Crystal field
in multielectron 3d metallic ions

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Crystal field

Crystal field theory : origin

Hans Bethe (1906-2005) [2]

(Nobel Prize in Physics 1967)

In **1929** (University of Tübingen) [1]

" Either we treat the crystal as a complete whole (spatial-periodic potential field and wave function) " *(F. Bloch theory)*

or

" one can start from **a free atom and treat its disturbance in the crystal** "

"the atom in the crystal is influenced by the other atoms by an **electric field** of certain symmetry" = **Crystal field**
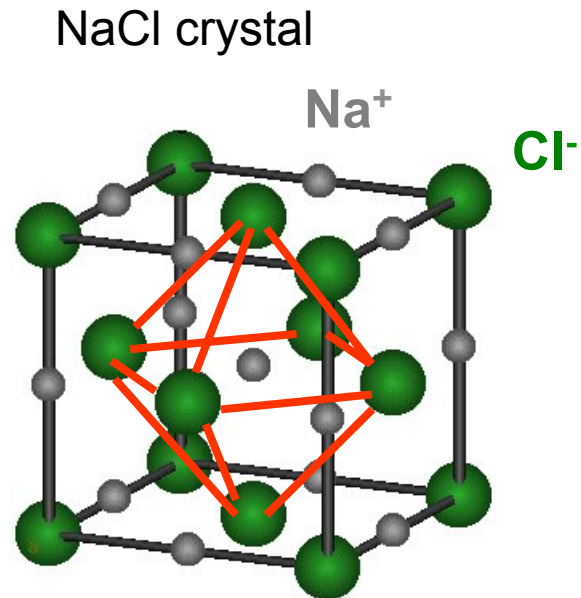
[1] H. Bethe, Annalen der Physik, 1929
[2] W. Kutzelnigg, Angew. Chem. 44, 25 (2005)

Crystal field : origin

Hans Bethe (1929) : Model used for NaCl crystal.

NaCl crystal

Na⁺ Cl⁻

Crystal field (CF)

Electric potential generated by the charges of the neighbor atoms
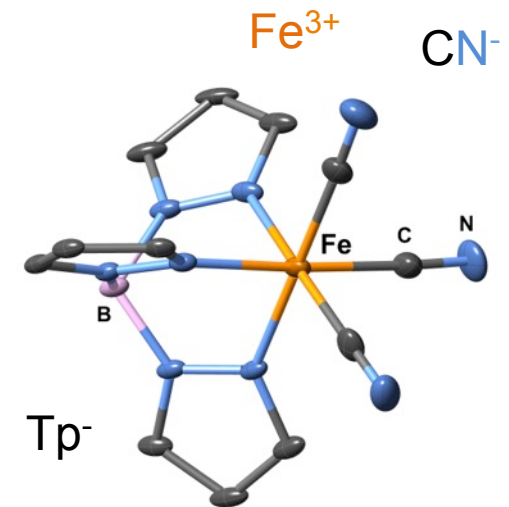
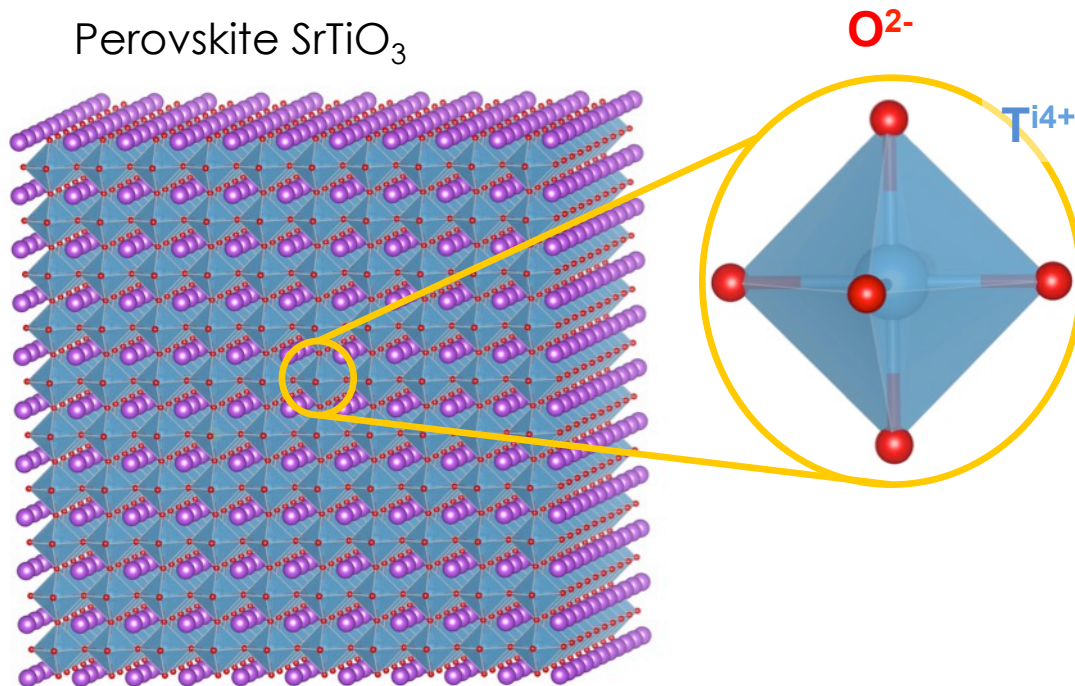Na⁺ ion surrounded by 6 Cl⁻ ions (nearest neighbors

➢ CF = Electrostatic potential produced by 6 negative charges:

$$V_{CF} = \sum_{i=1}^{6} \frac{e}{r_i}$$ *(r$_i$ = Na-Cl distance)*

➢ Depends on the local symmetry

H. Bethe, Annalen der Physik, 1929

Crystal field : origin

Analogy in solid-state or coordination complexes :
Consider the ligands as charged spheres

Perovskite $SrTiO_3$

O^{2-}

Ti^{4+}

Fe^{3+}

CN^-

Tp^-

Tp=tris-pyrazolyl borate

Crystal field model

- **Local model (restricted to the first neighbors /ligands)**

- **A purely *ionic* model for transition metal complexes.**

- **Ligands are considered as point charge.**

- **Predicts the pattern of splitting of d-orbitals.**

- **Used to rationalize spectroscopic and magnetic properties.**

II.1. Symmetries

Symmetry : responsible for many physical and spectroscopic properties of compounds

Group theory : powerful tool
- ➢   simplify calculations,
- ➢   predict some properties
- ➢   defines the language of labeling
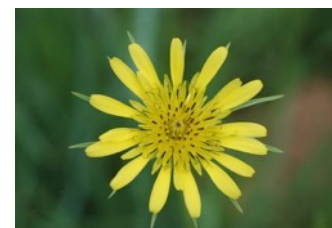
Symmetry operations : some notations to know

- **E**, the identity
- **C$_n$**, a rotation by an angle 2π/n;
- **σ** reflection in a plane, classified as
  - **σ$_h$**, reflection through a plane perpendicular to the axis of highest rotation symmetry, called *principal axis*
  - **σ$_v$,** reflection through a plane to which the principal axis belongs
  - **σ$_d$**, reflection through a plane to which the principal axis belongs, and bisecting the angle between the two-fold axes perpendicular to the principal axis.
- **S$_n$ = σ$_h$ ⊗ C$_n$**, improper rotation of an angle 2π/n
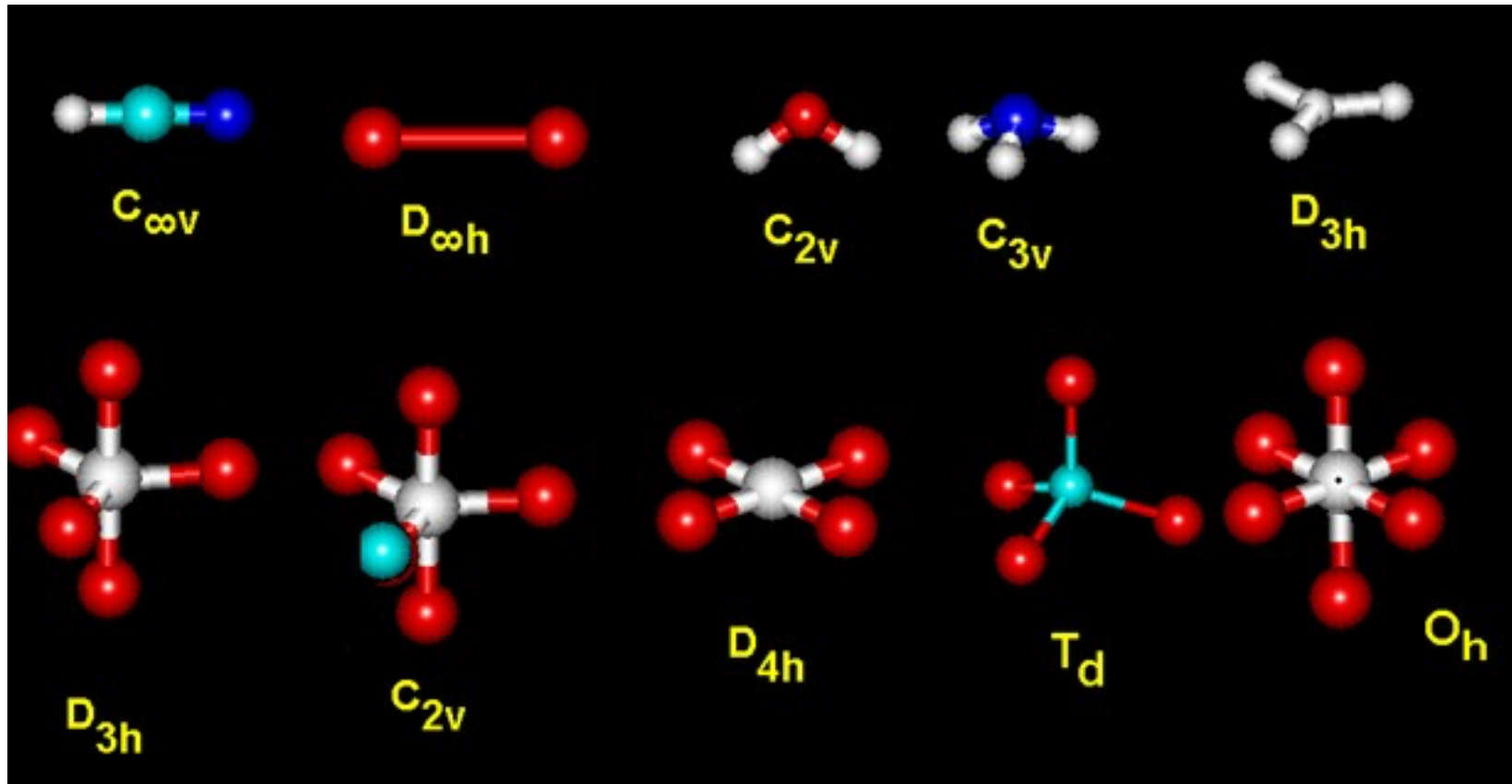- **I = S$_2$**, the inversion.

