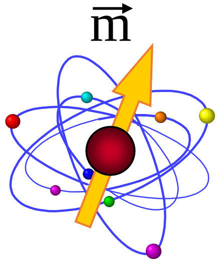
Lecture 8

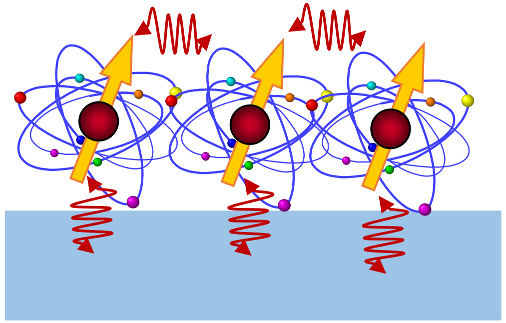
Dynamics for quantized spins:
Spin Hamiltonian

The spintronics "goose game"

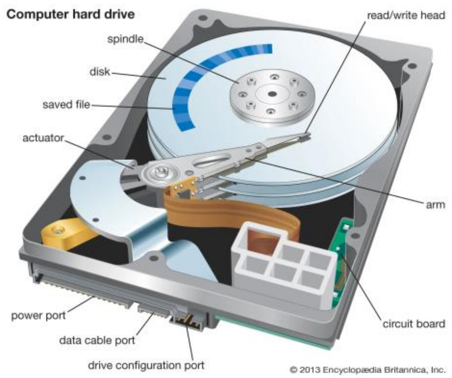
Atom magnetism

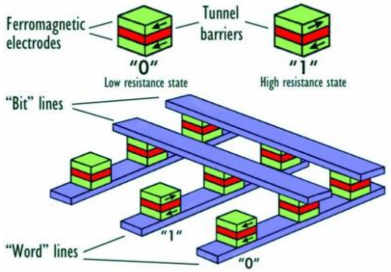


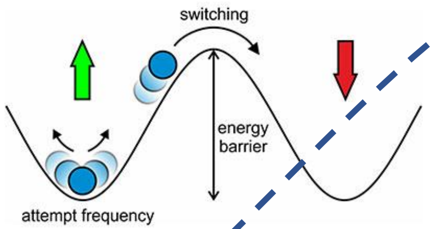
interactions between spins and with the supporting substrate



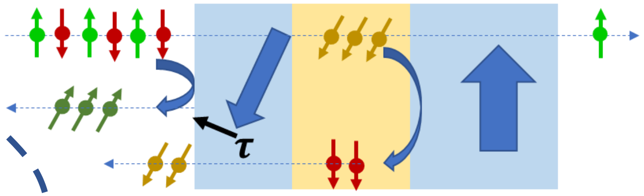
applications

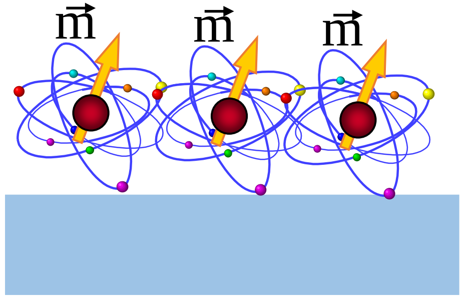




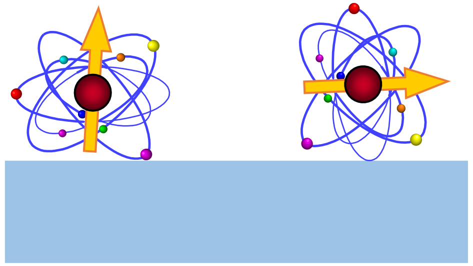


STT - SOT

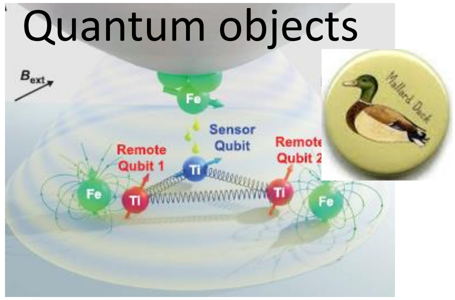




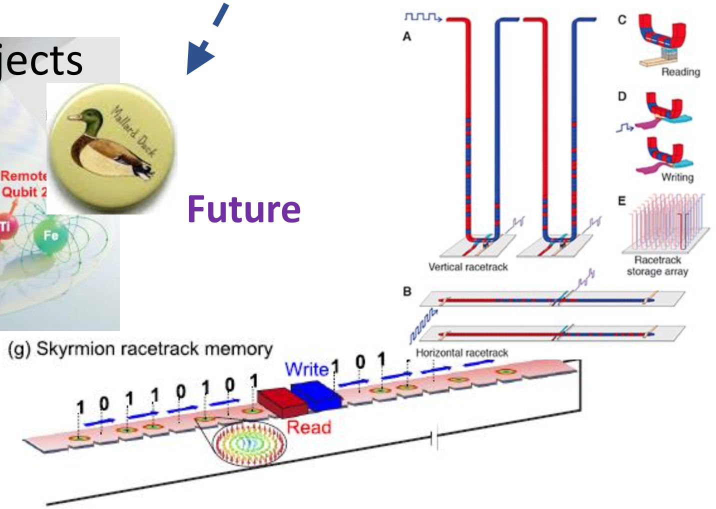
magnetic moment in a cluster and/or on a support



