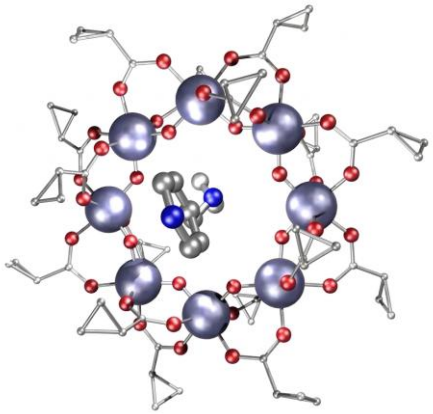
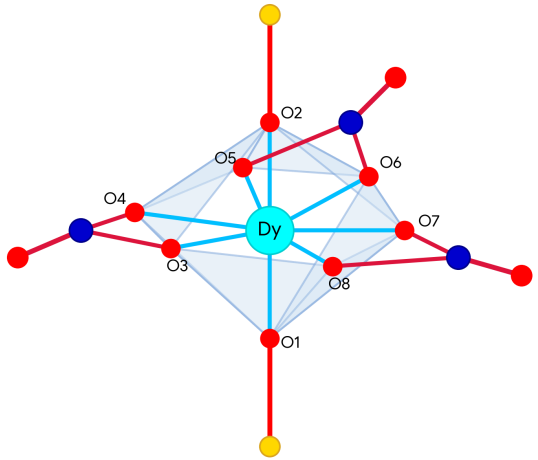
Università degli Studi di Pavia
Physics Department "Alessandro Volta"
PhD Course in Condensed Matter Physics

Quantum Coherence Time in Molecular Nanomagnets

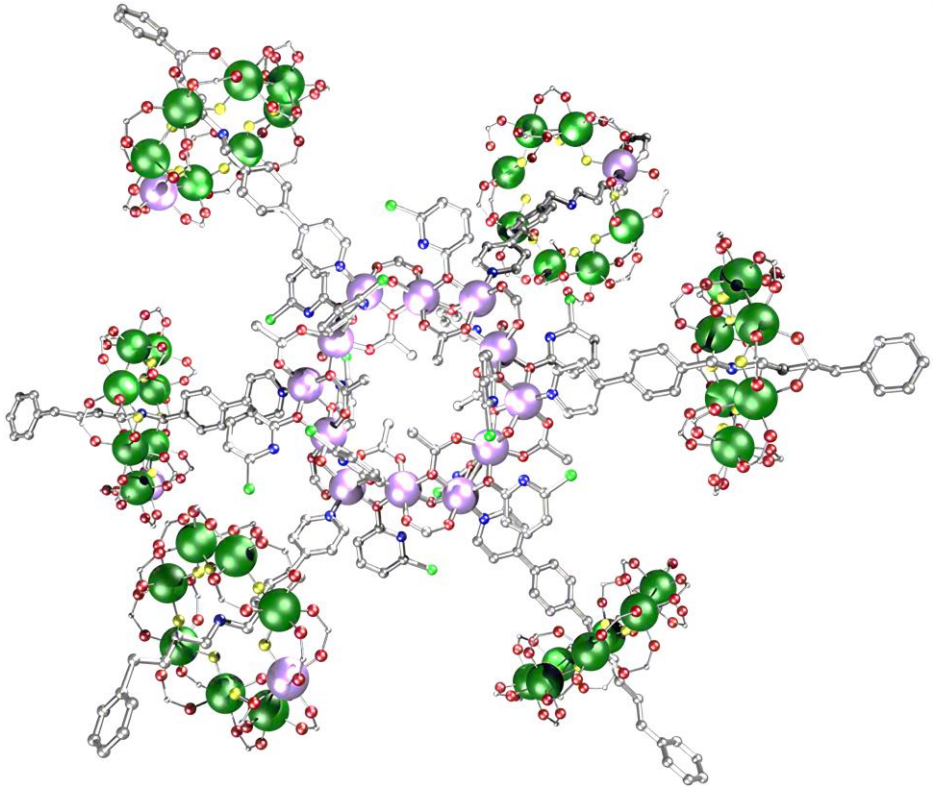
New Pathways to Qubit Computation



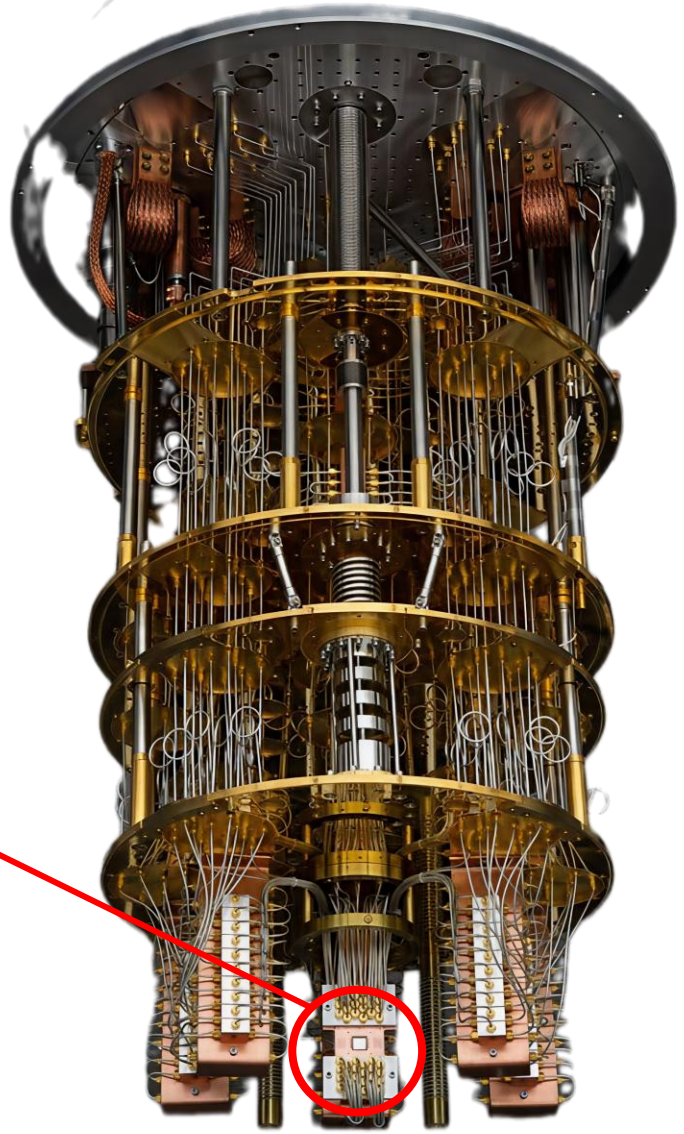


End-of-year seminar by: Martina Foresti
A.Y: 2025-2026

QUANTUM PROCESSING UNITS

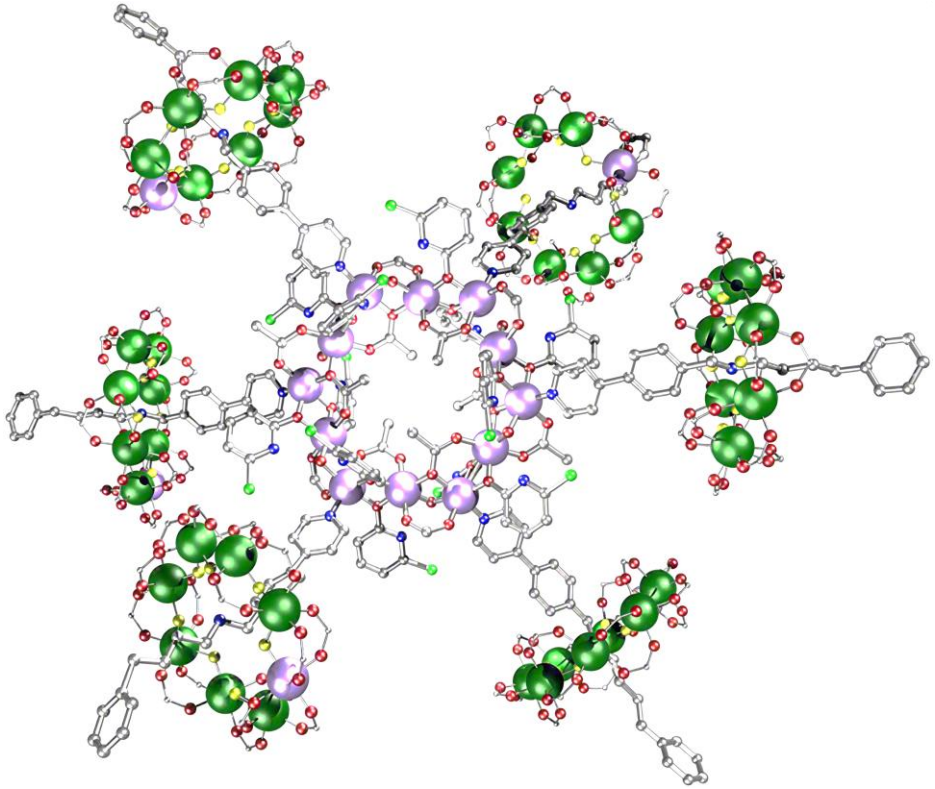


QPU

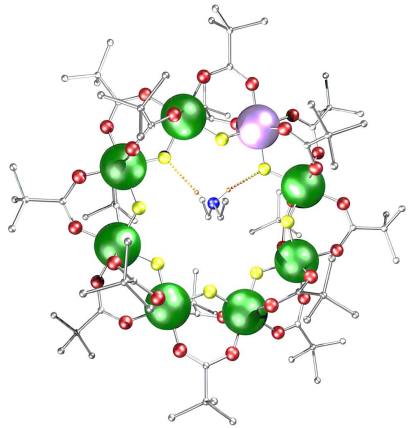


[1] S. J. Lockyer, et al. Chem. Eur. J., 0, e202501067 (2025)

QUANTUM PROCESSING UNITS



Molecular crystals
satisfy the
Di Vincenzo criteria

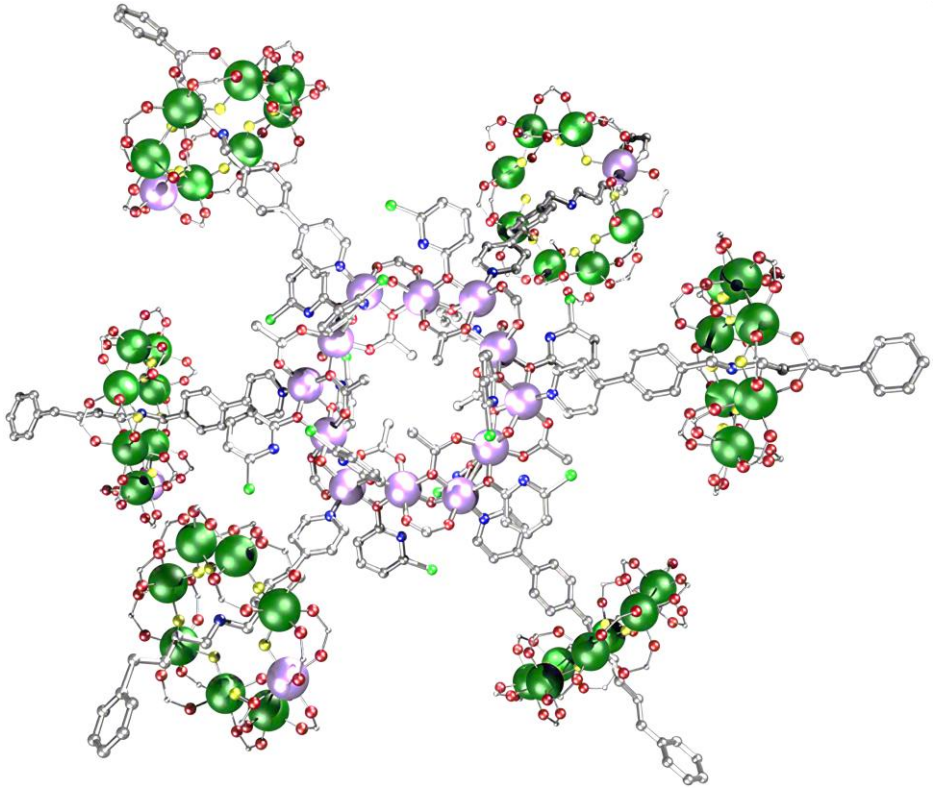


SMMs

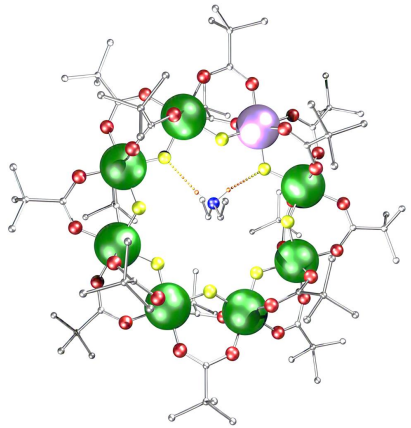
e.g. Cr_7Ni

[1] S. J. Lockyer, et al. Chem. Eur. J., 0, e202501067 (2025)

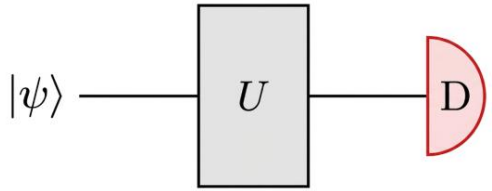
QUANTUM PROCESSING UNITS



Molecular crystals
satisfy the
Di Vincenzo criteria



SMMs

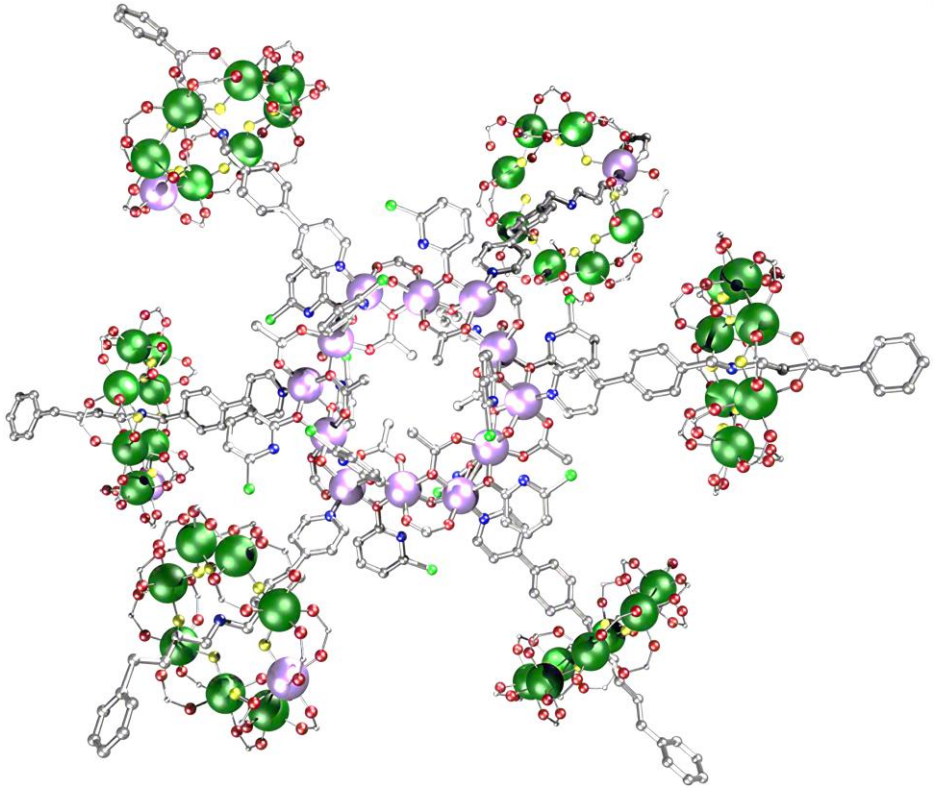


EPR

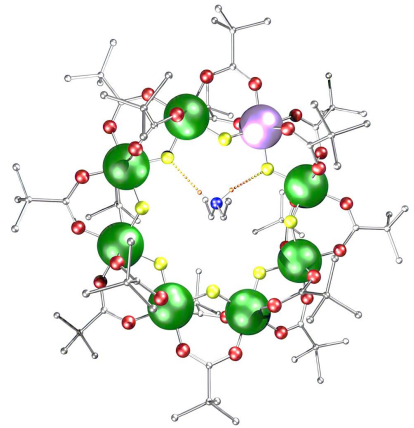
$\tau = 10^{-9}$ s

[1] S. J. Lockyer, et al. Chem. Eur. J., 0, e202501067 (2025)

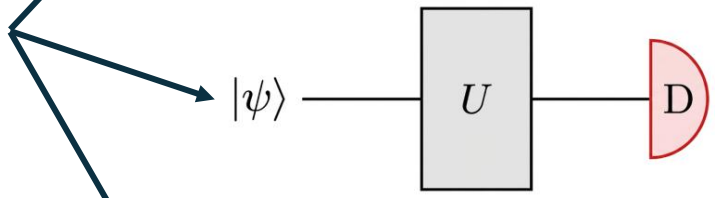
QUANTUM PROCESSING UNITS



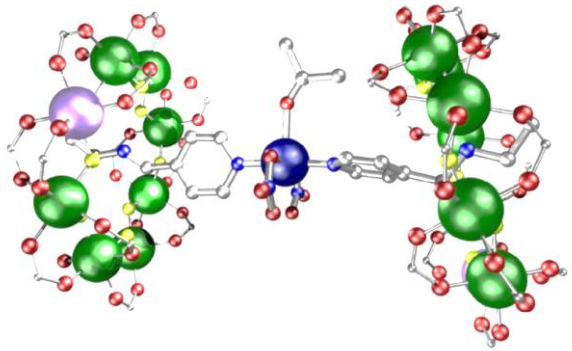
Molecular crystals
satisfy the
Di Vincenzo criteria