Quanty : http://www.quanty.org/physics_chemistry/point_groups
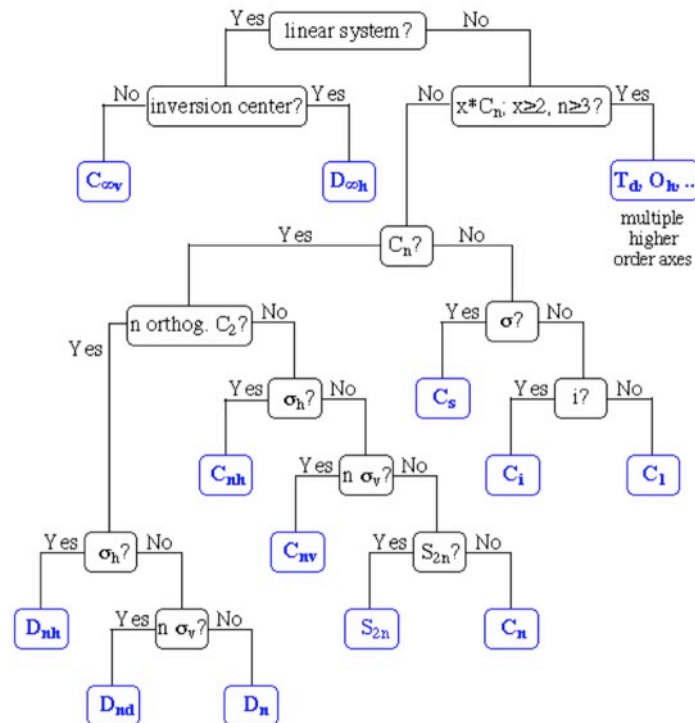
Symmetries : some point groups

◆ A group of symmetry is an ensemble of symmetry operations (group theory)
◆ Each group is labeled (in Schönfliess notation)

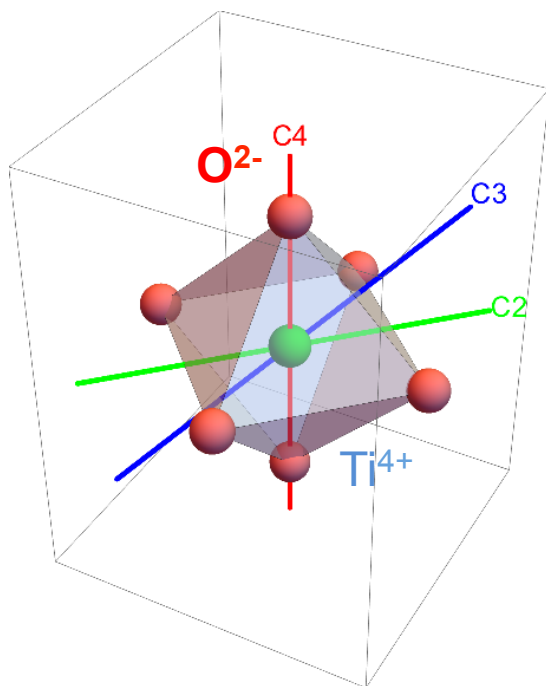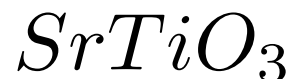◆ Each group has a table of representations

Symmetry tree

Quanty :
http://www.quanty.org/physics_chemistry/
point_groups#a_flow_diagram_to_determine_the_point_group

Octahedral symmetry: O_h

$SrTiO_3$

Character table

Symmetry elements

Basis functions

Group : O_h

	E	$8C_3$	$6C_2$	$6C_4$	$3C_2 = (C_4)^2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	linear, rotations	quadratic
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xz, yz, xy)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

Irreducible representation :
labeled the symmetry properties of a state in the group

Point groups: Quanty website

All you need is in the web page Quanty.org
http://quanty.org/physics_chemistry/point_groups

Point groups: Quanty / Orientation

Oh

http://quanty.org/physics_chemistry/point_groups/oh

Symmetries

$SrTiO_3$

$[TpFe^{III}(CN)_3]^-$

O²⁻ ... *(image)*

Octahedral
Group : O_h

Approximative
Trigonal group :
C_{3v}

II.2. Crystal field Hamiltonian

Crystal field Hamiltonian

CF potential : expanded on the normalized spherical harmonics

$$C_{k,m}(\theta, \phi) = \left(\tfrac{4\pi}{2k+1} \right)^{1/2} Y_{k,m}(\theta, \phi)$$

$$H_{CF} = \sum_{k=0}^{\infty} \sum_{m=-k}^{k} A_{k,m} C_k^m(\theta, \phi)$$

$A_{k,m}$ are the crystal field parameters

Sum over k infinity ?

➔ CF matrix element

CF matrix element

The crystal field potential

$$H_{CF} = \sum_{k=0}^{\infty} \sum_{m=-k}^{k} A_{k,m} C_k^m(\theta, \phi)$$

Basis function (one electron)

$$\phi_i(\mathbf{r}, \sigma) = \frac{1}{r} \underbrace{P_{n_i \ell_i}(r)}_{\text{Radial}} \underbrace{Y_{\ell,m}(\theta, \phi)}_{} \underbrace{\chi_{m_{s_i}}(\sigma)}_{\text{spin}}$$

Angular
Spherical harmonics

For an electron in orbital ℓ

$$\langle \phi_i | H_{CF} | \phi_j \rangle \propto \langle Y_{\ell, m_i} | C_{k,m} | Y_{\ell, m_j} \rangle$$

$$\propto \begin{pmatrix} \ell & k & \ell \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell & k & \ell \\ -m_i & m & m_j \end{pmatrix}$$

$$\neq 0 \text{ if } \boxed{k \text{ even } (2\ell + k \text{ even}), \ 0 \le k \le 2\ell}$$

Crystal field Hamiltonian

$$H_{CF} = \sum_{\substack{k=0, \\ k \ even}}^{2\ell} \sum_{m=-k}^{k} A_{k,m} C_{k,m}(\theta, \phi)$$

$$A_{k,m} = (-1)^m A^*_{k,-m}$$

Hermitian Hamiltonian

- -

Exemples

3d ion $\ell = 2$

$$k = 0, 2, 4$$

4f ion $\ell = 3$

$$k = 0, 2, 4, 6$$

Crystal field and symmetry

$$H_{CF} = \sum_{\substack{k=0, \\ k \ even}}^{2\ell} \sum_{m=-k}^{k} A_{k,m} C_{k,m}(\theta, \phi)$$

Point group $G=Oh$
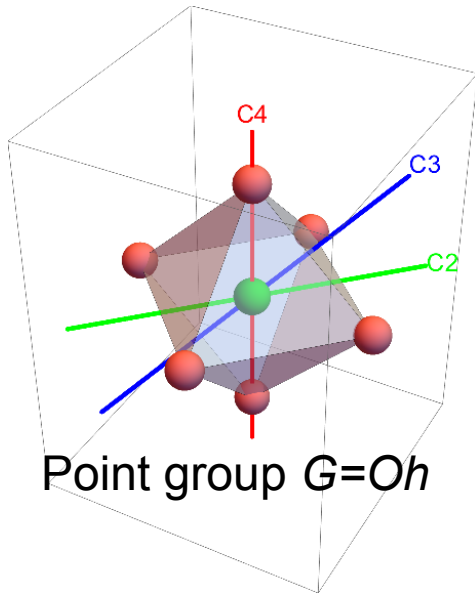
CF Hamiltonian belongs to G
    invariant under all symmetry operation of $G(O_i)$

$$O_i H_{CF} = H_{CF}$$

Some $A_{km} = 0$ due to symmetry

Crystal field Hamiltonian and symmetry

Example : O_h symmetry

$$O_i H_{CF} = H_{CF}$$
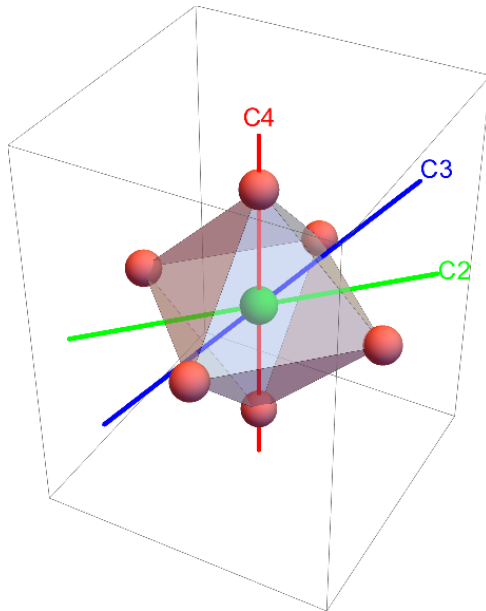
	E	$8C_3$	$6C_2$	$6C_4$	$3C_2 = (C_4)^2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1
E_g	2	-1	0	0	2	2	0	-1	2	0
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1
E_u	2	-1	0	0	2	-2	0	1	-2	0
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1

$$H_{CF} \in A_{1g}$$

Only 2 non-zero A_{km} :
A_{00}, A_{40}

$$H_{CF}^{O_h} = A_{4,0} C_4^0 + \sqrt{\frac{5}{14}} A_{4,0}(C_4^{-4} + C_4^4)$$

CF matrix
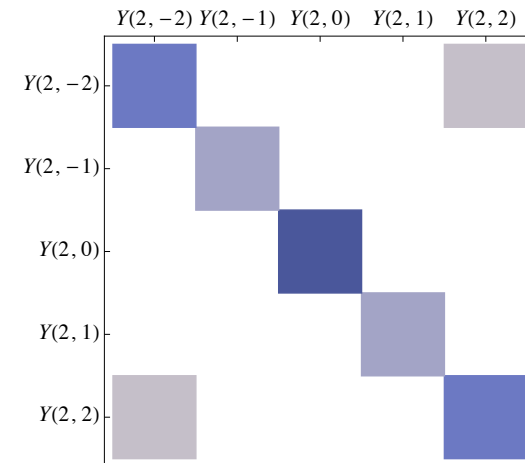
Notations for crystal field parameters

Vary from an author to the other

$$H_{CF} = \sum_{\substack{k=0, \\ k\ even}}^{2\ell} \sum_{m=-k}^{k} A_{k,m} C_{k,m}(\theta, \phi)$$ (Haverkort/Quanty)

$$H_{\mathrm{CF}}(\mathbf{r}) = \sum_{k=0}^{\infty} \sum_{m=-k}^{k} r^k A_{k,m} \, C_{k,m}(\theta, \phi) = \sum_{k=0}^{\infty} \sum_{m=-k}^{k} B_{k,m} \, C_{k,m}(\theta, \phi)$$

Parameters used mostly by chemist
Symmetry-dependent
(Balhausen, König, Kremer,..)