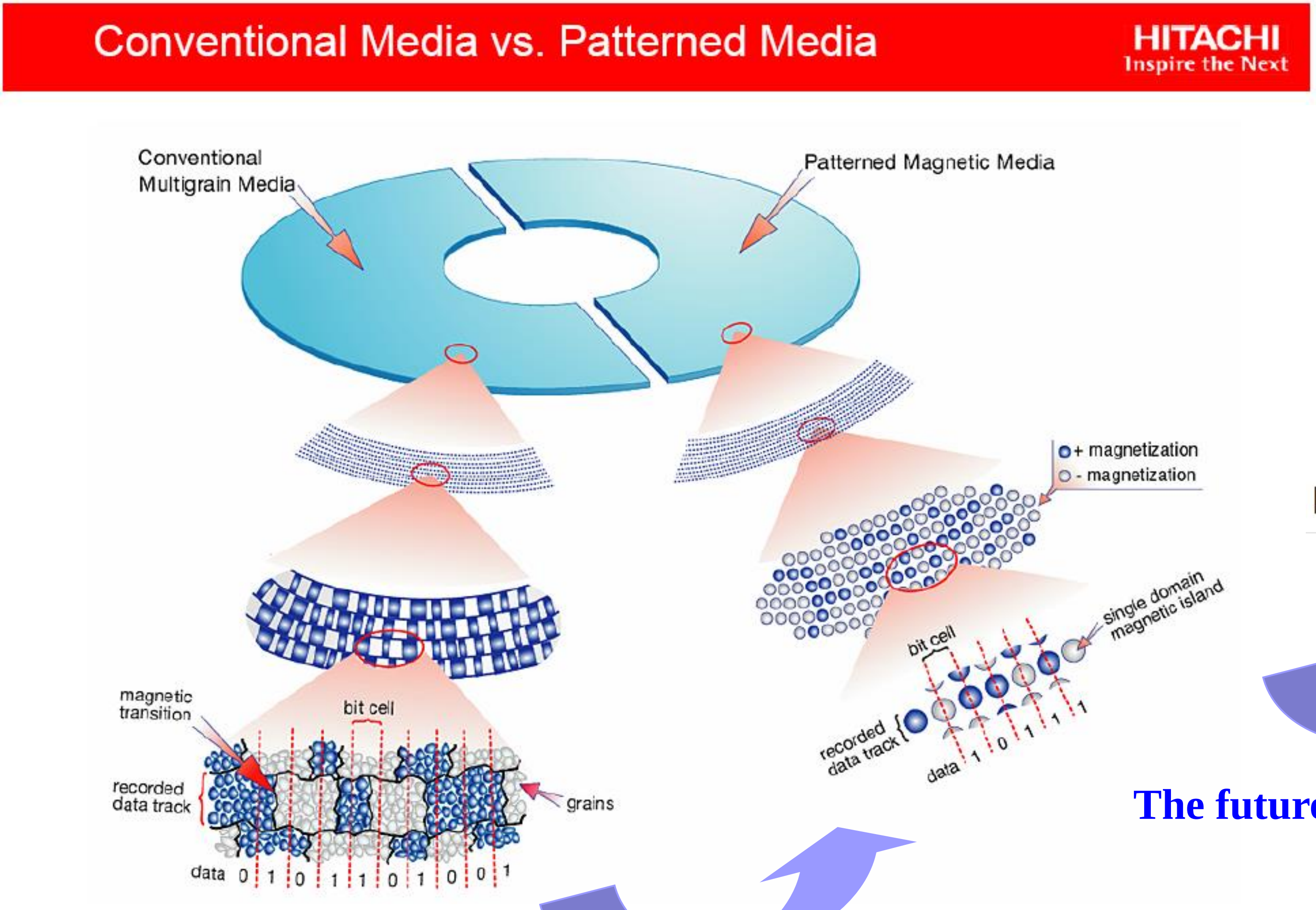
Magnetization easy axis

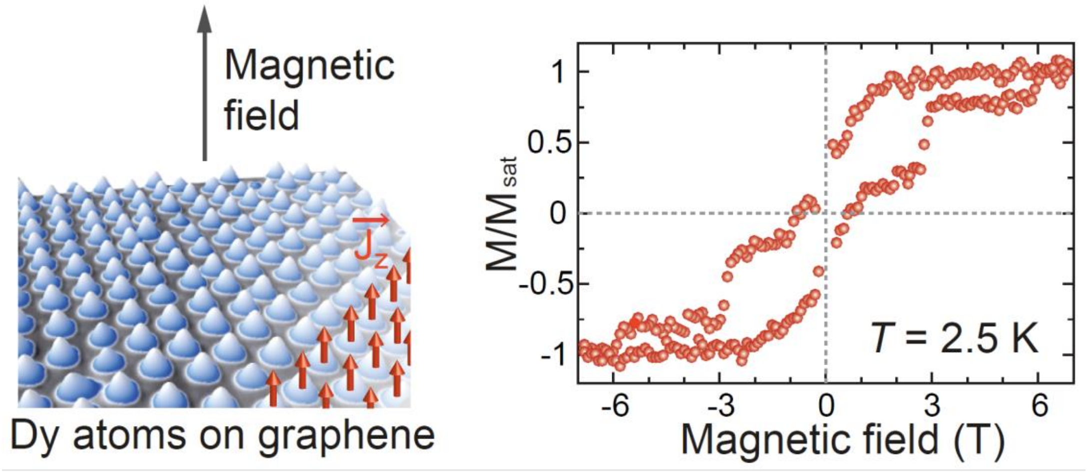


Future



From classic to quantum



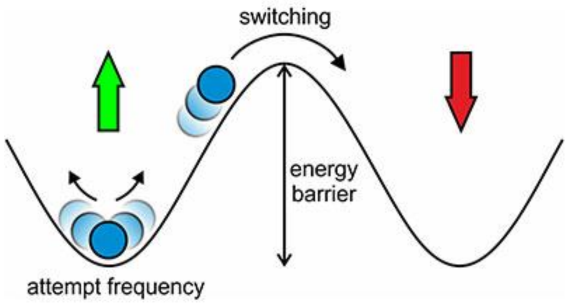


The future of the future: single atom per bit

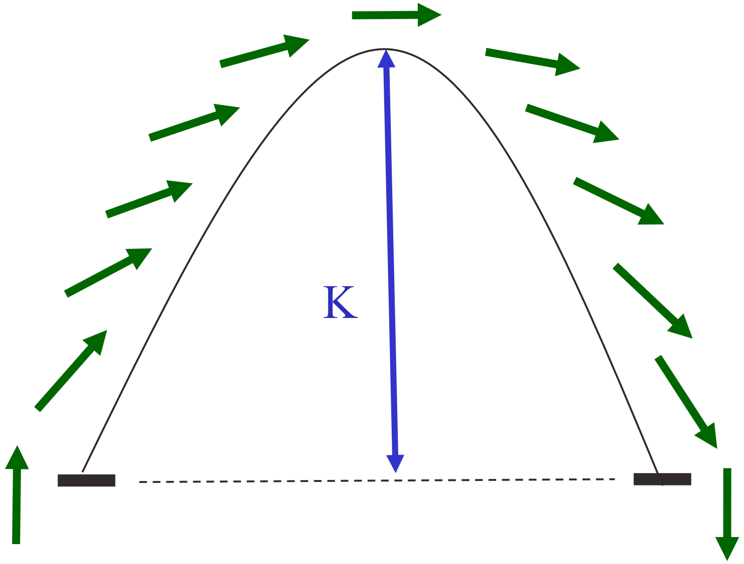
The future: single particle per bit

10.1021/acs.nanolett.6b03543

Spin reversal: classic *vs* quantum world

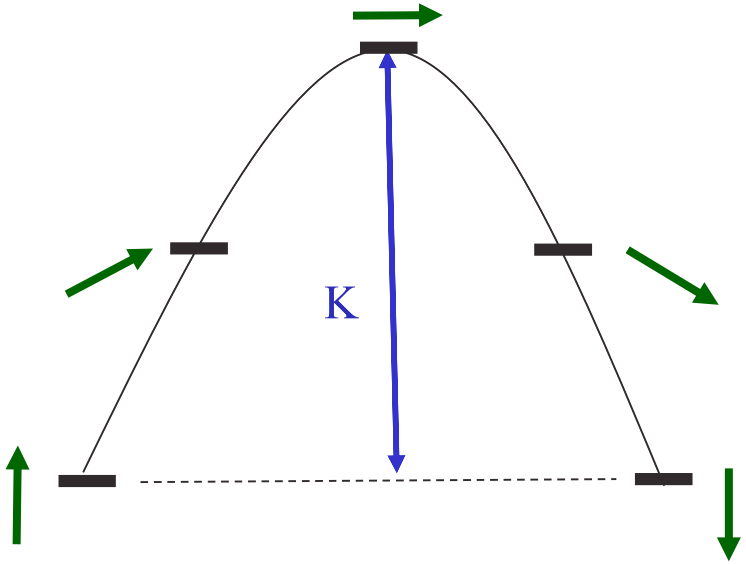


Classic



Continuous magnetization rotation: the magnetization rotates and passes through the hard axis direction

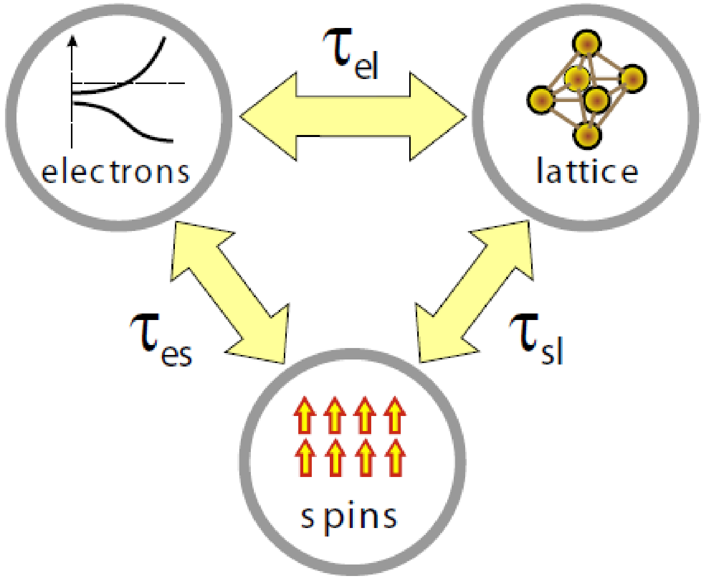
Quantum



Only a discrete number of states are available

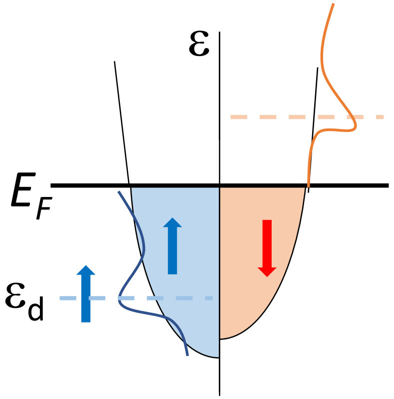
Interacting reservoirs

doi:10.1088/0034-4885/76/2/026501



Classic

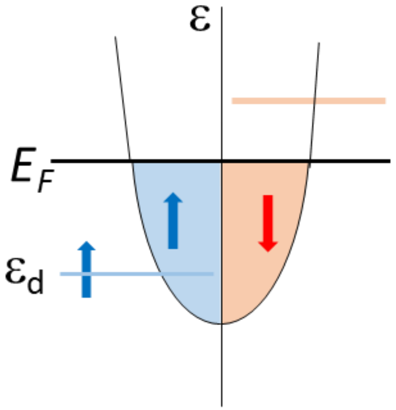
Ex.: Strong spin – electron hybridization



Strong spin – electron (phonon) hybridization $\Rightarrow$ continuous spin reversal models (ex.: LLG eq.)

Quantum

Ex.: poor spin – electron hybridization



Poor spin – electron (phonon) hybridization $\Rightarrow$ how do we model the spin reversal ?

Spin Hamiltonian

Transition metals $H_{tot} = H_{e\text{-}e} + H_{CF} + H_{SOC} + H_Z$ $\mathcal{H}_{\mathrm{sp-orb}} = \lambda \boldsymbol{L} \cdot \boldsymbol{S}$ $\mathcal{H}_Z = \mu_B(\boldsymbol{L} + 2\boldsymbol{S}) \cdot \boldsymbol{H}$

$H = H_{e\text{-}e} + H_{CF}$ $|\Gamma, \gamma\rangle |S, M_S\rangle$ Basis that diagonalize H (Γ is the orbital part)

SOC + Zeeman in second order perturbation theory

$$\mathcal{H}_{\mathrm{eff}} = \langle \Gamma, \gamma | \mathcal{H}_{\mathrm{sp-orb}} + \mathcal{H}_Z | \Gamma, \gamma \rangle$$
$$= 2\mu_B \boldsymbol{H} \cdot \boldsymbol{S} - \sum_{\Gamma', \gamma'} \frac{|\langle \Gamma', \gamma' | \mu_B \boldsymbol{H} \cdot \boldsymbol{L} + \lambda \boldsymbol{L} \cdot \boldsymbol{S} | \Gamma, \gamma \rangle|^2}{E_{\Gamma', \gamma'} - E_{\Gamma, \gamma}}$$

$$\mathcal{H}_{\mathrm{eff}} = 2\mu \boldsymbol{H} \cdot \boldsymbol{S} - 2\mu_B \lambda \sum_{\mu,\nu} \Lambda_{\mu\nu} S_\mu H_\nu - \lambda^2 \sum_{\mu,\nu} \Lambda_{\mu\nu} S_\mu S_\nu - \mu_B^2 \sum_{\mu,\nu} \Lambda_{\mu\nu} H_\mu H_\nu$$

$$\Lambda_{\mu\nu} = \sum_{\Gamma'\gamma'} \frac{\langle \Gamma, \gamma | L_\mu | \Gamma', \gamma' \rangle \langle \Gamma', \gamma' | L_\nu | \Gamma, \gamma \rangle}{E_{\Gamma', \gamma'} - E_{\Gamma, \gamma}}$$
$\mu, \nu = x, y, z$

$$\mathcal{H}_{\mathrm{eff}} = \sum_{\mu,\nu} (\mu_B g_{\mu\nu} H_\mu S_\nu - \lambda^2 \Lambda_{\mu\nu} S_\mu S_\nu - \mu_B^2 \Lambda_{\mu\nu} H_\mu H_\nu)$$

$g_{\mu\nu} = 2(\delta_{\mu\nu} - \lambda \Lambda_{\mu\nu})$ → $g_{\mu\mu} = 2$ only if $L = 0$ -> free electron

R. M. White, *Quantum theory of magnetism,* Springer (2007); M. Mostafanejad. Int. J. Quantum Chem. 2014, 114, 1495 DOI: 10.1002/qua.24721

$\Lambda_{\mu\nu}$ reflects the symmetry of the crystal.

$$\Lambda_{\mu\nu} = \sum_{\Gamma'\gamma'} \frac{\langle \Gamma, \gamma | L_\mu | \Gamma', \gamma' \rangle \langle \Gamma', \gamma' | L_\nu | \Gamma, \gamma \rangle}{E_{\Gamma',\gamma'} - E_{\Gamma,\gamma}}$$

The spin Hamiltonian must also display this symmetry:

in a cubic crystal $\Lambda_{xx} = \Lambda_{yy} = \Lambda_{zz}$.

For axial symmetry $\Lambda_{xx} = \Lambda_{yy} = \Lambda_{\perp}$ and $\Lambda_{zz} = \Lambda_{//}$

Neglecting $\mu_B^2 \Lambda_{\mu\nu} H_\mu H_\nu$

$$\mathcal{H}_{\text{eff}} = g_{||}\mu_B H_z S_z + g_{\perp}\mu_B (H_x S_x + H_y S_y) + D[S_z^2 - \frac{1}{3}S(S+1)] + \frac{1}{3}S(S+1)\left(2\Lambda_{\perp} + \Lambda_{||}\right)\lambda^2$$

$D = \lambda^2(\Lambda_{\parallel} - \Lambda_{\perp})$ contains all the information concerning the crystal field i.e. the orbital moment anisotropy

The Spin Hamiltonian is a phenomenological Hamiltonian with D, $g_{\parallel}$ and $g_{\perp}$ as parameters:

- D is used to describe the uni-axial anisotropy
- $g_{\parallel}$ and $g_{\perp}$ reflect the anisotropy of the orbital moment

