Calculation of EPR parameters by WFT

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Outline

Generalities

- EPR spectroscopy
- spin Hamiltonians
- SO-CASSCF based methods
- time reversal operator and symmetry properties

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- EPR spectroscopy
- spin Hamiltonians
- SO-CASSCF based methods
- time reversal operator and symmetry properties

Examples

- $NpCl_6^{2-}$ a fourfold degenerate ground state
- Ni^{2+} in pseudo octahedric environment : an almost threefold degenerate ground state

Generalities

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- magnetic moment $\vec{m}_L$ owing to the **orbital angular momentum** $\vec{L} = \sum_i \vec{l}_i$

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- rotational magnetic moment $\vec{m}_R$ owing to the **rotational angular momentum** of the molecule

Magnetoactive components of a molecule

For open shell molecules

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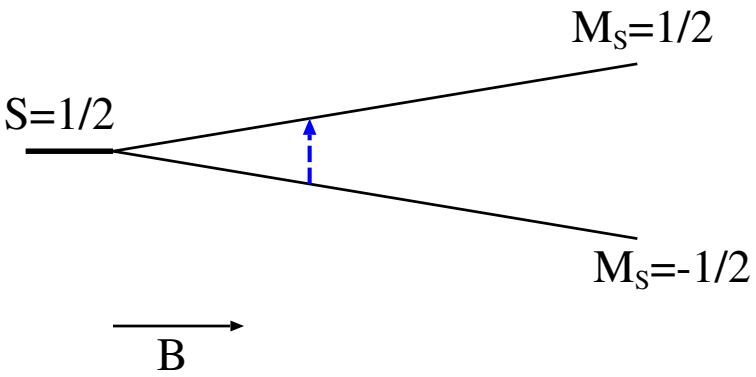
- magnetic moment $\vec{m}_S$ owing to the electron **spin angular momentum** $\vec{S} = \sum_i \vec{s}_i$

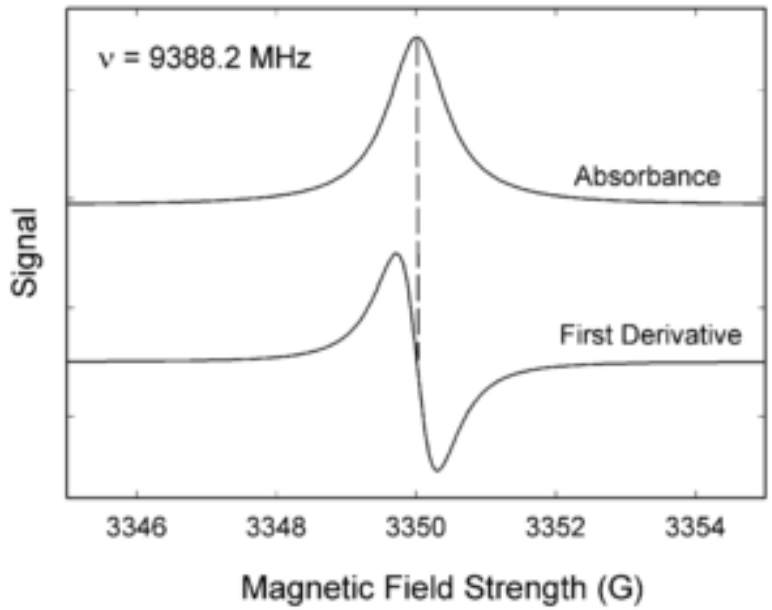
EPR : transitions between electronic Zeeman states

interaction of a magnetic moment $\vec{m}$ with an external magnetic field $\vec{B}$

$$H_{Ze} = -\vec{m}.\vec{B}$$

- for a pure spin doublet $S = 1/2$ with magnetic moment $\vec{m}_S = -\mu_B g_e \vec{S}$





$$h\nu = g_e \mu_B B_0$$

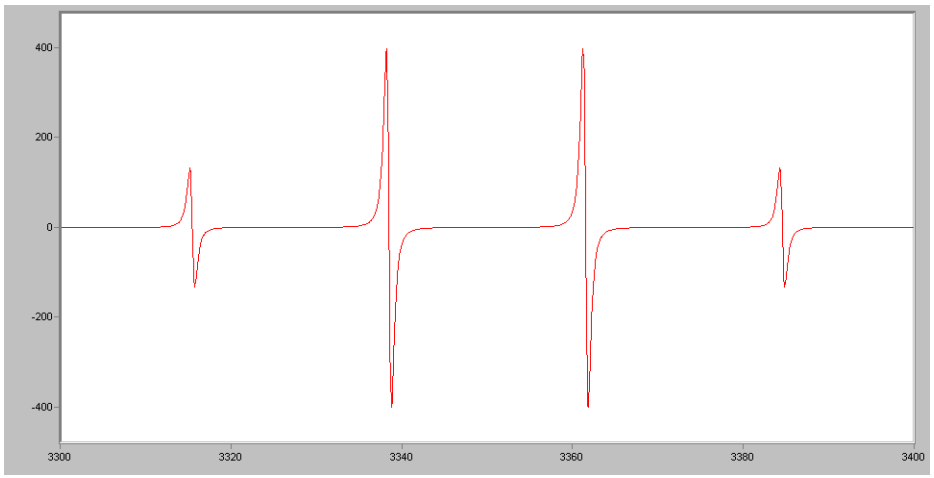
EPR : transitions between electronic Zeeman states

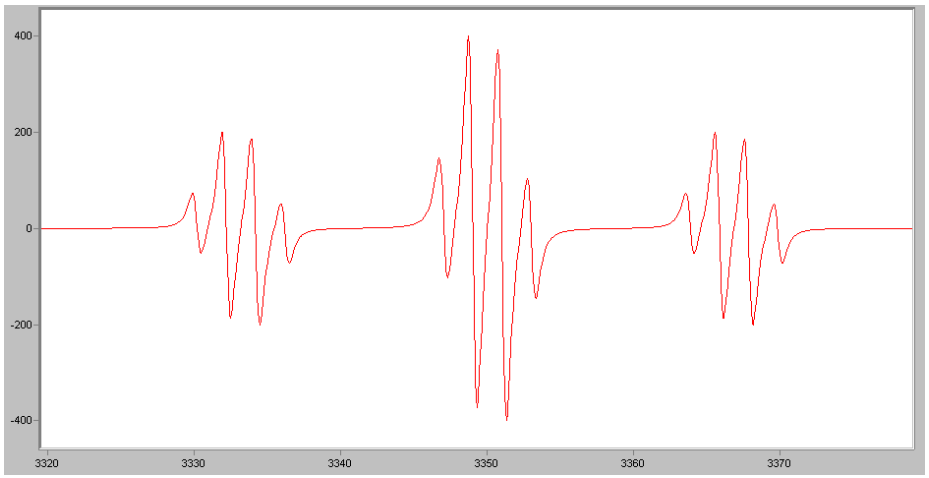
- microwaves region
  - for the X band, $\nu = 9388$ MHz
  - for a spin doublet $B = h\nu/g_e\mu_B$ =0.33 T and $h\nu$=0.076 cm^{-1}
- for non pure spin systems, $\vec{m} \neq \mu_B g_e \vec{S}$
- the magnetic moment depends on the direction $\Rightarrow$**anisotropy**
- for a magnetic field of $1\mathrm{T} = 10\,000$ G

$$\mu_B B = 0.46\mathrm{cm} - 1$$

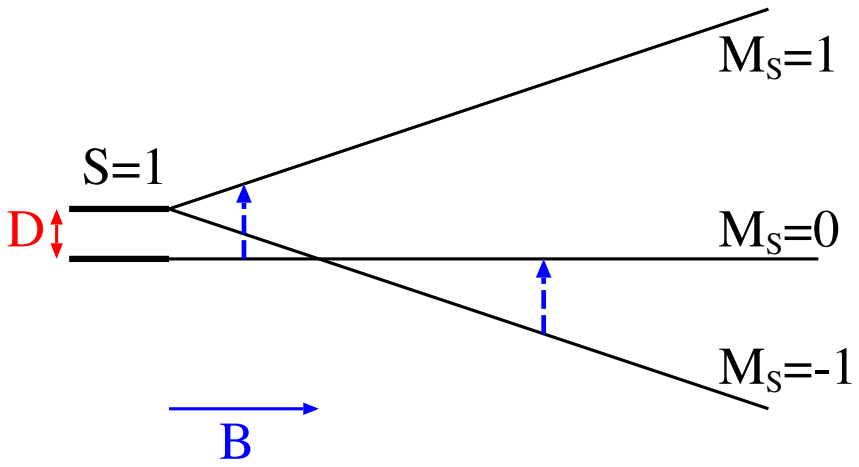
EPR : hyperfine coupling

- coupling with the spins I of the nuclei $\Rightarrow$ **hyperfine structure**
- $\vec{m}_I = \mu_N g_e \vec{I}$, since $\mu_N \ll \mu_B$, each electron Zeeman level is split into $2I+1$ lines





EPR : triplet state



- when $S \geq 1$, splitting of the M_S components in absence of magnetic field

zero-field splitting $\Rightarrow$ **fine structure**

- there are two transitions $M_S = -1 \rightarrow M_S = 0$ and $M_S = 0 \rightarrow M_S = 1$
- High Field High Frequency EPR
- one can deduce the ZFS energies and the Zeeman components

g-factors from experiment

- energy gap between Zeeman states in a magnetic field $\vec{B} = B\vec{n}$

$$\Delta E = g\mu_B B$$

- the g-factor depends on the direction of the magnetic field, this anisotropy is modelled by a spin Hamiltonian

$$H_S = \mu_B \vec{B}^{\dagger} \mathbf{.g.} \vec{\tilde{S}}$$

$$g = \pm \left[\vec{n}^{\dagger} \mathbf{.gg}^{\dagger} \mathbf{.} \vec{n} \right]^{1/2}$$

- Experiments give access to the tensor

$$G = gg^{\dagger}$$

- One defines the principal g-factors g_i from G_i the principal values of G

$$g_i = \pm\sqrt{G_i}$$

Determination of the sign of g-factors

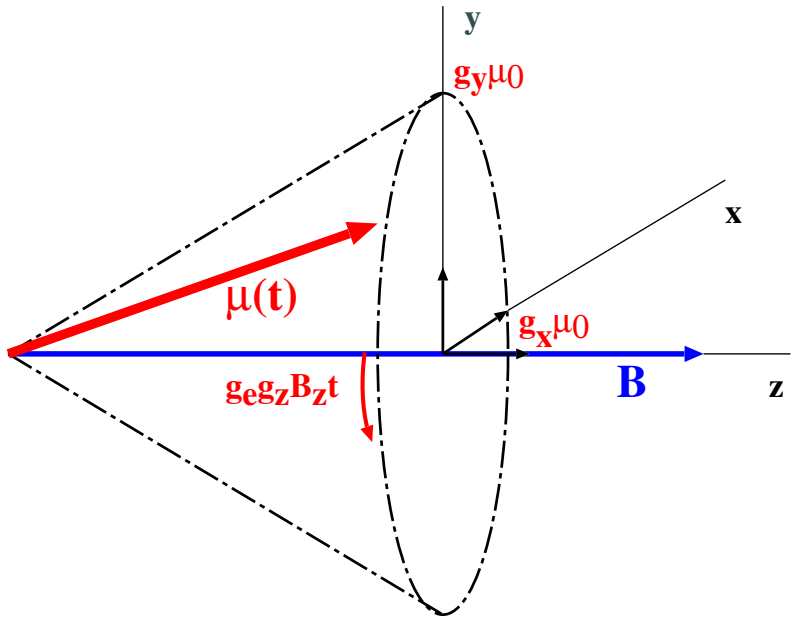
- by use of circularly polarized radiation, the relative intensities of a given transition using right- and left-handed senses give information about the sign of

$$g_x g_y g_z$$

- in the case of hyperfine coupling, when the sign of the hyperfine constant is known

Semiclassical approach: precession around a magnetic field

The anisotropy of the g-factors affects both the shape and the pulsation of the precession



magnetic field $\|$ to a principal axis z

the direction of the precession is defined by the sign of the product $g_x g_y g_z$

