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MOLECULAR MAGNETISM – A COMPUTATIONAL APPROACH

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Overview

Molecular magnetism and Single-Molecule Magnets

Theoretical methods used to describe the magnetic properties

Examples

Magnetism

Definitions: $\chi = \frac{\partial M}{\partial H}$

$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M})$
When χ is small, $\mathbf{B} \approx \mu_0\mathbf{H}$

χ – magnetic susceptibility
M – molar magnetization (moment per unit volume)
H – applied magnetic field.

When H is weak enough, χ is independent of H:

$$\mathbf{M} = \chi\mathbf{H}$$

$$M = -\frac{\partial E}{\partial H}$$

For a molecule with an energy spectrum $E_n (n = 1,2, \dots)$, we can define a *microscopic* magnetization

$$\mu_n = -\frac{\partial E_n}{\partial H}$$

The *macroscopic* magnetization is then

$$M = \frac{N \sum_n \left(-\frac{\partial E_n}{\partial H}\right) \exp(-E_n/kT)}{\sum_n \exp(-E_n/kT)}$$

Van Vleck formula

By expanding the energies E_n to the increasing powers of H:

$$E_n = E_n^{(0)} + E_n^{(1)} H + E_n^{(2)} H^2 + \cdots$$

and considering that $\frac{H}{kT} \ll 1$, one obtains:

$$M = \frac{NH \sum_n \left({E_n^{(1)}}^2 / kT - 2E_n^{(2)} \right) \exp\left(-E_n^{(0)} / kT \right)}{\sum_n \exp\left(-E_n^{(0)} / kT \right)}$$

and

$$\chi = \frac{N \sum_n \left({E_n^{(1)}}^2 / kT - 2E_n^{(2)} \right) \exp\left(-E_n^{(0)} / kT \right)}{\sum_n \exp\left(-E_n^{(0)} / kT \right)}$$

From the perturbation theory

$$E_n^{(1)} = \langle n | H_{Zeeman} | n \rangle$$

$$E_n^{(2)} = \sum_{m\prime} \frac{\left\langle n \left| \hat{H}_{Zeeman} \right| m \right\rangle^2}{E_n^{(0)} - E_m^{(0)}}$$

$$\chi = \frac{N \sum_n \left({E_n^{(1)}}^2 / kT - 2E_n^{(2)} \right) \exp\left(-E_n^{(0)} / kT \right)}{\sum_n \exp\left(-E_n^{(0)} / kT \right)}$$

When all energies E_n are linear in H (small field), the second-order terms vanish and the Van Vleck formula becomes:

$$\chi = \frac{N \sum_n \left({E_n^{(1)}}^2 / kT \right) \exp\left(-E_n^{(0)} / kT \right)}{\sum_n \exp\left(-E_n^{(0)} / kT \right)}$$

Free spin paramagnetism

Free spin-1/2

$$\hat{H}_{Zee} = \mu_B \mathrm{g}_e B_z \cdot \hat{S}_z$$

$$\mu_B = \frac{e\hbar}{2m_e} = 9.2740100657 \cdot 10^{-24}\ \mathrm{J} \cdot \mathrm{T}^{-1}$$

The eigenstates of $B_z \cdot S_z$ are $\pm B/2$

$$g_e \cong 2$$

The partition function is

$$Z = e^{-\beta\mu_B B} + e^{\beta\mu_B B}$$

The free energy is $F = -k_B T \ln Z$. The magnetic moment per spin is then

$$\mu = -\frac{\partial F}{\partial B} = \mu_B \tanh(\beta\mu_B B)$$

For many spins (n) per unit volume we define magnetization *M*.

At a small field, expanding the tanh for small argument:

$$\tanh x = x - \frac{x^3}{3} + \frac{2x^5}{15} - \frac{17x^7}{315} + \cdots$$

and using $B \approx \mu_0 H$, the magnetic susceptibility is

$$\chi = \lim_{H \to 0} \frac{\partial M}{\partial H} = \frac{n\,\mu_0 \mu_B^2}{k_B T} = \frac{C}{T}$$

This is the Curie law!

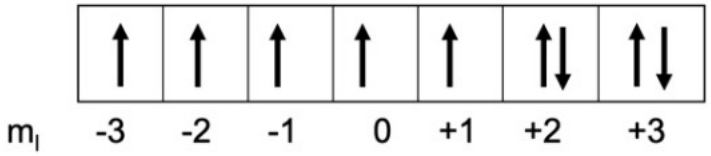
Hunds rules

- Electrons try to align their spins.
- Electrons try to maximize their total orbital angular momentum.
- Total angular momentum is:
  $J = L + S$ for *more* than half-filled orbitals
  $J = L - S$ for *less* than half-filled orbitals

Example: Dy^{3+} ion

Dy^0 ion has the electron configuration $[\mathrm{Xe}]6s^2 4f^{10}$

Dy^{3+} ion then has the configuration $[\mathrm{Xe}]4f^9$



$$L = 5;\ S = \frac{5}{2}$$

$$J = 15/2$$

Why do spins align?

$$\Psi(r_1, \sigma_1; r_2, \sigma_2) = \psi_{orb}(r_1, r_2)\chi_{spin}(\sigma_1, \sigma_2)$$

Ψ must be antisymmetric.

If spins align, $\chi_{spin}(\uparrow, \uparrow)$, symm.

Thus, ψ_{orb} must be antisymm.

$$\lim_{r_1 \to r_2} \psi_{orb}(r_1, r_2) \to 0$$

Electrons with aligned spins cannot get close to each other ⟶ the Coulomb energy is reduced.

Russel-Saunders terms (LS coupling)

A term symbol is denoted as

$$^{2S+1}L_J$$

L =	0	1	2	3	4	5	6	7	8	9	10
	S	P	D	F	G	H	I	K	L	M	N

For Dy^{3+} we have the following in the ground state

$$^{6}H_{15/2}$$

Multiplets for Equivalent p, d, and f Electrons

p Electrons

Configuration	Terms
p^1, p^5	^2P
p^2, p^4	^3P, ^1D, ^1S
p^3	^4S, ^2D, ^2P

d Electrons

Configuration	Terms
d^1, d^9	^2D
d^2, d^8	^3F, ^3P, ^1G, ^1D, ^1S
d^3, d^7	^4F, ^4P, ^2H, ^2G, ^2F, $2\times{}^2D$, ^2P
d^4, d^6	^5D, ^3H, ^3G, $2\times{}^3F$, ^3D, $2\times{}^3P$, ^1I, $2\times{}^1G$, ^1F, $2\times{}^1D$, $2\times{}^1S$
d^5	^6S, ^4G, ^4F, ^4D, ^4P, ^2I, ^2H, $2\times{}^2G$, $2\times{}^2F$, $3\times{}^2D$, ^2P, ^2S

f Electrons

Configuration	Terms
f^1, f^{13}	^2F
f^2, f^{12}	^3H, ^3F, ^3P, ^1I, ^1G, ^1D, ^1S
f^3, f^{11}	^4I, ^4G, ^4F, ^4D, ^2I, ^2K, ^2I, $2\times{}^2H$, $2\times{}^2G$, $2\times{}^2D$, ^2P
f^4, f^{10}	^5I, ^5G, ^5F, ^5D, ^5S, ^3M, ^3L, $2\times{}^3K$, $2\times{}^3I$, $4\times{}^3H$, $3\times{}^3G$, $4\times{}^3F$, $2\times{}^3D$, $3\times{}^3P$, ^1N, $2\times{}^1L$, ^1K, $3\times{}^1I$, $2\times{}^1H$, $4\times{}^1G$, ^1F, $4\times{}^1D$, $2\times{}^1S$
f^5, f^9	^6H, ^6F, ^6P, ^4M, ^4L, $2\times{}^4K$, $3\times{}^4I$, $3\times{}^4H$, $4\times{}^4G$, $4\times{}^4F$, $3\times{}^4D$, $2\times{}^4P$, ^4S, ^2O, ^2N, $2\times{}^2M$, $3\times{}^2L$, $5\times{}^2K$, $5\times{}^2I$, $7\times{}^2H$, $6\times{}^2G$, $7\times{}^2F$, $5\times{}^2D$, $4\times{}^2P$
f^6, f^8	^7F, ^5L, ^5K, $2\times{}^5I$, $2\times{}^5H$, $3\times{}^5G$, $2\times{}^5F$, $3\times{}^5D$, ^5P, ^5S, ^3O, ^3N, $3\times{}^3M$, $3\times{}^3L$, $6\times{}^3K$, $6\times{}^3I$, $9\times{}^3H$, $7\times{}^3G$, $9\times{}^3F$, $5\times{}^3D$, $6\times{}^3P$, ^1O, $2\times{}^1N$, $2\times{}^1M$, $4\times{}^1L$, $3\times{}^1K$, $7\times{}^1I$, $4\times{}^1H$, $8\times{}^1G$, $4\times{}^1F$, $6\times{}^1D$, ^1P, $4\times{}^1S$
f^7	^8S, ^6I, ^6H, ^6G, ^6F, ^6D, ^6P, ^4N, ^4M, $3\times{}^4L$, $3\times{}^4K$, $5\times{}^4I$, $5\times{}^4H$, $7\times{}^4G$, $5\times{}^4F$, $6\times{}^4D$, $2\times{}^4P$, $2\times{}^4S$, ^2O, $2\times{}^2N$, $4\times{}^2M$, $5\times{}^2L$, $7\times{}^2K$, $9\times{}^2I$, $9\times{}^2H$, $10\times{}^2G$, $10\times{}^2F$, $7\times{}^2D$, $5\times{}^2P$, $2\times{}^2S$

A given (L, S) term has the degeneracy (in absence of spin-orbit coupling)

$$(2L+1)\times(2S+1)$$

The term (L, S) splits into submultiplets (J, L, S), where each multiplet has the degeneracy $2J+1$ and

$$J = L+S, \ldots, |L-S|$$

Example: consider the ^3P term. Find the degeneracy of each level.

$S = 1$ and $L = 1$. Thus, $J = 2, 1, 0$.

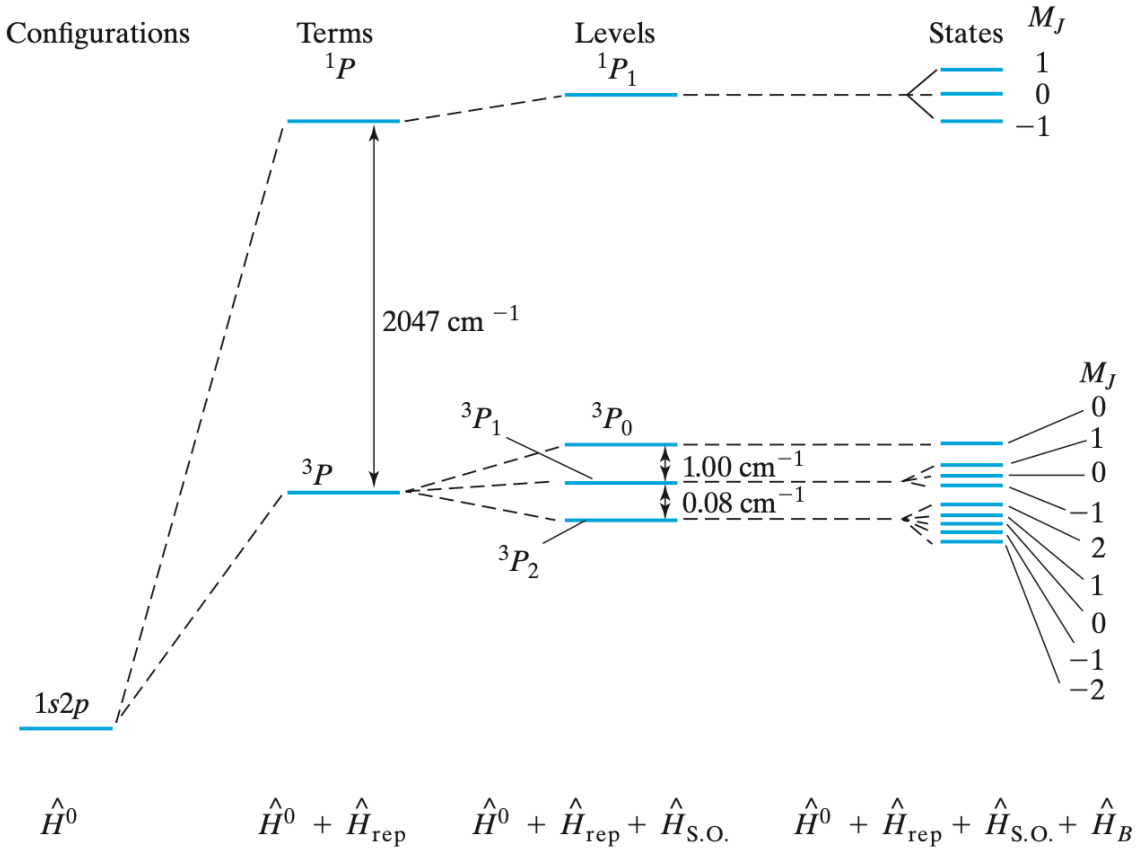
$^3P_2$ has $2J+1 = 5$ values of $M_J = -2, -1, 0, 1, 2$

$^3P_1$ has $2J+1 = 3$ values of $M_J = -1, 0, 1$

$^3P_0$ has $2J+1 = 1$ value of $M_J = 0$

9 states

Example: 1s2p helium configuration



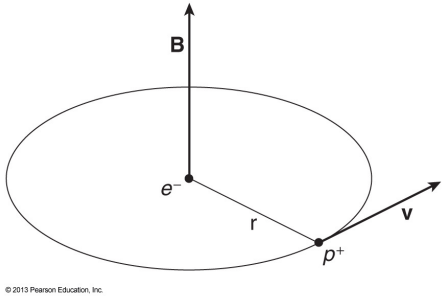
$$\hat{H}^0 = \sum_{i=1}^{n}\left(-\frac{\hbar^2}{2m_e}\nabla_i^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_i}\right)$$

$$\hat{H}_{\text{rep}} = \sum_i \sum_{j>i} \frac{e^2}{4\pi\varepsilon_0 r_{ij}}$$

$$\hat{H}_{\text{S.O.}} = \sum_{i=1}^{n} \xi_i \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i$$

$$\hat{H}_B = -\hat{\mathbf{m}} \cdot \mathbf{B} = -(\hat{\mathbf{m}}_L + \hat{\mathbf{m}}_S) \cdot \mathbf{B}$$

Spin-orbit coupling



$$\hat{H}_{\text{S.O.}} = \sum_i \zeta_i \mathbf{l}_i \cdot \mathbf{s}_i$$

where ζ is the spin-orbit coupling of the i^{th} electron.

ζ increases from the light to heavier elements!

Within the Russel-Saunders term ^{2S+1}L, the Hamiltonian can be written as

$$\hat{H}_{\text{S.O.}} = \lambda \mathbf{L} \cdot \mathbf{S}$$

where $\mathbf{L}$ and $\mathbf{S}$ are the total orbital and spin operators, and

$$\lambda = \pm \frac{\zeta}{2S}$$

The spin-orbit Hamiltonian is not diagonal in the uncoupled $|m_l m_s\rangle$ basis, but it is *diagonal* in the coupled $|jm_j\rangle$ basis.

$$\mathbf{J} = \mathbf{L} + \mathbf{S}$$

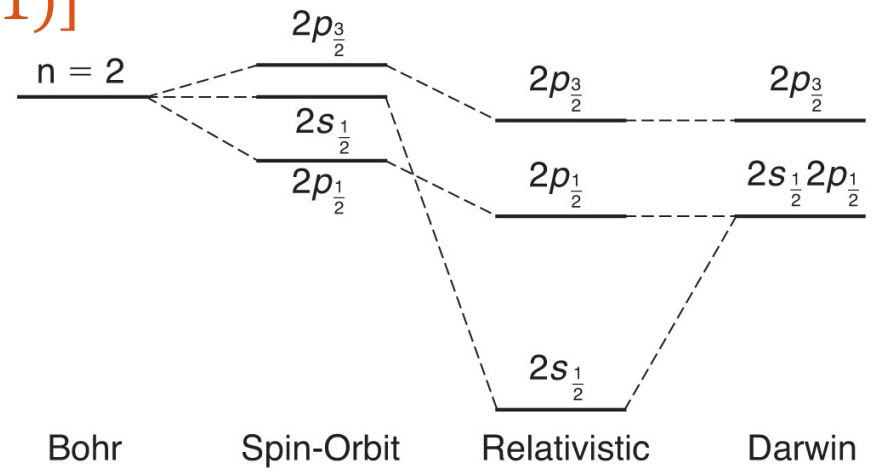
$$\mathbf{J}^2 = \mathbf{L}^2 + \mathbf{S}^2 + 2\mathbf{L}\cdot\mathbf{S}$$

$$\mathbf{L}\cdot\mathbf{S} = \frac{1}{2}\left(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2\right)$$

Thus, the first-order energy correction due to spin-orbit coupling is

$$E_{SO}^{(1)} = \langle H_{SO}\rangle = \langle jm_j|\lambda\mathbf{L}\cdot\mathbf{S}|jm_j\rangle = \frac{\lambda_{nl}}{2}\langle jm_j|\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2|jm_j\rangle$$

$$= \frac{\lambda_{nl}}{2}[j(j+1) - l(l+1) - s(s+1)]$$



Zeeman interaction

The total magnetic moment

$$\boldsymbol{\mu} = \boldsymbol{\mu}_S + \boldsymbol{\mu}_L = -\mathrm{g}_e \mu_B \mathbf{S} - \mathrm{g}_l \mu_B \mathbf{L}$$

The interaction Hamiltonian is

$$\hat{H}_{Zee} = -\boldsymbol{\mu} \cdot \mathbf{B} = \mu_B (\mathrm{g}_l \mathbf{L} + \mathrm{g}_e \mathbf{S}) \cdot \mathbf{B}$$

In a homogenous magnetic field along z axis

$$\hat{H}_{Zee} = \mu_B \left(\mathrm{g}_l \hat{L}_z + \mathrm{g}_e \hat{S}_z\right) \cdot B_z$$

Weak magnetic field

The Zeeman energy correction is

$$E_{Zee}^{(1)} = \langle jm_j | \hat{H}_{Zee} | jm_j \rangle$$

$$= \mu_B B \left(g_l \langle jm_j | \hat{L}_z | jm_j \rangle + g_e \langle jm_j | \hat{S}_z | jm_j \rangle \right)$$

The L_z and S_z operators are diagonal in the *uncoupled* basis $|m_l m_s\rangle$, that is connected to the *coupled* bases via the *Clebsch-Gordan* coefficients:

Tedious though!

$$|jm_j\rangle = \sum_{m_l m_s} |lsm_l m_s\rangle \langle lsm_l m_s | jm_j \rangle$$

More elegantly, we can use *Wigner-Eckhart theorem*

$$\langle jm_j|V_z|jm_j'\rangle = \frac{\langle jm_j|\mathbf{V}\cdot\mathbf{J}|jm_j\rangle}{j(j+1)}\langle jm_j|J_z|jm_j'\rangle$$

To use this theorem (*projection theorem*), we need to know the diagonal matrix elements, $\langle jm_j|\mathbf{V}\cdot\mathbf{J}|jm_j\rangle$.

$$\mathbf{J} = \mathbf{L} + \mathbf{S}$$

$$\mathbf{S} = \mathbf{J} - \mathbf{L}$$

squaring

$$\mathbf{S}^2 = \mathbf{J}^2 + \mathbf{L}^2 - 2\mathbf{L}\cdot\mathbf{J}$$

$$\mathbf{L}\cdot\mathbf{J} = \frac{1}{2}\left(\mathbf{J}^2 + \mathbf{L}^2 - \mathbf{S}^2\right)$$

Similarly,

$$\mathbf{S}\cdot\mathbf{J} = \frac{1}{2}\left(\mathbf{J}^2 + \mathbf{S}^2 - \mathbf{L}^2\right)$$

$$\langle jm_j|\mathbf{S}\cdot\mathbf{J}|jm_j\rangle = \frac{1}{2}[j(j+1)+s(s+1)-l(l+1)]$$

$$\langle jm_j|\mathbf{L}\cdot\mathbf{J}|jm_j\rangle = \frac{1}{2}[j(j+1)+l(l+1)-s(s+1)]$$

Using the projection theorem, we get

$$\langle jm_j|S_z|jm_j'\rangle = \frac{j(j+1)+s(s+1)-l(l+1)}{2j(j+1)}\langle jm_j|J_z|jm_j'\rangle$$

$$\langle jm_j|L_z|jm_j'\rangle = \frac{j(j+1)+l(l+1)-s(s+1)}{2j(j+1)}\langle jm_j|J_z|jm_j'\rangle$$

The first-order Zeeman energy correction

$$E_{Zee}^{(1)} = \langle jm_j|\hat{H}_{Zee}|jm_j\rangle = \mu_B B\left(\mathrm{g}_l\langle jm_j|\hat{L}_z|jm_j\rangle + \mathrm{g}_e\langle jm_j|\hat{S}_z|jm_j\rangle\right)$$

$$= \mu_B B\left(g_l\frac{j(j+1)+l(l+1)-s(s+1)}{2j(j+1)} + g_e\frac{j(j+1)+s(s+1)-l(l+1)}{2j(j+1)}\right)\langle jm_j|J_z|jm_j\rangle$$

$$= \mu_B B\left(g_l\frac{j(j+1)+l(l+1)-s(s+1)}{2j(j+1)} + g_e\frac{j(j+1)+s(s+1)-l(l+1)}{2j(j+1)}\right)m_j$$

This can be written as

$$E_{Zee}^{(1)} = g_j\mu_B B m_j$$

where

$$g_j = g_l\frac{j(j+1)+l(l+1)-s(s+1)}{2j(j+1)} + g_e\frac{j(j+1)+s(s+1)-l(l+1)}{2j(j+1)}$$

This is the Landé g factor

Hydrogen atom (weak field)

After considering the gyromagnetic ratios: $g_l = 1, g_e = 2$)

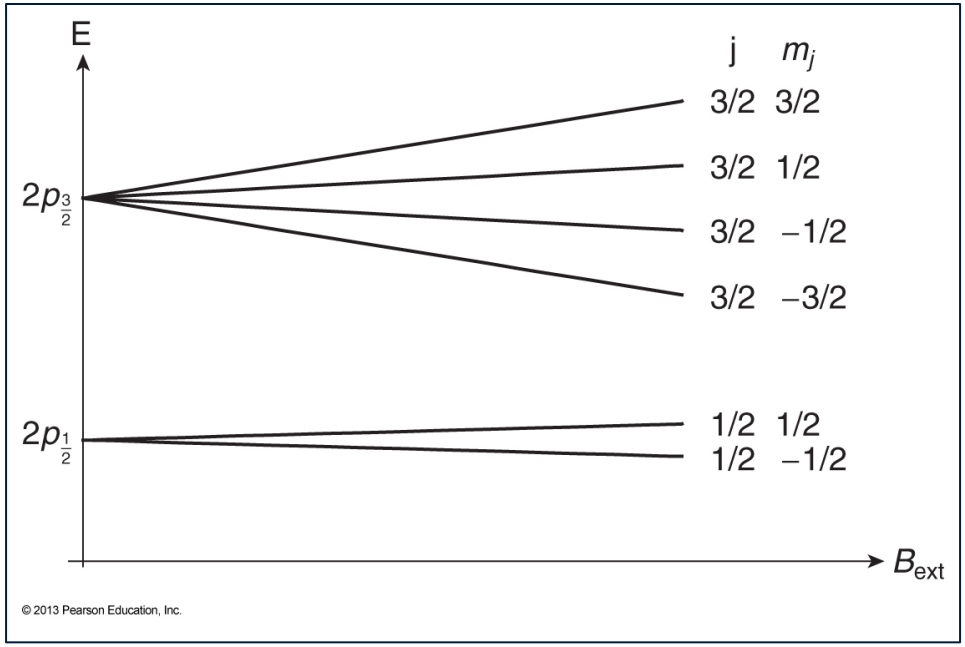
$$g_j = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$

For the hydrogen $2p$ state, we have

$L = 1; S = 1/2$ thus $J = \frac{3}{2}, \frac{1}{2}$

Therefore

$g_{\frac{3}{2}} = \frac{4}{3}$ and $g_{\frac{1}{2}} = \frac{2}{3}$



Strong magnetic field

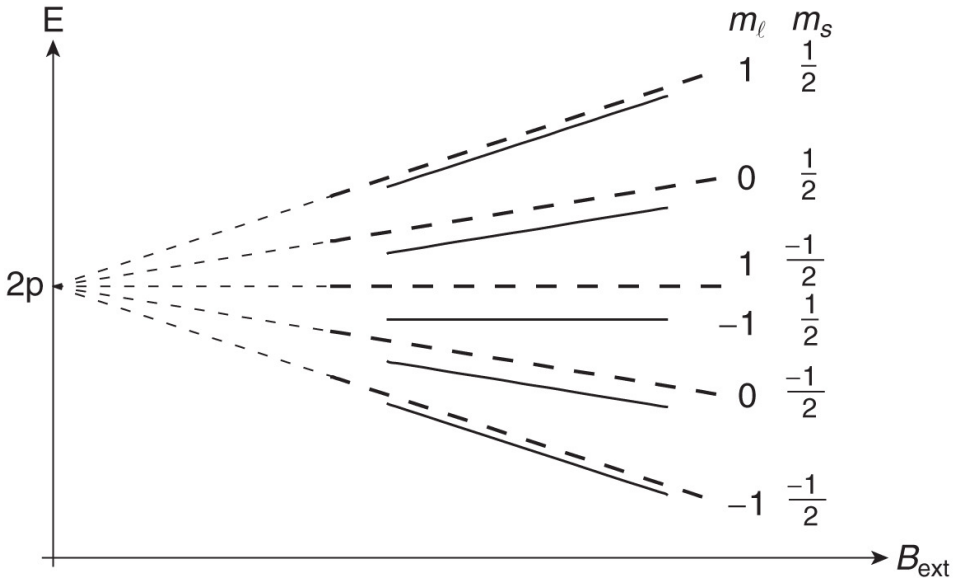
We should include the Zeeman Hamiltonian in the zeroth-order and treat the spin-orbit coupling as a perturbation

$$E_n^{(0)} = -\frac{Ryd}{n^2} + \langle m_l m_s | \hat{H}_{zee} | m_l m_s \rangle$$

