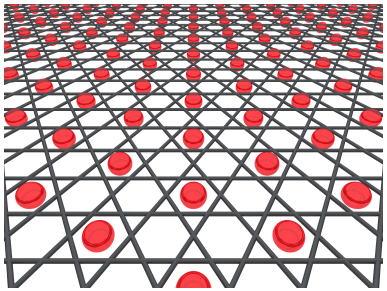
$|J_2/J_1| = 0.45$ – near critical, $|J_2/J_1| = 0.50$ – critical.

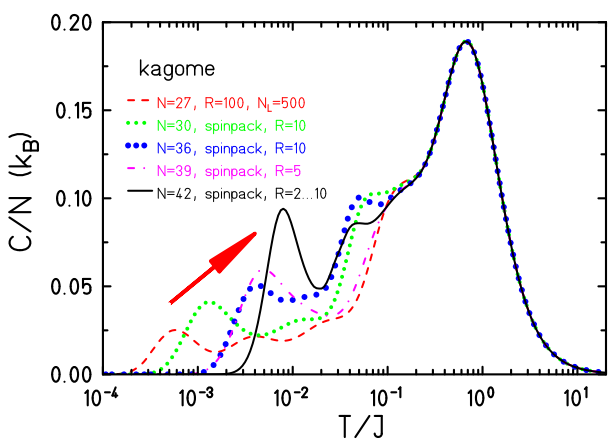
Frustration, technically speaking, works in your favour.

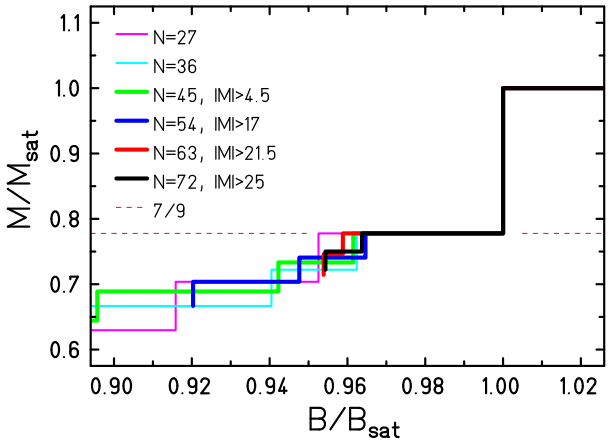
(1) J. Schnack, J. Richter, R. Steinigeweg, Phys. Rev. Research **2**, 013186 (2020)

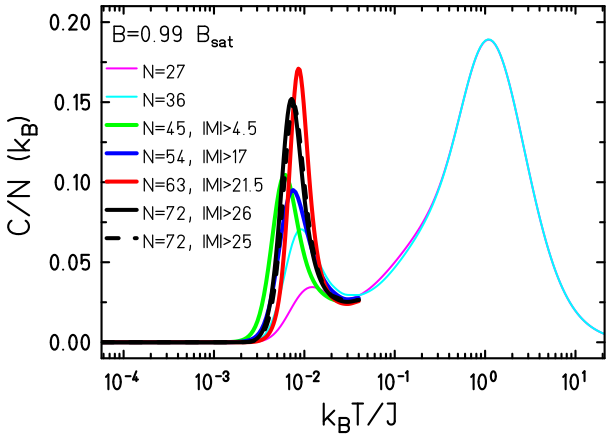
(2) J. Schnack, J. Richter, T. Heitmann, J. Richter, R. Steinigeweg, Z. Naturforsch. A 75, 465 (2020)

FTLM 4: kagome







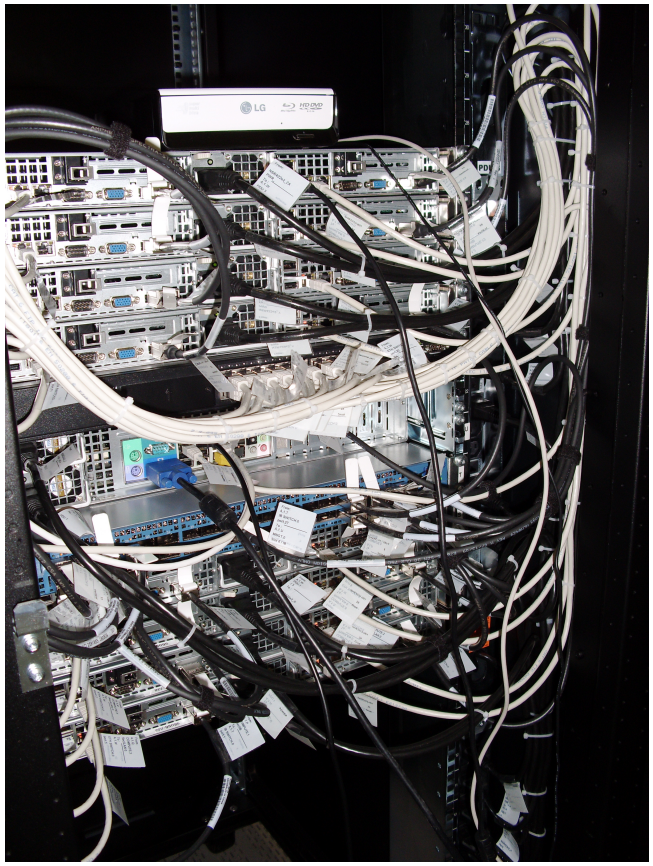


Specific heat of kagome with $N = 42$ – role of low-lying singlets, and magnon crystalization at high field.

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

(2) J. Schnack, J. Schulenburg, A. Honecker, J. Richter, Phys. Rev. Lett. 125, 117207 (2020)

Summary



- Magnetic molecules for storage, q-bits, MCE, and since they are nice.
- Toroidal magnetic molecules: perspectives not clear.
- Magnetism is much richer and more complicated than shown here. Talk focused on 3d ions with weak spin-orbit interaction.
- Typicality is a powerful approach.
- I could address Kramers systems at the black-board.

Many thanks to my collaborators







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Thank you very much for your attention.

The end.

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