Spin Hamiltonian

Model Hamiltonian

$$H_S = \vec{\tilde{S}}^{\dagger} \mathbf{.D.} \vec{\tilde{S}} + \mu_B \vec{B}^{\dagger} \mathbf{.g.} \vec{\tilde{S}}$$

- it is a **phenomenological relation** expressed with spin operators
- $\vec{\tilde{S}}$ **is a pseudo spin operator acting in the model space.**
- With spin-orbit coupling, the true spin operator $\vec{S}$ is not a good quantum number.
- In the case of a small spin-orbit coupling, $\vec{\tilde{S}} \approx \vec{S}$ (transition metal complexes)
- otherwise, the value of $\tilde{S}$ is chosen to suit the size of the model space
  - the size of the model space is $2\tilde{S}+1$ generated by the $\left|\tilde{M}_S\right\rangle$ functions

Spin Hamiltonian

spin algebra

- in the model space, algebra of spins

$$\begin{aligned}
\tilde{S}_z \left|\tilde{M}_{S\,z}\right\rangle &= M_S \left|\tilde{M}_{S\,z}\right\rangle \\
\tilde{S}_+ \left|\tilde{M}_{S\,z}\right\rangle &= M_S \sqrt{(\tilde{S}+\tilde{M}_S+1)(\tilde{S}-\tilde{M}_S)} \left|\tilde{M}_S+1\,z\right\rangle \\
\tilde{S}_- \left|\tilde{M}_{S\,z}\right\rangle &= M_S \sqrt{(\tilde{S}-\tilde{M}_S+1)(\tilde{S}+\tilde{M}_S)} \left|\tilde{M}_S-1\,z\right\rangle
\end{aligned}$$

- in other directions

$$\begin{aligned}
\tilde{S}_x \left|\tilde{M}_{S\,x}\right\rangle &= M_S \left|\tilde{M}_{S\,x}\right\rangle \\
\tilde{S}_y \left|\tilde{M}_{S\,y}\right\rangle &= M_S \left|\tilde{M}_{S\,y}\right\rangle \\
\tilde{S}_z \left|\tilde{M}_{S\,z}\right\rangle &= M_S \left|\tilde{M}_{S\,z}\right\rangle
\end{aligned}$$

- rotation in the spin space
  $\mathscr{R}$: rotation $z \to x \to y \to z$
  $\mathscr{R}'$: rotation $z \to y \to x \to z$

$$\begin{aligned}
\mathscr{R} \left|\tilde{M}_{S\,z}\right\rangle &= \left|\tilde{M}_{S\,x}\right\rangle \\
\mathscr{R}' \left|\tilde{M}_{S\,z}\right\rangle &= \left|\tilde{M}_{S\,y}\right\rangle
\end{aligned}$$

Spin Hamiltonian

EPR spin Hamiltonian

$$H_S = \vec{\tilde{S}}^{\dagger} \mathbf{.D.} \vec{\tilde{S}} + \mu_B \vec{B}^{\dagger} \mathbf{.g.} \vec{\tilde{S}}$$

- **D** is a two-rank tensor, usually traceless : the ZFS tensor
- **g** is in general not a tensor but $\mathbf{G} = \mathbf{g}\mathbf{g}^{\dagger}$ is
- the principal axis of **D** and **G** are not the same in general

Spin space and real space

- the spin space is an ideal world in which the algebra is well defined : "*all is for the best in the best of all possible worlds*" (Candide Voltaire)
- the phenomenological parameters can be extracted from experimental data by the fitting of physical observables.
  - the model is presupposed
- quantum chemical calculations
  1. validation of the model
  2. calculation of the parameters

WFT for open shell systems

- the wave function of an open shell system is **multideterminantal**
- for example 2 electrons in 2 orbitals a and b
  - a triplet $S = 1$

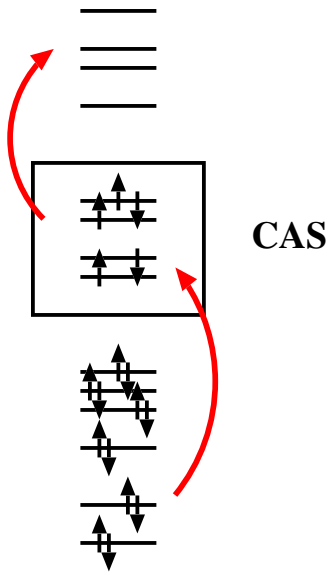
$$\begin{aligned} |1,1\rangle &= |ab| \\ |1,0\rangle &= \frac{1}{\sqrt{2}}\left(|a\bar{b}| + |\bar{a}b|\right) \\ |1,-1\rangle &= |\bar{a}\bar{b}| \end{aligned}$$

  - a singlet $S = 0$

$$|0,0\rangle = \frac{1}{\sqrt{2}}\left(|a\bar{b}| - |\bar{a}b|\right)$$

- in the case of no ZFS, $|1,1\rangle$ $|1,0\rangle$ and $|1,-1\rangle$ are degenerate, but the response to a magnetic field is different is different for the three components

CASSCF method



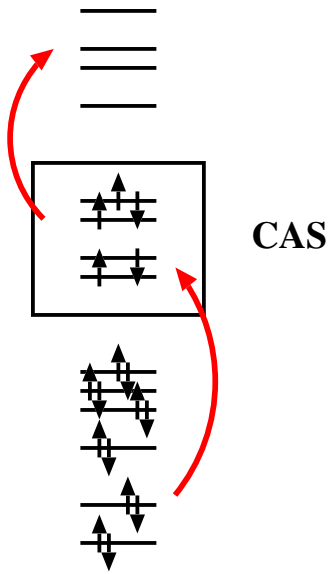
- **multireference**
  wave function of the Ith state

$$\Psi_I = \sum_{\kappa \in CAS} C_I^{\kappa} \Phi_{\kappa}$$

$\Phi_{\kappa} = |\phi_i \cdots \phi_l|$ Slater determinant

- **variational**
- **SCF procedure**
  optimization of the molecular orbitals at the same time as the C_I^{κ}

CASSCF method



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  optimization of the molecular orbitals at the same time as the C_I^κ

- scalar relativistic effects included
- the wave functions belong to an irrep of the simple group and have a well defined spin S $^{2S+1}\Gamma$
- **active orbitals**
  - at the least the open shell orbitals : non dynamical correlation
  - increase of the active in order to include some of the dynamical correlation variationnaly

dynamical correlation

- second order perturbation theory
  - CASPT2
  - NEVPT2
- Interaction Configuration
  - CAS-SDCI
  - DDCI

Spin-Orbit Coupling

- the spin-orbit matrix is written in the basis of the CASSCF $\{|\Psi_I, M_S\rangle\}$ wave functions and diagonalized

	$\|\Psi_1,S_1\rangle$	$\|\Psi_1,S_1-1\rangle$	$\cdots$	$\|\Psi_1,-S_1\rangle$	$\|\Psi_2,S_2\rangle$	$\cdots$	$\|\Psi_2,-S_2\rangle$	$\|\Psi_3,S_3\rangle$	$\cdots$
$\langle\Psi_1,S_1\|$	E_1								
$\langle\Psi_1,S_1-1\|$		E_1							
			E_1				H_{IJ}^{SO}		
$\langle\Psi_1,-S_1\|$				E_1					
$\langle\Psi_2,-S_2\|$					E_2				
						E_2			
$\langle\Psi_2,-S_2\|$			H_{JI}^{SO}				E_2		
$\langle\Psi_3,S_3\|$								E_3	
									E_3

- E_I SF energies (CASSCF, CASPT2, NEVPT2, CAS+SDCI ...)
- $H_{IJ}^{SOC} = \left\langle \Psi_K, M_S \middle| \hat{H}^{SO} \middle| \Psi_L, M_S' \right\rangle$ $\hat{H}^{SO}$ is the spin-orbit operator obtained from a 4c to 2 c transformation

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$\langle\Psi_1,S_1-1\|$		E_1							
			E_1				H_{IJ}^{SO}		
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						E_2			
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- the solutions belong to the irreps of the double group
  - wave functions are no more eigenfunctions of the spin
- one improves the quality of the calculations by increasing the number of SF roots

Response to a magnetic field

- Hamiltonian of a molecule in a permanent magnetic field $\vec{B}$ (to 1st order)

$$H = H^{ZF} - \vec{M} \cdot \vec{B} \qquad with \qquad \vec{M} = \sum_{i=el} \mu_B \left(\vec{r}_i \wedge \vec{j}_i \right)$$

with $\vec{r}_i$ and $\vec{j}_i$ position and current density of electron i

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- **in the non-relativistic limit**

$$\begin{aligned} \vec{M} = & \underbrace{\sum_{i=el} -\mu_B \left(\vec{l}_i + g_e \vec{s}_i\right)}_{-\mu_B \left(\hat{\vec{L}} + g_e \hat{\vec{S}}\right)} + -\tfrac{1}{4}\left(\vec{r}_i \wedge \vec{A}\right) \\ = & \qquad + \qquad diamag \end{aligned}$$

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- **for open shell system**

$$H = H^{ZF} + \mu_B \left(\vec{L} + g_e \vec{S}\right).\vec{B}$$

Magnetic moment matrix

1- Solution of the zero field (ZF) equation

$$H^{ZF}\left|\Psi_I\right\rangle = E_I\left|\Psi_I\right\rangle$$

2- Calculation of the **magnetic moment** matrix elements

$$\vec{m}_{IJ} = \mu_B\left\langle \Psi_I \left| \vec{L} + g_e\vec{S} \right| \Psi_J \right\rangle = \mu_B\left\langle \Psi_I \left| \vec{M} \right| \Psi_J \right\rangle$$

$$\mathbf{H} = \begin{array}{c|cccc} H^{ZF} & |\Psi_0\rangle & |\Psi_1\rangle & \cdots & |\Psi_N\rangle \\ \hline \langle\Psi_0| & E_0 & 0 & \cdots & 0 \\ \langle\Psi_1| & 0 & E_1 & & 0 \\ \vdots & \vdots & & \ddots & \\ \langle\Psi_N| & 0 & 0 & & E_N \end{array} + \begin{array}{c|cccc} -\vec{M} & \left|\Psi_0\right\rangle & |\Psi_1\rangle & \cdots & |\Psi_N\rangle \\ \hline \left\langle\Psi_0\right| & -\vec{m}_{00} & -\vec{m}_{01} & \cdots & -\vec{m}_{0N} \\ \langle\Psi_1| & -\vec{m}_{10} & -\vec{m}_{11} & & -\vec{m}_{1N} \\ \vdots & \vdots & & \ddots & \\ \langle\Psi_N| & -\vec{m}_{N0} & -\vec{m}_{N1} & & -\vec{m}_{NN} \end{array} . \vec{B}$$

Choice of the model space

H^{ZF}	$\|\Psi_0\rangle$	$\|\Psi_1\rangle$	$\|\Psi_2\rangle$	$\cdots$	$\|\Psi_N\rangle$
$\langle\Psi_0\|$	E_0	0		$\cdots$	0
$\langle\Psi_1\|$	0	E_1			0
$\langle\Psi_2\|$			E_2		0
$\vdots$	$\vdots$			$\ddots$	0
$\langle\Psi_N\|$	0	0			E_N

$+$

$-\vec{M}$	$\|\Psi_0\rangle$	$\|\Psi_1\rangle$	$\|\Psi_2\rangle$	$\cdots$	$\|\Psi_N\rangle$
$\langle\Psi_0\|$	$-\vec{m}_{00}$	$-\vec{m}_{01}$	$-\vec{m}_{02}$	$\cdots$	$-\vec{m}_{0N}$
$\langle\Psi_1\|$	$-\vec{m}_{10}$	$-\vec{m}_{11}$	$-\vec{m}_{12}$		$-\vec{m}_{1N}$
$\langle\Psi_2\|$	$-\vec{m}_{20}$	$-\vec{m}_{21}$	$-\vec{m}_{22}$		$-\vec{m}_{1N}$
$\vdots$	$\vdots$			$\ddots$	
$\langle\Psi_N\|$	$-\vec{m}_{N0}$	$-\vec{m}_{N1}$			$-\vec{m}_{NN}$

$\cdot \vec{B}$

- $E_3 - E_0 \gg \vec{m}_{IJ} \cdot \vec{B}$
- model space of size $2\tilde{S}+1$
- relationship between these matrices and the spin Hamiltonian simplified thanks to the properties of symmetry

Time reversal symmetry

Electric field vs magnetic field

Schrödinger equation of a particle with charge q

- in an electric field

$$i\hbar\frac{\partial\psi(r,t)}{\partial t} = \left[-\frac{\hbar^2}{2m}\nabla^2 + q\Phi(r)\right]\psi(r,t) \tag{1}$$

  $\psi^*(r,-t)$ is a solution of (1)

- in a magnetic field

$$i\hbar\frac{\partial\psi(r,t)}{\partial t} = \frac{1}{2m}\left[-i\hbar\nabla - \frac{q}{c}A(r)\right]^2\psi(r,t) \tag{2}$$

$\psi^*(r,-t)$ is not a solution of (2) but of the equation with reversed magnetic field

Time reversal operator Θ

- Θ is a **antilinear** and **antiunitary** operator

time reversal operator in $\vec{r}$ representation, for systems with spatial and spin degrees of freedom

$$\Theta = Ke^{-i\pi S_y/\hbar} = e^{-i\pi S_y/\hbar}K$$

where K is the conjugation operator.