SMMs

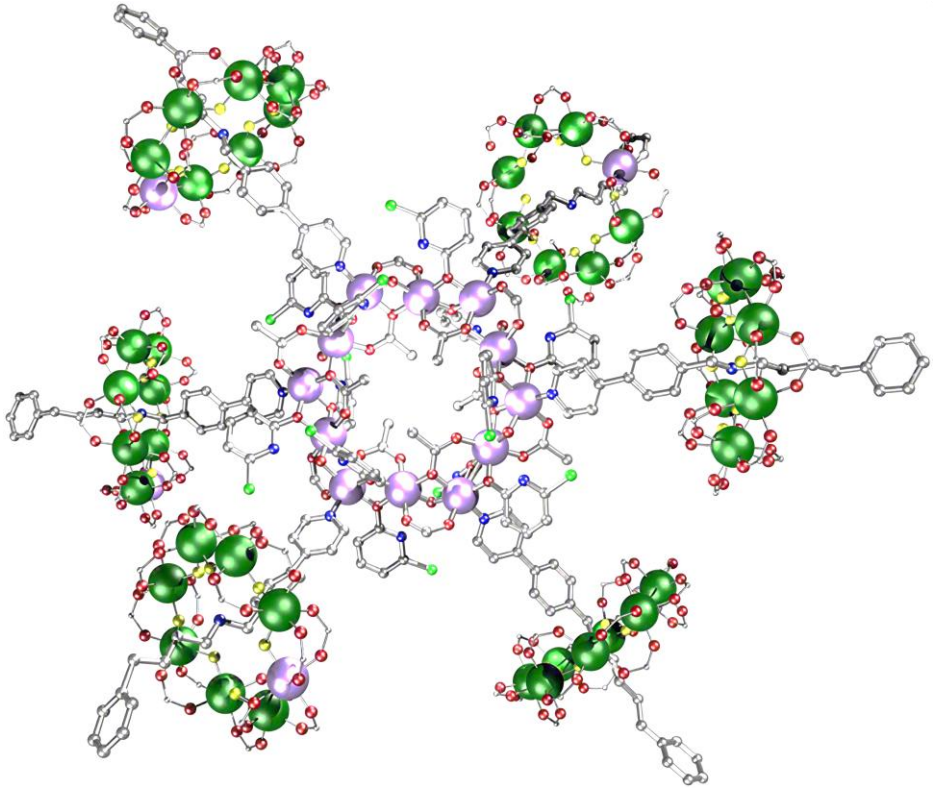


EPR

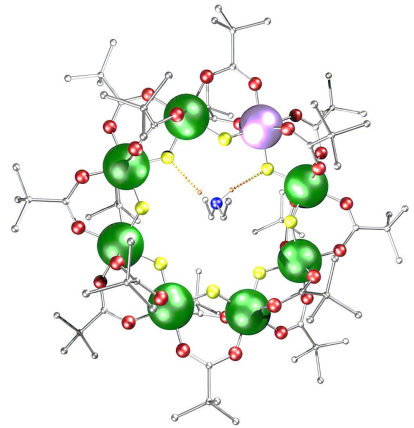


[1] S. J. Lockyer, et al. Chem. Eur. J., 0, e202501067 (2025)

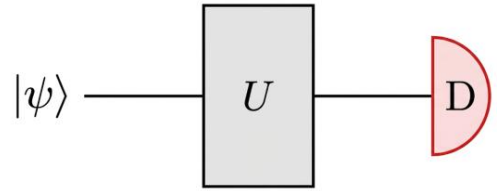
QUANTUM PROCESSING UNITS



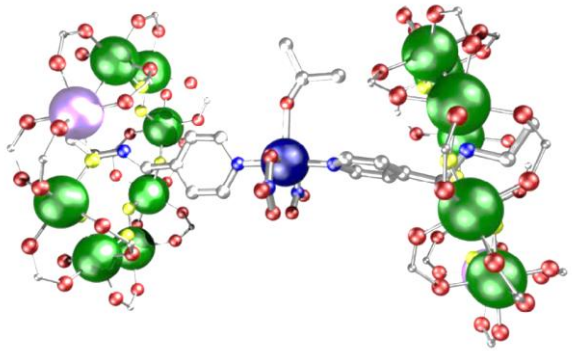
Molecular crystals
satisfy the
Di Vincenzo criteria



SMMs



EPR



$\tau_c \gg 10^{-9}$ s

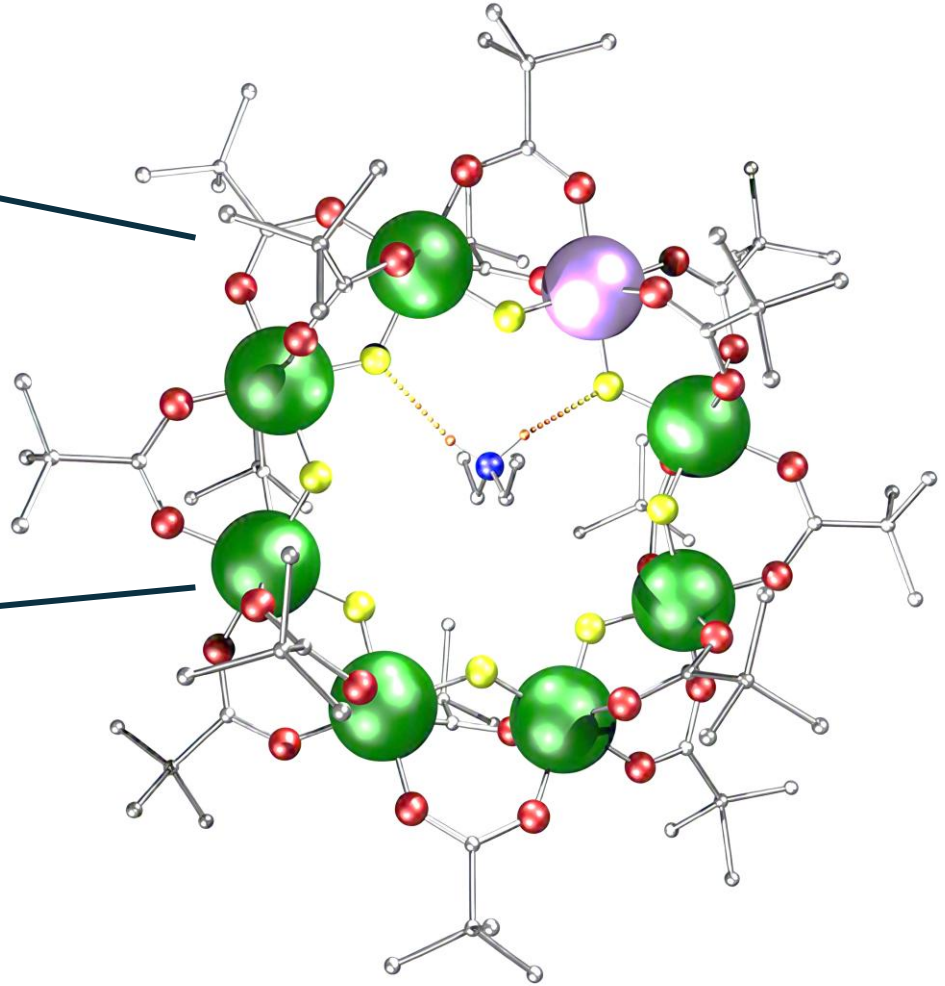
[1] S. J. Lockyer, et al. Chem. Eur. J., 0, e202501067 (2025)

SINGLE-MOLECULE MAGNETS

ORGANIC SHELL

METAL IONS

- 3d-TM
- Lanthanides



[1] S. J. Lockyer, et al. Chem. Eur. J., 0, e202501067 (2025)

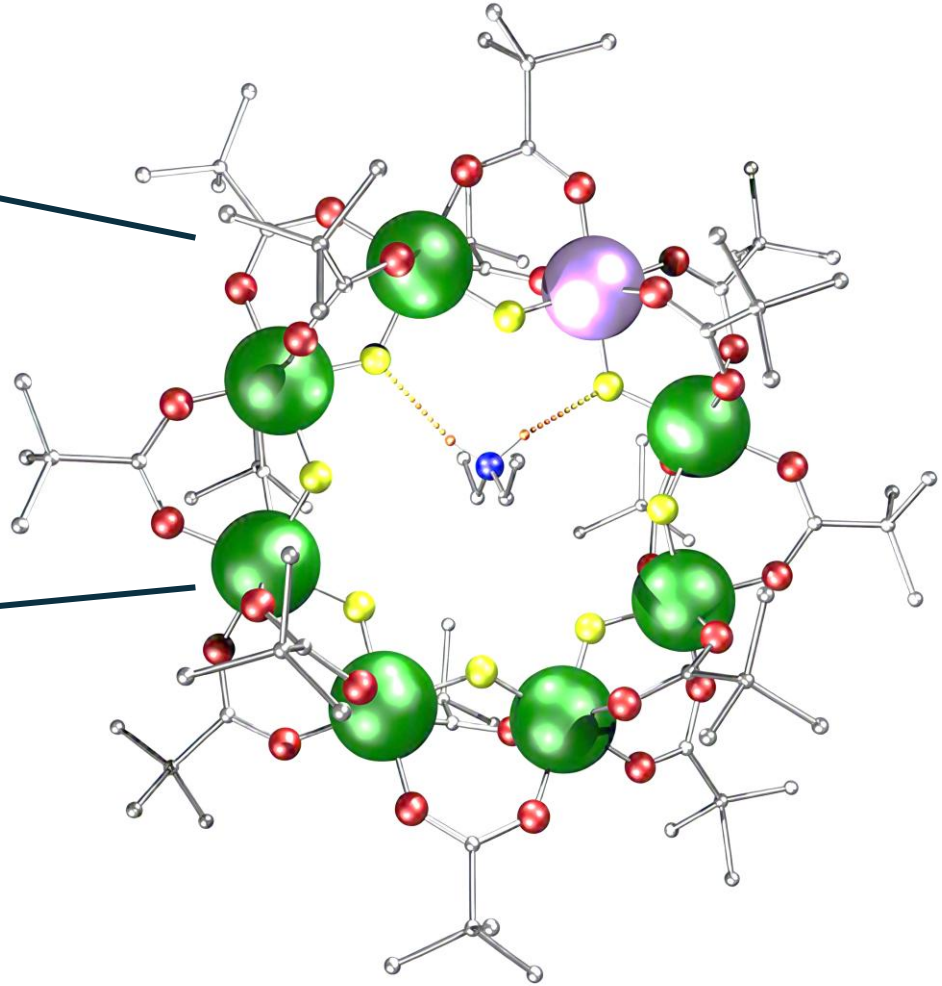
Spin-½ RINGS AS QUBITS

ORGANIC SHELL

- O, red
- N, blue
- C, grey
- H, omitted
- S, yellow

METAL IONS

- Cr, green
- Ni, violet



$Cr^{(III)}_7Ni^{(II)}$

$Cr^{(III)}$	**$Ni^{(II)}$**
S = 3/2	S = 1

AFM coupling

[1] S. J. Lockyer, et al. Chem. Eur. J., 0, e202501067 (2025)

Spin-½ RINGS AS QUBITS

SPIN HAMILTONIAN

HEISENBERG EXCHANGE

UNIAXIAL ANISOTROPY

ZEEMAN INTERACTION

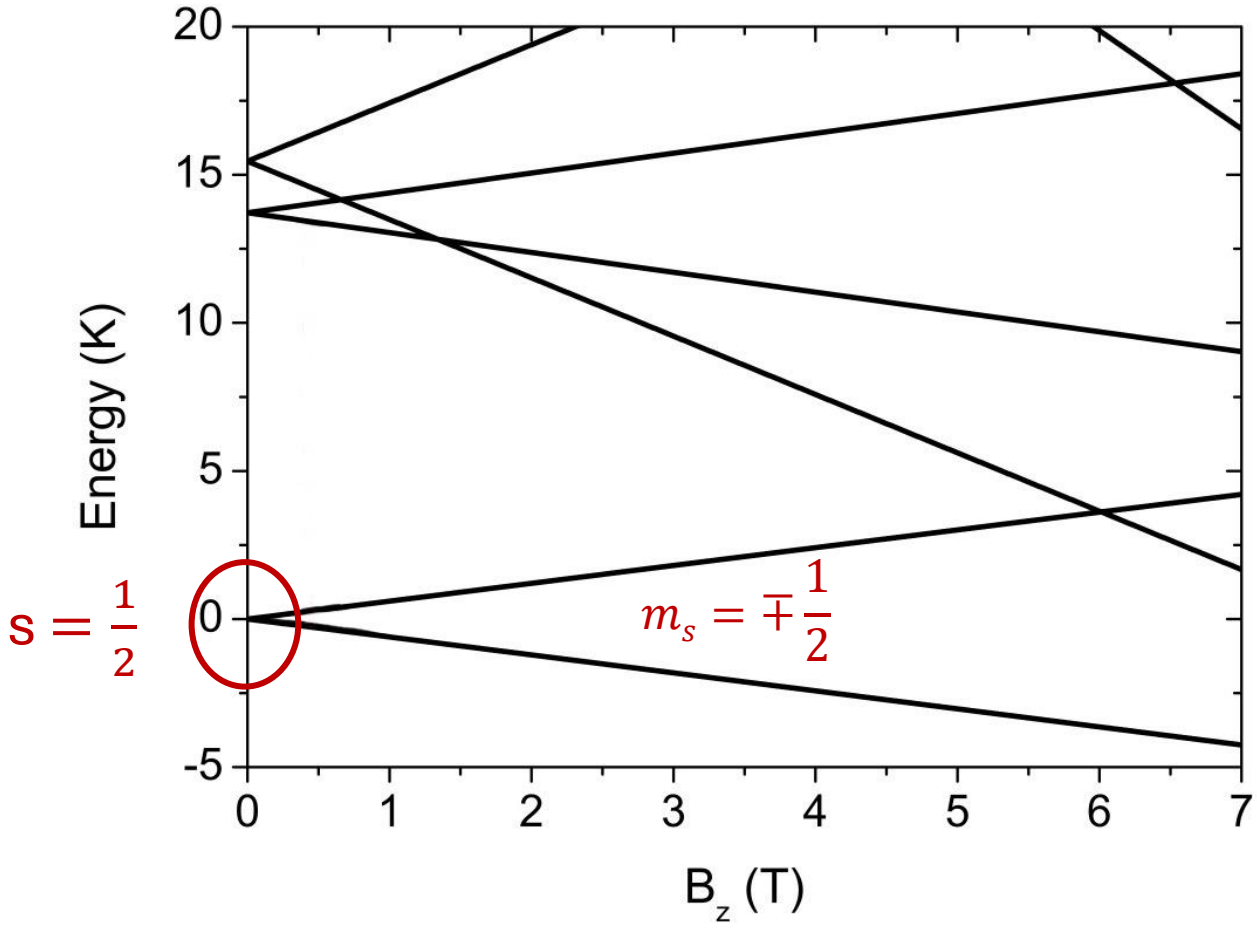
$$\hat{H} = \sum_{i,j}^{N.N.} J_{ij}\, \hat{\vec{s}_i} \cdot \hat{\vec{s}_j} + \sum_i D_i\, \hat{s}_{i,z}^2 + \sum_i \mu_B\, \vec{B}\, \vec{\vec{g}}_e \hat{\vec{s}_i}$$

Cr_7Ni: $J_{i,j}/K_B \simeq 22K$ [3]

[2] Adapted from W. Wu et al., Molecules, 30, 2522 (2025)
[3] H. Amiri et al., Phys. Rev. B 82, 144421 (2010)

Spin-½ RINGS AS QUBITS

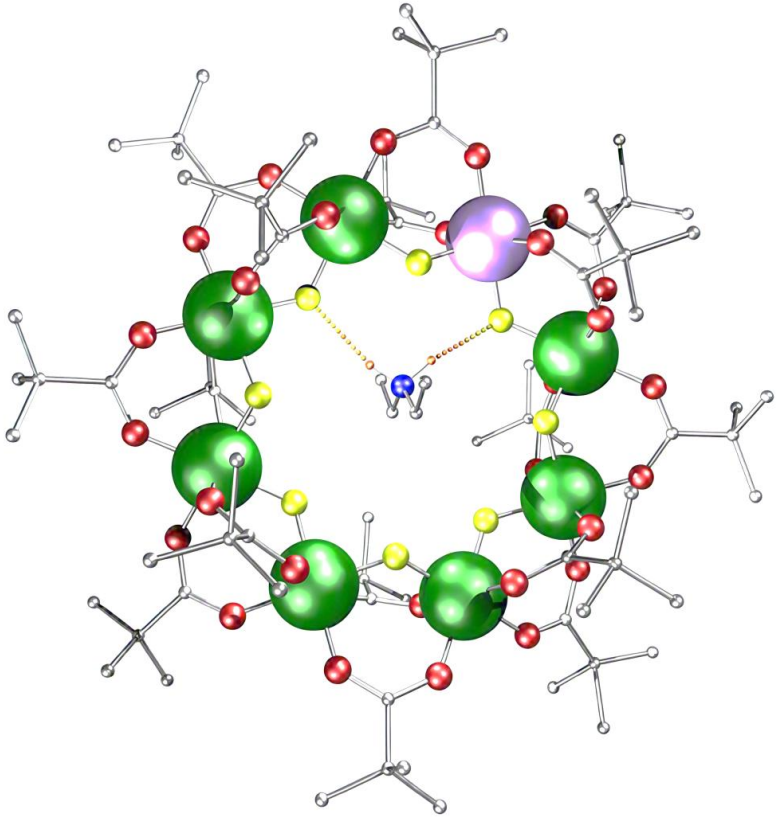
ENERGY LEVELS OF Cr_7Ni [4]



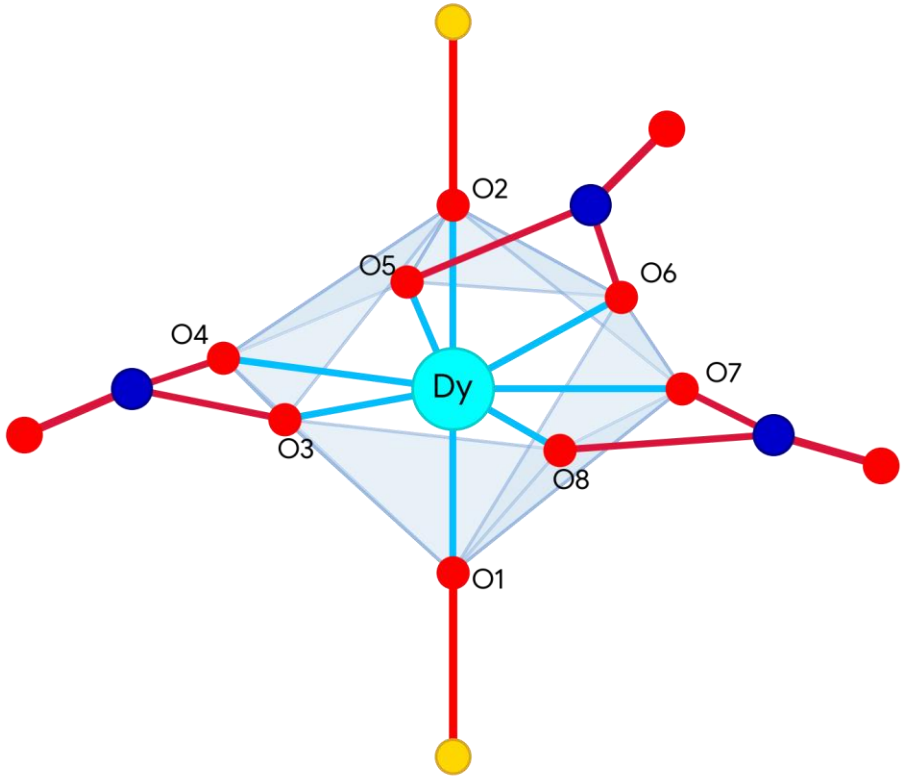
[4] A. Bianchi et al., Phys. Rev. B, 82,134403 (2010)

