Bielefeld theorists go Karlsruhe: Challenges and chances of 4f molecules

Jürgen Schnack, K. Irländer, D. Pister, J. Waltenberg, D. Westerbeck

Department of Physics – University of Bielefeld – Germany

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

Seminar talk, KIT
Karlsruhe, Germany, 29 April 2025

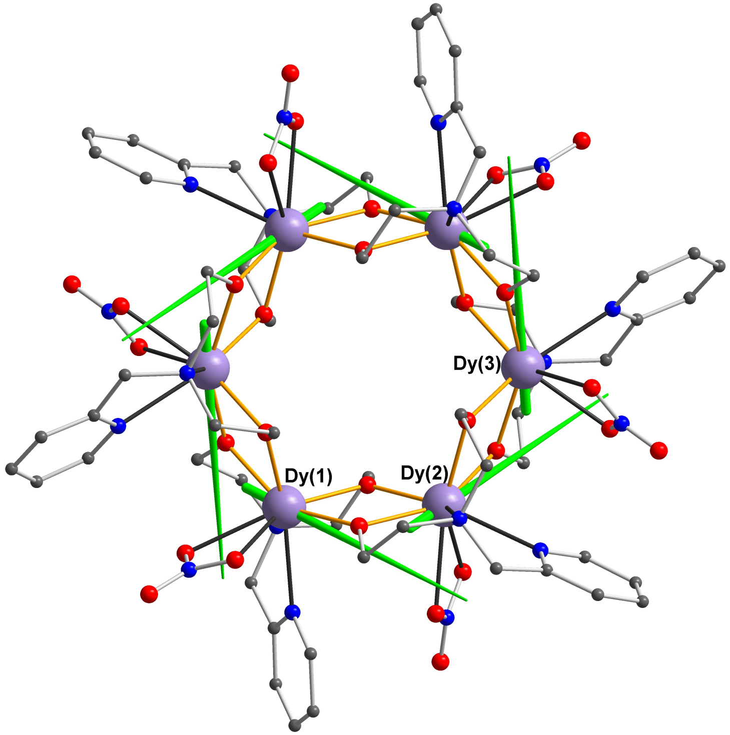
UNIVERSITÄT BIELEFELD
Fakultät für Physik

DFG

Funded by the European Union

lrz

Problem I: Can you please model this molecule for us?



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. Toroidal magnetic molecules
2. Bistability, tunneling, and stability
3. Clock transitions and decoherence
4. FTLM for very anisotropic spin systems

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

Toroidal magnetic molecules

Imagine . . .

Imagine someone tells you that
toroidal magnetic molecules
are superb building blocks
of quantum devices.

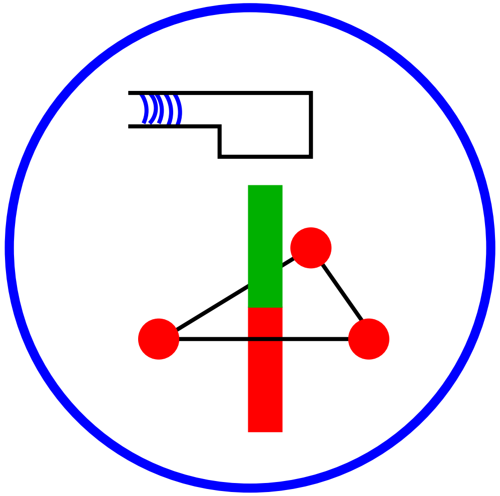
Would you buy one?

And, better don't ask ChatGPT.

Or would you first check such molecules?

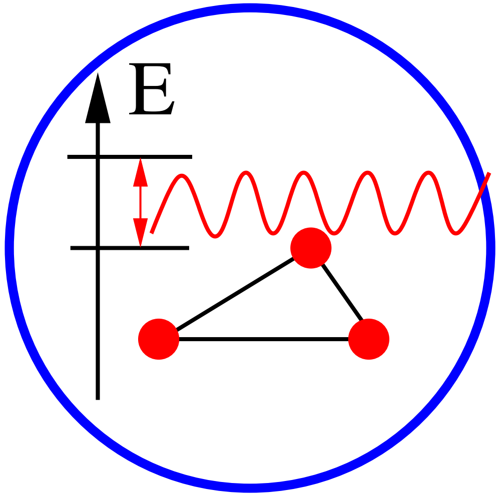
And if, what would you investigate?

Quantum devices – figures of merit



Memory unit

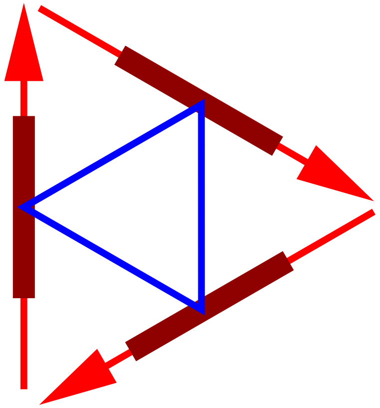
- requires bistability
- problem 1: quantum tunneling
- problem 2: stability against field fluctuations

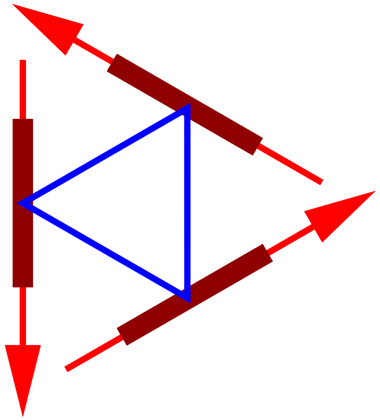


Q-bit

- requires coherence
- problem decoherence

Torodial magnetic molecules I





Model Hamiltonian

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

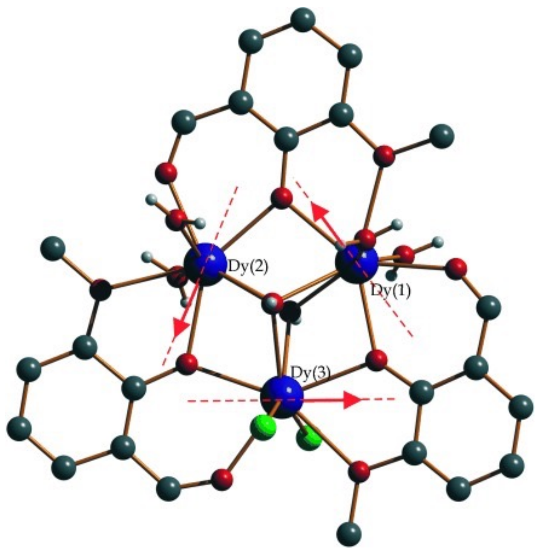
Toroidal magnetic moment

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

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

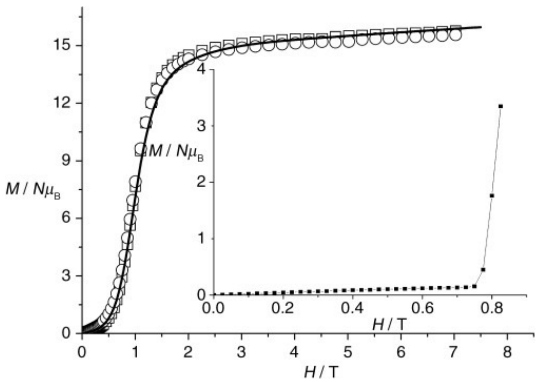


The Origin of Nonmagnetic Kramers Doublets in the Ground State of Dysprosium Triangles: Evidence for a Toroidal Magnetic Moment (1)

Kramers doublet – two states

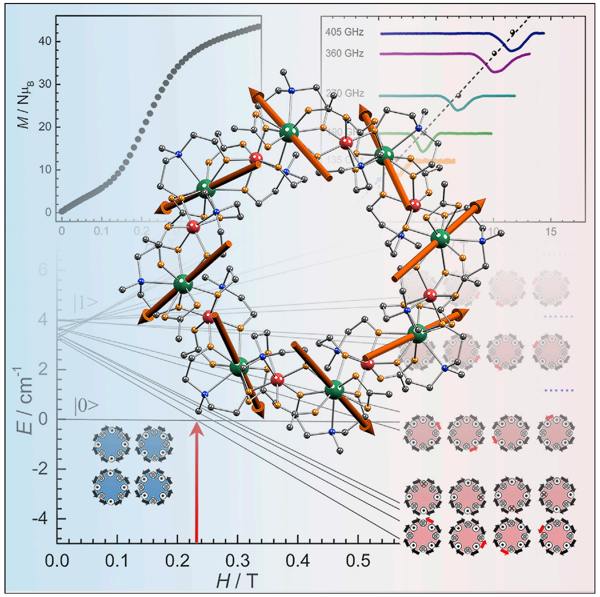
Toroidal magnetic moment – left/right rotating

Vanishing moment reduces crosstalk!