Ex. uni-axial system: energy scheme *vs B*

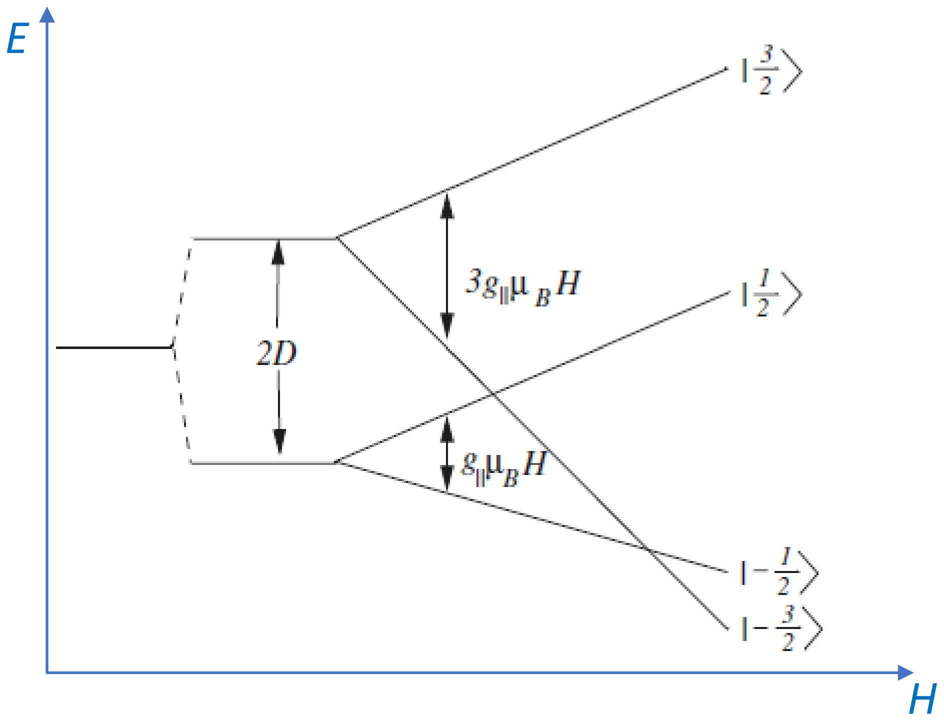
Example: axial symmetry ($C_{\infty v}$) and $H = (0, 0, H_z)$

$$H_{eff} = g_{\parallel}\mu_B(H_z S_z) + DS_z^2 + \frac{1}{3}S(S+1)[\lambda^2(\Lambda_\perp - \Lambda_\parallel) + \lambda^2(2\Lambda_\perp + \Lambda_\parallel)] = g_{\parallel}\mu_B(H_z S_z) + DS_z^2 + S(S+1)\lambda^2\Lambda_\perp$$

S = 3/2 and $D > 0$ (we can neglect the effect of $S(S+1)\lambda^2\Lambda_\perp$ since it is just a shift in energy)

$$H_{eff} = g_{\parallel}\mu_B(H_z S_z) + DS_z^2 \qquad D = \lambda^2(\Lambda_{||} - \Lambda_\perp)$$

$$\mathcal{H}_{\text{eff}} = \begin{array}{c} \\ \langle -\frac{3}{2}| \\ \langle -\frac{1}{2}| \\ \langle \frac{1}{2}| \\ \langle \frac{3}{2}| \end{array} \begin{array}{c} \begin{array}{cccc} |-\frac{3}{2}\rangle & |-\frac{1}{2}\rangle & |\frac{1}{2}\rangle & |\frac{3}{2}\rangle \end{array} \\ \begin{bmatrix} D - \frac{3}{2}g_{||}\mu_B H & 0 & 0 & 0 \\ 0 & -D - \frac{1}{2}g_{||}\mu_B H & 0 & 0 \\ 0 & 0 & -D + \frac{1}{2}g_{||}\mu_B H & 0 \\ 0 & 0 & 0 & D + \frac{3}{2}g_{||}\mu_B H \end{bmatrix} \end{array}$$

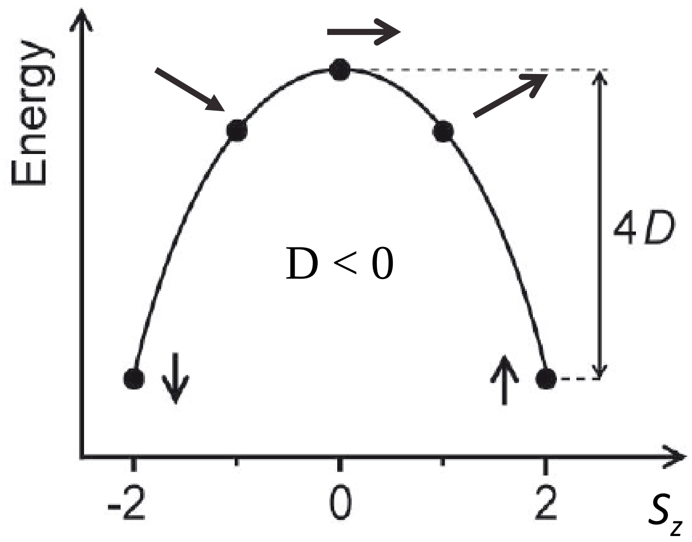


Energy barrier for reversal: uni-axial case

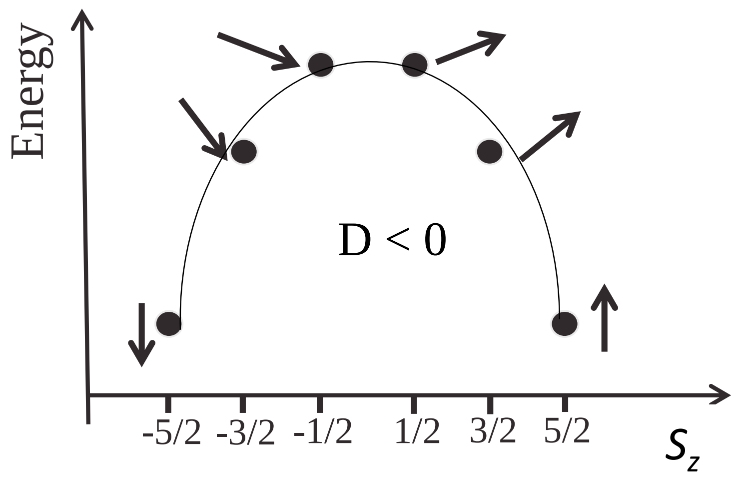
Energy barrier for spin reversal (E_b): easy axis along z

$E_b = DS_z^2$ (S integer)

S = 2



$E_b = D\left(S_z^2 - \frac{1}{4}\right)$ (S half-integer)



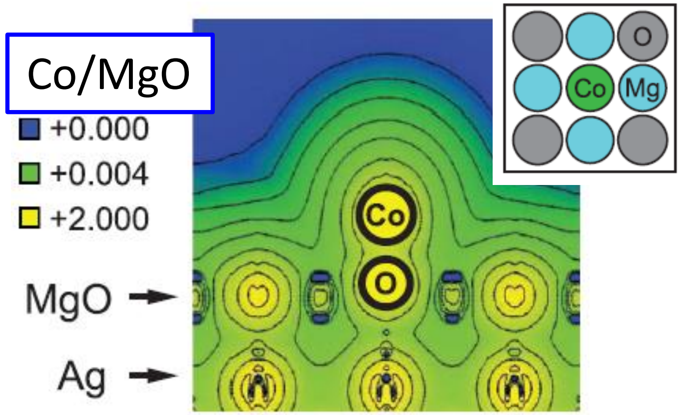
S = 5/2

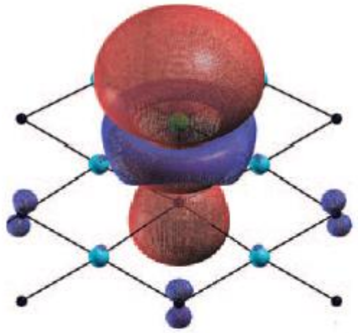
Co, Fe atoms on insulating substrates: MgO/Ag(100)

Charge distribution

Spin distribution

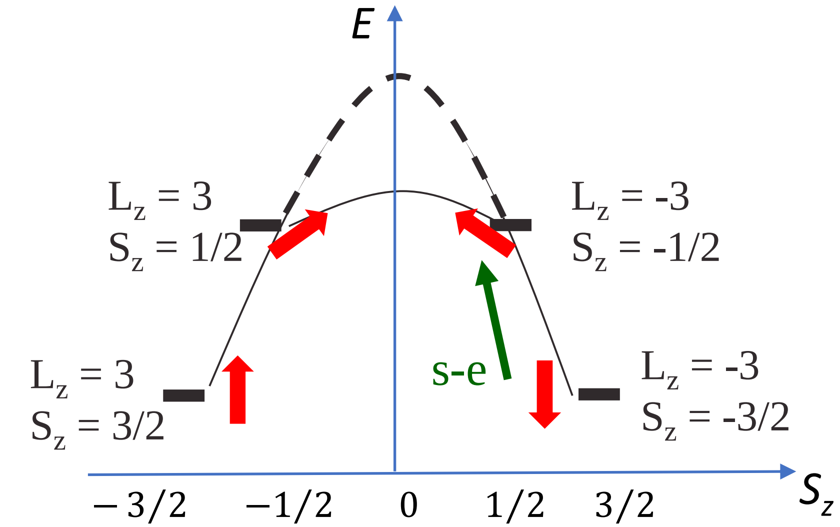
Majority Minority



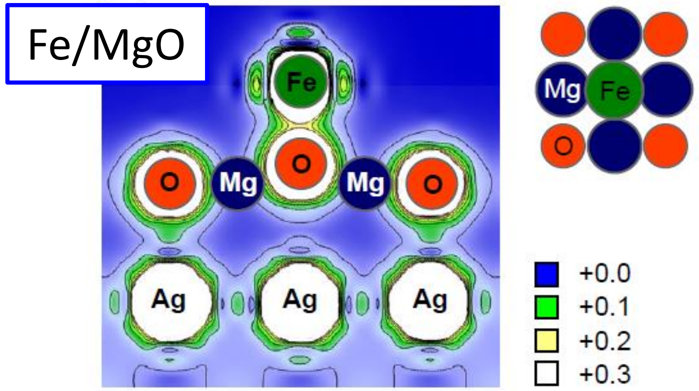


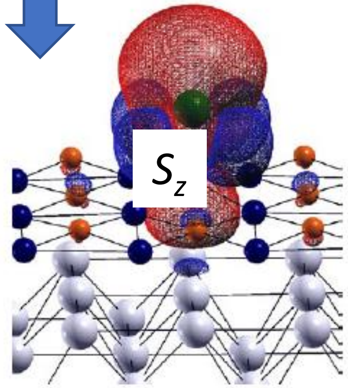
Axial (C_∞) crystal field

$$H_{eff} = g\mu_B S_z B + DS_z^2$$



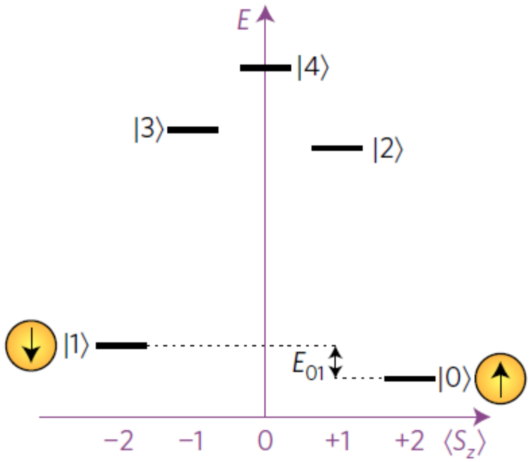
Different interactions with neighbors atoms for Co and Fe





C_{4v} crystal field

$$H_{eff} = g\mu_B S_z B + DS_z^2 + \cdots$$

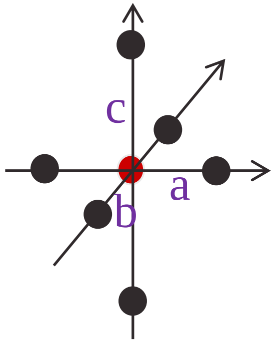


B_z = 2.5T

I.G. Rau *et al.* *Science* 988, **344** (2014); S. Baumann *et al.* Phys. Rev. Lett. **115**, 237202 (2015); DOI: 10.1038/NPHYS3965.

