Nanoscale superconductivity, fluxonics and photonics
K.U.Leuven Methusalem Group

Magnetic anisotropy in complexes and its *ab initio* description

Liviu F. Chibotaru and Liviu Ungur

Theory of Nanomaterials Group, Department of Chemistry,
Katholieke Universiteit Leuven

Magnetic Anisotropy workshop, Karlsruhe 11-12 October 2013

Outline:

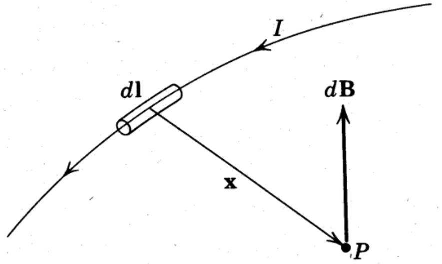
- Basic notions of atomic magnetism
- What is the magnetic anisotropy?
- When does it appear?
- How does it manifest in magnetic properties?

- Zeeman and ZFS interaction for weak s-o coupling: *spin* magnetic Hamiltonians
- ---- # ---- for intermediate/strong s-o coupling: *pseudospin* magnetic Hamiltonians
- Exchange interaction for weak s-o coupling: *spin* exchange Hamiltonians
- ---- # ---- for intermediate/strong s-o coupling: *pseudospin* exchange Hamiltonians
- The Lines' model
- The sign of the *g* tensor

- *Ab initio* calculations of electronic coupling of complexes
- Calculation methodology of anisotropic magnetic properties
- *SINGLE_ANISO* module for mononuclear complexes and fragments.
  Examples of applications.
- *POLY_ANISO* package for polynuclear complexes.
  Examples of applications.

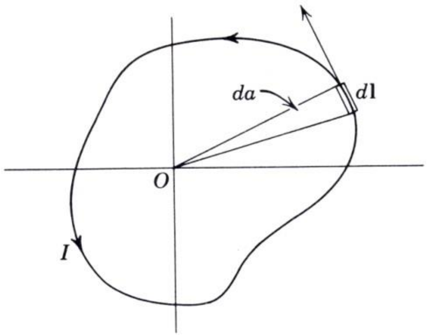
Classical magnetic and angular momenta

1) Currents induce magnetic field



Biot and Savart low: $$d\mathbf{B} = I\frac{d\mathbf{l}\times\mathbf{x}}{|\mathbf{x}|^3}$$

2) In finite systems → *loops* of currents:

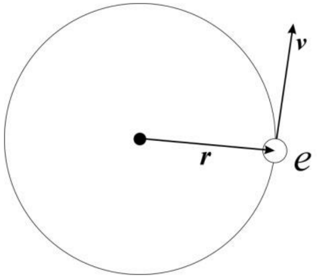


$$\mathbf{B} = \frac{3\mathbf{x}(\mathbf{x}\cdot\boldsymbol{\mu}) - |\mathbf{x}|^2\boldsymbol{\mu}}{|\mathbf{x}|^5}, \qquad \boldsymbol{\mu} = \frac{I}{2c}\oint \mathbf{x}\times d\mathbf{l} = \frac{I}{c}S\mathbf{e}_z$$

$$E_{\text{Zeeman}} = -\boldsymbol{\mu}\cdot\mathbf{H}_{\text{ext}}$$

magnetic moment

3) In atom → one electron in the Bohr's orbit:



$$I = e\frac{v}{2\pi r} \rightarrow \mu_z = \frac{e}{2mc}(r\cdot mv) = -\mu_{\text{B}}L_z$$

$$\boldsymbol{\mu} = -\mu_{\text{B}}\mathbf{L} \qquad \mathbf{L} = \mathbf{r}\times\mathbf{p} \qquad \mu_{\text{B}} = \frac{|e|}{2mc}$$

orbital angular moment

Bohr magneton

In quantum mechanics (one electron):

$$\hat{\boldsymbol{\mu}}_o = -\mu_B \hat{\mathbf{l}}, \qquad \hat{\mathbf{l}} - \text{in units of } \hbar \;\rightarrow\; \mu_B = \frac{\hbar|e|}{2mc}$$

For each electron: *internal* angular momentum $\hat{\mathbf{s}}$ (spin):

$$\hat{\boldsymbol{\mu}}_s = -g_s \mu_B \hat{\mathbf{s}} \quad g_s = 2.0023$$

Total magnetic moment:

$$\hat{\boldsymbol{\mu}} = \hat{\boldsymbol{\mu}}_o + \hat{\boldsymbol{\mu}}_s = -\left(\hat{\mathbf{l}} + 2\hat{\mathbf{s}}\right)\mu_B$$

Eigenstates (*quantization*) of angular momenta:

$$\hat{\mathrm{l}}_z |lm\rangle = m|lm\rangle \quad \hat{\mathbf{l}}^2 |lm\rangle = l(l+1)|lm\rangle, \quad \hat{\mathbf{l}}^2 = \hat{\mathrm{l}}_x^2 + \hat{\mathrm{l}}_y^2 + \hat{\mathrm{l}}_z^2$$

$$l = 0, 1, 2, \cdots \qquad m = -l, -l+1, \cdots, l \;\rightarrow\; 2l+1 \text{ definite projections}$$

$$\hat{\mathrm{s}}_z |sm_s\rangle = m_s|sm_s\rangle \quad \hat{\mathbf{s}}^2 |sm_s\rangle = s(s+1)|sm_s\rangle, \quad \hat{\mathbf{s}}^2 = \hat{\mathrm{s}}_x^2 + \hat{\mathrm{s}}_y^2 + \hat{\mathrm{s}}_z^2$$

$$s = \frac{1}{2} \qquad m_s = -\frac{1}{2}, \frac{1}{2}$$

Conservation of angular momenta in atoms

A physical quantity A is conserved if $\left[\hat{A},\hat{H}\right]=0$

One-electron atom (H)

$$\hat{H}=-\frac{\hbar^2}{2m}\Delta-\frac{Ze^2}{r} \qquad \Delta=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{\hat{\mathbf{l}}^2}{r^2}\ , \qquad \hat{\mathbf{l}}^2,\hat{l}_\alpha=f\left(\theta,\phi\right)$$

$$\Rightarrow \quad \left[\hat{\mathbf{l}},\hat{H}\right]=\left[\hat{\mathbf{s}},\hat{H}\right]=0 \qquad \Rightarrow \quad \mathbf{l},\mathbf{s} \text{ are conserved}$$

$$\hat{H}\varphi_{nlm}=\varepsilon_{nl}\varphi_{nlm} \qquad \varphi_{nlm}=R_{nl}\left(r\right)Y_{lm}\left(\theta,\phi\right) \qquad \psi_{nlmm_s}=\varphi_{nlm}\left(r,\theta,\phi\right)\chi_{m_s}\left(\sigma\right)$$

Many-electron atom:

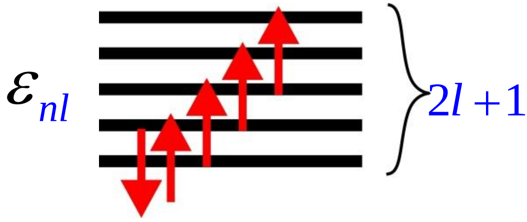
$$\hat{H}=\sum_{i=1}^{N_{el}}\left(-\frac{\hbar^2}{2m}\Delta_i-\frac{Ze^2}{r_i}\right)+\frac{1}{2}\sum_{i=1}^{N_{el}}\sum_{\substack{j=1\\(j\neq i)}}^{N_{el}}\frac{e^2}{\left|\mathbf{r}_i-\mathbf{r}_j\right|}$$

1) Independent electrons in the central field:

$$\hat{H}_0 = \sum_{i=1}^{n} \hat{H}_i, \qquad \hat{H}_i = -\frac{\hbar^2}{2m}\Delta_i - \frac{Ze^2}{r_i} + V(r_i),$$

$V(r_i)$ - average electrostatic field from all electrons

$$\left[\hat{\mathbf{l}}_i, \hat{H}_0\right] = \left[\hat{\mathbf{s}}_i, \hat{H}_0\right] = 0 \quad \Rightarrow \quad \mathbf{l}_i, \mathbf{s}_i \text{ are conserved}$$



nl configuration

2) Permutational symmetry of electrons:

Antisymmetrized w. f. are characterized by a *definite* total spin S

$\Rightarrow$ only the total spin $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2 + \cdots \mathbf{s}_n$ is conserved

3) Interacting electrons:

$$V_{\text{int}} = \frac{1}{2}\sum_{i\neq j}^{n} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i}^{n} V(r_i) \qquad \left[\hat{\mathbf{l}}_i, \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right] \neq 0, \quad \left[\hat{\mathbf{l}}_i + \hat{\mathbf{l}}_j, \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right] = 0$$

$\Rightarrow$ only the total orbital moment $\mathbf{L} = \mathbf{l}_1 + \mathbf{l}_2 + \cdots + \mathbf{l}_n$ is conserved

$\Rightarrow$ Solutions of SE are *terms* → definite L and S

4) Spin-orbit interaction

The interaction of electron spins with magnetic fields of their orbital motions:

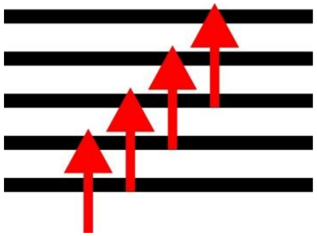
$$\hat{V}_{sl} = \sum_i \xi(r_i)\hat{\mathbf{l}}_i \cdot \hat{\mathbf{s}}_i, \qquad \xi(r_i) = \frac{\hbar^2}{2m^2c^2 r_i}\frac{\mathrm{d}U(r_i)}{\mathrm{d}r_i}, \qquad U(r_i) = -\frac{Ze^2}{r_i} + V(r_i)$$

Within a given electronic configuration

$$\hat{V}_{sl} = \sum_i \zeta \hat{\mathbf{l}}_i \cdot \hat{\mathbf{s}}_i, \qquad \zeta_{nl} = \int R_{nl}(r)^2 \xi(r) r^2 \mathrm{d}r, \qquad \zeta \sim Z^4$$

Within a given atomic term *LS*:

One should calculate $\left\langle \Psi_{LM_LSM_S} \middle| \hat{V}_{sl} \middle| \Psi_{LM_L'SM_S'} \right\rangle$



Hund's rule for the GS atomic term:

1) maximal S within a given configuration

2) maximal L possible for this S

$\Rightarrow$ For $n \leq$ half-filled shell $\rightarrow S = \frac{n}{2}$

$\Rightarrow$ $\Psi_{LM_LSM_S}$ are *symmetric* with respect to spin coordinates off all n electrons

$\Rightarrow$ The matrix elements of $\hat{\mathbf{s}}_i$ are the same for all $i = 1,..n$

Since $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2 + \cdots \mathbf{s}_n \;\rightarrow\;$ m.e.$\{\mathbf{s}_i\} =$ m.e.$\left\{\dfrac{\mathbf{S}}{n}\right\}$

$$\Rightarrow \quad \hat{V}_{sl} = \sum_i \zeta \hat{\mathbf{l}}_i \cdot \hat{\mathbf{s}}_i = \frac{\zeta}{n}\hat{\mathbf{S}} \cdot \sum_i \hat{\mathbf{l}}_i = \frac{\zeta}{n}\hat{\mathbf{S}} \cdot \hat{\mathbf{L}} = \lambda \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$$

Total angular momentum: $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$, $\left[\hat{\mathbf{J}}, \hat{V}_{sl}\right] = 0 \;\rightarrow\; \hat{\mathbf{J}}$ is conserved

Multiplets - eigenstates of $\hat{\mathbf{J}}^2, \hat{\mathrm{J}}_z$: Ψ_{JM_J}, $M_J = -J, -J+1, \cdots, J$

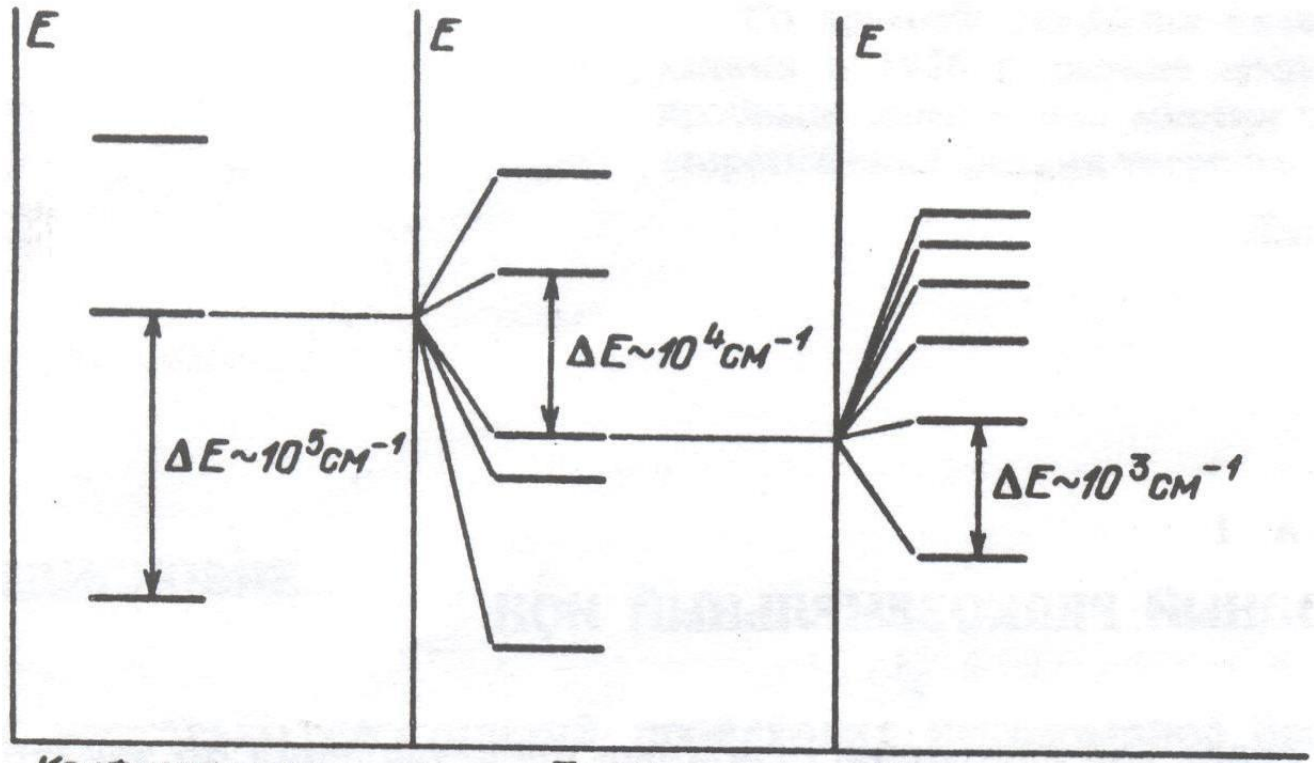
$$\lambda \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \frac{\lambda}{2}\left[\left(\hat{\mathbf{L}} + \hat{\mathbf{S}}\right)^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2\right] = \frac{\lambda}{2}\left[\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2\right]$$

$E_J = \dfrac{\lambda}{2}\left[J(J+1) - L(L+1) - S(S+1)\right]$, $\quad \Delta E_{J,J-1} = \lambda J$ - Lande rule

$n \leq$ h.f. : $\lambda > 0 \;\rightarrow\; J_{\mathrm{GS}} = |L - S|$ - normal multiplet structure

$n >$ h.f. : $\hat{V}_{sl} = -\zeta \sum_i \hat{\mathbf{l}}_i \cdot \hat{\mathbf{s}}_i \;\rightarrow\; \lambda < 0 \;\rightarrow\; J_{\mathrm{GS}} = |L + S|$ - inverted m.s.

Hierarchy of interactions in atoms

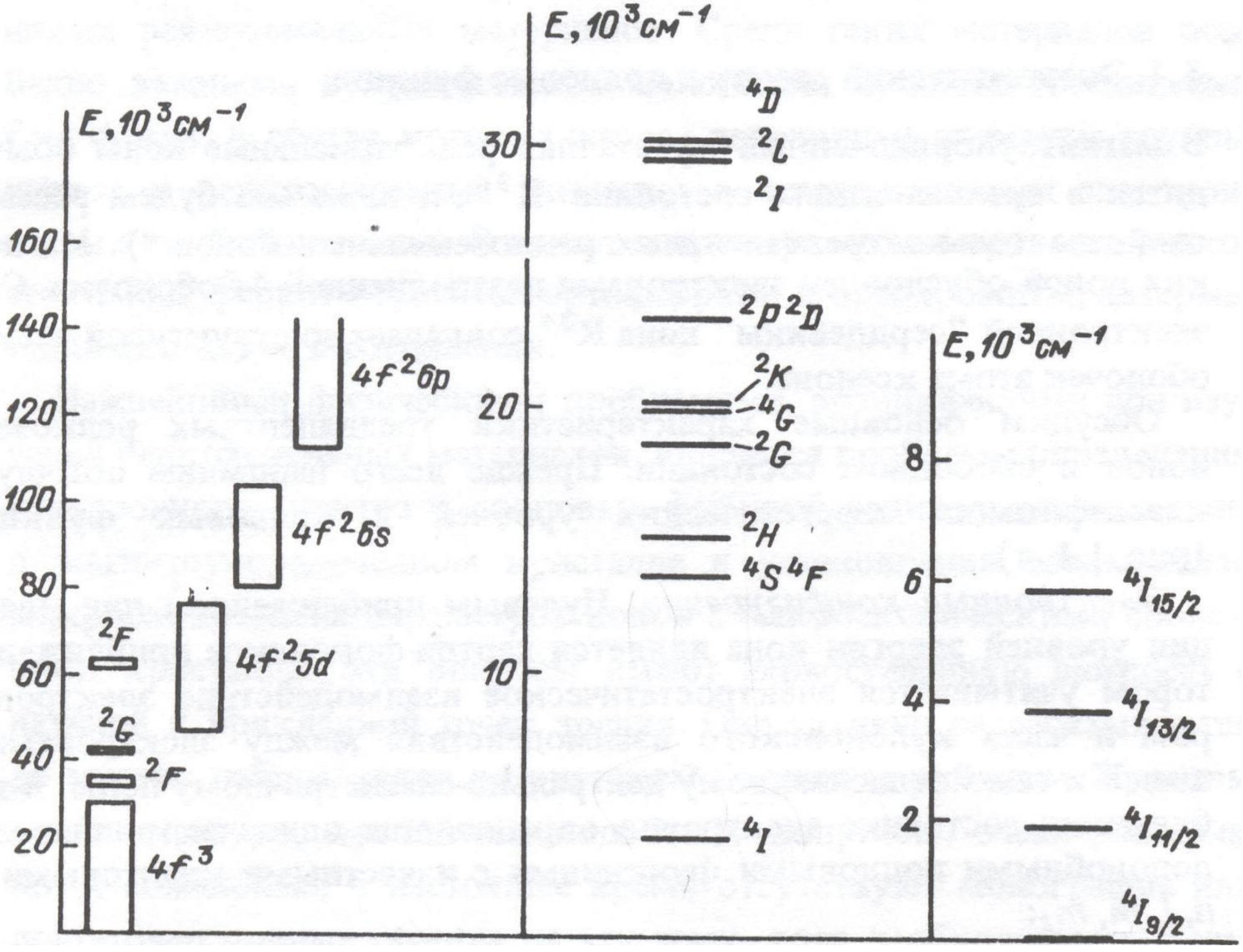


Configurations (shells)

Terms

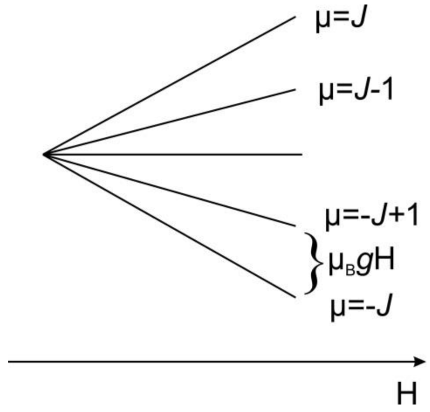
Multiplets

Example : Nd^{3+}



Configurations Terms Multiplets

Zeeman interaction



In applied homogeneous **H**: $\hat{V}_{\mathrm{Zee}} = -\boldsymbol{\mu}\cdot\mathbf{H} = \mu_{\mathrm{B}}\left(\hat{\mathbf{L}} + 2\hat{\mathbf{S}}\right)\cdot\mathbf{H}$

Spherical symmetry of atoms → rotational symmetry around **H**

Each multiplet J splits into $(2J+1)$ M_J-components || **H**:

$$E_{JM_J} = E_J + \mu_{\mathrm{B}}\langle JM_J|\hat{\mathbf{L}} + 2\hat{\mathbf{S}}|JM_J\rangle\mathbf{H} = E_J + \mu_{\mathrm{B}}\langle JM_J|\hat{J}_z + \hat{S}_z|JM_J\rangle H$$

$$= E_J + \mu_{\mathrm{B}}\left(M_J + \left\langle\hat{S}_z\right\rangle_{M_J}\right)H$$

Since J_z is the only conserving momentum → $\langle\mathbf{S}\rangle \,||\, \langle\mathbf{J}\rangle$ → $\langle\mathbf{S}\rangle_{M_J} = \mathrm{const}\cdot M_J$

One can prove: $\langle\mathbf{J}\cdot\mathbf{S}\rangle = \mathrm{const}\cdot\langle\mathbf{J}^2\rangle$ → const = $\langle\mathbf{J}\cdot\mathbf{S}\rangle / J(J+1)$

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

$\Rightarrow\quad E_{JM_J} = E_J + \mu_{\mathrm{B}} g M_J H, \qquad M_J = -J, -J+1, \cdots, J$ - Zeeman splitting

$g = 1 + \dfrac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$ - Lande (gyromagnetic) factor

Isotropy of space = degeneracy of $\left|JM\right\rangle$ after M

$$\left(M=-J,-J+1,\cdots,J\right)$$

Basic property of eigenfunctions of angular momentum $\left|JM\right\rangle$:

they have the same form w.r.t. all quantization axes:

Eigenfunctions of $\hat{\mathrm{J}}_z$: $\left|JM\right\rangle$

Eigenfunctions of $\hat{\mathrm{J}}_{z'}$: $\left|JM\right\rangle'$

$$\left|JM\right\rangle'=\sum_{M'=-J}^{J}D_{MM'}\left(\alpha\beta\gamma\right)\left|JM'\right\rangle$$

where $\alpha\beta\gamma$ - Euler angles of $x'y'z'$ relative to xyz

The same property also for **S** and **L**

$\Rightarrow$ Magnetic properties of consverved angular momenta are isotropic

Origin of magnetic anisotropy: removal of degeneracy after *M*

Atoms in a given multiplet state *J* are magnetically *isotropic*:
the Zeeman splitting is the same for *all directions* of the applied **H**

This is the consequence of the (2*J*+1) degeneracy of multiplets

Example: a d^2 configuration (l=2, L=3, S=1, J=2) in electric field (**E** || *z*)

splits into nondegenerate $|2,0\rangle$ and two degenerate $|2,\pm1\rangle$ and $|2,\pm2\rangle$ levels.