In the *uncoupled* basis, the spin-orbit corrections are

$$E_{SO}^{(1)} = \langle m_l m_s | \hat{H}_{SO} | m_l m_s \rangle = \lambda \langle m_l m_s | \mathbf{L} \cdot \mathbf{S} | m_l m_s \rangle$$

$$= \lambda \left\langle m_l m_s \left| \frac{1}{2}(L_+ S_- + L_- S_+) + L_z S_z \right| m_l m_s \right\rangle = \lambda m_l m_s$$

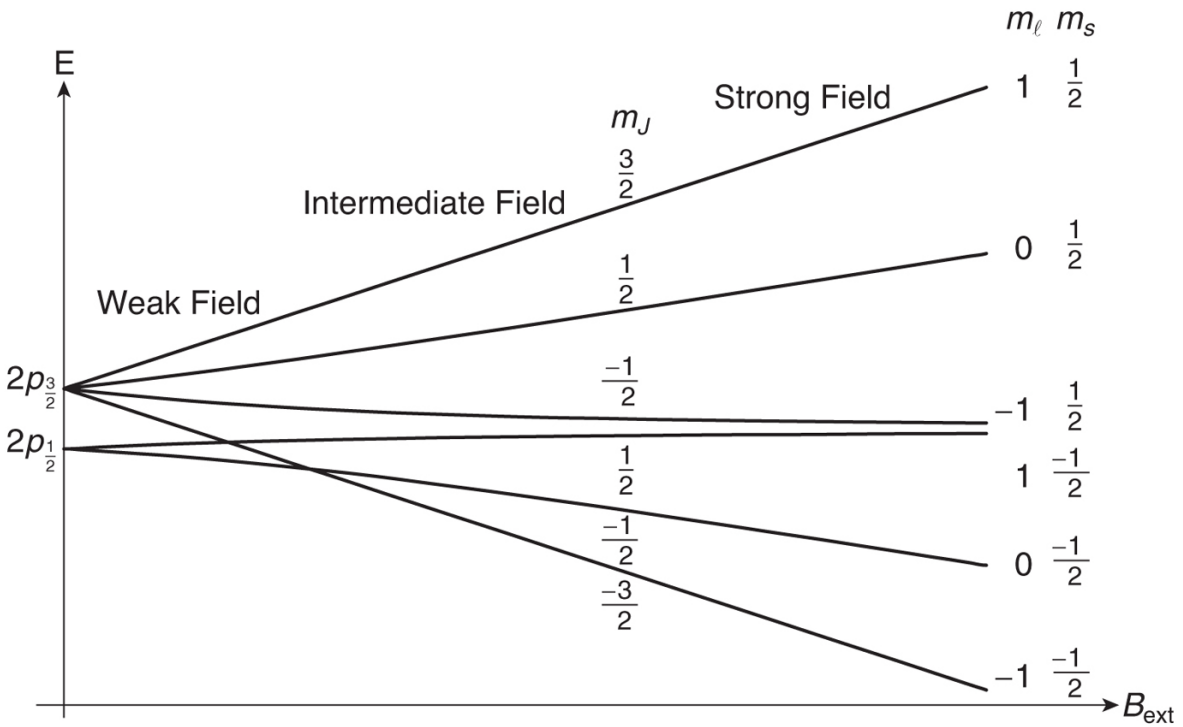


Intermediate magnetic field

In the uncoupled basis $|m_l m_s\rangle$, $\hat{H}_{Zee}$ is diagonal but $\hat{H}_{SO}$ is not diagonal and vice versa. We must diagonalize the entire perturbation Hamiltonian matrix, $H' = \hat{H}_{SO} + \hat{H}_{Zee}$

Exercise: build the matrix representing the perturbation Hamiltonian, H', in the *coupled* basis for the $2p$ states of hydrogen atom.

$$H' = \begin{pmatrix} -\lambda + 2\mu_B B & 0 & 0 & 0 & 0 & 0 \\ 0 & -\lambda + \frac{2}{3}\mu_B B & 0 & 0 & -\frac{\sqrt{2}}{3}\mu_B B & 0 \\ & & & & & \end{pmatrix} \begin{matrix} 3/2, 3/2 \\ 3/2, 1/2 \\ 3/2, -1/2 \\ 3/2, -3/2 \\ 1/2, 1/2 \\ 1/2, -1/2 \end{matrix}$$



Zeeman interaction (anisotropic cases)

For a free atom, the electronic magnetic moment can be written:

$$\mu_J = -g_J \mu_B \mathbf{J}$$

and the Zeeman Hamiltonian for the interaction with a field **B**:

$$\hat{H}_{Zee} = -(\mu_J \cdot \mathbf{B}) = g_J \mu_B (\mathbf{B} \cdot \mathbf{J})$$

In anisotropic cases:

$$\hat{H}_{Zee} = \mu_B (\mathbf{B} \cdot \mathbf{g} \cdot \tilde{\mathbf{S}})$$

$$= \mu_B \{ g_{xx} B_x \tilde{S}_x + g_{yy} B_y \tilde{S}_y + g_{zz} B_z \tilde{S}_z + g_{xy} B_x \tilde{S}_y + g_{yx} B_y \tilde{S}_x$$

$$+ g_{yz} B_y \tilde{S}_z + g_{zy} B_z \tilde{S}_y + g_{zx} B_z \tilde{S}_x + g_{xx} B_x \tilde{S}_z \}$$

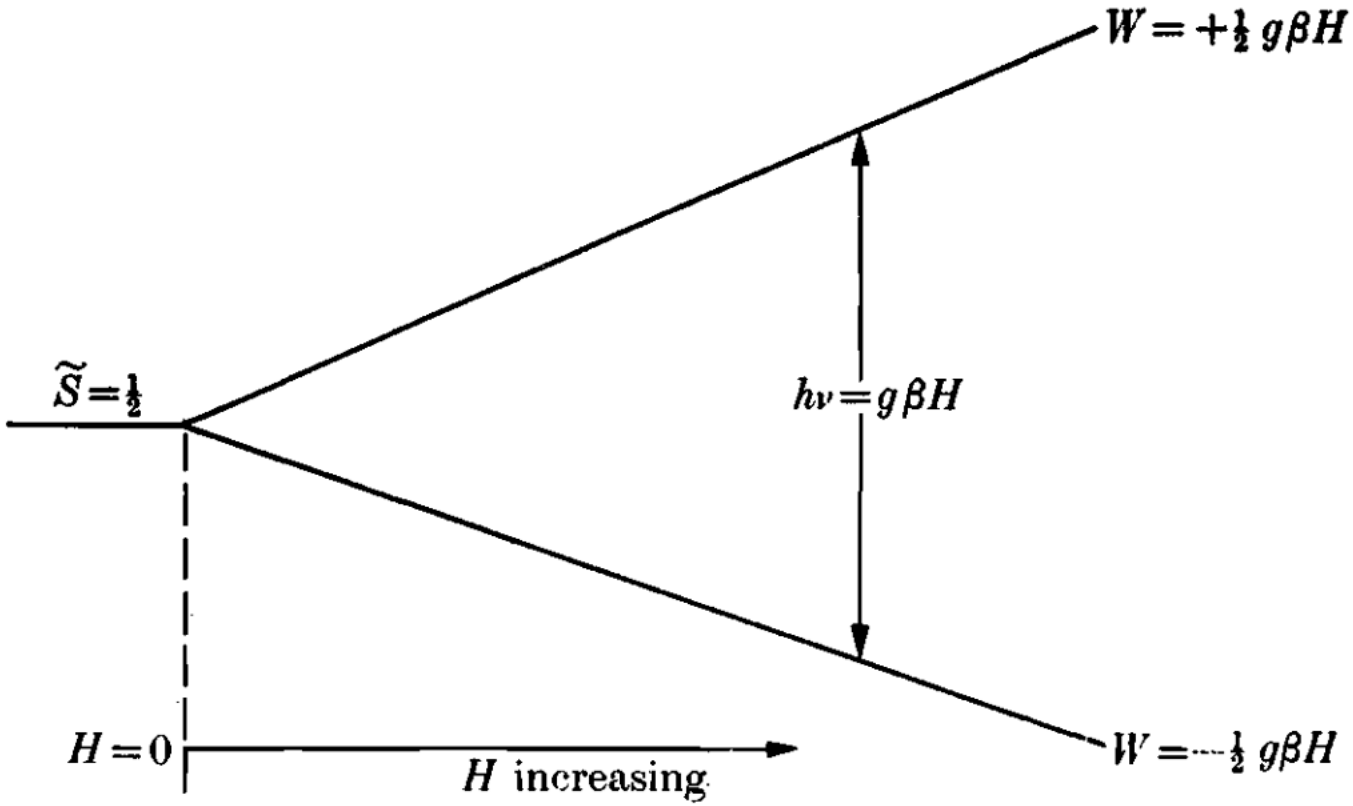
By choosing suitable x, y, z axes *(principal axes)*, in most cases the Hamiltonian acquires a simpler form:

$$\widehat{H}_{Zee} = \mu_B \{ g_{xx} B_x \tilde{S}_x + g_{yy} B_y \tilde{S}_y + g_{zz} B_z \tilde{S}_z \}$$

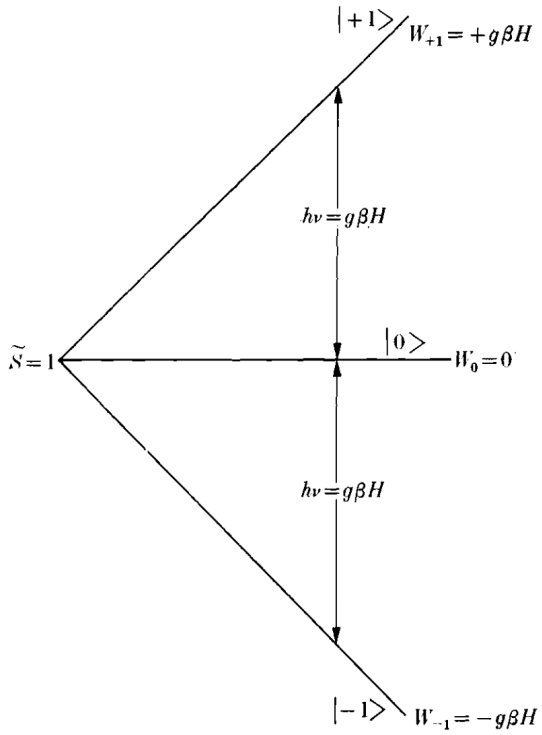
In axial symmetry

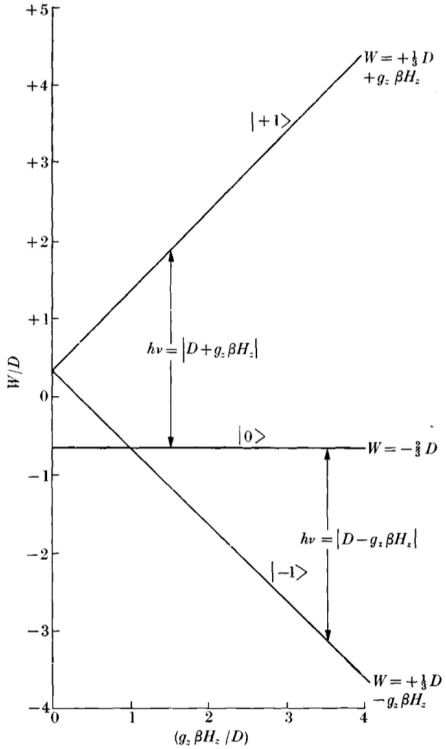
$$\left(g_{xx} = g_{yy} = g_{\perp}; g_{zz} = g_{\parallel} \right)$$

Energy levels for $\widetilde{S} = \frac{1}{2}$. Zeeman effect in an applied field, *H*.



Energy levels for $\tilde{s} = 1$ in the absence of any initial splitting of the levels, left (cubic symmetry) and lower symmetry (axial), right.





$$\hat{H}_{Zee} = \mu_B(\mathbf{B}\cdot\mathbf{g}\cdot\tilde{\mathbf{S}})$$

$$\hat{H}_{Zee} = \mu_B(\mathbf{B}\cdot\mathbf{g}\cdot\tilde{\mathbf{S}}) + D\left\{\tilde{S}_z^2 - \frac{1}{3}\tilde{S}(\tilde{S}+1)\right\}$$

Crystal-field splitting

The crystal field splitting can be described by the following Hamiltonian

$$\hat{H}_{CF} = \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}$$

where **D** is a symmetric tensor. Therefore, it has three orthogonal eigenvectors. Choosing the x, y, z axes parallel to these eigenvectors, **D** is diagonal and

$$\hat{H}_{CF} = D_{xx}S_x^2 + D_{yy}S_y^2 + D_{zz}S_z^2$$

Adding a constant to the Hamiltonian does not change physical properties. Thus, subtracting $\frac{1}{2}(D_{xx}+D_{yy})(S_x^2+S_y^2+S_z^2)=\frac{1}{2}(D_{xx}+D_{yy})S(S+1)$, we get

$$\hat{H}_{CF}=DS_z^2+E(S_x^2-S_y^2)$$

where

$$D=D_{zz}-\frac{1}{2}D_{xx}-\frac{1}{2}D_{yy};\quad E=\frac{1}{2}(D_{xx}-D_{yy})$$

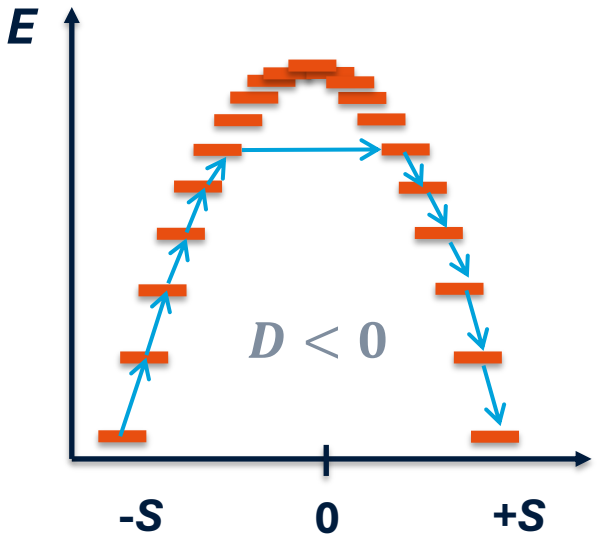
Subtracting the constant $DS(S+1)/3$ from the $\hat{H}_{CF}$, we obtain a traceless Hamiltonian ($\mathrm{Tr}\,H=0$):

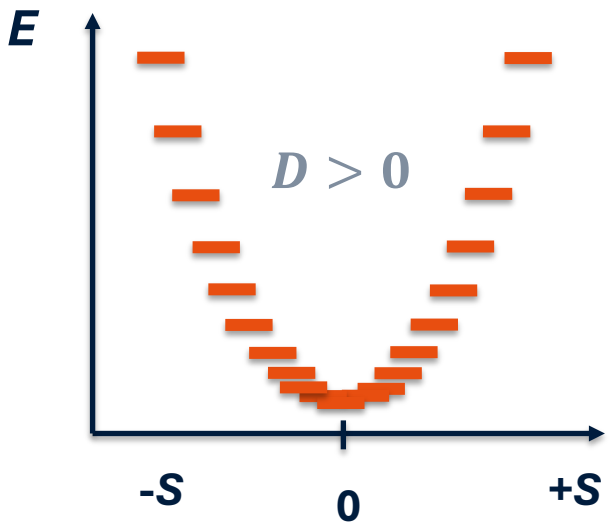
$$\hat{H}_{CF}=D\left[S_z^2-\frac{1}{3}S(S+1)\right]+E(S_x^2-S_y^2)$$

$$D = D_{zz} - \frac{1}{2}D_{xx} - \frac{1}{2}D_{yy}; \quad E = \frac{1}{2}\left(D_{xx} - D_{yy}\right)$$

When $D_{xx} = D_{yy} = D_{zz}$ $(cubic\ symmetry) \Rightarrow D = 0$. In axial symmetry, $D_{xx} = D_{yy} \Rightarrow E = 0$, therefore

$$\hat{H}_{CF} = DS_z^2$$





Higher terms

$\hat{H}_{CF} = \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}$ is the simplest Hamiltonian for CF splitting. We can include higher terms:

$$\hat{H}_{CF} = \sum_{N,k} B_N^k \mathbf{O}_N^k$$

where $N = 2, 4, 6, \ldots, 2S$
and B_N^k are parameters, and $\mathbf{O}_N^k$ are the Stevens operators (well tabulated):

$$O_2^0 = 3S_z^2 - s(s+1)$$

$$O_2^2 = \frac{1}{2}(S_+^2 + S_-^2)$$

$$O_4^0 = 35S_z^4 - [30s(s+1) - 25]S_z^2 + 3s^2(s+1)^2 - 6s(s+1)$$

...

Example: Ni(II) ion in axially distorted octahedral

The total spin Hamiltonian considering the CF splitting and Zeeman interaction is (assuming **D**- and **g**-tensors have the same principal axes)

$$\hat{H} = \mu_B \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{B} + \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}$$

$$= g_u \mu_B \mathbf{S}_u B_u + D\left[\mathbf{S}_z^2 - \frac{S(S+1)}{3}\right] + E\left(\mathbf{S}_x^2 - \mathbf{S}_y^2\right)$$

where u denotes the direction of the applied field.

When $\boldsymbol{B_z}$ **is parallel** to the unique axis, the Hamiltonian matrix is diagonal

$$\hat{H} = \begin{pmatrix} |1\rangle & |0\rangle & |-1\rangle \\ g_z \mu_B B_z + D & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -g_z \mu_B B_z + D \end{pmatrix}$$

Introducing those energies in the Van Vleck formula, $\chi = \frac{N\sum_n \left(E_n^{(1)^2}/kT\right)\exp\left(-E_n^{(0)}/kT\right)}{\sum_n \exp\left(-E_n^{(0)}/kT\right)}$, the magnetic susceptibility is

$$\chi_z = \frac{2Ng_z^2\mu_B^2}{kT}\frac{\exp(-D/kT)}{1+2\exp(-D/kT)}$$

When $\boldsymbol{B_x}$ **is perpendicular** to the unique axis, the Hamiltonian matrix is

$$\hat{H} = \begin{pmatrix} |1\rangle & |0\rangle & |-1\rangle \\ D & \sqrt{2}g_x\mu_B B_x/2 & 0 \\ \sqrt{2}g_x\mu_B B_x/2 & 0 & \sqrt{2}g_x\mu_B B_x/2 \\ 0 & \sqrt{2}g_x\mu_B B_x/2 & D \end{pmatrix}$$

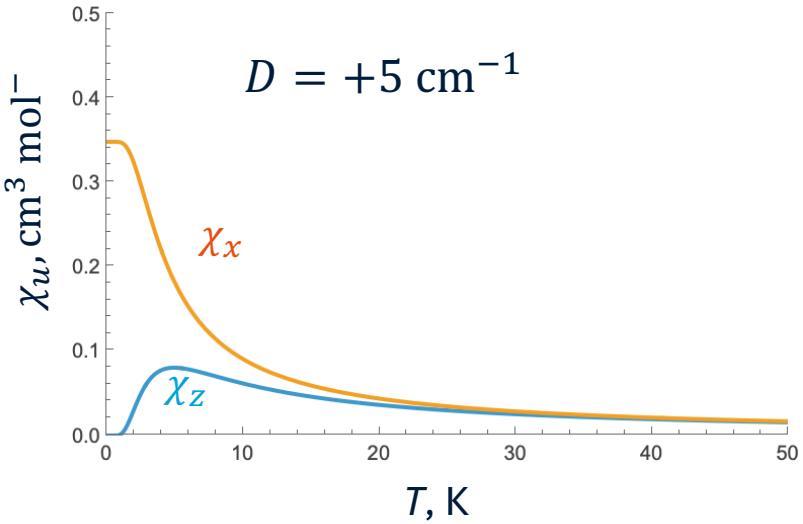
The eigenvalues are:

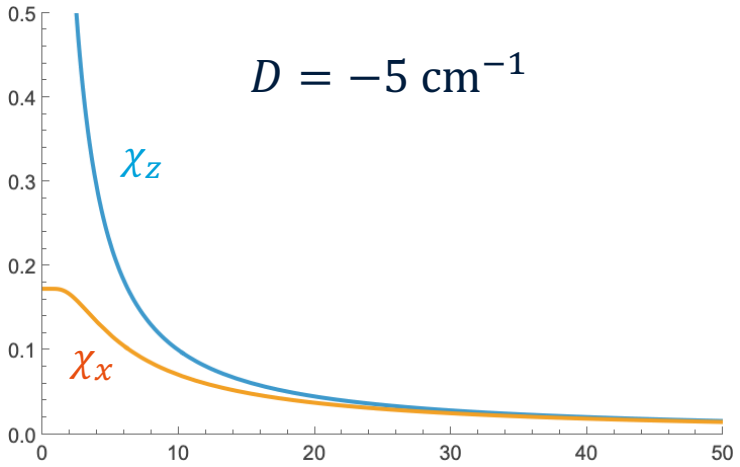
$$E_1 = D$$

$$E_{2,3} = \left(D \pm \sqrt{4 g_x^2 \mu_B^2 H_x^2 + D^2} \right) / 2$$

Assuming $|D| \gg g_x \mu_B H_x$, and using the Van Vleck equation, the perpendicular magnetic susceptibility is

$$\chi_x = \frac{2N g_x^2 \mu_B^2}{D} \frac{1 - \exp(-D/kT)}{1 + 2\exp(-D/kT)}$$





For powder susceptibility we can average it

$$\chi = \frac{2\chi_x + \chi_z}{3}$$

or more accurately

$$\chi = \frac{1}{4\pi}\int_0^{2\pi}\int_0^{\pi}\chi(\theta,\phi)\sin\theta\ d\theta d\phi$$

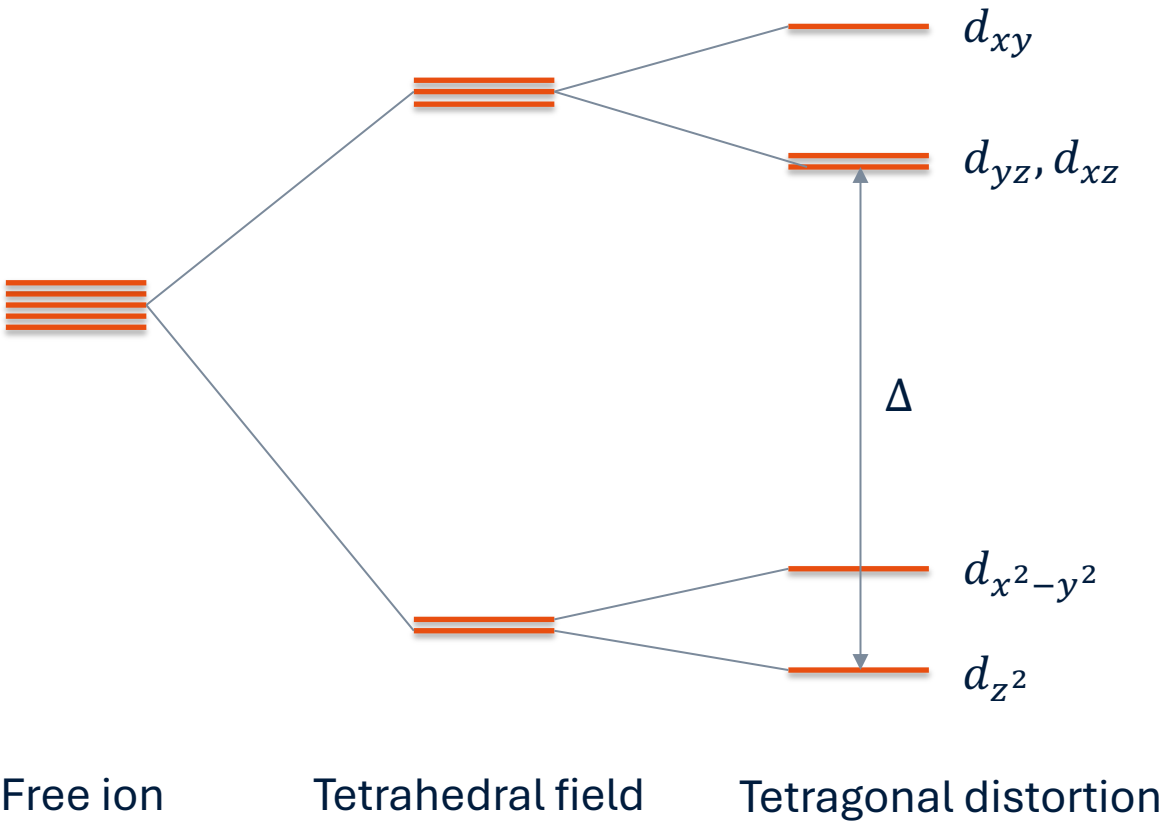
First-order orbital momentum (spin-orbit coupling important)

Examples:

- d^1 in distorted tetrahedral environment
- d^1 in octahedral environment

g-tensor of transition metal d^1 system.

Consider a d^1 ion in a distorted tetrahedral environment:



Some reminders

$$d_{x^2-y^2} = \frac{1}{\sqrt{2}}(|2,2\rangle + |2,-2\rangle)$$

$$d_{xy} = -\frac{i}{\sqrt{2}}(|2,2\rangle - |2,-2\rangle)$$

$$d_{xz} = -\frac{1}{\sqrt{2}}(|2,1\rangle - |2,-1\rangle)$$

$$d_{yz} = \frac{i}{\sqrt{2}}(|2,1\rangle + |2,-1\rangle)$$

$$d_{z^2} = |2,0\rangle$$

$$\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \frac{1}{2}\left(\hat{\mathbf{L}}_+\hat{\mathbf{S}}_- + \hat{\mathbf{L}}_-\hat{\mathbf{S}}_+ + \hat{\mathbf{L}}_z\hat{\mathbf{S}}_z\right)$$

$$\mathbf{S}_+ = \mathbf{S}_x + i\mathbf{S}_y$$

$$\mathbf{S}_- = \mathbf{S}_x - i\mathbf{S}_y$$

$$\mathbf{S}_+|S, M_S\rangle = [(S + M_S + 1)(S - M_S)]^{1/2}|S, M_S + 1\rangle$$

$$\mathbf{S}_-|S, M_S\rangle = [(S - M_S + 1)(S + M_S)]^{1/2}|S, M_S - 1\rangle$$

Same formulas apply for L by replacing S with L, and M_S with M_L.