10Dq for Oh
10Dq, Ds, Dt for D$_{4h}$
10Dq, Dσ, Dτ for D$_{3d}$ or C$_{3v}$

Parameters used in Quanty :
Orbital energies + off-diagonal elements
Symmetry-dependent

E$_{eg}$, E$_{t2g}$ for Oh
E$_{a1g}$, E$_{eg}$, E$_{b1g}$, E$_{b2g}$ for D$_{4h}$

Crystal field

1. Introduction / Definition
2. One electron (3d electron)
    1. Symmetries
    2. Hamiltonian

    3. Crystal field splitting of one 3d electron

3. Multi-electrons ion (3d electrons)
    1. The spherical ion :
    2. Crystal field
    3. Core hole spectroscopy : examples

4. Crystal field and magnetism
    1. Hamiltonian
    2. Magnetic moment (spin and orbit)
    3. Zeeman effect / paramagnetism

3d atomic orbitals

- Basis of atomic orbitals $\quad \phi_i(\mathbf{r}, \sigma) = \frac{1}{r} P_{n_i \ell_i}(r) \, Y_{\ell,m}(\theta, \phi) \, \chi_{m_{s_i}}(\sigma)$

- 3d shell : n=3, ℓ=2 $\qquad$ $2\ell+1$=5 basis functions ($-2 \leq m_\ell \leq 2$)

$$Y_{2,m}(\theta, \phi) \; with \; m = -2, -1, 0, 1, 2$$

- **3d orbitals** = real functions, linear combination of $Y_{2,m}(\theta, \phi)$

$$
\begin{aligned}
d_{xy} &= y_{2-2} = \frac{i}{\sqrt{2}}(Y_2^2 - Y_{-2}^2) = \sqrt{\frac{15}{4\pi}} \quad xy/r^2 \\
d_{yz} &= y_{2-1} = \frac{i}{\sqrt{2}}(Y_1^2 + Y_{-1}^2) = \sqrt{\frac{15}{4\pi}} \quad yz/r^2 \\
d_{3z^2-r^2} &= y_{20} = Y_2^0 \qquad\qquad = \sqrt{\frac{15}{4\pi}}\frac{1}{2\sqrt{3}} \, (3z^2 - r^2)/r^2 \\
d_{xz} &= y_{21} = \frac{1}{\sqrt{2}}(Y_1^2 - Y_{-1}^2) = \sqrt{\frac{15}{4\pi}} \quad xz/r^2 \\
d_{x^2-y^2} &= y_{22} = \frac{1}{\sqrt{2}}(Y_2^2 + Y_{-2}^2) = \sqrt{\frac{15}{4\pi}}\frac{1}{2} \quad (x^2 - y^2)/r^2
\end{aligned}
$$

d_{xy} $\qquad$ d_{yz} $\qquad$ d_{z2} $\qquad$ d_{xz} $\qquad$ d_{x2-y2}
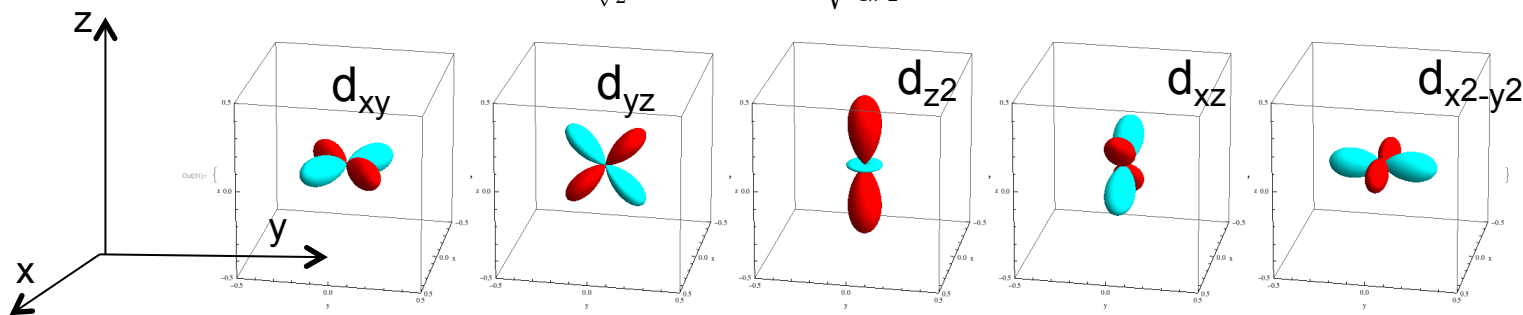
Crystal field splitting for O_h

$$H_{CF}^{O_h} = A_{4,0}C_{4,0} + \sqrt{\frac{5}{14}}A_{4,0}(C_{4,-4} + C_{4,4}) = 21D_qC_{4,0} + 21\sqrt{\frac{5}{14}}D_q(C_{4,-4} + C_{4,4})$$

1) CF matrix in $\{Y_{2,m}\}$ basis

$$|\ell\, m\rangle \equiv |2\, -2\rangle \qquad |2\, -1\rangle \qquad |2\, 0\rangle \qquad |2\, 1\rangle \qquad |2\, 2\rangle$$

$$\begin{pmatrix} A_{0,0} + \frac{1}{21}A_{4,0} & 0 & 0 & 0 & \frac{5}{21}A_{4,0} \\ 0 & A_{0,0} - \frac{4}{21}A_{4,0} & 0 & 0 & 0 \\ 0 & 0 & A_{0,0} + \frac{2}{7}A_{4,0} & 0 & 0 \\ 0 & 0 & 0 & A_{0,0} - \frac{4}{21}A_{4,0} & 0 \\ \frac{5}{21}A_{4,0} & 0 & 0 & 0 & A_{0,0} + \frac{1}{21}A_{4,0} \end{pmatrix}$$

2) Diagonalization

$$\begin{matrix} d_{x^2-y^2} & d_{z^2} & d_{yz} & d_{xz} & d_{xy} \end{matrix}$$

$$\begin{pmatrix} A_{0,0} + \frac{2}{7}A_{4,0} & 0 & 0 & 0 & 0 \\ 0 & A_{0,0} + \frac{2}{7}A_{4,0} & 0 & 0 & 0 \\ 0 & 0 & A_{0,0} - \frac{4}{21}A_{4,0} & 0 & 0 \\ 0 & 0 & 0 & A_{0,0} - \frac{4}{21}A_{4,0} & 0 \\ 0 & 0 & 0 & 0 & A_{0,0} - \frac{4}{21}A_{4,0} \end{pmatrix}$$

O_h crystal field splits the *d* orbitals in two groups

$$\{d_{x^2-y^2}, d_{z^2}\} \text{ and } \{d_{yz}, d_{xz}, d_{xy}\}$$

O_h Crystal field splitting of 3d electron
Use of group symmetry

Character table for O_h point group

	E	$8C_3$	$6C_2$	$6C_4$	$3C_2 = (C_4)^2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	linear, rotations	quadratic
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xz, yz, xy)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

$$\{d_{x^2-y^2}, d_{z^2}\} \in e_g$$
$$\{d_{yz}, d_{xz}, d_{xy}\} \in t_{2g}$$

> ➤ From the *Oh* group properties, one can guess the splitting of the d orbitals
> ➤ d orbitals are called e_g and t_{2g} *

[*] N.B. : lower case letter (e_g and t_{2g}) for one electron

O_h Crystal field splitting of 3d electron

$$E_{e_g} = A_{0,0} + \frac{2}{7}A_{4,0} = +6D_q$$
$$E_{t_{2g}} = A_{0,0} - \frac{4}{21}A_{4,0} = -4D_q$$

Towards the ligand : destabilized

$3d\ (\times 5)$

$e_g\ (\times 2)$

$+6Dq$

$10Dq$

$-4Dq$

$t_{2g}\ (\times 3)$

z y x d_{z^2}

z y x $d_{x^2-y^2}$

y x d_{xy}

y x d_{yz}

z y x d_{xz}
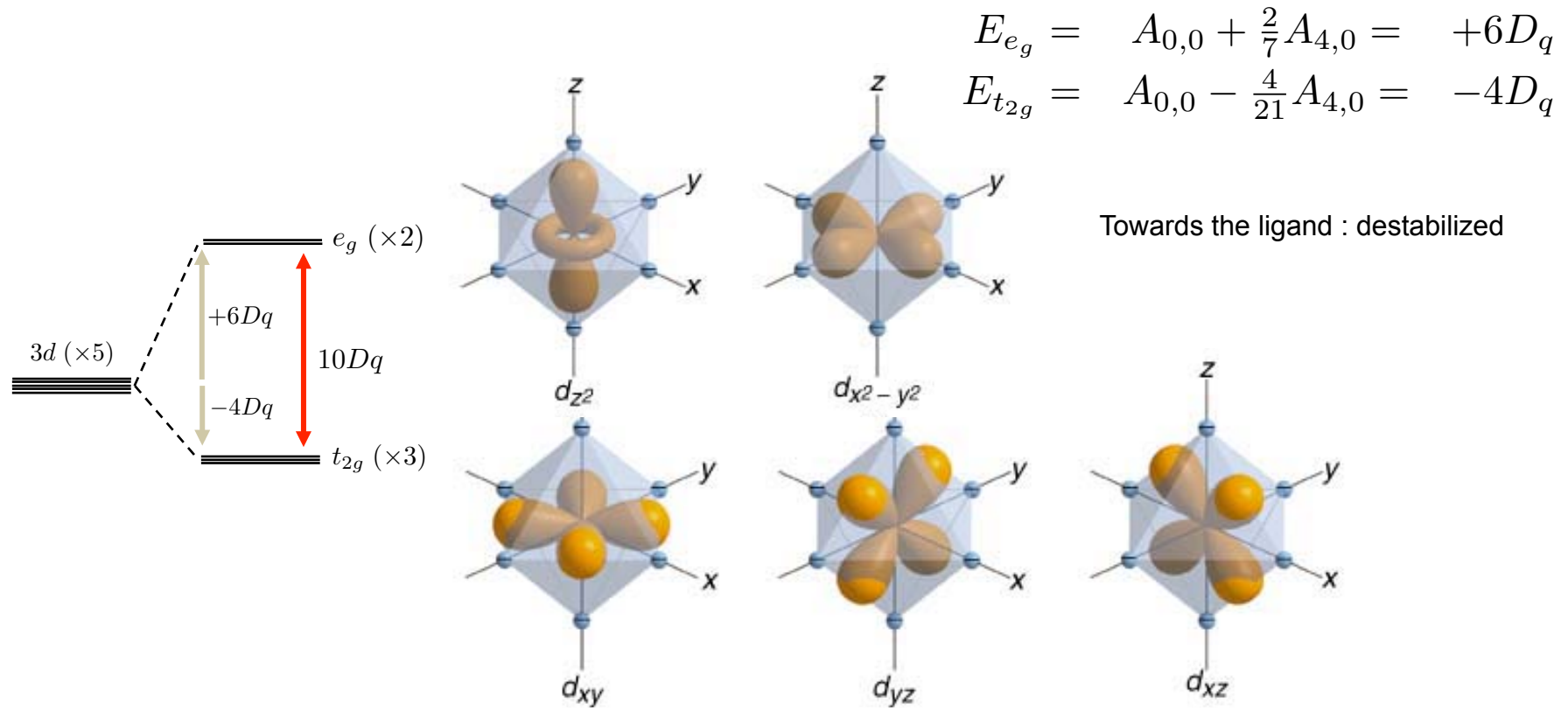
$10Dq \equiv$ Crystal field strength

(parameter)