Low symmetry cases

In general Λ_{xx} , Λ_{yy} , and Λ_{zz} are different (distorted octahedral symmetry)



$$H_{eff} = g_{\parallel}\mu_B(H_z S_z) + g_{\perp}\mu_B\left(H_x S_x + H_y S_y\right) + D S_z^2 + E(S_x^2 - S_y^2)$$

$$D = \lambda^2\left(\frac{1}{2}\Lambda_{xx} + \frac{1}{2}\Lambda_{yy} - \Lambda_{zz}\right) \approx \frac{\lambda^2}{\Delta E}(L_{\parallel} - L_z)$$

$$E = \lambda^2\left(\frac{1}{2}\Lambda_{xx} - \frac{1}{2}\Lambda_{yy}\right) \approx \frac{\lambda^2}{\Delta E}\left(L_x - L_y\right)$$

$$g_{\mu\nu} = 2(\delta_{\mu\nu} - \lambda\Lambda_{\mu\nu})$$

D and E are parameters describing the MAE, proportional to:

a) orbital anisotropy
b) Spin-orbit constant

$g_{\parallel}$ and $g_{\perp}$ contain also information about the orbital anisotropy

N.B.:

In the previous equations S should be considered as a sort of effective spin operator S* to be determined by fitting the data (for example: for rare earths $S^* = J$).

T. Schuh *et al.* Phys. Rev. B **84**, 104401 (2011); D. Dai *et al.,* J. Comput. Chem. **29**, 2187 (2008)

General expression for the CF

$$H_{eff} = H_{Zee} + \sum_{\substack{k=2 \\ even}}^{2l} \sum_{m=0}^{k} B_k^m O_k^m$$

O_k^m are the Stevens operators describing the CF in terms of J_z, J_+ and J_-

B_k^m are numerical coefficient to adjust (fitting parameters) the weight of each term

l is the orbital angular momentum of the considered shell; thus:
l = 3 for rare earth
l = 2 for 3d transition metals

m reflects the CF symmetry; for C_{nv} symmetry, $m = n \cdot i$ $\quad i = 0, 1, 2, \ldots$

Ex. For C_{3v} symmetric CF $\Rightarrow$ $H_{CF} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^3 O_4^3 + B_6^0 O_6^0 + B_6^3 O_6^3 + B_6^6 O_6^6$

Ex:

$O_2^0 = 3J_z^{\,2} - J(J+1);$ $\qquad B_2^0 = D/3$

$O_2^2 = ½\,(J_+^2 + J_-^2);$ $\qquad B_2^2 = 2E$

$O_4^0 = 35\,J_z^{\,4} - (30\,J(J+1) - 25)\,J_z^{\,2} + 3[J(J+1)]^2 - 6\,J(J+1);$

$O_4^3 = ¼\,[J_z(J_+^3 + J_-^3) + (J_+^3 + J_-^3)\,J_z];$

$O_4^4 = ½\,(J_+^4 + J_-^4);$

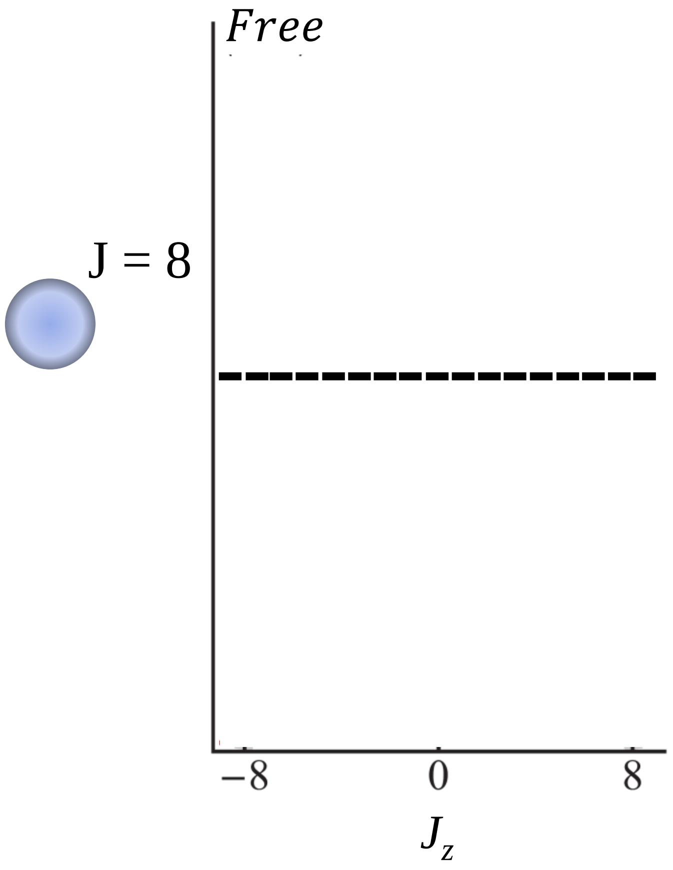
Ladder operators:

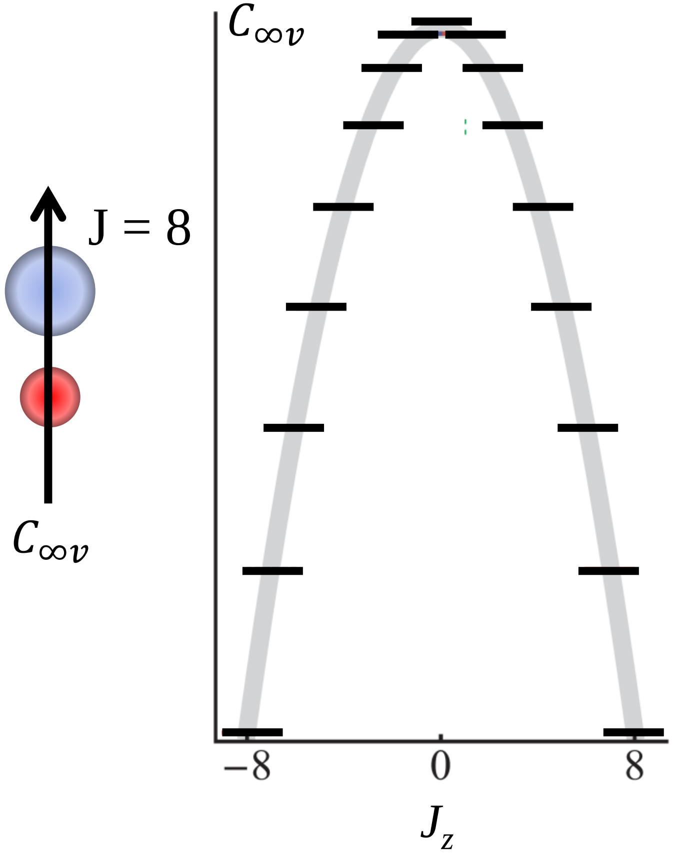
$$\hat{l}_\pm \,|Y_l^m\rangle = l_\pm\,|l,m\rangle = \sqrt{l(l+1) - m(m\pm 1)}\,|l, m\pm 1\rangle$$

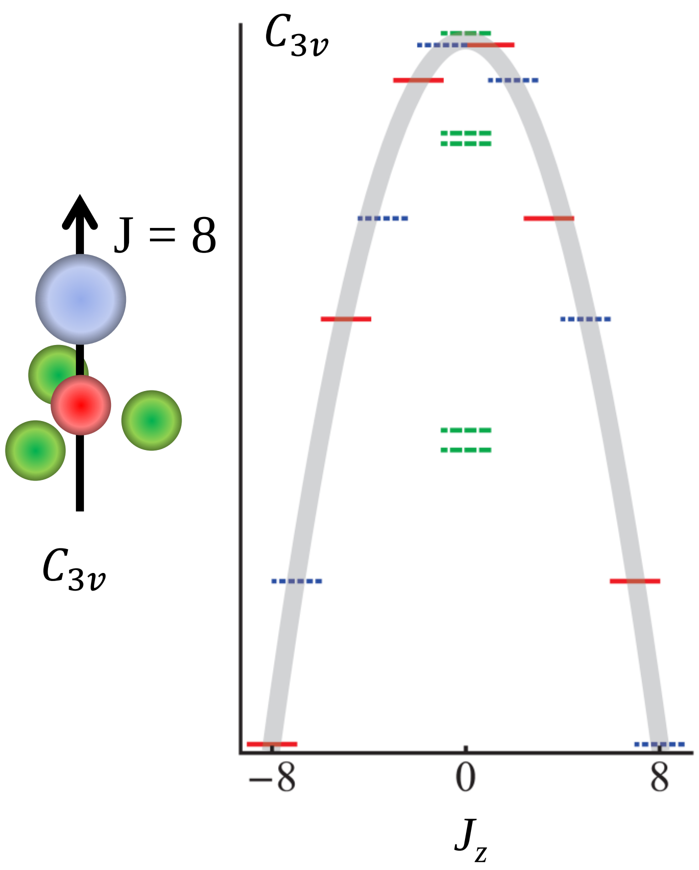
$$l_\pm^n\,|l,m\rangle = \underbrace{l_\pm l_\pm l_\pm \ldots l_\pm}_{\text{n times}}\,|l,m\rangle$$

For a list of Stevens parameter see: https://www2.cpfs.mpg.de/~rotter/homepage_mcphase/manual/node132.html

Energy scheme *vs* symmetry







Free atom:
The *2J+1* states (identified by J_z) are degenerate

Uniaxial anisotropy:
pure J_z states are split

Lower symmetry:
crystal field contains O_k^m terms in the Hamiltonian mixing J_z states separated by $\Delta J_z = m \cdot i \quad i = 0, 1, 2, \ldots$

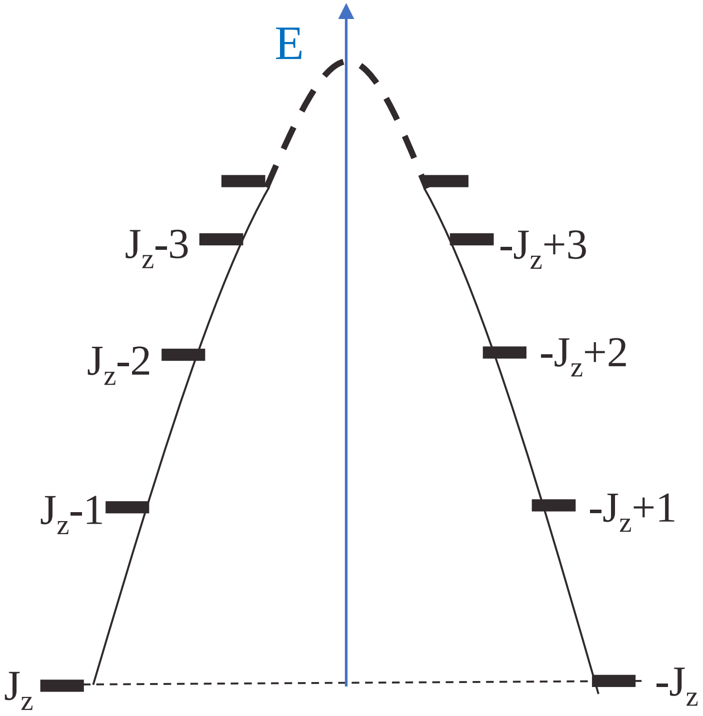
- Mixing of conjugate doublets to form singlets (forbidden for half integer *J* due to Kramer's theorem)
- Allowed spin transition across the barrier