In applied magnetic field: $\hat{V}_{\text{Zeeman}} = -\hat{\boldsymbol{\mu}}_{\text{at}} \cdot \mathbf{H} = \mu_{\text{B}} g_J \hat{\mathbf{J}} \cdot \mathbf{H}$

For the ground doublet $|2,\pm2\rangle$: $\hat{V}_{\text{Zeeman}} = \begin{pmatrix} 2\mu_{\text{B}} g_J H_z & 0 \\ 0 & -2\mu_{\text{B}} g_J H_z \end{pmatrix}$

GS orbital magnetic moment $\langle \hat{\boldsymbol{\mu}}_{\text{at}} \rangle = -\mu_{\text{B}} g_J \langle \hat{\mathbf{J}} \rangle = -\mu_{\text{B}} g_J \langle \hat{J}_z \rangle = \begin{cases} -2\mu_{\text{B}} g_J, & H_z > 0 \\ 0, & H_z = 0 \\ 2\mu_{\text{B}} g_J, & H_z < 0 \end{cases}$

Zeeman splitting: $\Delta E_{\text{Zee}} = 4\mu_{\text{B}} g_J H_z = 4\mu_{\text{B}} g_J H \cos\theta \quad \Rightarrow$ *anisotropic*

Magnetic anisotropy in mononuclear complexes

<u>Spin-orbit coupling</u> on metal ions leads to the following effects:

1. All spin levels corresponding to *S*>1/2 *become split* into:
   - Kramers doublets for half-integer spin
   - non-degenerate levels for integer spin

$$\hat{\mathrm{H}}_{\mathrm{ZFS}} = \sum_{\alpha,\beta} S_\alpha D_{\alpha\beta} S_\beta$$

D - tensor of *zero field splitting*

2. The Zeeman interaction becomes anisotropic, the gyromagnetic factor becomes a tensor:

$$g \rightarrow g_{\alpha\beta}$$

3. The magnetization becomes anisotropic, the susceptibility function becomes a tensor:

$$\chi(T,H) \rightarrow \chi_{\alpha\beta}(T,H), \qquad M_\alpha = \sum_\beta \chi_{\alpha\beta} H_\beta$$

Weak spin-orbit coupling effects

$\zeta/\Delta E_{CF} \sim 0.01 - 0.1$

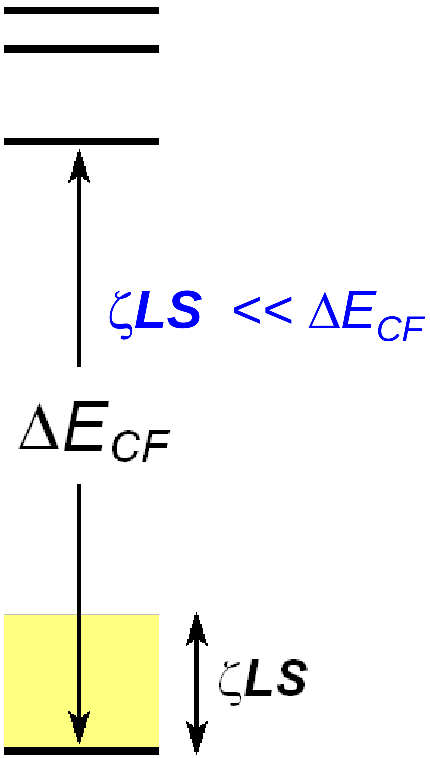
- Most of transition-metal ions - Cr^{3+}, Mn^{2+}, Fe^{3+}, Ni^{2+}

Magnetic centers have a spin-only ground state

- Magnetic moment has a spin origin
- The spin of the magnetic centers is a good quantum number

ZFS tensor is small

$\mathbf{D} \sim \zeta^2 /\Delta E_{CF}$



Perturbational treatment of spin-orbit coupling for $^{2S+1}\Gamma_0$

Effective Zeeman Hamiltonian: $\hat{\mathrm{H}}_{\mathrm{Zeeman}} = \sum_{\alpha\beta} S_\alpha g_{\alpha\beta} H_\beta$

Gyromagnetic tensor: $\mathbf{g} = g_e \mathbf{1} + \lambda \mathbf{\Lambda}$

Zero-field-splitting tensor: $\mathbf{D} = \lambda^2 \mathbf{\Lambda}$

where

$$\Lambda_{\alpha\beta} = \sum_i \frac{\langle \Gamma_0 | \hat{\mathrm{L}}_\alpha | \Gamma_i \rangle \langle \Gamma_i | \hat{\mathrm{L}}_\beta | \Gamma_0 \rangle}{E_0 - E_i}$$

$\hat{\mathrm{L}}_\alpha$, $\hat{\mathrm{L}}_\beta$ - Cartesian components of the total orbital momentum

Strong spin-orbit coupling effects

(quasi-) degenerate magnetic centers

= *unquenched* orbital moments

$\Delta E_{CF} \sim \zeta$

- *f* ions - lanthanides and actinides - Ce^{3+}, Nd^{3+}, Dy^{3+}, Yb^{3+}, U^{4+} et al.
- Some *d* ions and complexes – Co^{2+}, $[Mo^{III}(CN)_7]^{4-}$, $[Fe(CN)_6]^{3-}$.

- The total spin on magnetic centers is no longer a good quantum number

ZFS tensor is large

$\Rightarrow$ Pseudospin description

There are orbital states close to the ground one within the spin-orbit energy range

Non-perturbational treatment of spin-orbit coupling effects

1) Spin-orbit interactions are included in quantum chemistry calculations

$\Rightarrow$ exact treatment of zero field splitting of all molecular terms

2) All paramagnetic properties are expressed through *matrix elements* of magnetic moments operators:

$$\hat{\mathrm{H}}_{\mathrm{Zeeman}} = -\hat{\boldsymbol{\mu}} \cdot \mathbf{H}, \qquad \hat{\boldsymbol{\mu}} = -\mu_{\mathrm{B}} \sum_{i=1}^{N_{el}} \left(g_e \hat{\mathbf{s}}_i + \hat{\mathbf{l}}_i \right)$$

on calculated (exact) wave functions of spin-orbit-coupling multiplets

Exact derivation of pseudospin Hamiltonians $\hat{\mathrm{H}}_{\mathrm{Zee}}$ and $\hat{\mathrm{H}}_{\mathrm{ZFS}}$

1) Choice of the relevant manifold:

ab initio wave functions $\Psi_1, \Psi_2, \cdots \Psi_N \rightarrow 2\tilde{S}+1=N$

2) Definition of pseudospin (in a given coordinate system):

$$\Psi'_i = \sum_{n=1}^{N} c_{in}\Psi_n \rightarrow \left|\tilde{S}M\right\rangle \qquad \tilde{\mathrm{S}}_z\left|\tilde{S}M\right\rangle = M\left|\tilde{S}M\right\rangle$$

3) Decomposition of $\left\|\left\langle \Psi'_i \middle| \hat{\mu}_\alpha \middle| \Psi'_j \right\rangle\right\|$ and $\mathrm{H}_{\mathrm{ZFS}} = \left\|\sum_{n=1}^{N} c_{in}^{*} c_{jn} E_n\right\|$

in pseudospin matrices $\tilde{\mathrm{S}}_\alpha,\ \tilde{\mathrm{S}}_\alpha\tilde{\mathrm{S}}_\beta, \cdots \quad \alpha,\beta=\mathrm{x,y,z}$

Zeeman and ZFS tensors for various pseudospins

$$\hat{\mathrm{H}}_{\mathrm{Zee}} = -\boldsymbol{\mu}\cdot\mathbf{H}$$

$$\boldsymbol{\mu} = \boldsymbol{\mu}^1 + \boldsymbol{\mu}^3 + \boldsymbol{\mu}^5 + \ldots$$

S	μ	H_{ZFS}
1/2	μ^1	H^0
1	μ^1	H^2
3/2	$\mu^1 + \mu^3$	H^2
2	$\mu^1 + \mu^3$	H^2+H^4
5/2	$\mu^1 + \mu^3 + \mu^5$	H^2+H^4
3	$\mu^1 + \mu^3 + \mu^5$	$H^2+H^4+H^6$
7/2	$\mu^1 + \mu^3 + \mu^5 + \mu^7$	$H^2+H^4+H^6$
4	$\mu^1 + \mu^3 + \mu^5 + \mu^7$	$H^2+H^4+H^6+H^8$

Individual tensor components:

$$\hat{\mu}^1_\alpha = \sum_\beta g_{\alpha\beta}\hat{\tilde{S}}_\beta, \qquad g_{\alpha\beta} = g_{\beta\alpha},$$

$$\hat{\mu}^n_\alpha = \sum_{m=0}^{n}\left(b^\alpha_{nm}\hat{O}^m_n + c^\alpha_{nm}\hat{\Omega}^m_n\right)$$

$$\hat{\mathrm{H}}^2_{\mathrm{ZFS}} = \sum_\beta \hat{\tilde{S}}_\alpha D_{\alpha\beta}\hat{\tilde{S}}_\beta, \qquad D_{\alpha\beta} = D_{\beta\alpha},$$

$$\hat{\mathrm{H}}^n_{\mathrm{ZFS}} = \sum_{m=0}^{n}\left(e^\alpha_{nm}\hat{O}^m_n + f^\alpha_{nm}\hat{\Omega}^m_n\right)$$

$$\hat{O}^m_n = \frac{1}{2}\left(\hat{O}^{+m}_n + \hat{O}^{-m}_n\right), \quad \hat{\Omega}^m_n = \frac{1}{2i}\left(\hat{O}^{+m}_n - \hat{O}^{-m}_n\right)$$ - Stewens operators

$$\hat{O}^{\pm m}_n\left(\tilde{\mathbf{S}}\right) \sim Y_{n\pm m}\left(\tilde{\mathbf{S}}\right)$$ - spherical functions of $\tilde{S}_x, \tilde{S}_y, \tilde{S}_z$

Calculation of the parameters of pseudospin Hamiltonians

$$\left\langle \tilde{S}M \left| \hat{O}_n^{\pm m} \right| \tilde{S}M' \right\rangle = \frac{O_n^0\left(\tilde{S}\right)}{\sqrt{2\tilde{S}+1}} \frac{\sqrt{(2\tilde{S}-n)!(2\tilde{S}+n+1)!}}{(2\tilde{S})!} C_{\tilde{S}M'n\pm m}^{\tilde{S}M}$$

$$b_{nm}^{\alpha} = \frac{\left(2n+1\right)\mathrm{Sp}\left(\hat{\mu}_\alpha \hat{O}_n^m\right)}{\left\langle \tilde{S} \| O_n \| \tilde{S} \right\rangle^2} \qquad c_{nm}^{\alpha} = \frac{\left(2n+1\right)\mathrm{Sp}\left(\hat{\mu}_\alpha \hat{\Omega}_n^m\right)}{\left\langle \tilde{S} \| O_n \| \tilde{S} \right\rangle^2}$$

$$e_{nm} = \frac{\left(2n+1\right)\mathrm{Sp}\left(\hat{\mathrm{H}}_{\mathrm{ZFS}} \hat{O}_n^m\right)}{\left\langle \tilde{S} \| O_n \| \tilde{S} \right\rangle^2} \qquad f_{nm} = \frac{\left(2n+1\right)\mathrm{Sp}\left(\hat{\mathrm{H}}_{\mathrm{ZFS}} \hat{\Omega}_n^m\right)}{\left\langle \tilde{S} \| O_n \| \tilde{S} \right\rangle^2}$$

Definition of pseudospin for arbitrary $\tilde{S}$:

method of **A** tensor

$A_{\alpha\beta} = \frac{1}{2}\mathrm{Sp}\left\{\mu_\alpha \mu_\beta\right\}$, μ_α - $N \times N$ matrix of $\hat{\mu}_\alpha$ in arbitrary basis

Diagonalization:

$$\mathbf{R}_r^{\mathrm{main}} \mathbf{A} \left(\mathbf{R}_r^{\mathrm{main}}\right)^{-1} = \tilde{\mathbf{A}}_{\mathrm{diag}} \equiv \left\{\tilde{A}_{XX}, \tilde{A}_{YY}, \tilde{A}_{ZZ}\right\}$$

Main values of the g tensor $\left(N = 2\tilde{S}+1\right)$:

$$g_i = \frac{6}{\mu_{\mathrm{B}} \tilde{S}\left(\tilde{S}+1\right)\left(2\tilde{S}+1\right)} \sqrt{\tilde{A}_{ii}}, \quad i = X, Y, Z$$

Pseudospin eigenfunctions:

$\tilde{\mathrm{S}}_Z \left|\tilde{S} M\right\rangle = M \left|\tilde{S} M\right\rangle$ → *diagonalization of* μ_Z

Application: $\boldsymbol{\mu}^1 \gg \boldsymbol{\mu}^3, \boldsymbol{\mu}^5, \cdots$

Exchange interaction in polynuclear complexes

1) No spin-orbit coupling

Isotropic **spin** Hamiltonian: $\mathrm{H}_{exch} = -J\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2$

2) Weak spin-orbit coupling effects

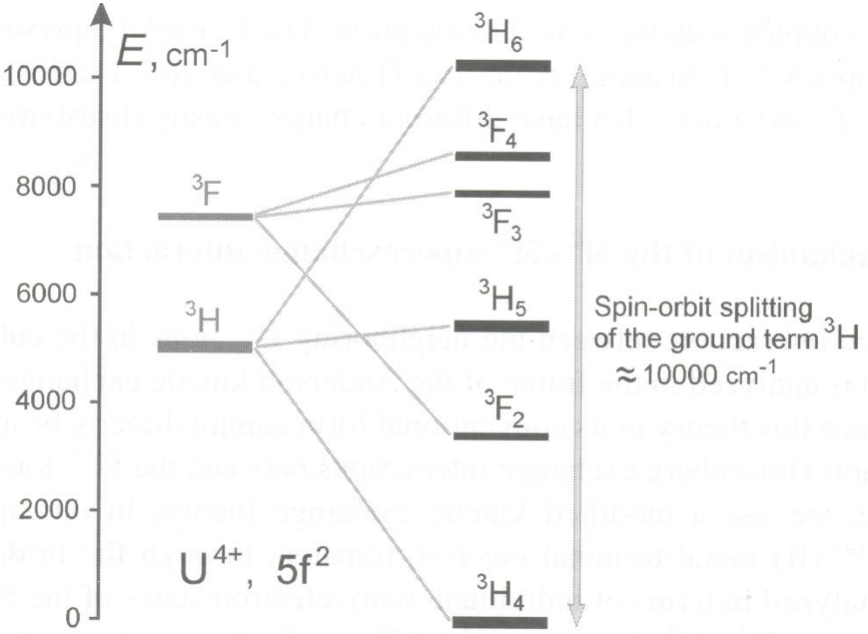
Anisotropic **spin** Hamiltonian: $\hat{\mathrm{H}}_{exch} = -J\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 + \mathbf{d} \cdot \hat{\mathbf{S}}_1 \times \hat{\mathbf{S}}_2 + \hat{\mathbf{S}}_1 \cdot \mathbf{J}_{symm} \cdot \hat{\mathbf{S}}_2$

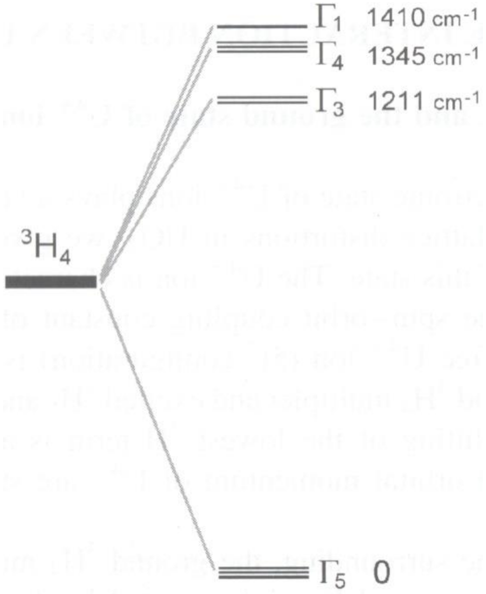
$$\mathbf{d} \sim J\frac{\lambda}{\Delta E_{CF}}, \quad \mathbf{J} \sim J\left(\frac{\lambda}{\Delta E_{CF}}\right)^2$$

3) Strong spin-orbit coupling effects

Anisotropic **pseudospin** Hamiltonian: $\hat{\mathrm{H}}_{exch} = \tilde{\mathbf{S}}_1 \cdot \mathbf{J} \cdot \tilde{\mathbf{S}}_2 + \textit{higher order terms}$

Pseudospin exchange Hamiltonians: $U^{4+} - U^{4+}$



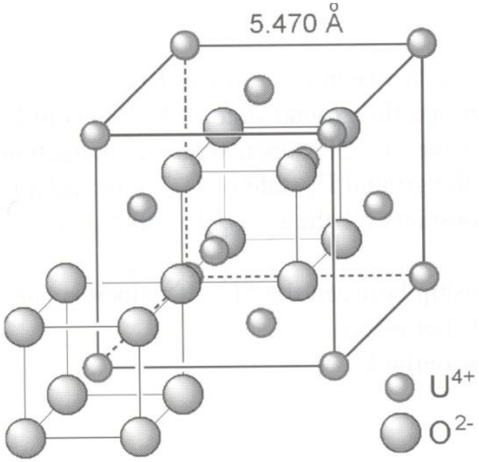


Ground state triplet: $\Gamma_5 \rightarrow \tilde{S} = 1$

$$\left|\Gamma_5,-1\right\rangle = \sqrt{\frac{7}{8}}\left|{}^3H_4,-3\right\rangle - \sqrt{\frac{1}{8}}\left|{}^3H_4,+1\right\rangle$$

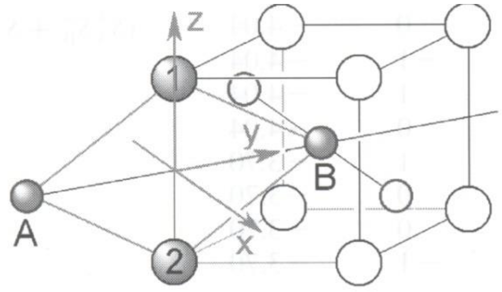
$$\left|\Gamma_5,0\right\rangle = \sqrt{\frac{1}{2}}\left|{}^3H_4,+2\right\rangle - \sqrt{\frac{1}{2}}\left|{}^3H_4,-2\right\rangle$$

$$\left|\Gamma_5,+1\right\rangle = \sqrt{\frac{7}{8}}\left|{}^3H_4,+3\right\rangle - \sqrt{\frac{1}{8}}\left|{}^3H_4,-1\right\rangle$$



$$\mathrm{H} = \mathrm{H}_{\mathrm{ZFS}} + \mathrm{H}^{(1)}_{\mathrm{exch}} + \mathrm{H}^{(2)}_{\mathrm{exch}} + \mathrm{H}^{(3)}_{\mathrm{exch}}$$

$$\mathrm{H}_{\mathrm{ZFS}} = D\left[\left(\tilde{\mathrm{S}}^z_A\right)^2 + \left(\tilde{\mathrm{S}}^z_B\right)^2\right] + E\left[\left(\tilde{\mathrm{S}}^x_A\right)^2 - \left(\tilde{\mathrm{S}}^y_A\right)^2 + \left(\tilde{\mathrm{S}}^x_B\right)^2 - \left(\tilde{\mathrm{S}}^y_B\right)^2\right]$$



$$D = -4.6\ \mathrm{cm}^{-1} \qquad E = 5.2\ \mathrm{cm}^{-1}$$

$$\mathrm{H}^{(1)}_{\mathrm{exch}} = J_x\tilde{\mathrm{S}}^x_A\tilde{\mathrm{S}}^x_B + J_y\tilde{\mathrm{S}}^y_A\tilde{\mathrm{S}}^y_B + J_z\tilde{\mathrm{S}}^z_A\tilde{\mathrm{S}}^z_B$$

$$J_x = 14.6\ \mathrm{cm}^{-1}, \quad J_x = 22.1\ \mathrm{cm}^{-1}, \quad J_z = 18.8\ \mathrm{cm}^{-1}$$

$$\mathrm{H}^{(2)}_{\mathrm{exch}} = j_1\tilde{\mathrm{S}}^x_A\tilde{\mathrm{S}}^x_B\left[\left(\tilde{\mathrm{S}}^z_A\right)^2 + \left(\tilde{\mathrm{S}}^z_B\right)^2\right] + j_2\tilde{\mathrm{S}}^y_A\tilde{\mathrm{S}}^y_B\left[\left(\tilde{\mathrm{S}}^z_A\right)^2 + \left(\tilde{\mathrm{S}}^z_B\right)^2\right] + j_3\tilde{\mathrm{S}}^x_A\tilde{\mathrm{S}}^x_B\left(\tilde{\mathrm{S}}^z_A\tilde{\mathrm{S}}^z_B\right) + j_4\tilde{\mathrm{S}}^y_A\tilde{\mathrm{S}}^y_B\left(\tilde{\mathrm{S}}^z_A\tilde{\mathrm{S}}^z_B\right)$$

$$j_1 = -0.3\ \mathrm{cm}^{-1}, \quad j_2 = 0.4\ \mathrm{cm}^{-1}, \quad j_3 = 0.8\ \mathrm{cm}^{-1}, \quad j_4 = -0.6\ \mathrm{cm}^{-1}$$

$$\mathrm{H}^{(3)}_{\mathrm{exch}} = q_1\mathrm{O}^{(1)}_A\mathrm{O}^{(1)}_B + q_2\mathrm{O}^{(2)}_A\mathrm{O}^{(2)}_B + q_3\mathrm{O}^{(3)}_A\mathrm{O}^{(3)}_B + q_4\left[\mathrm{O}^{(1)}_A\mathrm{O}^{(2)}_B + \mathrm{O}^{(1)}_A\mathrm{O}^{(2)}_B\right]$$

$$q_1 = 1.8\ \mathrm{cm}^{-1}, \quad q_2 = 2.6\ \mathrm{cm}^{-1}, \quad q_3 = 0.6\ \mathrm{cm}^{-1}, \quad q_4 = -0.2\ \mathrm{cm}^{-1}$$

$$\mathrm{O}^{(1)}_k = \left(\tilde{\mathrm{S}}^z_k\right)^2 - \tilde{S}\left(\tilde{S}+1\right)/3$$

$$\mathrm{O}^{(2)}_k = \left(\tilde{\mathrm{S}}^x_k\right)^2 - \left(\tilde{\mathrm{S}}^y_k\right)^2$$

$$\mathrm{O}^{(3)}_k = \left(\tilde{\mathrm{S}}^x_k\tilde{\mathrm{S}}^y_k + \tilde{\mathrm{S}}^y_k\tilde{\mathrm{S}}^x_k\right)$$

V.S. Mironov, L.F. Chibotaru, A. Ceulemans
Adv. Quant. Chem. **44**, 600-616 (2003)

Practical approach: combined exact-phenomenological treatment of anisotropic exchange in polynuclear complexes

- exact quantum chemical treatment of individual metal fragments

- Lines model treatment of exchange interactions:

1) introduce an effective $\hat{\mathrm{H}}_{\mathrm{exch}} = -\sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$

2) diagonalize $\hat{\mathrm{H}}_{\mathrm{exch}}$ in the basis of lowest SO multiplets on sites: $\{\Gamma_i\} \otimes \{\Gamma_j\}$

(J_{ij} - fitting parameters)

Advantages:

- contains one single Lines parameter for each exchange-coupled pair

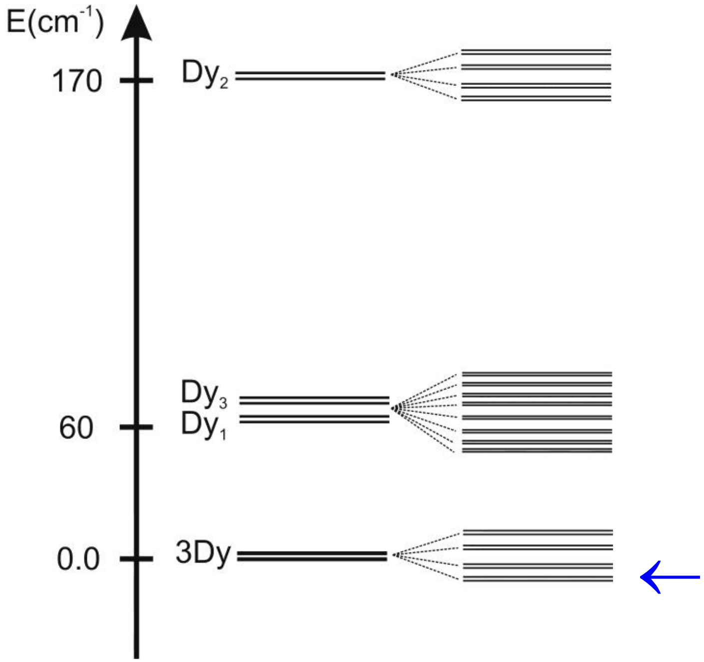
- becomes exact in the limit of isotropic and strongly anizotropic (Ising) interactions

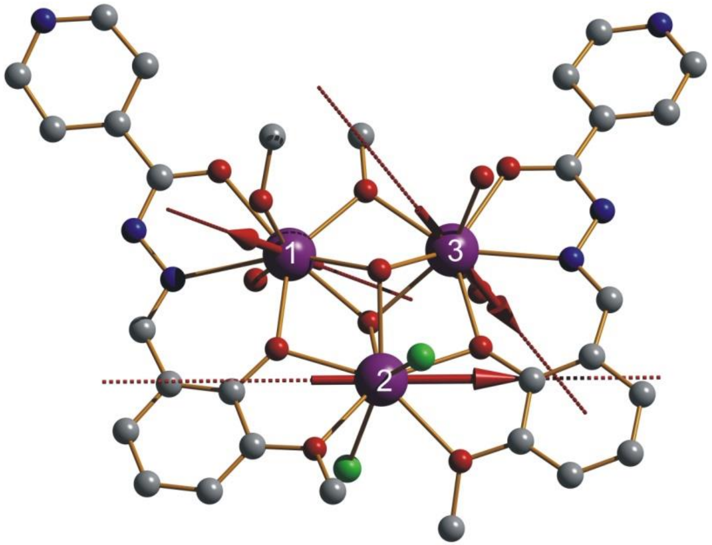
Polynuclear Ln complexes - weak exchange limit

CF splitting of multiplets on Ln ions >> exchange splitting

⇒ Non-collinear magnetic structure

Example: a Dy_3 complex



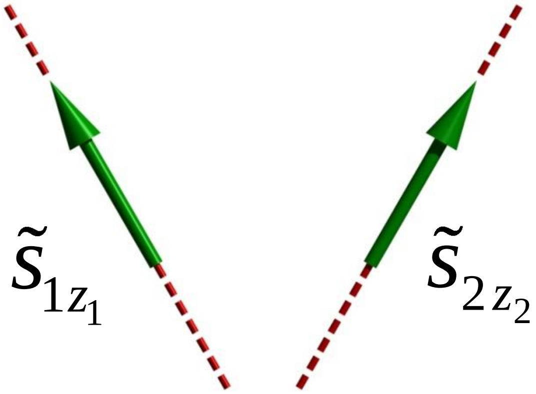


Anisotropic exchange interactions for axial ions

$$\left(\text{For two isotropic ions: } \hat{H}_{ex} = -J\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 = -J\left(\hat{S}_{1x}\hat{S}_{2x} + \hat{S}_{1y}\hat{S}_{2y} + \hat{S}_{1z}\hat{S}_{2z}\right)\right)$$

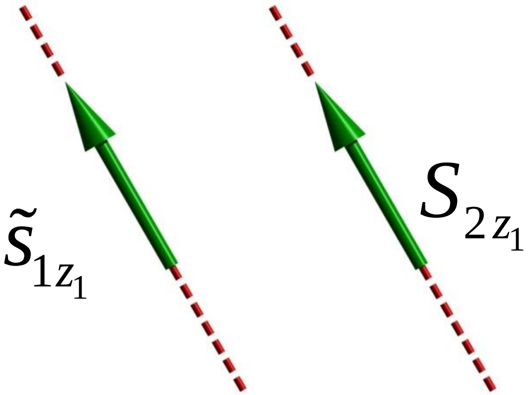
Ln - Ln:

$$\hat{H}_{ex} = -J\tilde{s}_{1z_1}\tilde{s}_{2z_2}$$



Ln - M,R:

$$\hat{H}_{ex} = -J\tilde{s}_{1z_1}S_{2z_1}$$



$\tilde{s}$ – axial

S – isotropic

Negative *g* factors in complexes with strong spin-orbit coupling effects

$$\hat{\boldsymbol{\mu}} = -g_L \mu_{\mathrm{B}} \hat{\mathbf{L}}, \quad g_L = 1$$

$$\hat{\boldsymbol{\mu}} = -g_s \mu_{\mathrm{B}} \hat{\mathbf{S}}, \quad g_s = 2.0023$$

$$\hat{\boldsymbol{\mu}} = -g_J \mu_{\mathrm{B}} \hat{\mathbf{J}}, \quad g_J = \frac{g_s + 1}{2} + (g_s - 1)\frac{S(S+1) - L(L+1)}{2J(J+1)} > 0$$

g>0 for conserved angular momenta

Sign[*g*] not evident for pseudospins

$\tilde{S} = 1/2 \;\rightarrow$ e.g. $(\Phi, \bar{\Phi})$ of a KD (crystal-field splitting of an atomic J)

Without symmetry $\rightarrow$ no *unique* way $\begin{pmatrix} \Phi \\ \bar{\Phi} \end{pmatrix} \Leftrightarrow \begin{pmatrix} |\tilde{S}\ 1/2\rangle \\ |\tilde{S}\ \text{-}1/2\rangle \end{pmatrix}$

$$\mu_\alpha = -\mu_{\mathrm{B}} \sum_\beta g_{\alpha\beta} \tilde{\mathrm{S}}_\beta , \qquad \tilde{\mathrm{S}}_\beta = \frac{1}{2}\sigma_\beta , \qquad \alpha, \beta = x, y, z$$

Dynamics of the magnetic moment in external **H**

$$\hat{\mathrm{H}}_{\mathrm{Zee}} = -\boldsymbol{\mu} \cdot \mathbf{H}$$

Diagonalization of ***g***:

$$x, y, z \rightarrow X, Y, Z$$

$$\left\| g_{\alpha\beta} \right\| \rightarrow g_X, g_Y, g_Z \qquad \Rightarrow \hat{\mathrm{H}}_{\mathrm{Zee}} = \mu_{\mathrm{B}} \sum_{i=X,Y,Z} g_i \tilde{\mathrm{S}}_i H_i$$

Equation of motion (M.H.L. Pryce, 1959) :

$$i\hbar \frac{d\hat{\mu}_X}{dt} = \left[\hat{\mu}_X, \hat{\mathrm{H}}_{\mathrm{Zee}} \right] = i\mu_{\mathrm{B}} g_X g_Y g_Z \left(\frac{1}{g_Z^2} \hat{\mu}_Z H_Y - \frac{1}{g_Y^2} \hat{\mu}_Y H_Z \right)$$

$\Rightarrow$ The direction of precession depends on Sign$\left[g_X g_Y g_Z \right]$

$g_X g_Y g_Z < 0$ was found in:

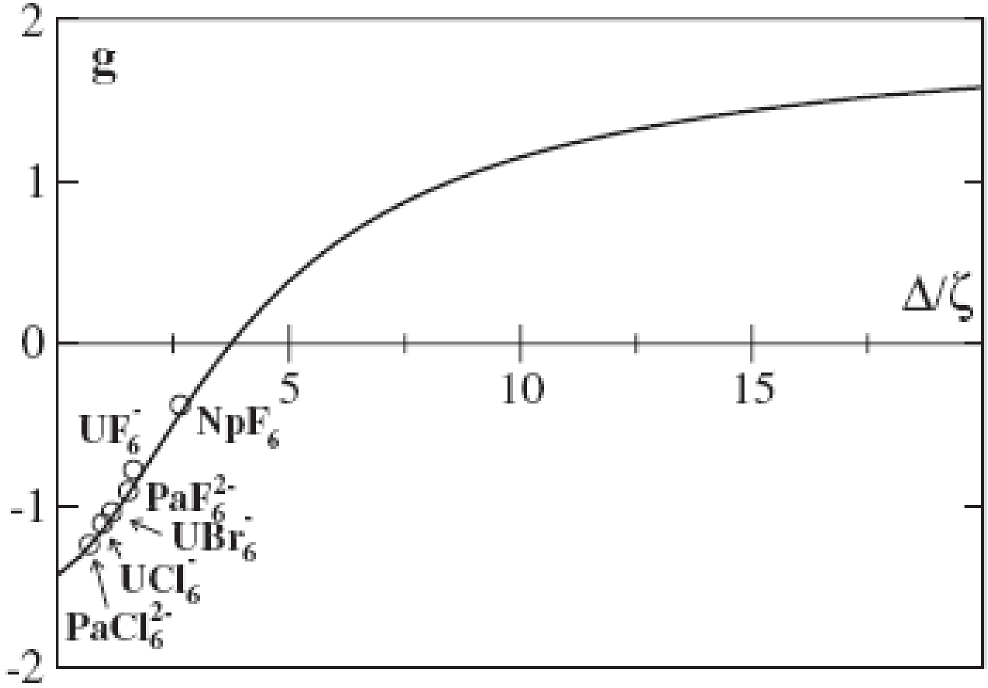
NpF_6 with circularly polarized light (1967)

UF_6^- with circularly polarized EPR (1967)

Ab initio calculation of $Sign\left[g_X g_Y g_Z\right]$

$$\frac{g_X g_Z}{g_Y} = -\frac{i}{\mu_B}\frac{\mu_X\mu_Z - \mu_Z\mu_X}{\mu_Y}$$ (L.Ungur, LC, PRL, 2012)

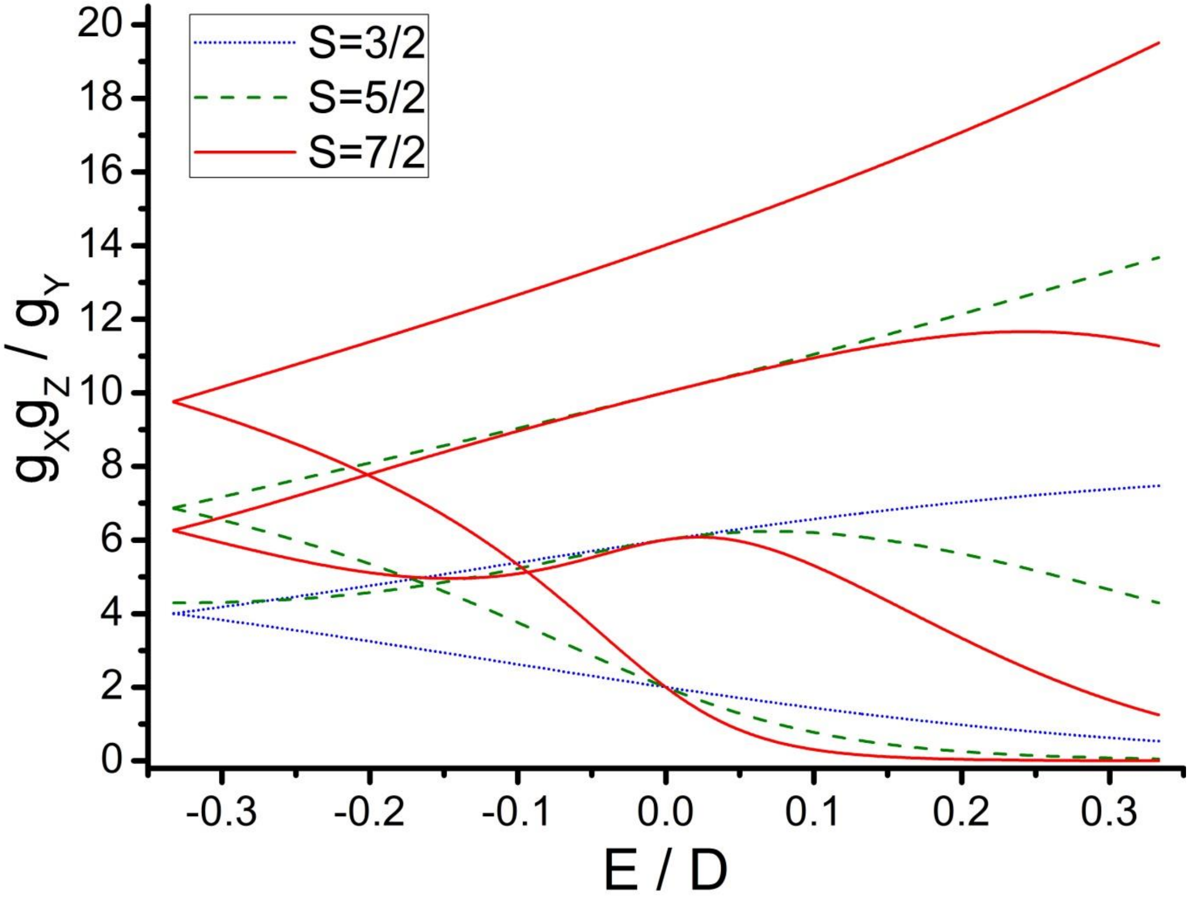
μ_i are matrices in RASSI-SO basis



L. Chibotaru, A. Ceulemans, H. Bolvin, *Phys. Rev. Lett.* **2008**

$Sign\left[g_X g_Y g_Z\right]$ for weak *s-o* coupling

$$\mathrm{H}_{\mathrm{ZFS}} = D\left[\mathrm{S}_Z^2 - S\left(S+1\right)\right] + E\left(\mathrm{S}_X^2 - \mathrm{S}_Y^2\right), \qquad \mu_\alpha \approx -g_e \mu_{\mathrm{B}} \mathrm{S}_\alpha$$



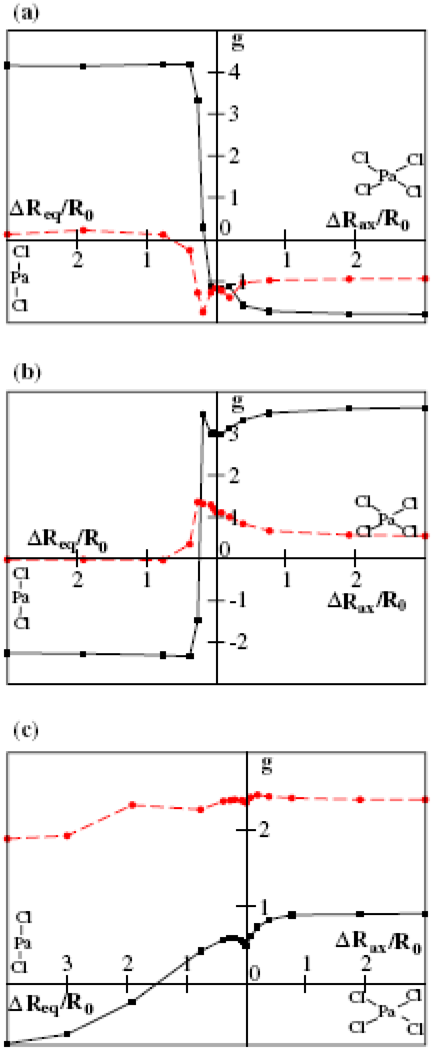
⇐ For individual Kramers doublets $\tilde{S} = 1/2$

Signs of individual g_i – unique definition of g tensors

L.Chibotaru, A. Ceulemans, H. Bolvin, *Phys. Rev. Lett.* **2008**

- use of symmetry: $\left|\tilde{S}M\right\rangle \Leftrightarrow \left|\Gamma\gamma\right\rangle$
- principle of adiabatic connection

Example: Tetragonally distorted $PaCl_6^{2-}$



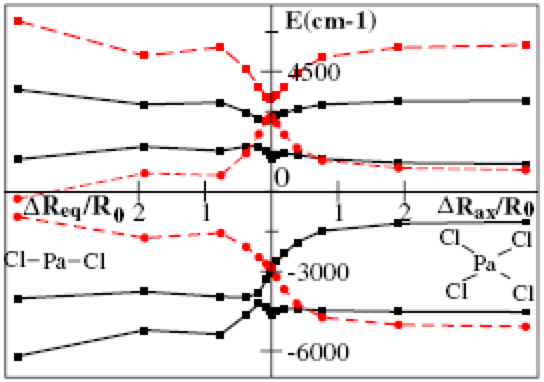
Γ_7 (GS)

Γ_7 (ES)

$g_\perp \rightarrow$

$g_\parallel \rightarrow$

Γ_6 (GS)



$\Gamma_6 \rightarrow$

$\Gamma_7 \rightarrow$

Ab initio calculation of magnetic properties of mononuclear complexes

What is an *ab initio* calculation?

Solves the Schrödinger Eq.: $\boldsymbol{\hat{H}\Psi = E\Psi}$

$\boldsymbol{\hat{H}}$ -- includes all possible interactions between the particles (electrons, nuclei)
$\boldsymbol{\Psi}$ -- contains all information about the electronic state of the system

- Uses ONLY the atomic coordinates as input
- Does NOT employ any experimental data / parameters / information

What is an ab initio calculation?

Exact solution → ***impossible.*** Approximations are needed…

Ψ -- single-determinant:

- Hartree-Fock (HF or SCF) -- **Ψ** is represented by one configuration;
- improvements: SCF + PT; SCF + CI; SCF + Coupled Clusters … etc;

Suitable for closed-shell systems! NOT applicable for open-shell systems!

Ψ -- many-determinants:

- Multiconfigurational Hartree-Fock (MCSCF)
- CASSCF is one of the existing multiconfigurational approaches;
- improvements: CASPT2; NEVPT2, DDCI

Suitable for open-shell systems! Computationally more difficult than HF!

Spin-orbit coupling is described by the DKH Hamiltonian in the AMFI approach, using CASSCF/CASPT2 states as input.

DFT ≠ is NOT ab initio, because the Exchange-Correlation Functional employed by DFT is fitted to a list of experimental data;

Relativistic *ab initio* computational methodology in MOLCAS

MOLCAS (www.molcas.org) - basic ab initio program package

- Get the atomic coordinates from the crystal structure file (CIF)
- Define the basis sets for all atoms: which already include scalar relativistic effects (ANO-RCC; ANO-DK3)
- Perform state – average CASSCF calculation of all spin states
- Use the RASSI-SO program to mix a large number (preferably all) of spin states by spin-orbit coupling

  Exact energy spectrum and wave functions + matrix elements of ***L***
- Use the SINGLE_ANISO program to compute the *g* tensor of the lowest groups of states, crystal field parameters of the lowest atomic multiplet, magnetic susceptibility and molar magnetization

Expression for magnetic susceptibility

Van-Vleck susceptibility expressed in terms of matrix elements of magnetic moment:

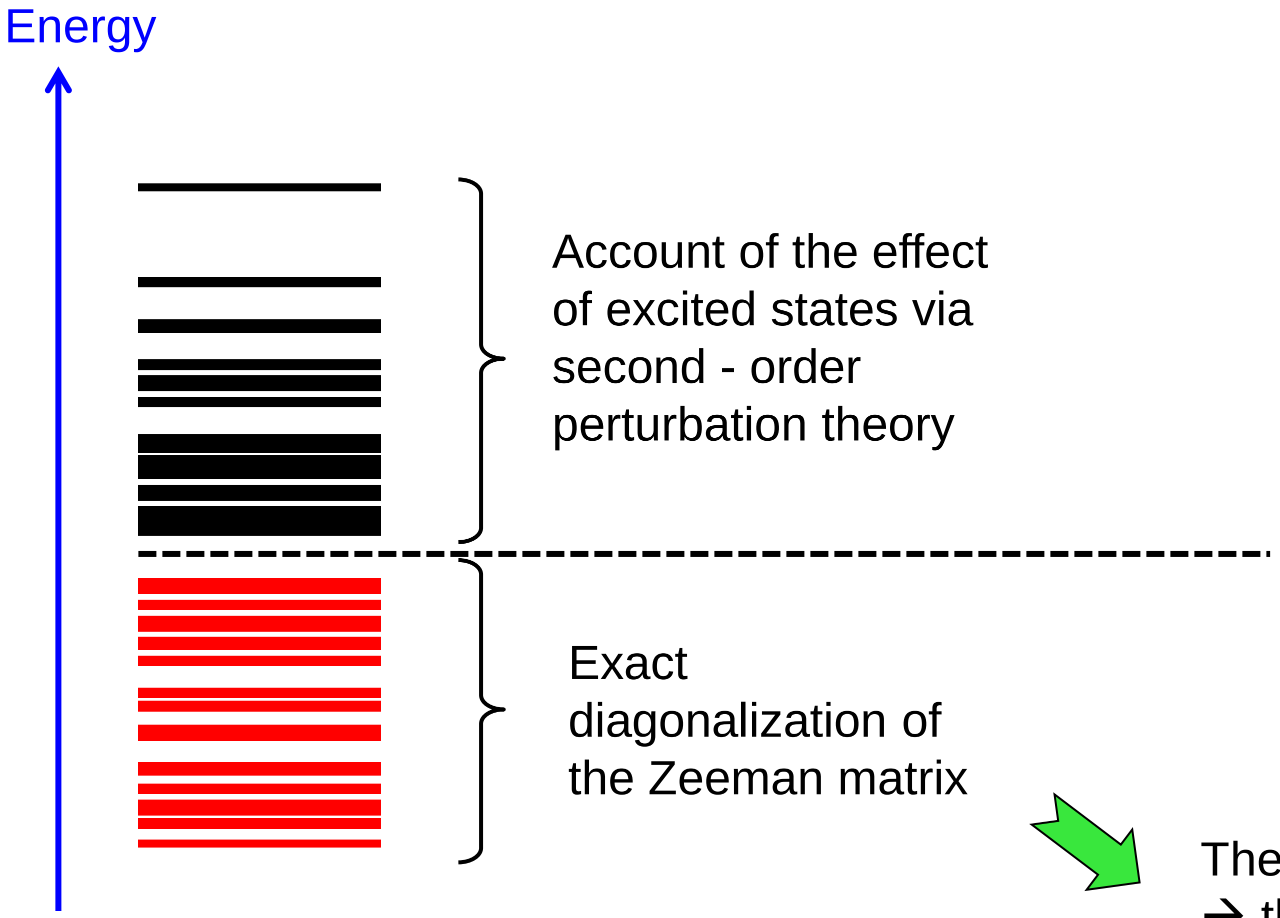
$$\chi_{\alpha\beta}T=\frac{N_A\mu_B^2}{k\sum_{i=1}^{NSS}e^{-\frac{E_i}{kT}}}\sum_{i=1}^{NSS}\left[\sum_{j=1}^{NSS}\left(\left\langle i\middle|\hat{\mu}_\alpha\middle|j\right\rangle\left\langle j\middle|\hat{\mu}_\beta\middle|i\right\rangle-\frac{kT\left(\left\langle i\middle|\hat{\mu}_\alpha\middle|j\right\rangle\left\langle j\middle|\hat{\mu}_\beta\middle|i\right\rangle+\left\langle j\middle|\hat{\mu}_\alpha\middle|i\right\rangle\left\langle i\middle|\hat{\mu}_\beta\middle|j\right\rangle\right)}{E_i-E_j}\right)\right]e^{-\frac{E_i}{kT}}$$

and

$$\chi T_{powder}=\frac{1}{3}\left(\chi T_{XX}+\chi T_{YY}+\chi T_{ZZ}\right).$$

For the calculation of magnetization we need the eigenvalues as function of magnetic field.