CLASSES OF SMMs

Transition-metal RINGS

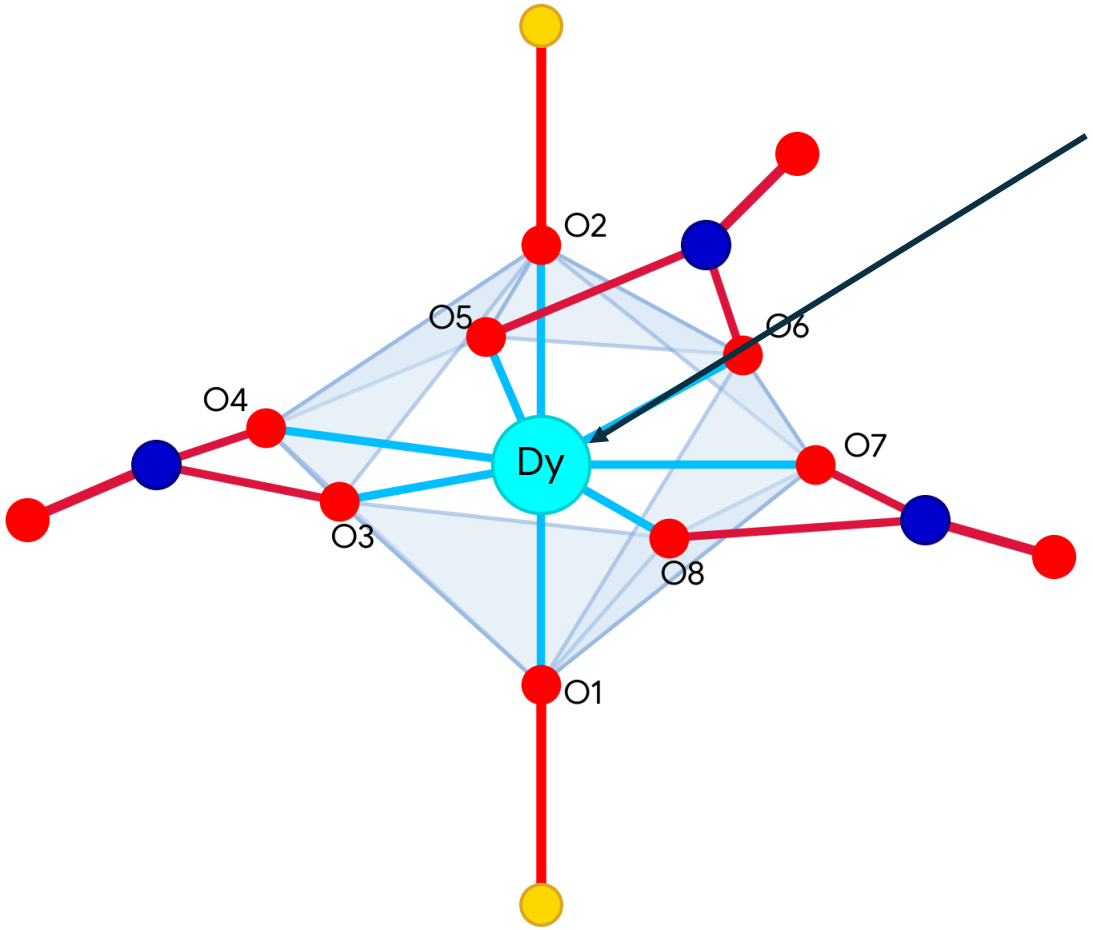


Lanthanide SIMs



[5] Adapted from J. Li et al., Inorg. Chem. 58, 2610 (2019)

Ln-SIMs AS QUBITS

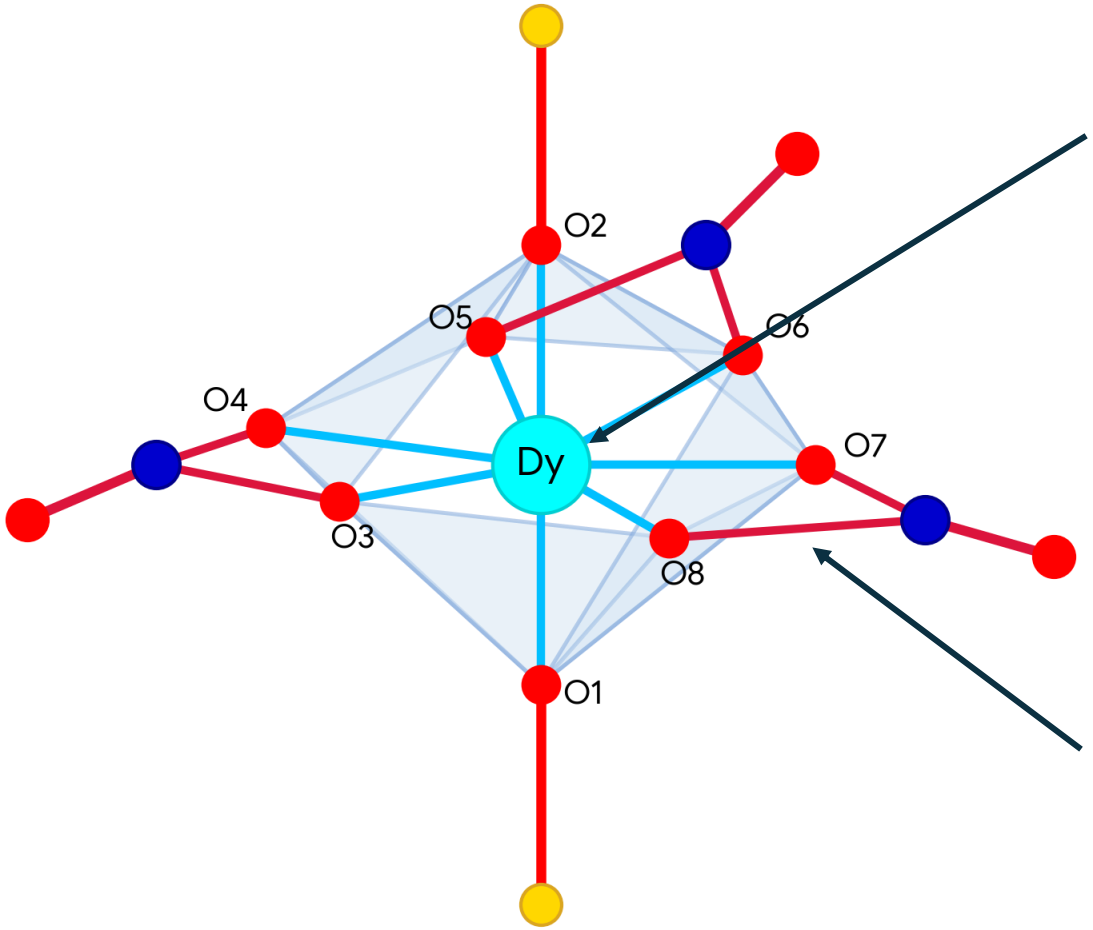


HIGH ANGULAR MAGNETIC MOMENT J

$$\sum_i \xi_i \vec{l_i} \cdot \vec{s_i}$$

[5] Adapted from J. Li et al., Inorg. Chem. 58, 2610 (2019)

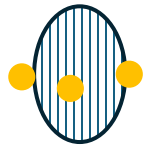
Ln-SIMs AS QUBITS



HIGH ANGULAR MAGNETIC MOMENT J

$$\sum_i \xi_i \vec{l_i} \cdot \vec{s_i}$$

OBLATE ELECTRONIC CLOUD:
equatorial ligands
to enhance anisotropy



[5] Adapted from J. Li et al., Inorg. Chem. 58, 2610 (2019)

Ln-SIMs AS QUBITS

SPIN HAMILTONIAN

UNIAXIAL ANISOTROPY

TRANSVERSE ANISOTROPY

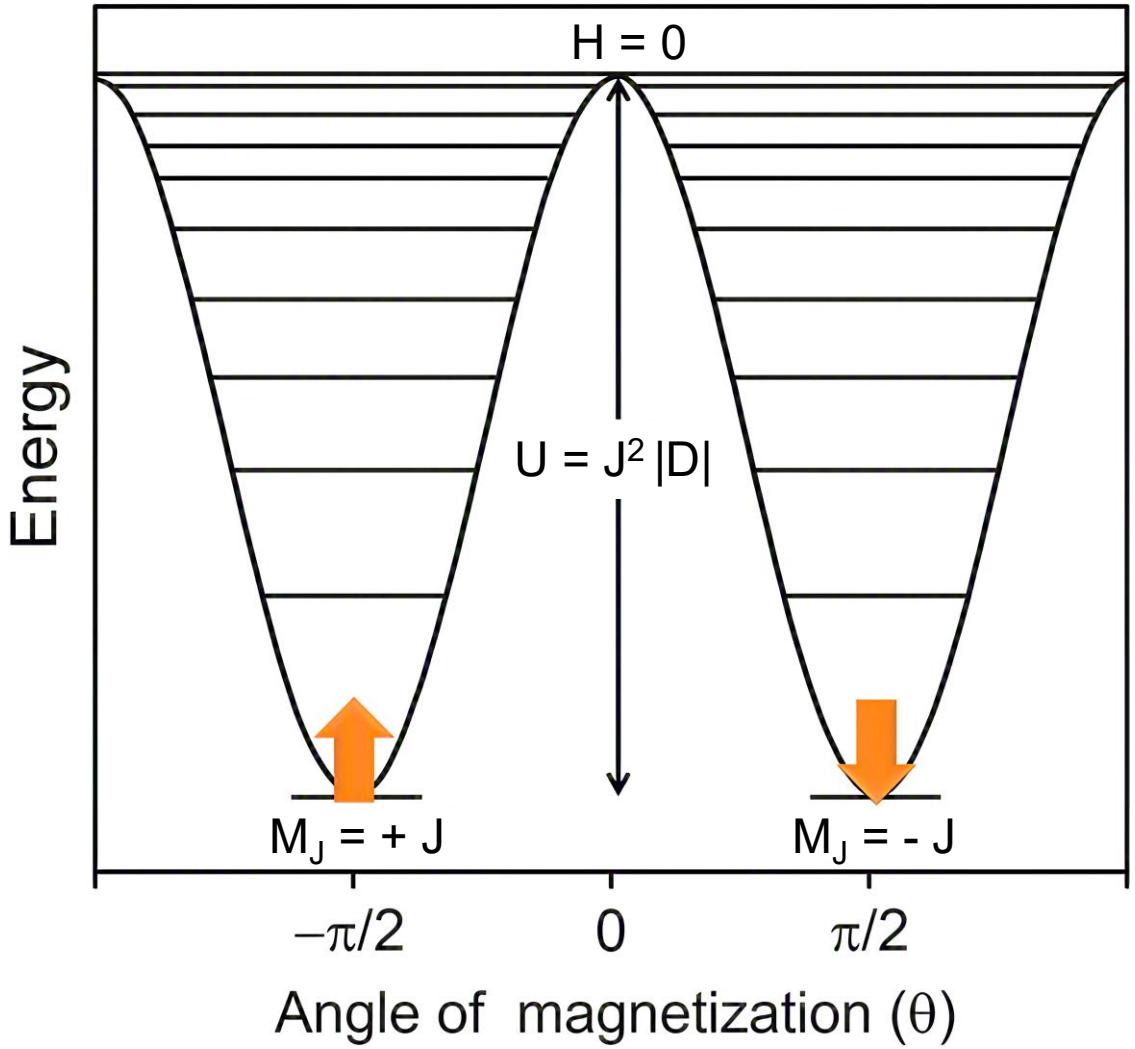
ZEEMAN INTERACTION

$$\hat{H} = \sum_i D_i \hat{\mathrm{j}}_{i,z}^2 + \left[E_i\left(\hat{\mathrm{j}}_{i,x}^2 - \hat{\mathrm{j}}_{i,y}^2\right)\right] + \sum_i \mu_B \vec{B} \vec{\vec{g}}_e \hat{\vec{\mathrm{j}}}_i$$

[2] Adapted from W. Wu et al., Molecules, 30, 2522 (2025)

Ln-SIMs AS QUBITS

ENERGY LEVELS
OF a Ln-SIM [6]



[6] J. Long et al., J.*Am. Chem. Soc. 135*, 17952 (2013)

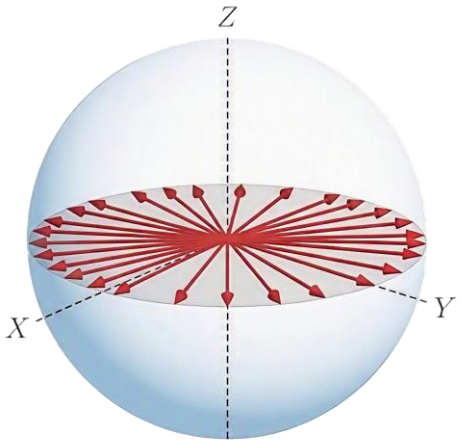
DECOHERENCE

"The coherence time τ_c is the period during which the system can store quantum information in a useful form, maintaining its spin in a fixed orientation." [7]

[7] Adapted from M. Affronte et al., Molecular Nanomagnets and Related Phenomena, *Song Gao ed. (2015)*

DECOHERENCE

ELECTRONIC T_2
(pulsed EPR)

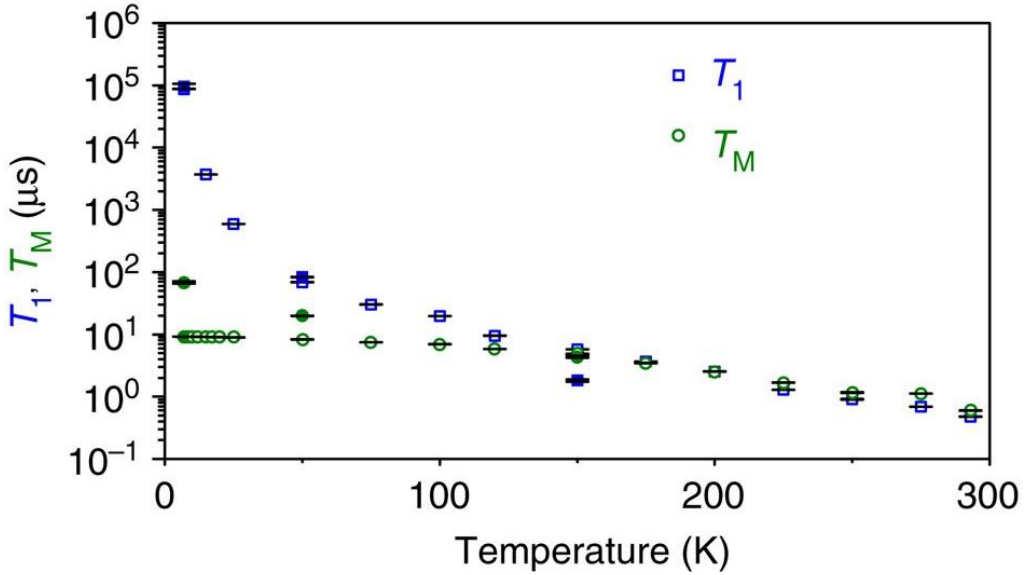


"The coherence time τ_c is the period during which the system can store quantum information in a useful form, maintaining its spin in a fixed orientation." [7]

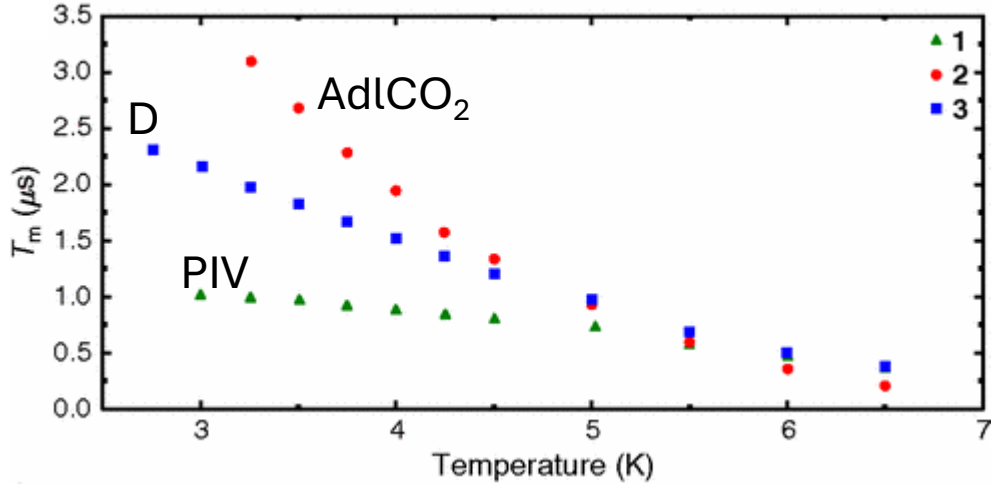
[7] Adapted from M. Affronte et al., Molecular Nanomagnets and Related Phenomena, *Song Gao ed. (2015)*

STATE OF THE ART

Longest: 68 μs for $(PPh_4)[Cu(mnt)_2]$ at T = 7 K [8]



Cr_7Ni: 3.2 μs at T = 3 K [9]



[8] K. Bader et al., Nat. Commun., 10, 1038 (2014)

[9] C.J. Wedge et al., Phys. Rev. Lett. 108, 107204 (2012)

RELAXATION MECHANISMS

$$\frac{1}{\tau_c} = AH^4T + CT^n + \frac{1}{\tau_0 \exp\left(\frac{\mathrm{U}}{K_B T}\right)} + \frac{B_1}{1 + B_2 H^2} + D \exp\left[-\left(\frac{K}{T}\right)^{\frac{1}{2}}\right]$$

[10] Adapted from A, Vieru et al., Ang. Chem. Int. Ed. 63, e202303146 (2024)