Symmetry of the Hamiltonian under time reversal

- Zero-field Hamiltonian

$$H = \frac{|p|^2}{2m} + V(\vec{r}) + f(r)\vec{L}.\vec{S}$$

  commutes with time reversal

- The angular momentum operators

$$\Theta \vec{M} \Theta^{\dagger} = -\vec{M} \qquad \vec{M} = \vec{L}, \vec{S}, \vec{J}$$

anticommutes with time reversal

Kramers degeneracy

- $\Theta^2 = e^{-2\pi i S_y/\hbar}$
- total spin rotation of angle 2π about the y-axis
  - for bosons $\Theta^2 = 1$
  - for fermions $\Theta^2 = -1$

Kramers degeneracy

- $\Theta^2 = e^{-2\pi i S_y/\hbar}$
- total spin rotation of angle 2π about the y-axis
  - for bosons $\Theta^2 = 1$
  - for fermions $\Theta^2 = -1$
- **$|\Psi\rangle$ and $\Theta|\Psi\rangle$ are degenerate**
- if $|\Psi\rangle$ is non degenerate

$$\Theta|\Psi\rangle = e^{i\alpha}|\Psi\rangle$$

$$\Theta^2|\Psi\rangle = \Theta e^{i\alpha}|\Psi\rangle = e^{-i\alpha}\Theta|\Psi\rangle = |\Psi\rangle$$

possible for bosons, not for fermions

Kramers degeneracy

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- total spin rotation of angle 2π about the y-axis
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$$\Theta|\Psi\rangle = e^{i\alpha}|\Psi\rangle$$

$$\Theta^2|\Psi\rangle = \Theta e^{i\alpha}|\Psi\rangle = e^{-i\alpha}\Theta|\Psi\rangle = |\Psi\rangle$$

  possible for bosons, not for fermions

- **In time-reversal invariant systems with an odd number of fermions, the energy levels have a degeneracy that is even.**
- Kramers degeneracy is lifted by any effect that breaks the time-reversal invariance, for example external magnetic fields.

Magnetic moment of a non-degenerate state

- if $|\Psi\rangle$is non degenerate

$$\begin{aligned}\left\langle \Psi \left| \vec{M} \right| \Psi \right\rangle &= \left\langle \Theta\Psi \left| \vec{M} \right| \Theta\Psi \right\rangle \\ &= -\left\langle \Psi \left| \vec{M} \right| \Psi \right\rangle \\ &= 0\end{aligned}$$

- **The magnetic moment of a non-degenerate state vanishes**

Time reversal

conclusion

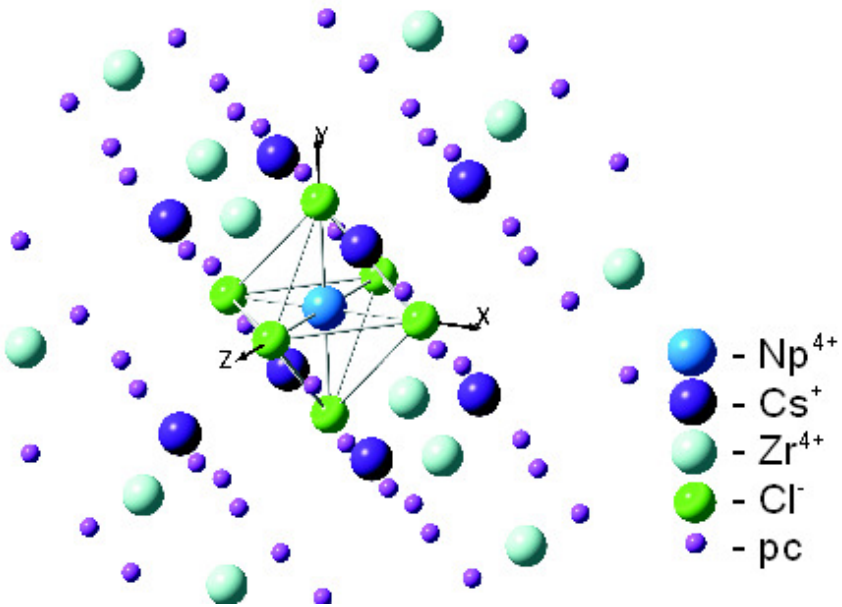
1. the magnetic moment operator is antisymmetrical towards time inversion

$$\Theta \vec{M} \Theta^{\dagger} = -\vec{M}$$

2. the zero-field energy of a system with an odd number of fermions have a degeneracy that is even. This degeneracy is lifted by external magnetic field.
3. The magnetic moment of a non-degenerate state vanishes

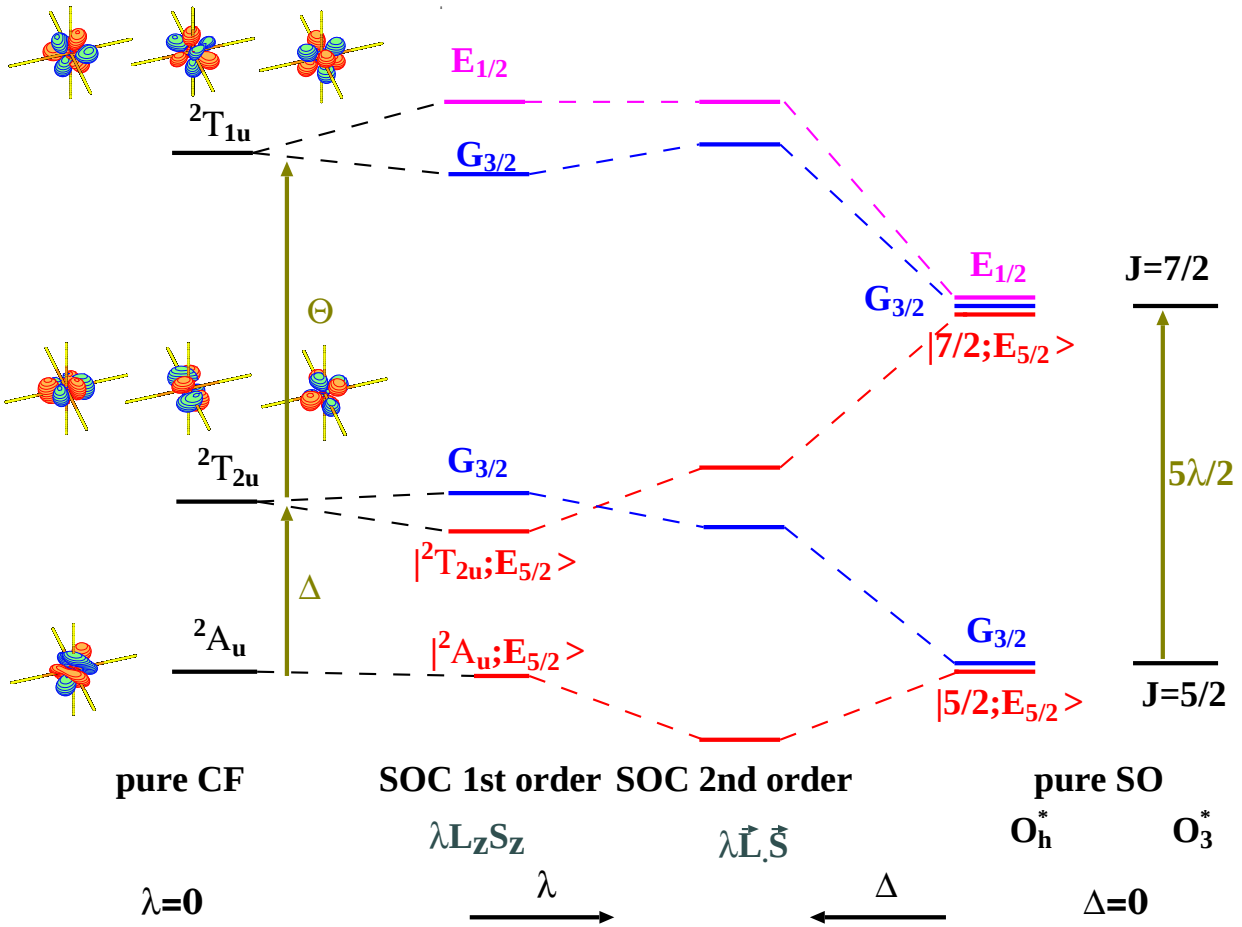
Example 1 : $NpCl_6^{2-}$

$NpCl_6^{2-}$
a Kramers quartet

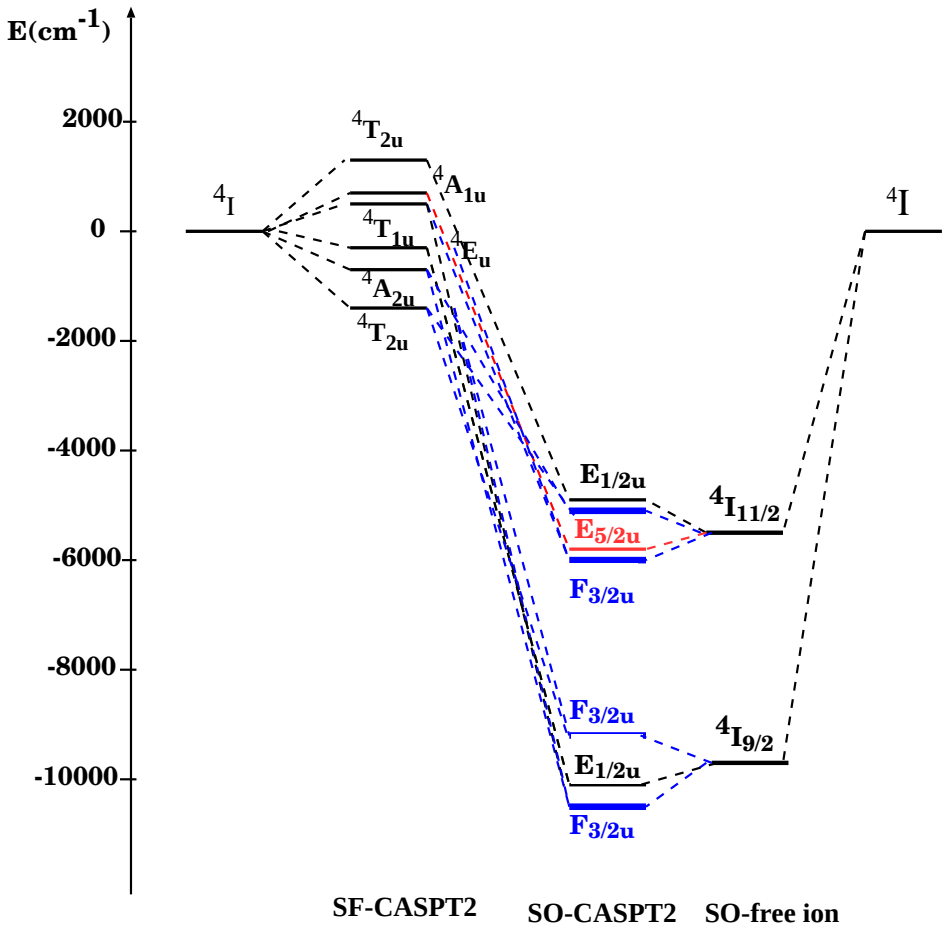


- $NpCl_6^{2-}$, configuration $(5f)^3$ cubic symmetry
- the ground state is of symmetry $F_{3/2u}$ (Γ_8)
- The highly symmetric lattice of diamagnetic Cs_2ZrCl_6 preserves the symmetry of the $F_{3/2u}$ state
- EPR spectrum (Bray, Bernstein, Dennis 1978)