The spin-orbit coupling mixes $|d_{z^2}\rangle$ with $|d_{yz}\rangle$ and $|d_{xz}\rangle$. First-order perturbation theory gives us

$$C_{0,i} = -\frac{\langle i|H'|0\rangle}{E_i - E_0}$$

Our first-order Hamiltonian is

$$H' = \zeta\, \mathbf{l}\cdot\mathbf{s}$$

Therefore

$$C_{0,i} = -\frac{\zeta}{\Delta}\langle i|\mathbf{l}\cdot\mathbf{s}|0\rangle$$

The first-order corrected ground state wavefunctions are:

$$|+\rangle = |d_{z^2},\alpha\rangle + \frac{\sqrt{3}}{2} i \frac{\zeta}{\Delta}|d_{yz},\beta\rangle + \frac{\sqrt{3}}{2}\frac{\zeta}{\Delta}|d_{xz},\beta\rangle$$

$$|-\rangle = |d_{z^2},\beta\rangle + \frac{\sqrt{3}}{2} i \frac{\zeta}{\Delta}|d_{yz},\alpha\rangle - \frac{\sqrt{3}}{2}\frac{\zeta}{\Delta}|d_{xz},\alpha\rangle$$

The Zeeman Hamiltonian is

$$\hat{H}_{Zee} = \mu_B(\mathbf{l} + g_e\mathbf{s}) \cdot \mathbf{B}$$

written in the basis of $|+\rangle$ and $|-\rangle$:

$\hat{H}_{Zee}$	$\|+\rangle$	$\|-\rangle$
$\langle+\|$	$\frac{1}{2}g_e\mu_B B_z$	$\frac{1}{2}\mu_B B_x(g_e - 6\zeta/\Delta) - \frac{1}{2}i\mu_B B_y(g_e - 6\zeta/\Delta)$
$\langle-\|$	$\frac{1}{2}\mu_B B_x(g_e - 6\zeta/\Delta) + \frac{1}{2}i\mu_B B_y(g_e - 6\zeta/\Delta)$	$-\frac{1}{2}g_e\mu_B B_z$

If the field is applied along z axis:

$$\Delta E_z = g_e\mu_B B_z$$

This corresponds to the free electron g-value.

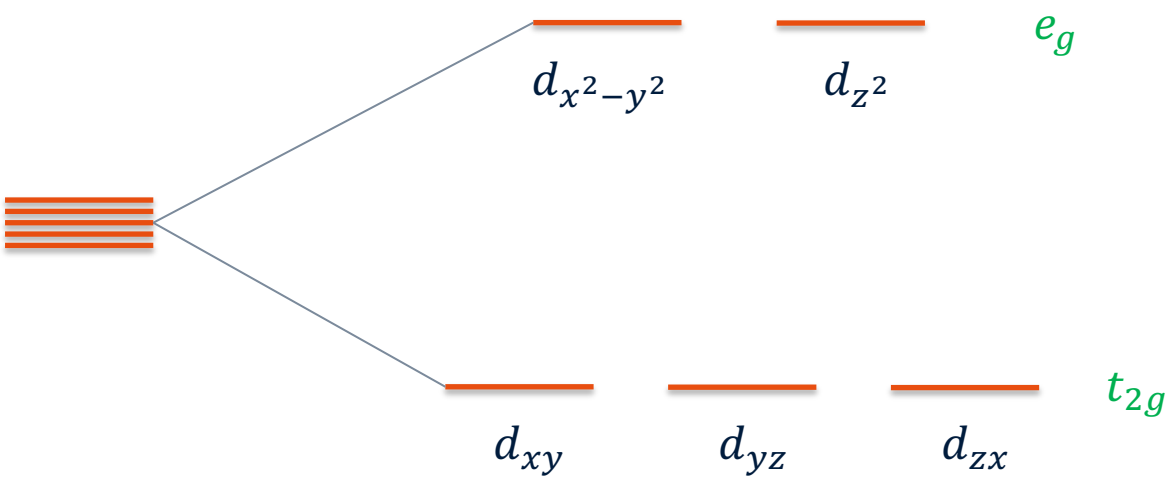
If the field is applied along x or y axes

$$\Delta E_x = \Delta E_y = (g_e - 6\zeta/\Delta)\mu_B B$$

$$g_\perp = (g_e - 6\zeta/\Delta); \qquad g_\parallel = g_e$$

d^1 in octahedral environment

In O_h symmetry the d orbitals split into t_{2g} and e_g levels.



Using the functions: $d_{xy}\alpha, d_{yz}\alpha, d_{zx}\alpha, d_{xy}\beta, d_{yz}\beta$, and $d_{zx}\beta$ as the basis set, the spin-orbit Hamiltonian, $\hat{H}_{SO} = \lambda \mathbf{L} \cdot \mathbf{S}$, becomes:

$$\widehat{H}_{\text{S.O.}} = \begin{array}{c|cccccc} & |d_{xy}\alpha\rangle & |d_{yz}\beta\rangle & |d_{zx}\beta\rangle & |d_{xy}\beta\rangle & |d_{yz}\alpha\rangle & |d_{zx}\alpha\rangle \\ \hline & 0 & \lambda/2 & -i\lambda/2 & 0 & 0 & 0 \\ & \lambda/2 & 0 & -i\lambda/2 & 0 & 0 & 0 \\ & i\lambda/2 & i\lambda/2 & 0 & 0 & 0 & 0 \\ & 0 & 0 & 0 & 0 & -\lambda/2 & -i\lambda/2 \\ & 0 & 0 & 0 & -\lambda/2 & 0 & i\lambda/2 \\ & 0 & 0 & 0 & i\lambda/2 & -i\lambda/2 & 0 \end{array}$$

Diagonalizing $\widehat{H}_{\text{S.O.}}$, we get

$$E = -\frac{\lambda}{2}$$

$$\psi_1 = \frac{\sqrt{6}}{6}\left(2d_{xy}\alpha - d_{yz}\beta - id_{zx}\beta\right)$$

$$\psi_2 = \frac{\sqrt{6}}{6}\left(2d_{xy}\beta + d_{yz}\alpha - id_{zx}\alpha\right)$$

$$\psi_3 = \frac{\sqrt{2}}{2}\left(d_{yz}\alpha + id_{zx}\alpha\right)$$

$$\psi_4 = \frac{\sqrt{2}}{2}\left(-d_{yz}\beta + id_{zx}\beta\right)$$

$$E = \lambda$$

$$\psi_5 = \frac{\sqrt{3}}{3}\left(d_{xy}\alpha + d_{yz}\beta + id_{zx}\beta\right)$$

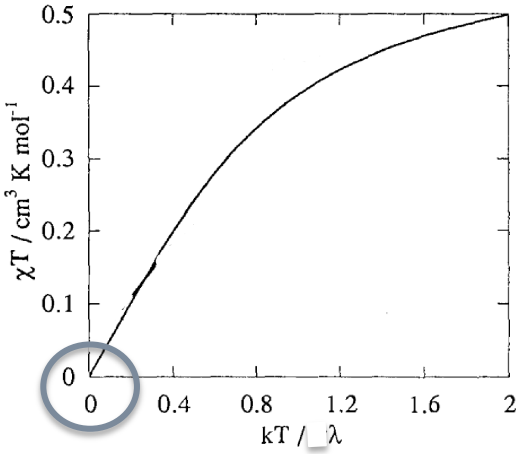
$$\psi_6 = \frac{\sqrt{3}}{3}\left(d_{xy}\beta - d_{yz}\alpha + id_{zx}\alpha\right)$$

Using the functions ψ_i as a basis set, the Zeeman Hamiltonian, $\hat{H} = \lambda \mathbf{L} \cdot \mathbf{S} + \mu_B(\mathbf{L} + g_e\mathbf{S}) \cdot B$, becomes:

$$\hat{H} = \begin{array}{c} \begin{matrix} |\psi_1\rangle & |\psi_2\rangle & |\psi_3\rangle & |\psi_4\rangle & |\psi_5\rangle & |\psi_6\rangle \end{matrix} \\ \begin{pmatrix} -\lambda/2 & 0 & 0 & 0 & 3\sqrt{2}\mu_B B/3 & 0 \\ & -\lambda/2 & 0 & 0 & 0 & -3\sqrt{2}\mu_B B/3 \\ & & -\lambda/2 & 0 & 0 & 0 \\ & & & -\lambda/2 & 0 & 0 \\ & & & & k\lambda - 3\mu_B B/3 & 0 \\ & & & & & k\lambda + 3\mu_B B/3 \end{pmatrix} \end{array}$$

Using the Van Vleck formula with the eigenvalues of the above Hamiltonian, one obtains

$$\chi = \frac{N\mu_B^2}{3KT} \; \frac{8 + \left(\frac{3\lambda}{kT} - 8\right)\exp\left(-\frac{3\lambda}{2kT}\right)}{\lambda/kT\left[2 + \exp\left(-\frac{3\lambda}{2kT}\right)\right]}$$



Does not obey Currie law.

Rare-Earth metal ions

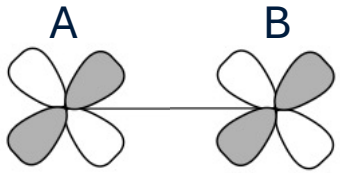
Perturbation theory not appropriate. Exact diagonalization of the SO Hamiltonian needed.

Spin-spin interactions

Direct exchange	Kinetic exchange	Super exchange
Double-exchange	Dipolar interaction	Dzyaloshinskii–Moriya

Potential (direct) exchange

Consider two orthogonal localized orbitals:



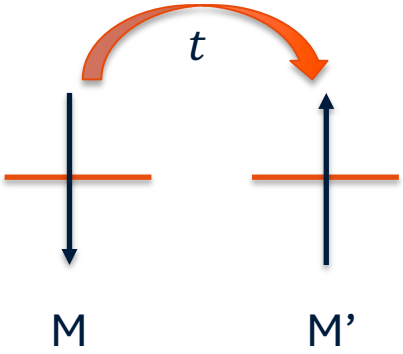
The direct exchange interaction stabilizes the *ferromagnetic* state:

$$K = \int \varphi_A^*(1)\varphi_B^*(2)\frac{e^2}{r_{12}}\varphi_A(2)\varphi_B(1)d\tau$$

Usually rather weak.

Kinetic exchange

Consider two nuclei M and M', with one *orbital* each and two opposite electrons in total. There are four possibilities:



$$|\uparrow,\downarrow\rangle \qquad |\downarrow,\uparrow\rangle \qquad |\uparrow\downarrow,\cdot\rangle \qquad |\cdot,\uparrow\downarrow\rangle$$

We can use the Hubbard Hamiltonian:

$$\hat{H} = -t \sum_{\langle j,l\rangle\sigma} \left(c_{j\sigma}^{\dagger} c_{l\sigma} + c_{l\sigma}^{\dagger} c_{j\sigma} \right) + U \sum_{j} n_{j\uparrow} n_{j\downarrow}$$

The Hubbard Hamiltonian in this basis is

$$\hat{H} = \begin{pmatrix} U & t & -t & 0 \\ t & 0 & 0 & t \\ -t & 0 & 0 & -t \\ 0 & t & -t & U \end{pmatrix} \qquad \begin{matrix} |\uparrow\downarrow,\cdot\rangle \\ |\uparrow,\downarrow\rangle \\ |\downarrow,\uparrow\rangle \\ |\cdot,\uparrow\downarrow\rangle \end{matrix}$$

Diagonalizing the Hamiltonian, we obtain:

$$E_1 = 0 \qquad \psi_1 = \frac{1}{\sqrt{2}}(|\uparrow,\downarrow\rangle + |\downarrow,\uparrow\rangle)$$

$$E_2 = U \qquad \psi_2 = \frac{1}{\sqrt{2}}(|\uparrow\downarrow,\cdot\rangle - |\cdot,\uparrow\downarrow\rangle)$$

$$E_{3,4} = \frac{1}{2}\left(U \pm \sqrt{U^2 + 16t^2}\right)$$

$$\psi_{3,4} = |\uparrow\downarrow,\cdot\rangle + |\cdot,\uparrow\downarrow\rangle - \left(\frac{U \mp \sqrt{16\,t^2 + U^2}}{4\,t}\right)|\uparrow,\downarrow\rangle - \left(\frac{-U \pm \sqrt{16\,t^2 + U^2}}{4\,t}\right)|\downarrow,\uparrow\rangle$$

If $U \gg t, \frac{1}{2}\left(U \pm \sqrt{U^2 + 16t^2}\right) \approx \frac{1}{2}\left[U \pm U\left(1 + \frac{8t^2}{U^2}\right)\right]$

This leads to the following energies:

$$E = 0; \quad U; \quad -4\frac{t^2}{U}; \quad U + 4\frac{t^2}{U}$$

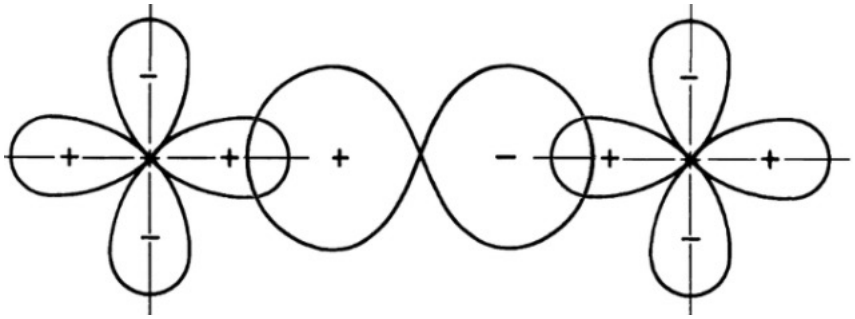
$E = 0$ corresponds to the triplet state

$E = -4\frac{t^2}{U}$ corresponds to the singlet state.

Therefore, the singlet-triplet gap is $J = -4\frac{t^2}{U}$

This is similar to the spin-1/2 Heisenberg exchange model (coming below)

Superexchange

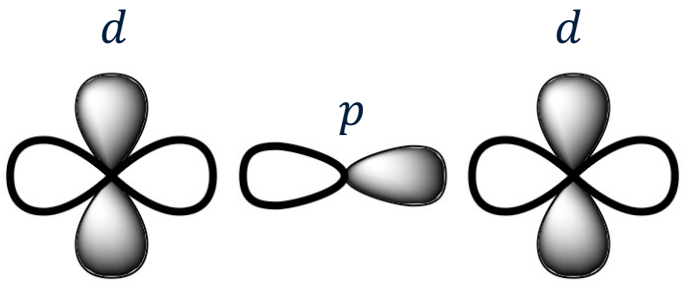


$$\hat{H}$$

$$= \epsilon_d \sum_{\sigma} \sum_{j} n_{j\sigma} + \epsilon_p \sum_{\sigma} n_{p\sigma} - t_{pd} \sum_{\sigma} \sum_{j} \left(c_{p\sigma}^{\dagger} c_{j\sigma} + c_{j\sigma}^{\dagger} c_{p\sigma} \right)$$

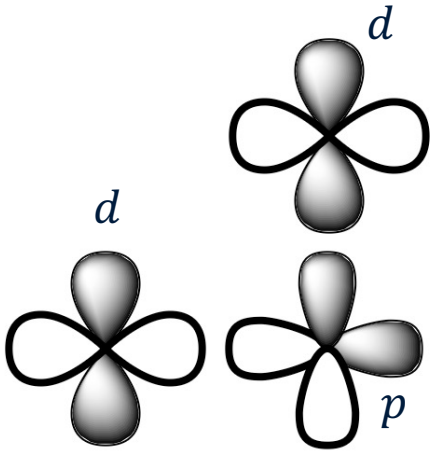
$$+ U_d \sum_{j} n_{j\uparrow} n_{j\downarrow}$$

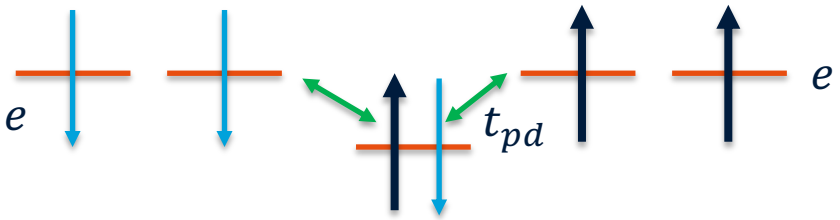
Goodenough-Kanamori rules

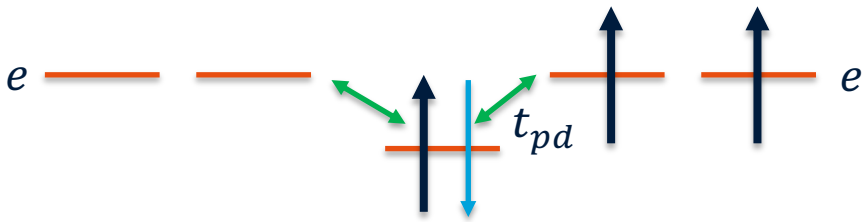


$$J \approx \frac{t_{dp}^4}{\Delta^2(2\Delta + U_p)}$$

$$\Delta = \varepsilon_d - \varepsilon_p$$







180º; Half-filled orbitals on both sides

Strong antiferromagnetic

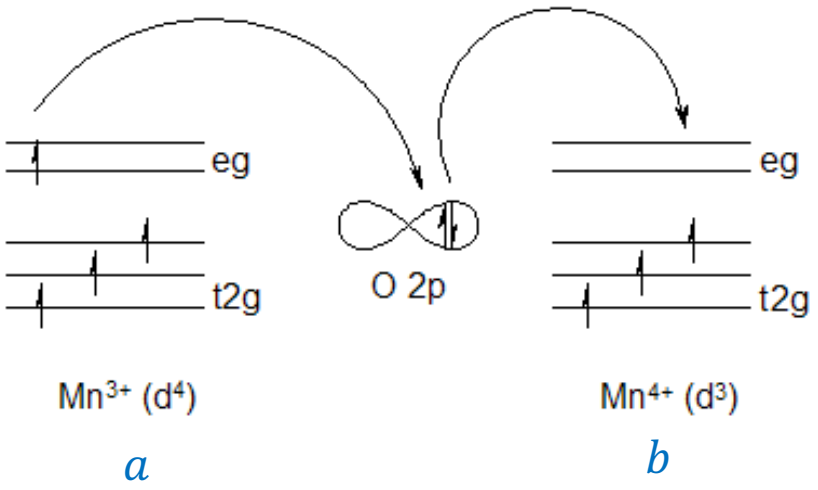
180º; one side occupied another empty

Weak ferromagnetic

90º; empty-half-filled orbitals on sides

Weak ferromagnetic

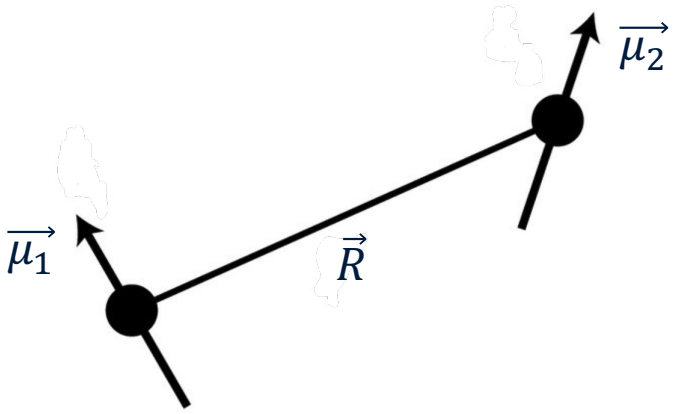
Double-exchange



$$E_{\pm}(S) = -t_{ab} + \frac{J}{2} \pm \frac{J}{2}\left(S_0 + \frac{1}{2}\right)$$

where S_0 is the spin of the configuration without hopping electrons ($S_0 = 3/2$).

Dipolar interaction



$$J_{12}^{dip} = \frac{\mu_B^2}{R^3}\left[\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2 - 3\frac{(\boldsymbol{\mu}_1 \cdot \mathbf{R})(\mathbf{R} \cdot \boldsymbol{\mu}_2)}{|R|^2}\right]$$

Rather weak. Important only when other exchange interactions are weaker.

Spin-spin interaction Hamiltonian

The interaction between two spins can be described by the following Hamiltonian (introduced by Heisenberg, Dirac, Van Vleck):

$$\hat{H}_{exch} = \mathbf{S}_i \cdot \mathbf{J}_{ij} \cdot \mathbf{S}_j$$

This can be rewritten as

$$\hat{H}_{exch} = -J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j + \mathbf{S}_i \cdot \mathbf{D}_{ij} \cdot \mathbf{S}_j + \mathbf{d}_{ij} \cdot \left(\mathbf{S}_i \times \mathbf{S}_j\right)$$

isotropic *anisotropic* *antisymmetric Dzyaloshinskii-Morya*

Isotropic exchange two spins-1/2

$$\widehat{H} = -J\mathbf{S}_1 \cdot \mathbf{S}_2 = J\left[\frac{1}{2}(\mathbf{S}_1^+\mathbf{S}_2^- + \mathbf{S}_1^-\mathbf{S}_2^+) + \mathbf{S}_1^z \cdot \mathbf{S}_2^z\right]$$

Write down the Hamiltonian in the basis:

$$|\uparrow\uparrow\rangle \qquad |\uparrow\downarrow\rangle \qquad |\downarrow\uparrow\rangle \qquad |\downarrow\downarrow\rangle$$

<u>Reminder:</u>

$$\mathbf{S}_+|S, M_S\rangle = [(S + M_S + 1)(S - M_S)]^{1/2}|S, M_S + 1\rangle$$

$$\mathbf{S}_-|S, M_S\rangle = [(S - M_S + 1)(S + M_S)]^{1/2}|S, M_S - 1\rangle$$

Broken-symmetry DFT

$$\hat{H}_{Spin} = -2J\hat{S}_A\hat{S}_B$$

Applying the relationship $\hat{S}^2 = (\hat{S}_A + \hat{S}_B)^2 = \hat{S}_A^2 + \hat{S}_B^2 + 2\hat{S}_A\hat{S}_B$ the spin Hamiltonian takes the form:

$$\hat{H}_{Spin} = -J(\hat{S}^2 - \hat{S}_A^2 - \hat{S}_B^2)$$

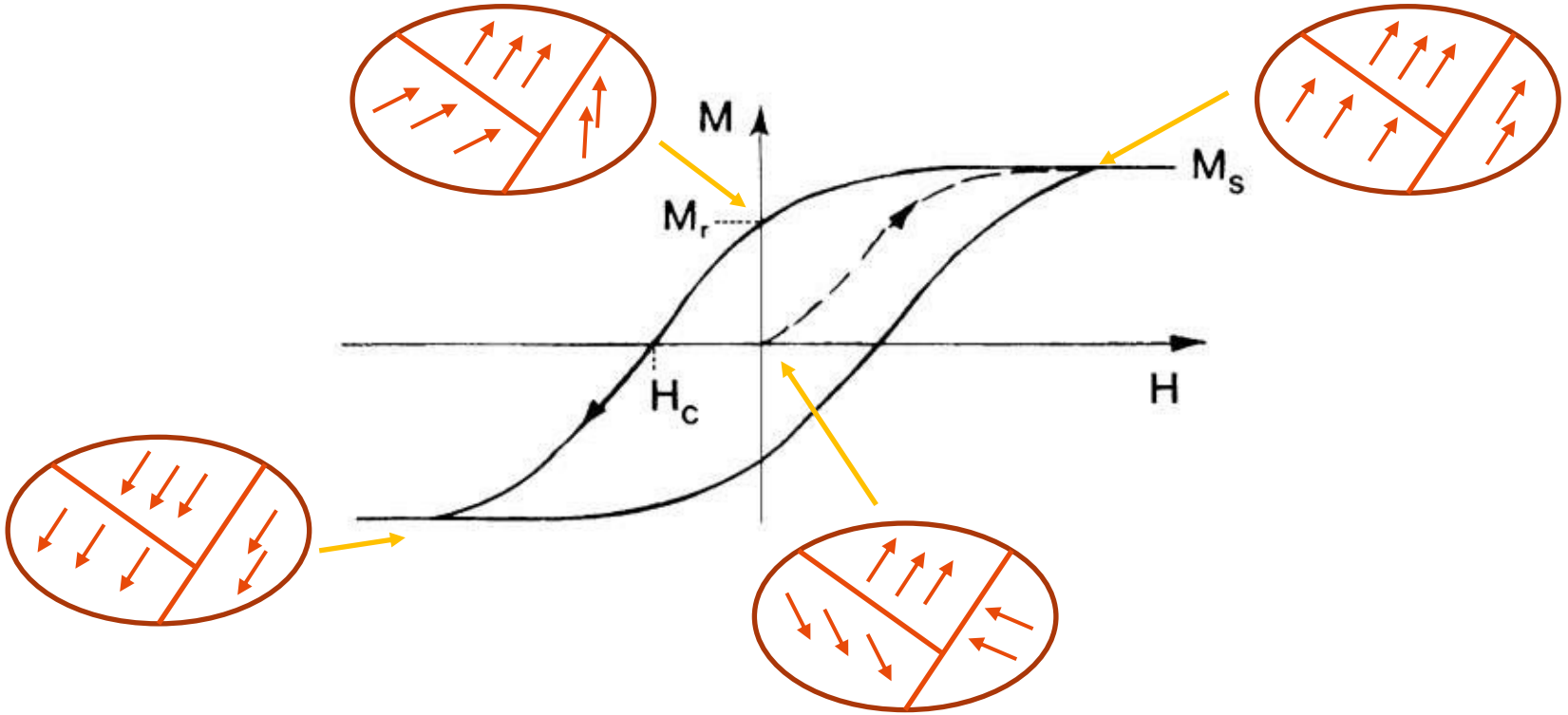
$$\langle \Psi_{BS} | \hat{H}_{Spin} | \Psi_{BS} \rangle = -J\left[\langle \hat{S}^2 \rangle_{BS} - S_A(S_A+1) - S_B(S_B+1)\right] = E_{BS}$$

$$\langle \Psi_{HS} | \hat{H}_{Spin} | \Psi_{HS} \rangle = -J\left[\langle \hat{S}^2 \rangle_{HS} - S_A(S_A+1) - S_B(S_B+1)\right] = E_{HS}$$

$$J = -\frac{E_{HS} - E_{BS}}{\langle \hat{S}^2 \rangle_{HS} - \langle \hat{S}^2 \rangle_{BS}}$$