QTM in Spin Hamiltonian description

See exercises: 8.1- 8.3

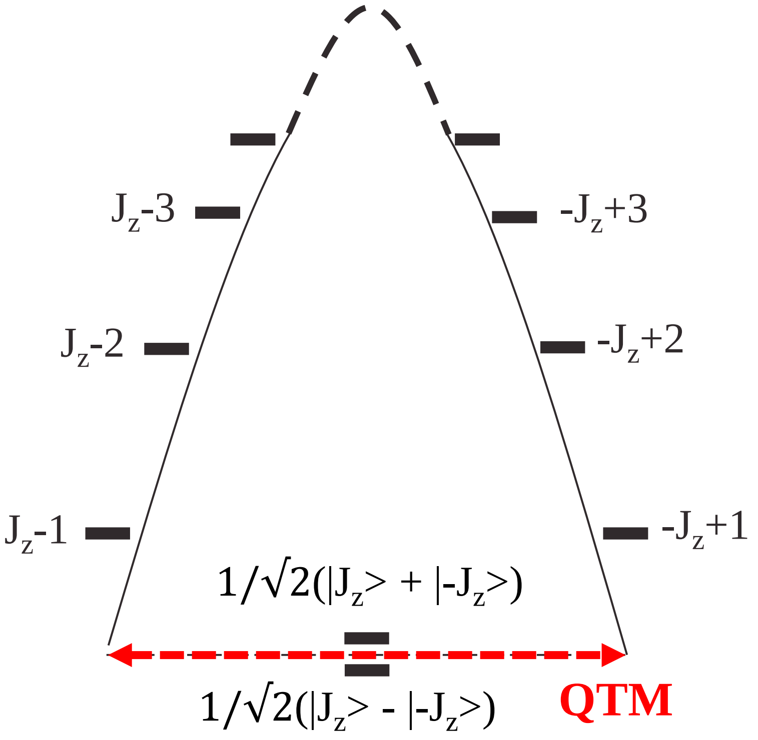
C_∞ symmetry: $H_{CF} = D\,J_z^2$

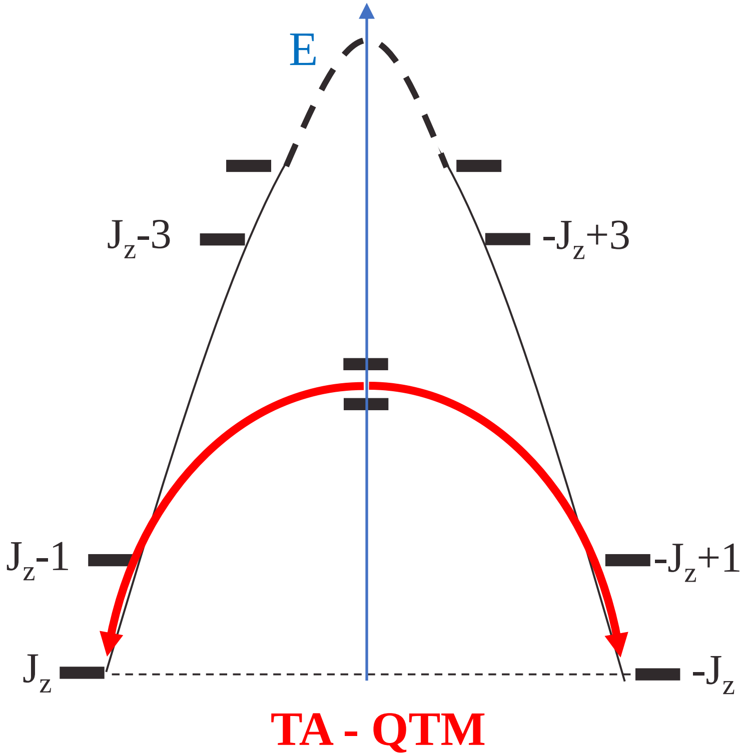
Pure J_z states -> No QTM



C_{nv} symmetry: $H_{CF} = D\,J_z^2 + E\,(J_+^n + J_-^n)$

$J_\pm^n$ operators mix states satisfying $J_z - J_{z'} = n \cdot i$ $i = 0, 1, 2, \ldots$ -> QTM or TA-QTM





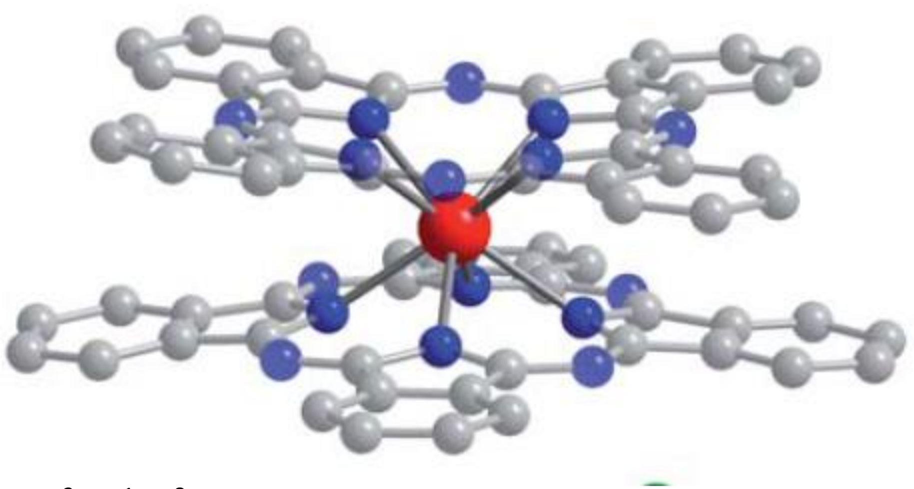
In case of QTM a net magnetization can not be stabilized in the ground state (the ground state is a superposition of spin-up and spin-down states) -> the particle can not be a bit

QTM: the TbPc2 case

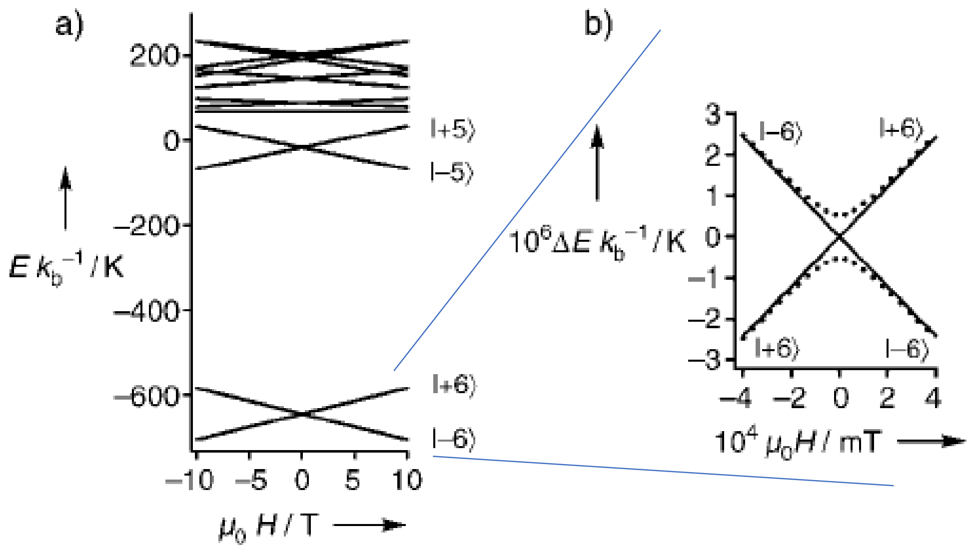
See exercise: 8.4

Chem. Sci., **2**, 2078 (2011)

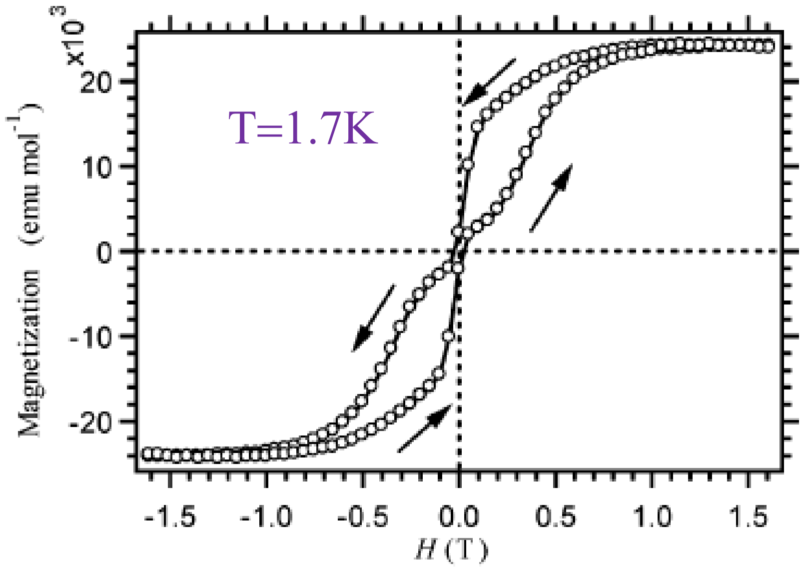
$TbPc_2$



Tb is in [Xe] $6s^2\ 5d^1\ 4f^8$ configuration



Angew. Chem. Int. Ed. **44**, 2931 –2935 (2005)



10.1021/jp0376065

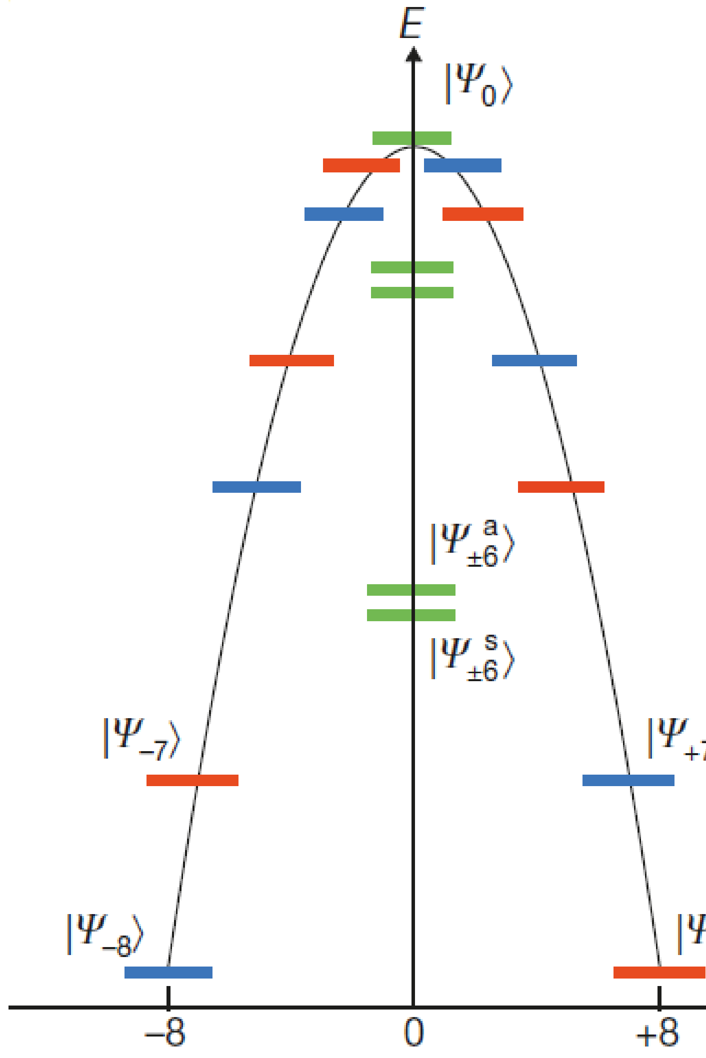
Split states by crystal field with symmetry C_{4v}

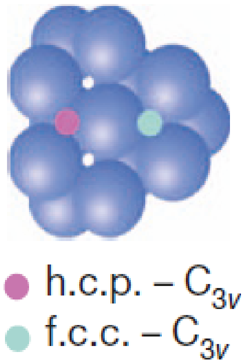
- O_4^4 and O_6^4 operators mix the two ground states at $B \approx 0$ (dotted lines show the *E vs B* of the mixed states, the continuous ones *E vs B* for the unperturbed states)
- States become pure (suppressed spin relaxation) already in a small field $\Rightarrow$ butterfly shaped hysteresis curve