Calculation of molar magnetization



Account of the effect of excited states via second - order perturbation theory

Exact diagonalization of the Zeeman matrix

Parameter to define size of the Zeeman matrix

The larger the Zeeman matrix → the more accurate Zeeman spectrum and the resulting molar magnetization

Expression for molar magnetization

$$\langle M\rangle_{\vec{H}_\gamma} = \frac{\sum_{m_H=1}^{NM}\left[\left\langle m_H\left|\hat{\vec{\mu}}_\gamma\right|m_H\right\rangle - \mu_B \sum_{n=NM+1}^{NSS}\frac{\sum_{\alpha=1}^{3}\left(\left\langle m_H\left|\hat{\vec{\mu}}_\alpha\right|n\right\rangle\left\langle n\left|\hat{\vec{\mu}}_\gamma\right|m_H\right\rangle + \left\langle n\left|\hat{\vec{\mu}}_\alpha\right|m_H\right\rangle\left\langle m_H\left|\hat{\vec{\mu}}_\gamma\right|n\right\rangle\right)\vec{H}_\gamma}{E_H(m_H)-E(n)}\right]e^{-\frac{E_H(m_H)}{kT}}}{\sum_{m_H=1}^{NM} e^{-\frac{E_H(m_H)}{kT}} + \sum_{n=1}^{NSS} e^{-\frac{E(n)}{kT}}} +$$

$$+\frac{\sum_{n=NM+1}^{NSS}\left[\frac{\mu_B}{kT}\sum_{j=1}^{NSS}\left(\sum_{\alpha=1}^{3}\left\langle n\left|\hat{\vec{\mu}}_\alpha\right|j\right\rangle\left\langle j\left|\hat{\vec{\mu}}_\gamma\right|n\right\rangle\right)\vec{H}_\gamma - \sum_{j=1}^{NSS}\frac{\sum_{\alpha=1}^{3}\left(\left\langle n\left|\hat{\vec{\mu}}_\alpha\right|j\right\rangle\left\langle j\left|\hat{\vec{\mu}}_\gamma\right|n\right\rangle + \left\langle j\left|\hat{\vec{\mu}}_\alpha\right|n\right\rangle\left\langle n\left|\hat{\vec{\mu}}_\gamma\right|j\right\rangle\right)\vec{H}_\gamma}{E(n)-E(j)}\right]e^{-\frac{E(n)}{kT}}}{\sum_{m_H=1}^{NM} e^{-\frac{E_H(m_H)}{kT}} + \sum_{n=1}^{NSS} e^{-\frac{E(n)}{kT}}}$$

where:

m_H – states obtained by diagonalization of the Zeeman matrix

$E_H(m_H)$ – the Zeeman energy of the state m_H

n, j – states unperturbed by magnetic field, i.e. the states which are higher in energy than the cut-off energy EM.

$E(n), E(j)$ – the spin-orbit energy of the states n and j.

Effect of intermolecular interaction on the magnetization vector and magnetic susceptibility

$$\hat{\mathrm{H}}_{Zee} = \sum_{\alpha}\left(-\hat{\mu}_{\alpha} H_{\alpha} - zJ'\hat{S}_{\alpha}\left\langle S_{\alpha}\right\rangle\right); \qquad \mathrm{E}_n = f\left(\left\langle S_{\alpha}\right\rangle\right)$$

$$\left\langle \vec{M}\right\rangle_{\vec{H}} = \frac{\sum_n \left\langle n\left|\vec{\mu}\right|n\right\rangle e^{-\frac{E_n}{kT}}}{\sum_n e^{-\frac{E_n}{kT}}}; \qquad \left\langle \vec{S}\right\rangle_{\vec{H}} = \frac{\sum_n \left\langle n\left|\vec{S}\right|n\right\rangle e^{-\frac{E_n}{kT}}}{\sum_n e^{-\frac{E_n}{kT}}}$$

Molar magnetization: Solve self-consistently the equation for $\left\langle \vec{S}\right\rangle_{\vec{H}}$ and then substitute E_n into the calculation of $\left\langle \vec{M}\right\rangle_{\vec{H}}$

The susceptibility tensor:

$$\chi_{\alpha\beta} = \chi_{\alpha\beta}^{(0)} + zJ'\sum_{\gamma}\mathbf{A}_{\alpha\gamma}\sum_{\delta}\left(\mathbf{1} - zJ'\mathbf{B}\right)^{-1}_{\gamma\delta}\mathbf{A}_{\delta\beta};$$

where $\chi_{\alpha\beta}^{(0)}$ – susceptibility tensor of the magnetic center alone

$$\mathrm{A}_{\alpha\beta} = \frac{\sum_n e^{-\frac{E_n}{kT}}\sum_{ij}\left[\frac{1}{kT}\left\langle n_i\left|\hat{\mu}_{\beta}\right|n_j\right\rangle\left\langle n_i\left|\hat{S}_{\alpha}\right|n_j\right\rangle - \sum_m \frac{\left\langle n_i\left|\hat{\mu}_{\beta}\right|m_j\right\rangle\left\langle m_j\left|\hat{S}_{\alpha}\right|n_i\right\rangle + \left\langle m_j\left|\hat{\mu}_{\beta}\right|n_i\right\rangle\left\langle n_i\left|\hat{S}_{\alpha}\right|m_j\right\rangle}{E_n - E_m}\right]}{\sum_n e^{-\frac{E_n}{kT}}}$$

$$B_{\alpha\beta} = \frac{\sum_n e^{-\frac{E_n}{kT}}\sum_{ij}\left[\frac{1}{kT}\left\langle n_i\left|\hat{S}_{\beta}\right|n_j\right\rangle\left\langle n_i\left|\hat{S}_{\alpha}\right|n_j\right\rangle - \sum_m \frac{\left\langle n_i\left|\hat{S}_{\beta}\right|m_j\right\rangle\left\langle m_j\left|\hat{S}_{\alpha}\right|n_i\right\rangle + \left\langle m_j\left|\hat{S}_{\beta}\right|n_i\right\rangle\left\langle n_i\left|\hat{S}_{\alpha}\right|m_j\right\rangle}{E_n - E_m}\right]}{\sum_n e^{-\frac{E_n}{kT}}}$$

Ab initio treatment of magnetism of mononuclear complexes and fragments

SINGLE_ANISO program

Magnetic properties

$\chi_{\alpha\beta}(T,H)$ - susceptibility tensor

$\chi(T,H)$ - powder susceptibility

$M_{\alpha}(T,H)$ - magnetization vector

$M(T,H)$ - powder magnetization

- Zeeman splitting

Crystal-Field for Ln

Pseudospin Hamiltonians

$D_{\alpha\beta}$ - second order ZFS tensor

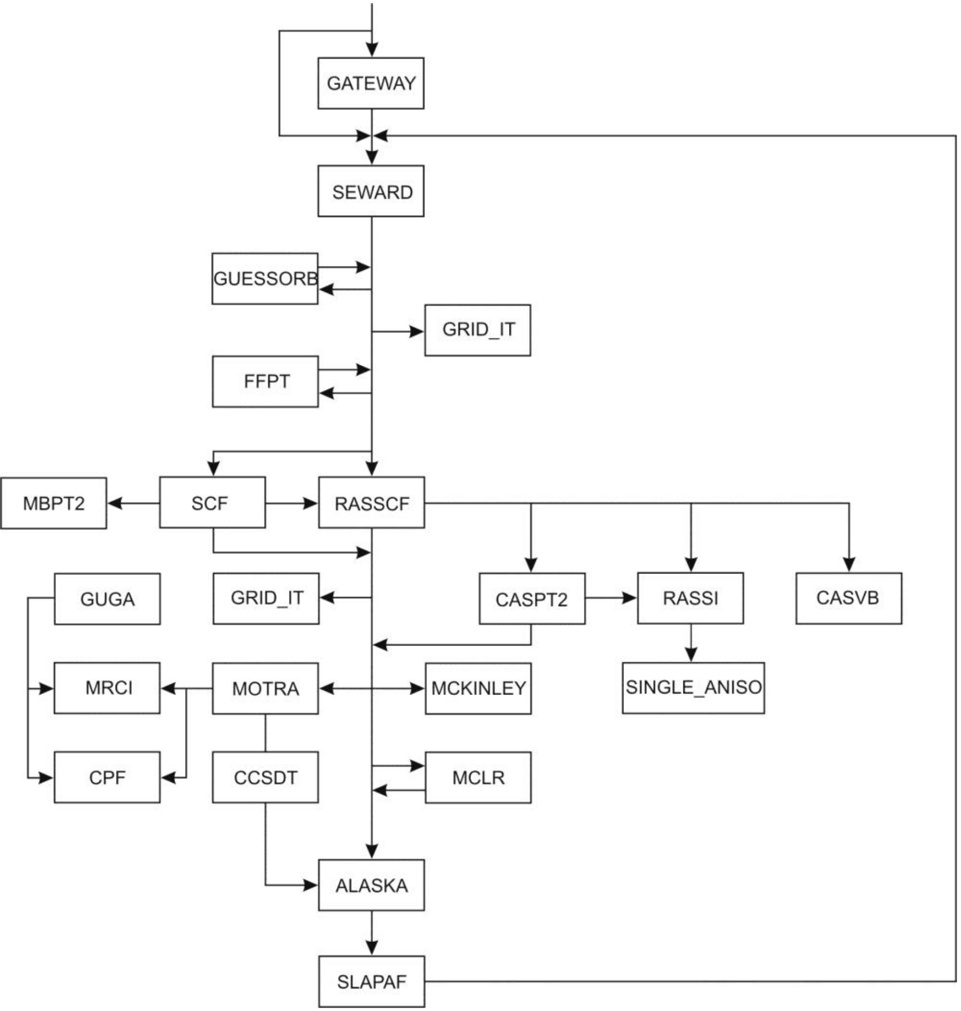
$g_{\alpha\beta}$ - first order gyromagnetic tensor

- Higher-order ZFS and Zeeman Hamiltonians

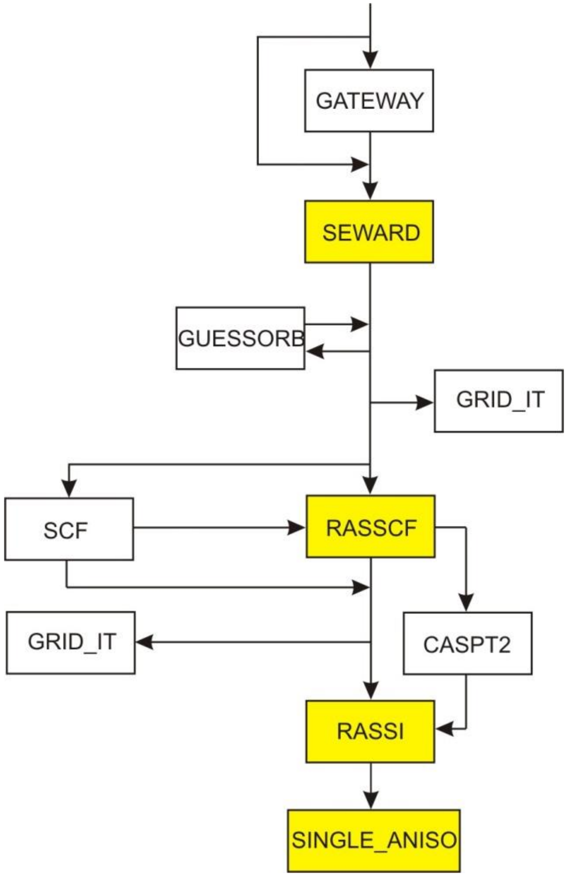
New: - the sign of the product $g_X g_Y g_Z$ is evaluated.

Now implemented in MOLCAS - 7.8

SINGLE_ANISO as a module in MOLCAS



Molcas flowchart



required programs to run before SINGLE_ANISO

Ab initio Crystal Field for Lanthanides

L. Ungur, L. F. Chibotaru, *J. Am. Chem. Soc.* , **2013**, submitted.

- Use the lowest CASSCF/RASSI wave functions $\{\Psi_n\}$ of the complex corresponding to the ground atomic multiplet on Ln

- Make the correspondence $\{\Psi_n\} \rightarrow \{|J,M>\}$:
  - Define the coordinate system and the main quantization axis;
  - Make the correspondence $\{\Psi_n\} \rightarrow \{|J,M>\}$ $\quad \left|\Psi_i\right\rangle = \sum_M c_{iM} \left|\tilde{J}, M\right\rangle$
  - Rewrite the CASSCF/RASSI matrix

$$\mathbf{H}_{\mathbf{CF}} = \sum_i^{2J+1} E_i \left|\Psi_i\right\rangle\left\langle\Psi_i\right| \qquad \left\langle M\right|\mathbf{H}_{\mathbf{CF}}\left|M'\right\rangle = \sum_i^{2J+1} E_i c_{iM}^* c_{iM'}$$

- Use the irreducible tensor technique to extract parameters of the Crystal-Field

Ab initio Crystal Field for Lanthanides

L. Ungur, L. F. Chibotaru, *J. Am. Chem. Soc.* , **2013**, submitted.

- Irreducible tensor operators:

$$O_n^m = \frac{1}{2}\left((-1)^m O_n^{+m} + O_n^{-m}\right) \qquad \Omega_n^m = \frac{1}{2i}\left((-1)^m O_n^{+m} - O_n^{-m}\right)$$

- The Crystal Field Matrix can be recovered as follows:

$$\mathbf{H}_{\mathbf{CF}} = \sum_{n=2,4,6} \alpha_n \left(\sum_{m=0}^{n} B_{nm}^{c} \mathbf{O}_{\mathbf{n}}^{\mathbf{m}} + \sum_{m=1}^{n} B_{nm}^{s} \Omega_{\mathbf{n}}^{\mathbf{m}} \right)$$

This is a **one-to-one mapping** of the *ab initio* calculated energy matrix!

The obtained set of parameters is **unique**!

Implemented in SINGLE_ANISO in MOLCAS 7.8

Ab initio Crystal Field for Lanthanides

L. Ungur, L. F. Chibotaru, *J. Am. Chem. Soc.* , **2013**, submitted.

- Extended Stevens Operators (ESO) as defined in:
  - Rudowicz, C.; J. Phys. C: Solid State Phys.,18 (1985) 1415-1430.
  - in the "EasySpin" function in MATLAB, www.easyspin.org.

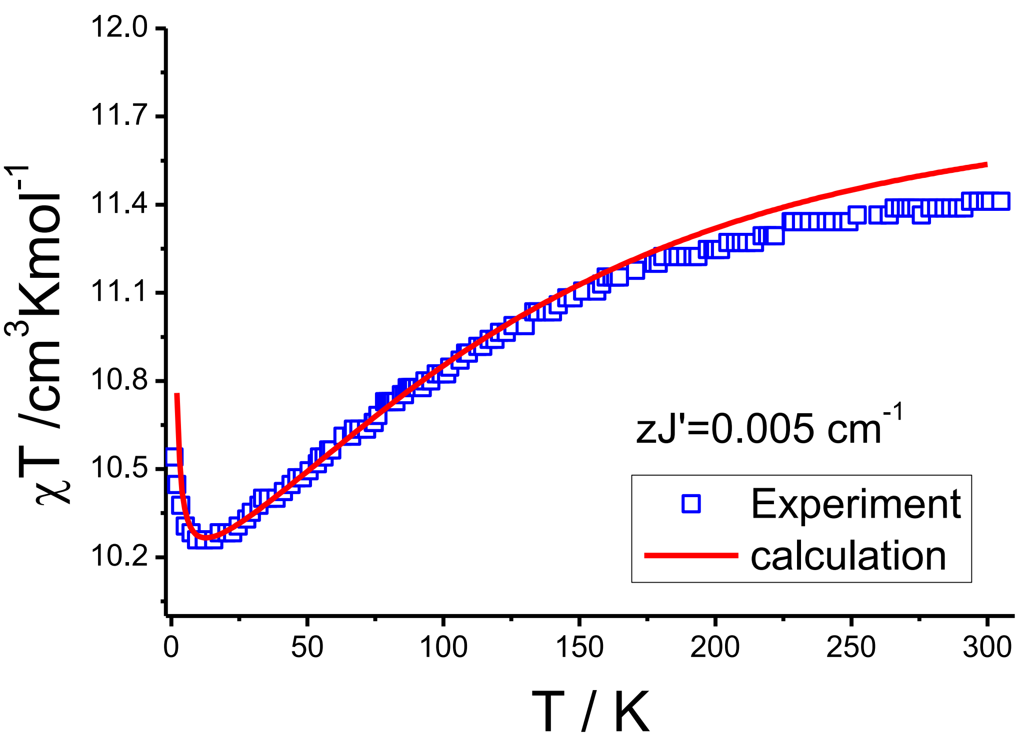
- The Crystal Field Matrix:

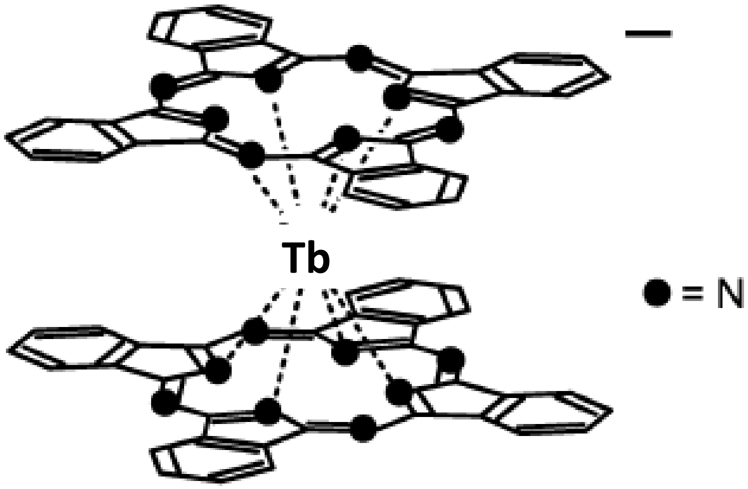
$$\mathbf{H}_{\mathbf{CF}} = \sum_{k,q} B_k^q \mathbf{O}_k^q$$

  - *k* - the rank of the ITO, = 2, 4, 6, 8,10,12.
  - *q* - the component (projection) of the ITO, = -*k*, -*k*+1, ... 0, 1, ... *k*;

Implemented in SINGLE_ANISO in MOLCAS 7.8

Ab initio extracted Crystal-Field: $[Tb(pc)_2]^-$

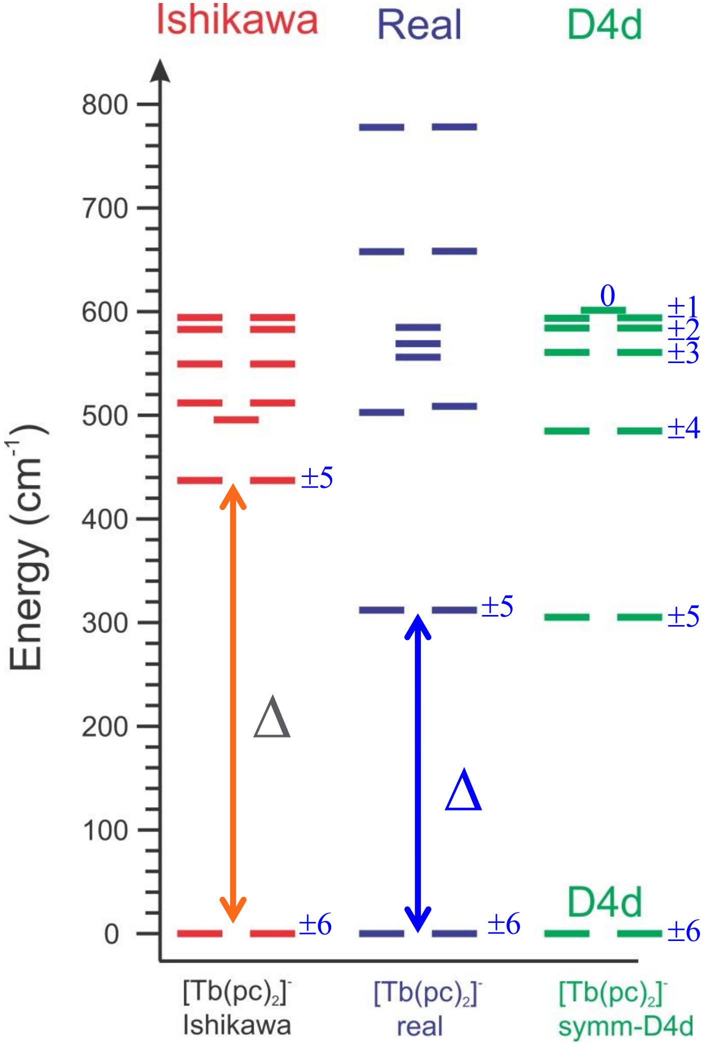




- CASSCF/RASSI calculations of the entire molecule with MOLCAS 7.8 package
- SINGLE_ANISO calculation of magnetic properties

Real *vs* symmetrized $[Tb(pc)_2]^-$

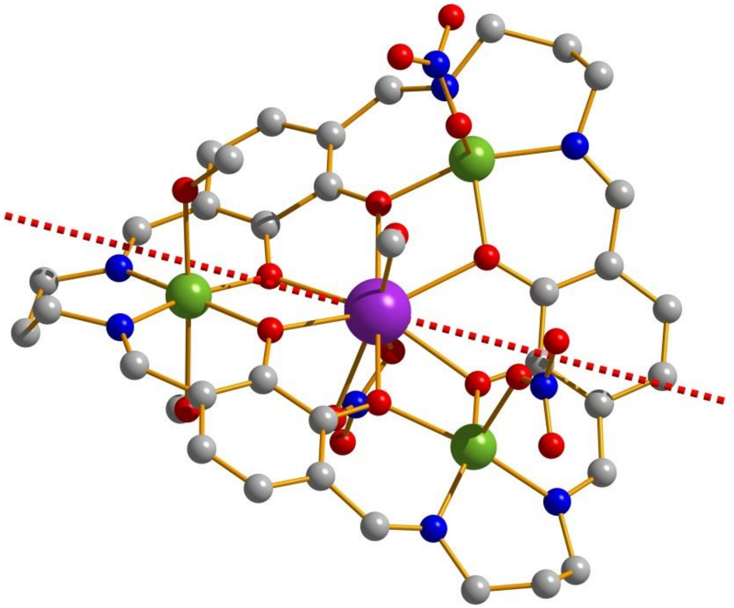
Ab initio

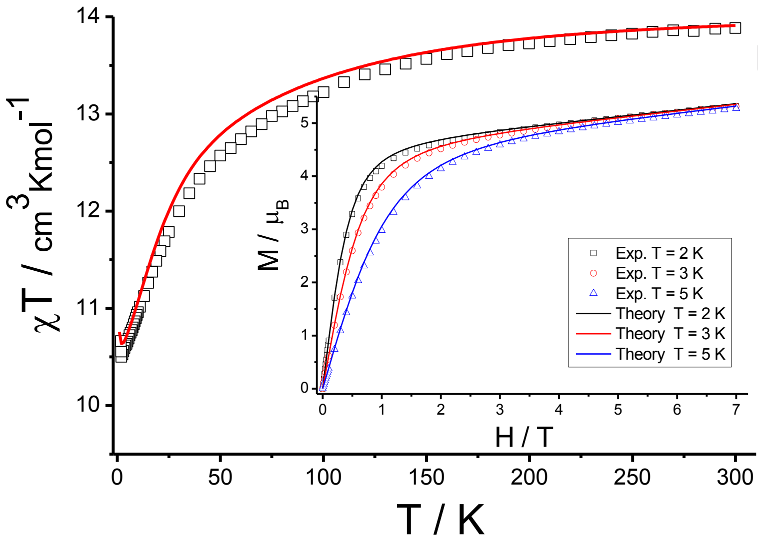


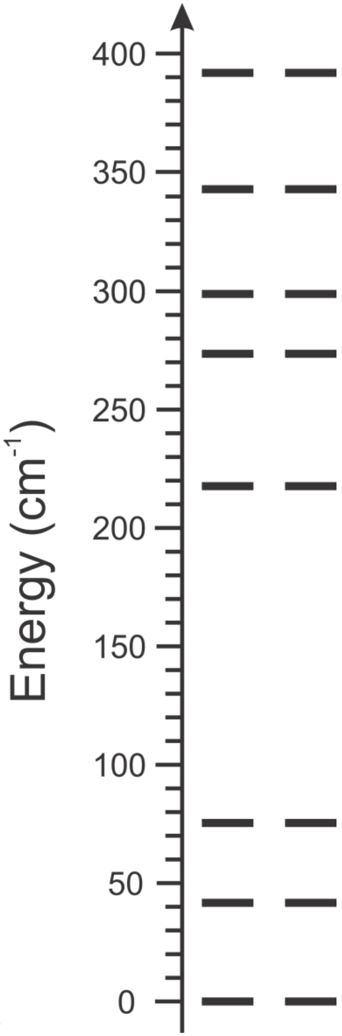
		Ishikawa		**Real**		**Symm- D4d**	
N	**M**	B^c_{nm}	B^s_{nm}	B^c_{nm}	B^s_{nm}	B^c_{nm}	B^s_{nm}
2	0	414.0	------	614.6	------	531.3	------
	1	0.0	0.0	-7.9	15.8	0.0	0.0
	2	0.0	0.0	5.0	227.0	0.0	0.0
4	0	-228.0	------	-98.2	------	-111.9	------
	1	0.0	0.0	-5.0	6.3	0.0	0.0
	2	0.0	0.0	2.3	54.7	0.0	0.0
	3	0.0	0.0	1.1	-2.7	0.0	0.0
	4	10.0	0.0	-18.6	4.7	0.0	0.0
6	0	33.0	------	-13.5	------	-7.3	------
	1	0.0	0.0	0.5	-0.8	0.0	0.0
	2	0.0	0.0	-0.3	25.4	0.0	0.0
	3	0.0	0.0	2.0	-2.0	0.0	0.0
	4	0.0	0.0	-4.3	1.2	0.0	0.0
	5	0.0	0.0	3.7	-3.8	0.0	0.0
	6	0.0	0.0	14.9	24.1	0.0	0.0

