Influence of the spin-phonon interaction on the tunneling gap of single-molecule magnets

Jürgen Schnack, K. Irländer, H.-J. Schmidt

Department of Physics – University of Bielefeld – Germany

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

”HIGH-SPIN MOLECULES AND MOLECULAR MAGNETS”
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Questions for today

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

1. Can the spin-phonon interaction open a tunneling gap?
2. Are there innocent phonons due to symmetry?

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

Model Hamiltonian (effective, spin-only, bilinear)

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

Exchange/Anisotropy Zeeman

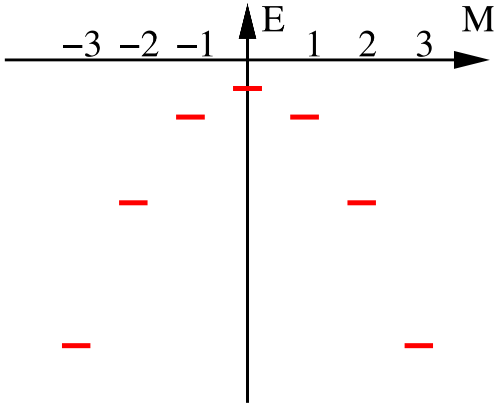
$\mathbf{J}_{ij}$: Heisenberg exchange, anisotropic exchange, and single-ion anisotropy.

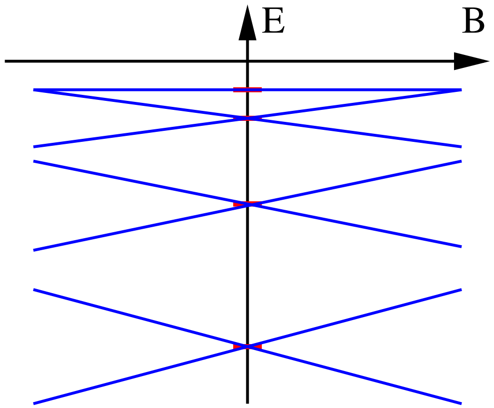
Isotropic Heisenberg Hamiltonian

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

Heisenberg Zeeman

Single-ion anisotropy – single spin I





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

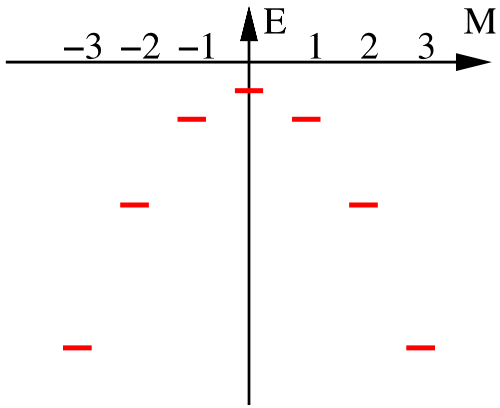
$D < 0$ easy axis, $D > 0$ hard axis;

eigenvectors: $|\, s, m\,\rangle$

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

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

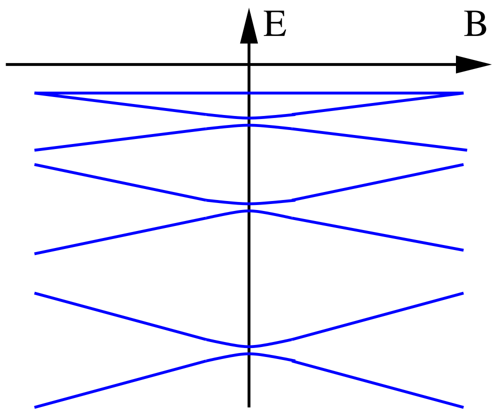
Single-ion anisotropy – single spin II



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

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

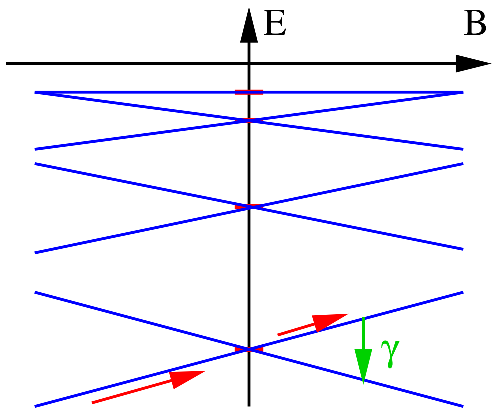
NO LONGER eigenvectors: $\mid s, m\,\rangle$