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

Torodial magnetic molecules III – Example 2



Single-Molecule Toroic Design through Magnetic Exchange Coupling (1)

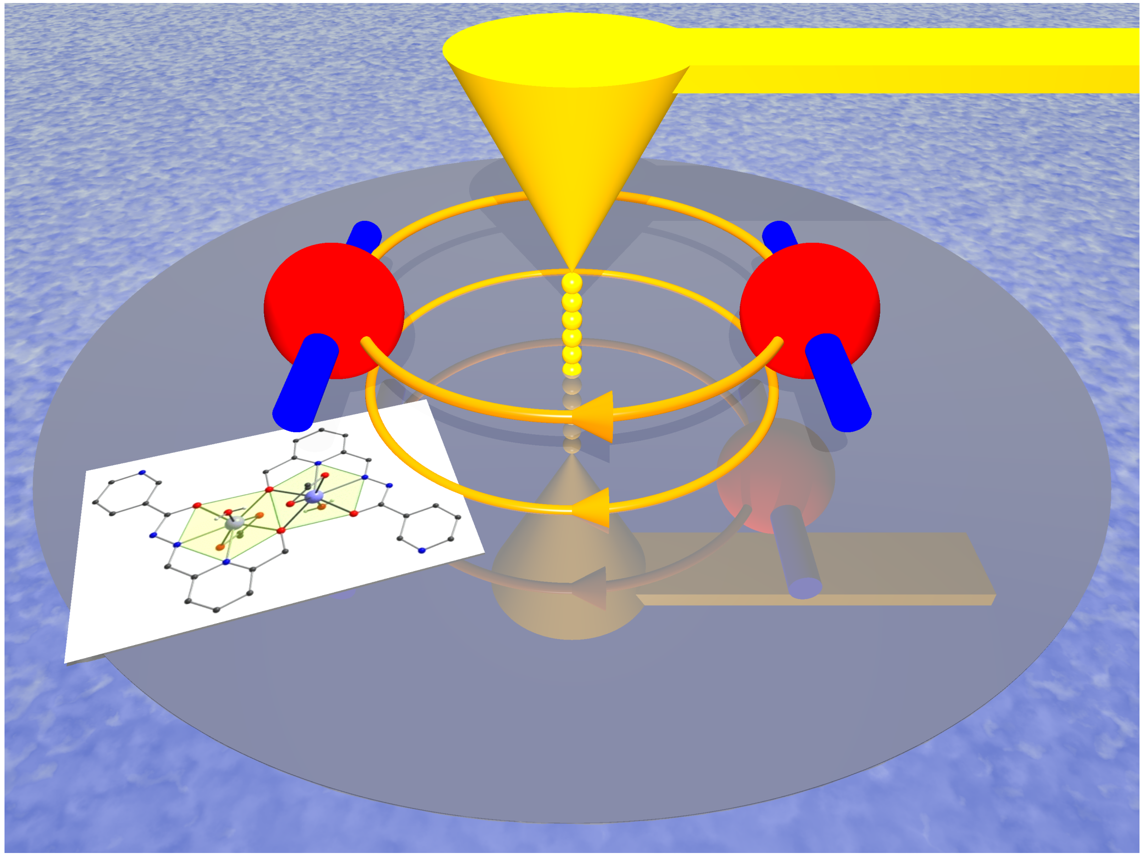
Rational design of toroidal molecules?

Role of exchange interaction?

Why here switchable by a homogeneus field?

(1) H.-L. Zhang, Y.-Q. Zhai, L. Qin, L. Ungur, H. Nojiri, and Y.-Z. Zheng, Matter **2**, 1481 (2020).

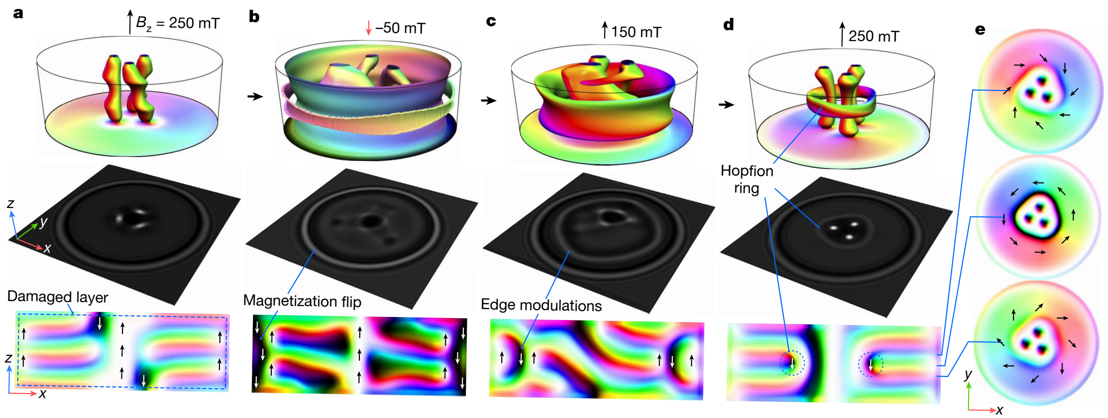
Torodial magnetic molecules IV – switching???



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

Kieran Hymas, Alessandro Soncini, arXiv:2504.08701: switching by homogeneous field + EPR.

Torodial magnetic molecules V – skyrmions and hopfions



Toroidal structures are *en vogue* (⇒ Manfred Fiebig):

- no/small crosstalk to neighboring units,
- may be of topological nature, i.e., protected, as e.g. skyrmions or hopfions,
- topological toroidal structures always build on the Dzyaloshinskii-Moriya interaction.

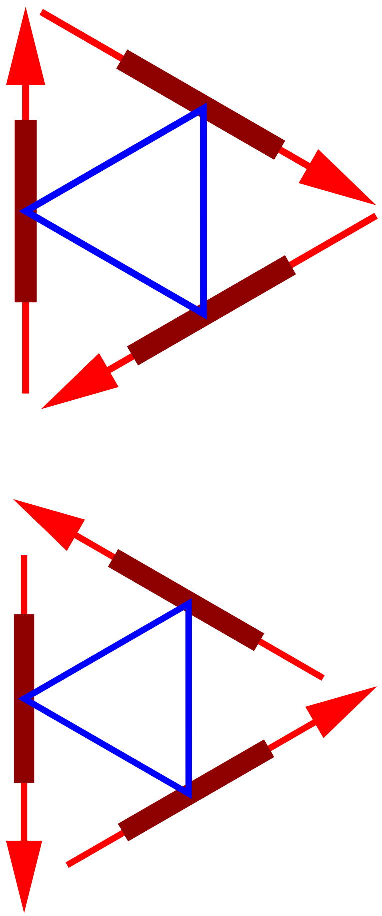
F. Zheng, N. S. Kiselev, F. N. Rybakov, L. Yang, W. Shi, S. Blügel, and R. E. Dunin-Borkowski, Nature **623**, 718 (2023).