RELAXATION MECHANISMS

NUCLEAR T_1
(pulsed NMR)

$$\frac{1}{T_1} = A \cdot \frac{\tau_c}{1 + \omega_L^2 \tau_c^2}$$

$$\frac{1}{\tau_c} = AH^4T + CT^n + \frac{1}{\tau_0 \exp\left(\frac{\mathrm{U}}{K_B T}\right)} + \frac{B_1}{1 + B_2 H^2} + D \exp\left[-\left(\frac{K}{T}\right)^{\frac{1}{2}}\right]$$

[10] Adapted from A, Vieru et al., Ang. Chem. Int. Ed. 63, e202303146 (2024)

RELAXATION MECHANISMS

1. SPIN-PHONON COUPLING

DIRECT RAMAN ORBACH

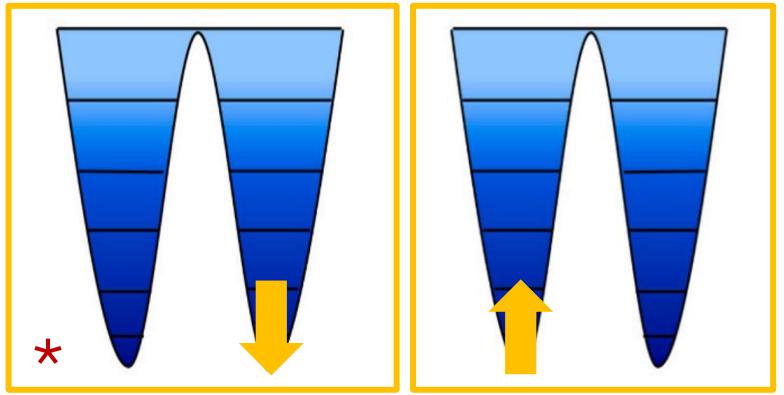
$$\frac{1}{\tau_c} = AH^4T + CT^n + \frac{1}{\tau_0 \exp\left(\frac{\mathrm{U}}{K_B T}\right)} + \frac{B_1}{1 + B_2 H^2} + D \exp\left[-\left(\frac{K}{T}\right)^{\frac{1}{2}}\right]$$

RELAXATION MECHANISMS

2. QUANTUM TUNNELING OF THE MAGNETIZATION *

QTM

$$\frac{1}{\tau_c} = AH^4T + CT^n + \frac{1}{\tau_0 \exp\left(\frac{U}{K_B T}\right)} + \frac{B_1}{1 + B_2 H^2} + D \exp\left[-\left(\frac{K}{T}\right)^{\frac{1}{2}}\right]$$



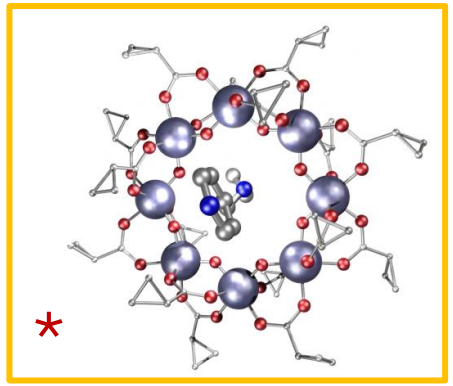
[11] Adapted from A. G. Bispo-Jr. Coord Chem Rev. 537, 216685 (2025)

RELAXATION MECHANISMS

3. FREE-CHARGE HOPPING *

FCH

$$\frac{1}{\tau_c} = AH^4T + CT^n + \frac{1}{\tau_0 \exp\left(\frac{\mathrm{U}}{K_B T}\right)} + \frac{B_1}{1 + B_2 H^2} + D \exp\left[-\left(\frac{K}{T}\right)^{\frac{1}{2}}\right]$$



*

[12] S. Lockyer et al., Chem. Eur. J., e71451 (2026)
[13] A. Rodin et al., Phys. Rev. B 80, 1 (2009)

PURPOSE OF PHD PROJECT

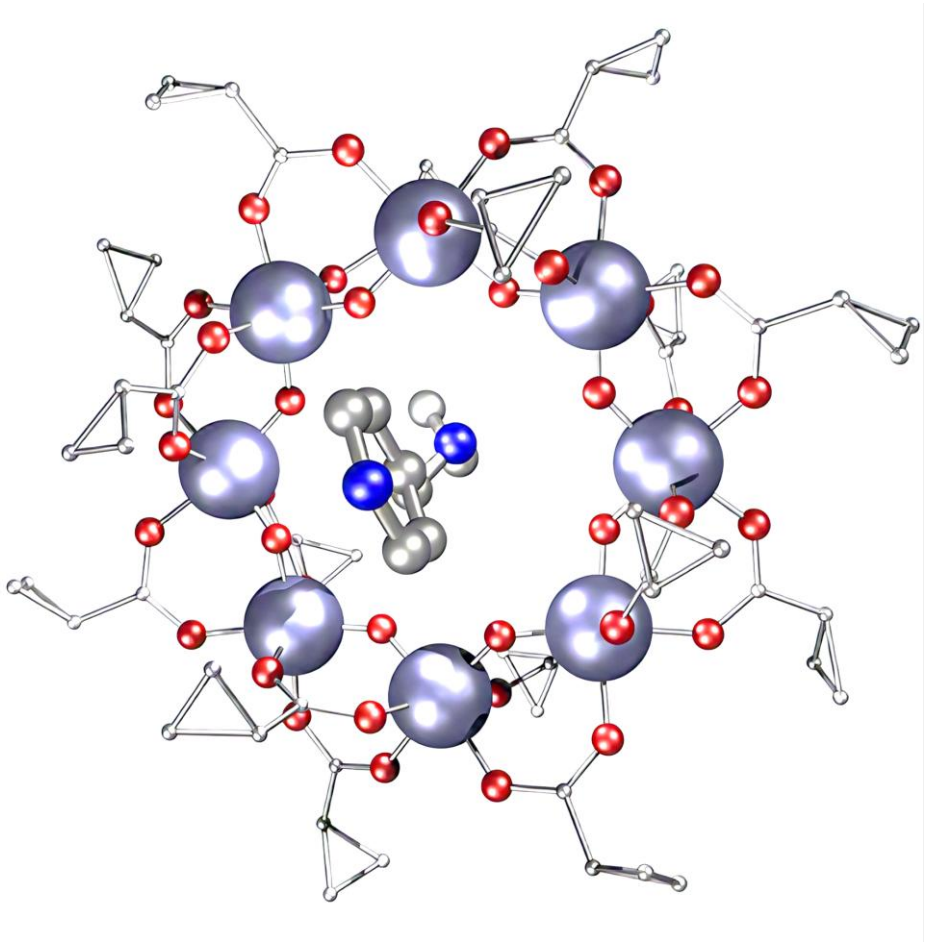
DETAILED EXPERIMENTAL INVESTIGATION
OF THE RELAXATION MECHANISMS
IN TWO NEW CLASSES OF SINGLE-MOLECULE MAGNETS.

Ti SPIN-½ RINGS

$Ti^{(IV)}{}_7Ti^{(III)}$

$Ti^{(IV)}$	$Ti^{(III)}$
S = 0	S = 1/2

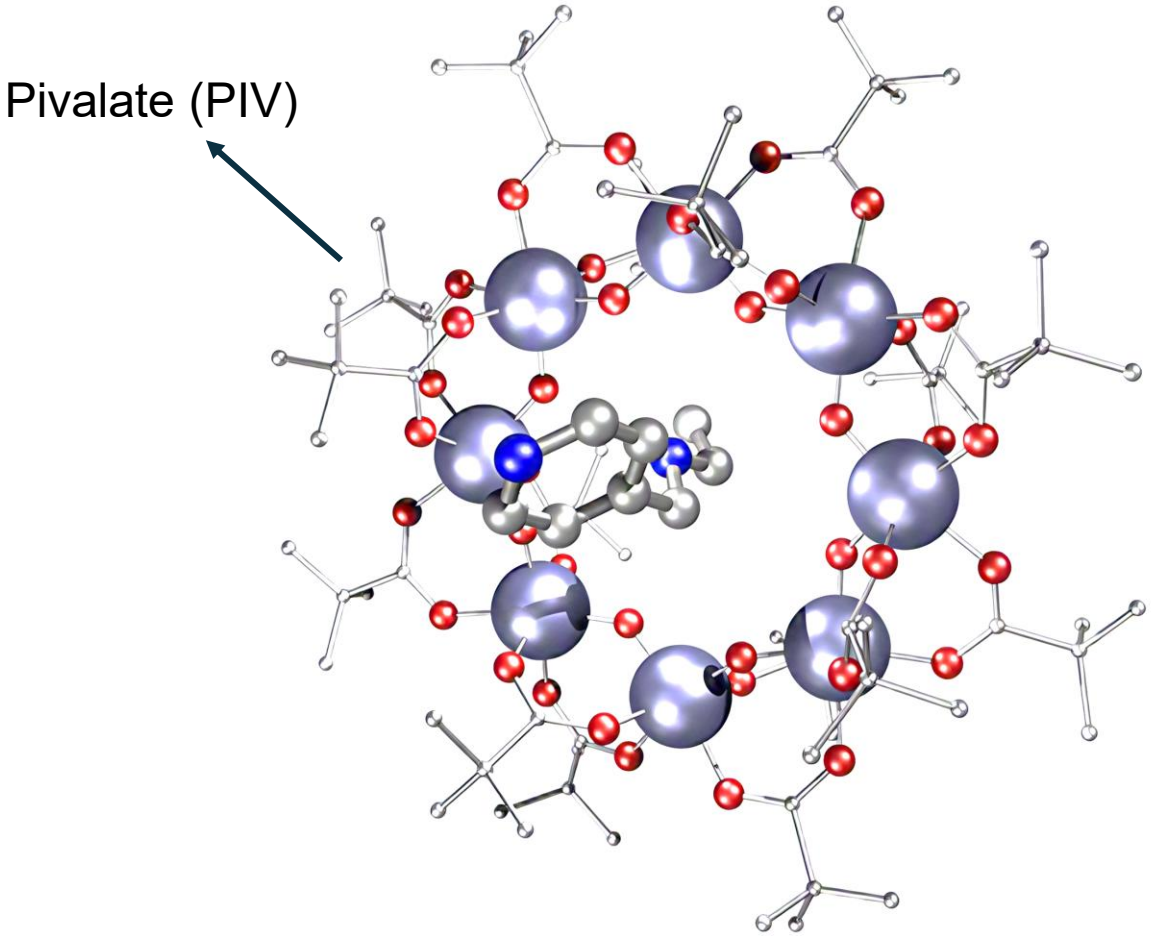
$Ti^{(IV)}{}_7Ti^{(III)}$



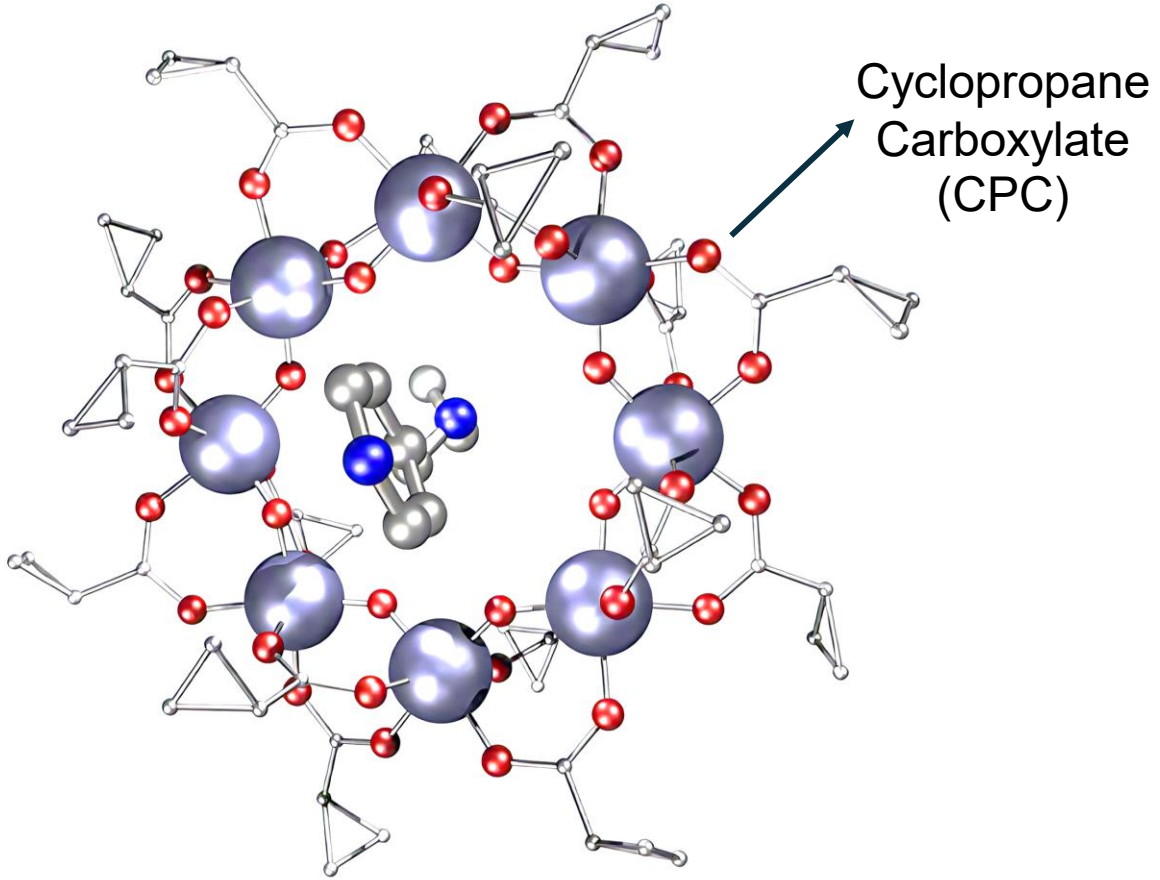
[12] S. Lockyer et al., Chem. Eur. J., e71451 (2026)

Ti SPIN-½ RINGS

$Ti^{(IV)}_7Ti^{(III)}$-PIV



$Ti^{(IV)}_7Ti^{(III)}$-CPC



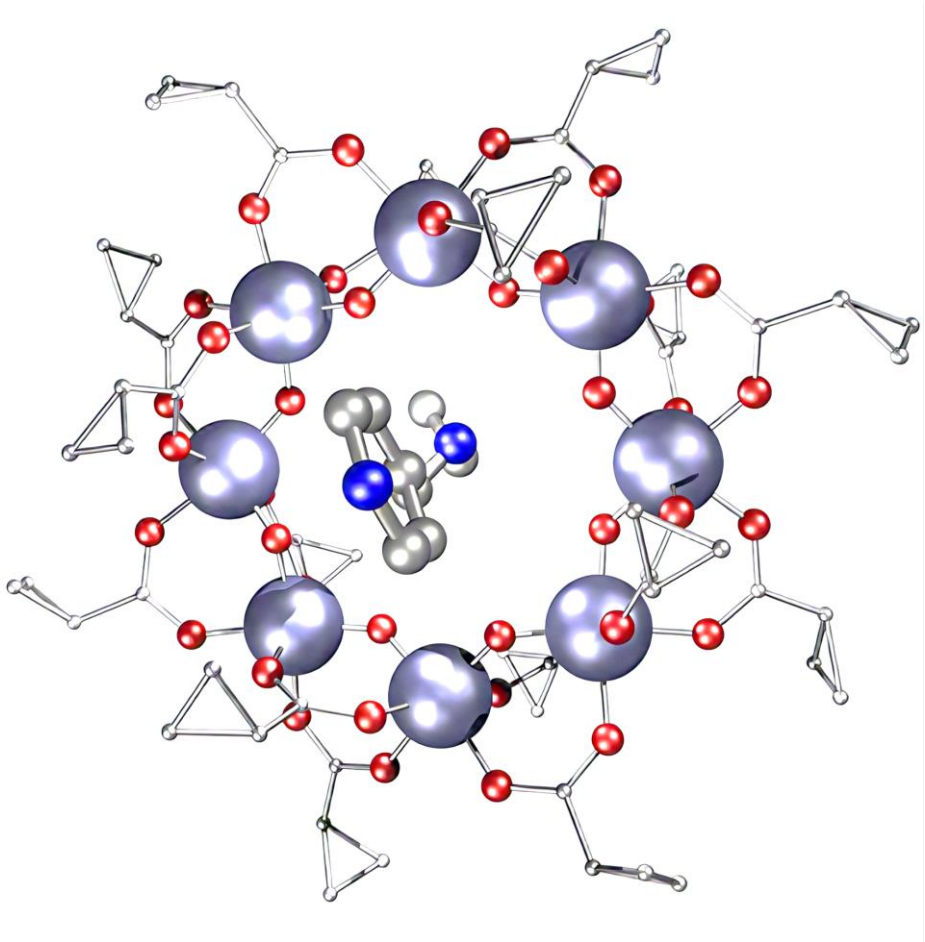
[12] S. Lockyer et al., Chem. Eur. J., e71451 (2026)

Ti SPIN-½ RINGS

$Ti^{(IV)}{}_7Ti^{(III)}$-CPC

NEW

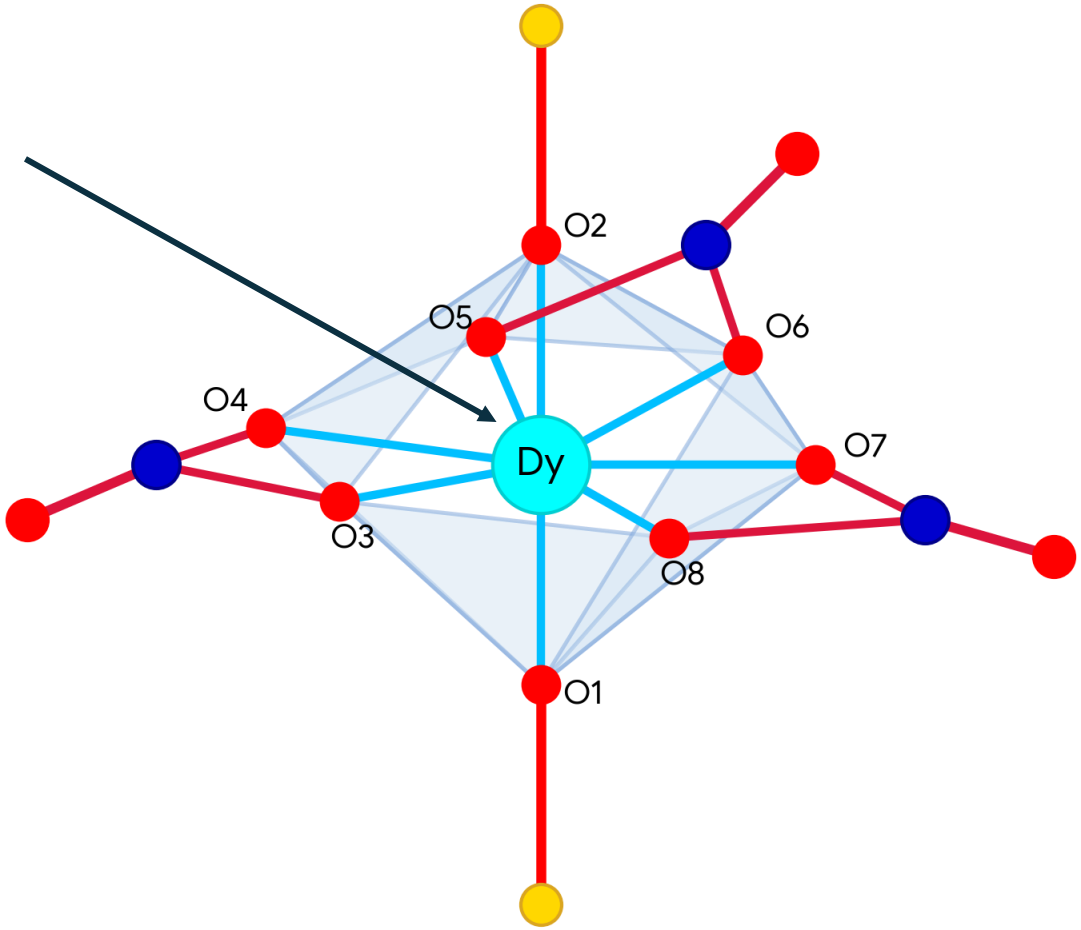
- 1 electron (not 23)
- Rigidity of ligands
- No methyl groups