O_h Crystal field splitting of 3d electron Parameters
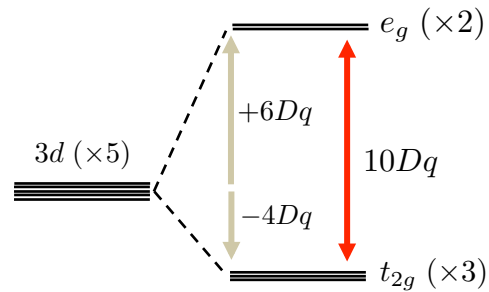
$$E_{e_g} = A_{0,0} + \tfrac{2}{7}A_{4,0} = +6D_q$$

$$E_{t_{2g}} = A_{0,0} - \tfrac{4}{21}A_{4,0} = -4D_q$$

Quanty : $A_{k,m}$ defined in function the orbital energies

$$A_{k,m} = \begin{cases} \tfrac{2}{5}E_{e_g} + \tfrac{3}{5}E_{t_{2g}} & k=0 \quad m=0 \\ \tfrac{21}{10}(E_{e_g} - E_{t_{2g}}) & k=4 \quad m=0 \\ \tfrac{21}{10}\sqrt{\tfrac{5}{14}}(E_{e_g} - E_{t_{2g}}) & k=4 \quad m=\pm 4 \\ 0 & \text{True} \end{cases}$$

Tetragonal (D$_{4h}$) crystal field

D$_{4h}$
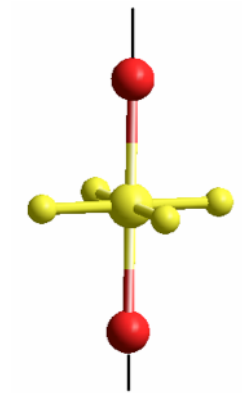
Elongated
or compressed O_h
along C$_4$ axis
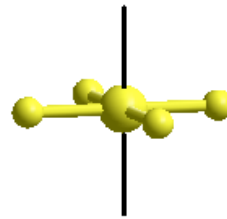
Square planar

Tetragonal (D_{4h}) crystal field

D_{4h}

Elongated
or compressed O_h
along C_4 axis

Square planar
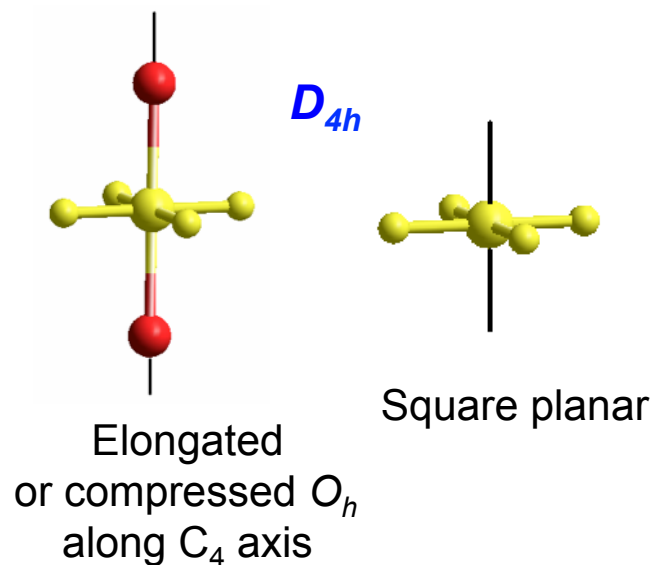
	E	$2C_4$ (z)	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	linears, rotations	quadratic
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		x^2-y^2
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	

From D_{4h} table, one predicts the 3d splitting in 4 groups

$$\{d_{z^2}\} \quad \in a_{1g}$$
$$\{d_{x^2-y^2}\} \quad \in b_{1g}$$
$$\{d_{xy}\} \quad \in b_{2g}$$
$$\{d_{xz}, d_{yz}\} \quad \in e_g$$

Tetragonal (D_{4h}) crystal field

$$H_{CF}^{D_{4h}} = A_{0,0}C_{0,0} + A_{2,0}C_{2,0} + A_{4,0}C_{4,0} + A_{4,4}(C_{4,-4} + C_{4,4})$$

CF matrix diagonal in the {d} basis

$$
\begin{array}{ccccc}
d_{x^2-y^2} & d_{z^2} & d_{yz} & d_{xz} & d_{xy}
\end{array}
$$

$$
\begin{pmatrix}
E_{a_{1g}} & 0 & 0 & 0 & 0 \\
0 & E_{b_{1g}} & 0 & 0 & 0 \\
0 & 0 & E_{e_g} & 0 & 0 \\
0 & 0 & 0 & E_{e_g} & 0 \\
0 & 0 & 0 & 0 & E_{b_{2g}}
\end{pmatrix}
$$

4 energy levels

Tetragonal (D_{4h}) crystal field splitting of 3d electron

$$H_{CF}^{D_{4h}} = A_{0,0}C_{0,0} + A_{2,0}C_{2,0} + A_{4,0}C_{4,0} + A_{4,4}(C_{4,-4} + C_{4,4})$$

O_h

D_{4h} (elongation)

b_{1g} ($d_{x^2-y^2}$)

$2D_s - D_t$

e_g

$2D_s - 6D_t$

a_{1g} (d_{z^2})

10Dq

10Dq

b_{2g} (d_{xy})

$2D_s - D_t$

t_{2g}

$-D_s + 4D_t$
e_g (d_{xz}, d_{yz})

increasing stretch along z ⟶
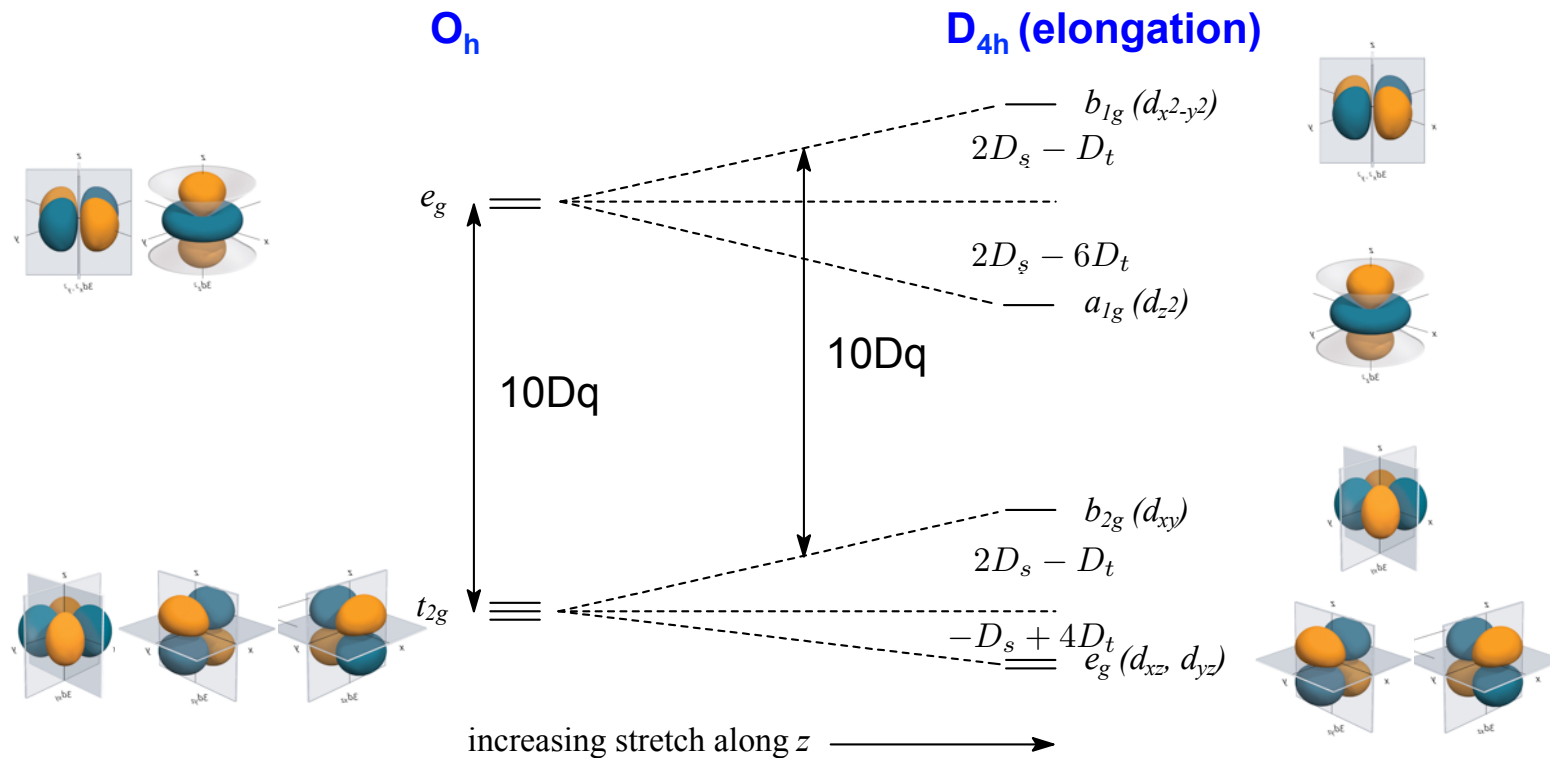
(*)The relation with Dq,Ds,Dt in König&Kremer « Ligand field. Energy diagram »

Crystal field Hamiltonian in Quanty

$$H_{CF}^{O_h} = A_{0,0}C_{0,0} + A_{4,0}C_{4,0} + \sqrt{\frac{5}{14}}A_{4,0}(C_{4,-4} + C_{4,4}) = 21D_qC_{4,0} + 21\sqrt{\frac{5}{14}}D_q(C_{4,-4} + C_{4,4})$$

1) Pre-defined CF potential

```
Akm = PotentialExpandedOnYlm("Oh",2,{0.6,-0.4});
OpptenDq = NewOperator("CF", NFermion, dIndexUp, dIndexDn, Akm);
```

The Oh potential is defined by:

$$A_{k,m} = \begin{cases} \frac{2}{5}E_{e_g} + \frac{3}{5}E_{t_{2g}} & k = 0 \quad m = 0 \\ \frac{21}{10}(E_{e_g} - E_{t_{2g}}) & k = 4 \quad m = 0 \\ \frac{21}{10}\sqrt{\frac{5}{14}}(E_{e_g} - E_{t_{2g}}) & k = 4 \quad m = \pm 4 \\ 0 & \text{True} \end{cases}$$

1) User made CF potential: Akm= $\{\{k_1, m_1, A_{k_1,m_1}\}, \{k_2, m_2, A_{k_2,m_2}\}, ..\}$

```
Akm = {{4,0,21/10},{4,-4,21/10sqrt(5/14)}, {4,4,21/10sqrt(5/14)}};
OpptenDq = NewOperator("CF", NFermion, dIndexUp, dIndexDn, Akm);
```

The parameter is 10Dq and the Hamiltonian writes $H_{CF} = 10Dq * OpptenDq$

To lower symmetries

O_h   1 parameter (10Dq)   2 energies

D_{4h}   3 parameters (10Dq,Ds,Dt)   4 energies

D_{3d}   3 parameters (10Dq,Dσ,Dτ)   3 energies

C_{2v}   9 parameters   😵   5 energies (5 orbtials)