$\Delta_{exp}=260\ cm^{-1}$

Ab initio extracted Crystal-Field: Dy^{3+} from $DyZn_3$

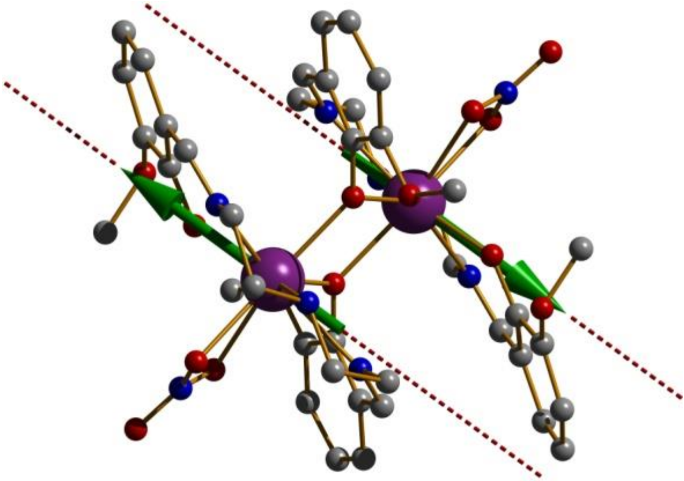


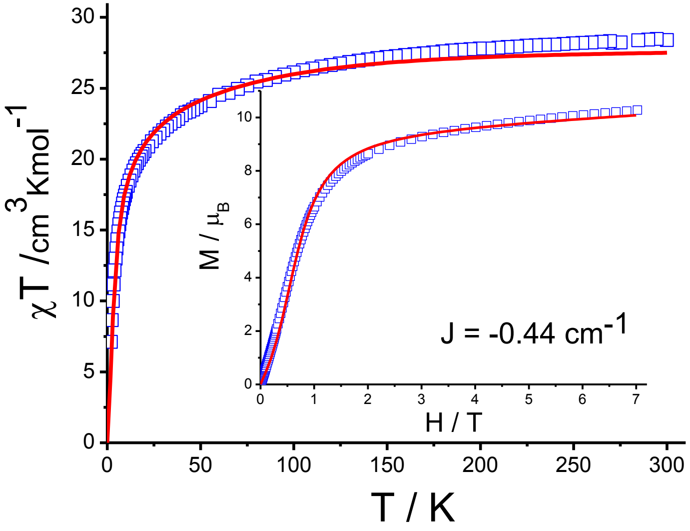


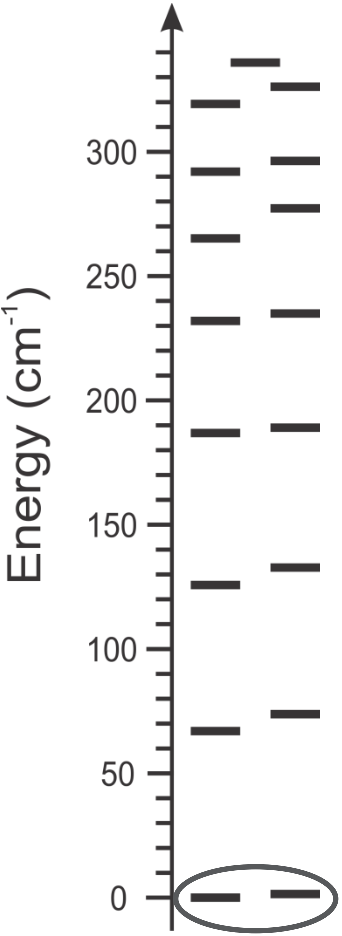


N	M	B^{c}_{nm}	B^{s}_{nm}
2	0	-136.1	------
	1	-11.7	-72.4
	2	352.9	35.1
4	0	-48.5	------
	1	-1.5	0.6
	2	85.9	-14.3
	3	-14.4	-34.0
	4	-97.6	30.2
6	0	11.9	------
	1	5.2	61.7
	2	-4.6	5.2
	3	13.8	50.5
	4	8.3	-1.2
	5	3.4	2.0
	6	22.5	-5.6

Ab initio extracted Crystal-Field: Ho^{3+} from Ho_2

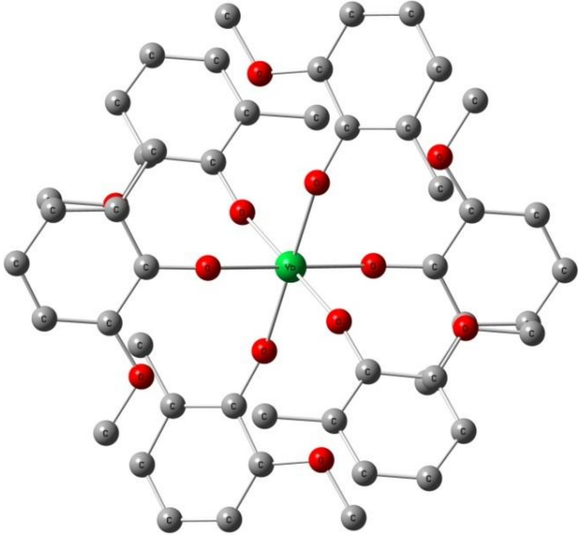


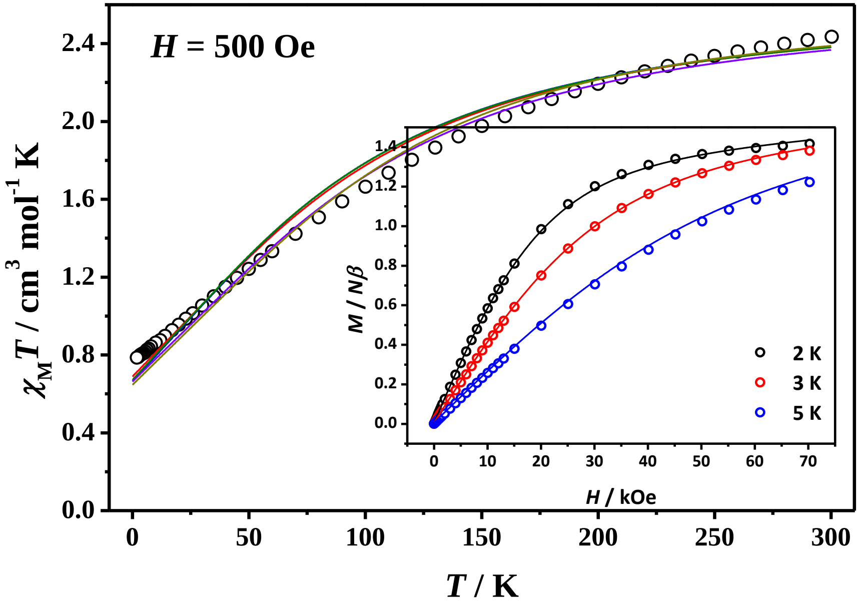




N	M	B^c_{nm}	B^s_{nm}
2	0	302.0	------
	1	32.3	-40.5
	2	130.3	-257.0
4	0	93.0	------
	1	5.4	4.8
	2	17.4	-83.5
	3	8.2	25.6
	4	-46.9	-53.0
6	0	8.6	------
	1	-27.9	25.0
	2	5.2	0.5
	3	-11.6	-30.6
	4	-12.8	5.8
	5	-12.8	-5.6
	6	-17.8	-17.9

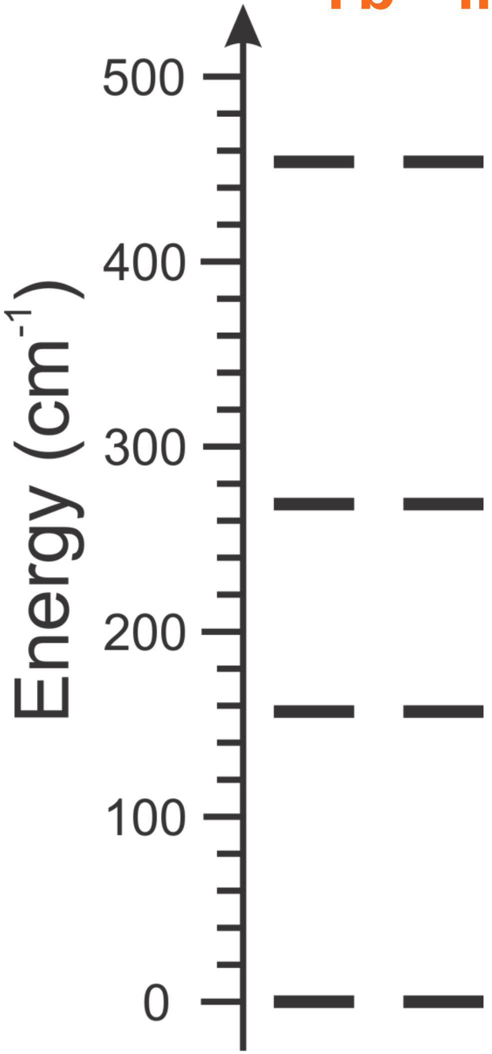
Ab initio extracted Crystal-Field: Yb^{3+} in an almost O_h environment





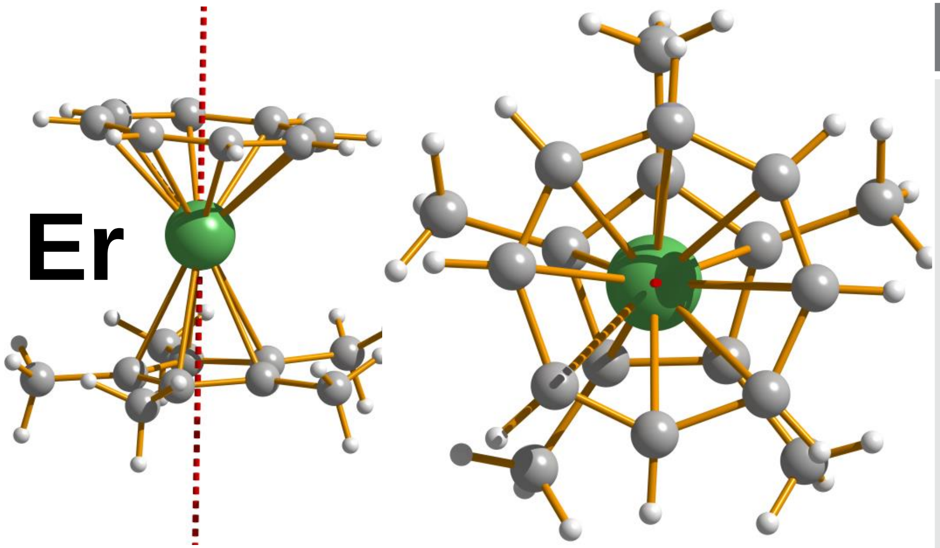
	S=1/2	KD (J=7/2)		g
^{2}F	0.0 49.7 87.7 346.0 477.4 524.8 572.0	0.0	g_X	**3.2098**
			g_Y	**2.6944**
			g_Z	**1.7634**
		187.9	g_X	1.9936
			g_Y	2.2654
			g_Z	3.6065
		300.0	g_X	0.1556
			g_Y	0.7852
			g_Z	3.1483
		485.0	g_X	1.8265
			g_Y	3.2849
			g_Z	4.8065

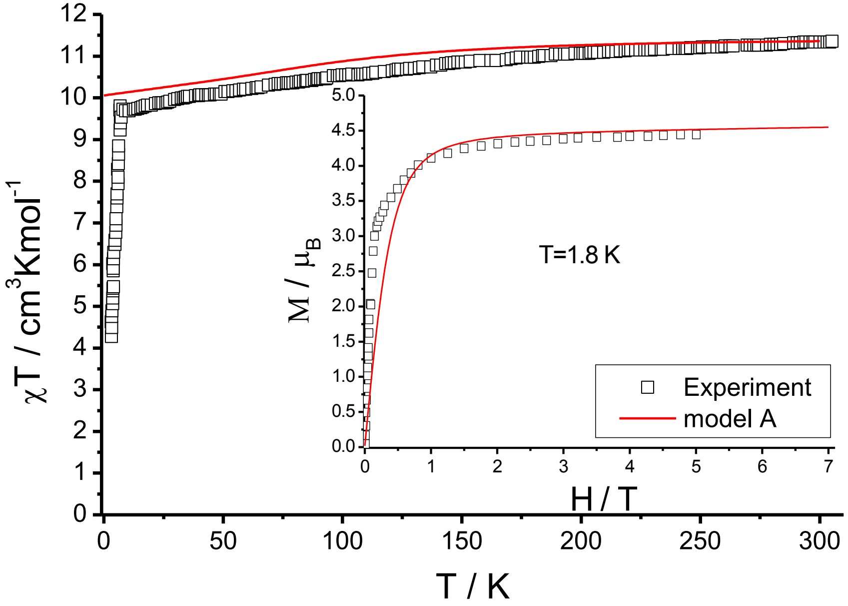
Ab initio extracted Crystal-Field: Yb^{3+} in an almost O_h environment



N	M	B^c_{nm}	B^s_{nm}
2	0	-42.3	-------
	1	-164.9	-11.1
	2	107.8	-50.7
4	0	-542.0	-------
	1	943.7	-881.5
	2	-33.6	858.4
	3	472.1	335.2
	4	1231.9	44.0
6	0	-11.9	-------
	1	7.9	-7.7
	2	1.6	-5.8
	3	-32.3	-27.8
	4	-4.6	3.0
	5	14.4	-6.8
	6	-2.6	24.0

Ab initio extracted Crystal-Field: [Cp*-Er-COT]$^-$

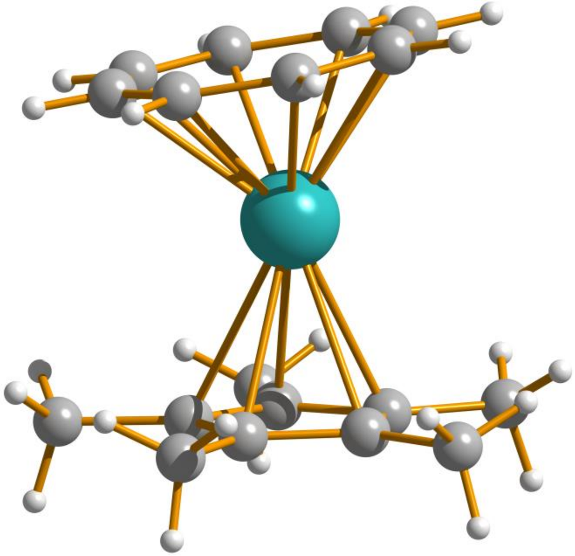


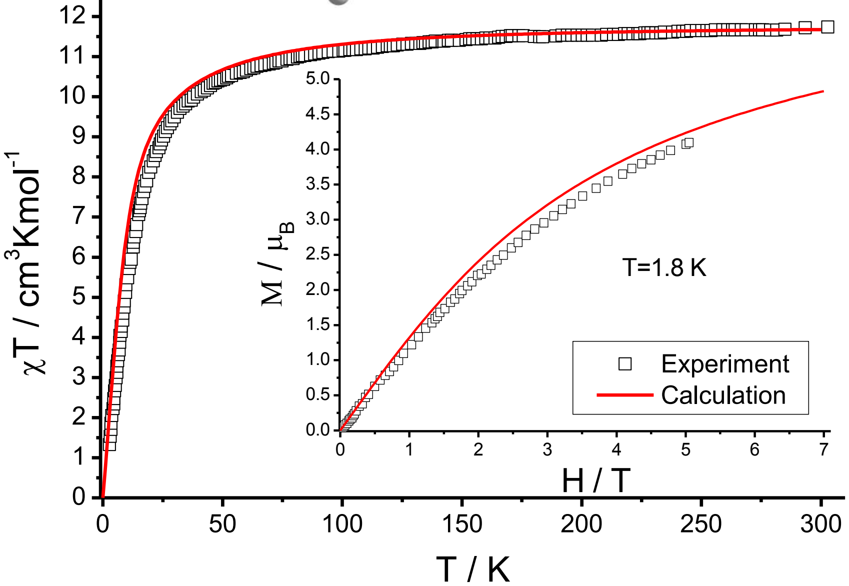


Energy	N	M	B^c_{nm}	B^s_{nm}
0.0	2	0	307.3	-----
0.0		1	157.3	2.7
177.5		2	-33.6	0.4
177.5	4	0	327.6	-----
192.3		1	101.3	5.7
192.3		2	-1.1	-1.6
206.8		3	2.6	0.2
206.8		4	3.3	1.9
225.9 225.9 242.6 242.6 268.5 268.5 319.5 319.5	6	0 1 2 3 4 5 6	22.8 -17.9 -1.2 0.8 -0.2 -9.5 -1.7	----- 0.2 0.0 0.0 0.1 -0.1 0.1

g_X = 0.0000849
g_Y = 0.0009137
g_Z = 17.9366602

Ab initio extracted Crystal-Field: [Cp*-Tb-COT]$^-$

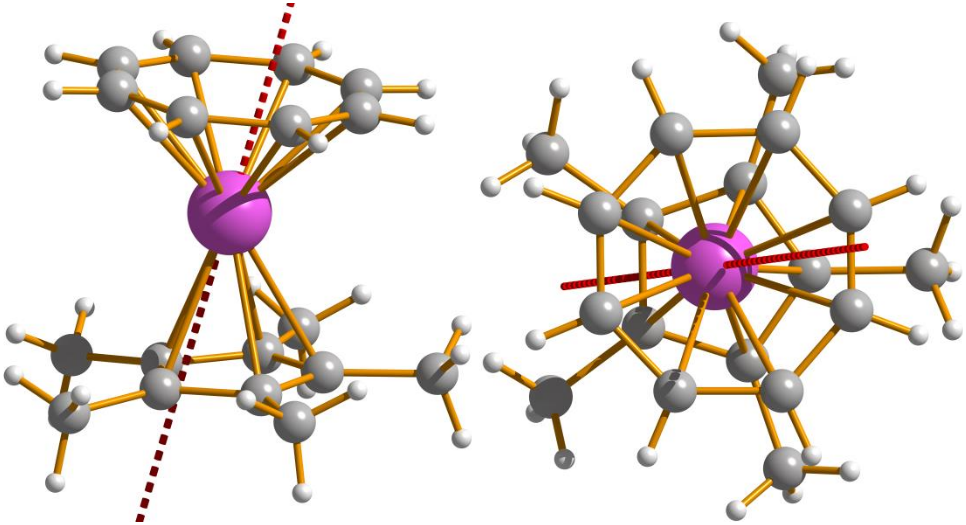


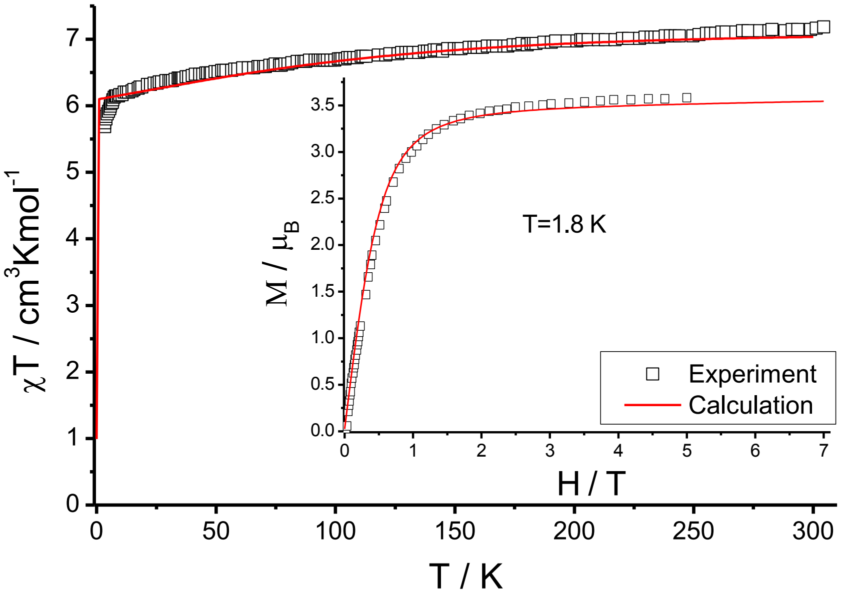


Energy
0.0
17.0
31.6
86.9
88.9
149.5
149.9
167.1
167.1
234.5
234.7
341.4
341.4

N	M	B^c_{nm}	B^s_{nm}
2	0	-211.8	-------
	1	15.3	-36.7
	2	-18.0	2.1
4	0	-66.6	-------
	1	-6.3	147.9
	2	60.4	5.1
	3	1.8	-13.6
	4	-0.8	-0.1
6	0	27.0	-------
	1	-2.4	3.7
	2	32.8	4.9
	3	6.3	-27.6
	4	-7.2	-1.0
	5	-2.0	4.5
	6	3.5	2.3

Ab initio extracted Crystal-Field: [Cp*-Tm-COT]$^-$





Energy	N	M	B^c_{nm}	B^s_{nm}
0.0	2	0	-317.0	-----
0.0		1	1.9	-3.2
215.2		2	38.8	64.8
215.8	4	0	-90.6	-----
295.9		1	-20.4	35.7
306.2		2	1.9	3.3
348.4		3	1.8	0.0
358.6		4	0.0	0.0
360.6	6	0	-8.3	-----
404.7		1	-14.1	25.4
411.4		2	5.6	9.1
436.4		3	5.1	0.0
437.7		4	0.1	0.0
		5	-1.9	-3.2
		6	-2.7	0.1

Semi *ab initio* calculation of magnetic properties of polynuclear complexes

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

- Employing a model fragmentation of the polynuclear complex.