V. Lohani, C. Hickey, J. Masell, and A. Rosch, Phys. Rev. X **9**, 041063 (2019).

Toroidal magnetic molecules

– very general thoughts –

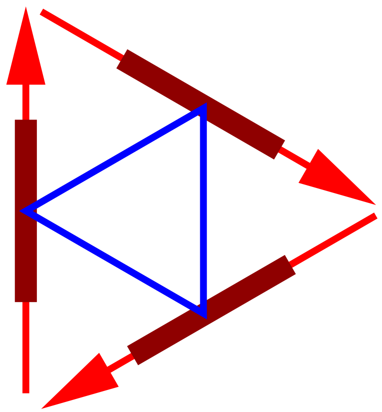
Torodial magnetic molecules – quantum aspects I

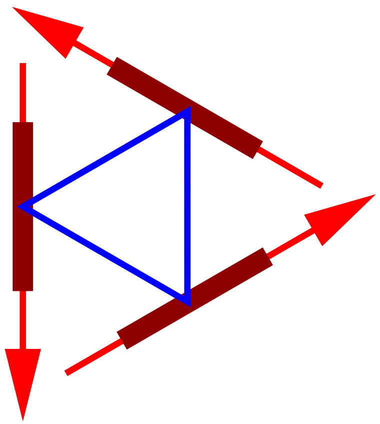


What is wrong with the picture on the left?

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

Torodial magnetic molecules – quantum aspects I





What is wrong with the picture on the left?

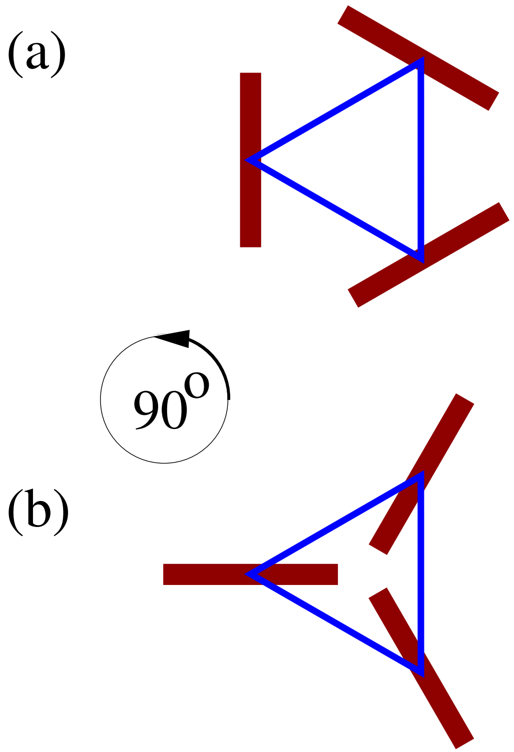
These classical/broken-symmetry states are (in most cases) not eigenstates in molecules!!!

Typically, eigenstates are superpositions such as

$$| \Psi \rangle \propto | \circlearrowright \rangle \pm | \circlearrowleft \rangle$$

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

Torodial magnetic molecules – quantum aspects II



Model Hamiltonian has got a symmetry!

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

One can rotate all anisotropy axes/tensors collectively together with the field about the same axis without altering the spectrum and many properties!

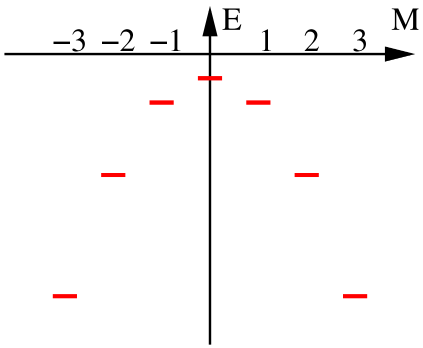
Toroidicity does not constitute something new for this Hamiltonian.

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

Bistability, tunneling, and stability against field fluctuations

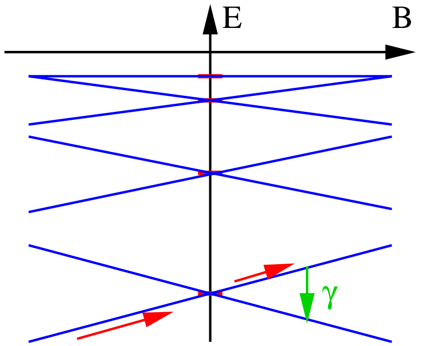
(Remember what we know from SMMs!)

Single-ion anisotropy and bistability I – good SMM



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

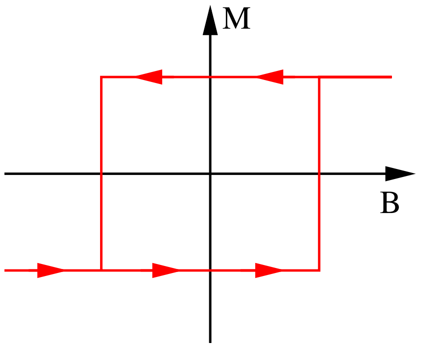
$D_i < 0$ collinear easy axes



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

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

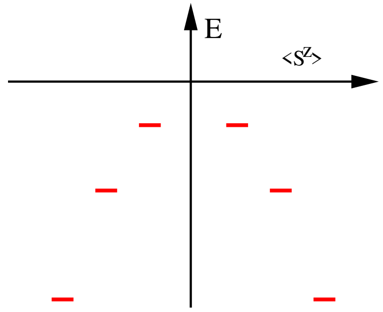
(strong exchange limit)



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

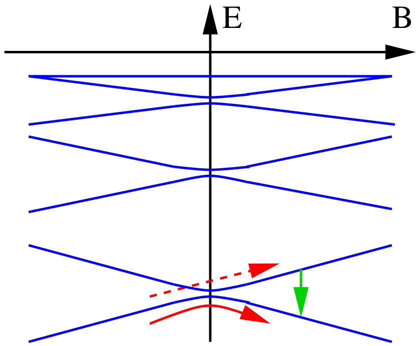
$\Rightarrow$ level crossings at $B = 0$
$\Rightarrow$ good hysteresis

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



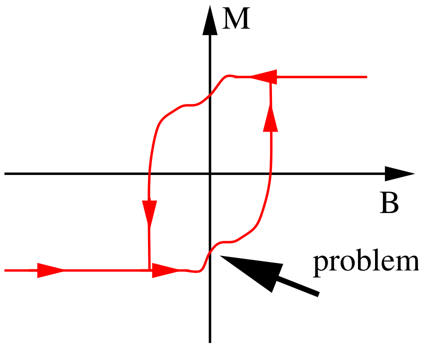
$$\underset{\sim}{H} = \sum_i \underset{\sim}{\vec{s}}_i \cdot \mathbf{D}_i \cdot \underset{\sim}{\vec{s}}_i + \mu_B B \sum_i g_i \underset{\sim}{s}_i^z + \underset{\sim}{H}_{\text{ferro int}}$$

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



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

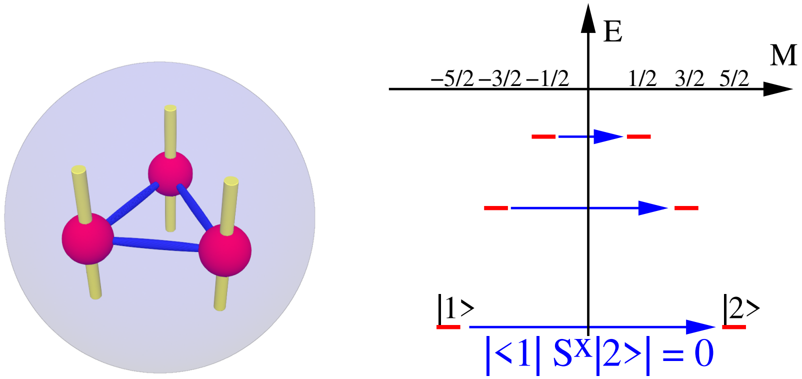
low-lying eigenvalues only approx. parabola (if at all)

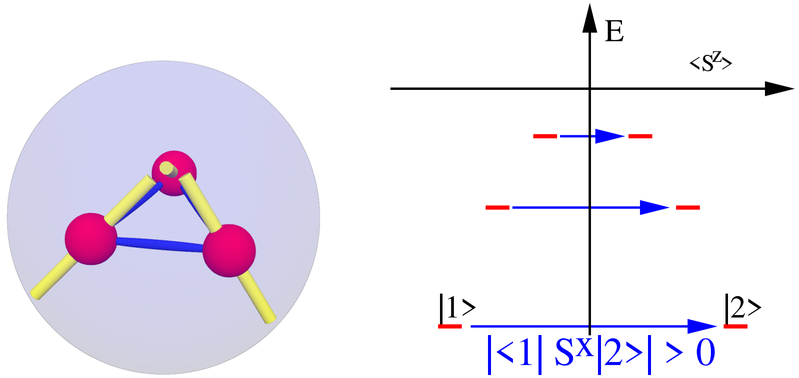


IMPORTANT: $[\underset{\sim}{H}, \underset{\sim}{S}^z] \neq 0$

$\Rightarrow$ 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

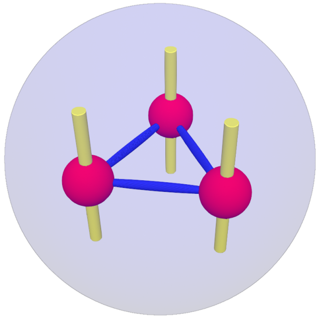
Non-collinear easy axes:

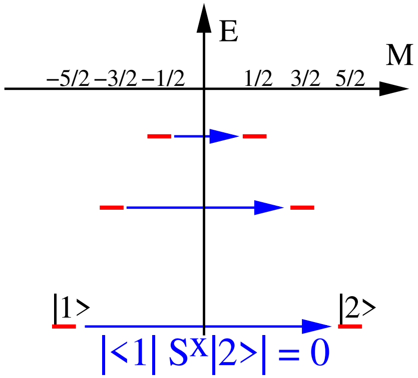
⇒ Tunneling gap for integer spin

⇒ (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).

Single-ion anisotropy and bistability IV – stability

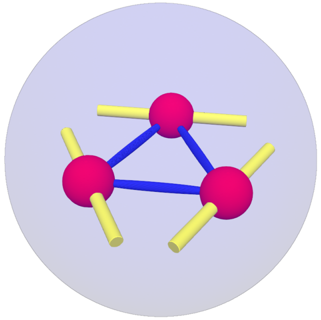


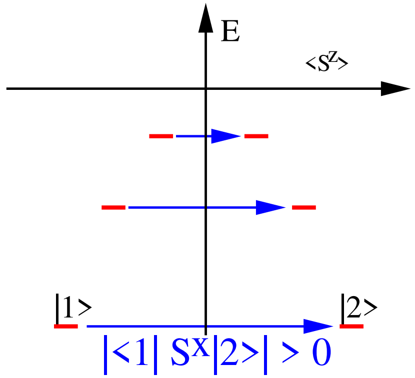


Collinear easy axes:

⇒ No tunneling gap

⇒ No transition matrix elements





Non-collinear easy axes:

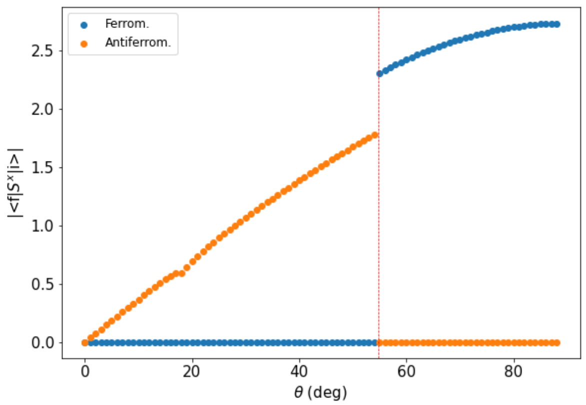
⇒ Tunneling gap for integer spin

⇒ (large) Transition matrix elements

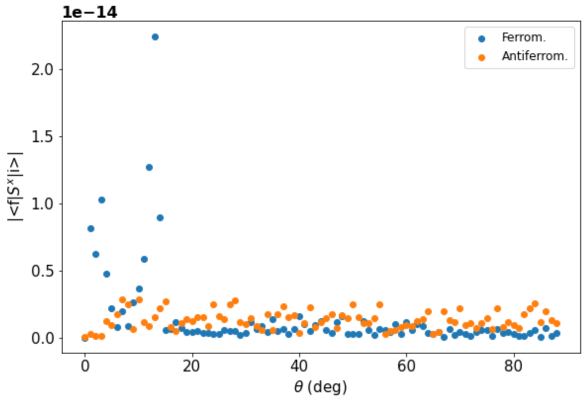
Toroidal moments are here!

Toroidal magnetic moments – There is hope!

Trimer s=2.5



Hexagon s=1.5



For gapped systems:

(1) Gap shrinks with increasing anisotropy!

(2) Gap shrinks with increasing spin!

(for all systems we investigated so far)

Transition matrix element:

(1) Vanishes for certain canting angles ($N = 2, 3, 4$)!

(2) Vanishes completely ($N = 6$)!

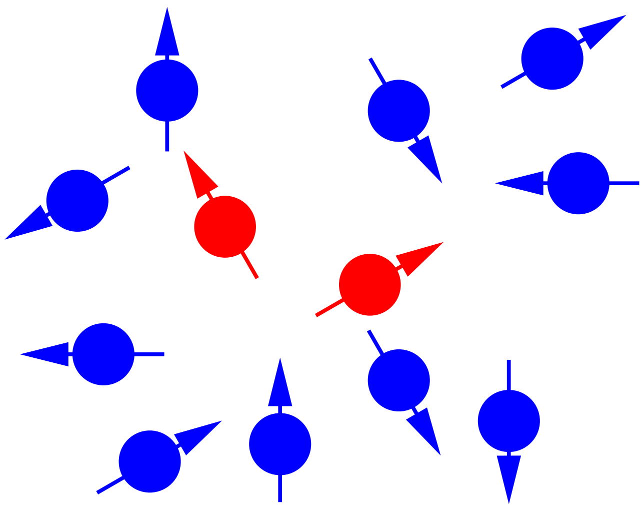
(work in progress)

$\Rightarrow$ Larger rings ($N > 4$) with larger spins might be preferential.

Master Theses of Daniel Pister and Jonas Waltenberg, Bielefeld University

Decoherence of (toroidal) clock transitions

Context



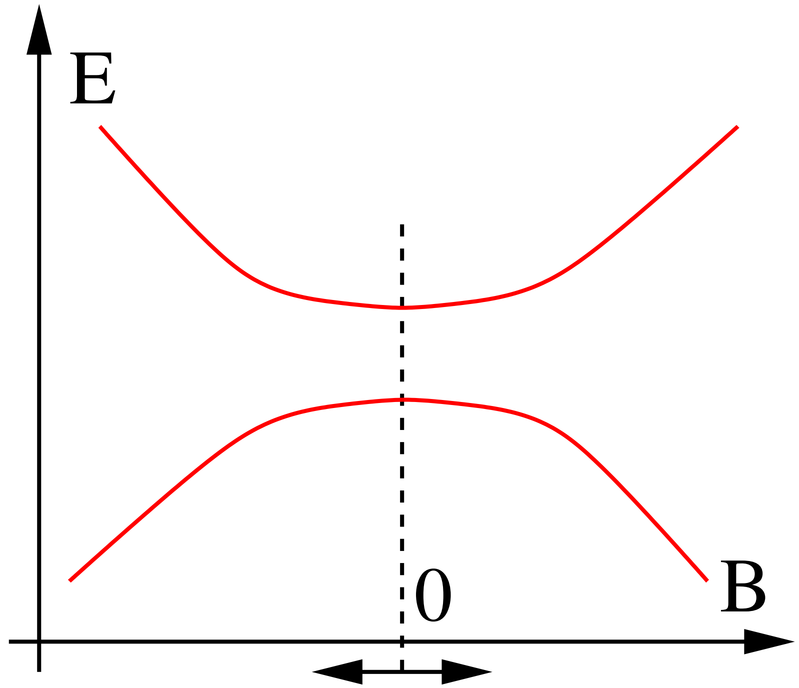
Investigation of decoherence of a subsystem if the combined system (including bath) is evolved via the time-dependent Schrödinger equation.

Employed measure of decoherence: reduced density matrix

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

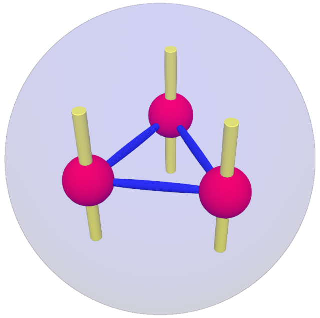
Typicality: unitary-time evolution of pure state approximates dynamics of density matrix.