Crystal field

Multi-electrons ions $3d^n$

A lot of physical-chemical properties are due to the crystal field

For example
- **Color**
- Magnetic properties

- Atomic number (Z)
- Number of electron (n) $3d^n$
- Crystal field strength ($\approx$10Dq) (ligand)

Ni^{2+} (d^8)

Ni(H$_2$0)$_6$

UV-visible Absorption spectroscopy

Transition Metal Ion Colors in Aqueous Solution

Multi-electrons ions : configuration

➢ **Electronic configuration**: complete simplified (open shell)

3d transition metal ions $\mathbf{1s^2 2s^2 2p^6\ 3d^n}$ $\mathbf{3d^n}$
4f rare earth ions $\mathbf{1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}\ 4f^n}$ $\mathbf{4f^n}$

➢ Filling of the 3d orbitals:

$2\ell+1=5$ $|\ell, m_\ell\rangle$ angular functions
$2s+1=5$ $|s m_s\rangle$ spin functions
$\Big\}$ 10 functions

$$\text{Nb states} = \binom{10}{n} = \frac{10!}{n!(10-n)!}$$

Example :

$3d^2$ ion (V^{3+}, Cr^{4+}) :

degenerate states : $C_{10}^2 = 45$

Some possibilites:

$m_l = -2 \quad -1 \quad 0 \quad 1 \quad 2$
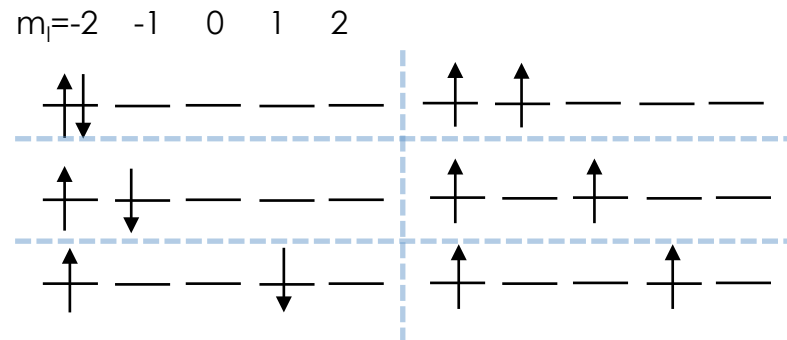
Multiplets

n electron in 10 d orbitals

$$\text{Nb states} = \frac{10!}{n!(10-n)!}$$

3d^2

m_l=-2 -1   0   1   2
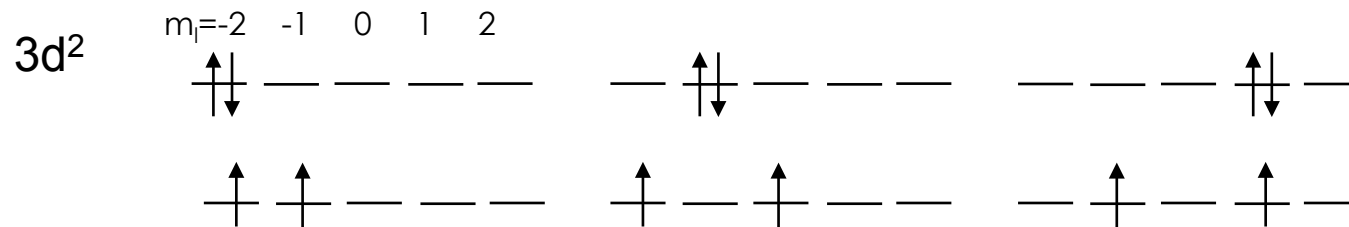
Degeneracy => **Multiplets (doublet, triplet,…)**

➔ **Name of the model :**

Crystal Field Multiplet (CFM)
Ligand Field Multiplet (LFM)

Hamiltonian of the ion with N electrons
Crystal field

$$H_{ion} = H_{cin} + H_{e-n} + H_{e-e} + H_{s-o} + H_{CF}$$

Free ion (spherical)   Crystal field

$$H_{cin} = \sum_{i=1}^{N} -\frac{h^2}{2m} \nabla_{r_i}^2$$ Total kinetic energy

$$H_{e-n} = \sum_{i=1}^{N} -\frac{Ze^2}{4\pi\varepsilon_0 r_i}$$ Coulomb attraction nuclei-electrons

$$H_{e-e} = \sum_{i<j=1}^{N} \frac{e^2}{4\pi\varepsilon_0 r_{ij}}$$ Electron-electron Coulomb repulsions

$$H_{s-o} = \sum_{i=1}^{N} \xi_i(r_i)\mathbf{l_i}\cdot\mathbf{s_i}$$ Spin-orbit coupling

Multi-electrons ions configuration and symmetry

d^2 ion in O$_h$ symmetry

Orbital degeneracy	3	6	3x2=6	3x2=6
Spin degeneracy	1 (S=0)	1 (S=0)	3 (S=1)	1 (S=0)

Hamiltonian of the ion with N electrons

Basis functions |Ψ>

- **Multi-electron functions for N electrons (configuration)**

  $$\Psi(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N)$$

- **Linear combination of Slater determinant built from the mono-electronic functions**

  $$\phi_i(\mathbf{r},\sigma) = \frac{1}{r} P_{n_i \ell_i}(r)\, Y_{\ell,m}(\theta,\phi)\, \chi_{m_{s_i}}(\sigma)$$

- **Anti-symmetric function to satisfy the Pauli principle**

Free ion with N electrons : basis functions

➢ **Functions $|\alpha(L,S)JM_J>$ = (L,S)J coupled functions**

✓ For N electrons, $\hat{L} = \sum\limits_{i=1}^{N} \hat{\ell}_i$

⚠ Sum is coupling

⚠ $\hat{\ell}_i \neq \ell_i$
$\hat{\ell}_i$ is the orbit operator defined by
$\hat{\ell}_{z,i}|\ell_i m_{\ell_i} >= m_{\ell_i}|\ell_i m_{\ell_i} >$
$\hat{\ell}_i^2|\ell_i m_{\ell_i} >= \ell_i(\ell_i + 1)|\ell_i m_{\ell_i} >$
$-\ell_i \leqslant m_{\ell_i} \leqslant \ell_i$

✓ Same definitions for $\hat{S}$ and $\hat{J}$

✓ $\hat{J} = \hat{L} \oplus \hat{S}$ operator associated with the spin-orbit coupling
$L - S \leqslant J \leqslant |L + S|$

Free 3d^n ion : basis functions, spectroscopic terms

No spin-orbit   **Basis functions |L,S,M$_L$,M$_S$>**

H_{cin}+H_{e-n}+H_{e-e} commutes with $\hat{L}^2, \hat{L}_z, \hat{S}^2, \hat{S}_z$
Common eigenfunctions with $\widehat{L}^2, \widehat{S}^2$

The energy of |α(L,S) > does not depend on M$_L$, M$_S$

Degeneracy of |α(L,S)> = (2L+1) (2S+1)

Orbital degeneracy   Spin degeneracy

Spectroscopic terms |L,S,M$_L$,M$_S$>

$^{2S+1}\Gamma$

S

letter for **L**
Γ=S pour L=0
Γ=P pour L=1
Γ=D pour L=2
Γ=F pour L=3

Ex: d^1

L=2, S=1/2

1 state ^{2}D
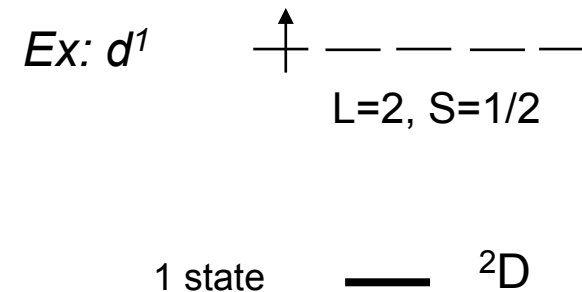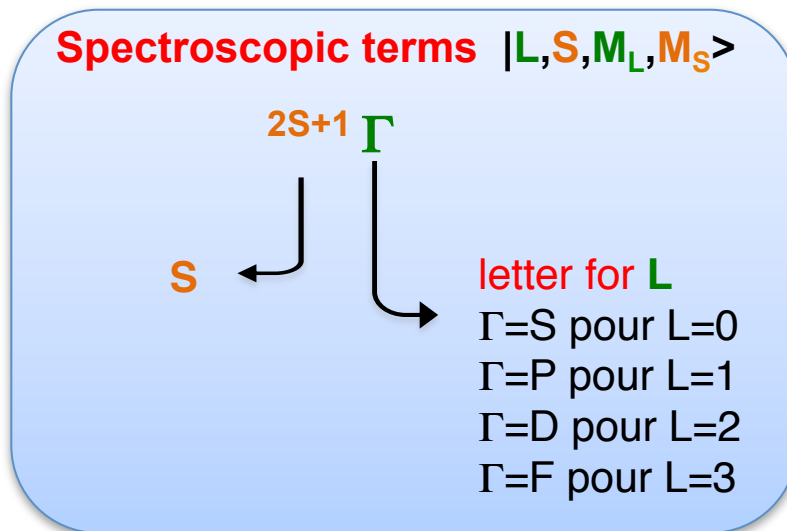
Free ion with N electrons : basis functions

Spin-orbit **Basis functions |(L,S)JM_J>**

> Common eigenfunctions with $\widehat{J}^2, \widehat{J}_z, \widehat{L}^2, \widehat{S}^2$

  $H_{cin}+H_{e\text{-}n}+H_{e\text{-}e}+H_{s\text{-}o}$ commutes with $\widehat{J}^2, \widehat{J}_z, \widehat{L}^2, \widehat{S}^2$

  ($H_{cin}+H_{e\text{-}n}+H_{e\text{-}e}$ commutes with $\hat{L}^2, \hat{L}_z, \hat{S}^2, \hat{S}_z$)