Classical magnets

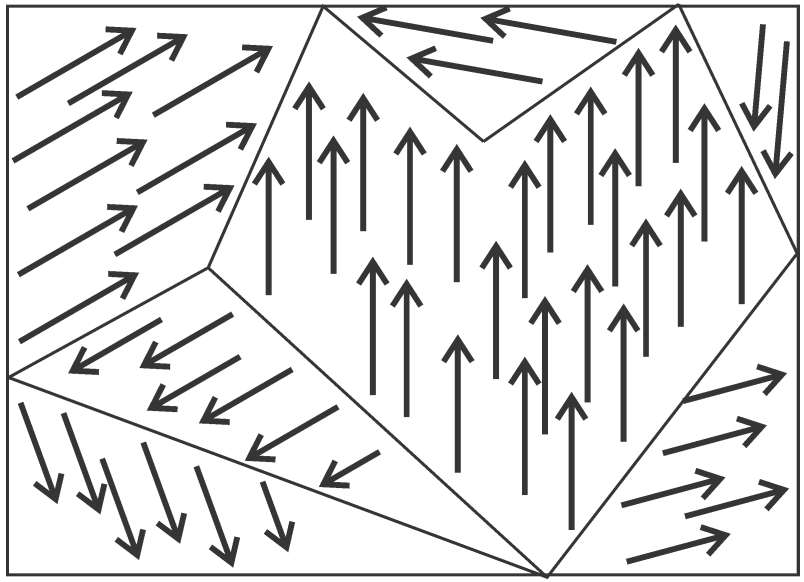
Bulk property



Blocking of magnetization in each domain is due to a macroscopic amount of spins

Relaxation time of magnetization in magnetic materials

Bulk magnet

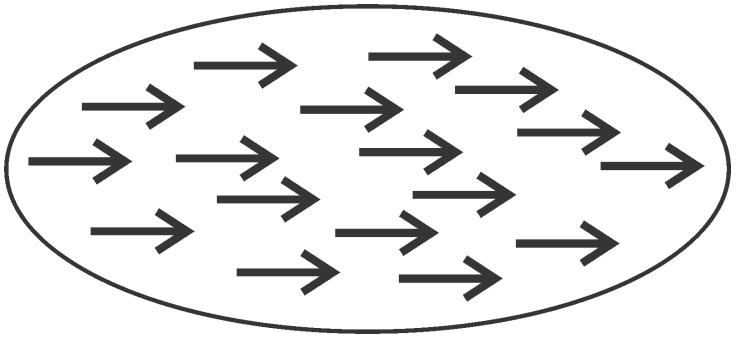


$\mu \approx 10^7$-10^8 μ_B

$\tau = \infty$

$T < T_C$

Magnetic nanoparticle

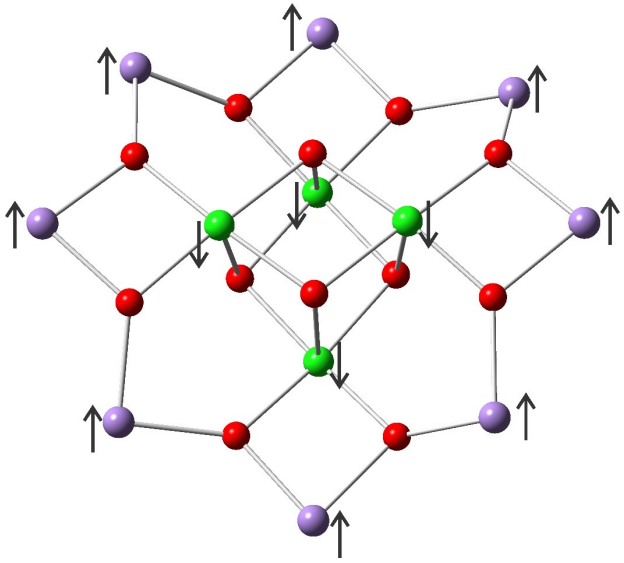


$\mu \approx 10^5$-10^6 μ_B

$\tau \rightarrow$ finite, very large

$T < T_C$

SMM

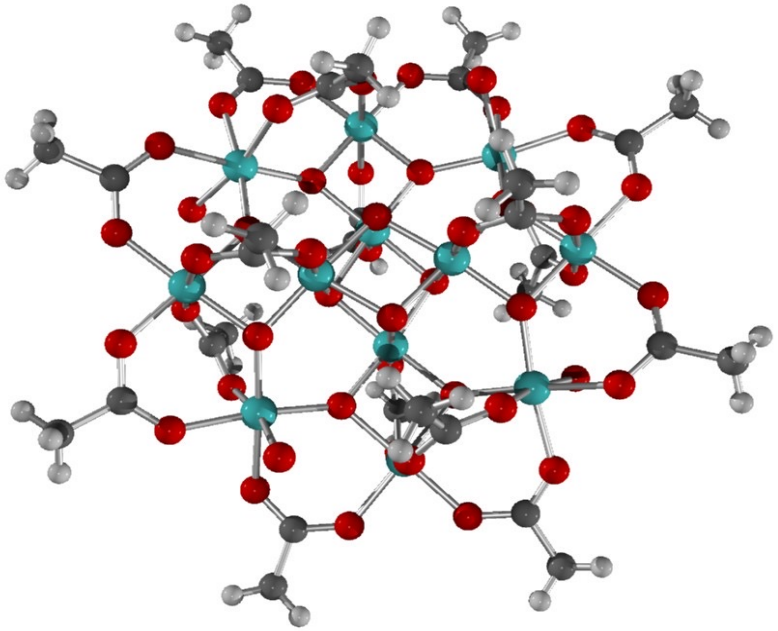


$\mu \approx$ 10-100 μ_B

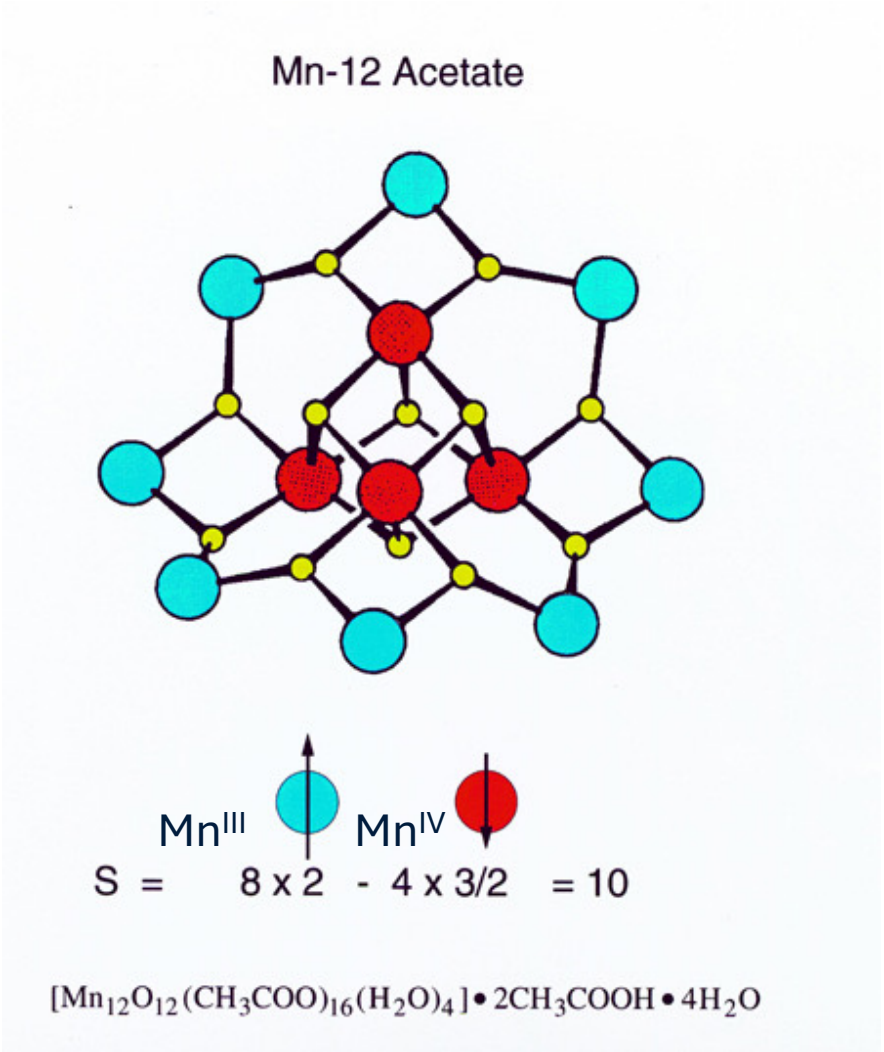
τ (Mn_{12})$\approx$1 month

(T=2.5 K)

First single molecule magnet (SMM): Mn_{12}-acetate

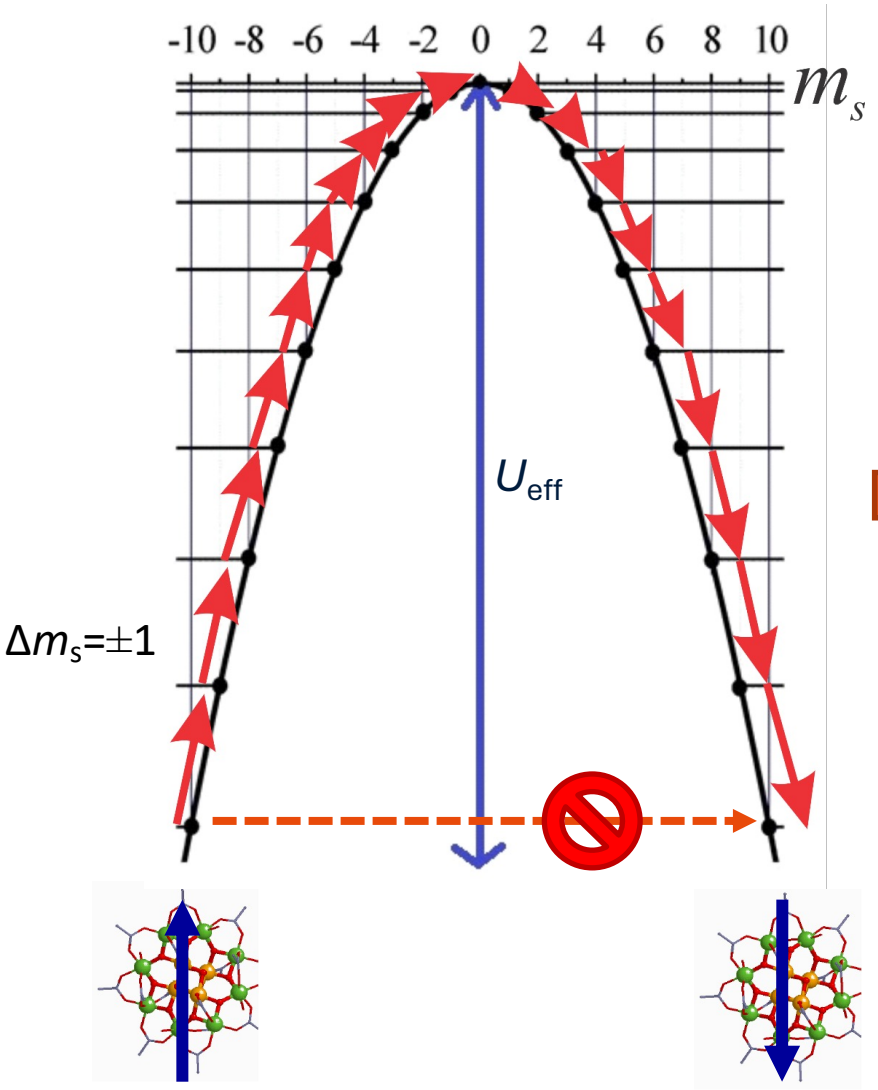


R. Sessoli et al, *Nature* **1993,** *365*, 141.



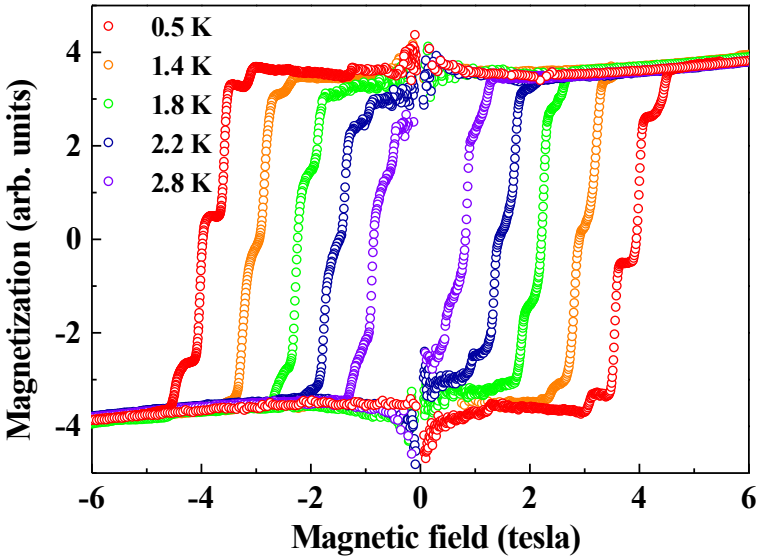
Well defined large spin (*S* = 10) at low temperatures (T < 10 K)

Mechanism of magnetization blocking



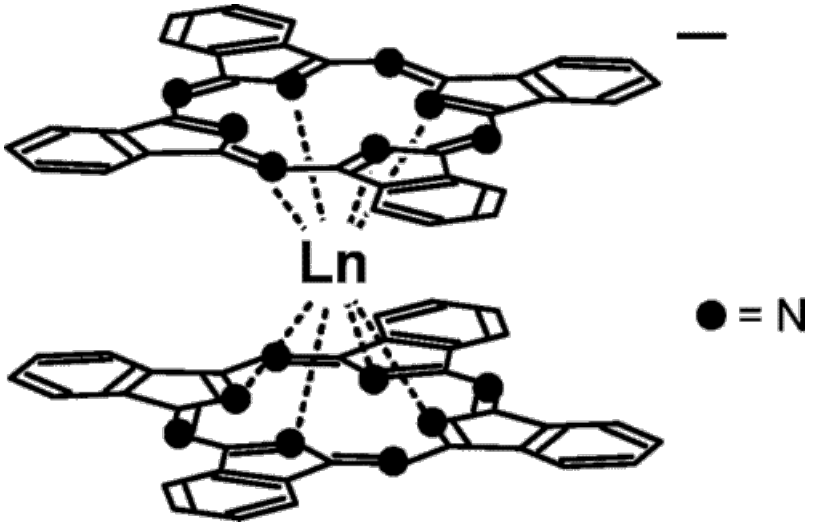
Blocking due to anisotropy

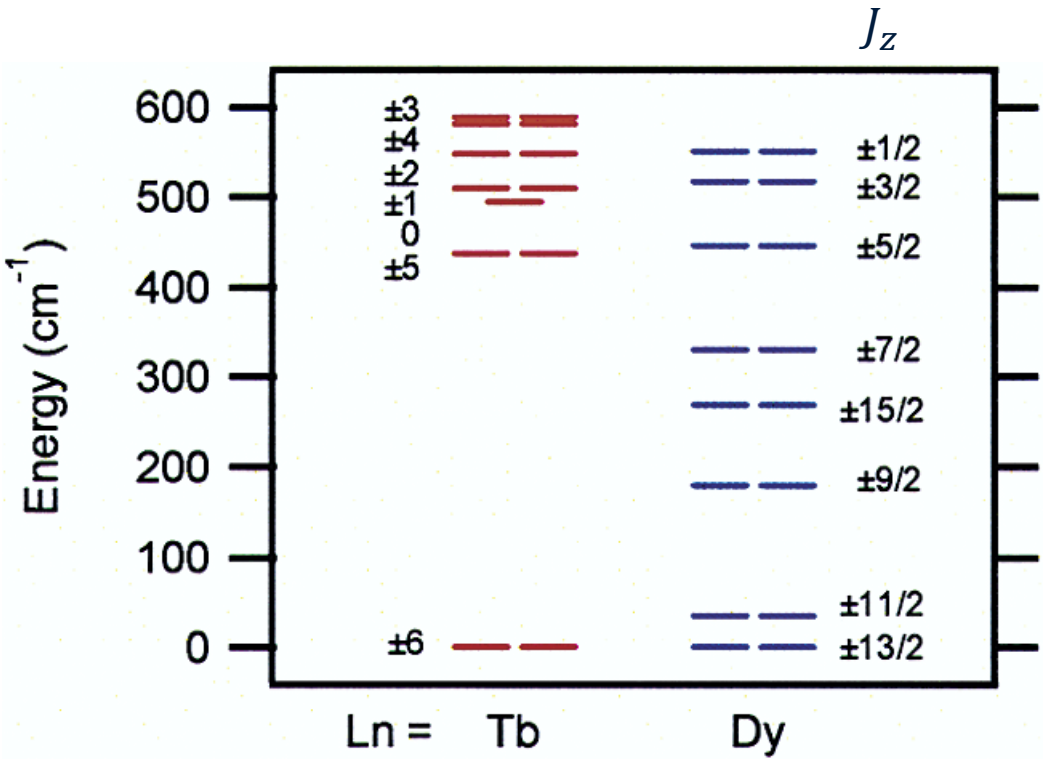
$$\hat{H}_{ZFS} = D\hat{S}_z^2 \qquad (D < 0)$$



Angew. Chem. Int. Ed. **2003**, 42, No. 3

First reported single-ion SMM





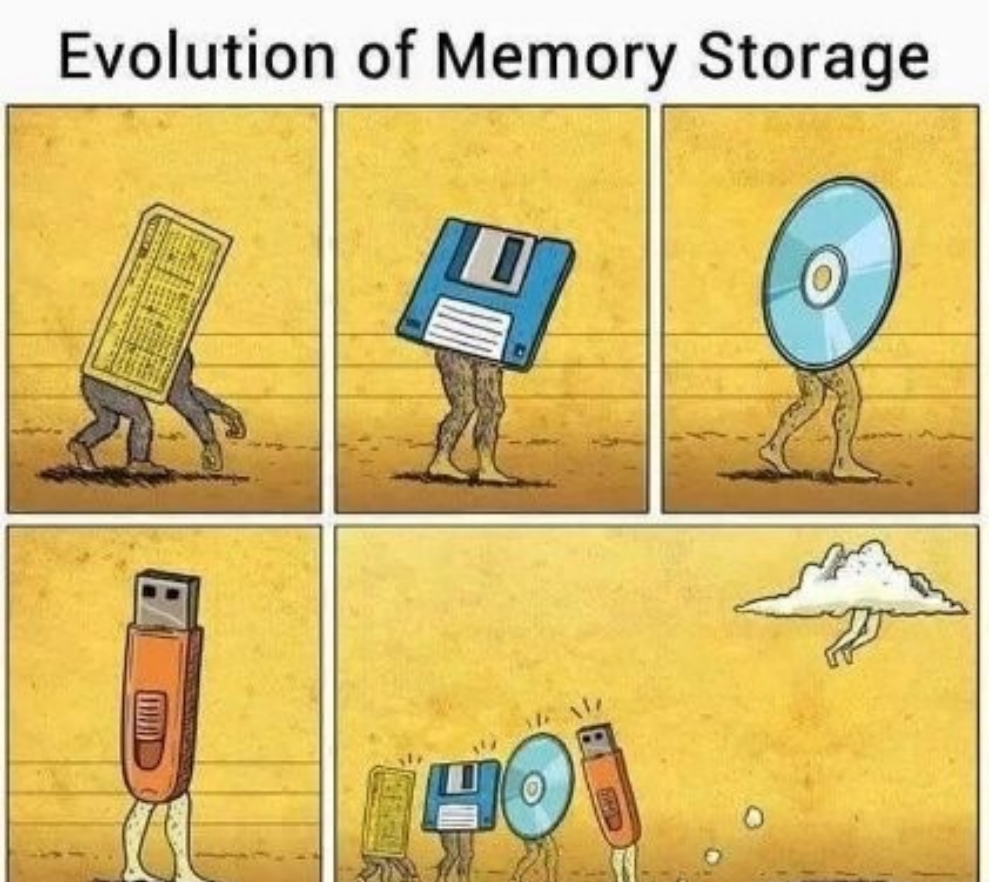
U_{eff}(Tb)=230 cm^{-1}

Blocking barrier originates from strong axial CF

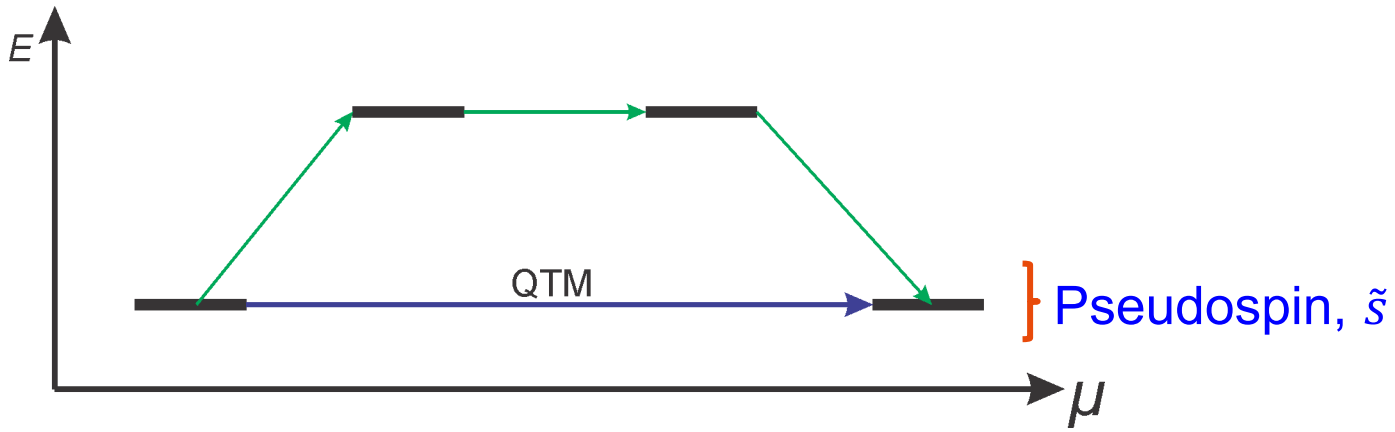
Ishikawa N. *et. al. J. Am. Chem. Soc.* **2003**, *125*, 8694

Why SMM?