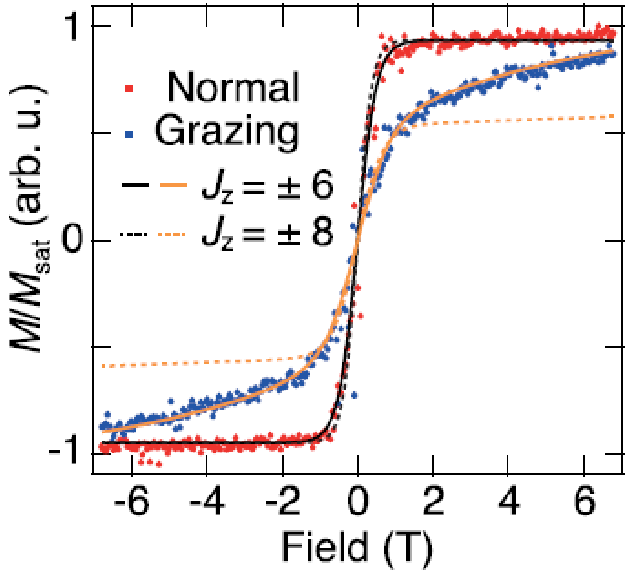
DFT prediction: stable magnetization (no QTM)

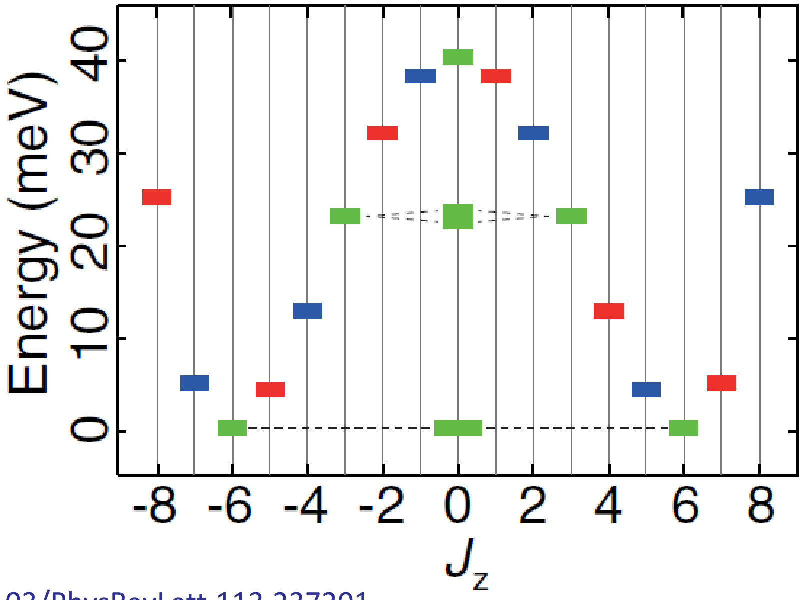
Ho/Pt(111)

Experiment: paramagnet due to QTM









doi:10.1038/nature12759

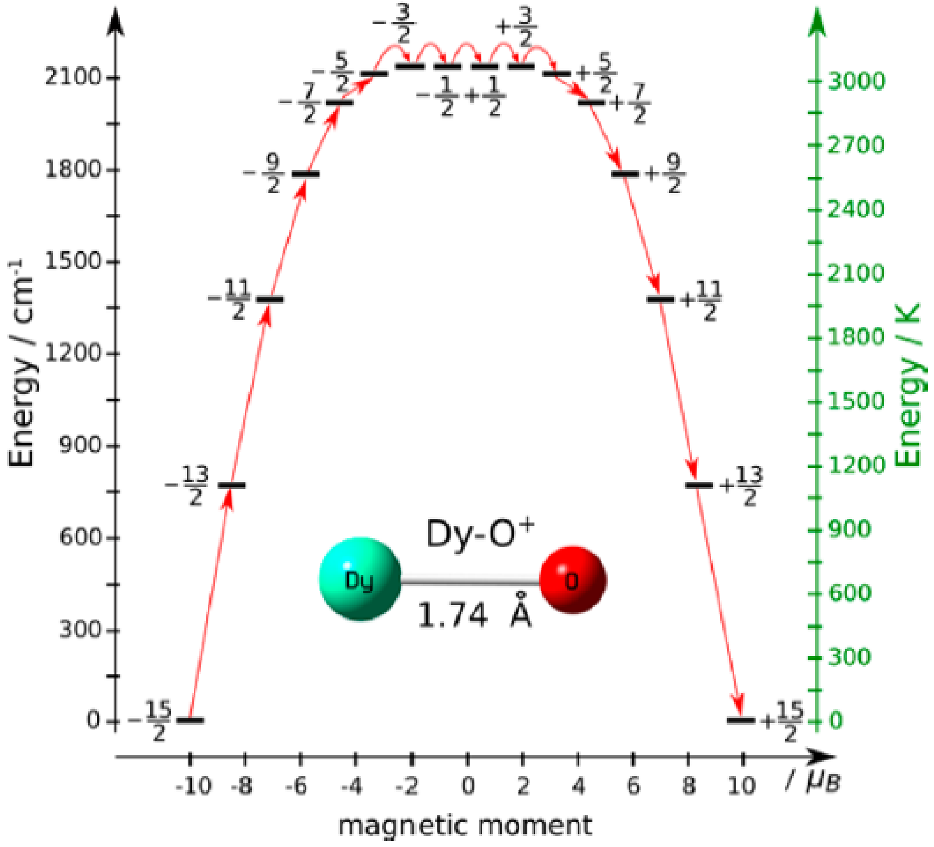
10.1103/PhysRevLett.113.237201

Long spin lifetime: avoided QTM

Depending on the CF symmetry, it can exist terms coupling J_z and $-J_z$ ground states via J_+ (J_-) operator -> quantum tunneling -> no stable magnetization

Ex.: CF with a significant O_4^3 (C_{3v}) term is not convenient for Dy^{3+} (J = 15/2) because J_+^3 links -15/2 -> -9/2 -> -3/2 -> 3/2 -> 9/2-> 15/2

Calculation for free-standing Dy-O

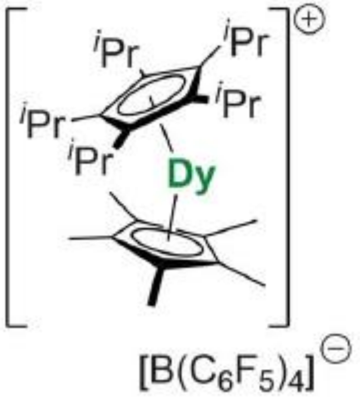


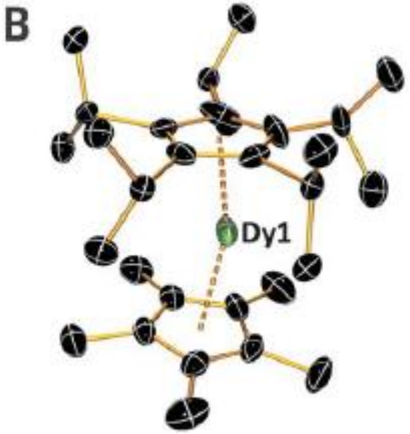
We can increase the barrier for spin reversal by judiciously choosing the coordination environment of the lanthanide ion.

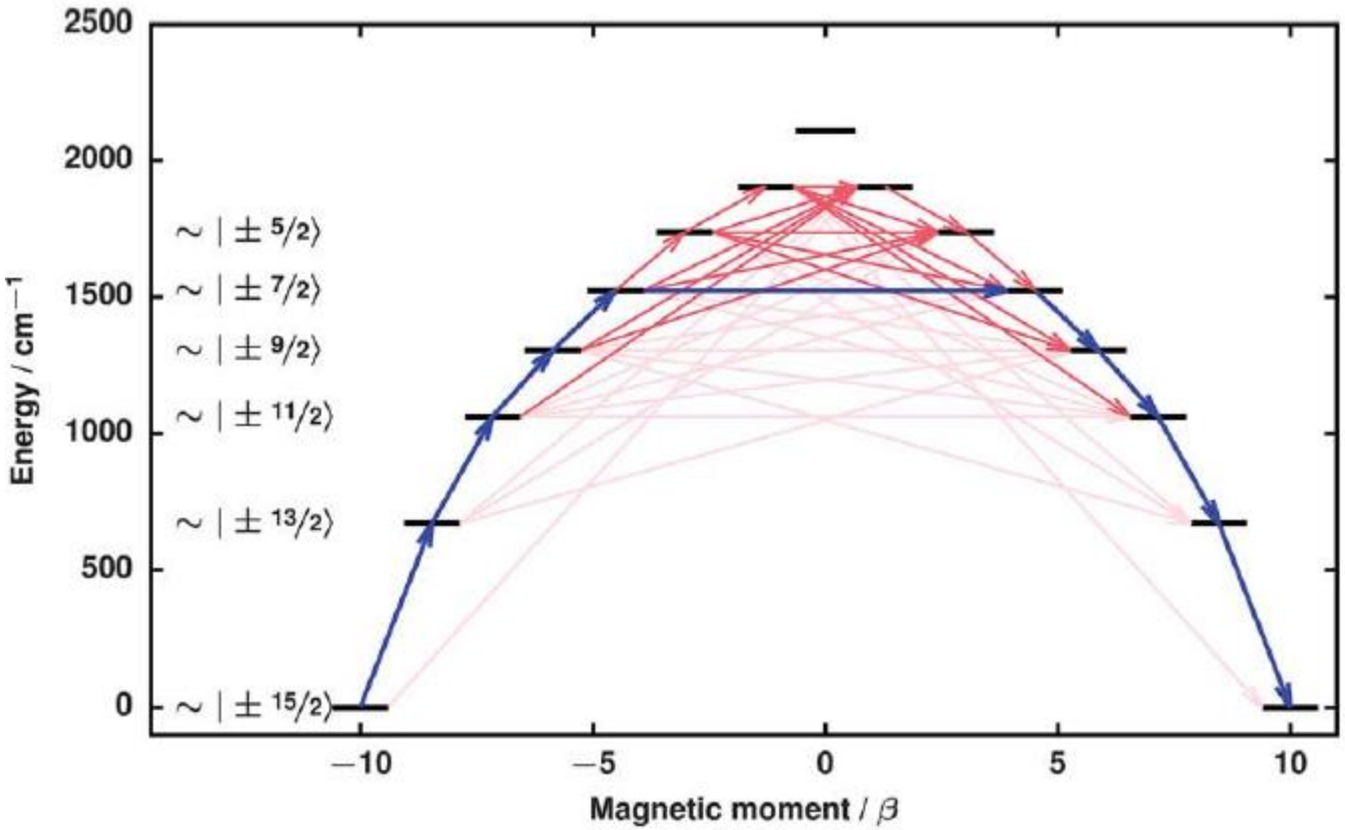
Axial CF -> only O_2^0, O_4^0 and O_6^0 terms -> no quantum tunneling

DOI: 10.1021/acs.inorgchem.6b01353

Molecular magnetic hysteresis at 80 K in dysprosocenium







CF mainly axial
Very small transverse terms of order 5
No QTM (forbidden split doublets due to Kramer's theorem)

Relaxation mechanisms. Blue arrows show the most probable relaxation route, and red arrows show transitions between states with less probable, but nonnegligible, matrix elements; darker shading indicates a higher probability