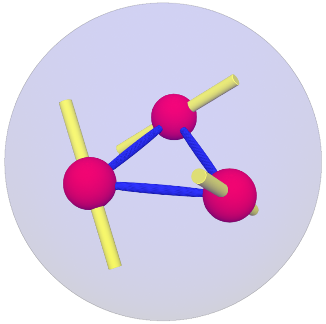
Concept of clock transitions

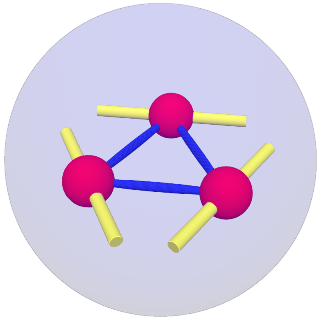


Fluctuations of B produce little effect on dynamics of superposition since ΔE of clock transition is independent of field at $B = 0$, at least to some order of a Taylor expansion.

Clock transitions with toroidal magnetic molecules







Model Hamiltonian II

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

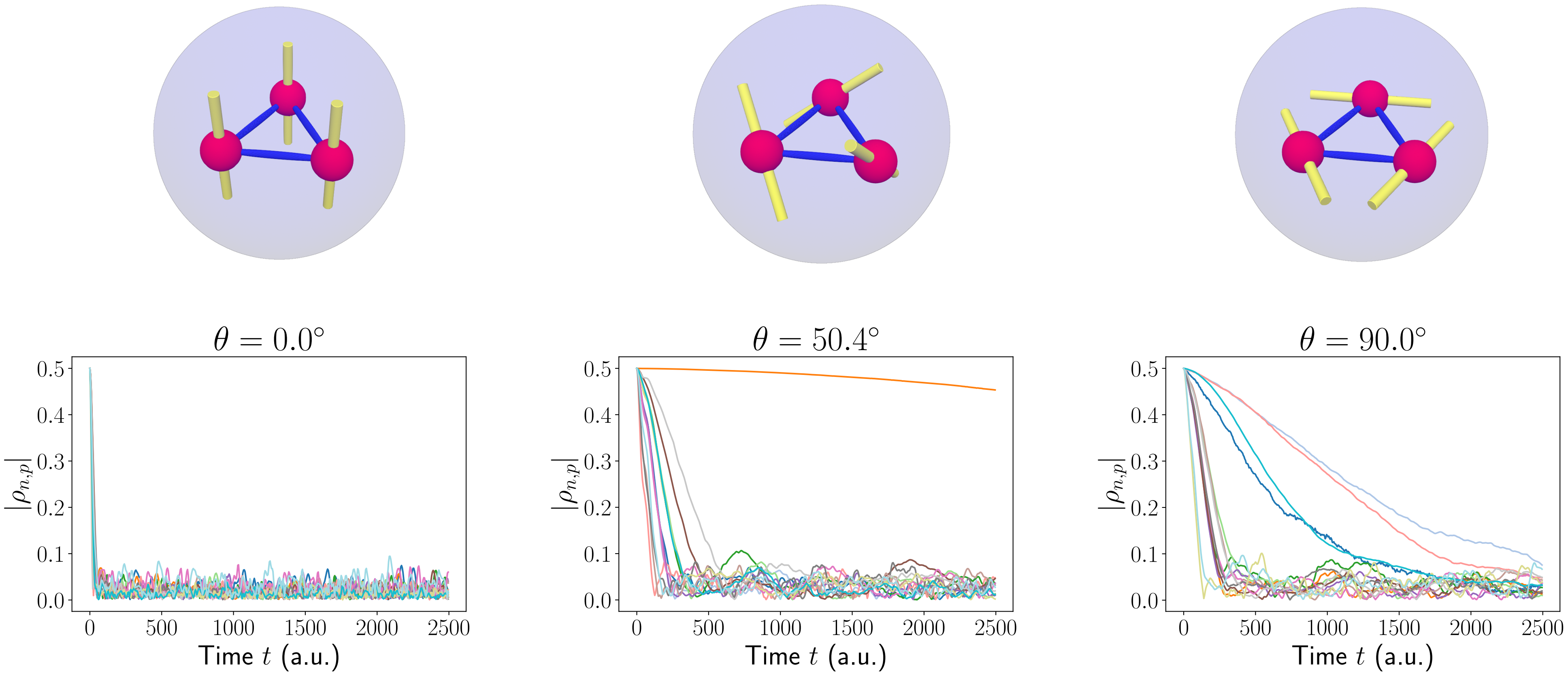
Reasonable parameters: weak J, strong D.
Dipolar interactions with and among $8 \dots 10$ bath spins.

Investigation as function of tilt angle

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

K. Irländer, J. Schnack, Phys. Rev. Research **5**, 013192 (2023).

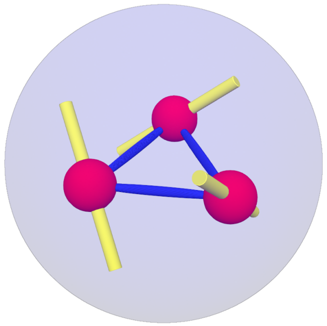
Clock transitions with toroidal magnetic molecules

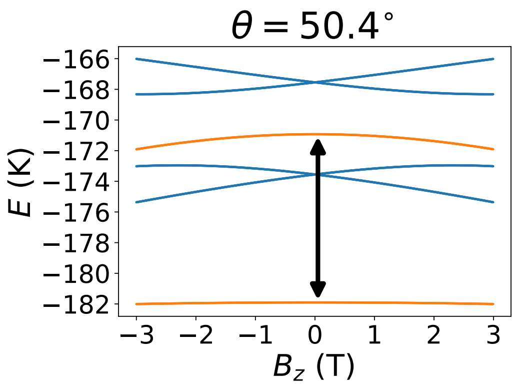


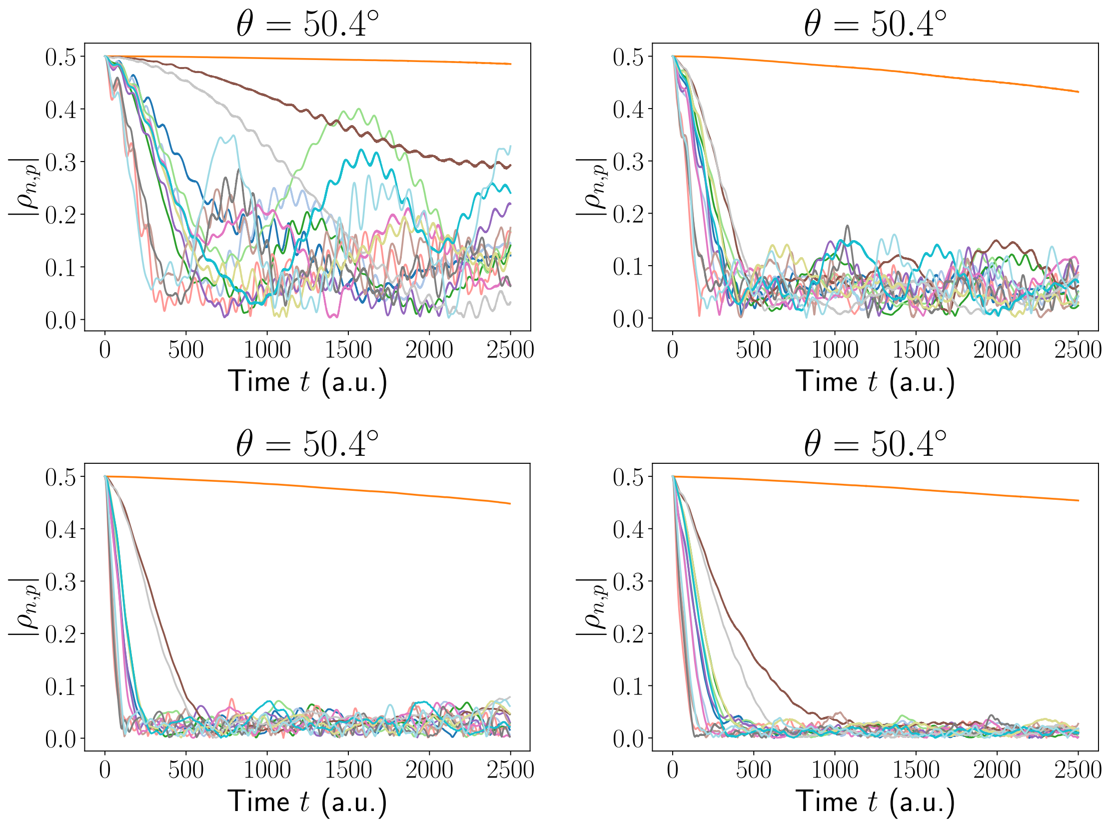
Time-evolution of all two-state superpositions of the lowest 6 states of the toroidal system (assuming we can excite them).