- Fundamental interest
- Molecular spintronics
- Quantum computing
- High-density information storage



Strong axiality as the reason of SMM behavior



Kramers

$$\Delta_{\text{tun}} = \frac{1}{2}\mu_{\text{B}}\sqrt{g_x^2 H_x^2 + g_y^2 H_y^2}$$

Ising

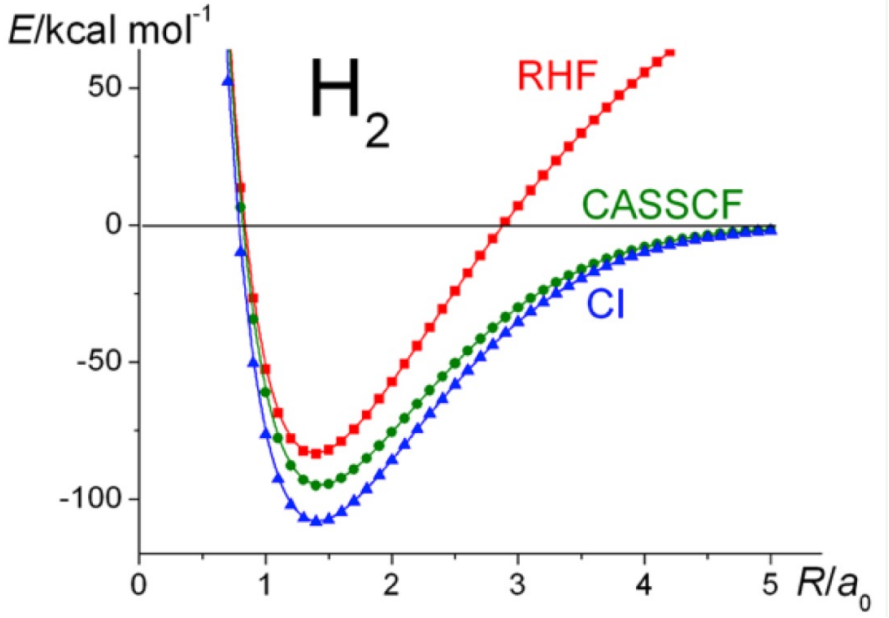
CF

Δ_{tun}(instrinsic)

Rate of quantum tunneling of magnetization:

g_x, g_y Δ_{tun} large	g_x, g_y Δ_{tun} small (axial)
QTM unquenched	QTM quenched
Not SMM	SMM

Theoretical methods

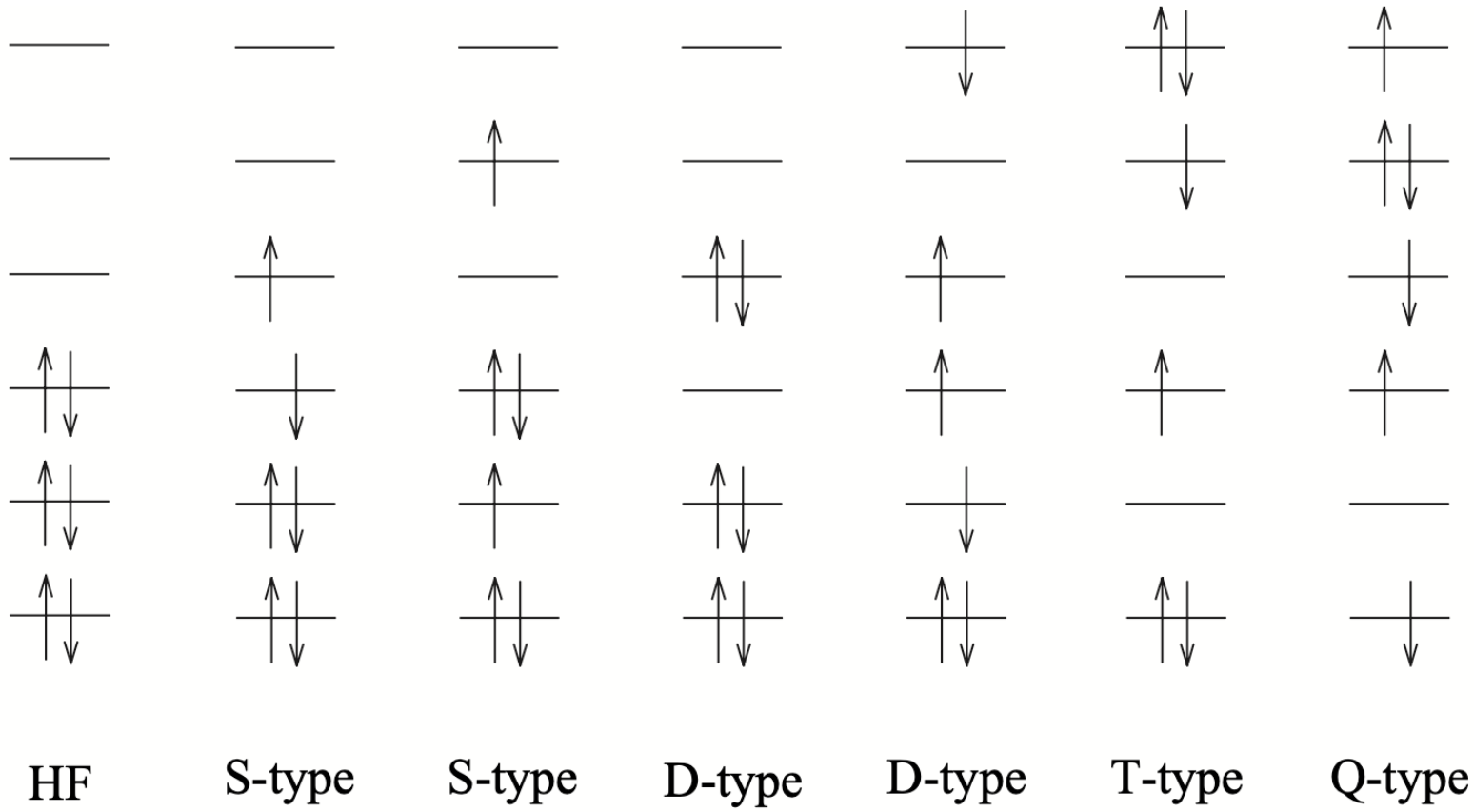


Bacskay, G.B. *Molecules* **2025**, *30*, 1154.

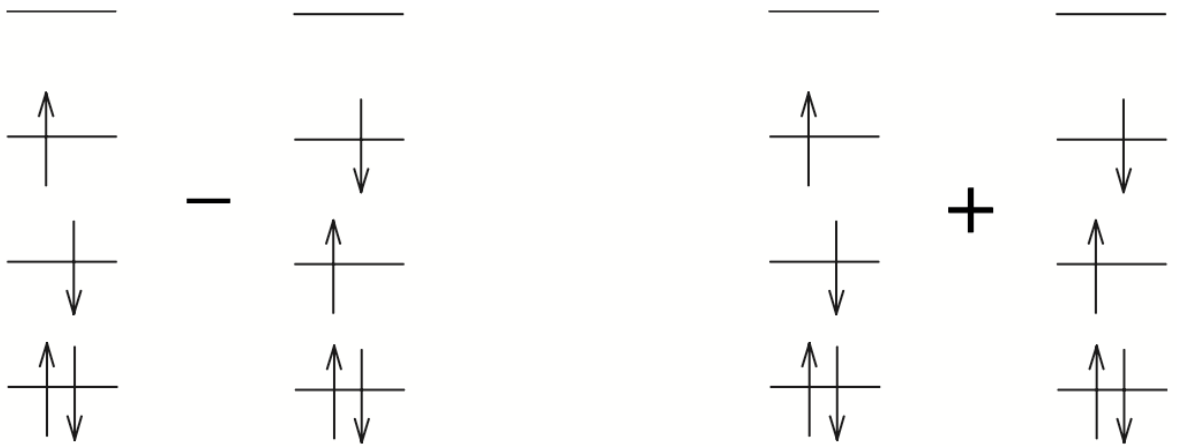
Multiconfigurational methods are needed:

$$\Psi = a_0\Phi_{\mathrm{HF}} + \sum_{i=1} a_i\Phi_i$$

Hartree-Fock (HF) and excited Slater determinants



Configurational State Functions (CSF)



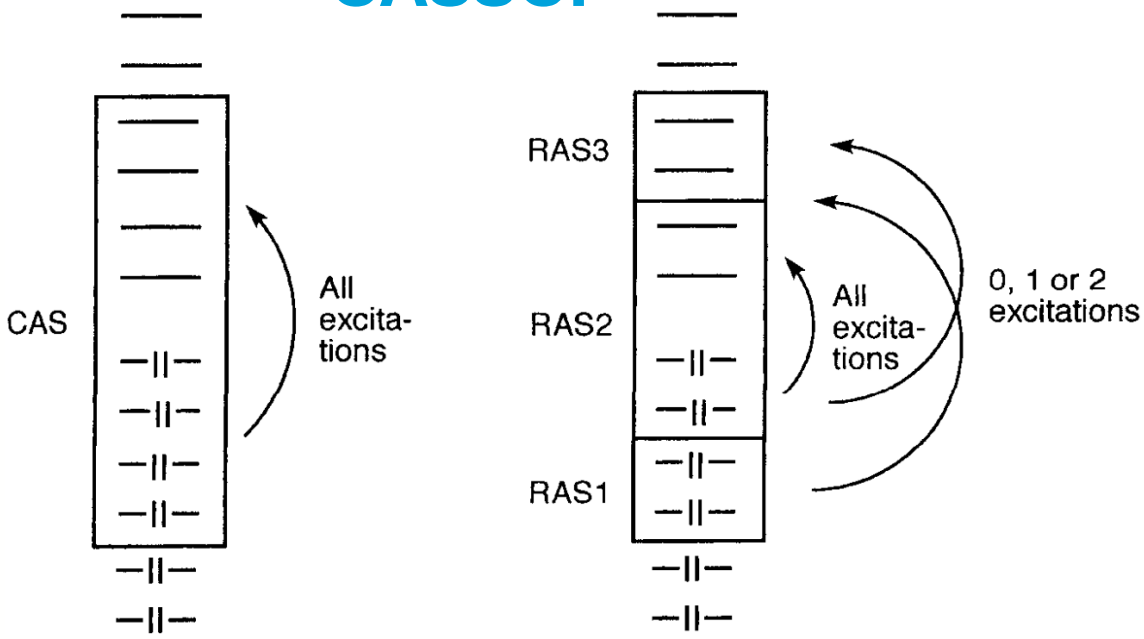
Singlet CSF

Triplet CSF

$S_z = 0$ for both determinants.

Only the linear combinations ($\pm$) become eigenfunctions of $\mathbf{S}^2$ operator.

Complete Active Space Self-Consistent Field
CASSCF



For M active orbitals, N active electrons and a total spin S (Weyl's formula)

$$\#_{\mathrm{CAS}} = \frac{2S+1}{M+1}\binom{M+1}{\frac{N}{2}-S}\binom{M+1}{\frac{N}{2}+S+1}$$

$$\binom{n}{k} = \frac{n!}{k!\,(n-k)!}$$

$\#_{\mathrm{CAS}}$ **grows very fast!**

What to include in the active space?

- Depends on the problem
- *Organic* molecules: usually all π orbitals
- *Transition* metal complexes: all d-orbitals. *Double-shell effect* for the first row of atoms.
- In complexes with very *covalent bonds*, we should include also p orbitals (more expensive though).
- *Lanthanide* complexes: usually 4f orbitals.
- *Actinide* complexes: usually 5f, 6d and 7s orbitals.

Spin-orbit-Restricted Active Space State Interaction SO-RASSI

$$\Psi_i = \sum_{rSM} c_{i,SM}^{\mathrm{RASSI}} \Psi_{rSM}^{\mathrm{CASSCF}}$$

- $c_{i,SM}^{\mathrm{RASSI}}$ are obtained via the exact diagonalization of the spin-orbit coupling matrix in RASSI.
- This approach treats SO coupling in an **exact** way, even for systems with *multi-configurational* nature.
- Second-order perturbation theory (earlier slides) is only valid for systems with weak spin-orbit coupling effects.

Ab initio calculation of the *g*-tensor for pseudospin $\tilde{S} = 1/2$: SINGLE_ANISO/Molcas

- Zeeman Hamiltonian is written in an arbitrary basis (Ψ_1, Ψ_2) and diagonalized for an arbitrary magnetic field, $\mathbf{B} = (\xi_x, \xi_y, \xi_z)B$.
- The obtained eigenvalues are:

$$E_{Zee} = -\lambda B, \qquad \lambda_{\pm} = \pm\left(\sum_{\alpha\beta} \xi_\alpha A_{\alpha\beta} \xi_\beta\right)^{1/2}$$

$$A_{\alpha\beta} = -\frac{1}{2}\left(|\mu_\alpha \mu_\beta| + |\mu_\beta \mu_\alpha|\right)$$

$$|\mu_\alpha \mu_\beta| \equiv \begin{vmatrix} (\mu_\alpha)_{11} & (\mu_\alpha)_{12} \\ (\mu_\beta)_{21} & (\mu_\beta)_{22} \end{vmatrix}$$

$$\boldsymbol{g_i} = \pm\frac{\boldsymbol{2}}{\boldsymbol{\mu_B}}\sqrt{\widetilde{\boldsymbol{A}}_{\boldsymbol{ii}}}, \qquad i = X, Y, Z$$

Maastricht University

L.F. Chibotaru, L. Ungur. *J. Chem. Phys.* **137**, 064112 (2012)

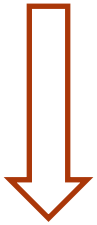
Two steps of *ab initio* description of exchange coupling constants

- Low-lying multiplets localized at magnetic sites are considered in the first place.
- Exchange interaction between the localized multiplets at different sites is treated subsequently.

Ab initio treatment of mononuclear fragments

CASSCF/SO-RASSI

Spin-orbital multiplets

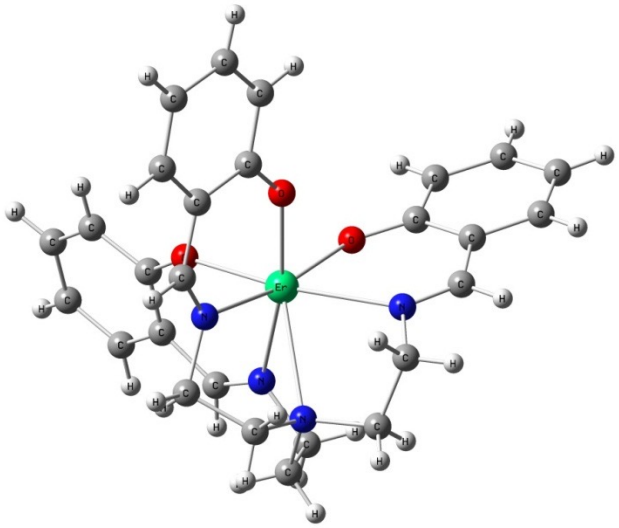


SINGLE_ANISO

- *g*-tensor
- ZFS parameters
- *X* magnetic susceptibility
- *M* magnetization
- .....

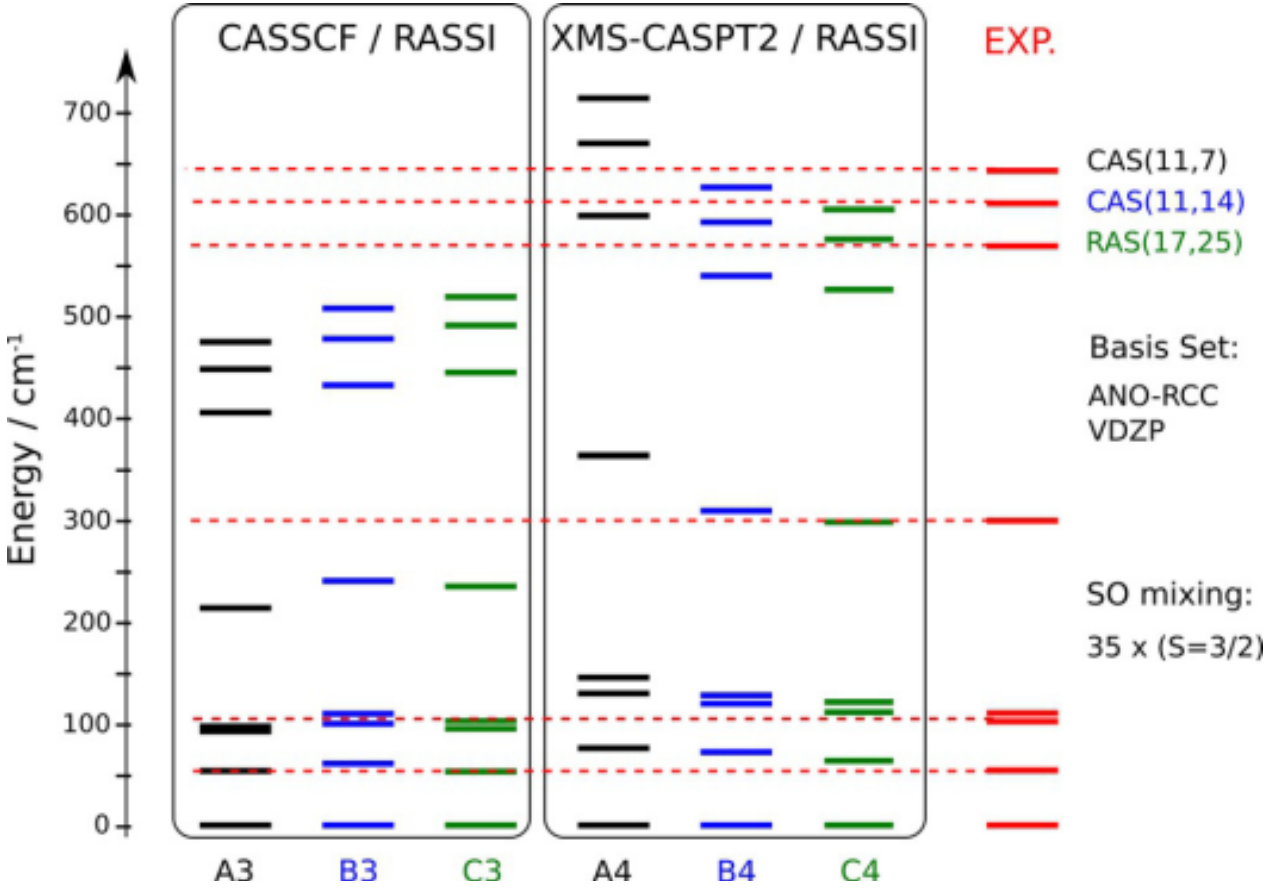
http://molcas.org/documentation/manual

Accuracy of *ab initio* calculated energies



Synthesis: B. M. Flanagan et al. *Inorg. Chem.* **2001**, 40, 5401.

Luminescence: K.S. Pedersen et al. *Chem. Sci.*, **2014**, 5, 1650.



L. Ungur, L. F. Chibotaru, *Chem. Eur. J.* **2017**, *23*, 3708.

Semi - *ab initio* treatment of magnetism in polynuclear complexes and fragments

Fragment 1 | Fragment 2 | ... | Fragment N

Lines model for the exchange interaction

$$-J_{\text{Lines}}\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j$$

J { from fitting / from BS-DFT

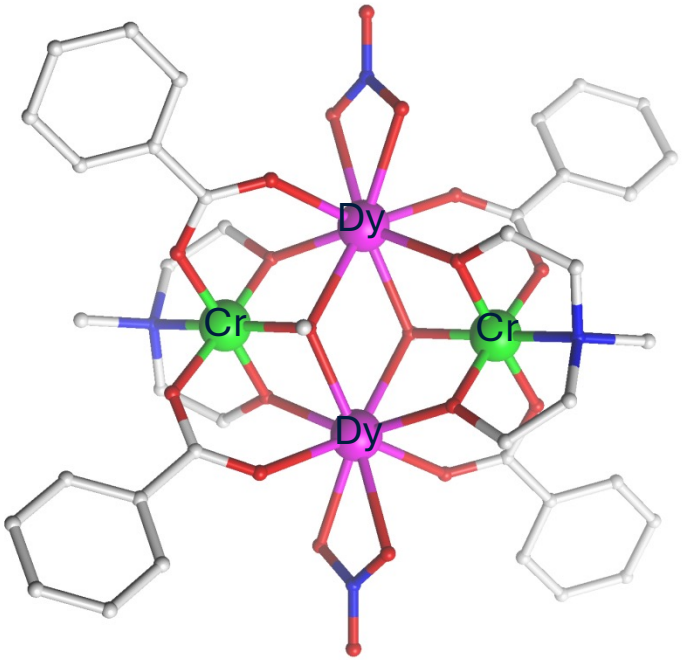
POLY_ANISO

- Exchange spectrum
- *g*-tensor
- *X* magnetic susceptibility
- *M* magnetization
- ....

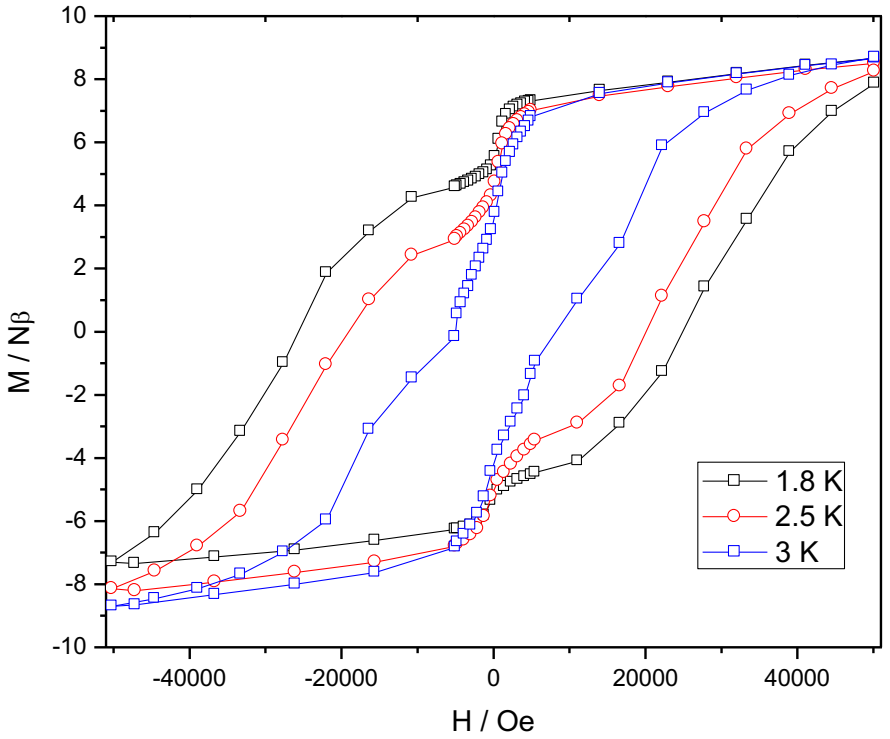
L. Ungur, and L. F. Chibotaru, Computational Modelling of the Magnetic Properties of Lanthanide Compounds. In: *Lanthanides and Actinides in Molecular Magnetism* (Wiley-VCH, 2015)


examples

I) A $\{Cr^{III}_2Dy^{III}_2\}$ Single-Molecule Magnet: Enhancing the Blocking Temperature through 3*d* Magnetic Exchange



U_{eff}=54 cm^{-1}

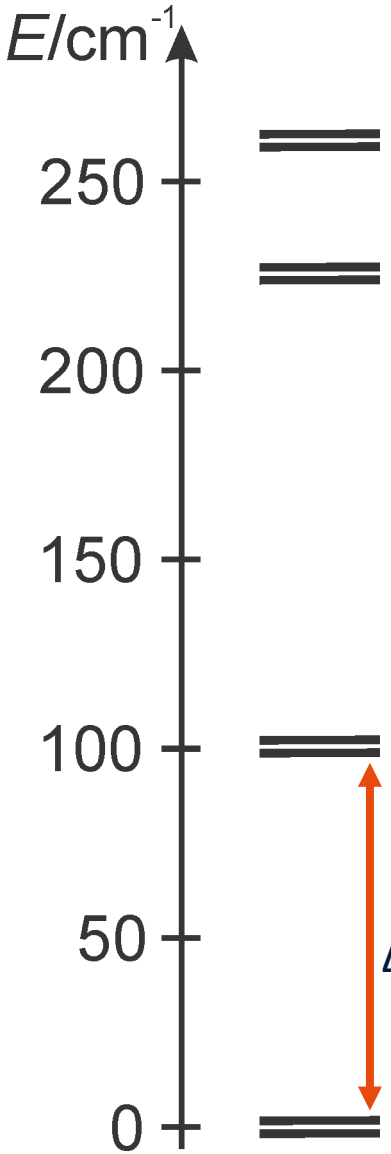


Why Cr_2Dy_2 ⟹ Hysteresis **?**

Co_2Dy_2 ⟹ No hysteresis

S.K. Langley, D.P. Wielechowski, V. Vieru et al. *Angew. Chem. Int. Ed.* **2013**, 52, 12014.

Dy fragment calculations



KD		E, cm^{-1}	g-factor
1	g_x	0	0.002
	g_y		0.003
	g_z		19.9
2	g_x	101	0.1
	g_y		0.1
	g_z		17.2

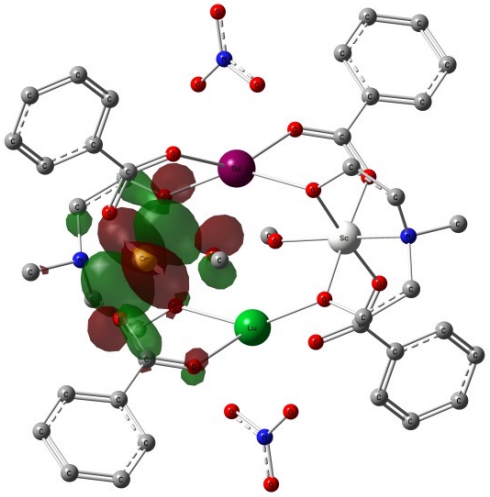
axial

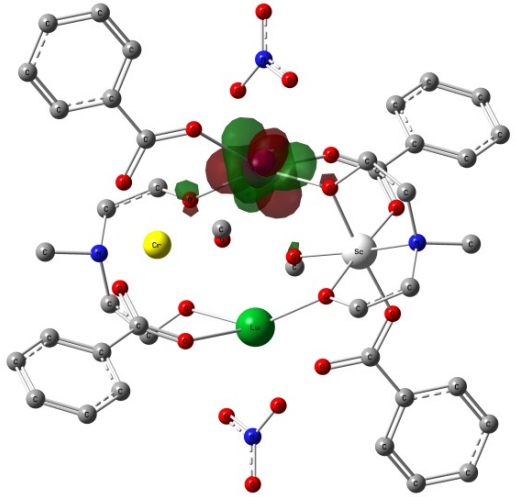
Experimental blocking barrier is not of CF type (U_{eff}=54 cm^{-1})

Exchange Interaction

$$\widehat{H} = -\left(-J_{dip}^{Dy1-Dy1'} + J_{exch}^{Dy1-Dy1'}\right)\tilde{s}_{Dy1,Z}\tilde{s}_{Dy1',Z} - \left(-J_{dip}^{Cr1-Cr1'} + J_{exch}^{Cr1-Cr1'}\right)\vec{S}_{Cr1}.\vec{S}_{Cr1'} -$$
$$3J_{dip}^{Cr-Cr'}S_{Cr1,Z}S_{Cr1',Z}$$
$$-J_{dip}^{Dy1-Cr1}\left[(1-3\cos^2\theta)\tilde{s}_{Dy1,Z}S_{Cr1,Z} - 3\sin\theta\cos\theta\,\tilde{s}_{Dy1,Z}S_{Cr1,Y}\right] - J_{dip}^{Dy1'-Cr1}\left[(1-\right.$$
$$\left.3\cos^2\theta)\tilde{s}_{Dy1',Z}S_{Cr1,Z} + 3\sin\theta\cos\theta\,\tilde{s}_{Dy1',Z}S_{Cr1,Y}\right] - J_{dip}^{Dy1-Cr1'}\left[(1-3\cos^2\theta)\tilde{s}_{Dy1,Z}S_{Cr1',Z} -\right.$$
$$\left.3\sin\theta\cos\theta\,\tilde{s}_{Dy1,Z}S_{Cr1',Y}\right] - J_{dip}^{Dy1'-Cr1'}\left[(1-3\cos^2\theta)\tilde{s}_{Dy1',Z}S_{Cr1',Z} + 3\sin\theta\cos\theta\,\tilde{s}_{Dy1',Z}S_{Cr1',Y}\right] -$$
$$J_{exch}^{Dy1-Cr1}\tilde{s}_{Dy1,Z}S_{Cr1,Z} - J_{exch}^{Dy1'-Cr1}\tilde{s}_{Dy1',Z}S_{Cr1,Z} - J_{exch}^{Dy1-Cr1'}\tilde{s}_{Dy1,Z}S_{Cr1',Z} - J_{exch}^{Dy1'-Cr1'}\tilde{s}_{Dy1',Z}S_{Cr1',Z}$$