Guo et al., Science 362, 1400–1403 (2018)

RE atoms on top-O site on MgO: almost axial CF

EPFL

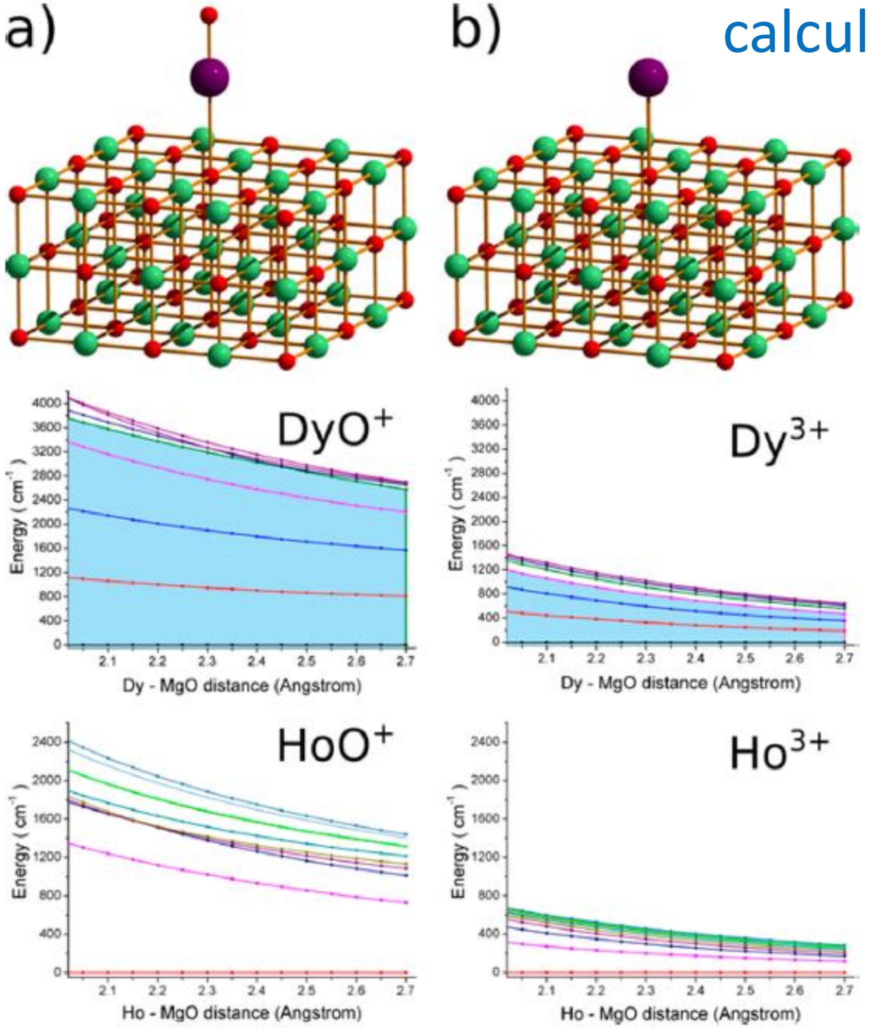


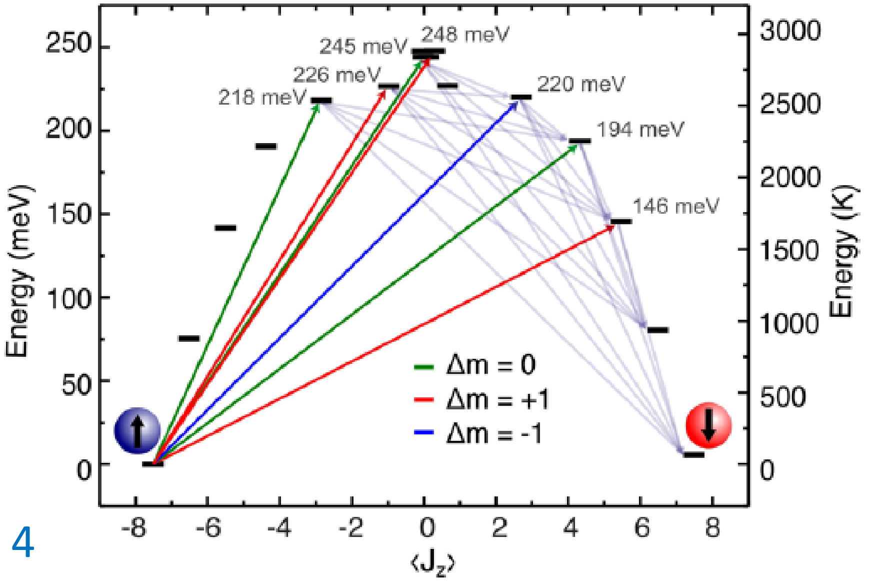
Figure 9. Comparison of the blocking barrier of $[LnO]^+$ (a) with a blocking barrier of Ln^{3+}, where Ln = Dy and Ho, (b) deposited on the MgO surface. For these illustrative calculations, it was assumed that $[LnO]^+$ is oriented perpendicularly to the plane of the surface. Lines in the plots represent the energies of the low-lying $J = {}^{15}/_2$ (Dy) and $J = 8$ (Ho) CF multiplet states.

DOI: 10.1021/acs.inorgchem.6b01353

calculation

experiment

Dy^{3+} on MgO
($4f^9 \Rightarrow$ J=15/2)



Mainly axial CF

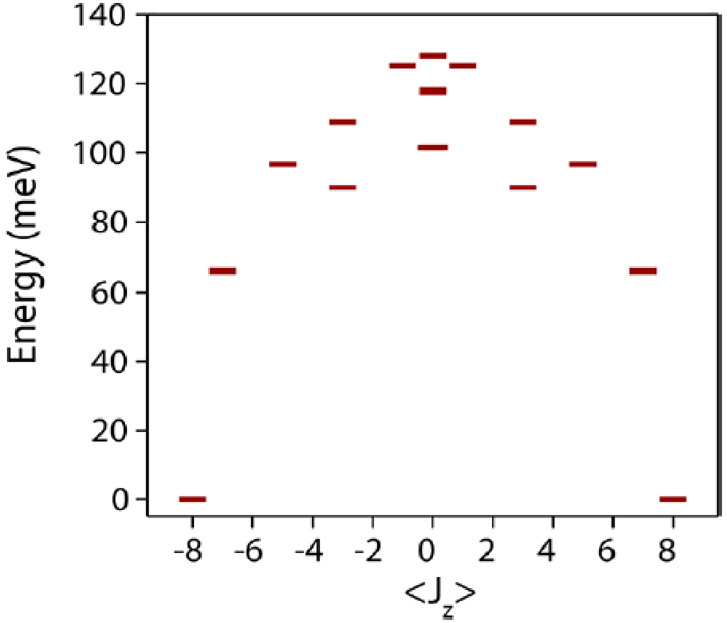
Very small transverse terms of order 4

(negligible QTM for Ho)

Spin lifetime of several days at 2K for both Ho and Dy

10.1103/PhysRevLett.121.027201

Ho^{3+} on MgO
($4f^{10} \Rightarrow$ J=8)



$1\ eV \approx 8000\ cm^{-1}$

https://doi.org/10.1038/s41467-021-24465-2; https://doi.org/10.1021/acs.nanolett.1c02744; https://doi.org/10.1021/acsnano.1c05026

Transitions induced by spin-phonon and spin-electron scattering

See exercise: 8.5

Phonons are distortions of the crystal field -> $H_{spin-phonon} = a\,(J_+ , J_-) + b\,(J_+^2, J_-^2)$

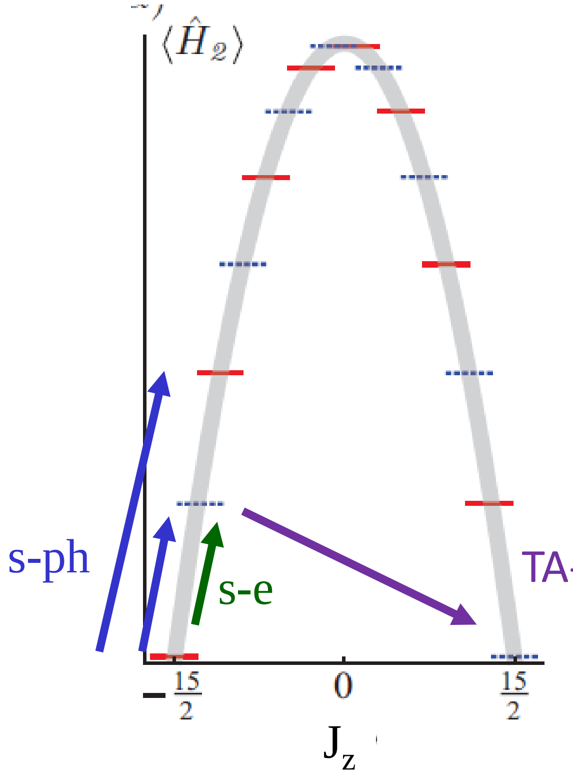
Spin-phonon scattering (s-ph) induces transitions between states differing by $\Delta J_z = \pm 1, 2$

A. Fort, et al. Phys. Rev. Lett. **80**, 612 (1998)

Electrons have spin $\sigma = 1/2$ -> $H_{spin-electron} = J_{exc} J_z \sigma_z + 1/2\, J_{exc} (J_+ \sigma_- + J_- \sigma_+)$

Spin-electron scattering (s-e) induces transitions between states differing by $\Delta J_z = \pm\; 0, 1$

C. Hubner *et al.*, Phys. Rev.B **90**, 155134 (2014)



Example:

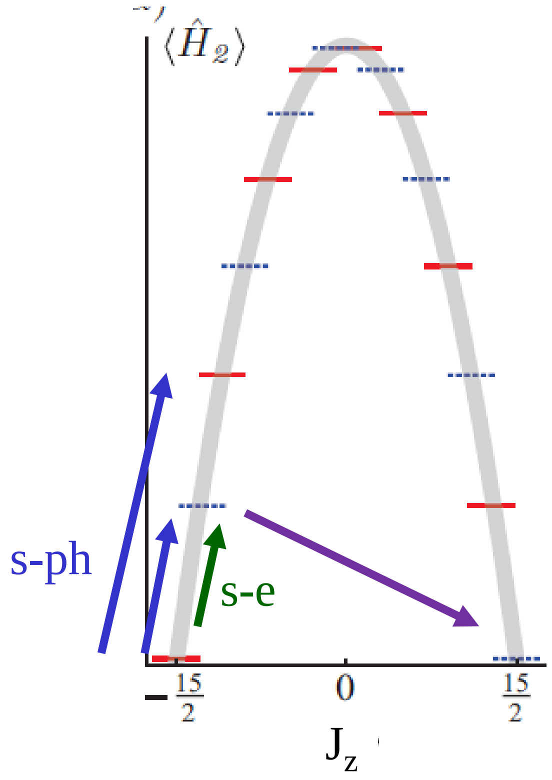
CF with C_{2v} symmetry + interaction with conduction electrons + interaction with phonons

$$H_2 = D J_z^2 + E (J_+^2 + J_-^2) + J_{exc} J_z \sigma_z + 1/2\, J_{exc} (J_+ \sigma_- + J_- \sigma_+) + \alpha (J_+, J_-) + \beta (J_+^2, J_-^2)$$

TA-QTM: spin reversal via first excited state and not via the top of the barrier

Magnetization is stable only if QTM, electron and phonon transitions are forbidden