5*f* orbitals in an octahedric environment



SO-CASPT2 results



- CAS(3,7) ($5f^3$ configuration)
- SO-RASSI calculation : 35 quartets and 84 doublets
- the ground state is of $F_{3/2u}$ symmetry (four-fold degenerate)
- the ZFS is due to the splitting of the $^4I_{9/2}$ term of the free ion by the ligands

Crystal field theory

- crystal field operator in an octahedric environment

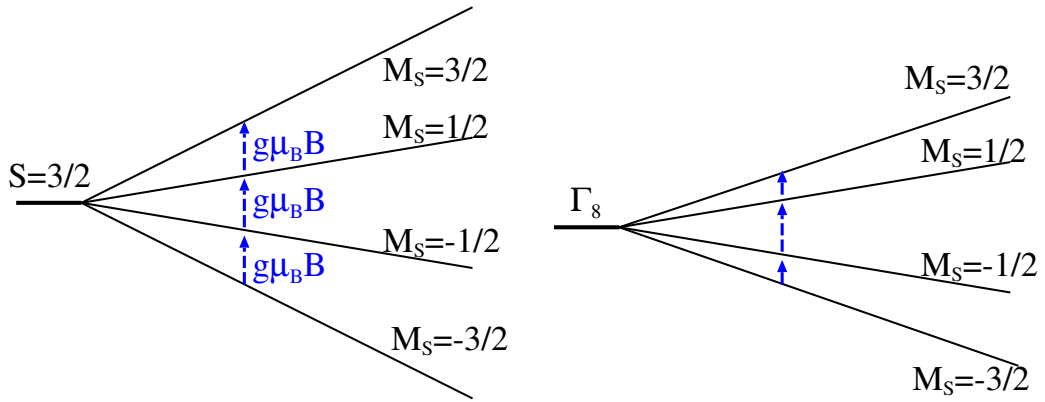
$$\begin{aligned}\hat{V}_{CF} &= \beta(J)\,A_4\left\langle r^4\right\rangle\left(\hat{O}_4^0(J)+5\,\hat{O}_4^4(J)\right)+\gamma(J)\,A_6\left\langle r^6\right\rangle\left(\hat{O}_6^0(J)-21\,\hat{O}_6^4(J)\right)\\ &= W\left[x\,\frac{\hat{O}_4}{F(4)}+(1-|x|)\,\frac{\hat{O}_6}{F(6)}\right]\end{aligned}$$

in cm^{-1}

	SO-CASSCF	SO-CASPT2	exp
$F_{3/2u}$	0	0	0
$E_{1/2u}$	327	266	
$F_{3/2u}(2)$	1094	1115	982
$E_{5/2u}$	5738	5980	5836
x	0.70	0.73	
W	-19	-20	
$A_4 < r^4 >$	784	833	
$A_6 < r^6 >$	59	55	

a Kramers quartet

- **the ground state is 4-fold degenerate** $\Rightarrow \widetilde{S} = \frac{3}{2}$



Spin Hamiltonian

$$H_S = \mu_B g \vec{B}^{\dagger} . \vec{\tilde{S}} + \mu_B G \left[B_x \tilde{S}_x^3 + B_y \tilde{S}_y^3 + B_z \tilde{S}_z^3 \right]$$

- x y and z are equivalent : $\mathbf{g}$ is isotropic
- One adds cubic terms to take into account the contribution of angular momentum

model matrices

basis set $\left|\tilde{\frac{3}{2}}\right\rangle \left|\tilde{\frac{1}{2}}\right\rangle \left|-\tilde{\frac{1}{2}}\right\rangle \left|-\tilde{\frac{3}{2}}\right\rangle$

$$\mathbf{M}_x = \begin{pmatrix} 0 & -\sqrt{3}(\frac{1}{2}g+\frac{7}{8}G) & 0 & -\frac{3}{4}G \\ -\sqrt{3}(\frac{1}{2}g+\frac{7}{8}G) & 0 & -(g+\frac{5}{2}G) & 0 \\ 0 & -(g+\frac{5}{2}G) & 0 & -\sqrt{3}(\frac{1}{2}g+\frac{7}{8}G) \\ -\frac{3}{4}G & 0 & -\sqrt{3}(\frac{1}{2}g+\frac{7}{8}G) & 0 \end{pmatrix}$$

$$\mathbf{M}_y = \begin{pmatrix} 0 & i\sqrt{3}(\frac{1}{2}g+\frac{7}{8}G) & 0 & -i\frac{3}{4}G \\ -i\sqrt{3}(\frac{1}{2}g+\frac{7}{8}G) & 0 & i(g+\frac{5}{2}G) & 0 \\ 0 & -i(g+\frac{5}{2}G) & 0 & i\sqrt{3}(\frac{1}{2}g+\frac{7}{8}G) \\ i\frac{3}{4}G & 0 & -i\sqrt{3}(\frac{1}{2}g+\frac{7}{8}G) & 0 \end{pmatrix}$$

$$\mathbf{M}_z = \begin{pmatrix} -\frac{3}{2}g-\frac{27}{8}G & 0 & 0 & 0 \\ 0 & -\frac{1}{2}g-\frac{1}{8}G & 0 & 0 \\ 0 & 0 & \frac{1}{2}g+\frac{1}{8}G & 0 \\ 0 & 0 & 0 & \frac{3}{2}g+\frac{27}{8}G \end{pmatrix}$$

SO-CASPT2 matrices

basis set $|\Psi_1\rangle|\Psi_2\rangle|\Psi_3\rangle|\Psi_4\rangle$

$$\mathbf{M}_x = \begin{pmatrix} -0.174 & -0.088+0.10i & 0.572+0.003i & -0.254+0.044i \\ -0.088-0.101i & 0.174 & -0.258+0.005i & -0.561+0.114i \\ 0.572-0.003i & -0.258-0.005i & 0.348 & 1.033-1.447i \\ -0.254-0.044i & -0.561-0.114i & 1.033+1.447i & -0.348 \end{pmatrix}$$

eigenvalues -2.028 2.028 0.096 -0.096

$$\mathbf{M}_y = \begin{pmatrix} 0.886 & 0.194-0.827i & 0.950-0.079i & 0.112+0.139i \\ 0.194+0.827i & -0.886 & 0.083-0.158i & -0.947i+0.107i \\ 0.950+0.079i & 0.083+0.158i & 0.413 & 0.131+0.737i \\ 0.112-0.139i & -0.947-0.107i & 0.131-0.737i & -0.413 \end{pmatrix}$$

eigenvalues -2.028 2.028 0.096 -0.096

$$\mathbf{M}_z = \begin{pmatrix} -0.331 & -0.986i-1.251i & -0.430-0.134i & 0.236+0.614i \\ -0.986+1.251i & 0.331 & 0.11321-0.64851I & 0.396-0.215i \\ -0.430+0.134i & 0.113+0.648i & 0.369 & 0.1235-0.197i \\ 0.236-0.614i & 0.396+0.215i & 0.1235+0.197i & -0.369 \end{pmatrix}$$

eigenvalues -2.028 2.028 0.096 -0.096

SO-CASPT2 matrices in M_z eigenvectors

basis set $R|\Psi_1\rangle\, R|\Psi_2\rangle\, R|\Psi_3\rangle\, R|\Psi_4\rangle$

$$\mathbf{M}_x = \begin{pmatrix} 0.000 & 0.799-0.248i & 0.000 & 0.440-0.378i \\ 0.799+0.248i & 0.000 & -1.025-1.155i & 0.000 \\ 0.000 & -1.025+1.155i & 0.000 & -0.260+0.795i \\ 0.440+0.378i & 0.000 & -0.260-0.795i & 0.000 \end{pmatrix}$$

$$\mathbf{M}_y = \begin{pmatrix} 0.000 & -0.247-0.799i & 0.000 & 0.378+0.440i \\ -0.247+0.799i & 0.000 & -1.155+1.026i & 0.000 \\ 0.000 & -1.155-1.026i & 0.000 & 0.795+0.261i \\ 0.378-0.440i & 0.000 & 0.795-0.261i & 0.000 \end{pmatrix}$$

$$\mathbf{M}_z = \begin{pmatrix} 2.026 & 0.000 & 0.000 & 0.000 \\ 0.000 & -0.096 & 0.000 & 0.000 \\ 0.000 & 0.000 & 0.096 & 0.000 \\ 0.000 & 0.000 & 0.000 & -2.026 \end{pmatrix}$$

SO-CASPT2 matrices in M_z eigenvectors, M_x real

basis set $R'|\Psi_1\rangle\, R'|\Psi_2\rangle\, R'|\Psi_3\rangle\, R'|\Psi_4\rangle$

$$\mathbf{M}_x = \begin{pmatrix} 0.000 & 0.837 & 0.000 & 0.588 \\ 0.837 & 0.000 & 1.556 & 0.000 \\ 0.000 & 1.556 & 0.000 & 0.837 \\ 0.588 & 0.000 & 0.837 & 0.000 \end{pmatrix}$$

$$\mathbf{M}_y = \begin{pmatrix} 0.000 & -0.837i & 0.000 & 0.588i \\ 0.837i & 0.000 & -1.556i & 0.000 \\ 0.000 & 1.556i & 0.000 & -0.837i \\ -0.588i & 0.000 & 0.837i & 0.000 \end{pmatrix}$$

$$\mathbf{M}_z = \begin{pmatrix} 2.042 & 0.000 & 0.000 & 0.000 \\ 0.000 & -0.104 & 0.000 & 0.000 \\ 0.000 & 0.000 & 0.104 & 0.000 \\ 0.000 & 0.000 & 0.000 & -2.042 \end{pmatrix}$$

- these three matrices match the three model matrices with g=-0.406 G=0.785
- EPR experimental values g= -0.516 G= 0.882

EPR parameters

- there are two sets of parameters that math the model matrices corresponding to the transformation

$$\left\{\Psi_{3/2} \leftrightarrow \Psi_{-1/2}; \Psi_{-3/2} \leftrightarrow \Psi_{1/2}\right\}$$

. This leads to a set of new parameters $g' = (-40g - 91G)/12$ and $G' = (4g + 10G)/3$. The existence of these two solutions was already pointed out by Bleaney.