> The energy of $|\alpha(L,S)JM_J>$ does not depend on M_J

  Degeneracy of $|\alpha(L,S)JM_J>$ = 2J+1

Spectroscopic terms |L,S,M_L,M_S>

$^{2S+1}\Gamma_J$

S

letter for **L**
Γ=S pour L=0
Γ=P pour L=1
Γ=D pour L=2
Γ=F pour L=3

Ex: d¹

L=2, S=1/2
J=3/2,5/2

2 states

$^2D_{5/2}$

$^2D_{3/2}$

Free ion : $3d^2$ ion

m_l=-2   -1   0   1   2
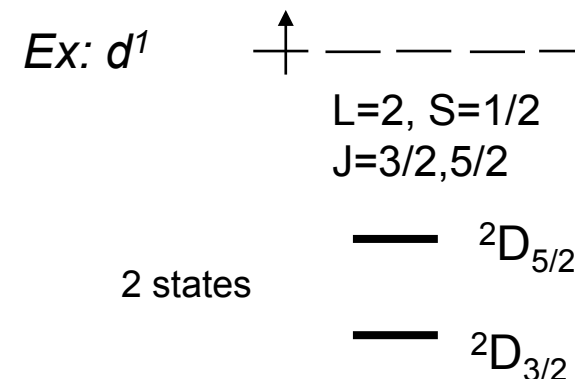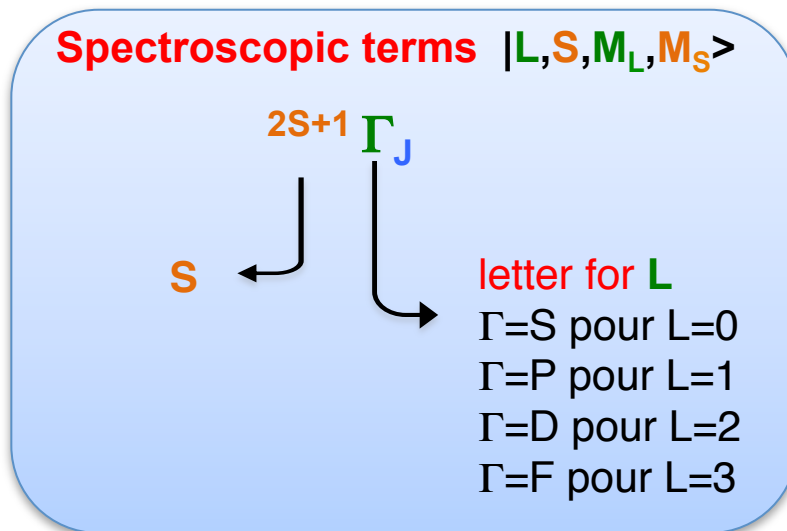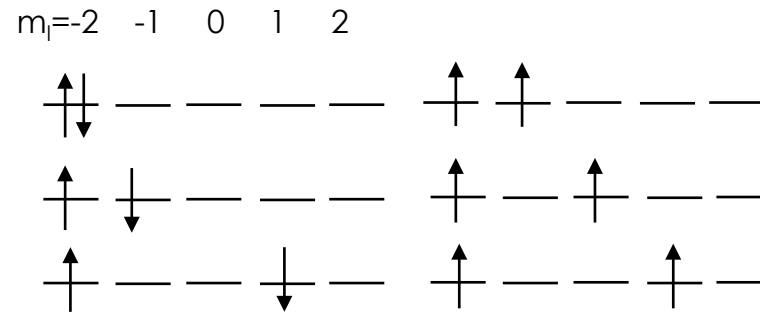
$$\hat{L} = \hat{\ell} \otimes \hat{\ell} \qquad 0 \leqslant L \leqslant 2\ell = 4$$

$$S, P, D, F, G \quad \text{terms}$$

$$\hat{S} = \hat{s} \otimes \hat{s} \qquad 0 \leqslant S \leqslant 2s = 1$$

Spin doublet or triplet

5 terms

$$^1G, \ ^3F, \ ^1D, \ ^3P, \ ^1S$$

Ground state (Hund's rules)

Free ion
Spectroscopic terms for $3d^2$ ion

Energy

^1S $^1S_0$

^1G
^3P
$3d^2$
^1D

$^1G_4$
$^3P_2$ $^3P_1$ $^3P_0$
$^1D_2$

^3F $^3F_4$ $^3F_3$ $^3F_2$

No Spin-orbit   Spin-orbit

$\approx 3/2\,\zeta_{3d}$ $^3F_4$

$\approx -1/2\,\zeta_{3d}$ $^3F_3$

$\approx -2\,\zeta_{3d}$ $^3F_2$

*Landé interval rule (neglect off diagonal coupling)

$$\Delta E = \frac{\zeta_{3d}}{2}J$$

Ground state given by third Hund's rule
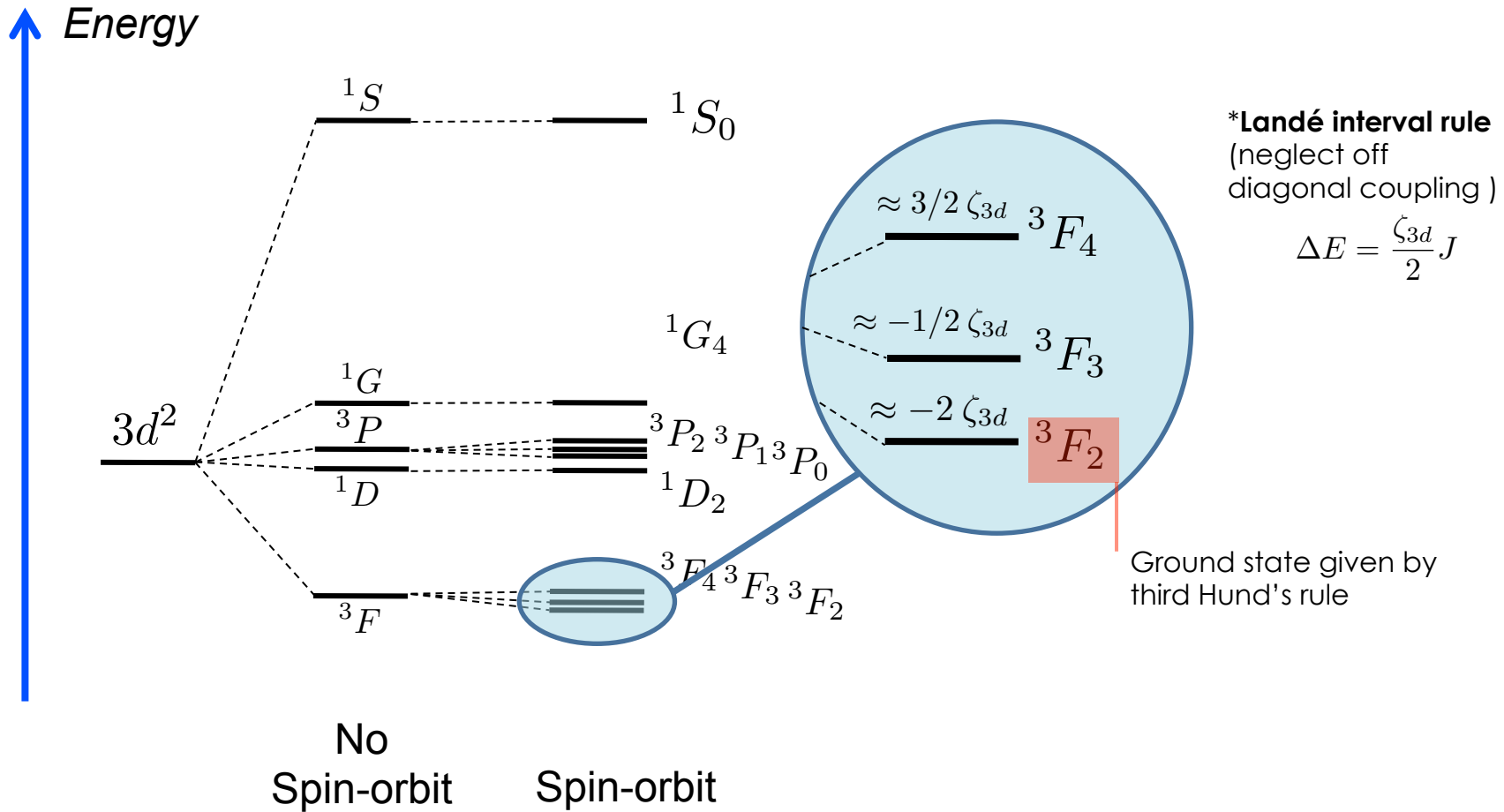
Crystal field : basis function

➢ **Basis functions**

Spherical symmetry:
$$|\alpha(L,S)\ J\ M_J>$$
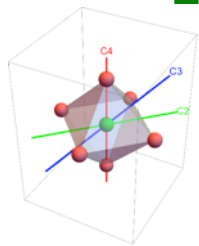
Local symmetry around the ion → point group *G*:
Basis functions of the representations of group G
$$|\alpha(L,S)\ J\ \Gamma\ \gamma>$$
Γ irreducible representation of G
$\Gamma\gamma$ basis function of G

➢ Thole's code uses group theory and the $\{\Gamma\}$ basis (TTMULT, CTM4XAS)

➢ **Quanty**

- uses group theory only for crystal field potential building

- uses **spherical $\{Y_{l,m}\}$ basis** and not the $\{\Gamma\}$ basis.

- although Quanty is a many body code, the basis set is defined by one particle

- uses $\{\Gamma\}$ to label the states (spectroscopic terms)

Crystal field and group theory
Matrix elements

$H_{CF} \in A_{1(g)}$ *   (fully symmetric representation of group **G**)

g only for centro-symmetric group

$$\langle (L_i, S_i) J_i \Gamma_i | H_{CF} | (L_j, S_j) J_j \Gamma_j \rangle \neq 0$$

$$\text{if } \Gamma_i \otimes \Gamma_{H_{CF}} \otimes \Gamma_j \ni A_{1(g)}$$
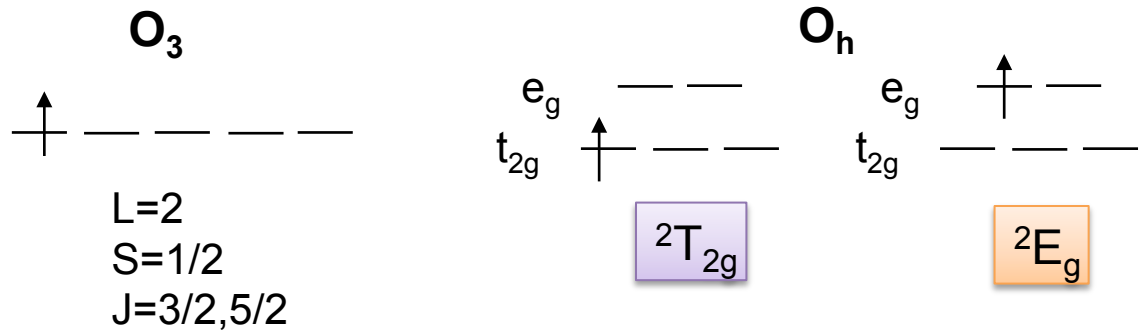
$$\text{if } \Gamma_i \otimes A_{1(g)} \otimes \Gamma_j = \Gamma_i \otimes \Gamma_j \ni A_{1(g)}$$