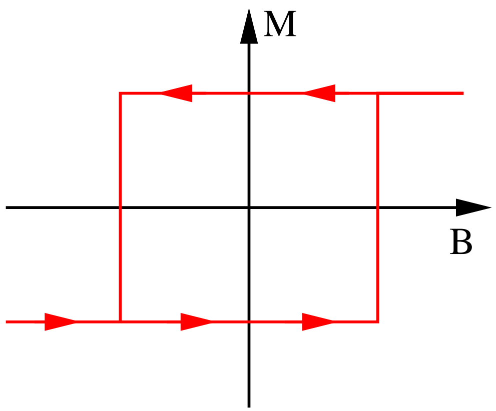


eigenvalues are more complicated functions of $\vec{B} = B\vec{e}_z$: $E_\mu(B)$

IMPORTANT: $[\underset{\sim}{H}, \underset{\sim}{s}^z] \neq 0 \Rightarrow$ avoided level crossings at $B = 0$ for integer spins
(otherwise Kramers degeneracy)

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





Goal: single-molecule magnets (SMM)

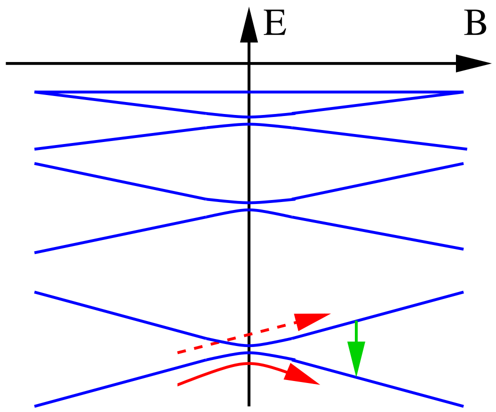
$$\underset{\sim}{H} = \sum_i D_i (\underset{\sim}{s}_i^z)^2 + \mu_B B \sum_i g_i \underset{\sim}{s}_i^z + \underset{\sim}{H}_{\text{ferro int}}$$

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.

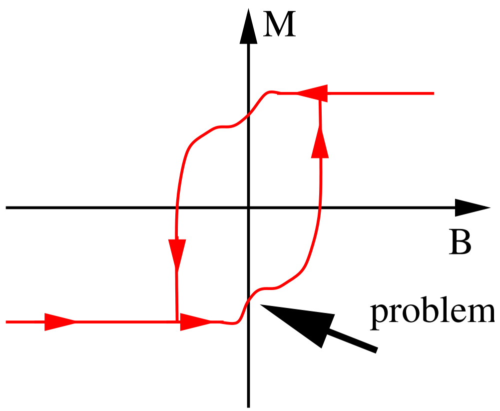
Bistability – general system – NO $\underset{\sim}{S}^z$-symmetry



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

$\mathbf{D}_i$ individual anisotropy tensors

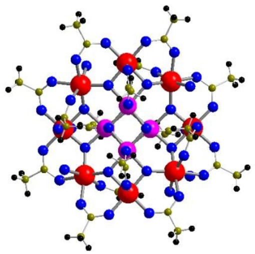
$\Rightarrow$ low-temperature TIME-DEPENDENT hysteresis closes at $B = 0$ – not bistable & bad for storage



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

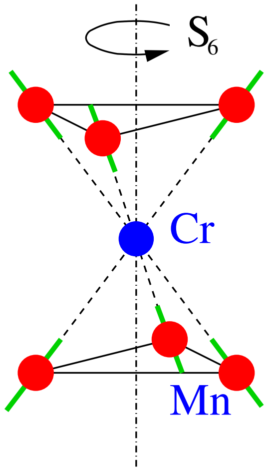
slow change of $B \Rightarrow$ system follows ground state, compare Landau-Zener-Stückelberg or slow/fast train at switch

Bistability – state of the art



Today's major goals:

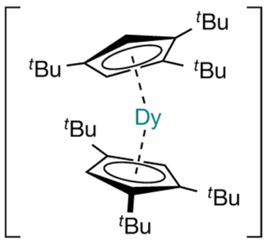
ferromagnetic spin-spin interaction



uniaxial anisotropy tensors

symmetry that does not permit E-terms

PERSISTENT PROBLEM: phonons



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

Can spin-phonon interaction induce a tunneling gap?