- from the spin and orbital moment matrices one gets
  - spin contribution g_S= 0.027 G_s= -0.250
  - orbital contribution g_L= -0.460 G_S=1.285
- the orbital and spin contributions are opposite as they are in the free ion : $J = L - S$
- the magnetic moments are very different from the free ion one $\tilde{S} \neq S$

$$\begin{aligned} \left\langle \Psi_{\pm 3/2} \left| M_z \right| \Psi_{\pm 3/2} \right\rangle &= \mp 2.04 \neq \mp \frac{3}{2} g_e \\ \left\langle \Psi_{\pm 1/2} \left| M_z \right| \Psi_{\pm 1/2} \right\rangle &= \pm 1.05 \neq \mp \frac{1}{2} g_e \end{aligned}$$

EPR parameters : conclusion

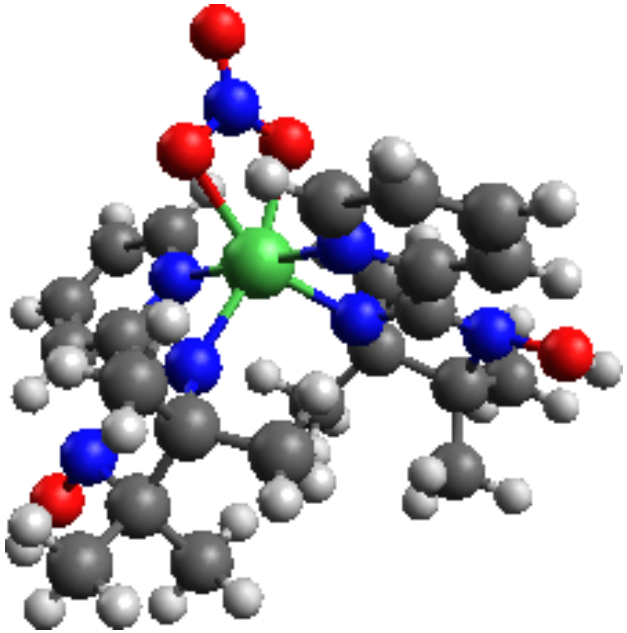
- **validation of the Spin Hamiltonian**
- We have found the correspondance between the model space and the real space

$$\begin{aligned}
\left|\frac{\tilde{3}}{2}\right\rangle &\leftrightharpoons \left|\Psi_{3/2}\right\rangle = R'\left|\Psi_1\right\rangle \\
\left|\frac{\tilde{1}}{2}\right\rangle &\leftrightharpoons \left|\Psi_{1/2}\right\rangle = R'\left|\Psi_2\right\rangle \\
\left|-\frac{\tilde{1}}{2}\right\rangle &\leftrightharpoons \left|\Psi_{-1/2}\right\rangle = R'\left|\Psi_3\right\rangle \\
\left|-\frac{\tilde{3}}{2}\right\rangle &\leftrightharpoons \left|\Psi_{-3/2}\right\rangle = R'\left|\Psi_4\right\rangle
\end{aligned}$$

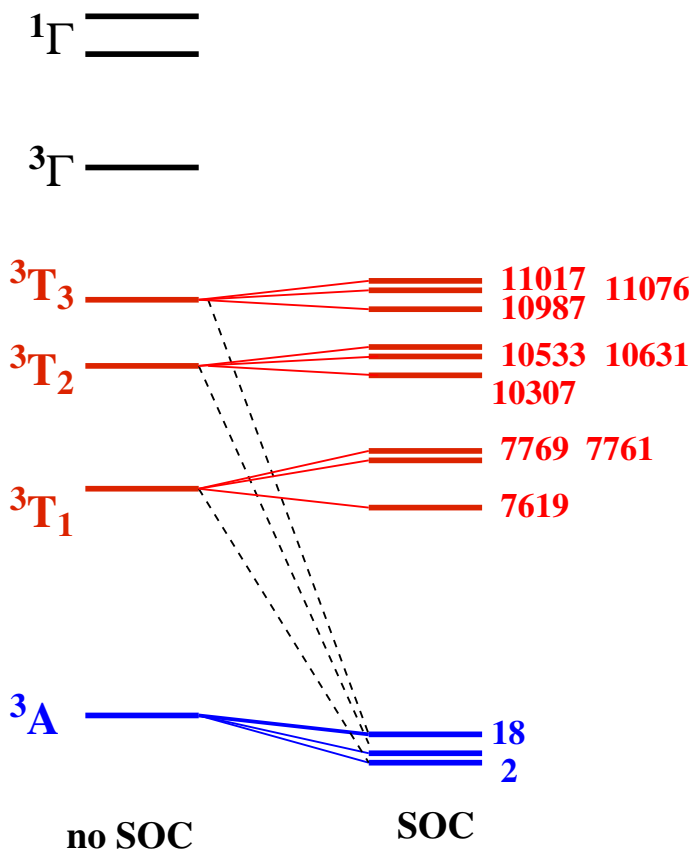
- extraction of g and G in reasonable agreement with experimental values

Example 2 : Pseudooctahedric N(II)

Pseudooctahedric Ni(II) complex : $\tilde{S} = 1$



$Ni(II)(himpy)_2NO_3$ $3d^8$

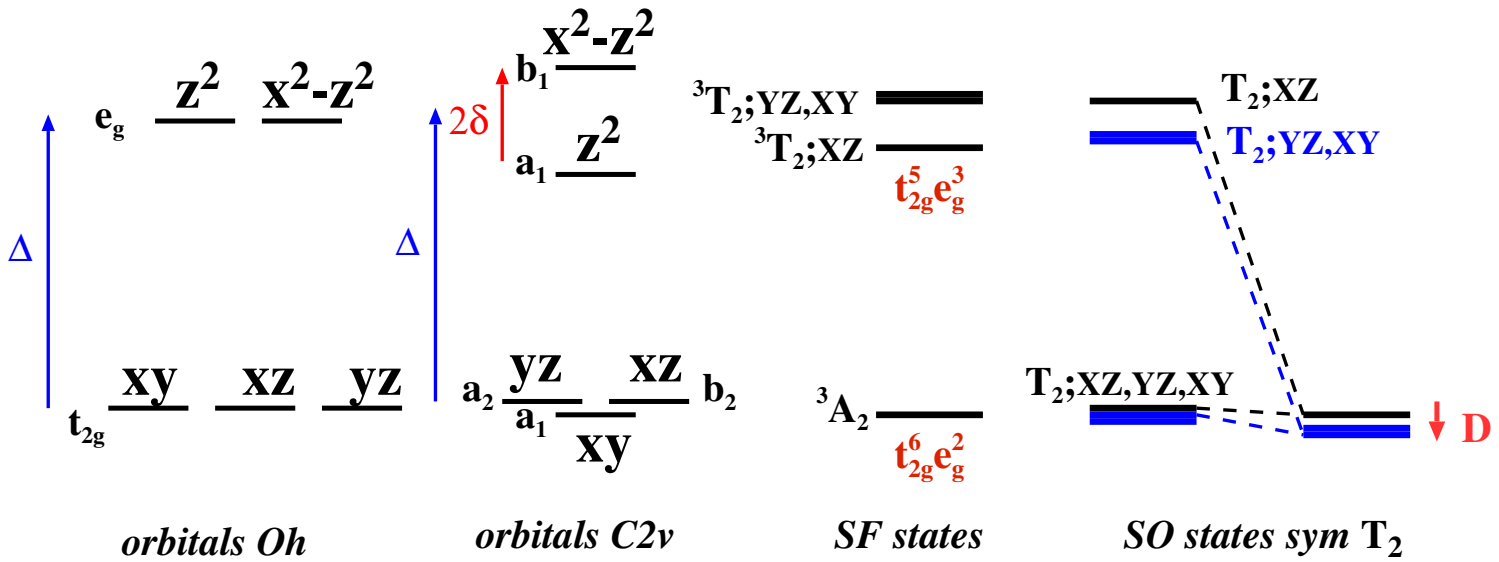


- without spin-orbit : pure spin, isotropic
- spin-orbit : some orbital moment of the excited states $\Longrightarrow$ anisotropic
- model space $\tilde{S} = 1$

SO-CASPT2 calculation

- $3d^8$ configuration
- minimal active space CAS(8,5) 8 electrons in the 5 3*d* orbitals

pseudo octahedric symmetry



Active space

- CAS(8,10) doubled d shell active space, increased by a set of $3d'$ orbitals for a better description of the dynamical correlation within the d orbitals.
- CAS(12,12) augmented with the two bonding orbitals of the ligands eg-type orbitals
- SO-RASSI with 10 triplets and 15 singlets

		SF $\Delta E(\mathrm{cm}^{-1})$			ZFS $\Delta E(\mathrm{cm}^{-1})$	
		$^3T_1$	$^3T_2$	$^3T_3$	E_1	E_2
CAS(8,5)	SCF	6213	8196	8558	2.26	16.46
	PT2	7921	9099	9849	3.15	8.72
CAS(8,10)	SCF	6675	8795.	9193.	2.18	15.24
	PT2	7752	10088.	10504.	**0.96**	**12.01**
CAS(12,12)	SCF	6699.	9291.	9764	2.03	17.04
	PT2	7680	10578.	10938	2.18	16.92
exp					**0.34**	**10.70**

Spin Hamiltonian

$$H_S = \vec{\tilde{S}}^{\dagger} \mathbf{.D.} \vec{\tilde{S}} + \mu_B \vec{B}^{\dagger} \mathbf{.g.} \vec{\tilde{S}}$$

- In the frame of the principal axis of the ZFS tensor D

$$H_S^{ZF} = \frac{1}{2}\left(D_x \tilde{S}_x^2 + D_y \tilde{S}_y^2 + D_z \tilde{S}_z^2\right)$$

- basis set for the spin space $|0_x\rangle$, $|0_y\rangle$, $|0_z\rangle$

$$\begin{aligned} |0_x\rangle &= \mathscr{R}|0_z\rangle = \frac{1}{\sqrt{2}}(-|1_z\rangle + |-1_z\rangle) \\ |0_y\rangle &= \mathscr{R}'|0_z\rangle = \frac{i}{\sqrt{2}}(|1_z\rangle + |-1_z\rangle) \end{aligned}$$

$$\begin{aligned} H_S^{ZF}|0_x\rangle &= \frac{1}{2}(D_y + D_z) = E_x^0 \\ H_S^{ZF}|0_y\rangle &= \frac{1}{2}(D_x + D_z) = E_y^0 \\ H_S^{ZF}|0_z\rangle &= \frac{1}{2}(D_x + D_y) = E_z^0 \end{aligned}$$

Spin Hamiltonian

$$H_S = \vec{\tilde{S}}^{\dagger} \mathbf{.D.} \vec{\tilde{S}} + \mu_B \vec{B}^{\dagger} \mathbf{.g.} \vec{\tilde{S}}$$

S_x	$\lvert 0_x\rangle$	$\lvert 0_y\rangle$	$\lvert 0_z\rangle$
$\langle 0_x\rvert$	0	0	0
$\langle 0_y\rvert$	0	0	$-i$
$\langle 0_z\rvert$	0	i	0

S_y	$\lvert 0_x\rangle$	$\lvert 0_y\rangle$	$\lvert 0_z\rangle$
$\langle 0_x\rvert$	0	0	i
$\langle 0_y\rvert$	0	0	0
$\langle 0_z\rvert$	$-i$	0	0

S_z	$\lvert 0_x\rangle$	$\lvert 0_y\rangle$	$\lvert 0_z\rangle$
$\langle 0_x\rvert$	0	$-i$	0
$\langle 0_y\rvert$	i	0	0
$\langle 0_z\rvert$	0	0	0

- with a magnetic field $\vec{B} = B_x \vec{e}_x + B_y \vec{e}_y + B_z \vec{e}_z$

H_S	$\lvert 0_x\rangle$	$\lvert 0_y\rangle$	$\lvert 0_z\rangle$
$\langle 0_x\rvert$	E_x^0	$-i\mu_B g B_z$	$i\mu_B g B_y$
$\langle 0_y\rvert$	$i\mu_B g B_z$	E_y^0	$-i\mu_B g B_x$
$\langle 0_z\rvert$	$-i\mu_B g B_y$	$i\mu_B g B_x$	E_z^0