K. Irländer, J. Schnack, Phys. Rev. Research **5**, 013192 (2023).

Clock transitions with toroidal magnetic molecules



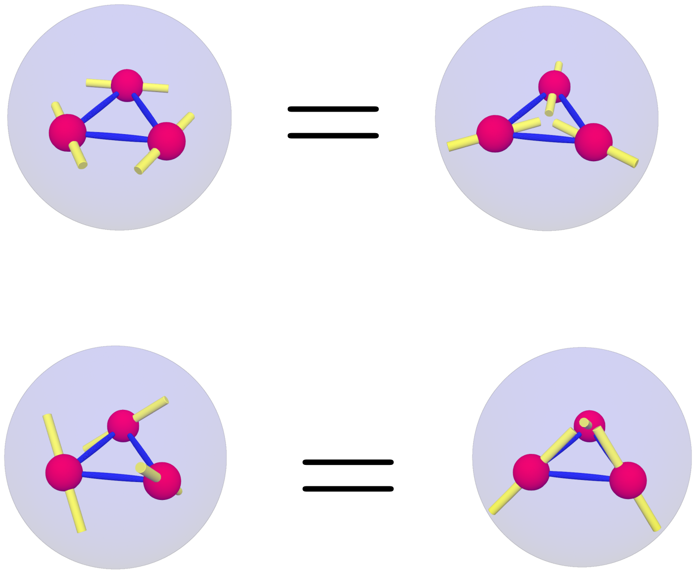




Decoherence as function of size of the bath (4, 6, 8, 10).

K. Irländer, J. Schnack, Phys. Rev. Research **5**, 013192 (2023).

Decoherence of toroidal magnetic molecules



- Toroidal structure irrelevant, i.e. not correlated with desired properties (for Heisenberg interactions and non-collinear easy axes).
- Canted, near orthogonal anisotropy axes optimal in our example, i.e., they show longest coherence.
- Dipolar interactions between system spins do not alter the picture.

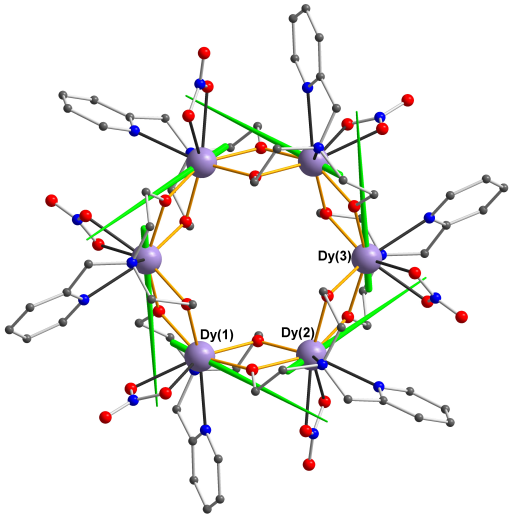
D. Pister, K. Irländer, D. Westerbeck, and J. Schnack, Phys. Rev. Research **4**, 033221 (2022).

K. Irländer, J. Schnack, Phys. Rev. Research **5**, 013192 (2023).

Typicality approach to molecular magnetism

Problem II: strong spin-orbit interaction

Lanthanides feature very strong spin-orbit interaction!



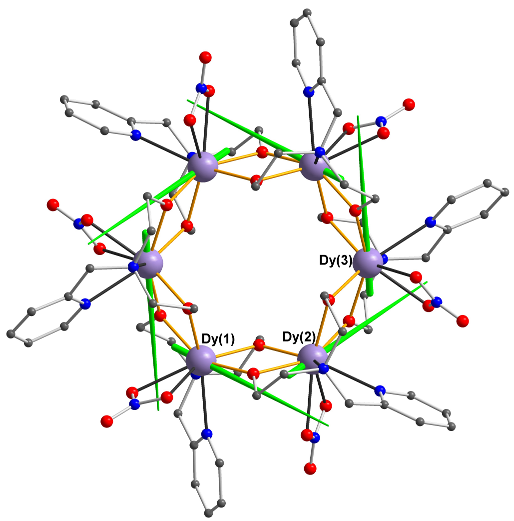
Possible modelling (by experts):

- CASSCF: wave function method, electrons and effective nucleus, quasi exact; restricted to one magnetic ion; little effective insight (1).
- Low-spin effective multicenter models with very anisotopic g-matrices; approximate. Single-ion anisotropy remodelled as Zeeman anisotropy for every energy eigenstate (1).

(1) Chibotaru, Ungur, Lunghi, Rajaraman, Soncini, . . .

Problem II: strong spin-orbit interaction

Lanthanides feature very strong spin-orbit interaction!



Possible modelling (by experts):

- CASSCF: wave function method, electrons and effective nucleus, quasi exact; restricted to one magnetic ion; little effective insight (1).

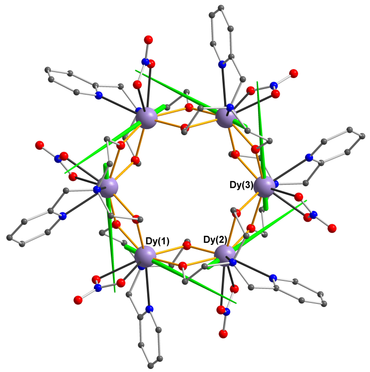
- Low-spin effective multicenter models with very anisotopic g-matrices; approximate. Single-ion anisotropy remodelled as Zeeman anisotropy for every energy eigenstate (1).

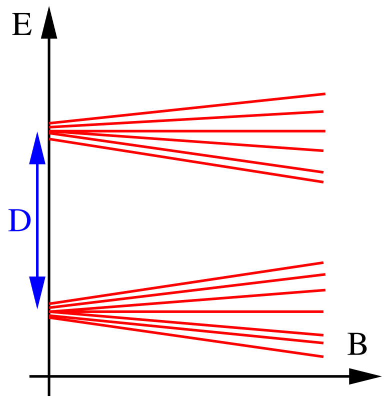
- Effective multicenter models formulated with j, strong-single ion anisotropy and isotropic g; approximate. Allows for more general single-ion anisotropies and, hopefully, better description of mixed 3d/4f systems.

(1) Chibotaru, Ungur, Lunghi, Rajaraman, Soncini, . . .

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.

Finite-temperature Lanczos method in one slide

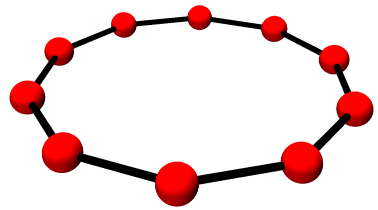
$$Z(T,B) \approx \langle\, r \,|\, e^{-\beta \underset{\sim}{H}} \,|\, r \,\rangle \approx \sum_{n=1}^{N_L} e^{-\beta \epsilon_n^{(r)}} |\langle\, n(r) \,|\, r \,\rangle|^2$$