$J_{dip}^{Dy1-Dy1'} = \frac{\mu_B^2 g_{Dy,Z}^2}{R_{Dy1-Dy1'}^3} = 2.5$; $J_{dip}^{Cr1-Cr1'} = \frac{\mu_B^2 g_{Cr}^2}{R_{Cr1-Cr1'}^3} = 0.34$; $J_{dip}^{Dy_i-Cr_j} = \frac{\mu_B^2 g_{Dy,Z} g_{Cr}}{R_{Dy_i-Cr_j}^3} = 5.2$ cm-1





Exctracted from BS-DFT:

J (Dy1-Dy1')=1.00 cm^{-1}

J (Cr1-Cr1')=0.12 cm^{-1}

J (Dy1-Cr1)=-26.0 cm^{-1}

J (Dy1-Cr1'=-32.5 cm^{-1}

Strong overlap ⟹ Strong kinetic AF coupling

Blocking of Magnetization Barrier

Ising Hamiltonian for low-lying states:

$$\hat{H} = -J_{Dy1-Dy1'}\tilde{s}_{Dy1,Z}\tilde{s}_{Dy1',Z} - J_{Dy1-Cr1}\left(\tilde{s}_{Dy1,Z}S_{Cr1,Z} + \tilde{s}_{Dy1',Z}S_{Cr1',Z}\right) - J_{Dy1-Cr1'}\left(\tilde{s}_{Dy1,Z}S_{Cr1',Z} + \tilde{s}_{Dy1',Z}S_{Cr1,Z}\right) - J_{Cr1,Z-Cr1',Z}S_{Cr1,Z}S_{Cr1',Z}$$

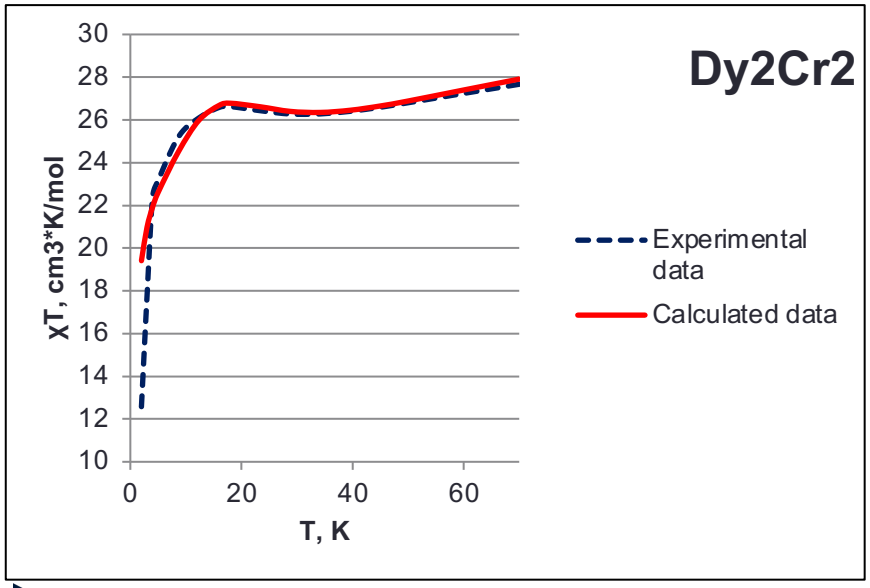
Fitted values:

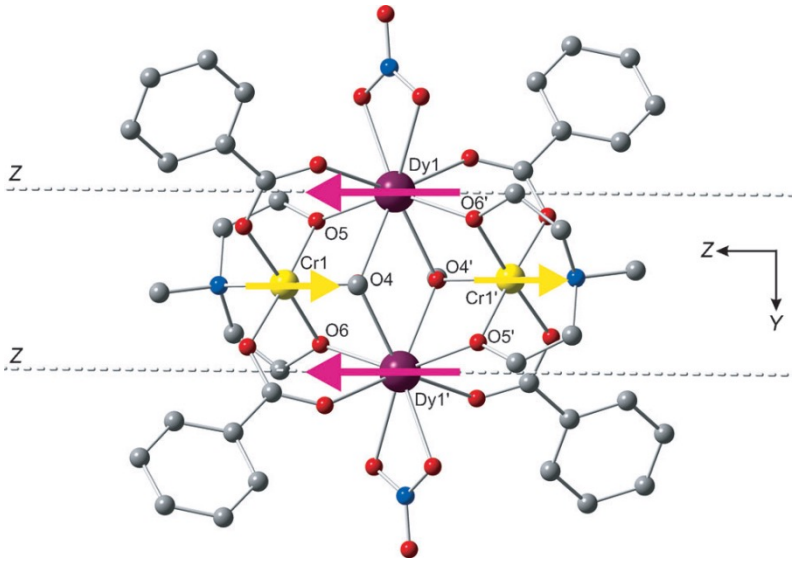
J (Dy1-Dy1')=1.00 cm^{-1}

J (Cr1-Cr1')=0.10 cm^{-1}

J (Dy1-Cr1)=-20.5 cm^{-1}

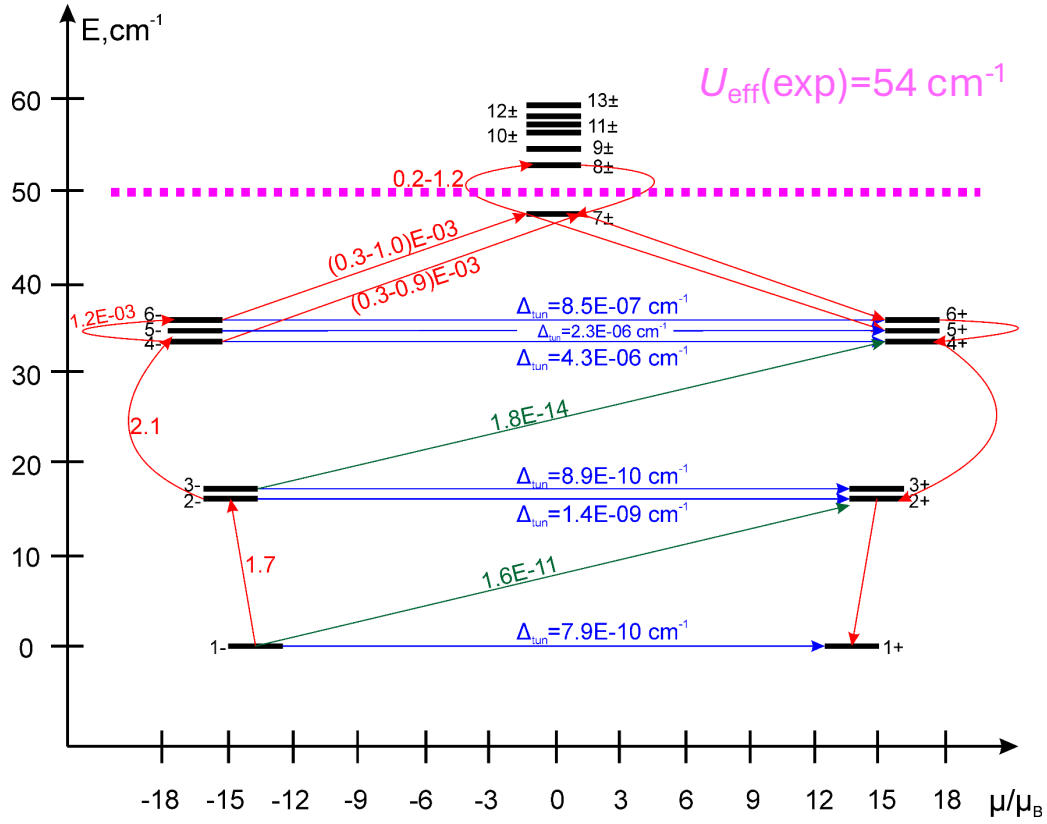
J (Dy1-Cr1'=-17.0 cm^{-1}





Low-lying exchange spectrum and relaxation path

Cr_2Dy_2



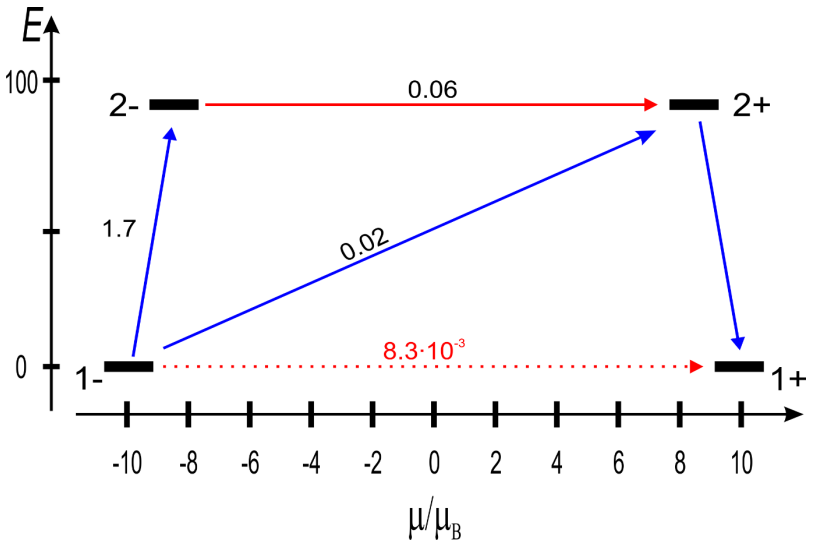
U_{eff}(exp)=54 cm^{-1}

Multi-level exchange-type barrier

⇩

Magnetic hysteresis

Co_2Dy_2



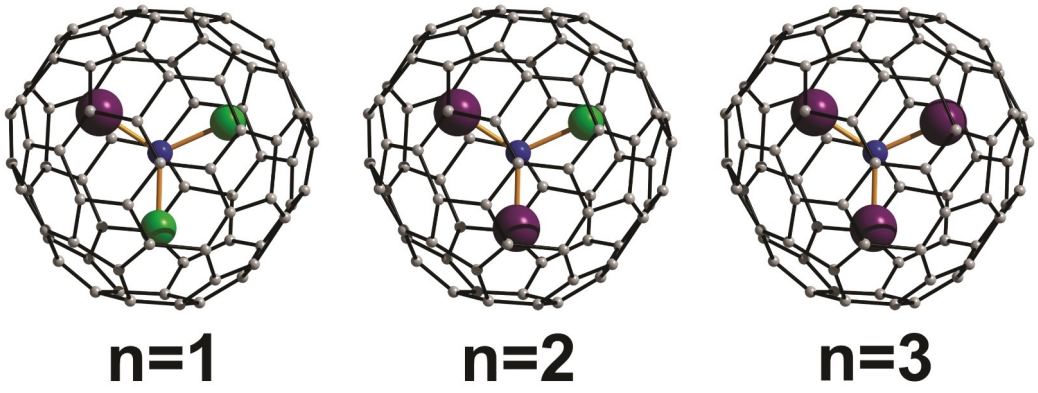
Barrier originates from <u>one</u> excited state on individual Dy center

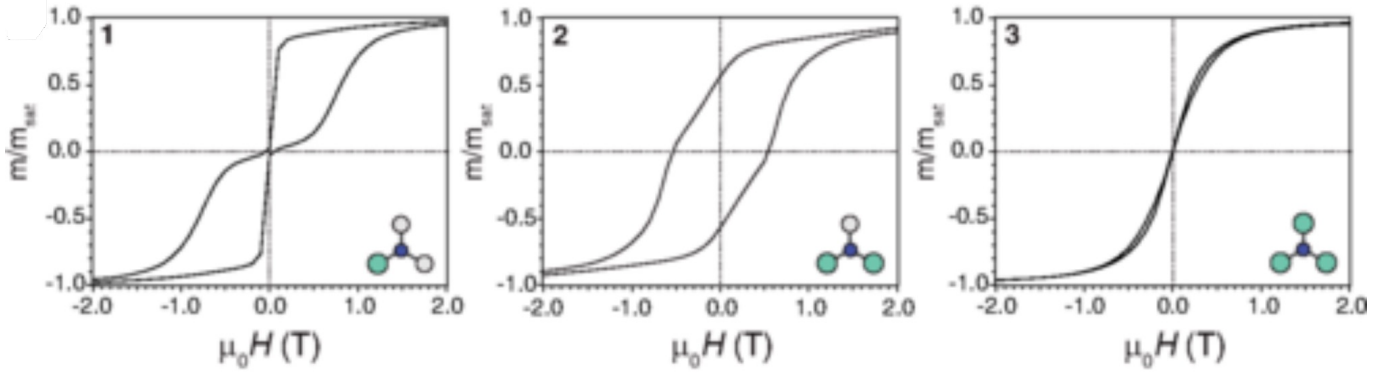
⇩

Lack of magnetic hysteresis

S.K. Langley et al. *Inorg. Chem*. **2012**, 51, 11873

II) Key Role of Frustration in Suppression of Magnetization Blocking in $Dy_nSc_{(3-n)}N@C_{80}$

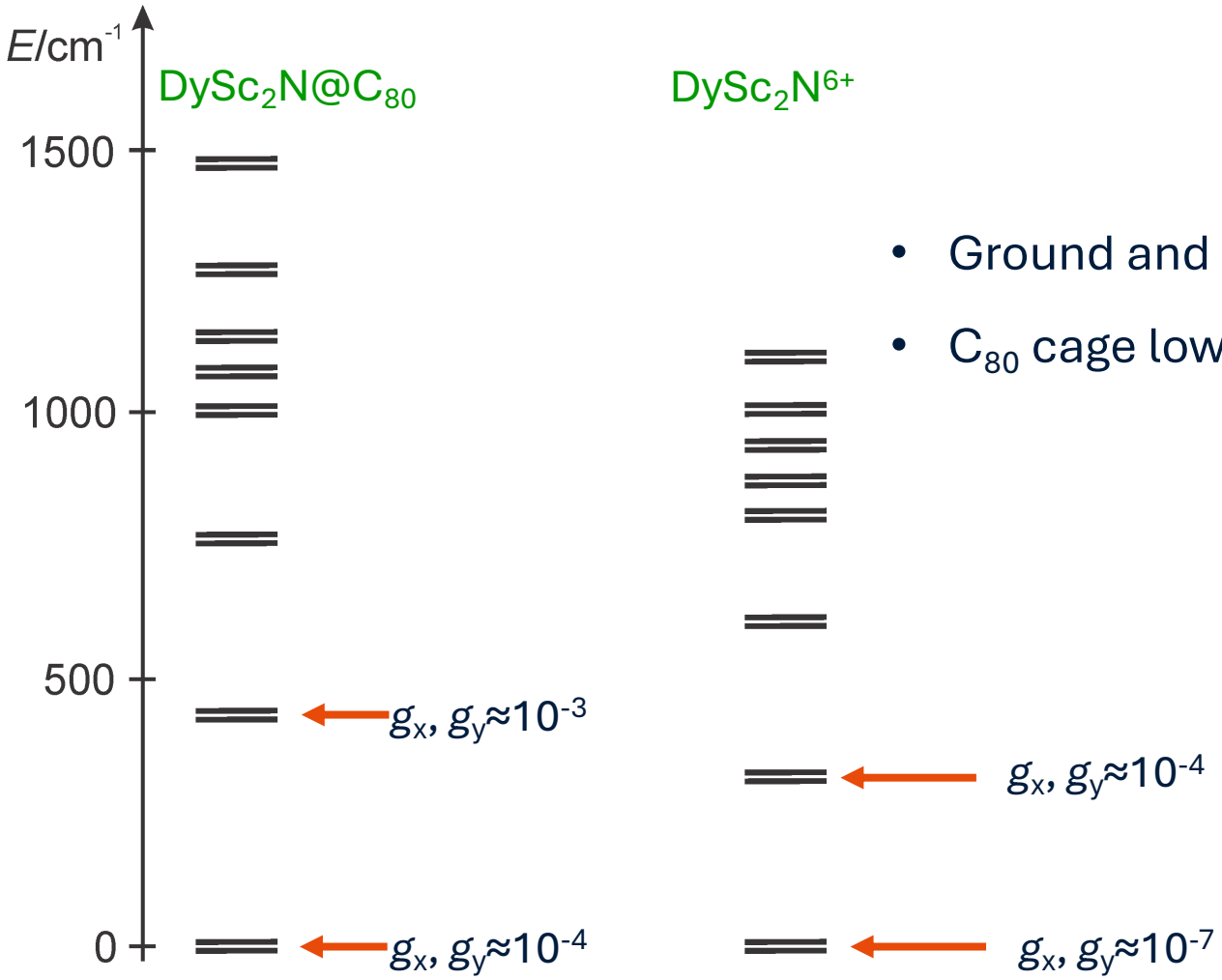




Why is n=3 the worst SMM?

V. Vieru *et al. J. Phys. Chem. Lett.*, **2013**, *4* (21), 3565.

Calculated multiplet spectrum of $DySc_2N@C_{80}$



- Ground and 1st excited KD are very axial
- C_{80} cage lowers the axiality

Magnetic interactions

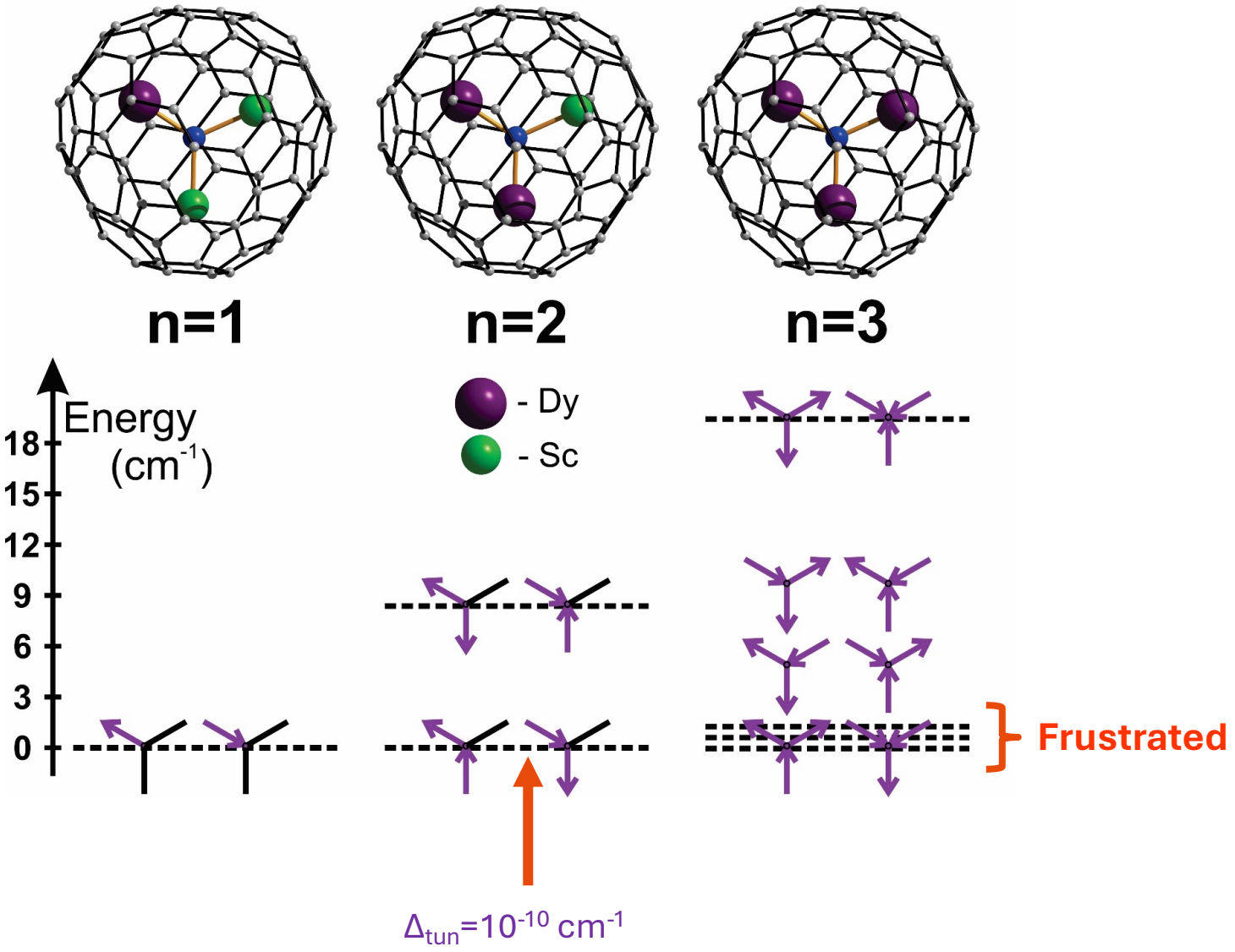
$$\hat{H} = \sum_{<ij>} (J_{dip}^{ij} + J_{\text{Ising}}^{ij}) \tilde{S}_{Zi} \tilde{S}_{Zj}$$

Strong axiality ⟹ Ising model

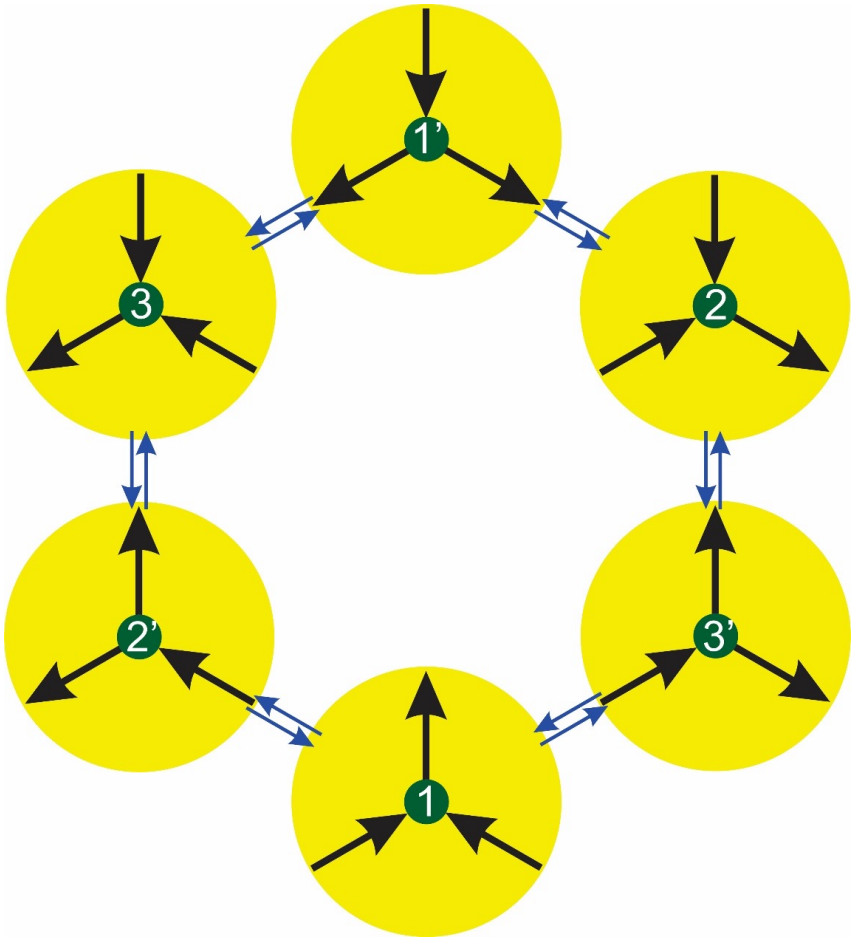
Interaction		$Dy_2ScN@C_{80}$	$Dy_3N@C_{80}$
J_{dip} (cm^{-1})	Dy1-Dy2	6.4	6.7
	Dy1-Dy3	---	6.8
	Dy2-Dy3	---	7.0
J_{exch} (cm^{-1})	Dy1-Dy2	10.8	12.2
	Dy1-Dy3	---	12.1
	Dy2-Dy3	---	14.0

dipolar - exact
exchange – BS DFT

Low-lying exchange spectrum



Connection of the lowest six magnetic states in $Dy_3N@C_{80}$



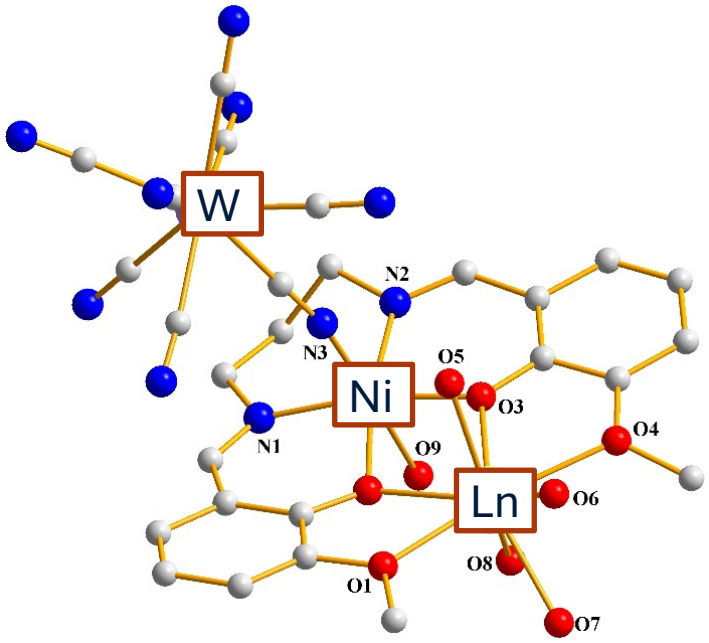
States are connected via single-momentum flips

Good SMM

Avoid frustration

Magnetic Properties and Theoretical Investigation of a Series of Ni^{II}-Ln^{III}-W^{V}

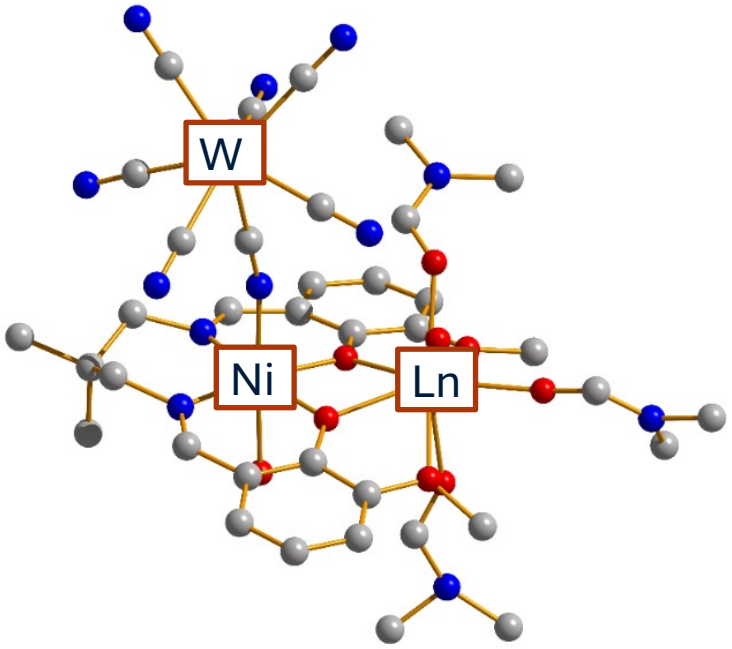
I series



Ln=Gd,Tb,Dy

None SMM

II series



Ln=Gd,Tb,Dy,Ho,Er

Tb complex SMM

Why is only TbNiW SMM?