Collaboration: group of Prof. Richard Winpenny from University of Manchester (UK)

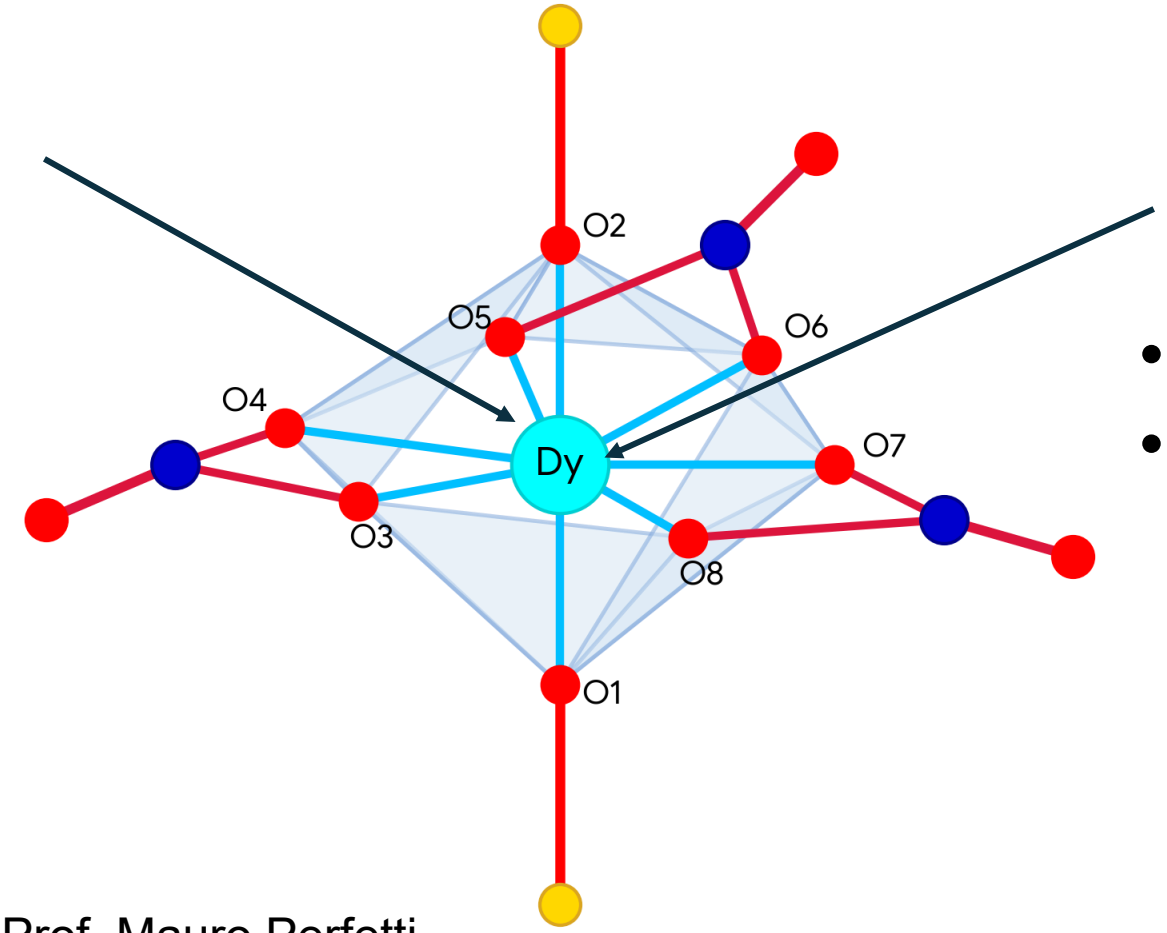
Ln-based SIMs

- Dy $J = \frac{15}{2}$
- Er $J = \frac{11}{2}$

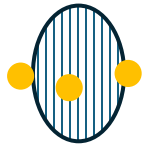


Ln-based SIMs

- Dy $J = \frac{15}{2}$
- Er $J = \frac{11}{2}$



NEW
HEXAGONAL BY-PIRAMID

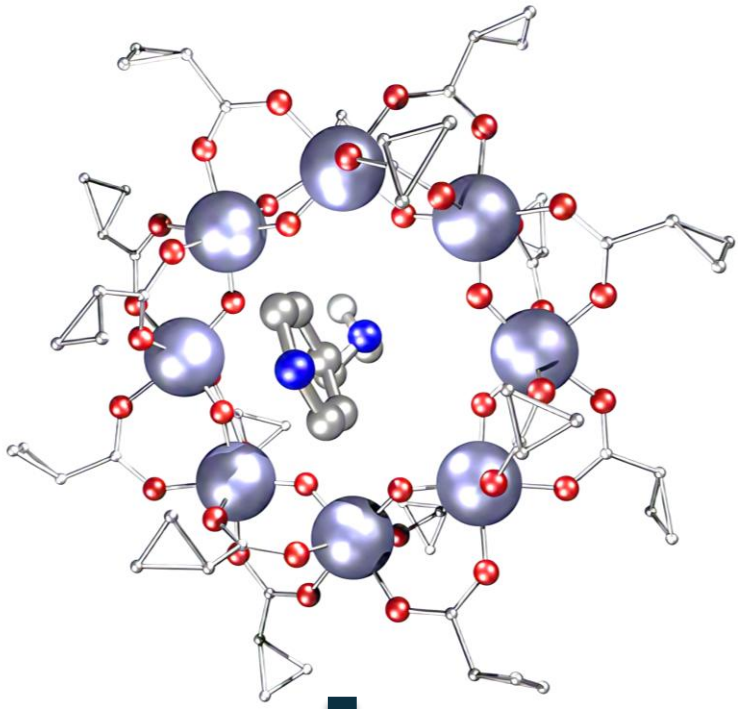


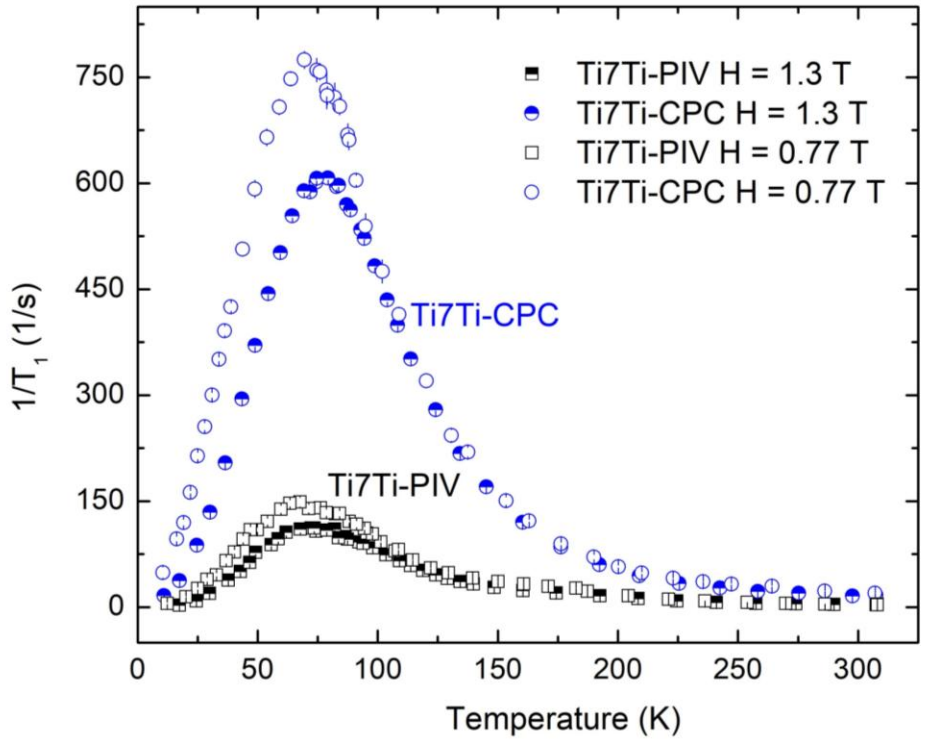
- No QTM
- High Anisotropy

Collaboration: group of Prof. Mauro Perfetti from University of Firenze (IT)

NEXT STEPS WITHIN THE PROJECT

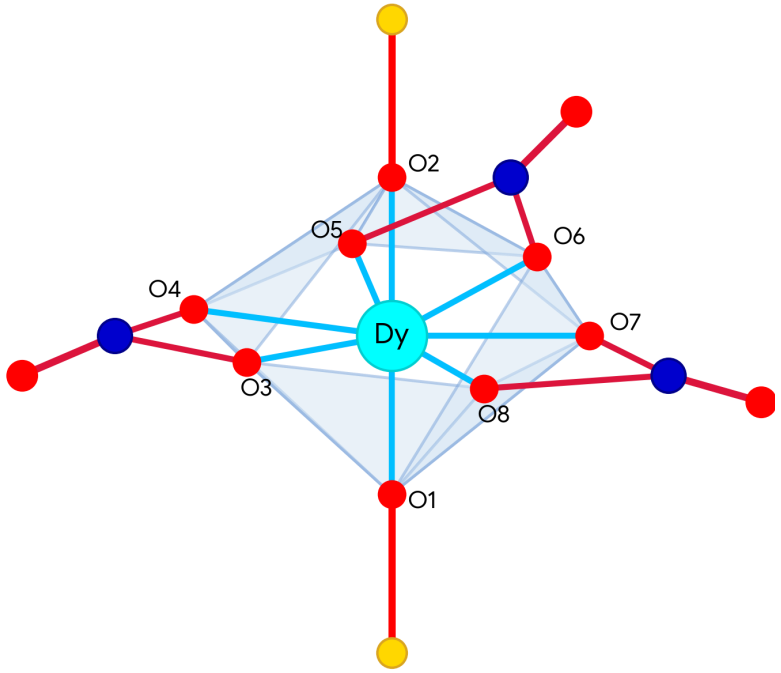
$$\frac{1}{T_1} = A \cdot \frac{\tau_c}{1 + \omega_L^2 \tau_c^2}$$



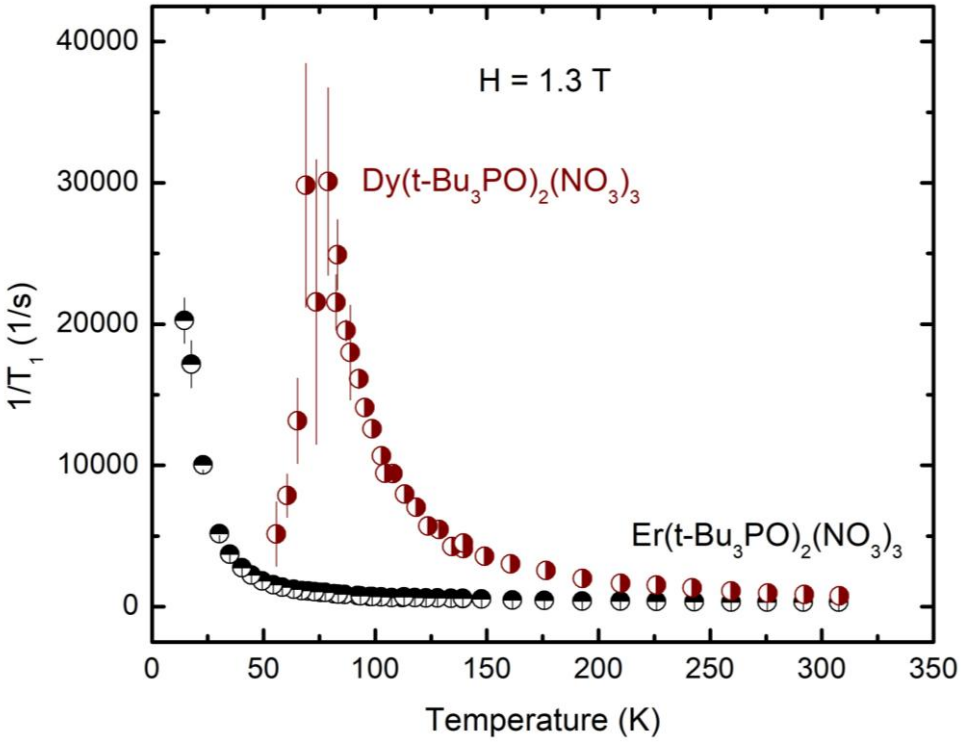


DIRECT DETERMINATION OF COHERENCE TIME with PULSED EPR

NEXT STEPS WITHIN THE PROJECT



WIPE-OUT EFFECT



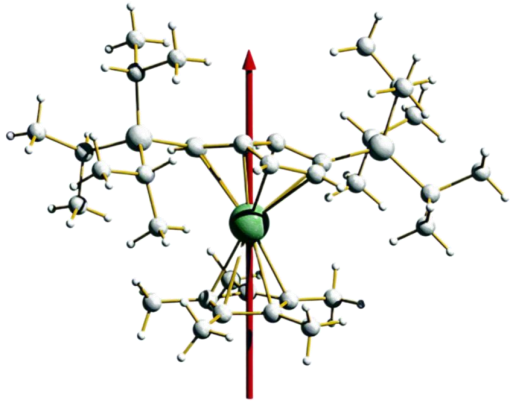
DEEPER DETERMINATION OF DECOHERENCE MECHANISMS with LF-μSR

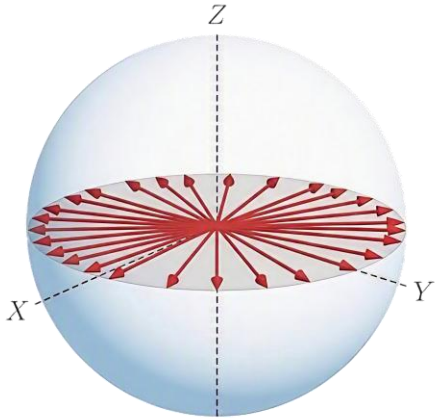
Thank you for your kind attention!

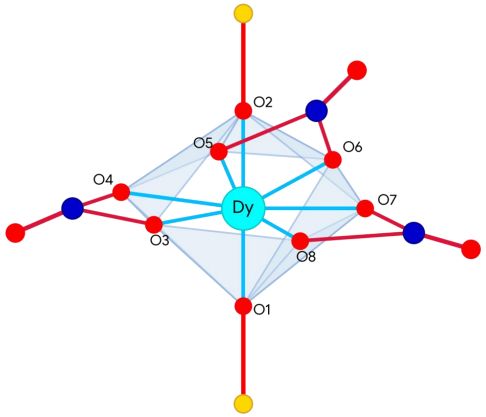
MOLECULAR MAGNETISM

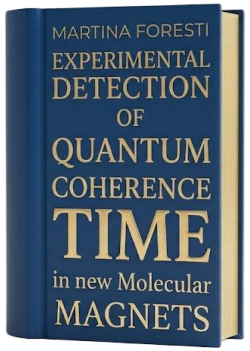
"MM is the interdisciplinary area where chemists design and synthesize materials of increasing complexity based on feedback interaction with physicists, who want to observe phenomena of purely quantum origin, as well as magnetic properties typical of bulk materials". [1]

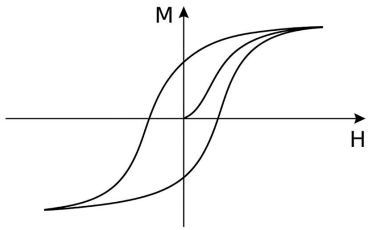
[1] R. Sessoli, D. Gatteschi et al., Molecular Nanomagnets (1998)