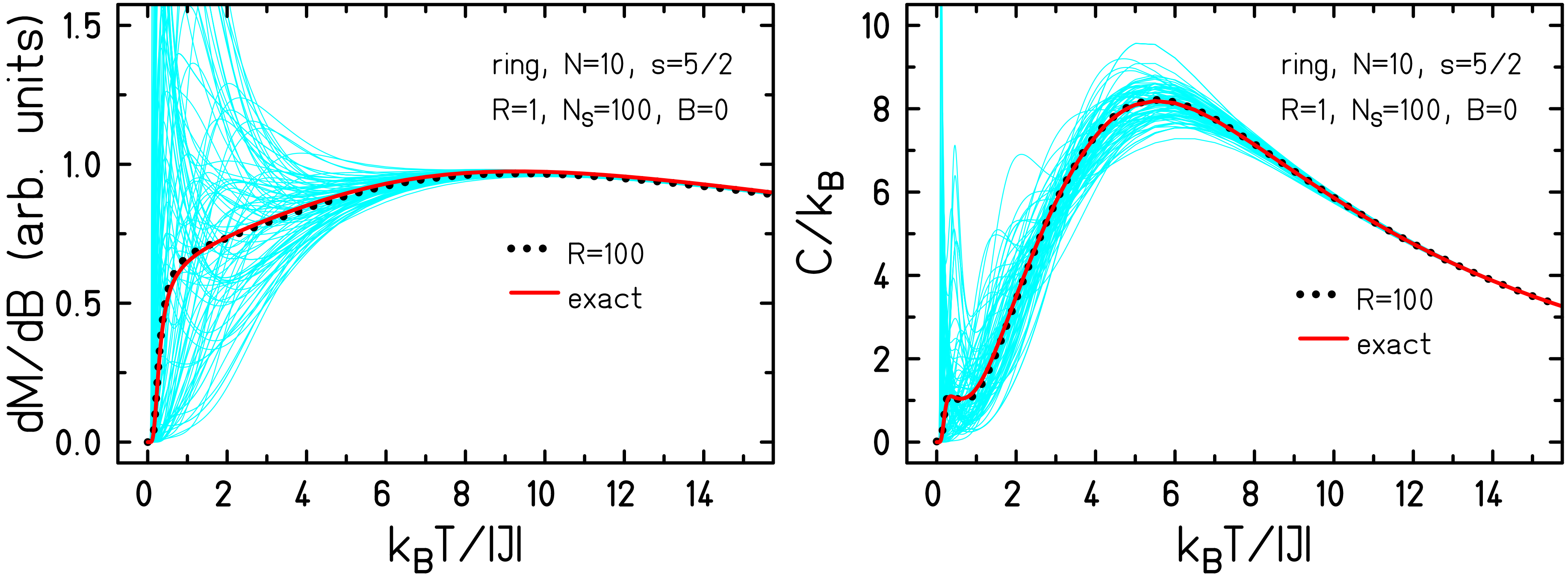
$$O^{\mathrm{r}}(T,B) \approx \frac{\langle\, r \,|\, \underset{\sim}{O} e^{-\beta \underset{\sim}{H}} \,|\, r \,\rangle}{\langle\, r \,|\, e^{-\beta \underset{\sim}{H}} \,|\, r \,\rangle}$$

- $|\, r \,\rangle$ 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



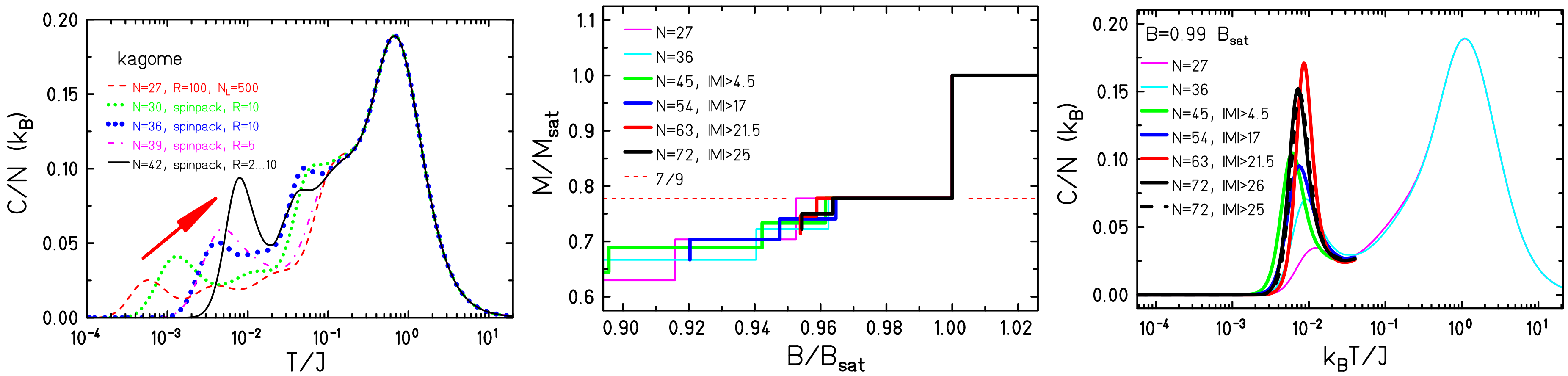


(1) J. Schnack, J. Richter, R. Steinigeweg, Phys. Rev. Research **2**, 013186 (2020).

(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)

FTLM 4: kagome (using spinpack)

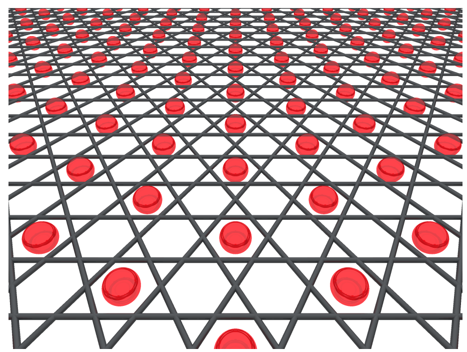


Specific heat of kagome with $N = 42$ – role of low-lying singlets

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

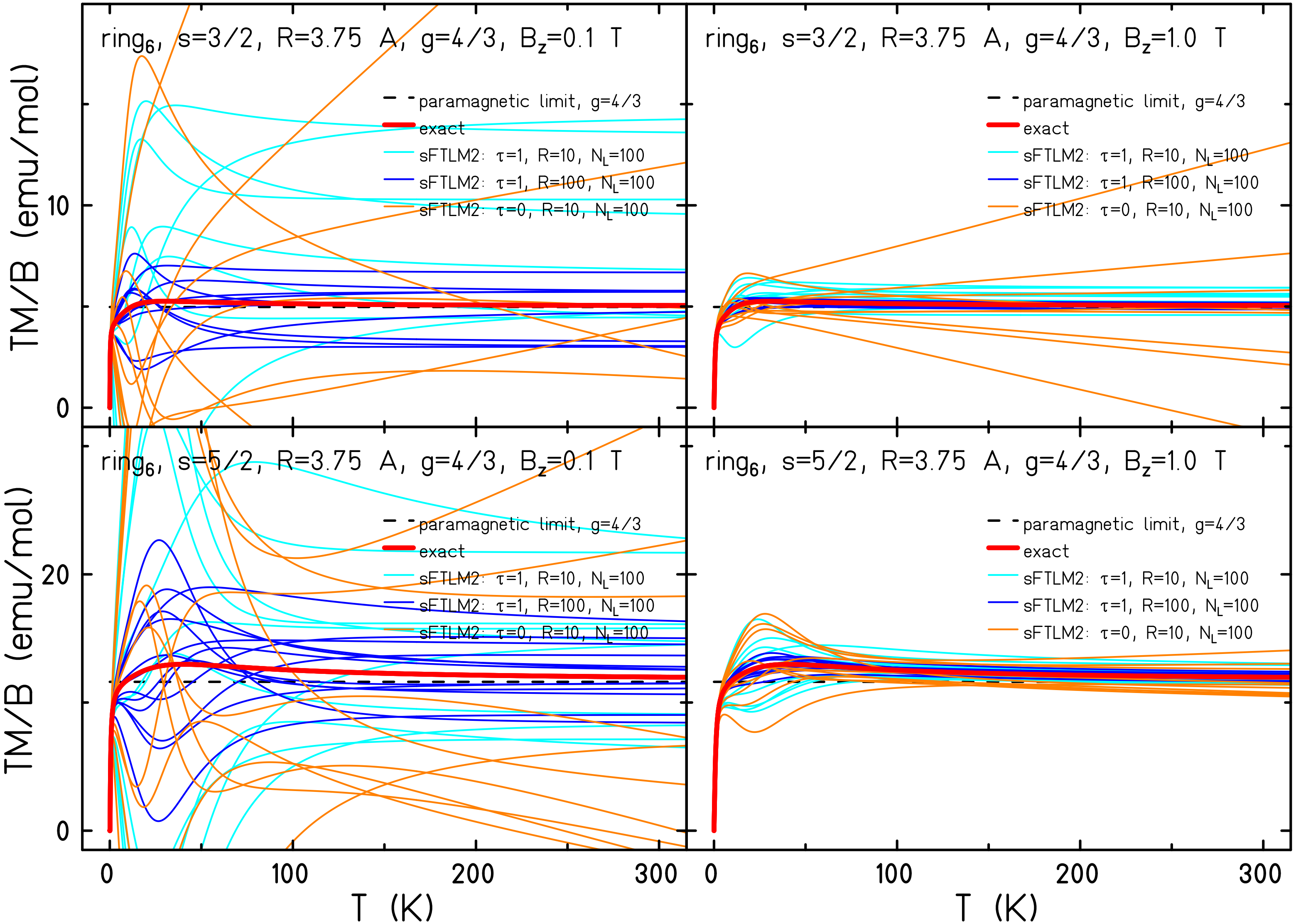
Magnon crystalization at high field.