Master eqs. to describe the dynamics



$$\frac{dP_m}{dt} = \sum_{m=1}^{2J+1} P_{m'}\Gamma_{mm'}^{s-el} - \sum_{m'=1}^{2J+1} P_m\Gamma_{mm'}^{s-el} + \sum_{m=1}^{2J+1} P_{m'}\Gamma_{mm'}^{s-ph} - \sum_{m'=1}^{2J+1} P_m\Gamma_{mm'}^{s-ph} + \Gamma_{m,-m}^{QTM}(P_{-m} - P_m)$$

P_m is the population of the state *m*

$\Gamma_{mm'}^{s-el(ph)}$ is the transition rate between states *m* and *m'* induced by a spin-electron (spin-phonon) scattering

$$\Gamma_{mm'}^{s-el(ph)} = \langle m | H_{CF} + H_{s-el} + H_{s-ph} | m' \rangle \, D(E)^{el(ph)} \, F\left(\frac{E}{k_B T}\right)^{el(ph)}$$

Interaction Hamiltonian matrix element between *m* and *m'* states

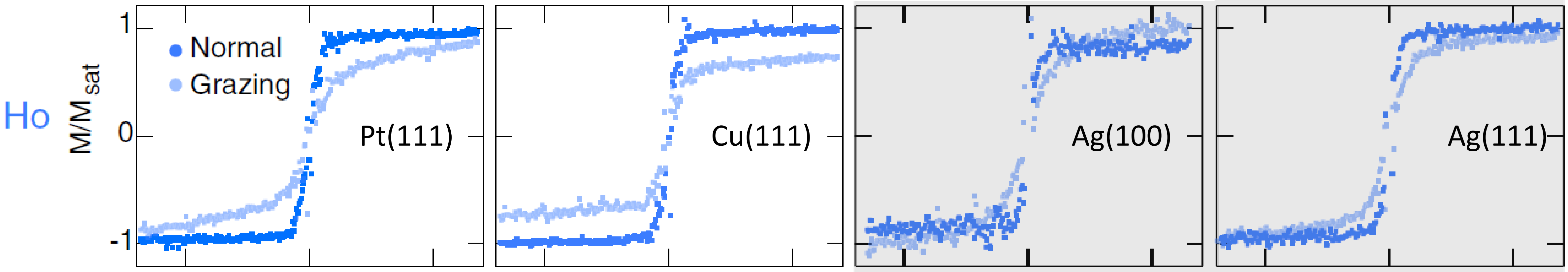
Electron (phonon) DOS

Fermi-Dirac (Bose-Einstein) function

A. Fort, et al. Phys. Rev. Lett. **80**, 612 (1998)

Effect of a decoupling layer

An Ho atom shows paramagnetic behavior when adsorbed on metal surfaces

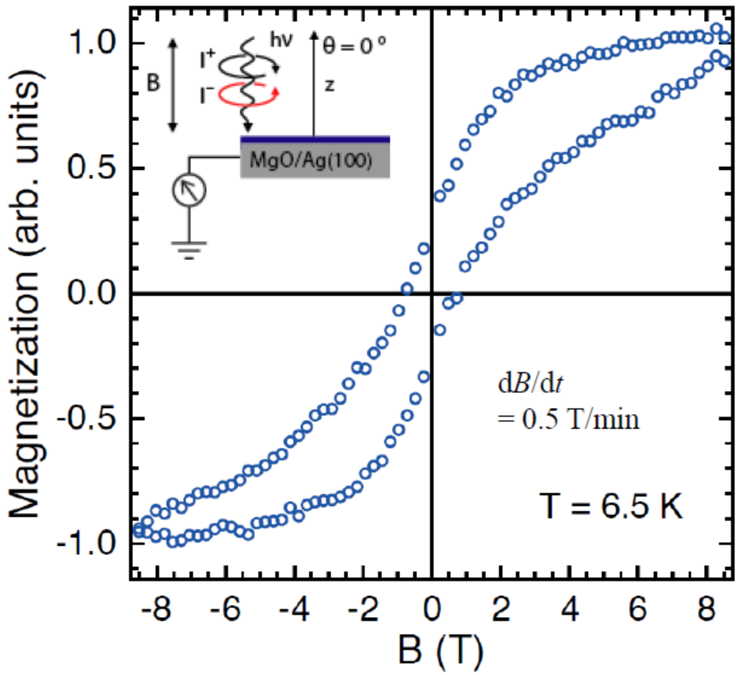


10.1103/PhysRevB.96.224418

Ho atom shows hysteresis (long spin lifetime) when adsorbed on top-O site on a MgO/Ag(100)

Consequence of reduced:
- spin-phonon scattering (MgO is stiff)
- spin-electron scattering (MgO is an insulator)

$D(E)^{el(ph)}$ is small

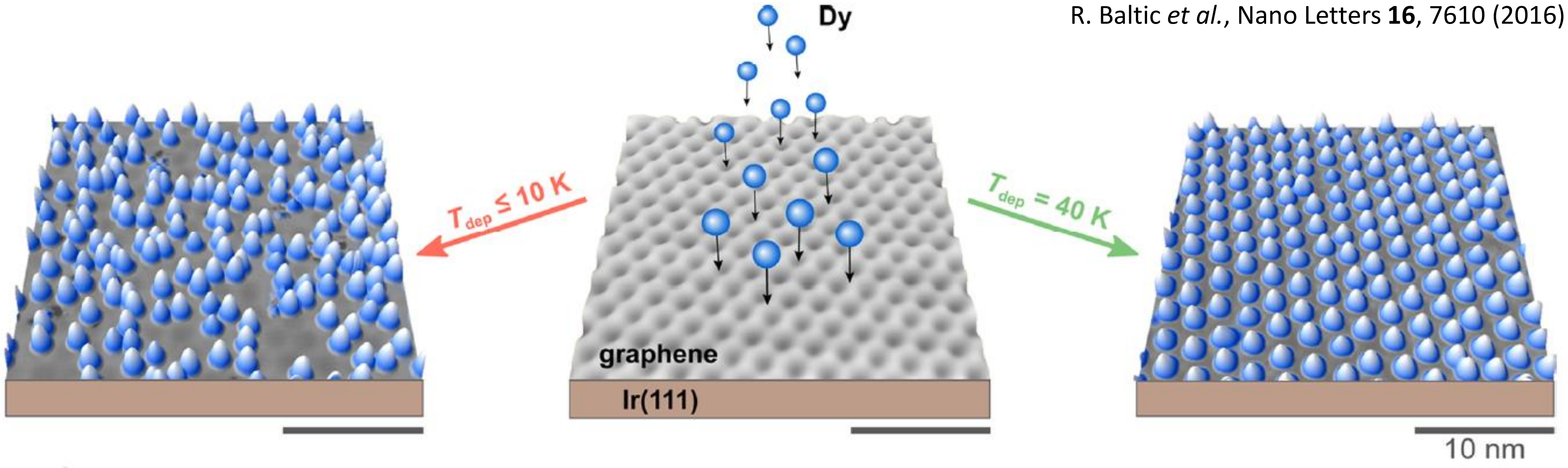


F. Donati *et al.*,Science **315**, 319 (2016).

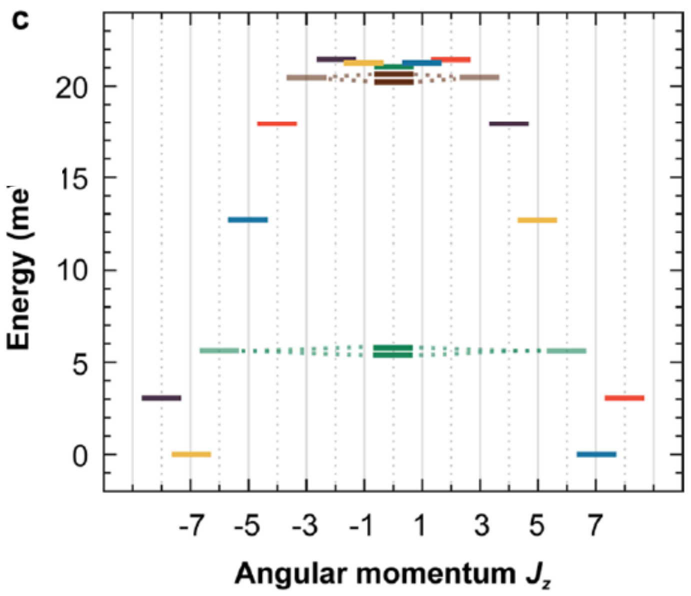
Lattice of single atom magnets

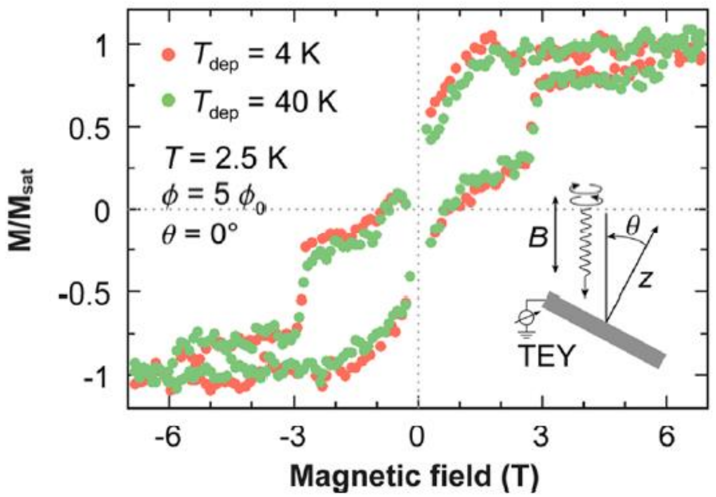
R. Baltic *et al.*, Nano Letters **16**, 7610 (2016)

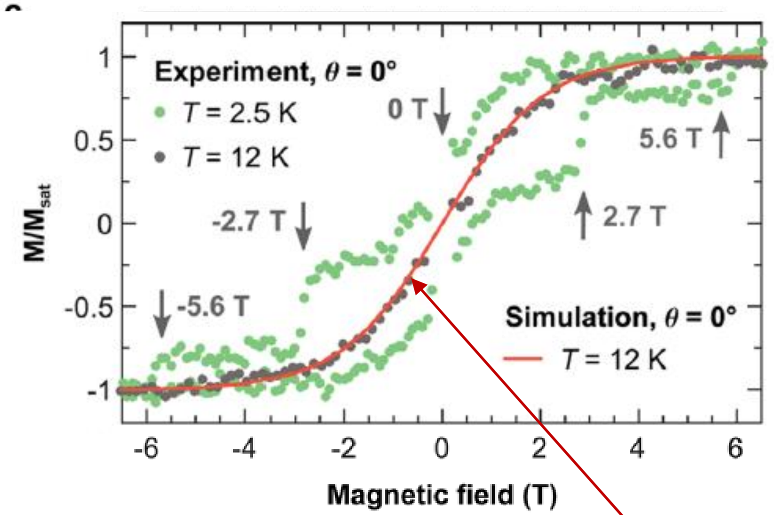
- Dy on graphene has an electronic configuration similar to the gas phase: [Xe] $6s^2\ 4f^{10}$ configuration $\Rightarrow J = 8$
- Dy adsorbs in the center of a graphene hexagon (hollow site) $\Rightarrow$ CF with C_{6v} symmetry



CF with C_{6v} symmetry







$$F\left(\frac{E}{k_B T}\right)^{el(ph)}$$

TA-QTM -> M ≠ 0 at B = 0 T, and T low enough (< 10 K)

Graphene decouples from the soft metallic support: reduced spin-phonon and spin-electron scattering ($D(E)^{el(ph)}$ is small)