Crystal field mixes J states if $\quad \Gamma_i \otimes \Gamma_j \ni A_{1(g)}$
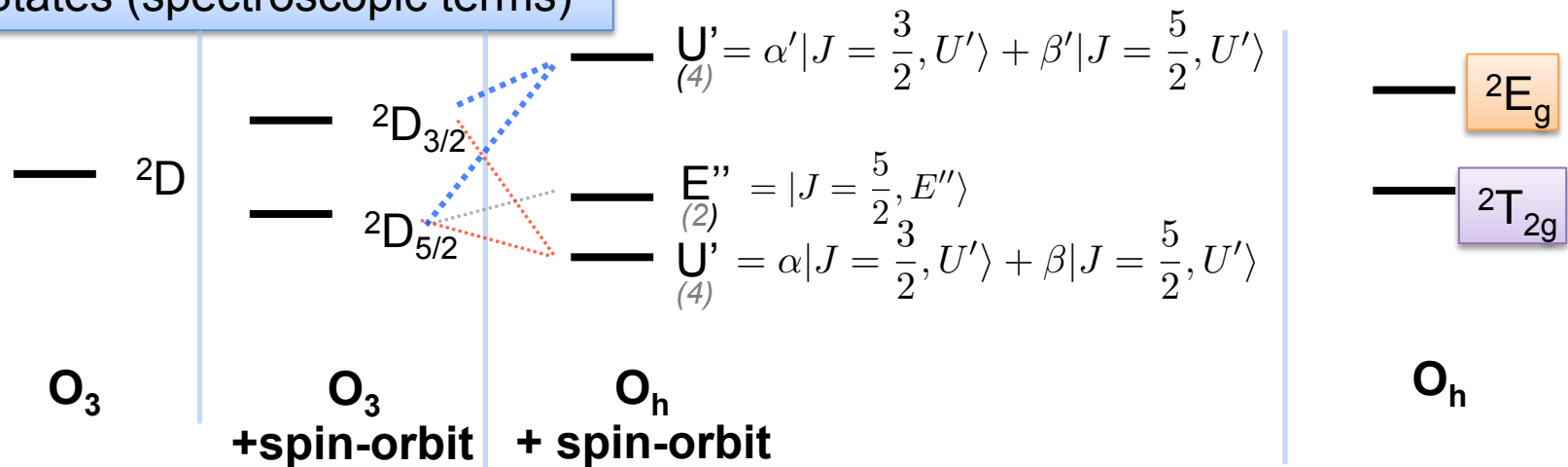
(group multiplication table)

Ex: d^1 (d^9) ion in O_h symmetry

Orbitals

O_3

$L=2$
$S=1/2$
$J=3/2,5/2$

O_h

e_g

t_{2g}

$^2T_{2g}$

e_g

t_{2g}

^2E_g

States (spectroscopic terms)

^2D

$^2D_{3/2}$

$^2D_{5/2}$

U' = $\alpha'|J = \frac{3}{2}, U'\rangle + \beta'|J = \frac{5}{2}, U'\rangle$
(4)

E'' = $|J = \frac{5}{2}, E''\rangle$
(2)

U' = $\alpha|J = \frac{3}{2}, U'\rangle + \beta|J = \frac{5}{2}, U'\rangle$
(4)

^2E_g

$^2T_{2g}$
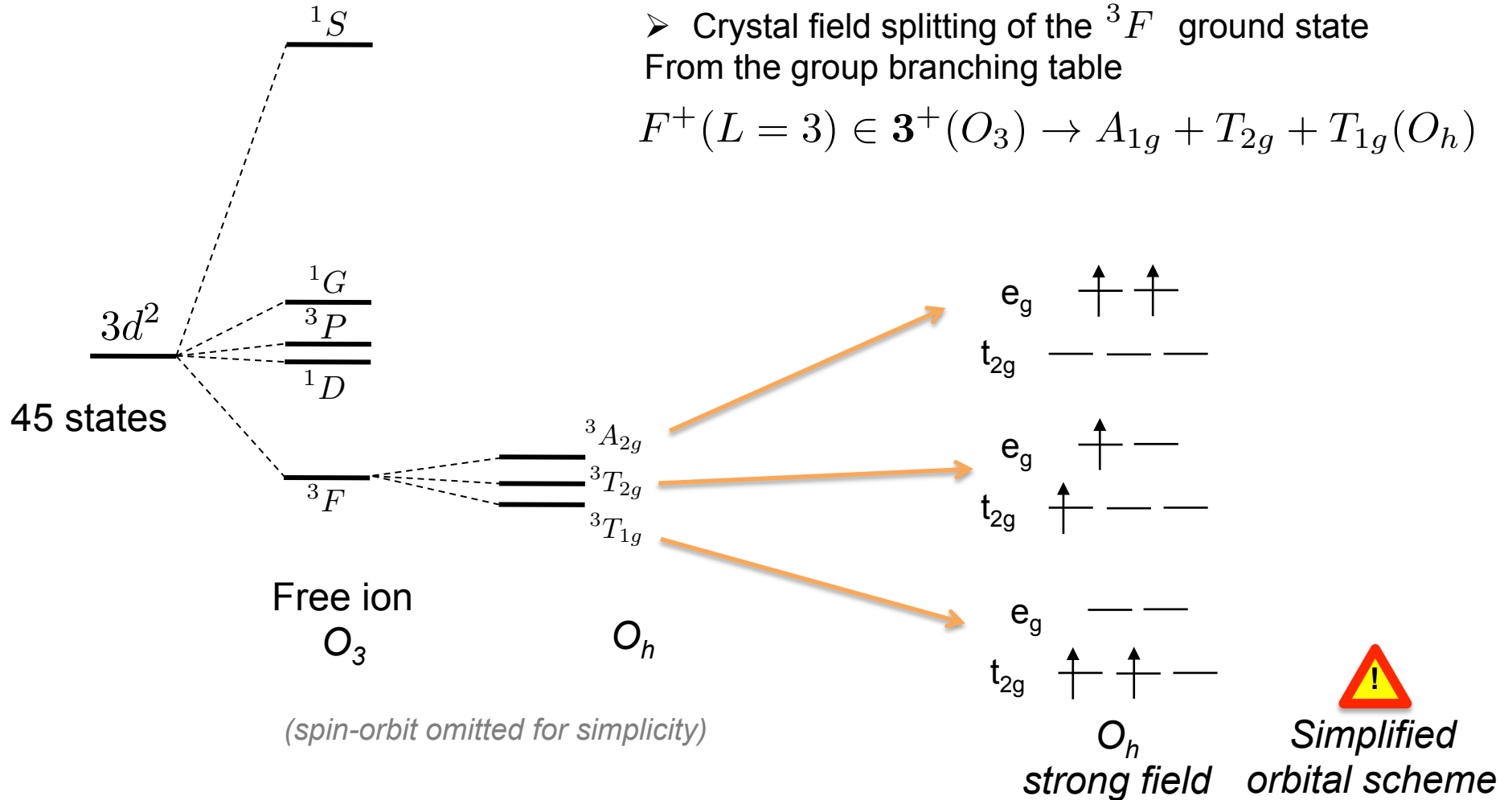
O_3

O_3
+spin-orbit

O_h
+ spin-orbit

O_h

⟹ *J states mixed by CF and SO*

Crystal field and group theory

Example: d^2 ion in O_h symmetry

^1S

> Crystal field splitting of the ^3F ground state
> From the group branching table

$$F^+(L=3) \in \mathbf{3}^+(O_3) \to A_{1g} + T_{2g} + T_{1g}(O_h)$$

$3d^2$

^1G
^3P
^1D

45 states

e_g

t_{2g}

$^3A_{2g}$
$^3T_{2g}$
$^3T_{1g}$

^3F

e_g

t_{2g}

Free ion
O_3

O_h

e_g

t_{2g}

(spin-orbit omitted for simplicity)

O_h
strong field

Simplified
orbital scheme

From the multi-electronic state, one can get the electron density on the orbitals of the group (it is not necessary integer)
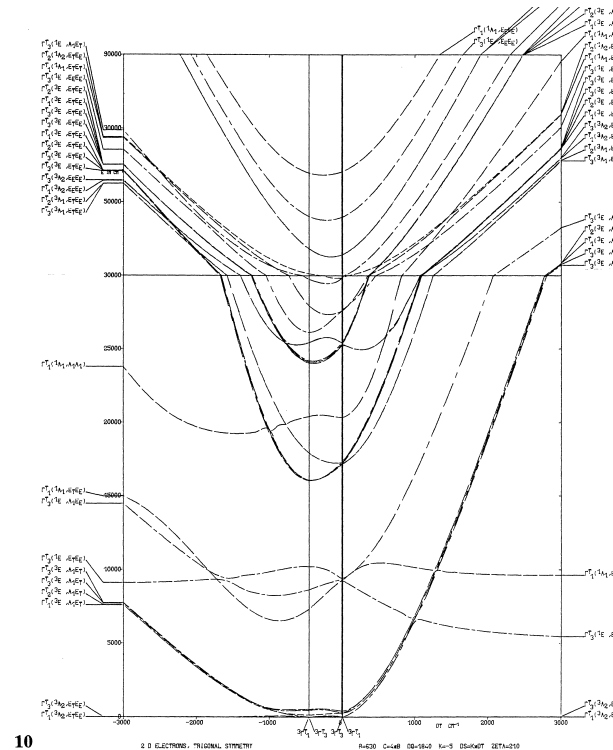
Crystal field : energy diagram

➢ Plot of the **energy** of spectroscopic terms $(^{2S+1}\Gamma \text{ or } ^{2S+1}\Gamma_J)$

as function of **crystal field parameter (10Dq,Ds,…)** (and B Racah parameter (*))

➢ **Tanabe-Sugano diagram (1954)**

$O_h(T_d)$, no spin-orbit
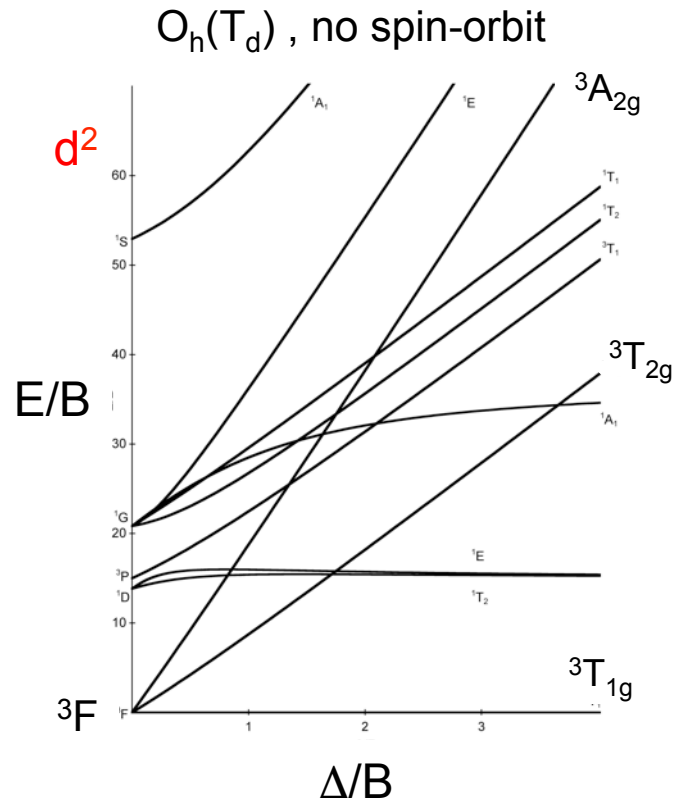
➢ **König&Kremer (1970)**

Low symmetries+spin-orbit

(*)B Racah parameters related to the slater integrals (electronic repulsions)

$$A = F^0(3d,3d) - \frac{49}{441}F^4(3d,3d)$$
$$B = \frac{1}{49}F^2(3d,3d) - \frac{5}{441}F^4(3d,3d)$$
$$C = \frac{35}{441}F^4(3d,3d)$$