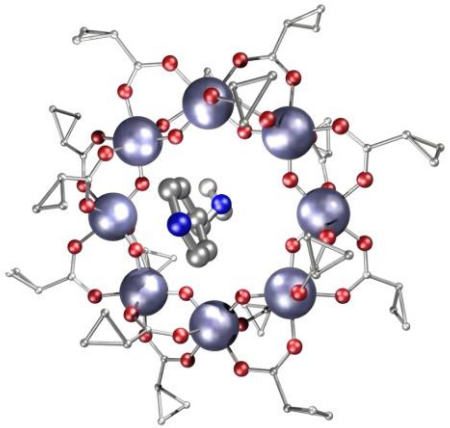



Z
X
Y


O2
O5
O6
O4
Dy
O7
O3
O8
O1

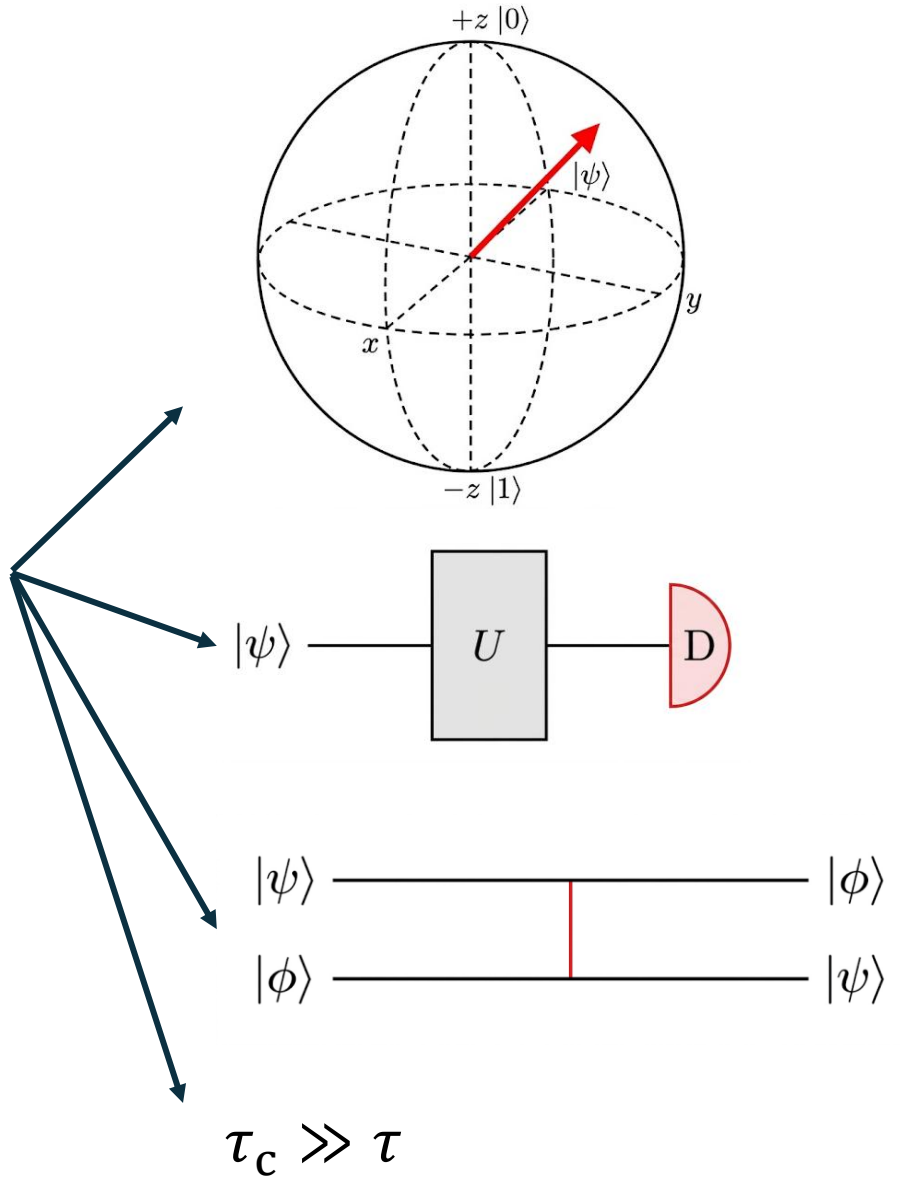

MARTINA FORESTI
EXPERIMENTAL
DETECTION
OF
QUANTUM
COHERENCE
TIME
in new Molecular
MAGNETS


M
H



QPUs

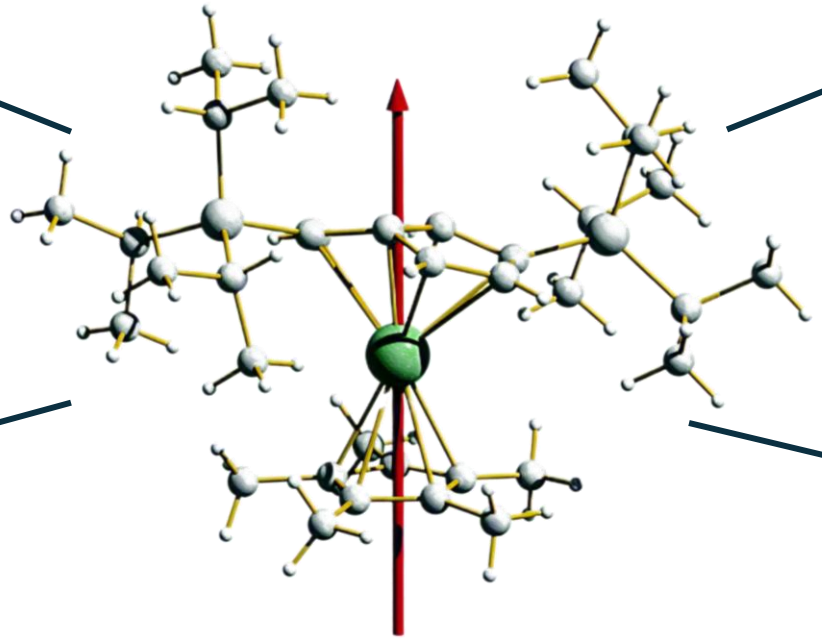
QPUs satisfy the Di Vincenzo criteria



SMMs as QUBITS

ROBUSTNESS OF THE QUANTUM STATE

QUANTUM CONTROL through CHEMISTRY



SCALABILITY

CONTROL AND READING via EPR

Adapted from A. Kilpatrick et al. Chem. Commun. 54, 7085 (2018)

NET HAMILTONIAN

SPIN HAMILTONIAN

HEISENBERG EXCHANGE

UNIAXIAL ANISOTROPY

BIAXIAL ANISOTROPY

ZEEMAN INTERACTION

$$\hat{H} = \sum_{i,j}^{N.N.} J_{ij}\,\hat{\vec{s}_i}\cdot\hat{\vec{s}_j} + \sum_i \left[D_i \hat{s}_{i,z}^2 + E_i\left(\hat{s}_{i,x}^2 - \hat{s}_{i,y}^2\right)\right] + \sum_i \mu_B\,\vec{B}\,\vec{\vec{g}}_e\,\hat{\vec{s}_i} +$$

$$+ \sum_{i,j} A_{ij}\,\hat{\vec{s}_i}\cdot\hat{\vec{I}_j} + \sum_j \mu_N\,\vec{B}\,\vec{\vec{g}}_N\,\hat{\vec{I}_j} + \sum_i \xi_i\,\vec{l_i}\cdot\vec{s}_i$$

HYPERFINE INTERACTION

ZEEMAN INTERACTION nuclear

SPIN-ORBIT COUPLING

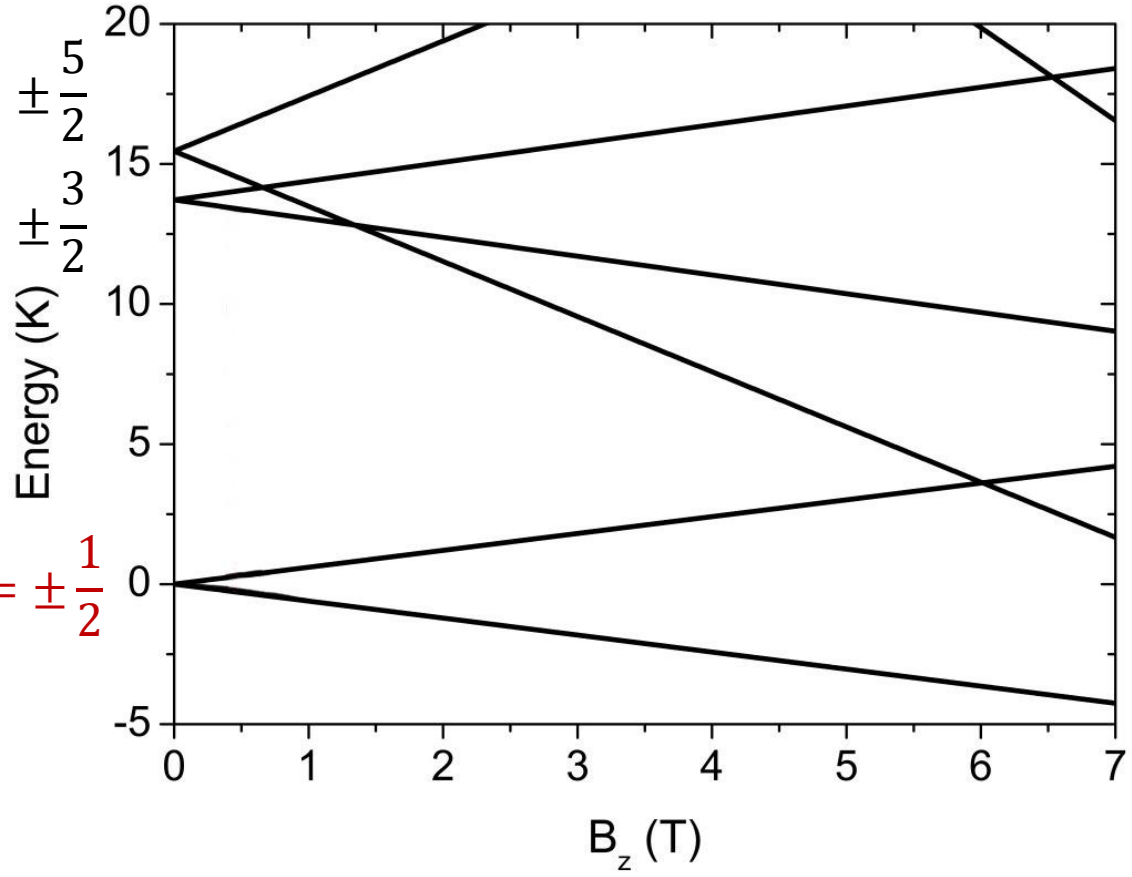
[2] Adapted from W. Wu et al., Molecules, 30, 2522 (2025)

MAGNETIC BEHAVIOUR of RINGS

$s = \frac{5}{2};\ m_s = \pm\frac{5}{2}$

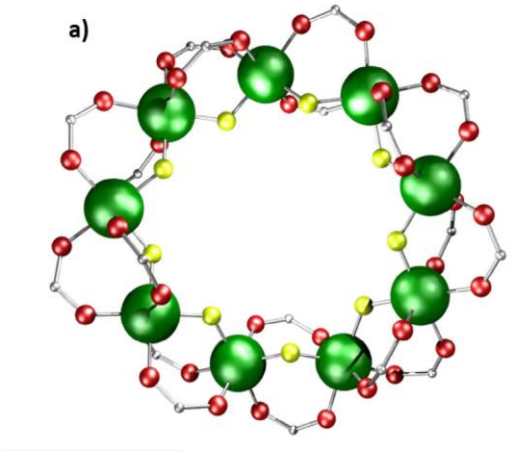
$s = \frac{3}{2};\ m_s = \pm\frac{3}{2}$

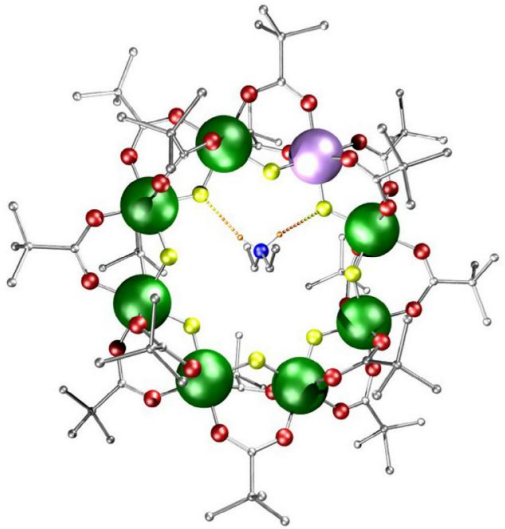
$s = \frac{1}{2};\ m_s = \pm\frac{1}{2}$



[4] A. Bianchi et al., Phys. Rev. B, 82,134403 (2010)

MAGNETIC BEHAVIOUR of RINGS

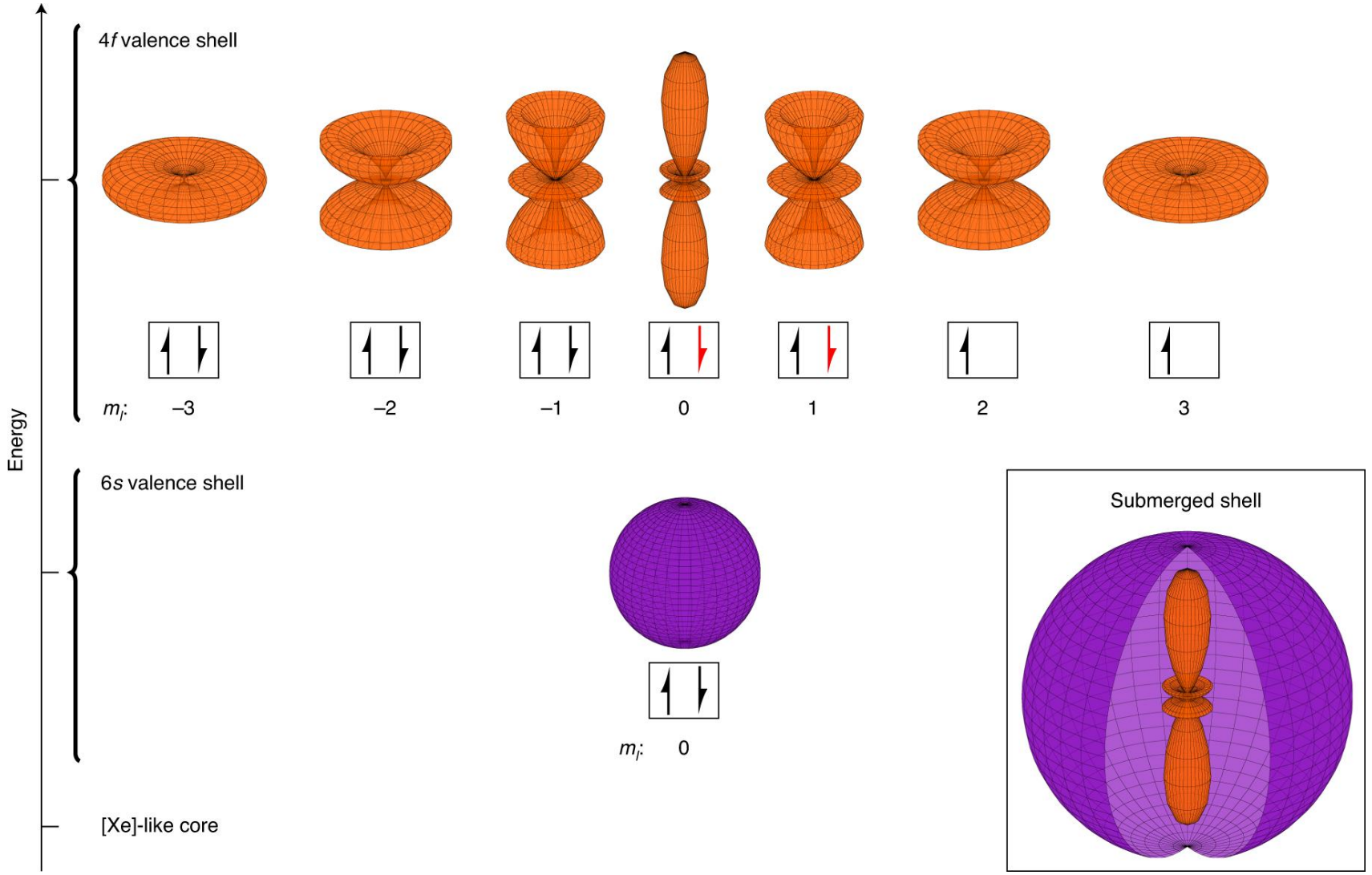




Atoms: [1]
- Cr, green
- Ni/Fe/Cd, lilac
- O, red
- N, blue
- F, yellow
- C, grey
- H, omitted for clarity

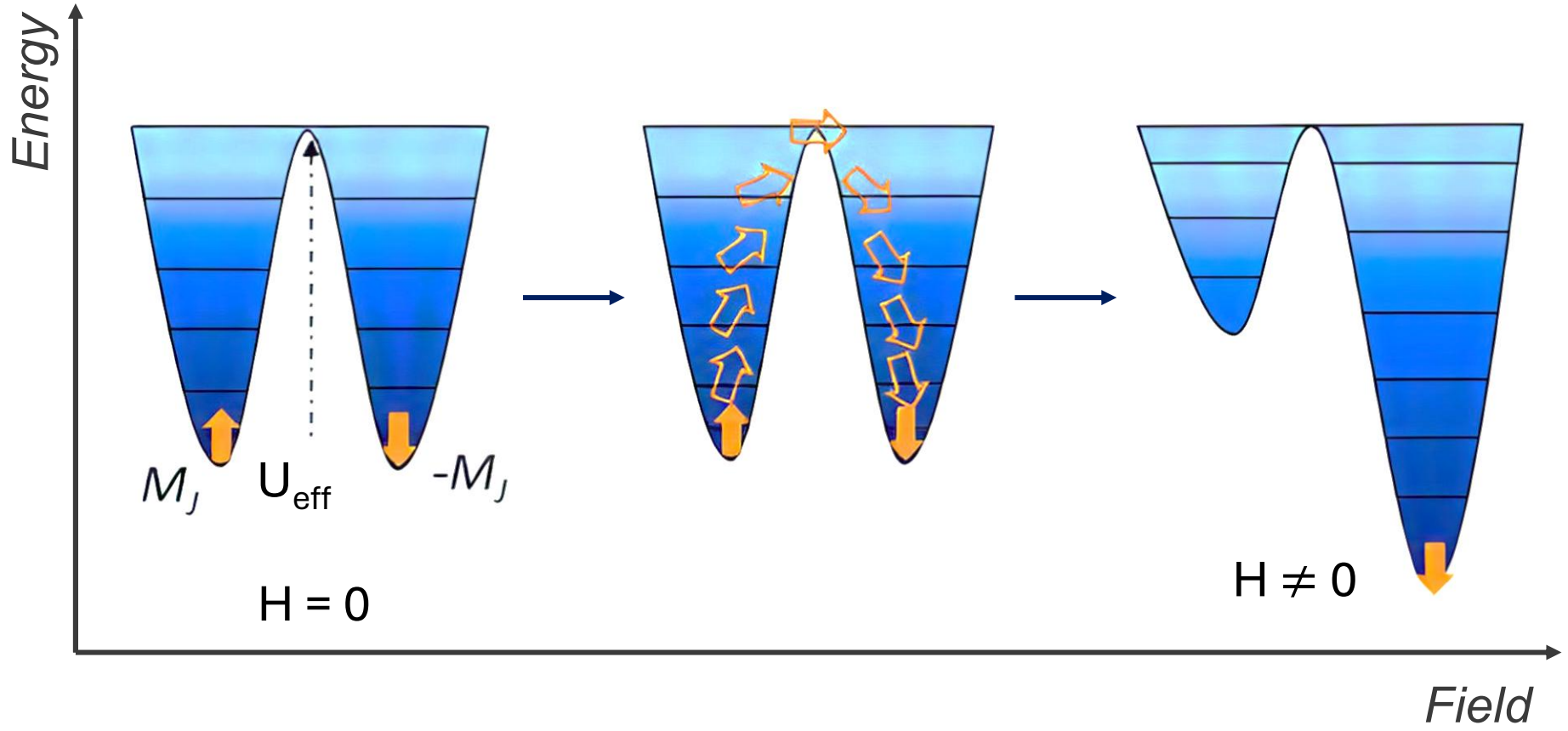
Molecule	Valence	Spin (low T)	Interest
Cr_8	Cr(III) $S = 3/2$	0	AFM chain; dope supramolecular assemblies [1]
Cr_7Cd	Cd(0)	3/2	Qudit
Cr_7Ni	Ni(II) and $S = ½$	½	Qubit
Cr_7Fe	Fe(II) and $S = ½$	½	Qubit