Spin-phonon interaction – DFT view of the problem

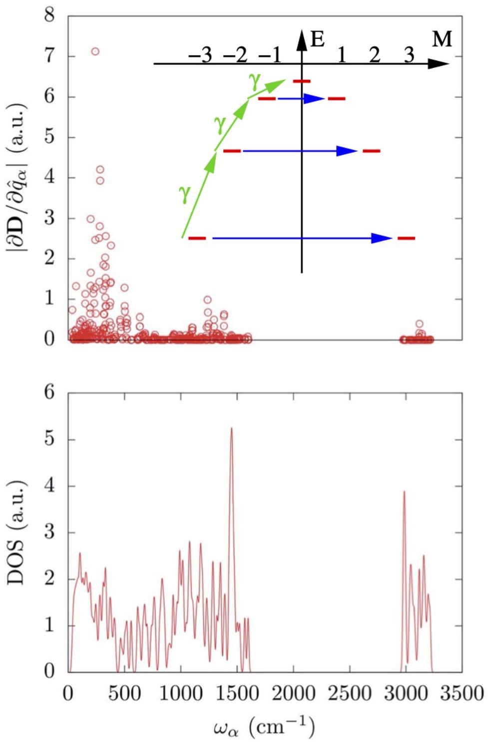


Fig. 2 Top panel: calculated spin-phonon coupling coefficients projected onto the normal modes basis set and displayed as a function of the modes frequency. Bottom panel: DFT calculated density of states for the Γ-point normal modes of vibration.

Calculate structure by means of DFT (1)

Calculate phonon density of states by means of DFT + molecular dynamics (1,2,3)

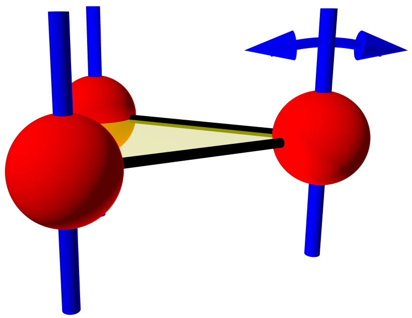
Calculate coupling coefficients from DFT (2,3,4)

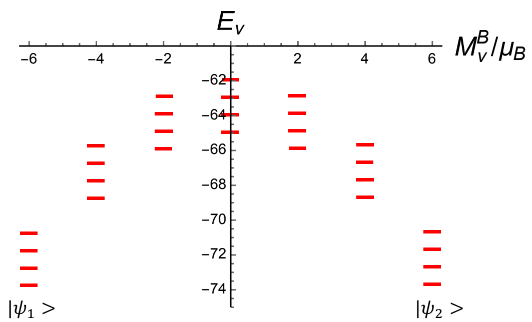
Perturbation picture: set up rate equations for phonon transitions between eigenstates of unperturbed spin Hamiltonian (2,3)

ADVANTAGE: many realistic phonons

(1) A. V. Postnikov, J. Kortus, and M. R. Pederson, physica status solidi (b) **243**, 2533 (2006).
(2) A. Lunghi and S. Sanvito, Science Advances **5**, eaax7163 (2019).
(3) A. Albino, S. Benci, L. Tesi, M. Atzori, R. Torre, S. Sanvito, R. Sessoli, and A. Lunghi, Inorg. Chem. **58**, 10260 (2019); ⇒ figure.
(4) D.A.S. Kaib, S. Biswas, K. Riedl, S.M. Winter, R. Valentí, Phys. Rev. B **103**, L140402 (2021).

Spin-phonon interaction – our question





Can phonons induce a tunnel splitting?

Know that non-collinear easy axes produce tunnel splitting

Set up special phonon modes that tilt easy axes in plane with C_3 axis out of uniaxial alignment

ADVANTAGE: quantum many-body solution for spins and phonons

$\Rightarrow$ correlated spin-phonon states:

$$|\,\Psi_\nu\,\rangle = \sum c^\nu_{m_1,m_2,m_3,n_1,n_2,n_3}\,|\,m_1,m_2,m_3,n_1,n_2,n_3\,\rangle$$

(1) K. Irländer and J. Schnack, Phys. Rev. B **102**, 054407 (2020).