- the states do not have any magnetic moment since they are non degenerate

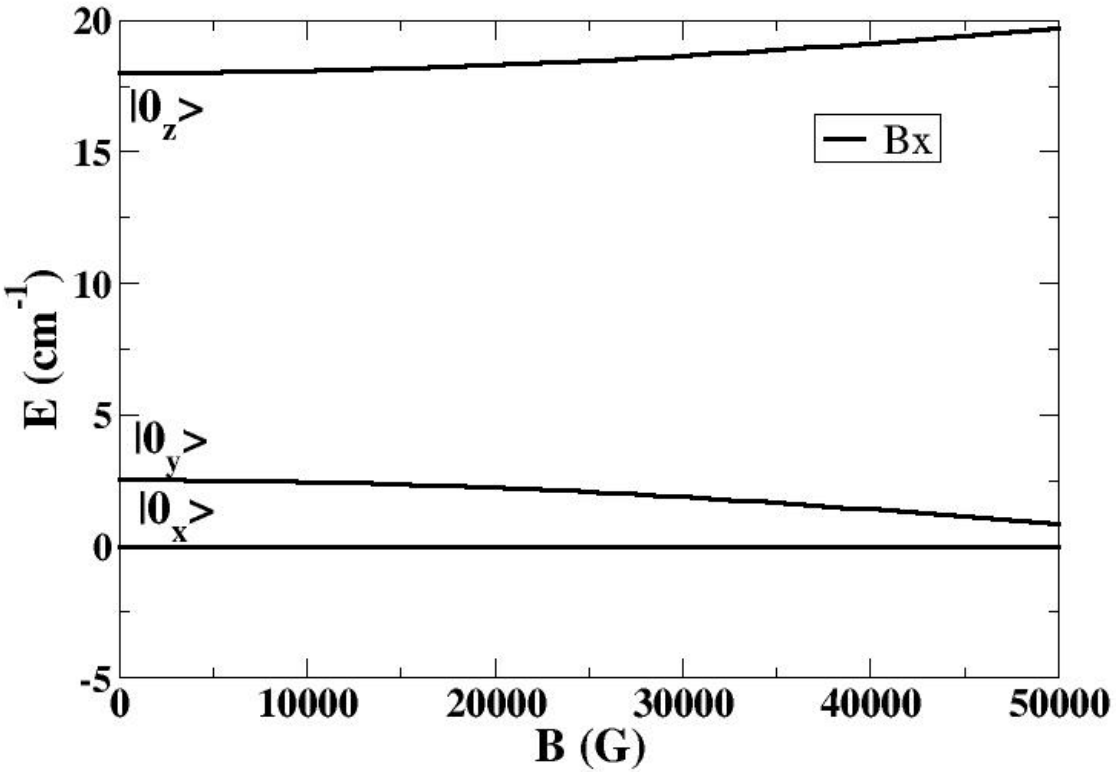
Spin Hamiltonian

- a magnetic field in direction x induces a coupling between $|0_y\rangle$ and $|0_z\rangle$ and induces a magnetic moment, even more that $E_z - E_y$ is small.

H_S	$\|0_x\rangle$	$\|0_y\rangle$	$\|0_z\rangle$
$\langle 0_x\|$	E_x^0	0	0
$\langle 0_y\|$	0	E_y^0	$i\mu_B g B_x$
$\langle 0_z\|$	0	$-i\mu_B g B_x$	E_z^0

Spin Hamiltonian

Spin Hamiltonian energies with E_x^0=0 E_y^0=2.5 E_z^0=18.0 and g=2.3



Spin Hamiltonian

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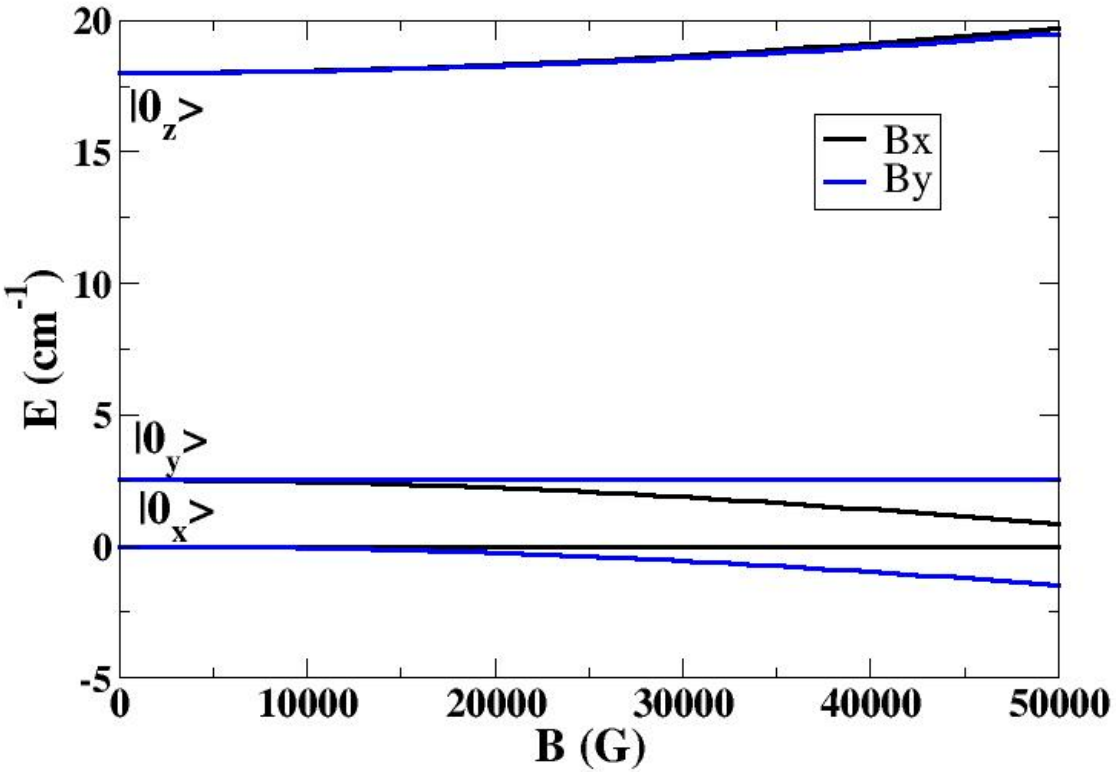

Spin Hamiltonian

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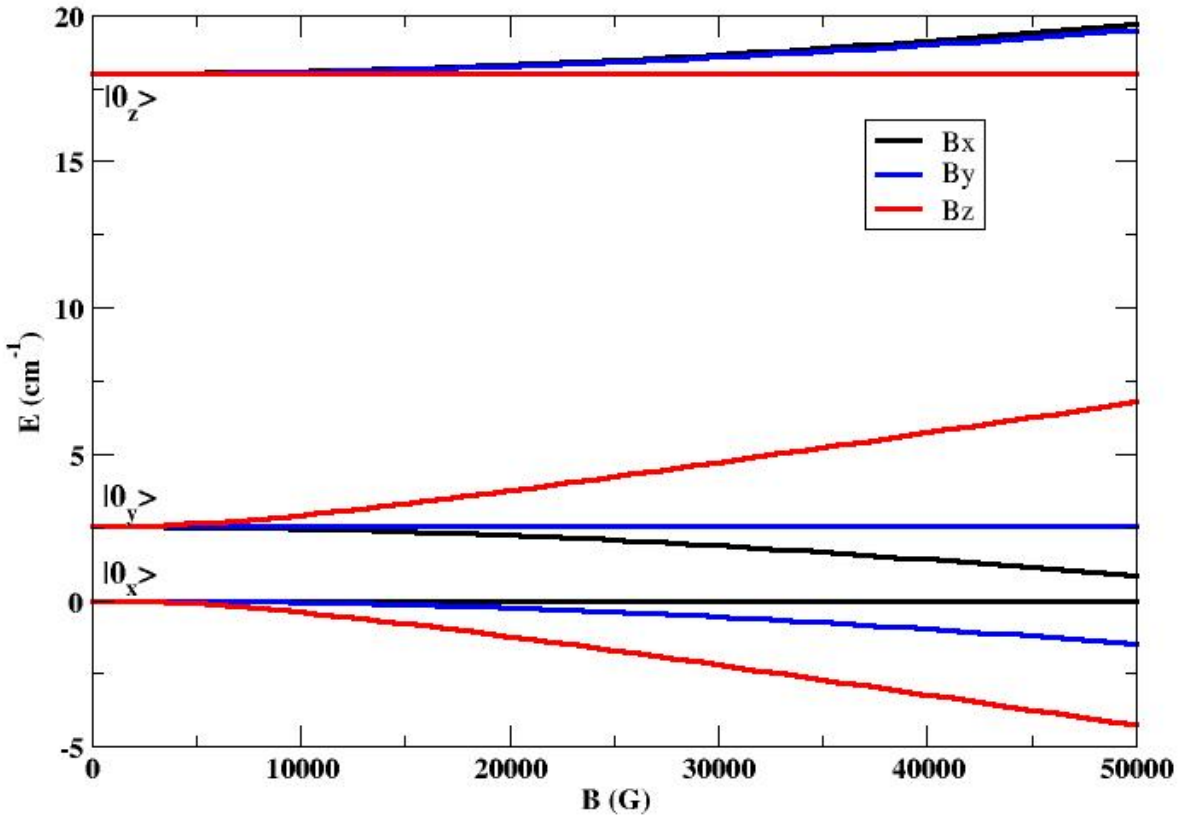

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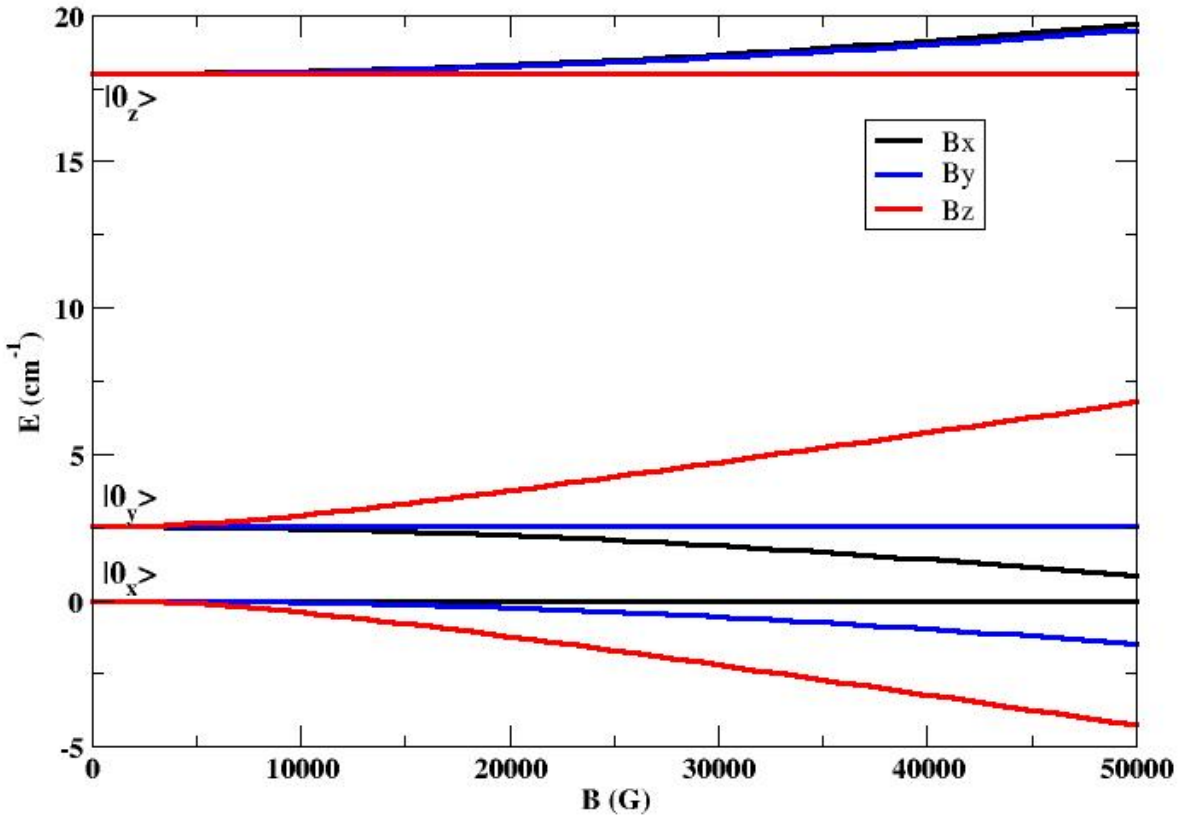

z is the axis of **easy magnetization**

Calculation of the D tensor

- without spin-orbit coupling the three components $\left|^3A,1\right\rangle$ $\left|^3A,0\right\rangle$ and $\left|^3A,-1\right\rangle$ are degenerate
- with spin-orbit

$$
\begin{aligned}
|\Psi_1\rangle &= c_{11}\left|^3A,1\right\rangle + c_{12}\left|^3A,0\right\rangle + c_{13}\left|^3A,-1\right\rangle + \sum_{I,M_S} c_{1IMS}\left|^3\Gamma_I,M_S\right\rangle + \sum_{IJ} c_{1J}\left|^1\Gamma_J,0\right\rangle \\
|\Psi_2\rangle &= c_{21}\left|^3A,1\right\rangle + c_{22}\left|^3A,0\right\rangle + c_{23}\left|^3A,-1\right\rangle + \sum_{I,M_S} c_{2IMS}\left|^3\Gamma_I,M_S\right\rangle + \sum_{IJ} c_{2J}\left|^1\Gamma_J,0\right\rangle \\
|\Psi_3\rangle &= c_{31}\left|^3A,1\right\rangle + c_{32}\left|^3A,0\right\rangle + c_{33}\left|^3A,-1\right\rangle + \sum_{I,M_S} c_{2IMS}\left|^3\Gamma_I,M_S\right\rangle + \sum_{IJ} c_{3J}\left|^1\Gamma_J,0\right\rangle
\end{aligned}
$$

  with energies E_1, E_2 and E_3.
- Since the spin-orbit is a small perturbation, $c_{i1}^2 + c_{i2}^2 + c_{i3}^2$ close to 1.