LANTHANIDE OAM



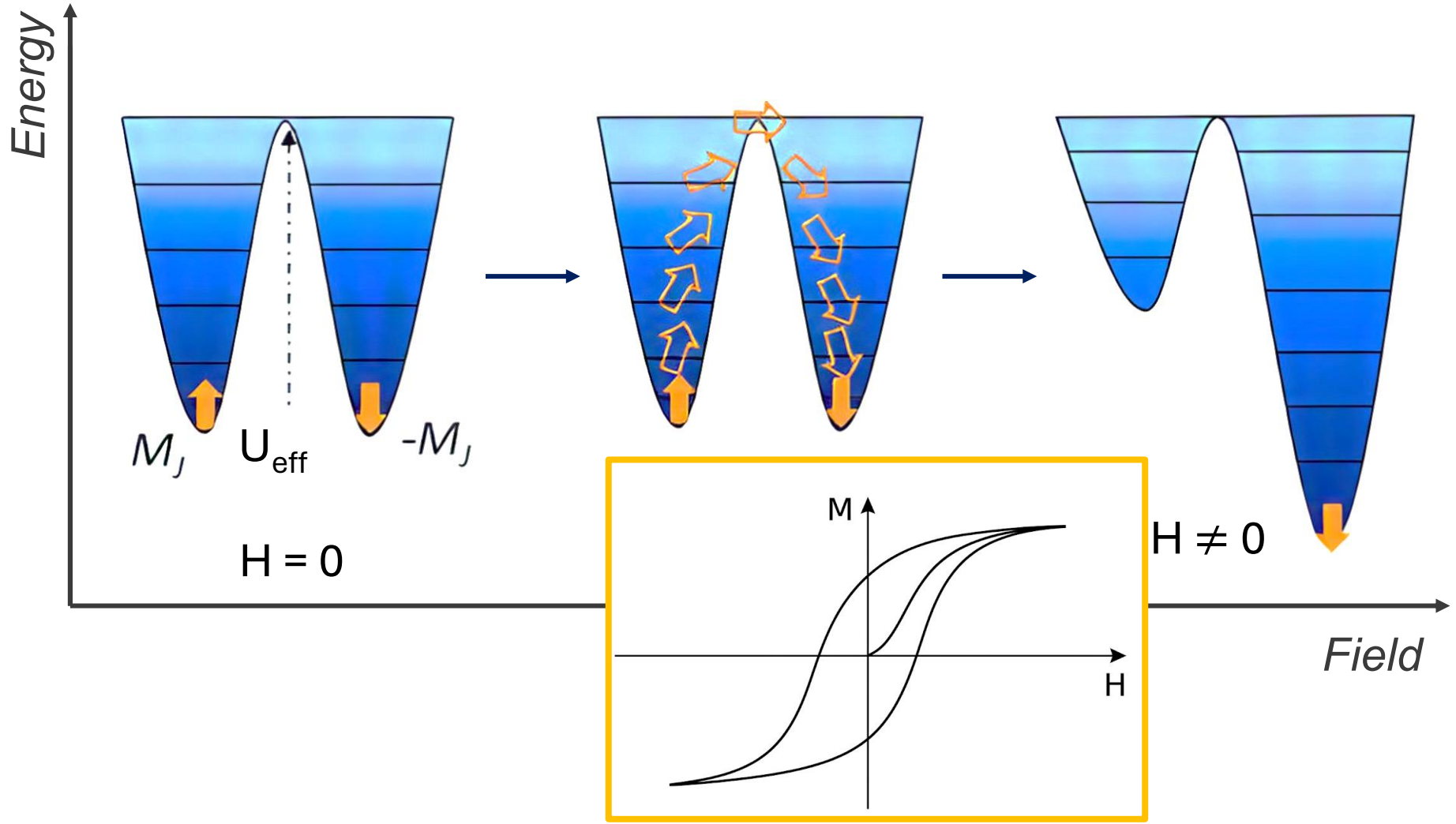
Norcia, M.A., Ferlaino, F. *Nat. Phys.* **17**, 1349–1357 (2021)

Ln-SIMs AS QUBITS

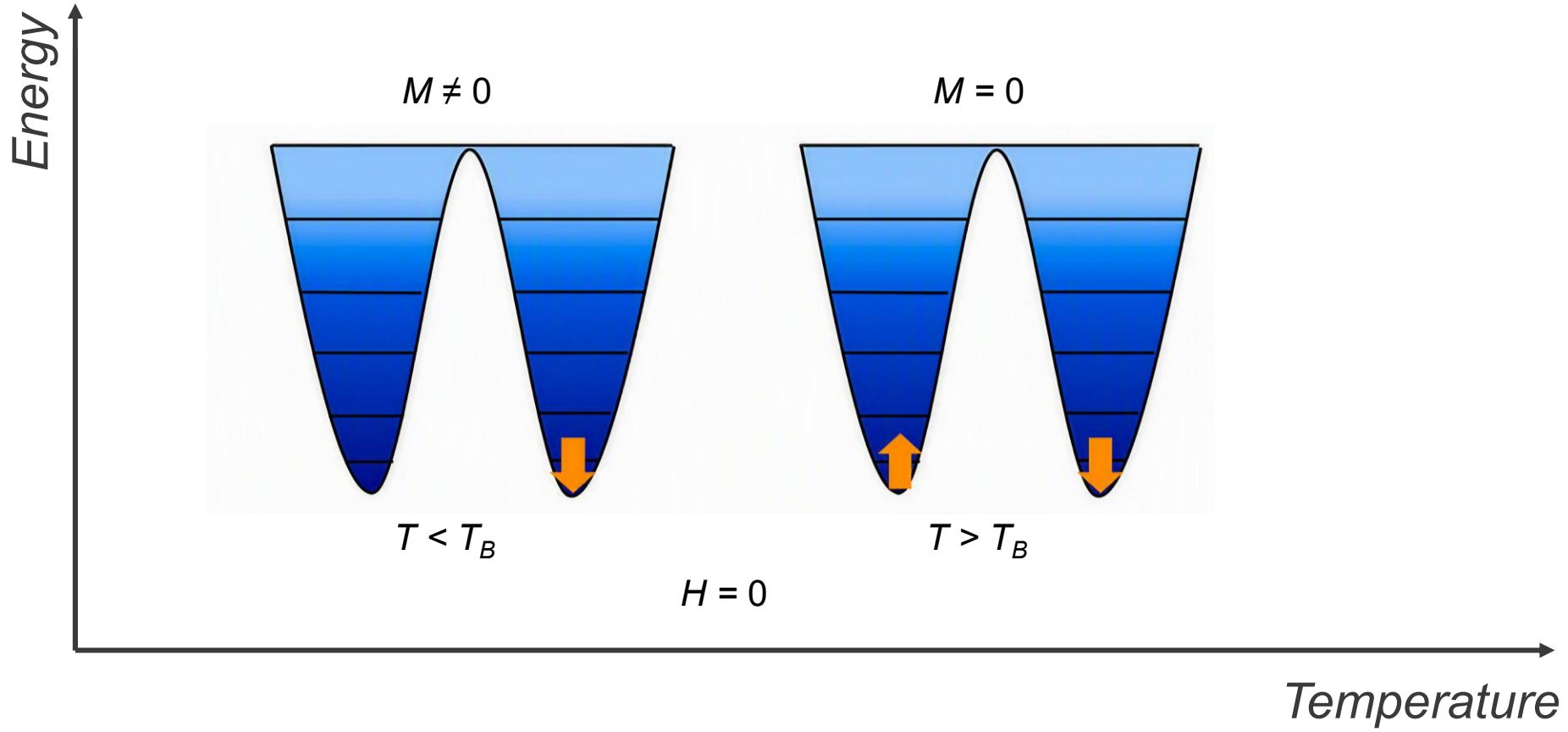


[5] Adapted from A. G. Bispo-Jr. Coord Chem Rev. 537, 216685 (2025)

Ln-SIMs AS QUBITS

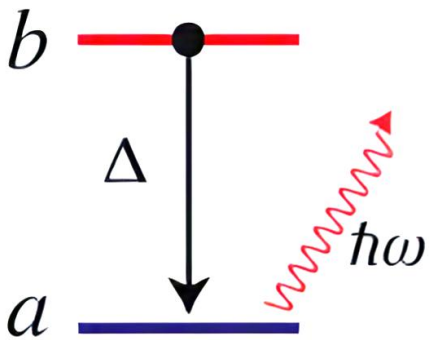


Ln-SIMs AS QUBITS



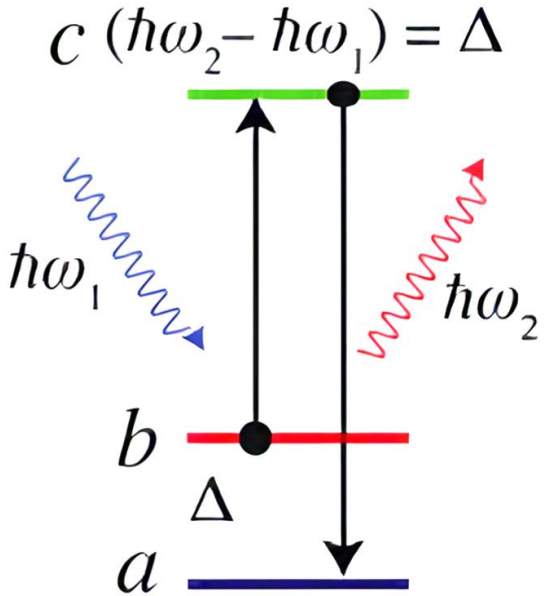
[5] Adapted from A. G. Bispo-Jr. Coord Chem Rev. 537, 216685 (2025)

SPIN-PHONON COUPLING



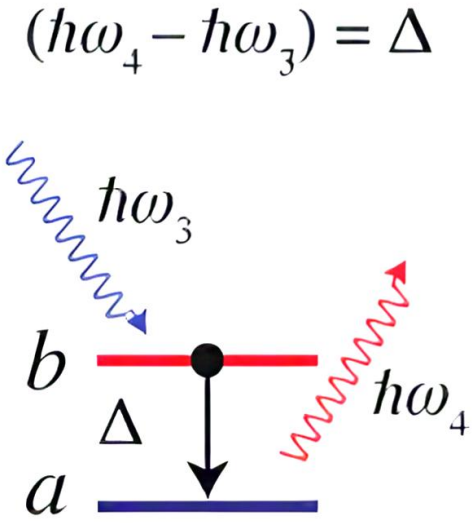
Direct

$$AH^4T$$



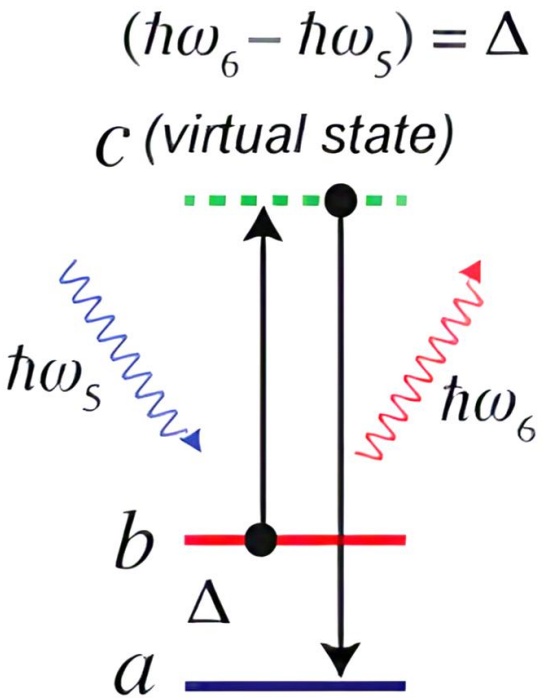
Orbach

$$\frac{1}{\tau_0 exp\left(\frac{U_{eff}}{K_B T}\right)}$$



First order Raman

$$CT^n$$

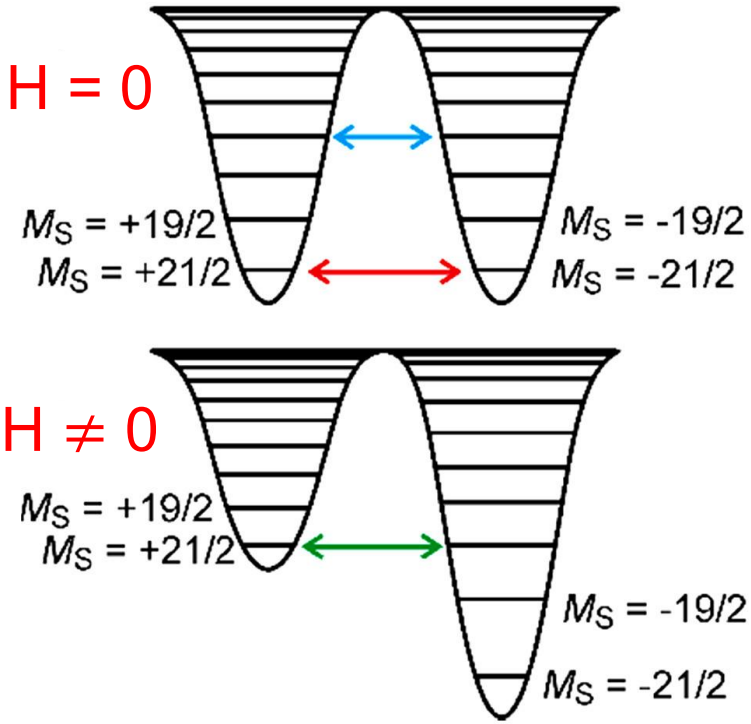


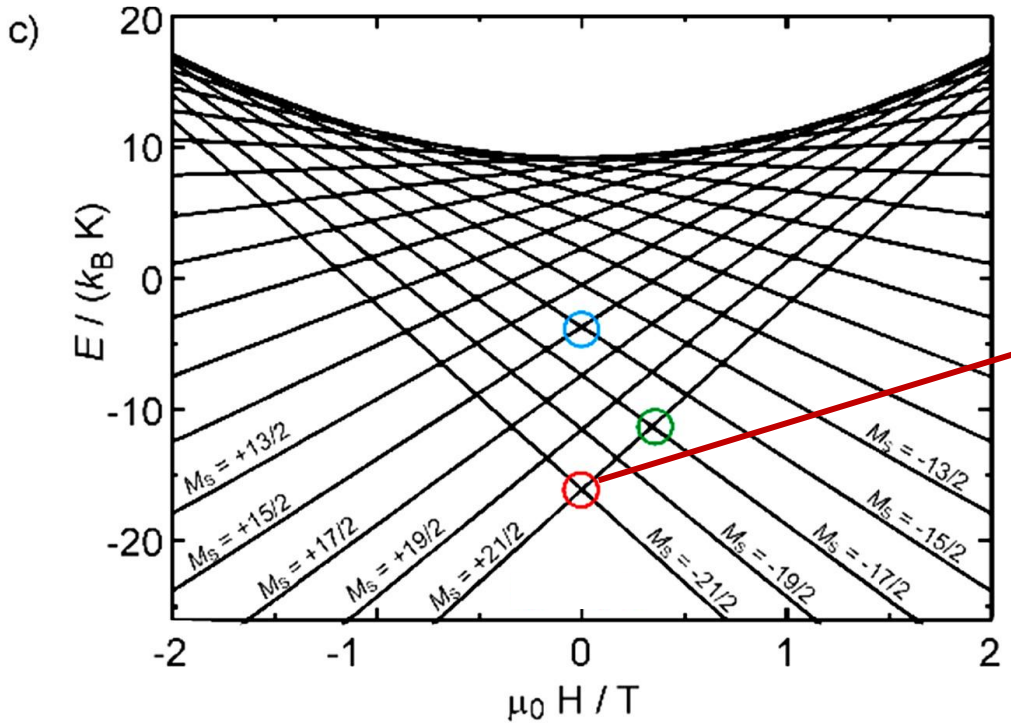
Second order Raman

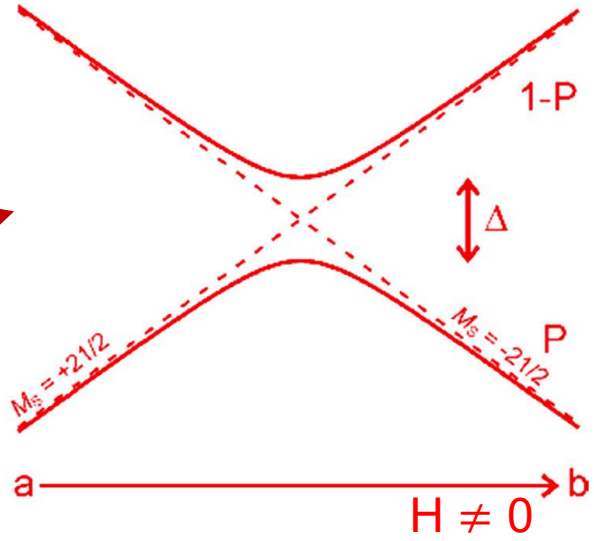
$$D\frac{exp\left(\frac{-h\omega}{K_B T}\right)}{\left(exp\left(\frac{-h\omega}{K_B T}\right)-1\right)^2}$$