- *Ab initio* treatment of individual fragments:

CASSCF → (CASPT2) → RASSI-SO → SINGLE_ANISO

SINGLE_ANISO produces an input file for POLY_ANISO.

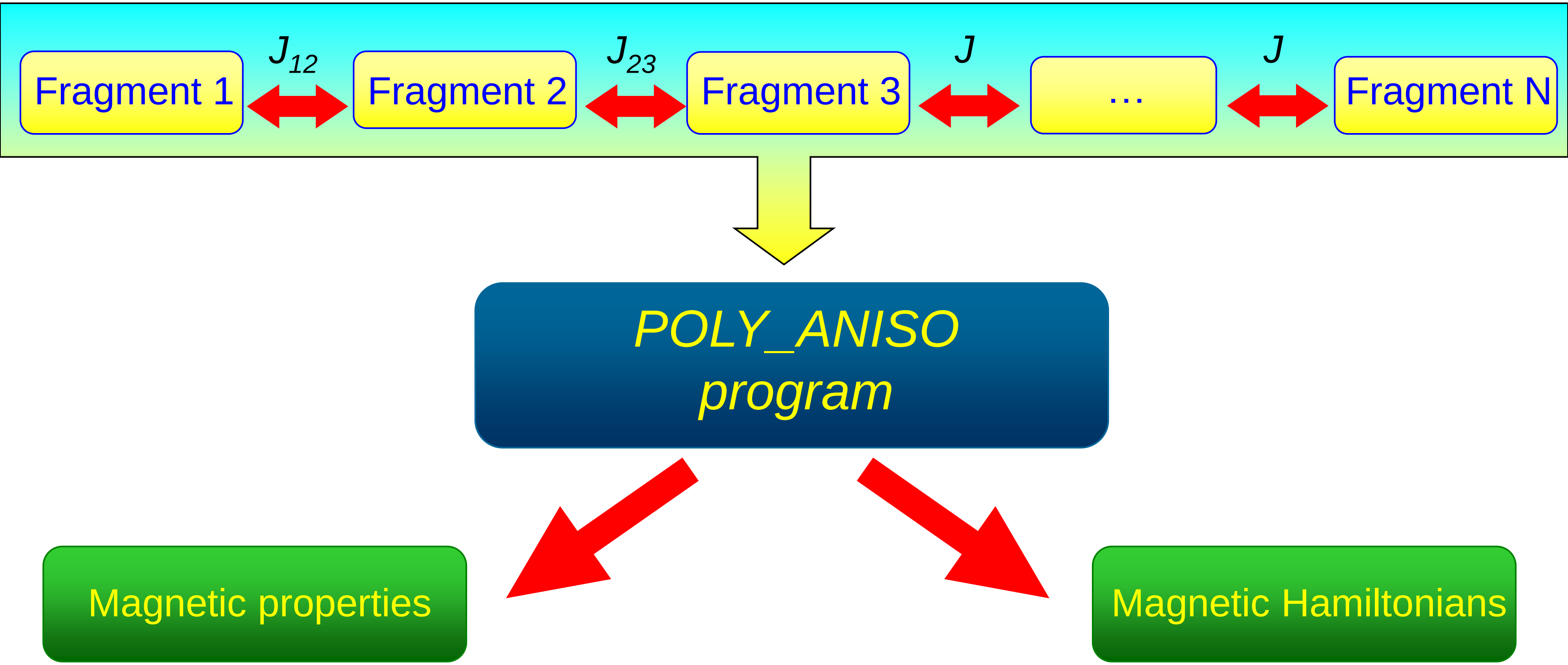
- Lines model: → Treatment of exchange interactions

1. Introduce an effective $\hat{\mathrm{H}}_{\mathrm{exch}} = -\sum_{ij} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j$
2. The dipolar magnetic coupling can be considered exact: $\frac{\mu_B^2\left(\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2 - 3(\boldsymbol{\mu}_1\mathbf{r}_1)\cdot(\boldsymbol{\mu}_2\mathbf{r}_2)\right)}{r^3}$
3. Diagonalize $\hat{\mathrm{H}}_{\mathrm{exch}}$ in the basis of lowest spin–orbit states on sites $\{\Gamma_i\}\otimes\{\Gamma_j\}$

(J_{ij} - fitting parameters)

4. Calculate all magnetic properties and parameters of magnetic Hamiltonians

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



Fragment 1 J_{12} Fragment 2 J_{23} Fragment 3 J … J Fragment N

POLY_ANISO
program

Magnetic properties

Magnetic Hamiltonians

$\chi_{\alpha\beta}(T,H);\ \chi(T,H)$

$M_{\alpha}(T,H);\ M(T,H)$

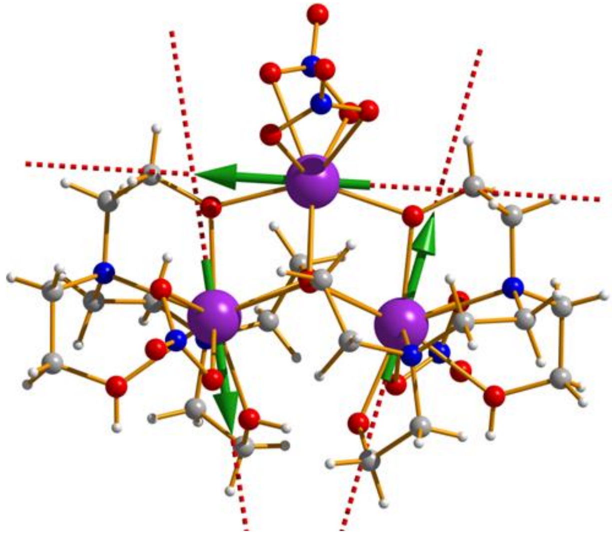
Zeeman splitting

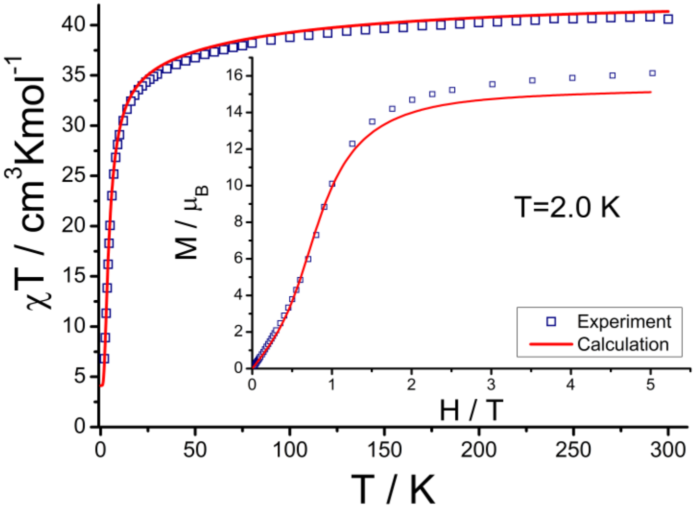
$D_{\alpha\beta}$ - tensor; $g_{\alpha\beta}$ - tensor

- Higher-order ZFS and gyromagnetic tensors

Dy_3 isosceles triangle:

Y.-X. Wang, W. Shi, H. Li, Y. Song, L. Fang, Y. Lan, A. K. Powell, W. Wernsdorfer, L. Ungur, L. F. Chibotaru, M. Shenc, P. Cheng, *Chem. Sci.*, **2012**, *3*, 3366-3370.



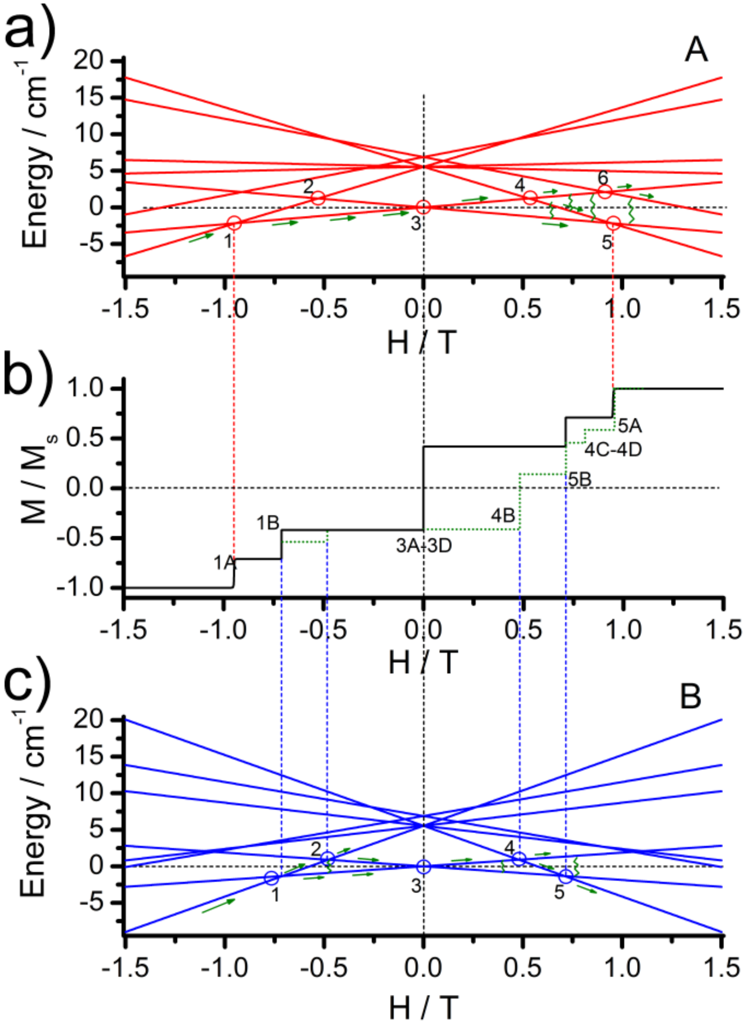


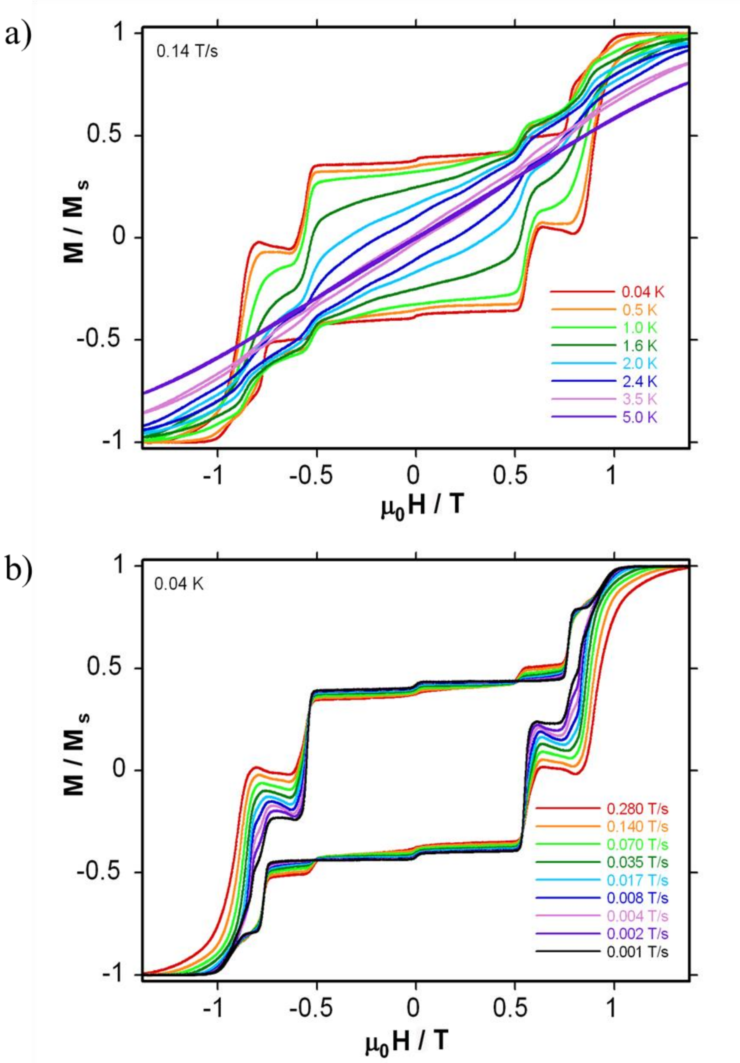
KD	Dy1	Dy2	Dy3
1	0.000	0.000	0.000
2	108.778	239.577	225.784
3	202.571	459.170	485.721
4	286.735	546.174	634.670
5	322.050	587.706	672.382
6	385.913	642.290	711.704
7	458.087	709.691	753.551
8	524.465	979.880	834.336
Main values of the g-tensor for the lowest doublets			
g_X	0.0528	0.0020	0.0024
g_Y	0.0793	0.0024	0.0028
g_Z	19.7092	19.8247	19.8525
Angle between the main magnetic axis g_Z and the Dy_3 plane (degrees)			
	6.657	0.568	10.398

Interaction	J_{exch}	J_{dip}	$J_{exch} + J_{dip}$
1-2	1.608	5.428	7.036
2-3	1.608	5.293	6.901
3-1	1.311	2.959	4.270

Dy_3 isosceles triangle:

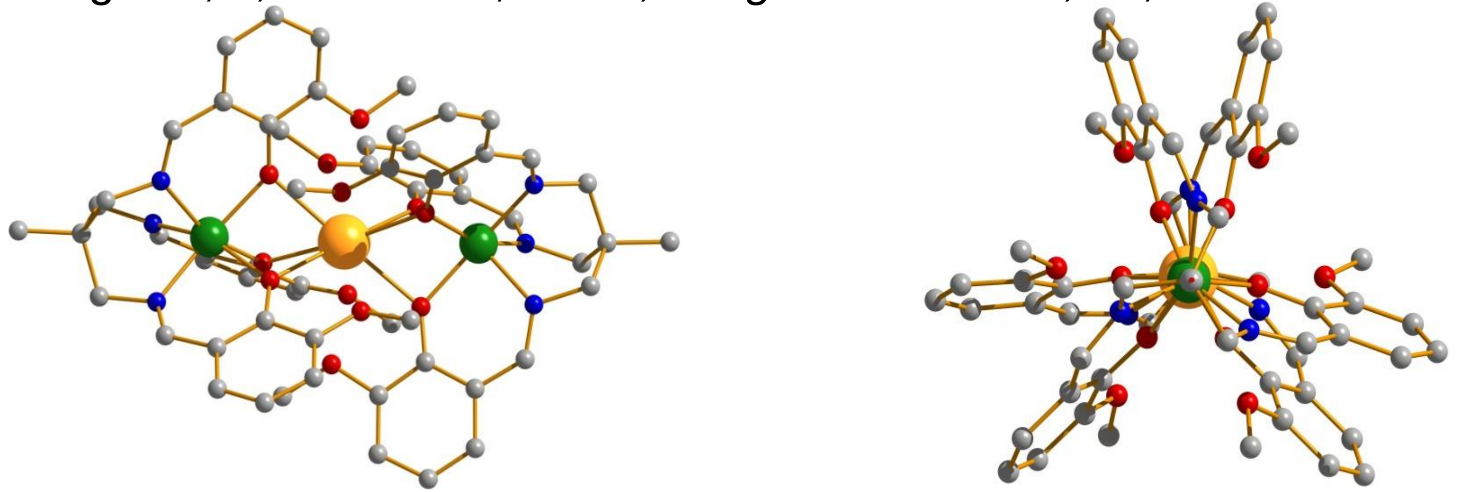
Y.-X. Wang, W. Shi, H. Li, Y. Song, L. Fang, Y. Lan, A. K. Powell, W. Wernsdorfer, L. Ungur, L. F. Chibotaru, M. Shenc, P. Cheng, *Chem. Sci.*, **2012**, *3*, 3366-3370.

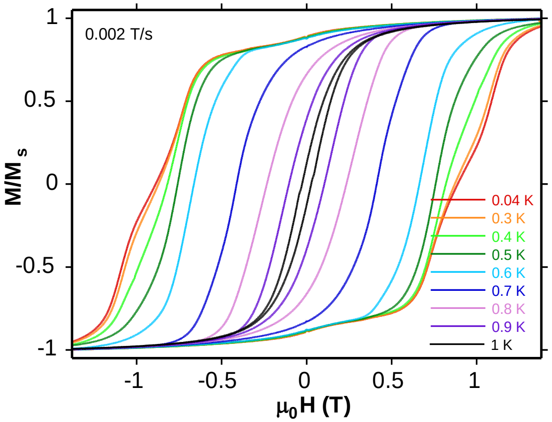




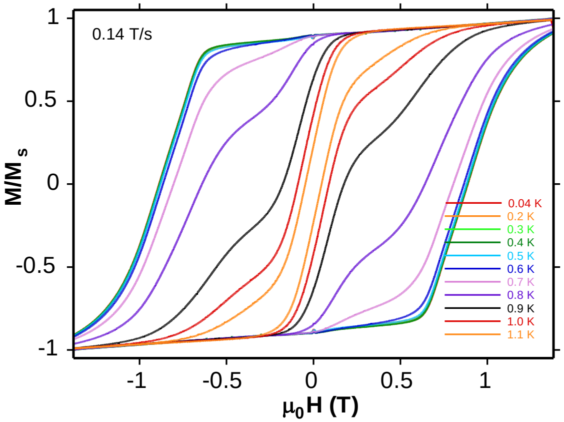
Isostructural series of mixed 4f-3d SMM’s : Co-Ln-Co, Ln = Gd, Tb, Dy

Yamaguchi,T.; Costes JP, et. al., *Inorg. Chem.* **2010**, *49*, 9125–9135.

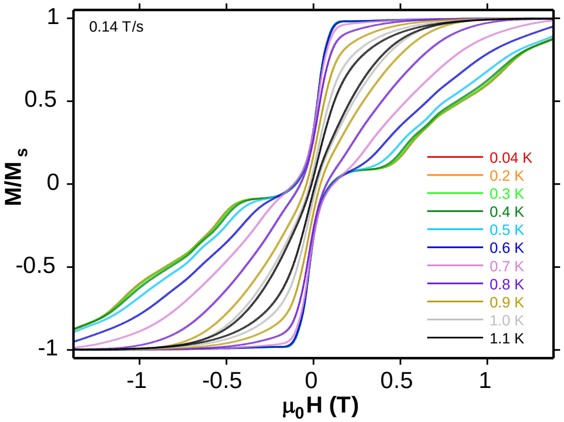




Co-Gd-Co

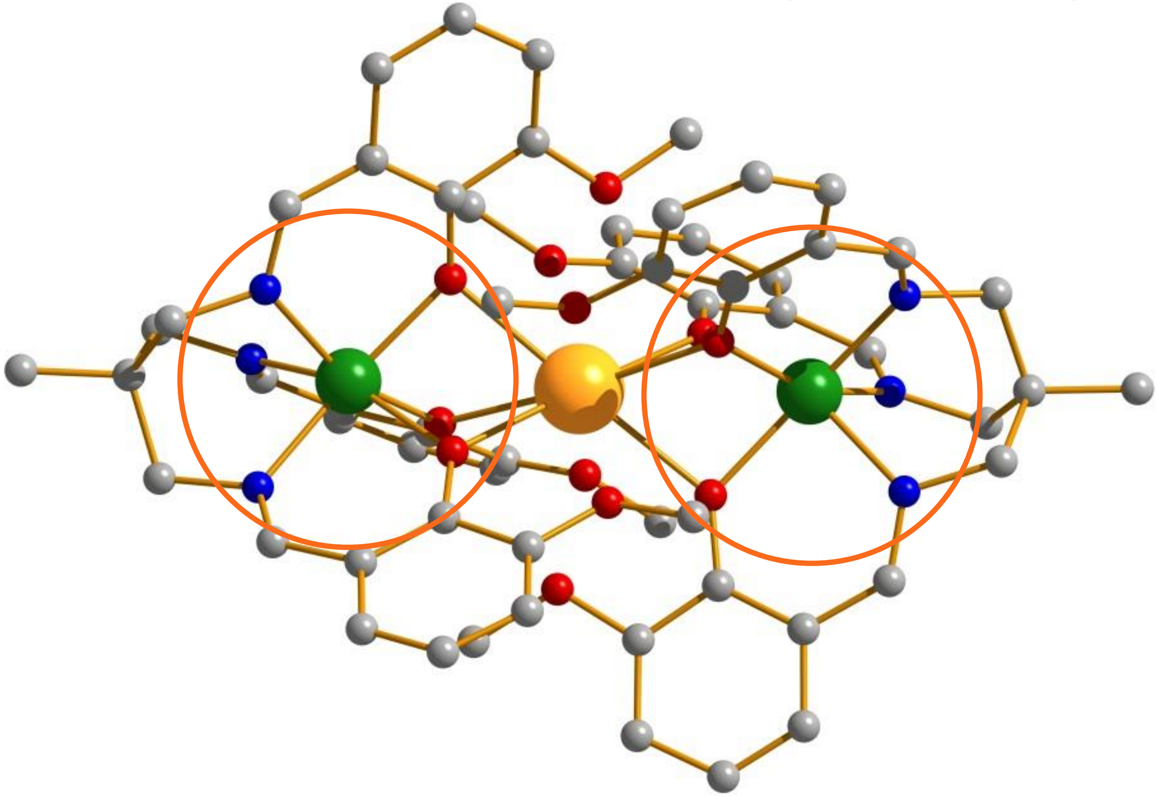


Co-Tb-Co



Co-Dy-Co

Isostructural series of mixed 4f-3d SMM's : Co-Ln-Co, Ln = Gd, Tb, Dy



The approximate symmetry of the first coordination sphere of Co^{2+} centers is a distorted trigonal prism

The SMM behavior is mainly due to the strong anisotropy on Co^{2+} centers

Co-Gd-Co > Co-Tb-Co > Co-Dy-Co

Ab initio calculation of Co fragments (CASSCF-calculations)

2S+1	CoGdCo		CoTbCo		CoDyCo	
	Co1	Co2	Co1	Co2	Co1	Co2
4	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**
	49.6	**120.0**	**170.6**	**89.0**	**95.2**	**56.6**
	3410.2	3551.6	3477.2	3412.4	4142.0	4033.8
	7868.3	8384.0	8153.9	7985.3	7195.5	7510.5
	8167.9	8417.1	8175.9	8224.8	7381.0	7567.4
	8959.1	9364.8	9082.5	8994.5	8262.2	8512.8
	16091.0	16784.3	16287.7	16157.6	13963.9	14595.8
	23555.8	23965.2	23691.6	23732.3	23018.0	23165.0
	23655.9	24108.9	23814.0	23784.3	23083.2	23382.7
	23980.6	24166.4	24083.1	23893.2	23314.7	23497.5
2	14594.1	14367.8	14594.9	14592.0	15865.5	15530.8
	14783.7	14488.8	14751.3	14723.2	16017.1	15640.9
	19775.6	19798.0	19790.9	19828.5	19925.2	19861.0
	19854.3	19873.0	19956.5	19864.4	19946.6	19933.8
	20396.0	20473.7	20475.6	20409.4	20382.5	20395.8
	21012.2	21125.9	21105.9	21036.6	21020.6	21039.2
	21134.3	21161.3	21159.1	21152.1	21063.3	21074.8
	21643.7	21710.8	21699.4	21648.4	22124.4	22031.2
	25940.3	26268.2	26080.7	26015.9	25266.8	25498.3
	26112.0	26282.4	26201.6	26129.2	26035.9	26105.2
	…	…	…	…	…	…