Spin-phonon interaction – Hamiltonian

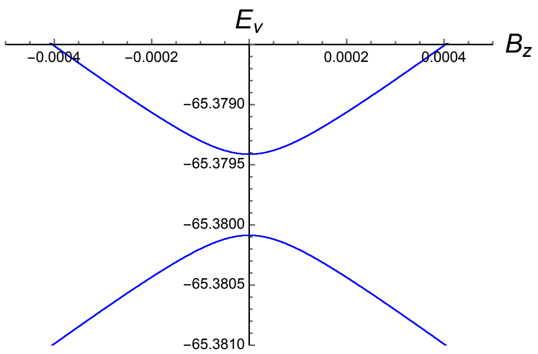
$$
\begin{aligned}
\underset{\sim}{H} \quad = \quad & -2J\left(\underset{\sim}{\vec{s}}_1\cdot\underset{\sim}{\vec{s}}_2+\underset{\sim}{\vec{s}}_2\cdot\underset{\sim}{\vec{s}}_3+\underset{\sim}{\vec{s}}_3\cdot\underset{\sim}{\vec{s}}_1\right)\\
& +\underset{\sim}{\vec{s}}_1\cdot\mathbf{D}_1(\underset{\sim}{\theta}_1)\cdot\underset{\sim}{\vec{s}}_1+\underset{\sim}{\vec{s}}_2\cdot\mathbf{D}_2(\underset{\sim}{\theta}_2)\cdot\underset{\sim}{\vec{s}}_2+\underset{\sim}{\vec{s}}_3\cdot\mathbf{D}_3(\underset{\sim}{\theta}_3)\cdot\underset{\sim}{\vec{s}}_3\\
& +\omega_1\left(\underset{\sim}{a}_1^\dagger\underset{\sim}{a}_1+\frac{1}{2}\right)+\omega_2\left(\underset{\sim}{a}_2^\dagger\underset{\sim}{a}_2+\frac{1}{2}\right)+\omega_3\left(\underset{\sim}{a}_3^\dagger\underset{\sim}{a}_3+\frac{1}{2}\right)\\
& +g\mu_B\cdot\vec{B}\cdot\left(\underset{\sim}{\vec{s}}_1+\underset{\sim}{\vec{s}}_2+\underset{\sim}{\vec{s}}_3\right)
\end{aligned}
$$

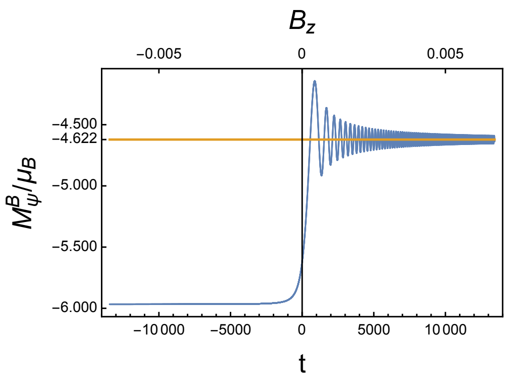
$$
\mathbf{D}_i(\underset{\sim}{\theta}_i) \quad = \quad D\,\vec{e}_i(\underset{\sim}{\theta}_i,\phi_i)\otimes\vec{e}_i(\underset{\sim}{\theta}_i,\phi_i)
$$

$$
\underset{\sim}{\theta}_i \quad = \quad \theta_{i,0}+\alpha\left(\underset{\sim}{a}_i^\dagger+\underset{\sim}{a}_i\right)\ , \qquad \theta_{i,0}=0,
$$

i.e., zero mean tilt

Spin-phonon interaction – our result (applies to integer spins)





Can phonons induce a tunnel splitting?

$\Rightarrow$ Yes, they can!

Ground state, practically, does not contain any phonons, nevertheless tunneling occurs. Coupling to zero-point motion suffices (2).

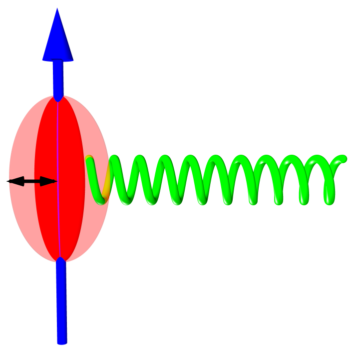
BAD NEWS: It is not enough to cool quantum devices, you have to prevent the coupling to disturbing sources at all.

Side remark: result probably already known in field of vibronic coupling (Atanasov, Shrivastava, Tsukerblat, Coronado).