Calculation of the D tensor

effective Hamiltonian technique

- effective Hamiltonian matrix in the $\left|^3A,1\right\rangle$ $\left|^3A,0\right\rangle$ $\left|^3A,-1\right\rangle$ target space

$$H^{eff} = \mathbf{C}^{-1}\mathbf{E}\mathbf{C}$$

$C_{ij} = c_{ij}\ i,j = 1,3$
$E_{ij} = E_i\delta_{ij}$

- properties of effective Hamiltonian

$$\begin{aligned} H^{eff}P\left|\Psi_1\right\rangle &= E_1P\left|\Psi_1\right\rangle \\ H^{eff}P\left|\Psi_2\right\rangle &= E_2P\left|\Psi_2\right\rangle \\ H^{eff}P\left|\Psi_3\right\rangle &= E_3P\left|\Psi_3\right\rangle \end{aligned}$$

$P = \sum_{M_S}\left|^3A,M_S\right\rangle\left\langle^3A,M_S\right|$ projector on the target space

Calculation of the D tensor

basis set $\left|^3A,1\right\rangle \left|^3A,0\right\rangle \left|^3A,-1\right\rangle$

$$\mathbf{H}^{eff} = \begin{pmatrix} 0.155 & -0.373+0.453i & 3.211+1.293i \\ -0.373-0.453i & 3.048 & 0.373-0.453i \\ 3.211-1.293i & 0.373+0.453i & 0.155 \end{pmatrix}$$

Calculation of the D tensor

basis set $\left|^3A,1\right\rangle \left|^3A,0\right\rangle \left|^3A,-1\right\rangle$

$$\mathbf{H}^{eff} = \begin{pmatrix} 0.155 & -0.373+0.453i & 3.211+1.293i \\ -0.373-0.453i & 3.048 & 0.373-0.453i \\ 3.211-1.293i & 0.373+0.453i & 0.155 \end{pmatrix}$$

basis set $\left|\tilde{1}\right\rangle \left|\tilde{0}\right\rangle \left|-\tilde{1}\right\rangle$

$$\mathbf{H}_S = \begin{pmatrix} \frac{1}{2}\left(D_{xx}+D_{yy}+4D_{zz}\right) & \frac{1}{\sqrt{2}}\left(D_{zx}-iD_{zy}\right) & \frac{1}{2}\left(D_{xx}-D_{yy}-2iD_{xy}\right) \\ \frac{1}{\sqrt{2}}\left(D_{zx}+iD_{zy}\right) & D_{xx}+D_{yy} & \frac{1}{\sqrt{2}}\left(-D_{zx}+iD_{zy}\right) \\ \frac{1}{2}\left(D_{xx}-D_{yy}+2iD_{xy}\right) & \frac{1}{\sqrt{2}}\left(-D_{zx}-iD_{zy}\right) & \frac{1}{2}\left(D_{xx}+D_{yy}+4D_{zz}\right) \end{pmatrix}$$

Calculation of the D tensor

basis set $\left|^3A,1\right\rangle \left|^3A,0\right\rangle \left|^3A,-1\right\rangle$

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basis set $\left|\tilde{1}\right\rangle \left|\tilde{0}\right\rangle \left|-\tilde{1}\right\rangle$

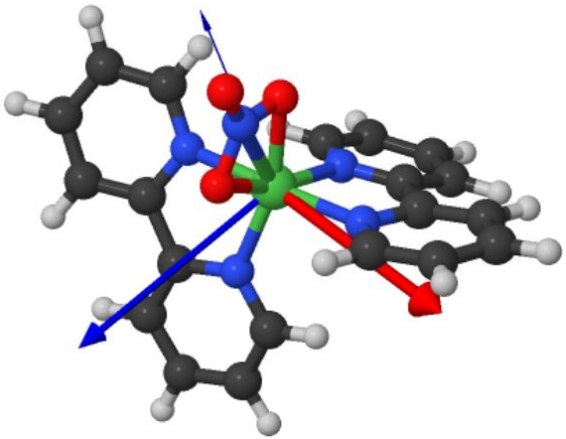
$$\mathbf{H}_S = \begin{pmatrix} \frac{1}{2}\left(D_{xx}+D_{yy}+4D_{zz}\right) & \frac{1}{\sqrt{2}}\left(D_{zx}-iD_{zy}\right) & \frac{1}{2}\left(D_{xx}-D_{yy}-2iD_{xy}\right) \\ \frac{1}{\sqrt{2}}\left(D_{zx}+iD_{zy}\right) & D_{xx}+D_{yy} & \frac{1}{\sqrt{2}}\left(-D_{zx}+iD_{zy}\right) \\ \frac{1}{2}\left(D_{xx}-D_{yy}+2iD_{xy}\right) & \frac{1}{\sqrt{2}}\left(-D_{zx}-iD_{zy}\right) & \frac{1}{2}\left(D_{xx}+D_{yy}+4D_{zz}\right) \end{pmatrix}$$

- comparison of the two matrices $\rightarrow$ all the elements of the **D** tensor

$$\mathbf{D} = \begin{pmatrix} 3.055 & 1.293 & 0.527 \\ 1.293 & -3.367 & -0.640 \\ 0.527 & -0.640 & 0.311 \end{pmatrix}$$

Calculation of the D tensor

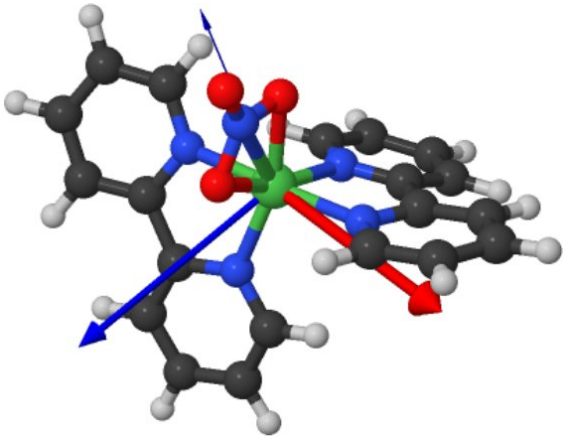
- the diagonalization of **D** leads to the magnetic axis



red = easy axis

Calculation of the D tensor

- the diagonalization of **D** leads to the magnetic axis



red = easy axis

- this method needs a description by a two-step method for which the spin-orbit coupling is introduced a posteriori

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Calculation of the g factors

model matrices

basis set $|0_x\rangle|0_y\rangle|0_z\rangle$

$$\mathbf{M}_x = \begin{pmatrix} 0 & -ig_{xz} & ig_{xy} \\ ig_{xz} & 0 & -ig_{xx} \\ -ig_{xy} & ig_{xx} & 0 \end{pmatrix}$$

$$\mathbf{M}_y = \begin{pmatrix} 0 & -ig_{yz} & ig_{yy} \\ ig_{yz} & 0 & -ig_{yx} \\ -ig_{yy} & ig_{yx} & 0 \end{pmatrix}$$

$$\mathbf{M}_z = \begin{pmatrix} 0 & -ig_{zz} & ig_{zy} \\ ig_{zz} & 0 & -ig_{zx} \\ -ig_{zy} & ig_{zx} & 0 \end{pmatrix}$$

Calculation of the D tensor

calculated matrices

basis set $|\Psi_1\rangle|\Psi_2\rangle|\Psi_3\rangle$

$$\mathbf{M}_x = \begin{pmatrix} 0 & 0.002 & -0.001 \\ 0.002 & 0 & 0.636 - 2.106i \\ -0.001 & 0.636 + 2.106i & 0 \end{pmatrix}$$

$$\mathbf{M}_y = \begin{pmatrix} 0 & 2.234 + 0.247i & -0.003 - 0.001i \\ 2.234 - 0.247i & 0 & -0.002i \\ -0.003 + 0.001i & 0.002i & 0 \end{pmatrix}$$

$$\mathbf{M}_z = \begin{pmatrix} 0 & -0.004 & 2.032 + 0.868i \\ -0.004 & 0 & 0.001i \\ 2.032 - 0.868i & -0.001i & 0 \end{pmatrix}$$

Calculation of the D tensor

calculated matrices after rotation

basis set $|\Psi_1\rangle\ e^{i\alpha}\,|\Psi_2\rangle\ e^{i\beta}\,|\Psi_3\rangle$

$$\mathbf{M}_x = \begin{pmatrix} 0 & 0.002i & 0.002i \\ -0.002i & 0 & 2.200i \\ -0.002i & -2.200i & 0 \end{pmatrix}$$

$$\mathbf{M}_y = \begin{pmatrix} 0 & -0.004i & 2.210i \\ 0.004i & 0 & -0.002i \\ 2.210i & 0.002i & 0 \end{pmatrix}$$

$$\mathbf{M}_z = \begin{pmatrix} 0 & 2.248i & 0.004i \\ -2.248i & 0 & 0.002i \\ -0.004i & -0.002i & 0 \end{pmatrix}$$

basis set $|0_x\rangle|0_y\rangle|0_z\rangle$

$$\mathbf{M}_x^S = \begin{pmatrix} 0 & -ig_{xz} & ig_{xy} \\ ig_{xz} & 0 & -ig_{xx} \\ -ig_{xy} & ig_{xx} & 0 \end{pmatrix}$$