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

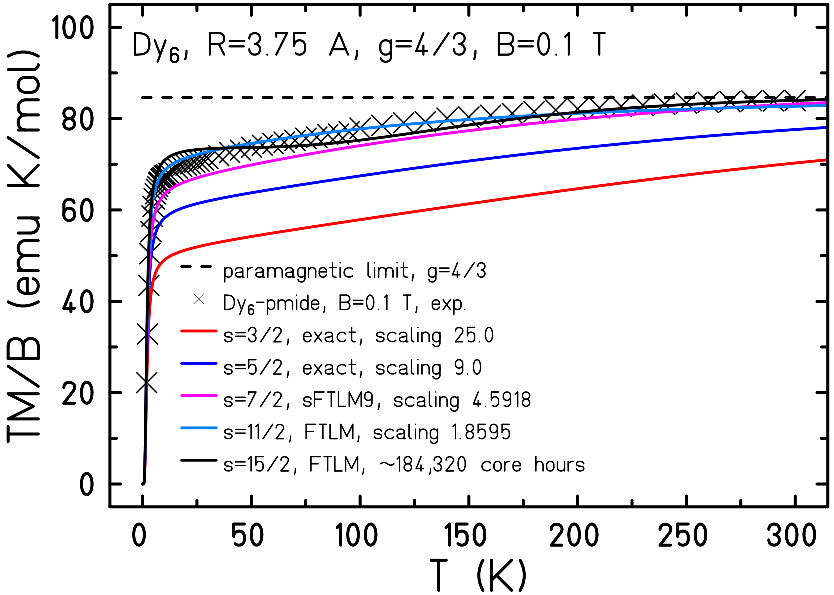


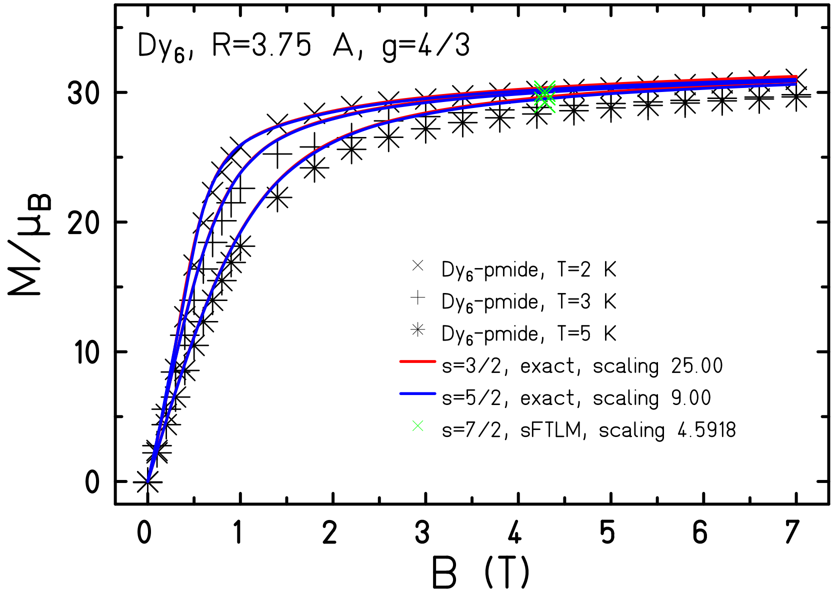
. . . and many more results with Johannes Richter.

Problem III – FTLM converges badly for anisotropic models



Dy_6 – results



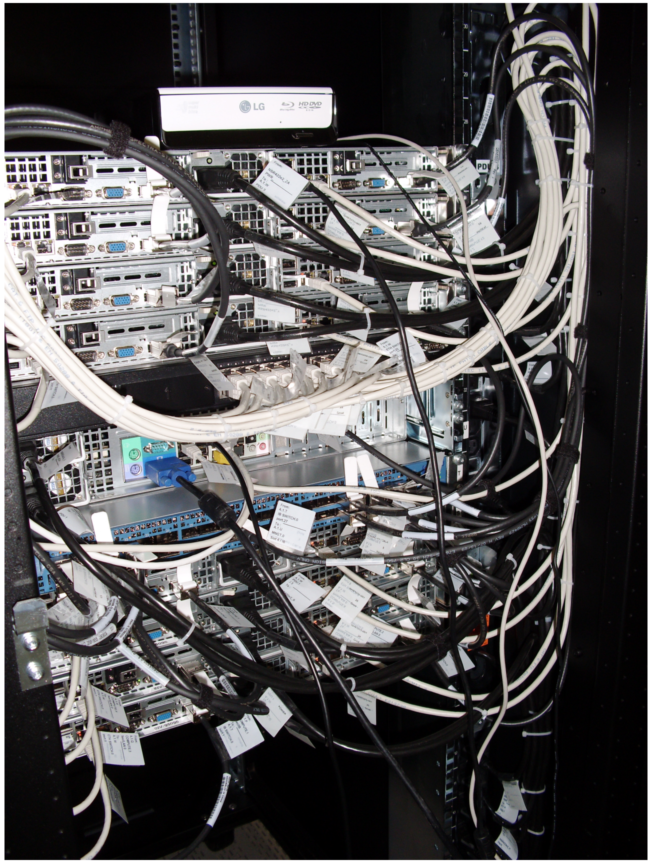


1. Use pairs of time-reversed random vectors (1).

2. Use symmetric version of FTLM (2):
$$\mathrm{Tr}\left(\underset{\sim}{Q} e^{-\beta \underset{\sim}{H}}\right) = \mathrm{Tr}\left(e^{-\beta \underset{\sim}{H}/2} \underset{\sim}{Q} e^{-\beta \underset{\sim}{H}/2}\right) \approx \langle\, r \,|\, e^{-\beta \underset{\sim}{H}/2} \underset{\sim}{Q} e^{-\beta \underset{\sim}{H}/2} \,|\, r \,\rangle \,.$$

(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 ⇒ To-Do-List



- Toroidal magnetic molecules: relaxation and decoherence measurements needed.
- Are there ions with large DM and large easy-axis anisotropy D?
- sFTLM on its way to deliver results.

Many thanks to my collaborators


- C. Beckmann, M. Czopnik, T. Glaser, O. Hanebaum, Chr. Heesing, M. Höck, K. Irländer, N.B. Ivanov, H.-T. Langwald, A. Müller, H. Schlüter, R. Schnalle, Chr. Schröder, J. Ummethum, P. Vorndamme, J. Waltenberg, D. Westerbeck (Bielefeld)
- K. Bärwinkel, T. Heitmann, R. Heveling, H.-J. Schmidt, R. Steinigeweg (Osnabrück)
- M. Luban (Ames Lab); 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, C. Anson, W. Wernsdorfer (Karlsruhe); J. Wosnitza (Dresden-Rossendorf); J. van Slageren (Stuttgart); R. Klingeler (Heidelberg); O. Waldmann (Freiburg); U. Kortz (Bremen)

Thank you very much for your attention.

The end.

Molecular Magnetism Web

www.molmag.de

Highlights. Tutorials. Who is who. Conferences.