Ab initio calculation of Co fragments (RASSI –calculations)

	CoGdCo		**CoTbCo**		**CoDyCo**	
	Co1	Co2	Co1	Co2	Co1	Co2
	0.0	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**
	248.6	**242.2**	**235.8**	**246.5**	**257.8**	**258.6**
	536.5	**549.0**	**565.8**	**544.1**	**570.6**	**558.8**
	852.0	**856.1**	**868.0**	**857.3**	**896.0**	**883.8**
	3771.5	3880.7	3786.4	3756.8	4467.1	4381.7
	3847.3	3954.7	3862.0	3832.8	4549.2	4460.8
	8240.1	8646.4	8393.3	8328.2	7528.7	7815.0
	8303.5	8749.4	8498.0	8400.1	7626.4	7931.2
	8612.5	8856.8	8602.7	8654.1	7842.7	8059.1
	8676.8	8967.1	8713.2	8726.5	7932.6	8171.5
	9398.1	9767.6	9469.3	9415.4	8712.6	8976.7
	9426.7	9794.4	9495.7	9445.9	8732.9	8988.8

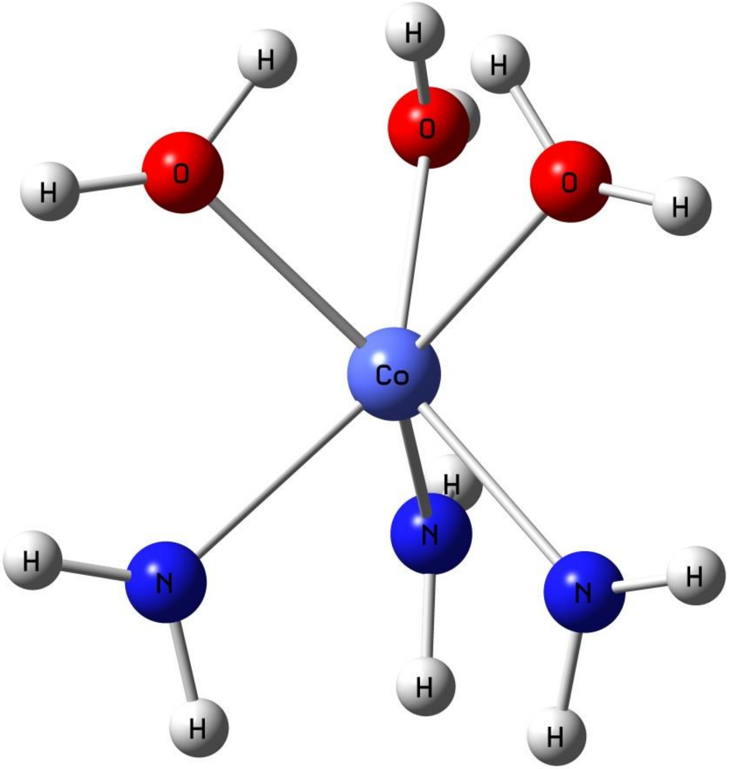
Ab initio calculation of Co fragments (SINGLE_ANISO)

KD		CoGdCo			
		Co1		Co2	
		E	g	E	g
1	g_X	0.000	0.4197	0.000	0.4066
	g_Y		0.4233		0.4155
	g_Z		**9.2928**		**9.2570**
2	g_X	248.686	0.5064	242.221	1.4578
	g_Y		0.9614		1.9117
	g_Z		5.2042		4.9886
3	g_X	536.549	0.6653	549.084	0.9821
	g_Y		0.8109		1.6751
	g_Z		1.2123		1.7170
4	g_X	852.041	0.0425	856.123	0.0063
	g_Y		0.0639		0.0258
	g_Z		2.7922		2.8266

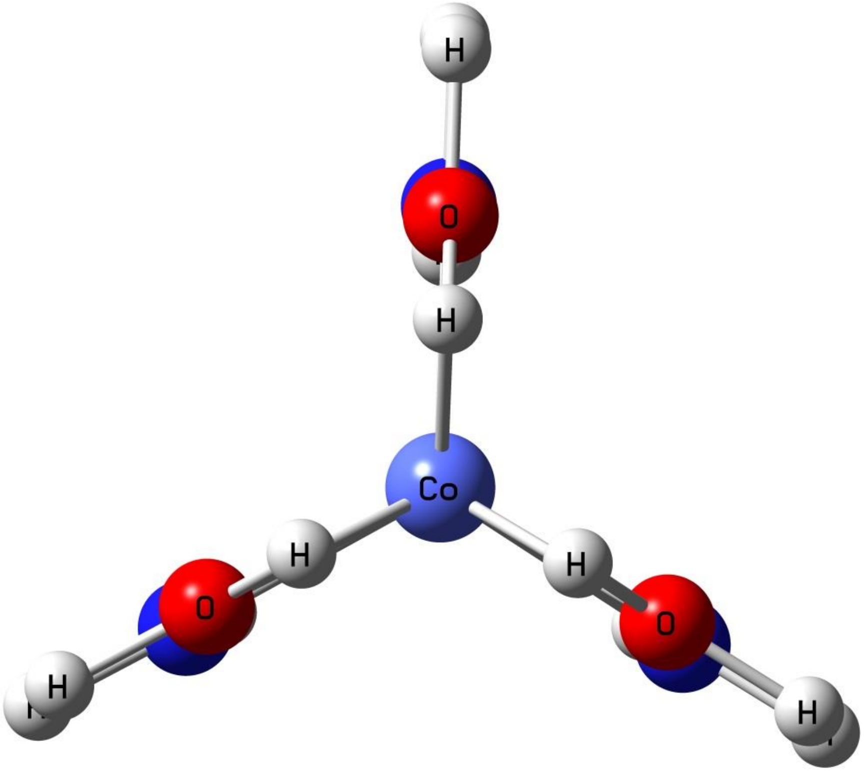
The Co^{2+} centers have an unquenched orbital moment in the ground state:

$$\langle L_Z \rangle \approx 1.6 \mu_B$$

Unquenched orbital moment of Co^{2+} in a perfect prismatic environment



CoO_3N_3 core has original geometry from X-Ray experiment. The H atoms saturate the broken O-C or N-C bonds.



$CoO_3N_3H_{12}$ fragment was symmetrized towards C_{3v} symmetry.

Unquenched orbital moment of Co^{2+} in a perfect prismatic environment

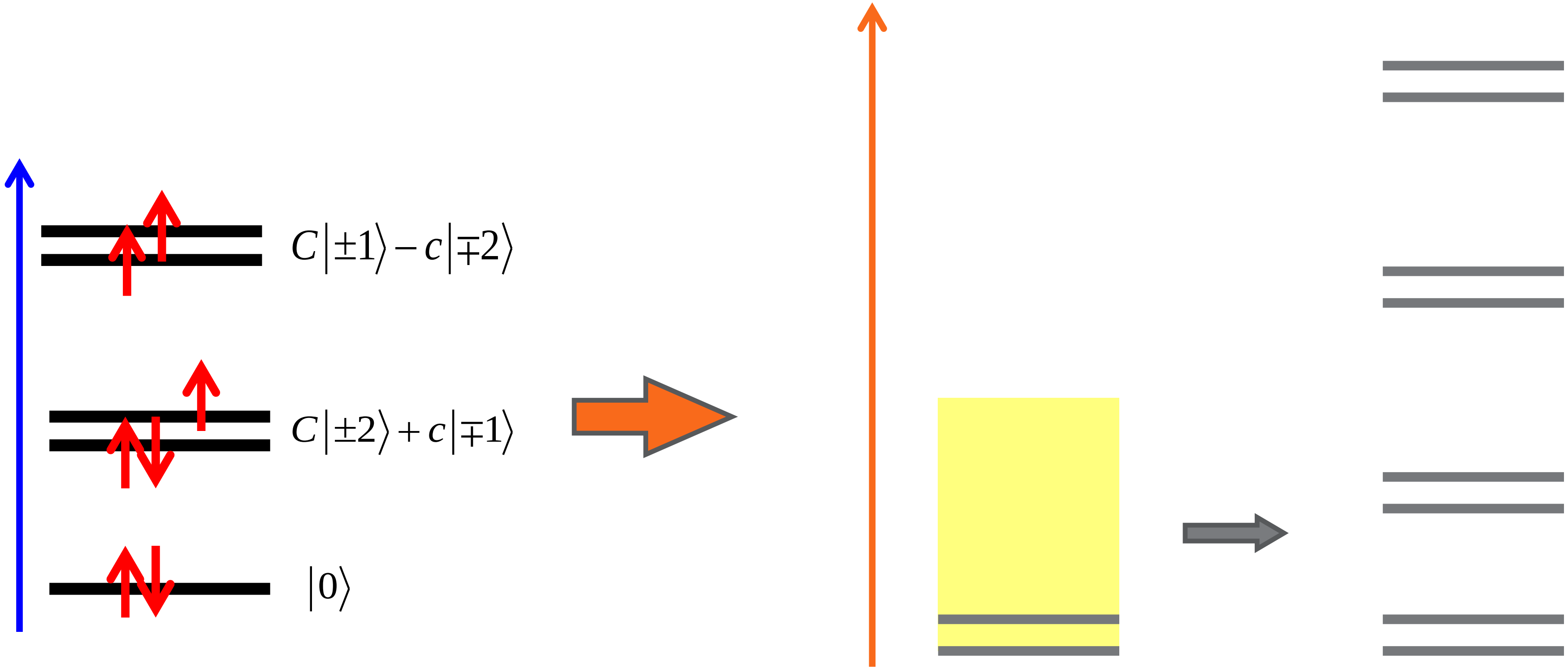
	Original geometry			
	SFS	KD		g
4	**0.0**	0.0	g_X	0.1858
	78.3		g_Y	0.1865
	4637.8		g_Z	**9.5528**
	5814.7	260.2	g_X	1.0181
	6009.0		g_Y	1.2129
	7592.0		g_Z	5.4266
	…			
2	16956.6	573.5	g_X	1.0486
	17122.0		g_Y	1.1674
	19763.0		g_Z	1.4079
	19785.4	908.7	g_X	0.0265
	20304.1		g_Y	0.0537
	20775.8		g_Z	2.5510
	…			

$\langle L_Z \rangle \approx 1.8\mu_B$

	Symmetrized C_{3v} geometry			
	SFS	KD		g
4	**0.000**	0.0	g_X	0.0066
	0.010		g_Y	0.0066
	5508.5		g_Z	**9.8032**
	5508.5	286.3	g_X	0.0032
	7512.6		g_Y	0.0035
	7810.3		g_Z	5.8128
	9433.9			
	…			
2	19124.9	613.3	g_X	0.0001
	19124.9		g_Y	0.0001
	19658.3		g_Z	1.8155
	19658.3	976.7	g_X	0.0108
	20423.0		g_Y	0.0108
	20423.0		g_Z	2.1910
	…			

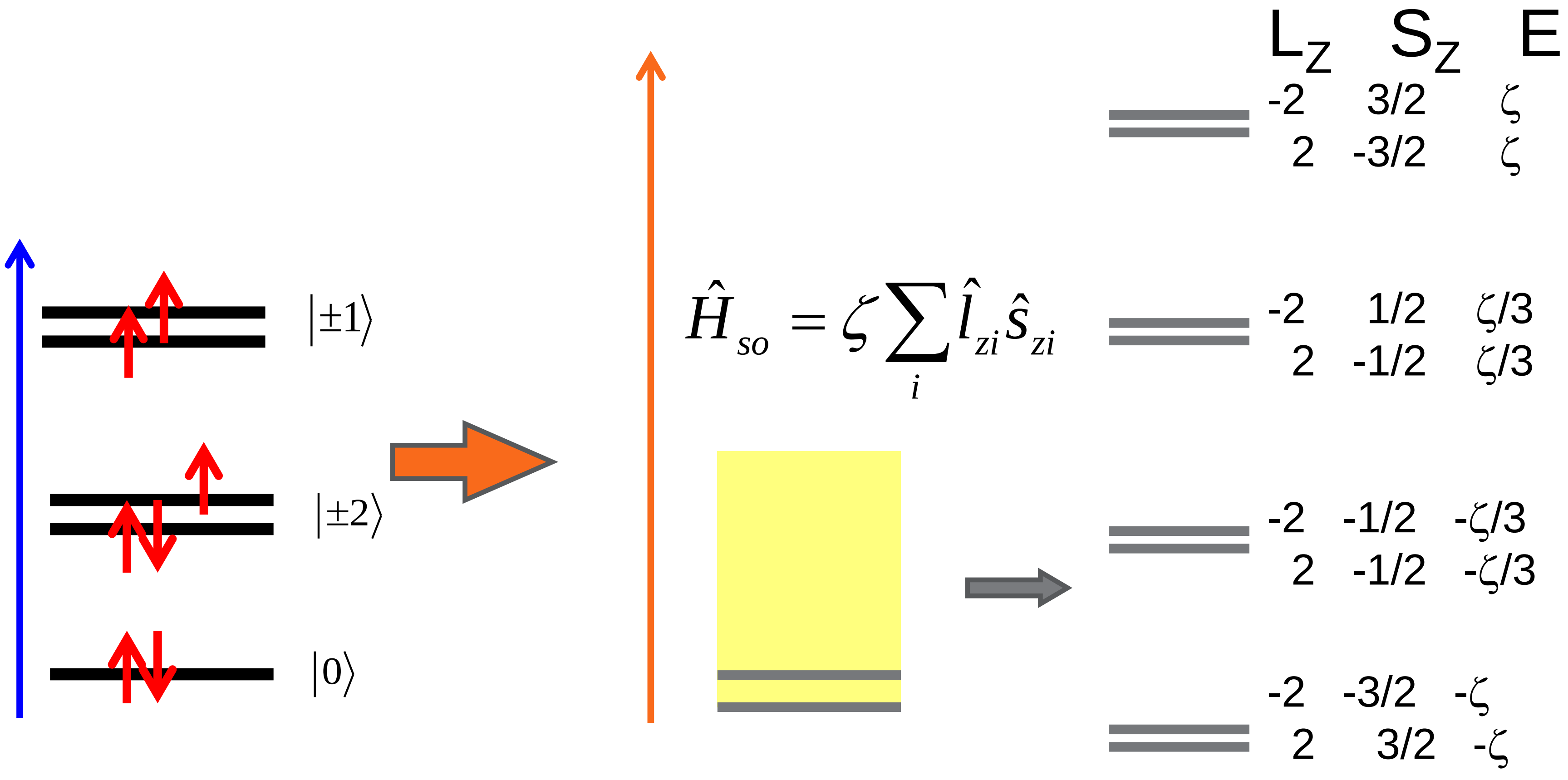
$\langle L_Z \rangle \approx 1.9\mu_B$

Unquenched orbital moment of Co^{2+} in a perfect trigonal prismatic environment



For a d^7 configuration
in a trigonal prismatic environment → $\langle L_z \rangle < 2$

Unquenched orbital moment of Co^{2+} in a perfect higher-order prismatic environment



$$\hat{H}_{so} = \zeta \sum_i \hat{l}_{zi} \hat{s}_{zi}$$

L_Z	S_Z	E
-2	3/2	ζ
2	-3/2	ζ
-2	1/2	$\zeta/3$
2	-1/2	$\zeta/3$
-2	-1/2	$-\zeta/3$
2	-1/2	$-\zeta/3$
-2	-3/2	$-\zeta$
2	3/2	$-\zeta$

higher-order

$$\langle L_Z \rangle = 2$$

Unquenched orbital moment of $[Mo(CN)_7]^{4-}$

Mironov, L.F. Chibotaru, A. Ceulemans, *J. Am. Chem. Soc*, 2003, 125, 9750-9760

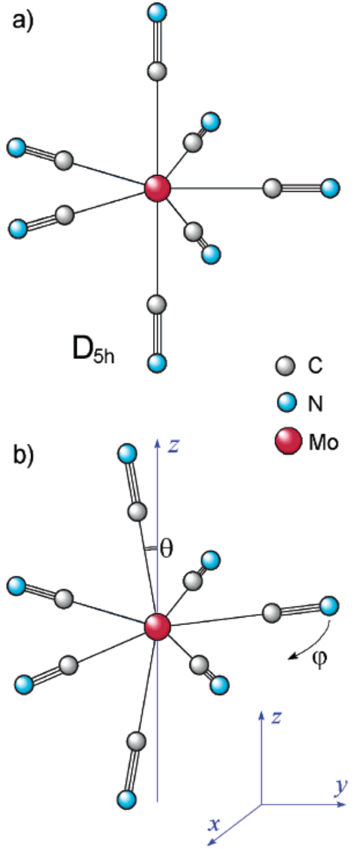


Figure 1. Structure of the $[Mo(CN)_7]^{4-}$ heptacyanometalate: (a) the idealized pentagonal bipyramid (D_{5h} symmetry group) and (b) real distorted bipyramid; the polar (θ) and azimuthal (φ)

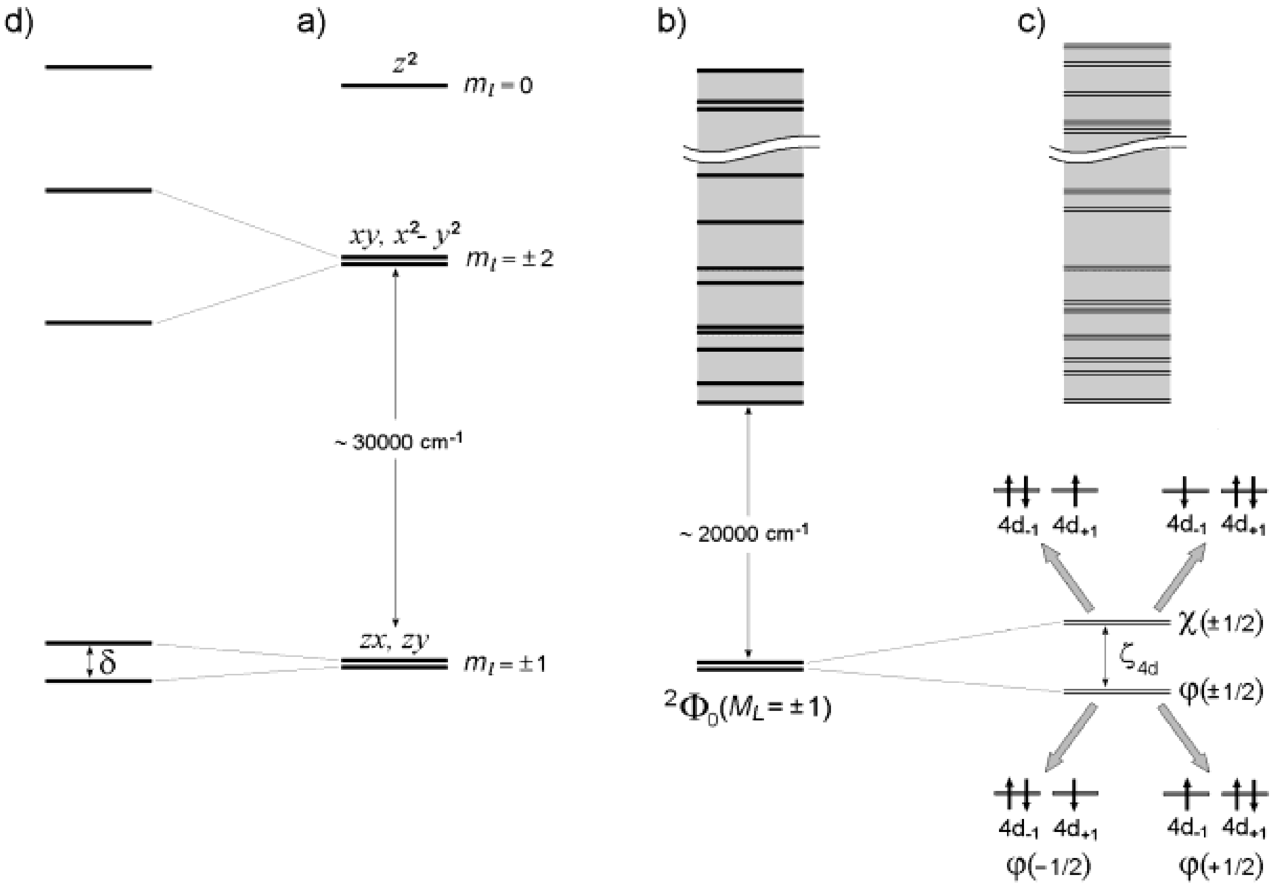
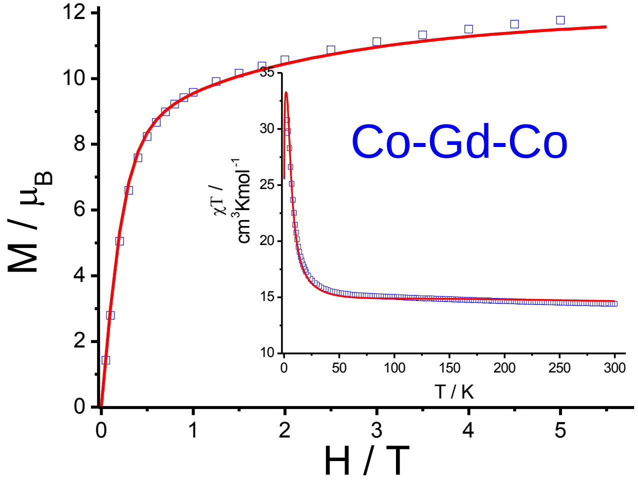
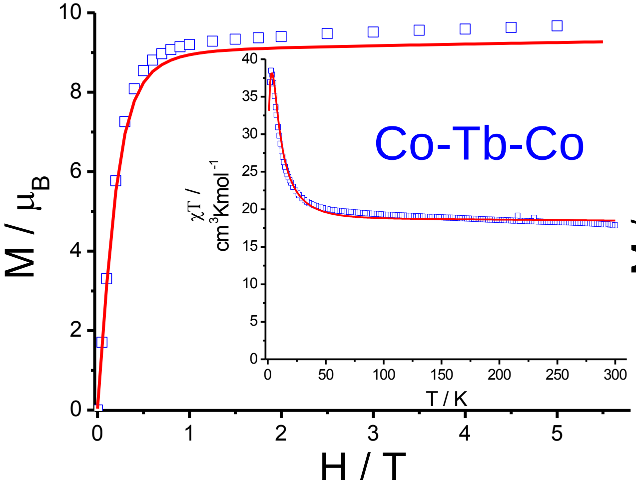


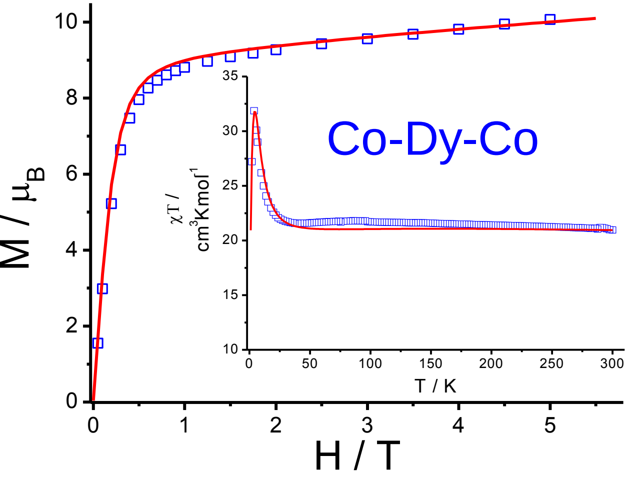
Figure 3. Electronic structure of the $[Mo(CN)_7]^{4-}$ heptacyanometalate: (a) Mo 4d orbital energies in a regular D_{5h} pentagonal bipyramid, (b) the energy spectrum of MoIII($4d^3$) in the D_{5h} bipyramid without spin-orbit coupling, and (c) the energy spectrum of MoIII($4d^3$) in the D_{5h} bipyramid with the spin-orbit coupling. The orbital composition of the ground φ(±1/2) and excited χ(± 1/2) Kramers doublets is shown; (d) the splitting of 4d orbital energies in distorted $[Mo(CN)_7]^{4-}$ complexes.