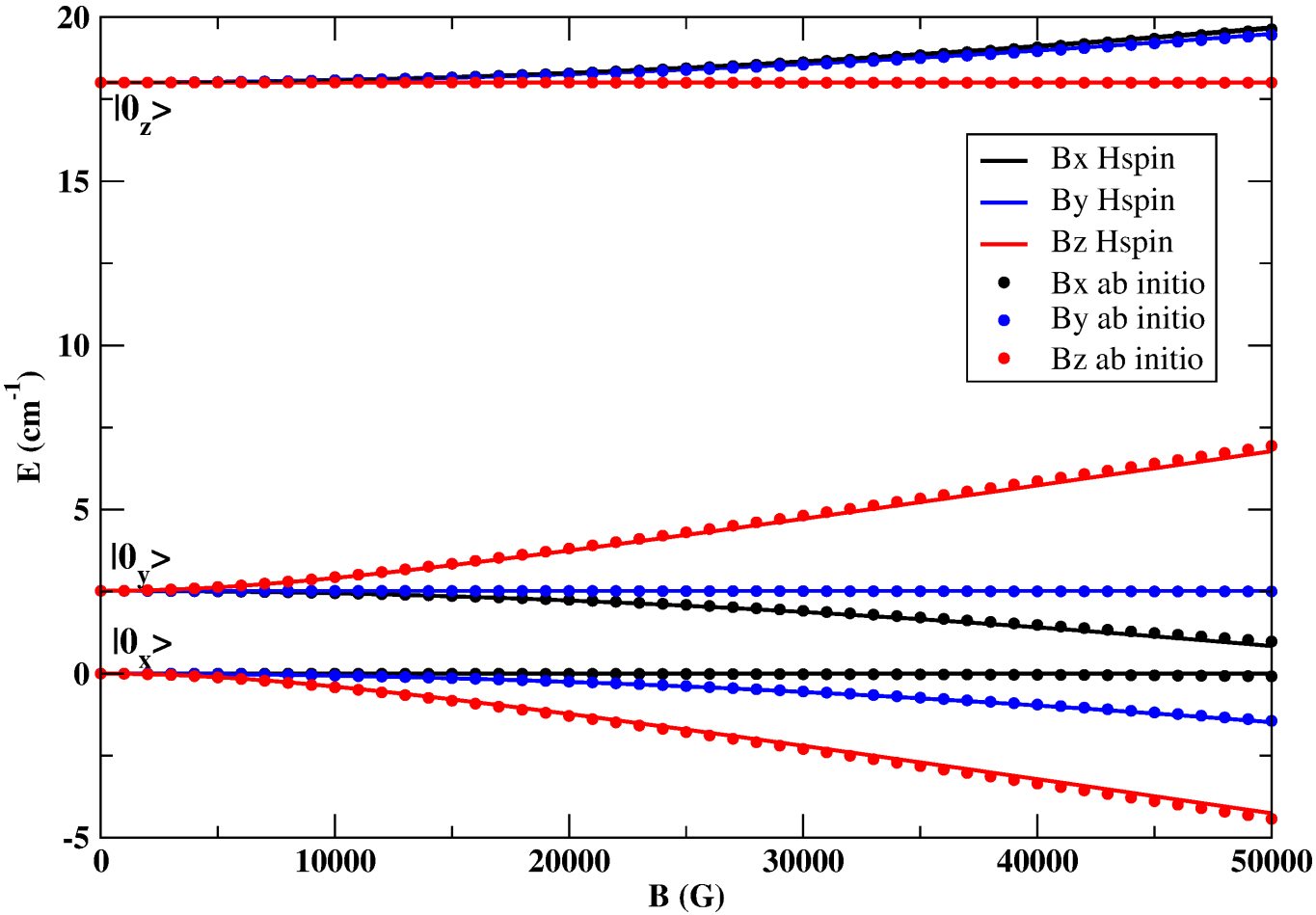
$$\mathbf{M}_y^S = \begin{pmatrix} 0 & -ig_{yz} & ig_{yy} \\ ig_{yz} & 0 & -ig_{yx} \\ -ig_{yy} & ig_{yx} & 0 \end{pmatrix}$$

$$\mathbf{M}_z^S = \begin{pmatrix} 0 & -ig_{zz} & ig_{zy} \\ ig_{zz} & 0 & -ig_{zx} \\ -ig_{zy} & ig_{zx} & 0 \end{pmatrix}$$

Calculation of the D tensor

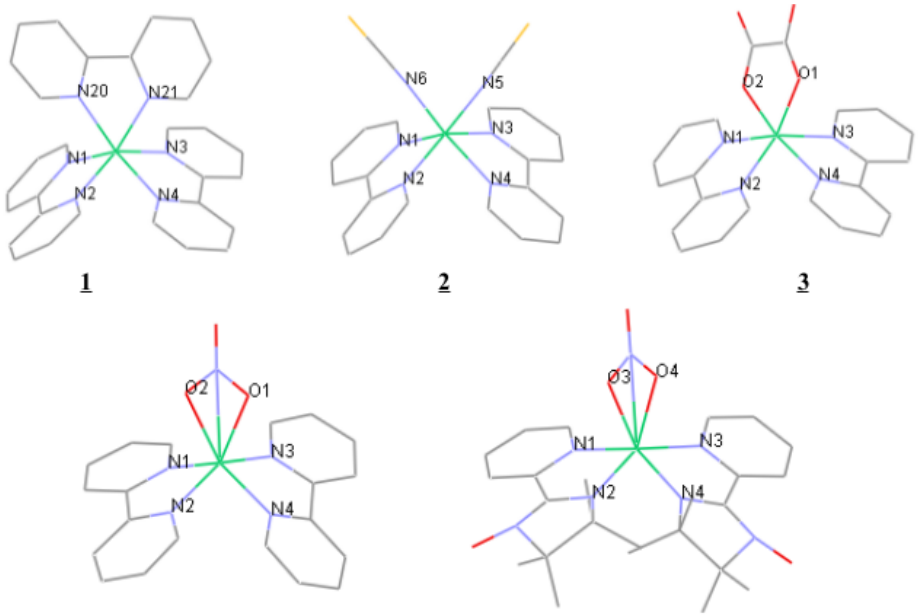
- one builds $\mathbf{g}$
- one deduces $\mathbf{G} = \mathbf{g}\mathbf{g}^{\dagger}$
- one gets the principal axis of $\mathbf{g}$ and the g factors
- $g_1 = 2.200$ $g_2 = 2.248$ $g_3 = 2.210$
- principal axis of G close to those of D

Spin Hamiltonian versus ab initio



Pseudooctahedric Ni(II) complexes

the series



		1	2	3	4	5
		$Ni(bipy)_3$	$Ni(bipy)_2(NCS)_2$	$Ni(bipy)_2ox$	$Ni(bipy)_2NO_3$	NiL_2NO_3
exp	X-Ni-X	79	91	80	60	60
	D (cm^{-1})	-1.18	-1.74	-1.44	-5.82	-10.00
	E/D	0.17	0.24	0.04	0.04	0.07
SO-CASPT2	D (cm^{-1})	-2.807	-3.55	-3.59	-5.62	-11.52
	E/D	0.18	0.48	0.27	0.26	0.04

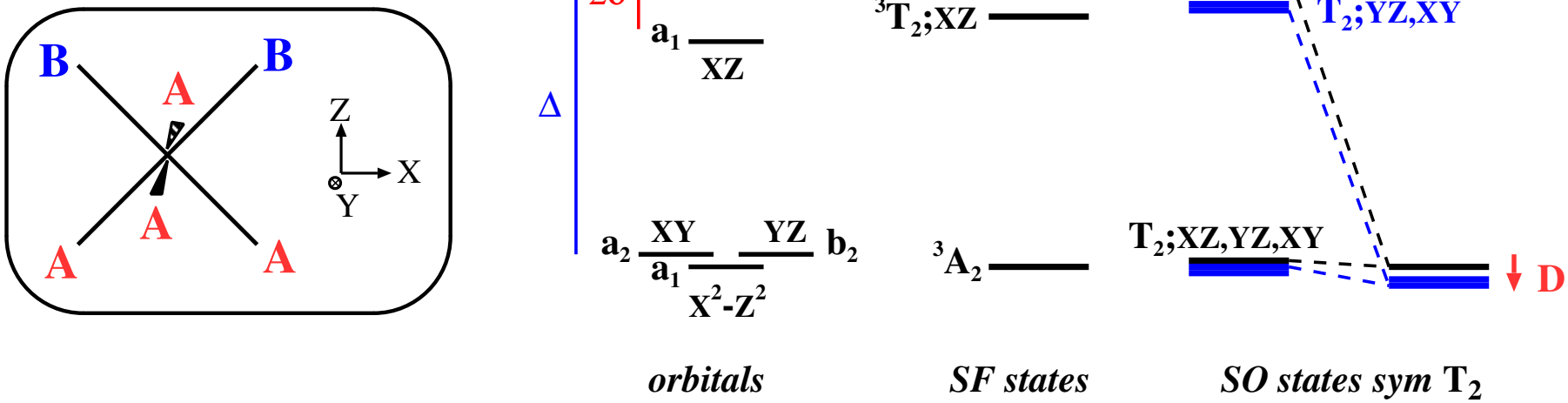
Crystal field : $\mathscr{O}_h$ symmetry

T_2	${}^3A_2(t_{2g}^6 e_g^2)$	${}^3T_2(t_{2g}^5 e_g^3)$
	0	$\sqrt{2}\lambda$
	$\sqrt{2}\lambda$	Δ

$$
\begin{aligned}
\left|{}^3T_2; T_2; xy\right\rangle &= \frac{1}{\sqrt{2}}\left(-\left|T_2; xz\right\rangle \otimes \left|0\right\rangle_x + \left|T_2; yz\right\rangle \otimes \left|0\right\rangle_y\right) \\
\left|{}^3T_2; T_2; yz\right\rangle &= \frac{1}{\sqrt{2}}\left(-\left|T_2; xy\right\rangle \otimes \left|0\right\rangle_y + \left|T_2; xz\right\rangle \otimes \left|0\right\rangle_z\right) \\
\left|{}^3T_2; T_2; xz\right\rangle &= \frac{1}{\sqrt{2}}\left(\left|T_2; xy\right\rangle \otimes \left|0\right\rangle_x - \left|T_2; yz\right\rangle \otimes \left|0\right\rangle_z\right)
\end{aligned}
$$

$$
\begin{aligned}
E_{xy}^{SO} &= \frac{1}{2}\left(E_{xz}^{SF} + E_{yz}^{SF}\right) = \Delta \\
E_{yz}^{SO} &= \frac{1}{2}\left(E_{xy}^{SF} + E_{xz}^{SF}\right) = \Delta \\
E_{xz}^{SO} &= \frac{1}{2}\left(E_{xy}^{SF} + E_{yz}^{SF}\right) = \Delta
\end{aligned}
$$

Crystal field : $\mathscr{C}_{2v}$ symmetry



spin-free		spin-orbit	
$^3A_2$	2Δ	$T_2; XZ, YZ, XY$	2Δ
$^3T_2, XZ$	$3\Delta - \frac{1}{2}\delta$	$T_2; XZ$	$3\Delta + \frac{1}{4}\delta$
$^3T_2, YZ$ $^3T_2, XY$	$3\Delta + \frac{1}{4}\delta$	$T_2; YZ$ $T_2; XY$	$3\Delta - \frac{1}{8}\delta$

$D < 0 \Longrightarrow \delta > 0 \Longrightarrow$ A is a better σ donnor as B

Crystal field : $\mathscr{C}_{2v}$ symmetry

spectrochemical series bipy>NCS^->ox >$NO3^-$

energies in cm^{-1}

		$Ni(bipy)_3$	$Ni(bipy)_2(NCS)_2$	$Ni(bipy)_2ox$	$Ni(bipy)_2NO_3$	NiL_2NO_3
exp	X-Ni-X	79	91	80	60	60
	D	-1.18	-1.74	-1.44	-5.82	-10.00
th	D	-2.807	-3.55	-3.59	-5.62	-11.52
	Δ	9426	8318	8171	8581	7725
	δ	329	658	87	2194	2326
	δ/Δ	0.034	0.079	0.010	0.255	0.301

$\tilde{S} = 1$: Conclusions

- for transition metal complexes with a quenched orbital momentum and $S = 1$
- the anisotropic magnetic properties are due to the zero field splitting since the Zeeman interaction is almost isotropic
- the anisotropy is larger with a scheme $E_x \simeq E_y \ll E_z$

Two step methods

summary

- ☺
- the symmetry of the wave function is well defined
- the wave functions of all the components of degenerate states are known
- use of the single symmetry to describe dynamical correlation : cheaper and usual machinery
- ☹
- a lot of SF excited states needs to be calculated for the correct description of the ground state
- not systematic improvement of the calculation
- for lanthanide and actinide, crystal field is a perturbation of the SOC

Conclusions

- from the matrices of magnetic moments, one gets all information about the response to an external magnetic field.
- restriction to a model space $\Longrightarrow$ spin Hamiltonian parameters
- for the calculation of the ZFS tensor, needs a two-step method
- the results are satisfactory but numerical accuracy not reached

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