(1) K. Irländer and J. Schnack, Phys. Rev. B **102**, 054407 (2020).
(2) F. Ortu *et al.*, Dalton Trans. **48**, 8541 (2019).

Innocent spin-phonon interaction due to symmetry

SUSY spin-phonon interaction (applies to integer spins)



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

Special phonons that modify only:

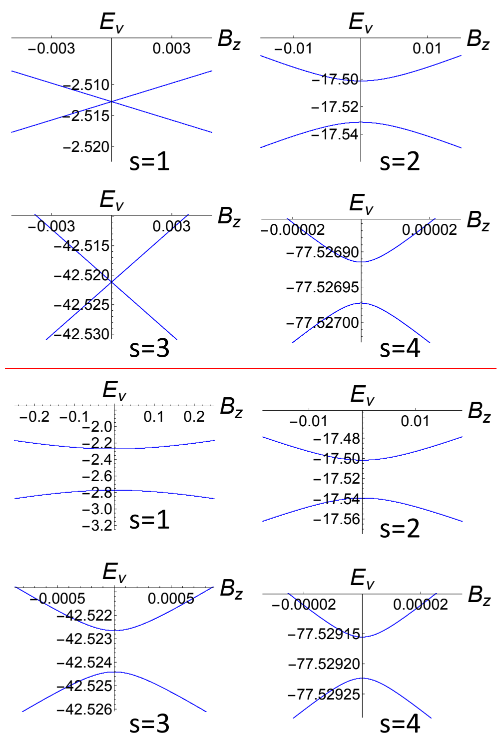
L: $E = \alpha\left(\underset{\sim}{a}^\dagger + \underset{\sim}{a}\right)$ or Q: $E = \alpha\left(\underset{\sim}{a}^\dagger + \underset{\sim}{a}\right)^2$

L: tunneling gap for even s, no gap for odd s.

This is not Kramers, but related to another symmetry.

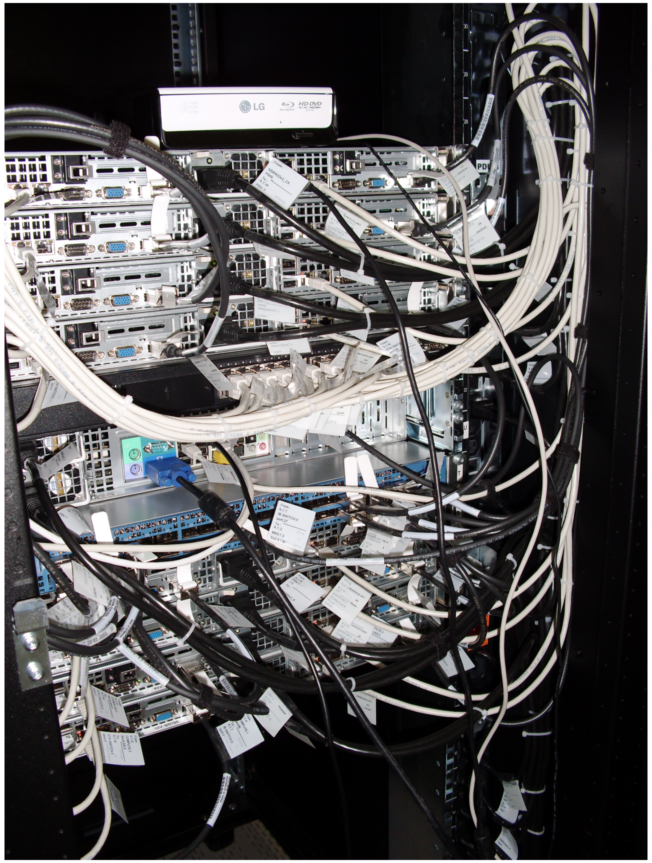
Q: tunneling gap for all s.

RESULT: very interesting behavior; there are some phonons that do not produce a tunneling gap thanks to the way they couple. SUSY at work.



(1) K. Irländer, H.-J. Schmidt, J. Schnack, Eur. Phys. J. B **94**, 68 (2021)

Summary



- Magnetic molecules for storage, q-bits, MCE, and since they are nice.
- SMM challenges: quantum tunneling and phonons
- Magnetism is much richer and more complicated than shown here. Talk focused on 3d ions with weak spin-orbit interaction.

Many thanks to my collaborators

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Thank you very much for your attention.

The end.

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