V. Vieru et al. *Inorg. Chem.* **2016**, *55*, 12158.

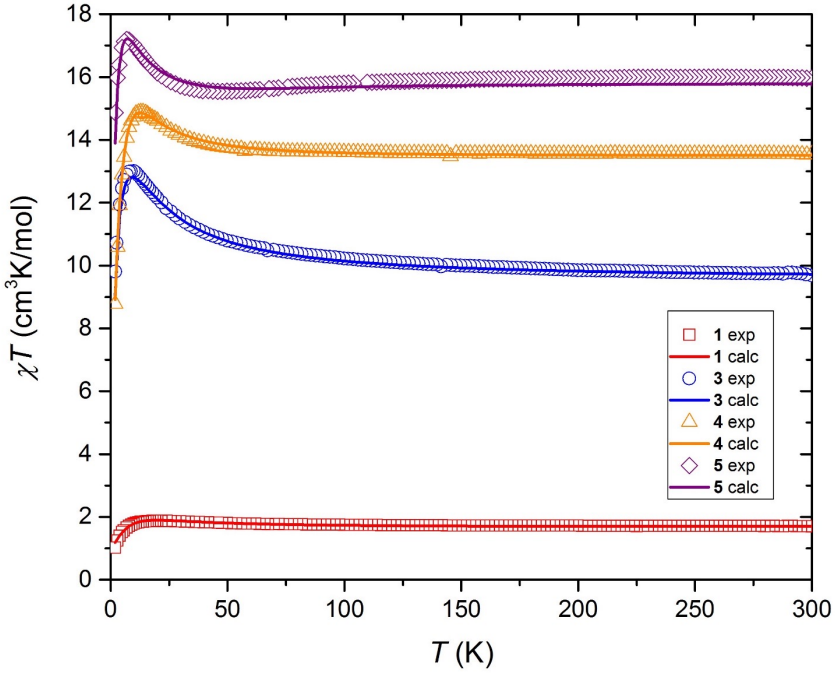
Low-lying multiplets on Ln sites of NiLnW

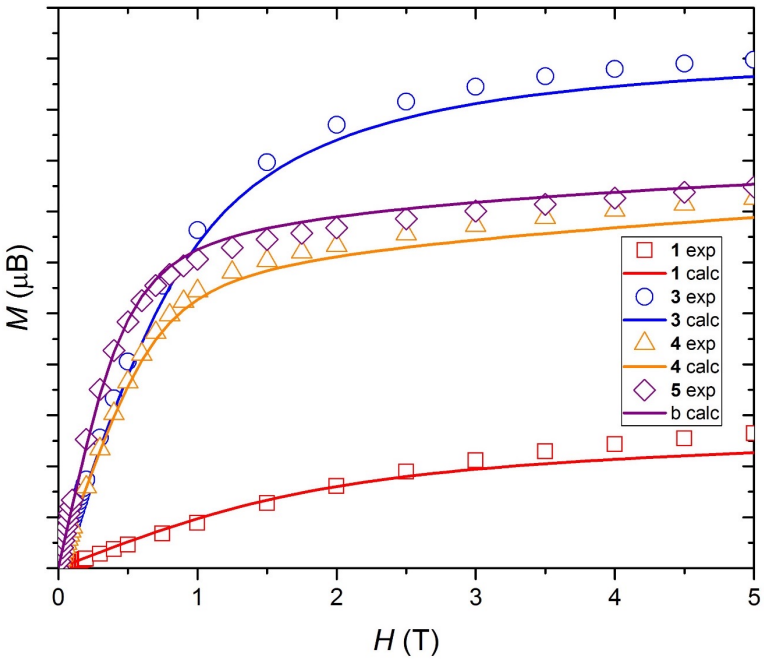
Complex	NiDyW	NiTbW a	NiTbW b
Center	Dy center*	Tb center	Tb center
CF levels, cm^{-1}	0 119 174 214 …	0 1.0 (large) 75 84 …	0 0.01 (small) 199 200 …
g-factors in the ground multiplet			
g_x g_y g_z	large: 0.02 large: 0.03 19.8	0 0 17.5	0 0 17.9
	Not SMM		SMM

*Kramers doublets

Calculation of magnetic properties

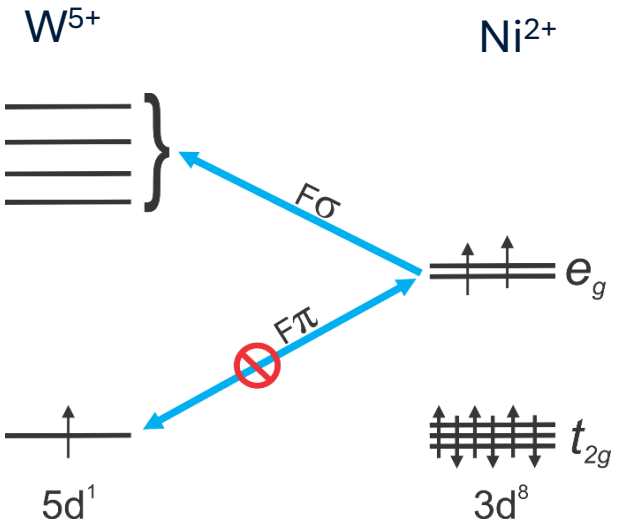
$$\hat{H}_{\text{Lines}} = -J_{Ni-Ln}\hat{\mathbf{S}}_{Ni}\cdot\hat{\mathbf{S}}_{Ln} - J_{Ni-W}\hat{\mathbf{S}}_{Ni}\cdot\hat{\mathbf{S}}_{W}$$





Pair/Compound	NiYW (1)	NiGdW (3)	NiTbW (4)	NiDyW (5)
J_{Lines}(Ni-Ln), cm^{-1}	-	3.46	3.0	2.5
J_{Lines}**(Ni-W)**, cm^{-1}	**16.08**	**21.6**	**22.0**	**24.0**

Origin of strong ferromagnetic coupling in Ni-W pair



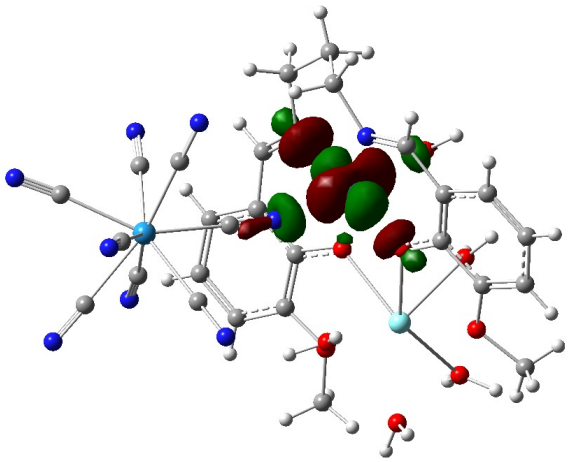
Goodenough + direct exchange

⇩

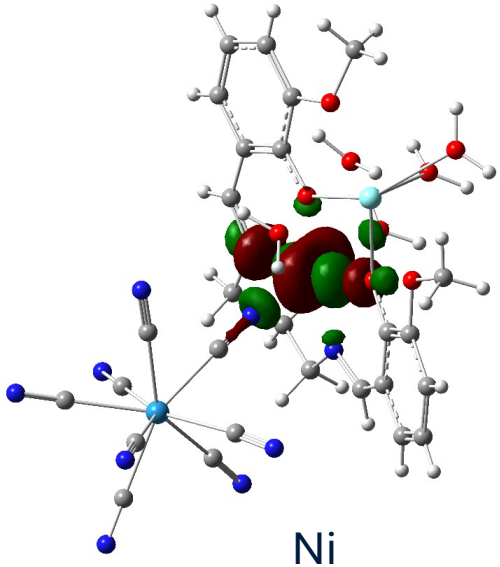
Strong ferromagnetism

Kinetic AF mechanism is suppressed

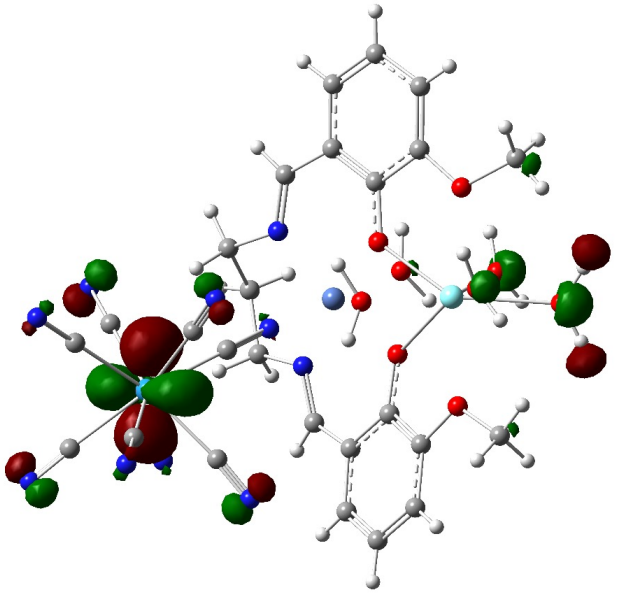
(L.F. Chibotaru *et. al.*, ACIE **2001**,40,4429)



Ni



Ni



W

Axiality of the lowest exchange doublets in NiLnW

Ising doublet:

Complex	NiGdW a	NiGdW b	NiDyW a	NiDyW b	NiErW
Δ_{tun}, cm^{-1}	0.004	0.009	0.002	0.009	0.06

large ⟹ Not SMM

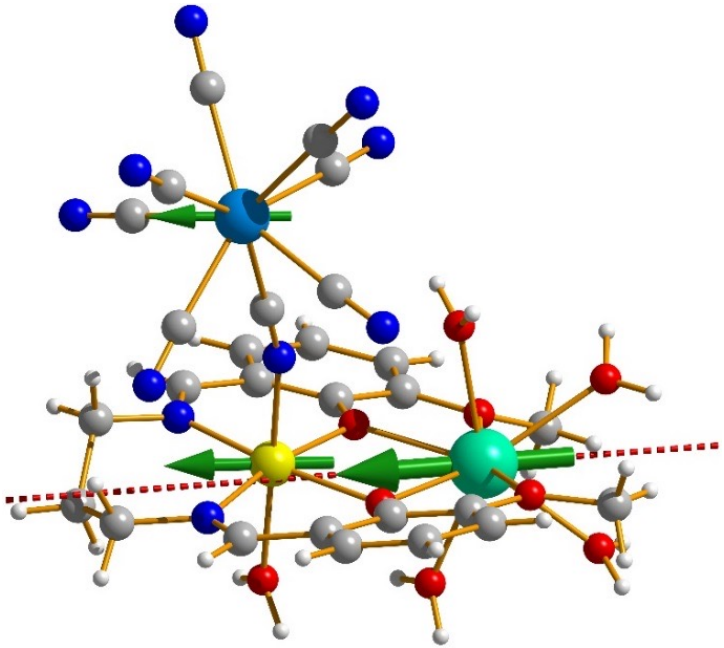
Kramers doublet:

g-factor	NiTbW	NiTbW **a**	NiTbW **b**	NiHoW
g_x	0.2	0.03	0.002	1.8
g_y	0.3	0.03	0.003	3.5
g_z	23.5	23.2	23.5	11.2

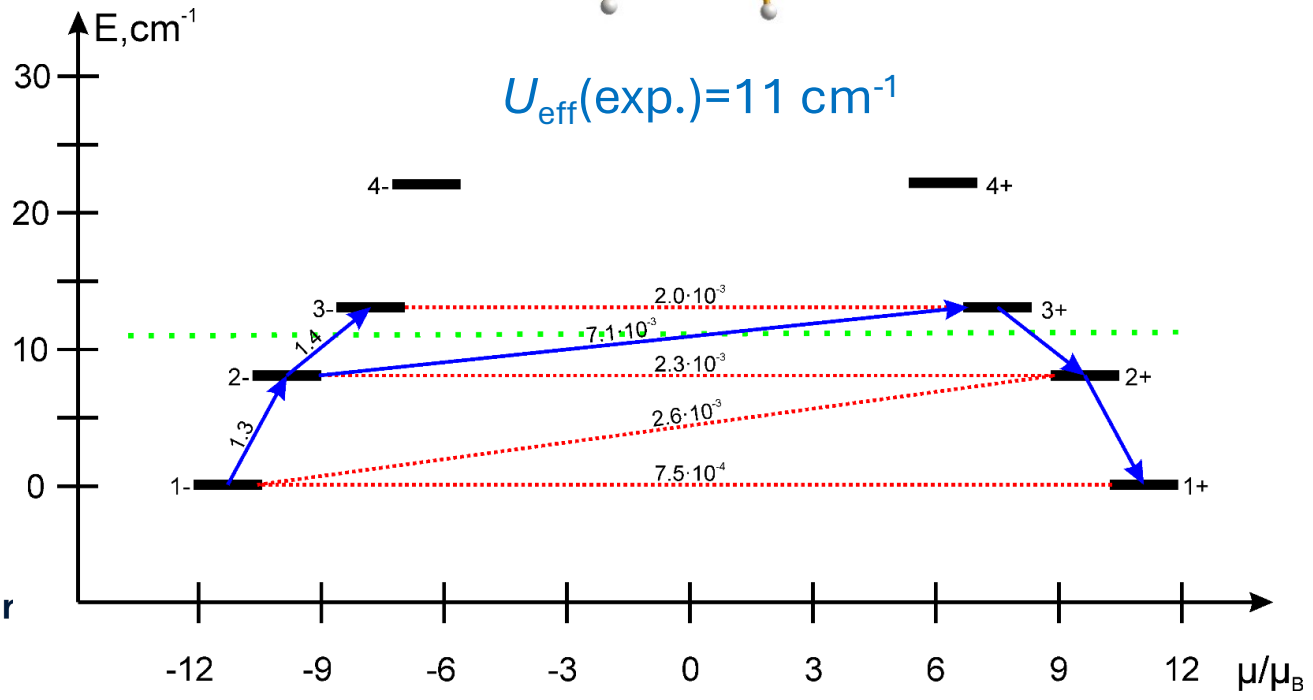
small ⟹ SMM

Ab initio calculations explain why only one complex is SMM

Magnetization blocking in the NiTbW complex



U_{eff}(exp.)=11 cm^{-1}



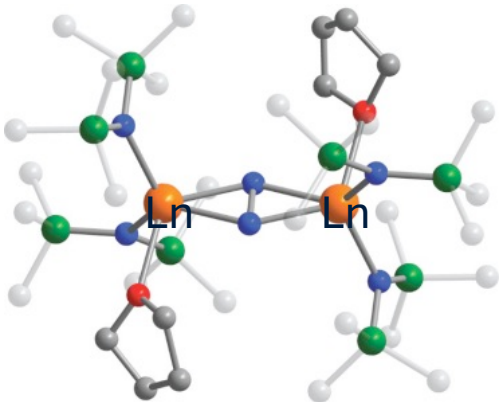
Prospects for Enhancing the SMM Performance of Polynuclear Complexes

g-factors of the ground exchange doublet of NiTbW complex under different anisotropy at Ni(II) site.

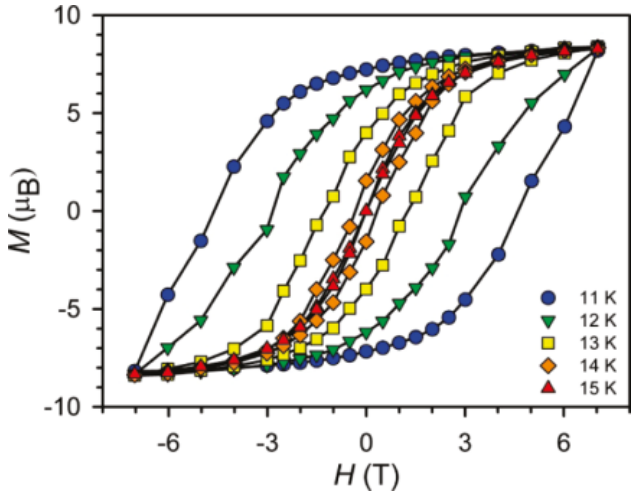
Ni-isotrop	D(Ni) ∥ Z(Tb)	D(Ni): Z arbitrary	-D(Ni) ∥ Z(Tb)	Unmodified
2.5×10^{-5}	0.0033	0.0046	6.0×10^{-5}	0.0020
2.5×10^{-5}	0.0041	0.0053	6.1×10^{-5}	0.0025
23.7	22.4	22.0	23.7	23.5

⇒ Coupling of weakly anisotropic magnetic units to strongly anisotropic ones (lanthanide ions) will result in a drastic enhancement of SMM properties.

Giant exchange interaction in mixed lanthanides



Ln^{3+}-N_2^{3-}-Ln^{3+},
Ln=Gd, Tb, Dy, Ho, Er



Strongest magnetic coupling

Tb complex shows hysteresis up to 14 K

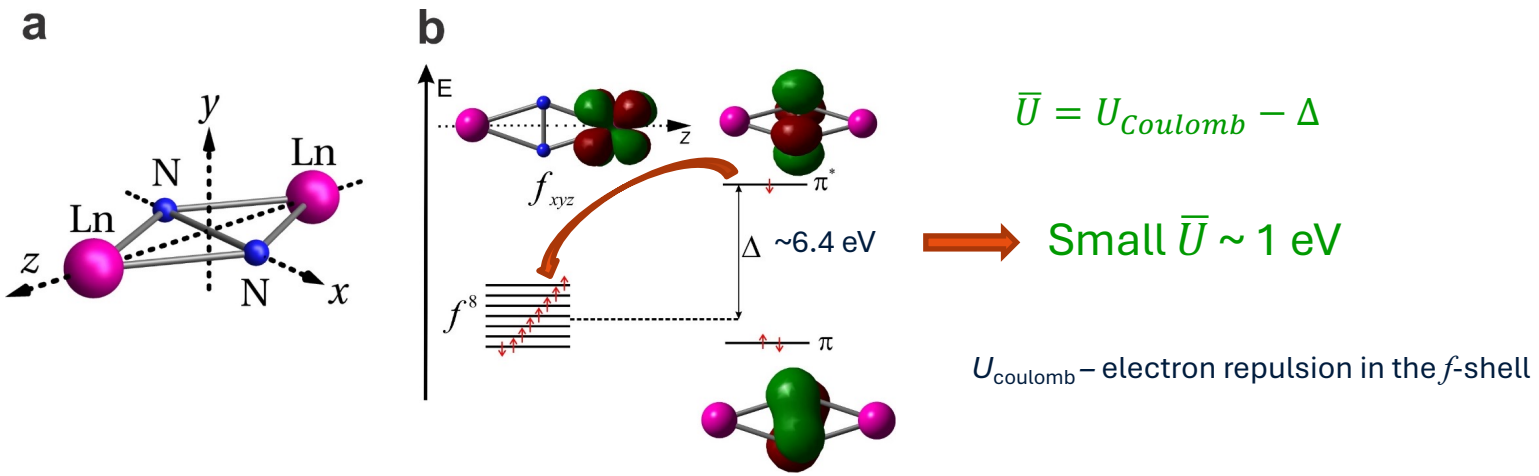
Exp.:J. Rinehart, *et al*., *Nat. Chem.* **3**, 538 (2011), *J. Am. Chem. Soc*. **133**, 14236 (2011).

Origin of unusual exchange interaction and magnetization blocking?

V. Vieru, N. Iwahara, L. Ungur, L. F. Chibotaru. *Scientific Reports*, **6**, 24046 (2016).

Exchange mechanism

- BS-DFT calculated J for the Gd compound (-21.4 cm^{-1}) ~ exp. J (-27 cm^{-1})
- Transfer parameters t and the averaged electron promotion energy $\overline{U}$ extracted from DFT



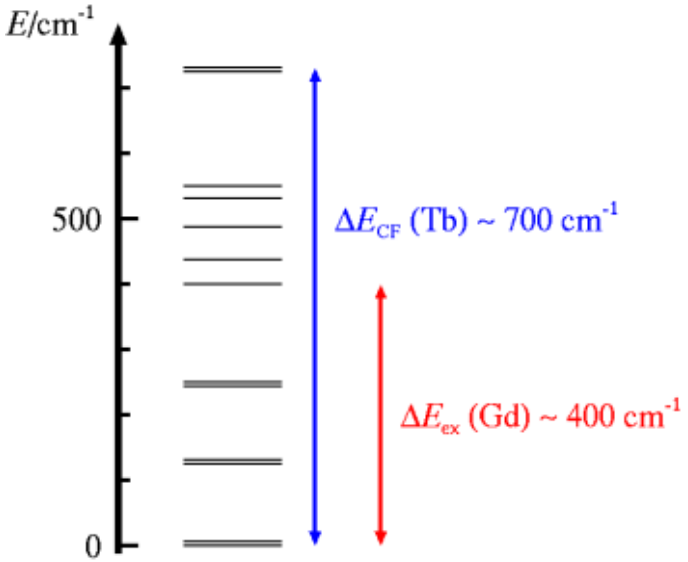
$\overline{U} = U_{Coulomb} - \Delta$

Small $\overline{U}$ ~ 1 eV

$U_{coulomb}$ – electron repulsion in the f-shell

Large Δ, small $\overline{U}$ ⇒ **Strong kinetic exchange** $J \sim -t^2/\overline{U}$

Crystal-field splitting on Ln sites



For Ln=Tb, Dy, Ho, Er:

- strong kinetic exchange interaction
- strong magnetic anisotropy

$$\Delta E_{CF} \approx \Delta E_{ex}$$

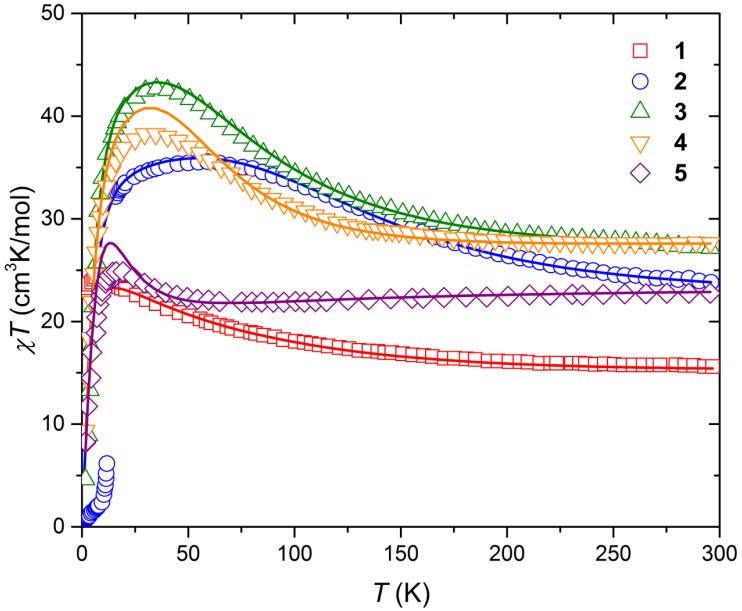
⇩

All components of the *J* multiplet have to be involved in the exchange interaction.