QUANTUM TUNNELING

e.g. $S = 21/2$ with easy-axis anisotropy







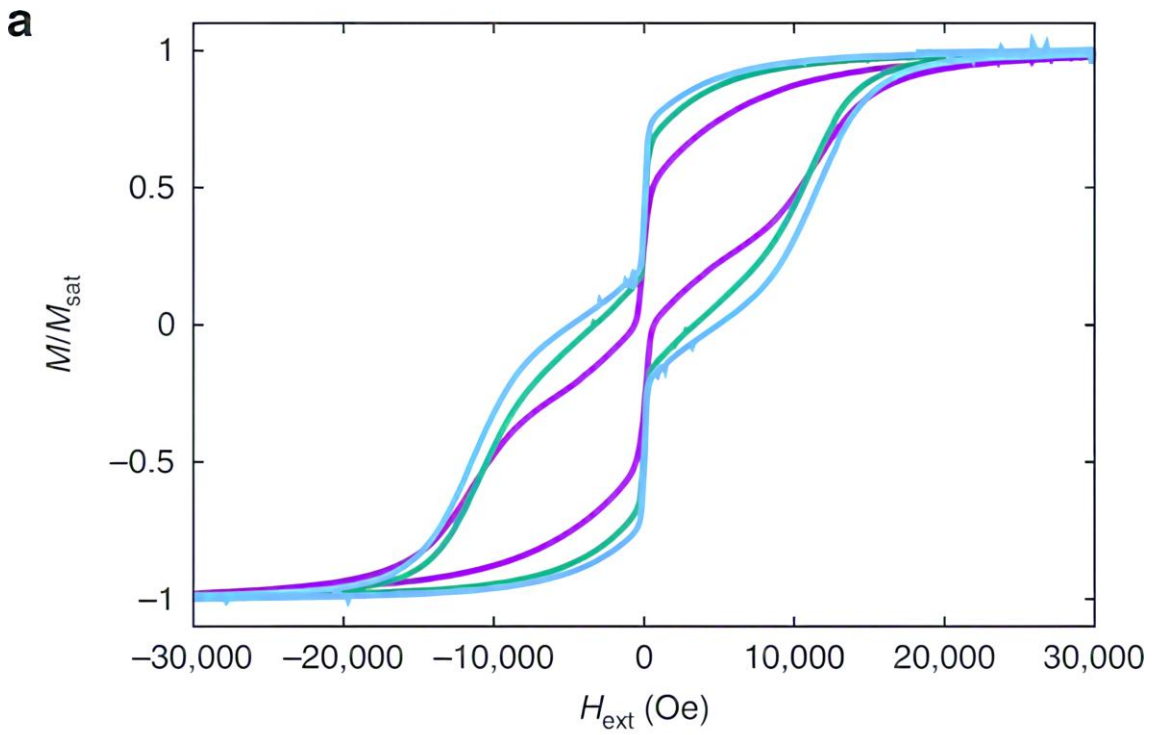
QTM pathways

- red: GS-QTM
- blue: thermal-assisted QTM
- green: field-induced QTM

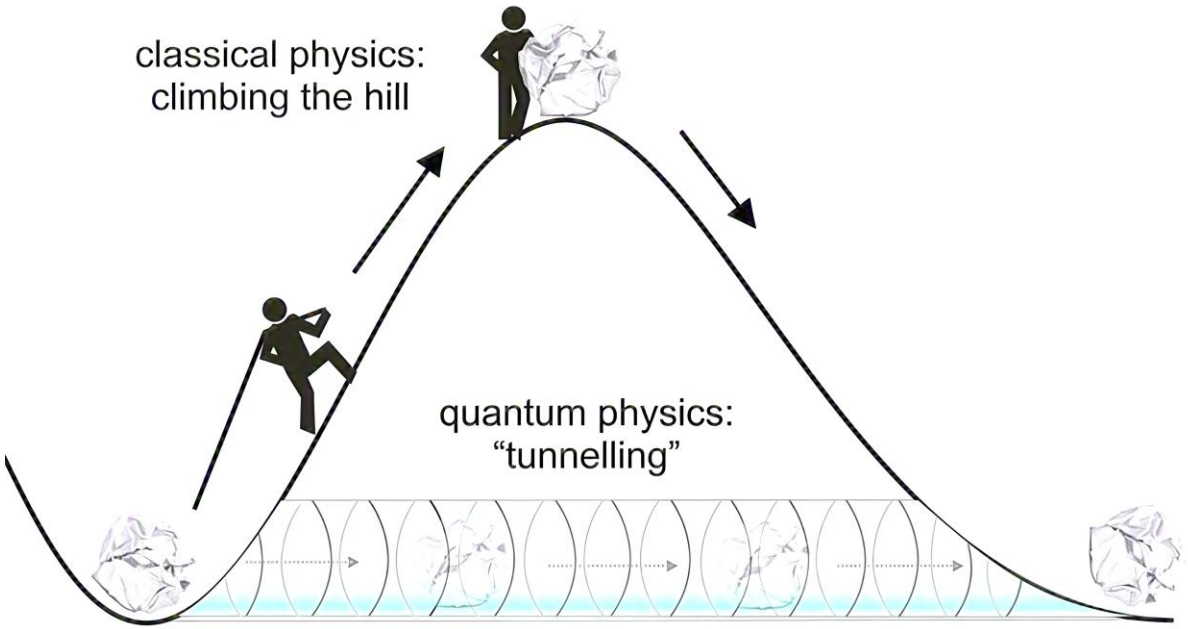
Zeeman diagram with QTM

Landau-Zener diagram

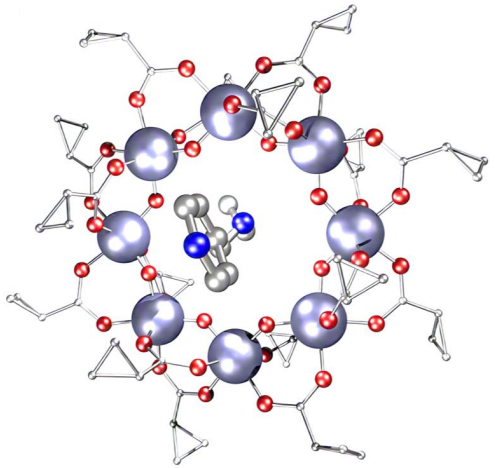
QUANTUM TUNNELING



Y.S. Ding et al., *Nat. Commun.* **9**, 3134 (2018)

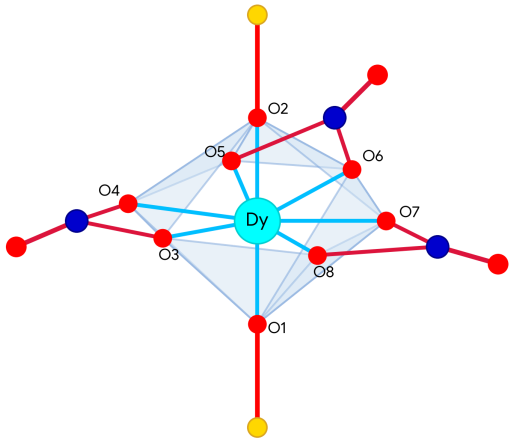


CHEMICAL FORMULAS



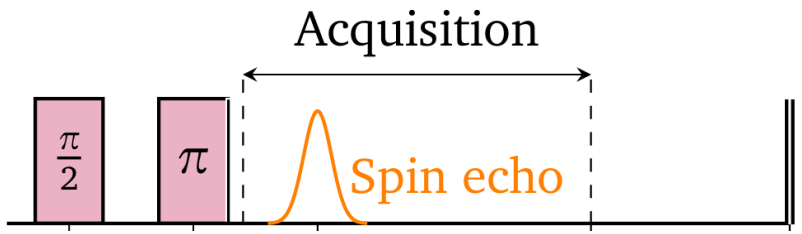
$[py\text{-}CH_2NH_2Et]^+[Ti_7^{(III)}Ti^{(IV)}O_8(CPC)_{16}]$

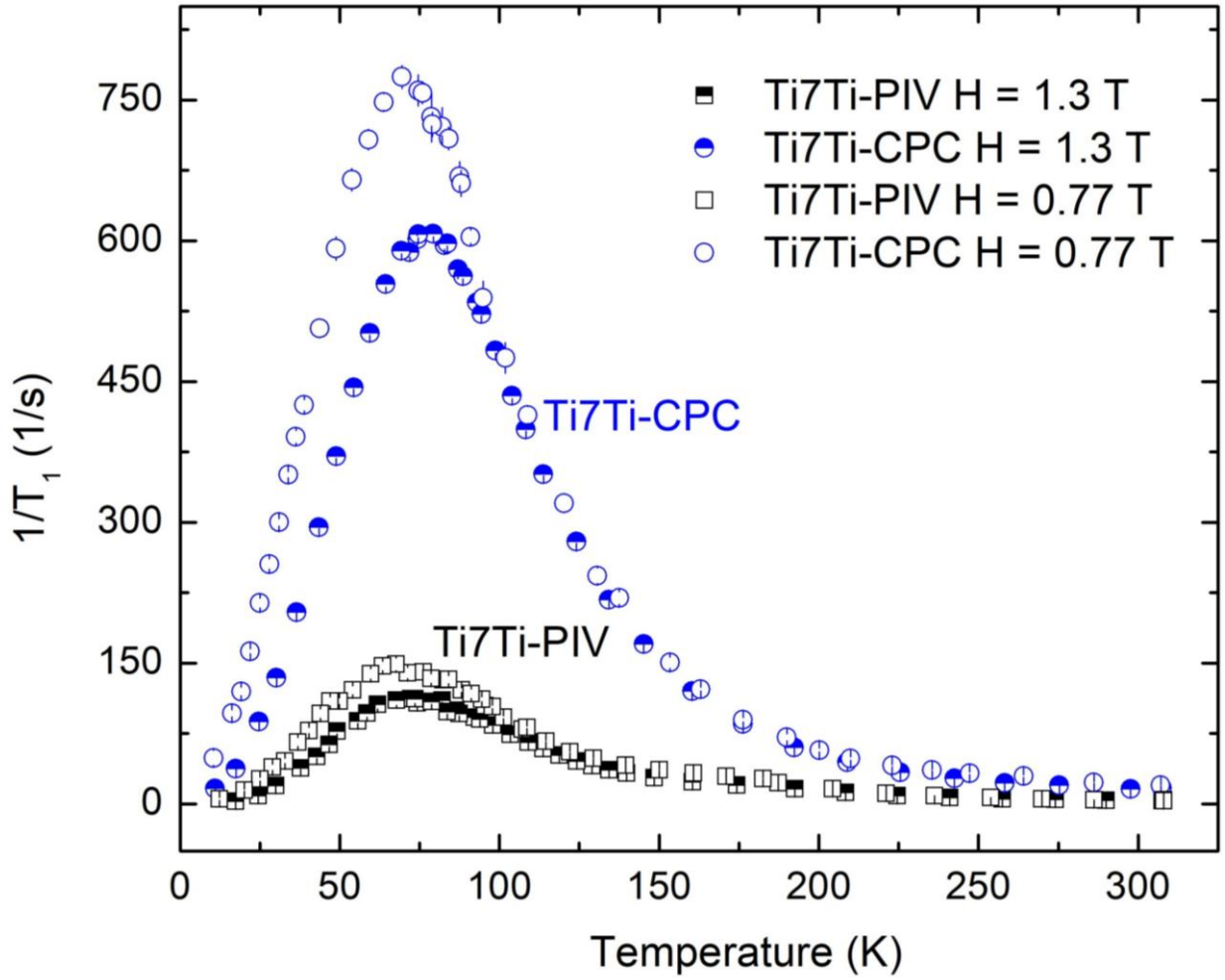
py= pyridyl
CPC = cyclopropane carboxylate $(CH_2)_3CHCOOH$
Piv = pivalate = trimethyl acetic acid $(CH_3)_3CCOOH$



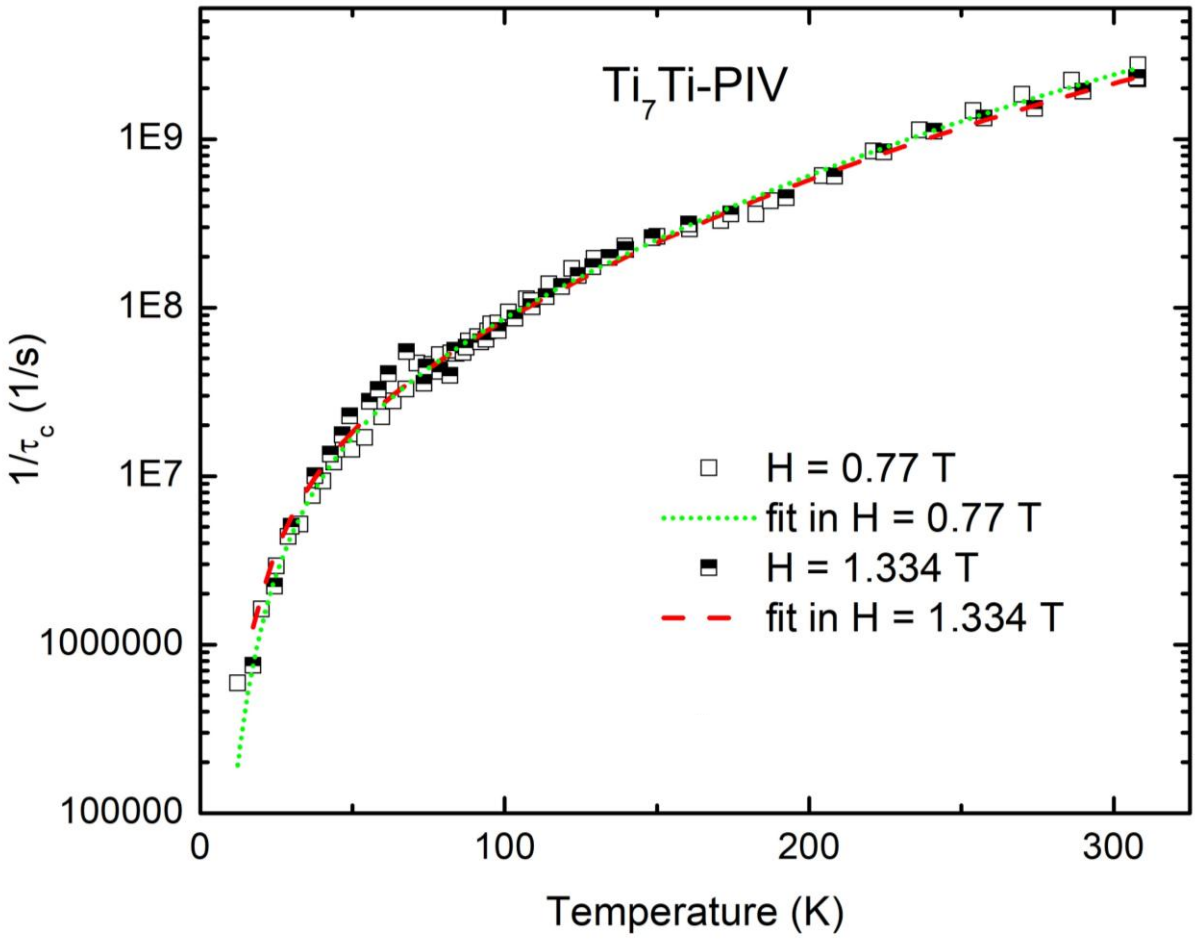
$Ln(t\text{-}BuPO_2)_2(NO_3)_3$

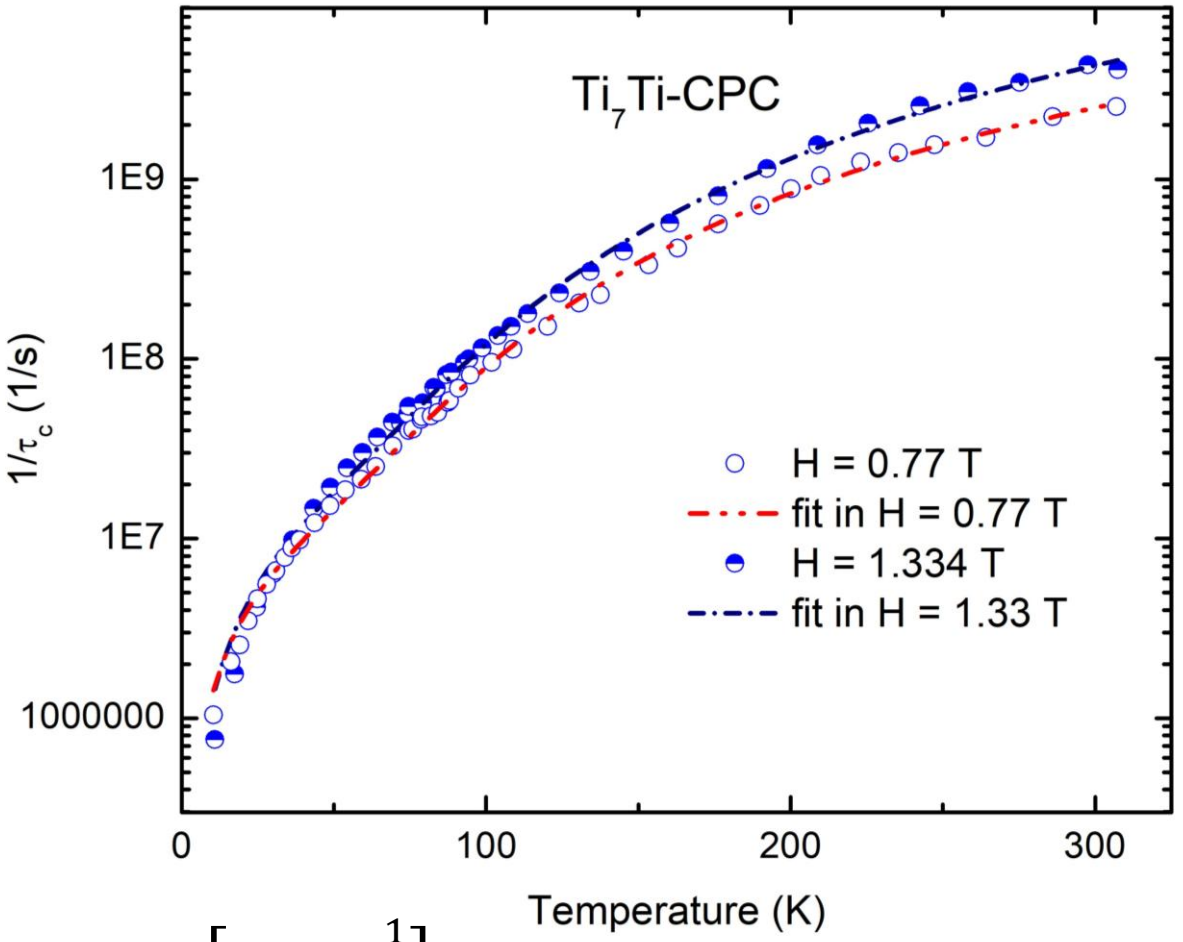
EXPERIMENTAL DATA





EXPERIMENTAL DATA





$$\frac{1}{\tau_c} = CT^n + D\exp\left[-\left(\frac{K}{T}\right)^{\frac{1}{2}}\right]$$

In preparation …