Ab initio based calculation of magnetism in Co-Gd-Co, Co-Tb-Co and Co-Dy-Co (Poly_Aniso routine)

$$H_{exch} = -J_1\left(S_{Co1}\cdot S_{Ln} + S_{Co2}\cdot S_{Ln}\right) - J_2 S_{Co1}\cdot S_{Co2}$$





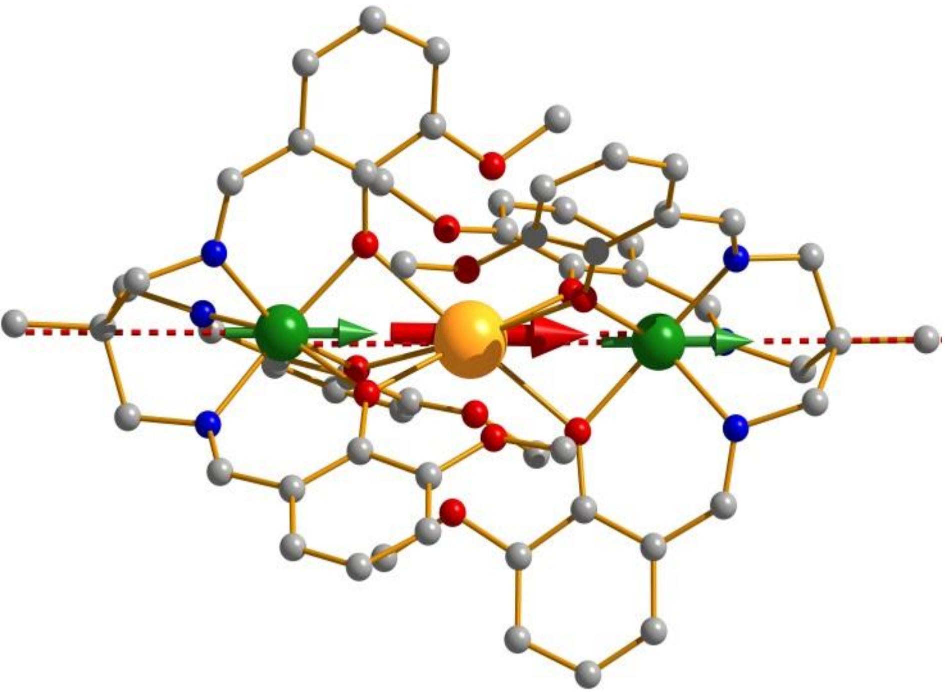


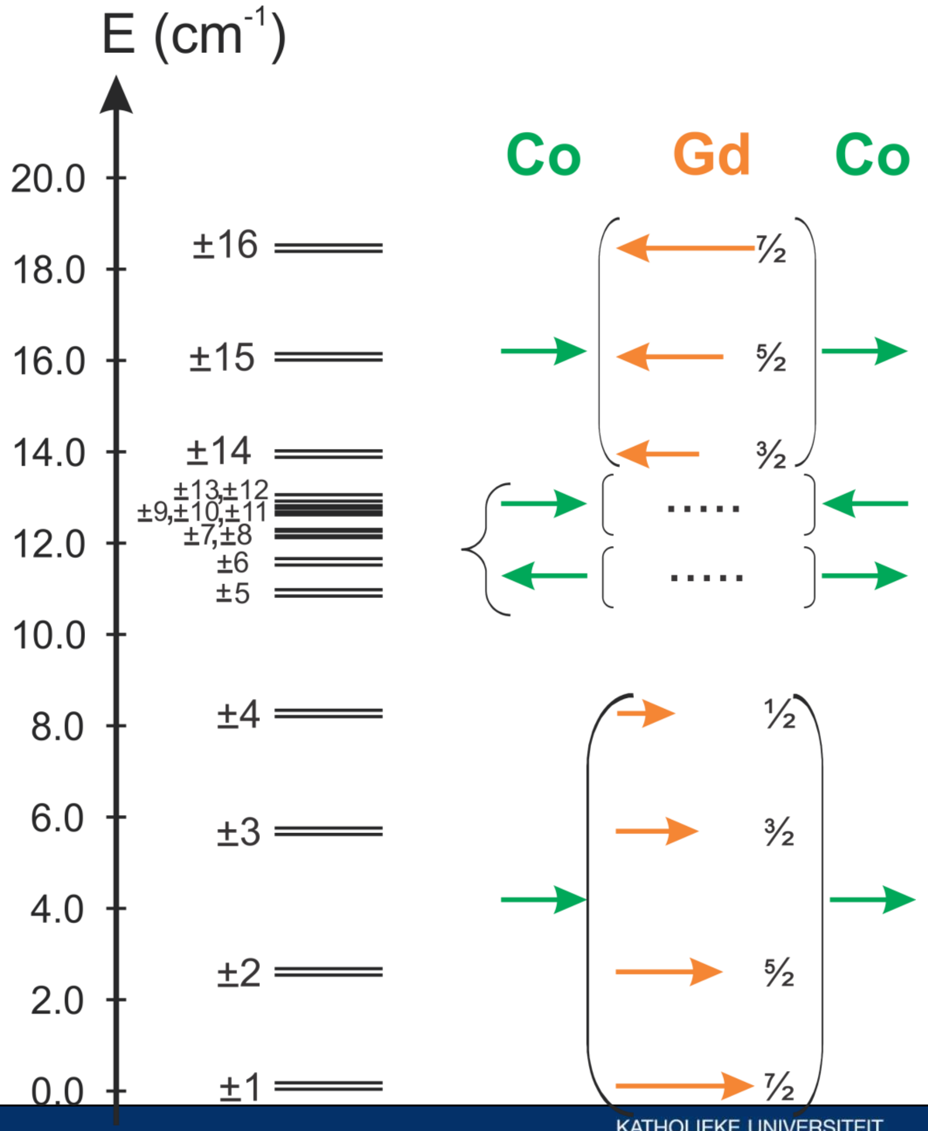
J_1 = +0.90 cm^{-1}
J_2 = +0.60 cm^{-1}
zJ = -0.0005 cm^{-1}

J_1 = +1.10 cm^{-1}
J_2 = +0.35 cm^{-1}
zJ = -0.0005 cm^{-1}

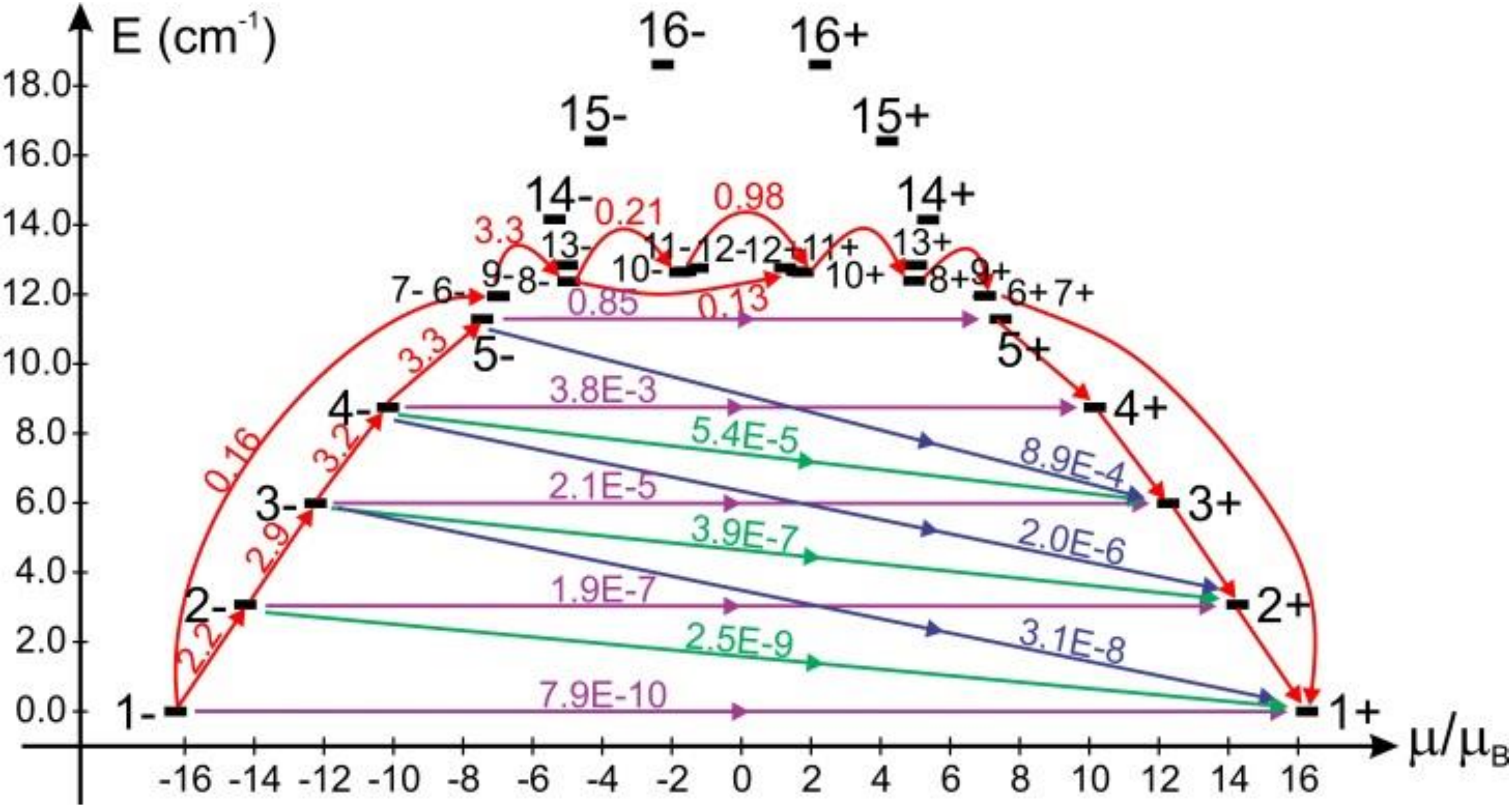
J_1 = +1.25 cm^{-1}
J_2 = +0.50 cm^{-1}
zJ = -0.0005 cm^{-1}

Exchange energy spectrum and orientation of local magnetic moments in Co-Gd-Co

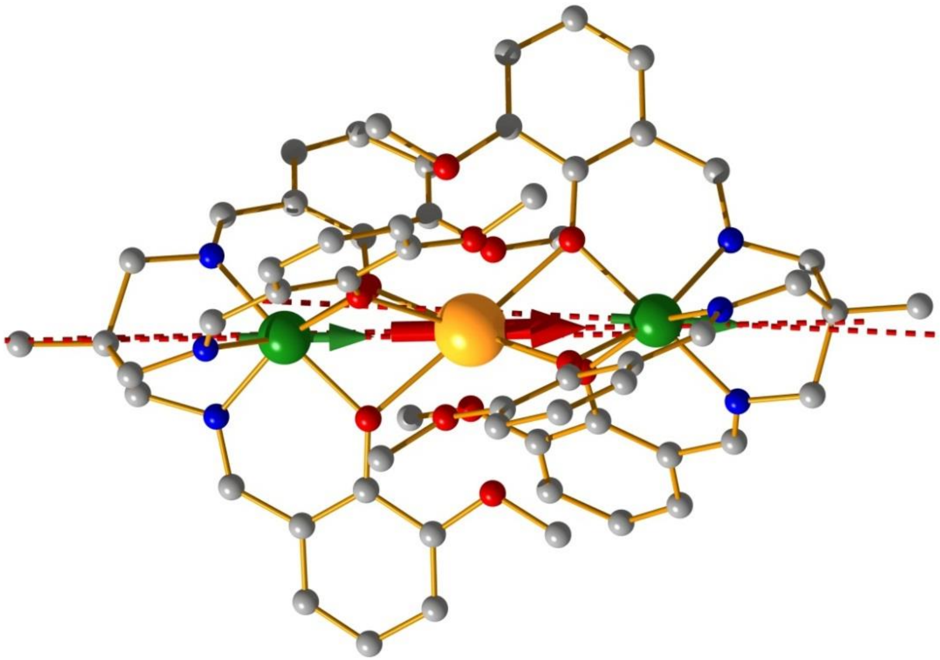


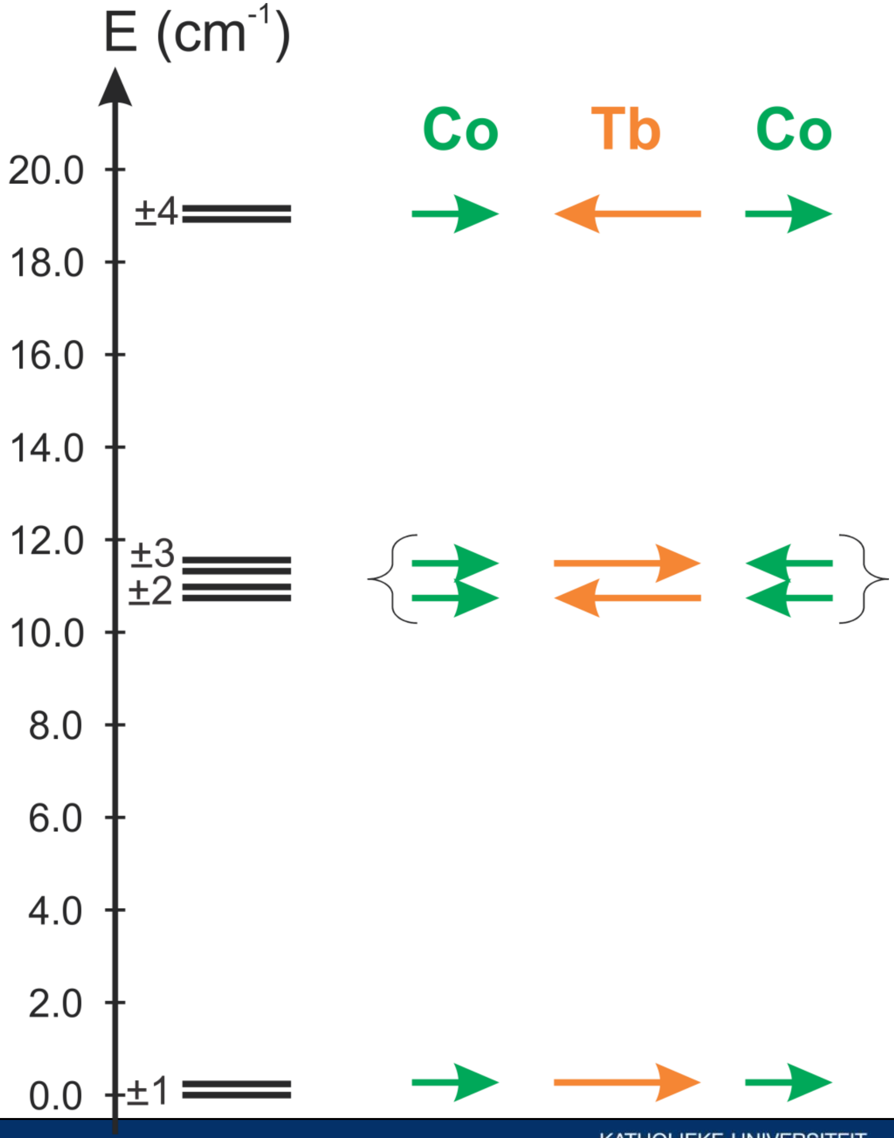


Structure of the blocking barrier in Co-Gd-Co

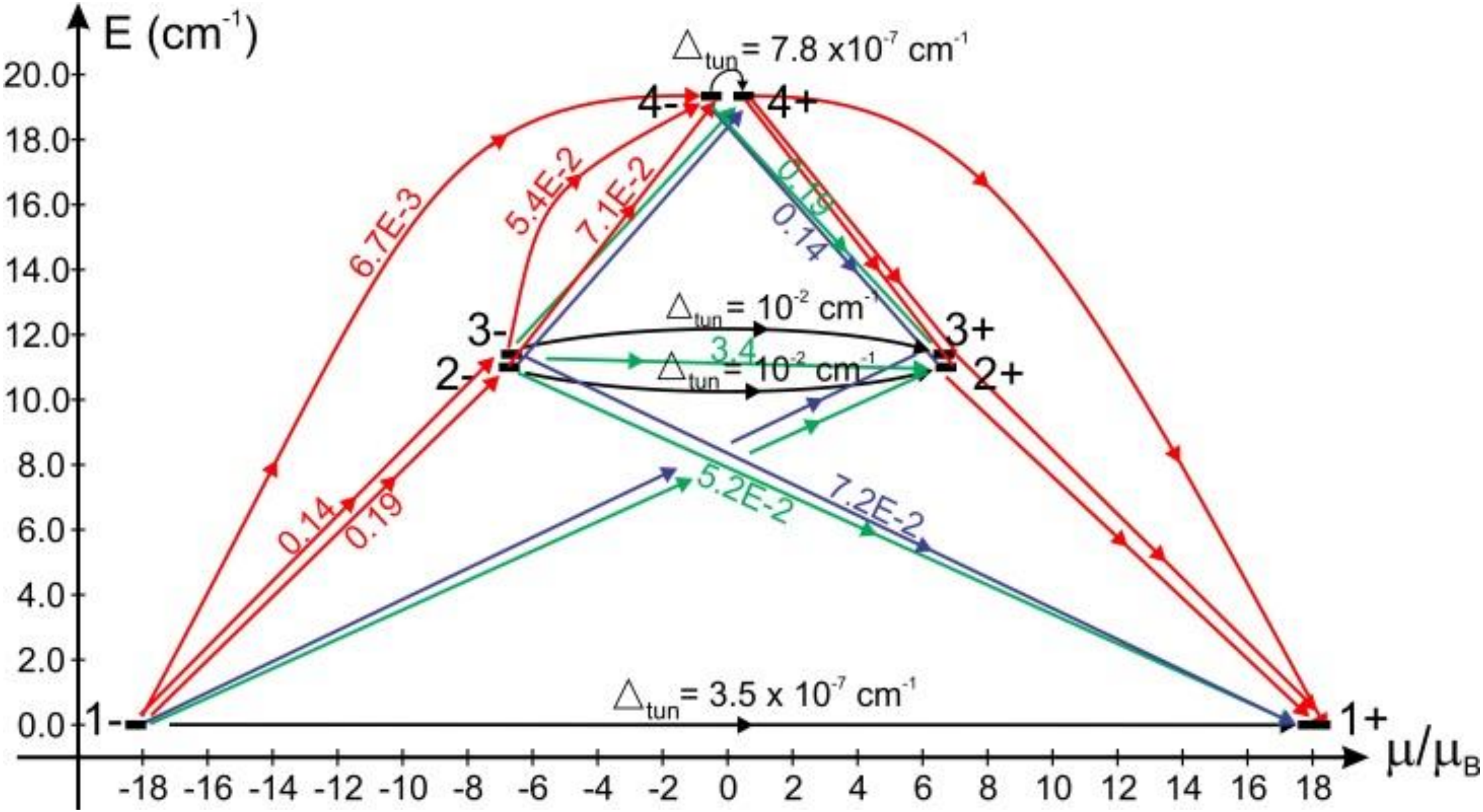


Exchange energy spectrum and orientation of local magnetic moments in Co-Tb-Co

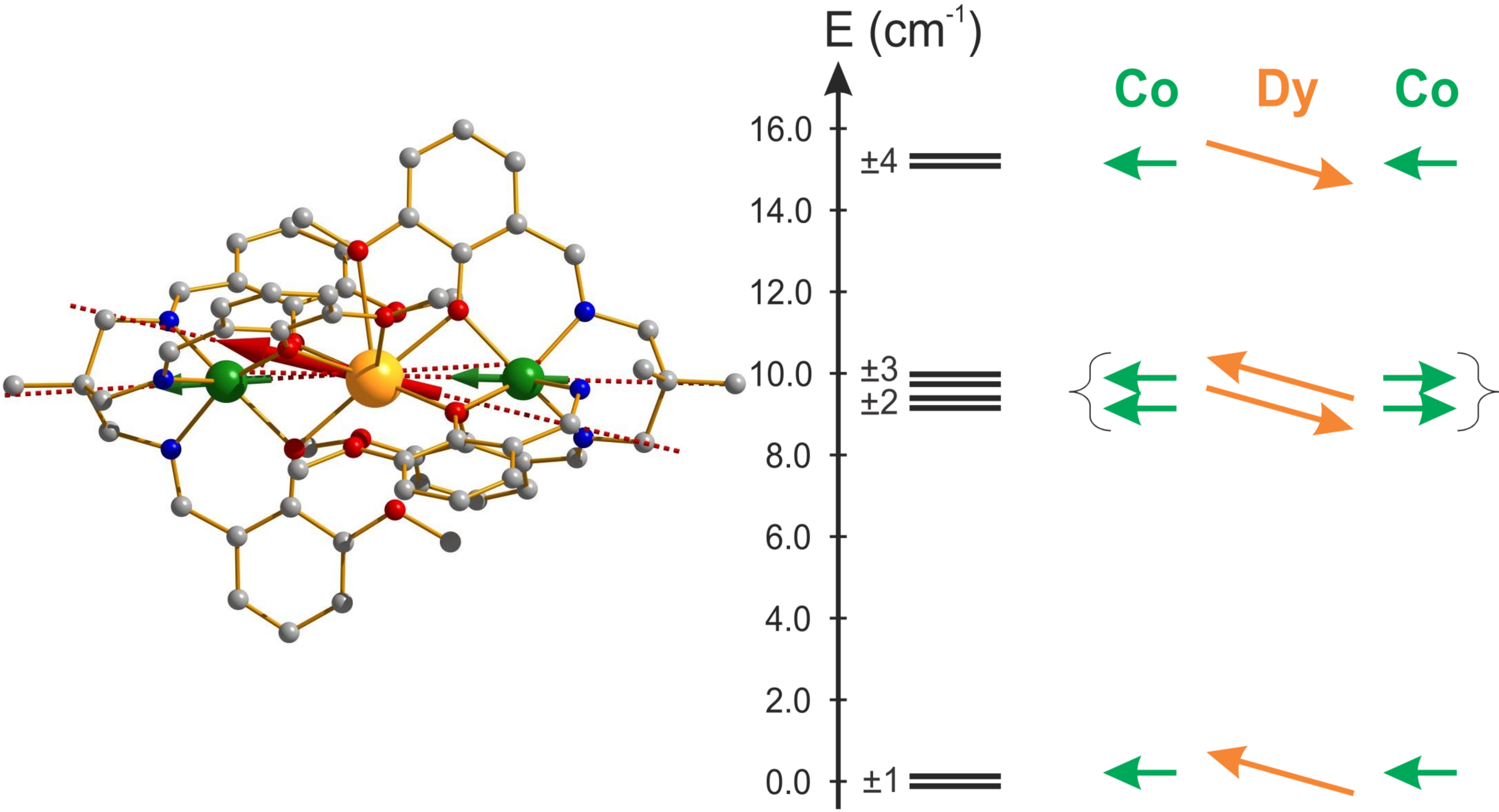




Structure of the blocking barrier in Co-Tb-Co



Exchange energy spectrum and orientation of local magnetic moments in Co-Dy-Co



Structure of the blocking barrier in Co-Dy-Co