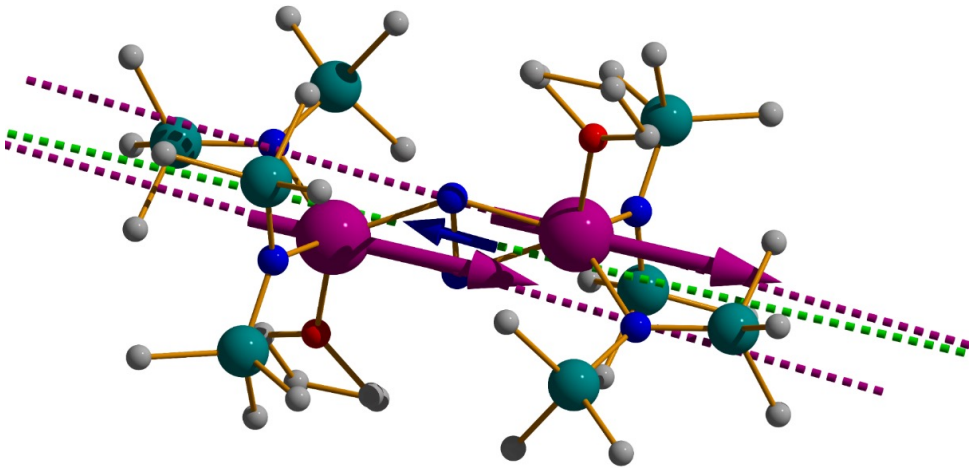
$$\hat{H}_{exch} = \sum_{i=1,2} \sum_{k=1,3,5,7} \sum_{q,q'} \gamma_{kq1q'} \frac{O_k^q(\hat{\mathbf{J}}_i)\hat{S}_{q'}}{O_k^0(J_i)S} \neq \gamma \hat{\mathbf{J}} \cdot \hat{\mathbf{S}}$$

N. Iwahara and L. F. Chibotaru, *Phys. Rev. B* **91**, 174438 (2015)

Magnetic properties



Magnetic susceptibility for H =1 T



Magnetic moments in the ground exchange state

Structure of the exchange interaction

$$\hat{H}_{\text{ex}} = \sum_{i=1,2} \sum_{k,q,q'} \mathcal{J}_{kq1q'} \frac{O_k^q(\hat{\mathbf{J}}_i)\hat{S}_{q'}}{O_k^0(J_i)S}$$

TABLE II. Calculated exchange parameters $\mathcal{J}_{kq1q'}$ (cm^{-1}) for the complexes **1**- **5**.

k	q	q'	$\mathcal{J}_{kq1q'}$				
			1 (Gd)	**2** (Tb)	**3** (Dy)	**4** (Ho)	**5** (Er)
1	0	0	94.9	95.8	70.8	55.4	24.2
1	±1	∓1	−94.9	−95.8	−70.8	−55.4	−24.2
3	0	0	0.0	13.4	−10.6	−4.4	5.0
3	±1	∓1	0.0	8.2	−6.5	−2.7	3.0
3	±3	±1	0.0	10.6	−8.4	−3.5	3.9
5	0	0	0.0	17.0	−16.0	−1.6	4.2
5	±1	∓1	0.0	−12.8	8.4	6.8	−6.1
5	±3	±1	0.0	−2.5	7.5	−7.6	3.4
5	±4	0	0.0	5.7	−0.8	−7.5	5.0
5	±5	∓1	0.0	−13.5	11.5	3.2	−4.4
7	0	0	0.0	0.3	−3.3	4.6	−2.3
7	±1	∓1	0.0	−0.2	2.5	−3.5	1.7
7	±3	±1	0.0	0.2	−2.2	3.0	−1.5
7	±4	0	0.0	−0.4	5.1	−7.1	3.5
7	±5	∓1	0.0	0.6	−7.2	10.0	−5.0

1st rank part:

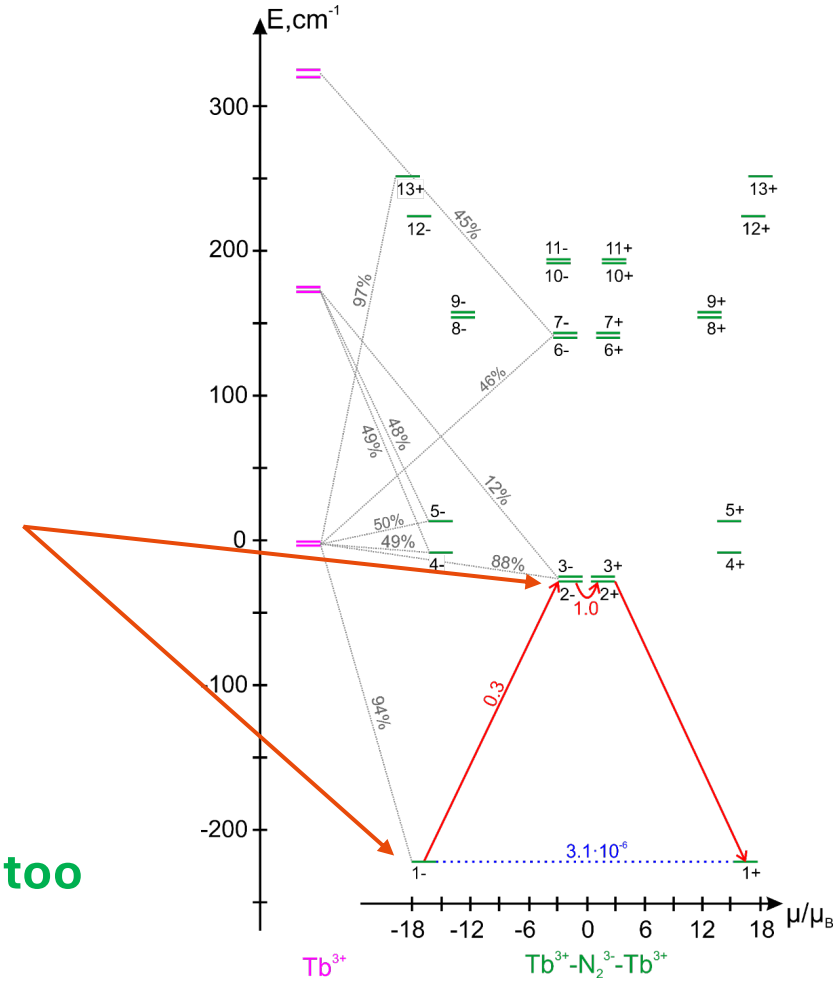
- Dominant
- Isotropic Heisenberg type

Higher order terms:

Not negligible

Nature of low-lying exchange states

Largest contribution comes from the ground CF doublet



Excited CF states contribute too

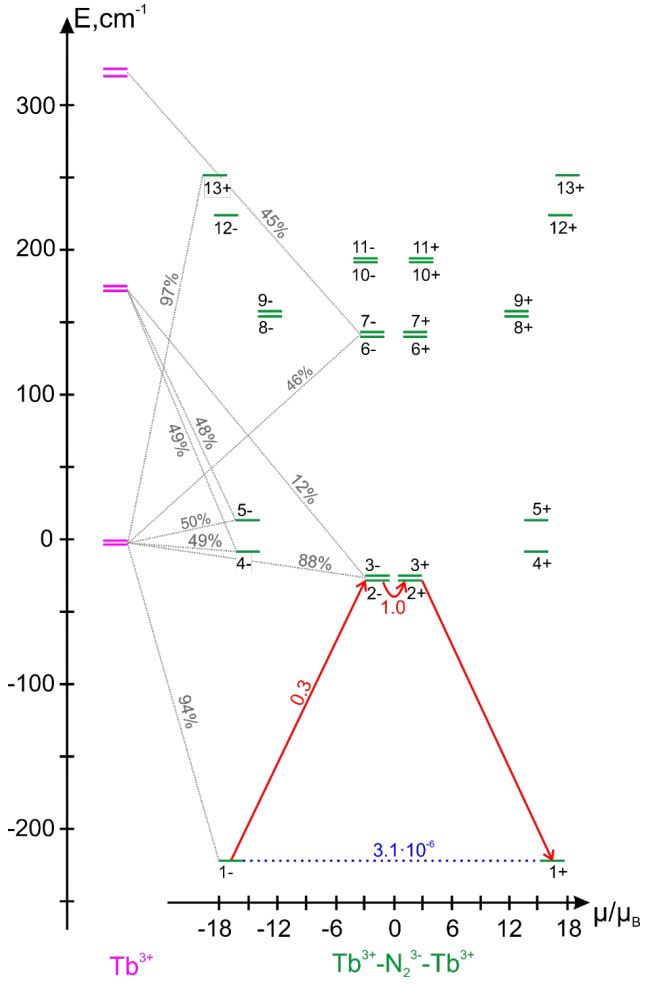
Mechanism of the relaxation of magnetization

- Rate of quantum tunneling of magnetization:

	Tb	Dy	Er	Ho
Rate of QTM	Small	Small	Large	The largest
Magnetic hysteresis	Yes	Yes	Yes Weak	No

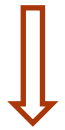
- Barrier for magnetization relaxation at high T, cm^{-1}:

	Tb	Dy	Ho	Er
E_{barr}(exp)	227	123	73	36
E_{barr}(calc)	208	121	105	28

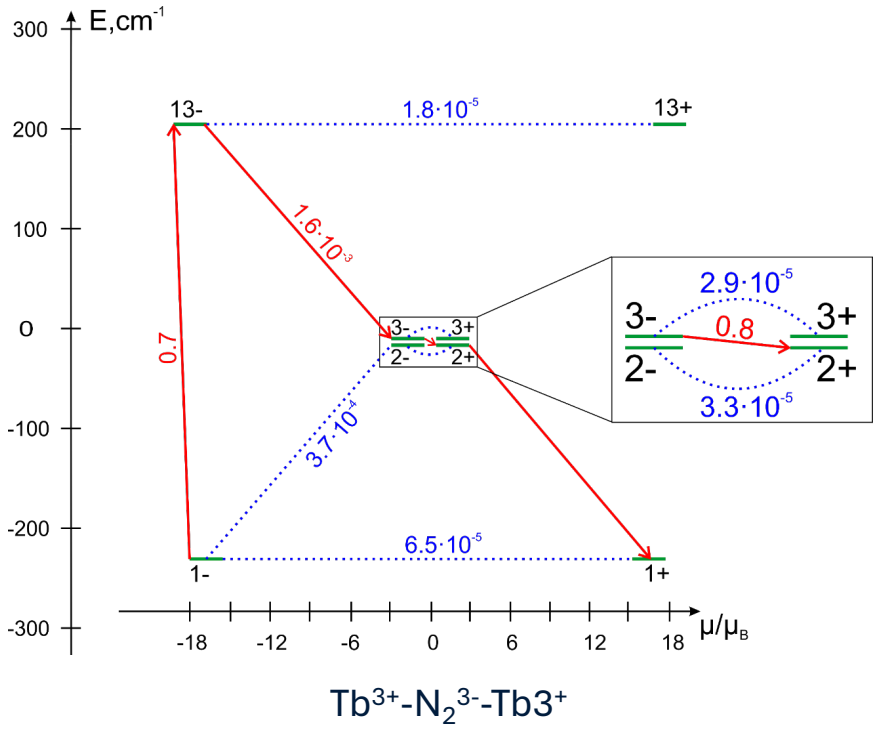


Influence of excited CF states on the height of the blocking barrier

Exchange mixing of the excited CF levels excluded



- Relaxation goes via the excited states
- **Two times larger barrier**

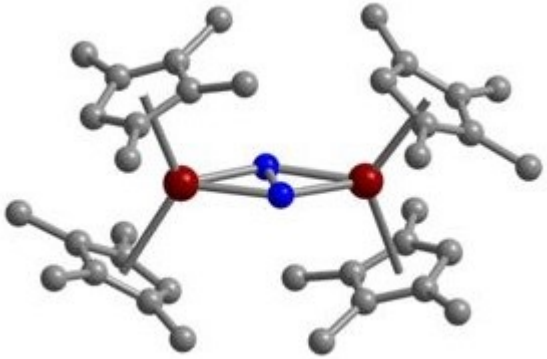


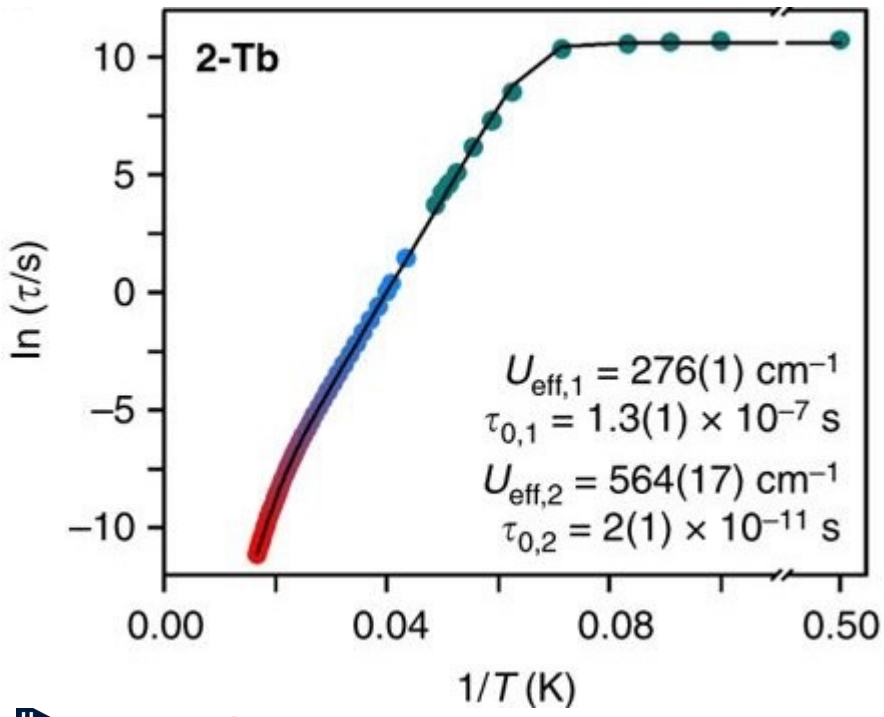
Tb^{3+}-N_2^{3-}-$Tb3^+$

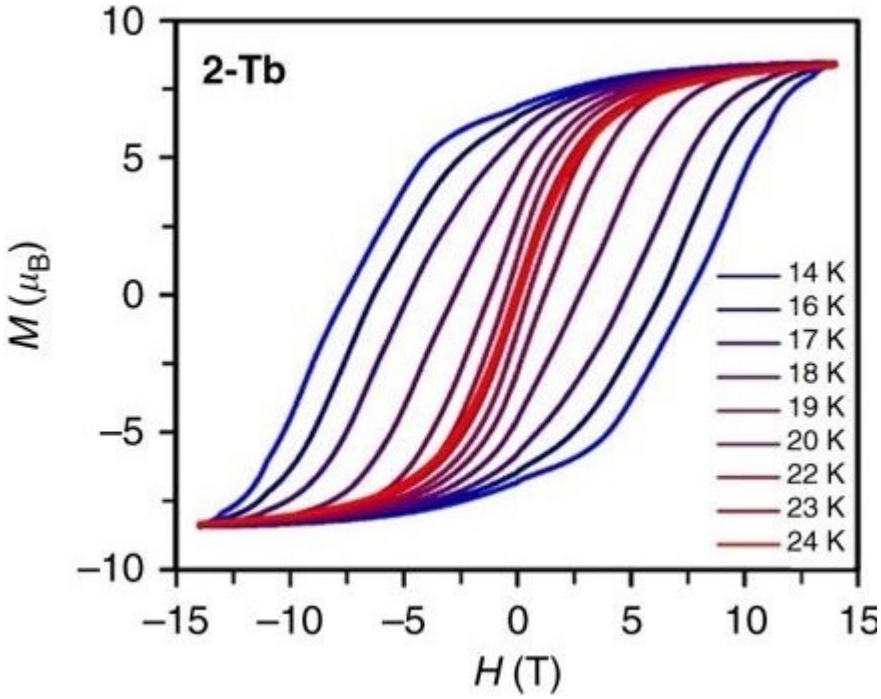
Large CF
Large exchange

Good SMM

This prediction was confirmed: higher axiality larger barrier

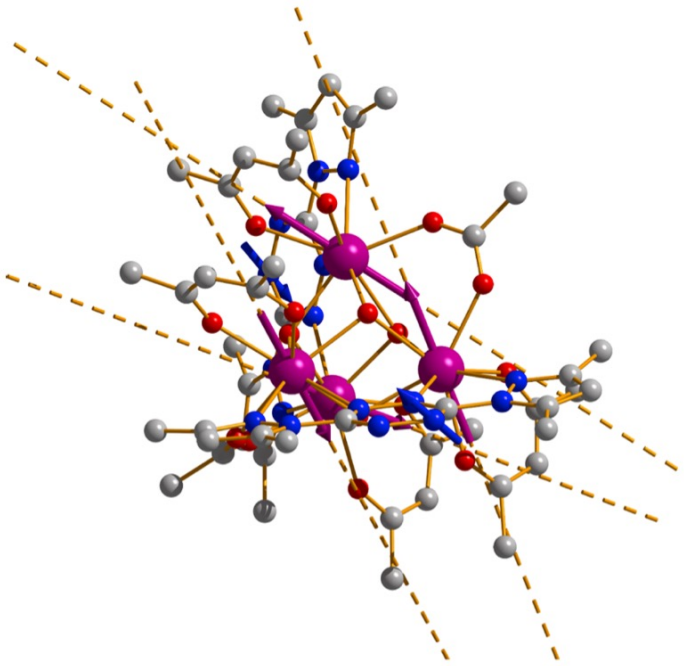






S. Demir et al. *Nature Communications*, ***2017***, *8*, 2144.

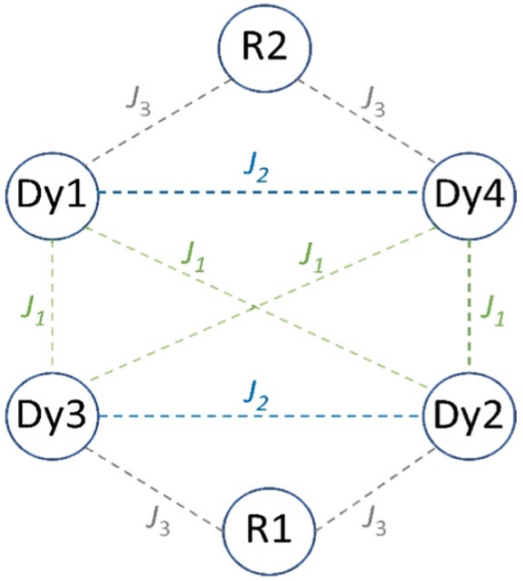
Magnetization of a Multimolecular Single Crystal of Radical-Bridged [Dy^{III}_4] Cubane



KD		Dy[a]	Dy[a]
1		0	0
2		95	109
3		150	197
4		216	272
5		264	318
6		322	396
7		466	521
8		586	636
g-tensor of the ground and first excited KDs			
1	g_x	0.00073	0.037
	g_y	0.052	0.095
	g_z	19.2	19.2
2	g_x	0.75	0.53
	g_y	1.23	0.79
	g_z	16.1	15.7

[a]Two symmetry inequivalent Dy ions.

J. Phys. Chem. C 2018, 122, 20, 11128–11135



$$\hat{H}_{tot} = \hat{H}_{dip} + \hat{H}_{exch}$$

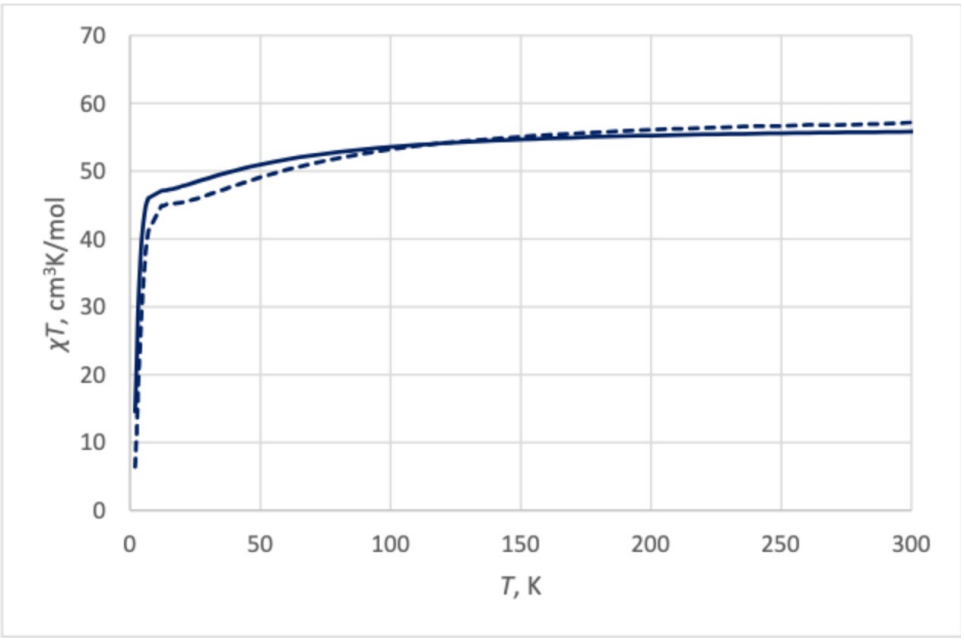
$$\hat{H}_{exch} = -J_1(\hat{\mathbf{S}}_{Dy1}\cdot\hat{\mathbf{S}}_{Dy2} + \hat{\mathbf{S}}_{Dy1}\cdot\hat{\mathbf{S}}_{Dy3} + \hat{\mathbf{S}}_{Dy2}\cdot\hat{\mathbf{S}}_{Dy4} + \hat{\mathbf{S}}_{Dy3}\cdot\hat{\mathbf{S}}_{Dy4}) - J_2(\hat{\mathbf{S}}_{Dy1}\cdot\hat{\mathbf{S}}_{Dy4} + \hat{\mathbf{S}}_{Dy2}\cdot\hat{\mathbf{S}}_{Dy3}) - J_3(\hat{\mathbf{S}}_{Dy1}\cdot\hat{\mathbf{S}}_{R2} + \hat{\mathbf{S}}_{Dy4}\cdot\hat{\mathbf{S}}_{R2} + \hat{\mathbf{S}}_{Dy3}\cdot\hat{\mathbf{S}}_{R1} + \hat{\mathbf{S}}_{Dy2}\cdot\hat{\mathbf{S}}_{R1})$$

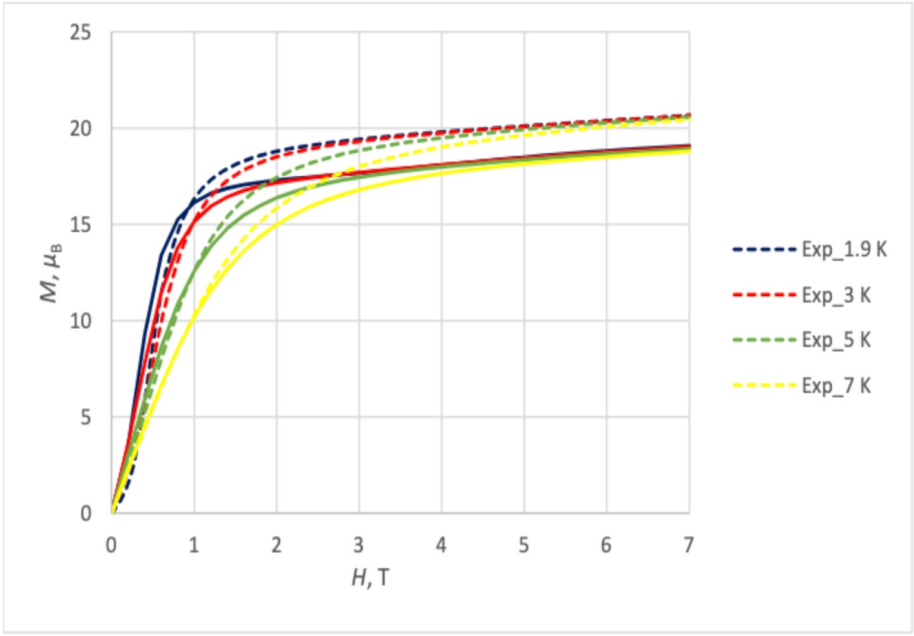
pair	J_{dip}	J_{exch}	$J = J_{dip} + J_{exch}$
Dy1−Dy2	−2.56	−0.096	−2.66
Dy1−Dy3	−0.92	−0.11	−1.03
Dy1−Dy4	−2.85	−0.47	−3.32
Dy1−R2	−0.30	−15.26	−15.56
Dy3−Dy4	−2.17	−0.080	−2.25
Dy3−R1	−0.27	−15.24	−15.51

Table 3. Energy of the Low-Lying Exchange States of 1 and Main *g*-Factor of the Ground and First Excited Exchange Doublets

energy (cm^{-1})	*g*-factor
0	g_z = 12.3
0.000000	
3.483231	g_z = 68.4
3.483231	
7.920883	
7.920887	
7.920921	
7.920926	
8.127443	
8.127447	
8.127494	
8.127497	
...	

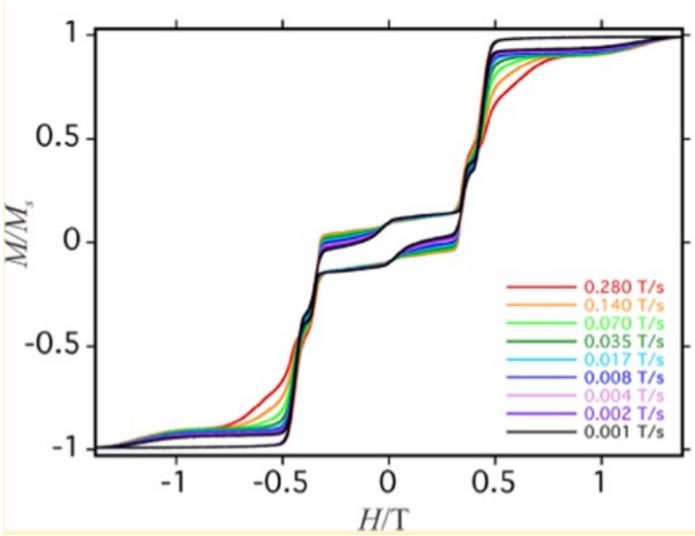
Experimental vs. calculated magnetic data

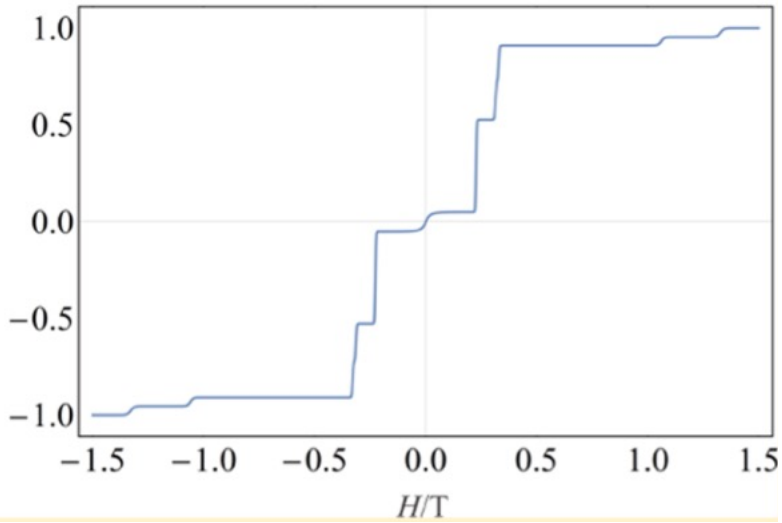




Single crystal experimental vs. calculated magnetization

$$M_\alpha(\mathbf{H},\, T) = \sum_r \frac{\sum_{l,m} \mu_B g_z^{(l)} m \vec{e}_r^{\,(l)} \cdot \vec{\xi}_\alpha \; e^{-E_{rlm}/kT}}{\sum_{l,m} e^{-E_{rlm}/kT}}$$





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