Crystal field : energy diagram

➤ Plot of the **energy** of spectroscopic terms $\left({}^{2S+1}\Gamma \text{ or } {}^{2S+1}\Gamma_J \right)$

as function of **crystal field parameter (10Dq,Ds,…)** (and B Racah parameter (*))
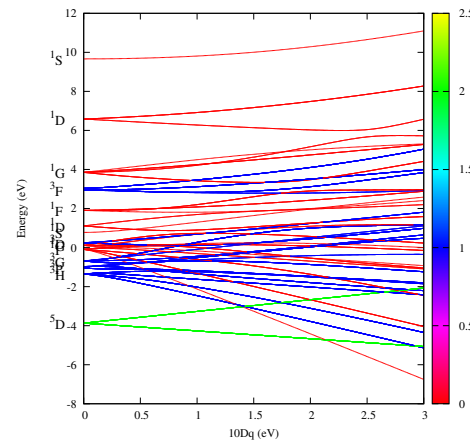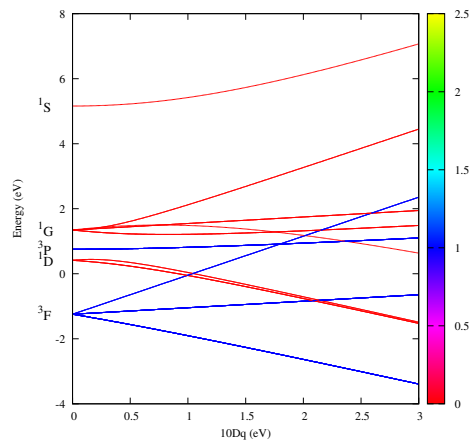
➤ **Tanabe-Sugano diagram (1954)**

$O_h(T_d)$, no spin-orbit

➤ **König&Kremer (≈1970)**

Low symmetries+spin-orbit

Tutorial Monday afternoon :
02_Energy_Level_Diagram_Tanabe-Sugano.Quanty

Crystal field : multi-electron and orbitals

Multi-electron ions

- **Spectroscopic terms :** $\Gamma_i \in G$

Term written with capital letter in Mulliken notation. *Ex :* A_{1g}, T_2

or Koster notation : Γ_i

- **Electron density / orbitals**

ex : $e_g^{5.8} t_{2g}^{1.2}$

- **L,S,J,M$_L$,M$_S$,M$_J$ not « good » quantum numbers.**

Expectation values**:**

$$\langle \Gamma_i | \hat{O} | \Gamma_i \rangle$$
$$\text{with } \hat{O} = L_z, S_z, \dots$$

One electron/orbitals

- **Orbitals :** $\gamma_i \in G$

Small letter

ex: e_g, t_{2g}

$$a_{1g}, e_2$$

Crystal field multiplet applied to core hole spectroscopies

Calculations including the core-hole (ex : $2p^5 3d^{n+1}$, $3d^9 4f^{n+1}$,…)

Transitions : electric dipole, electric quadrupole, magnetic dipole…

✓ **Racah/Bander** (Theo Thole) : core of **CTM4XAS** (Frank de Groot)

Based on group theory (Butler "Point group symmetry applications")

Difficult to modified the core in order to adapt to new spectroscopies since

Theo Thole died in1996

✓ **Quanty** (Mauris Haverkort) : core of **Crispy** (Marius Retegan)
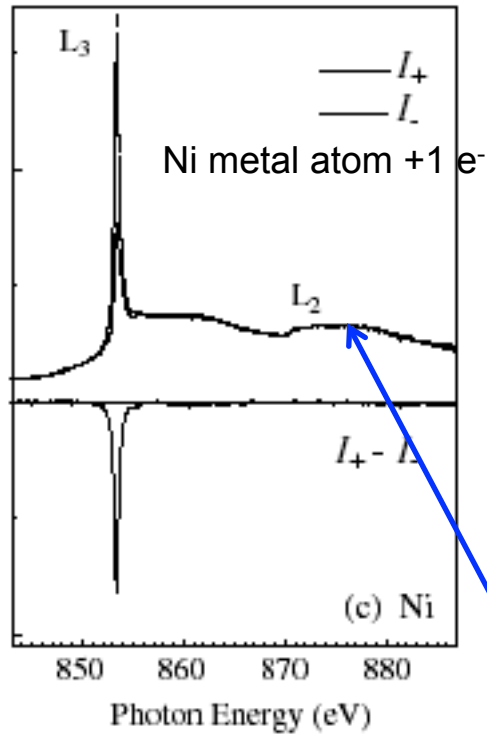
and CTM4RIXS (Frank de Groot)

Flexible for the need of the new spectroscopies/physical properties

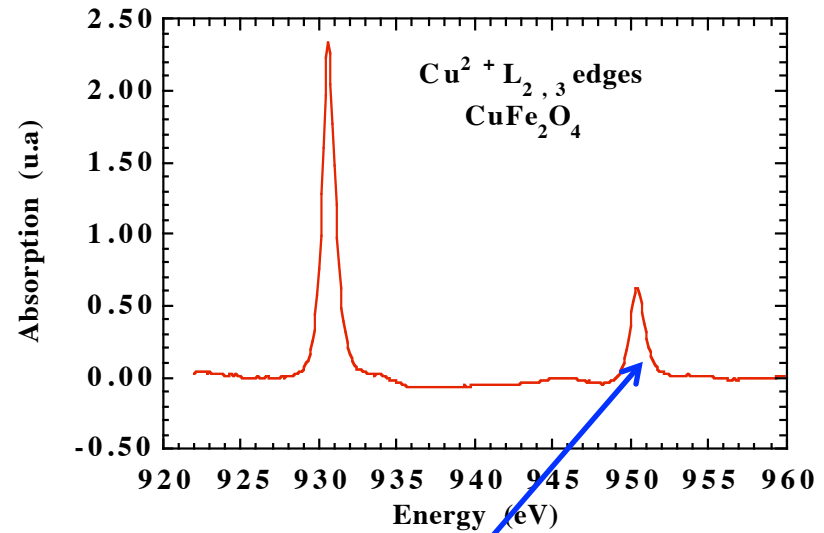# *Example of crystal field effect*

From spherical to Oh symmetry

Example of crystal field effect:
d^9 ion at $L_{2,3}$ edges (2p->3d)

$3d^9$
Spherical symmetry

$3d^9$
$\approx O_h$ symmetry

No L_2

L_2
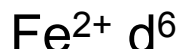
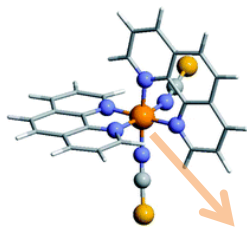Can be understood via symmetry consideration using group theory
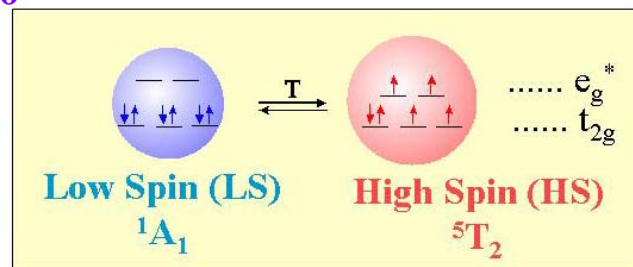
Example of crystal field effect

Spin crossover

Example of crystal field effect : spin crossover

Color

Fe^{II}(phen)$_2$(NCS)$_2$

Fe^{2+} d^6

T = 77 K
Low spin S = 0

T = 300 K
High spin S = 2

Low Spin (LS)
$^1A_1$

High Spin (HS)
$^5T_2$

...... e$_g$*
...... t$_{2g}$

Energy

HS

LS

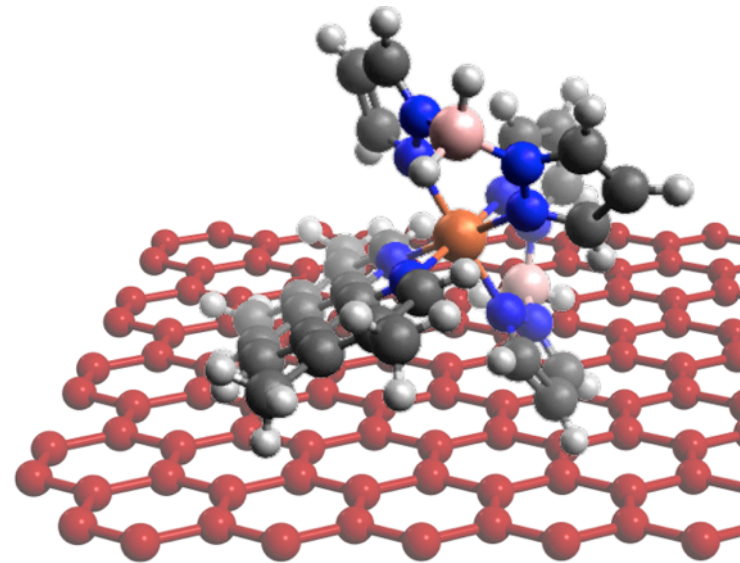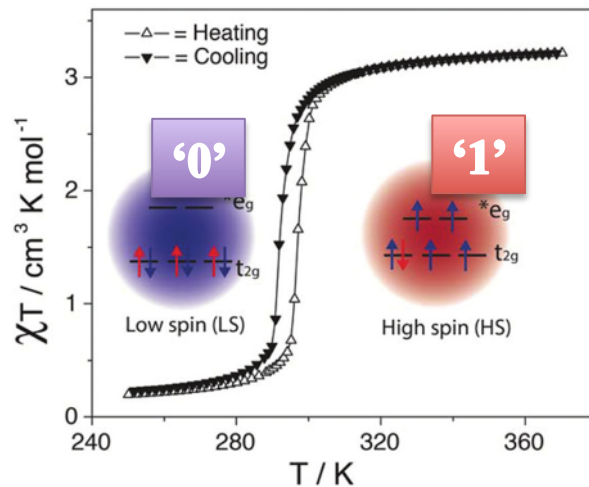$\Delta E_{HL} \approx k_B T$

Δr_{HL}

r$_{Fe-N}$
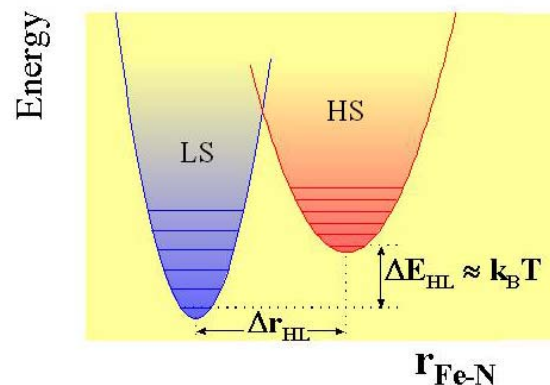
Fe-N distance

CF strength

Color change

Ex of application: thermochromic painting

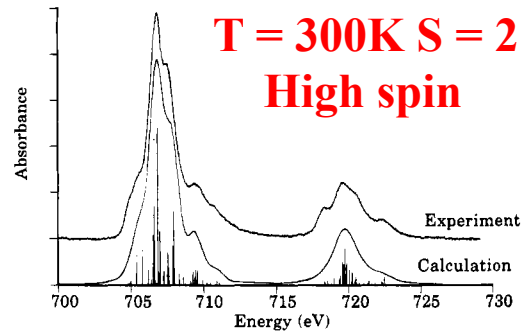# *Example of crystal field effect : spin crossover*

Magnetism:

- switch between "0"(LS) and "1"(HS)
- driven by external stimuli (temperature, light, …)
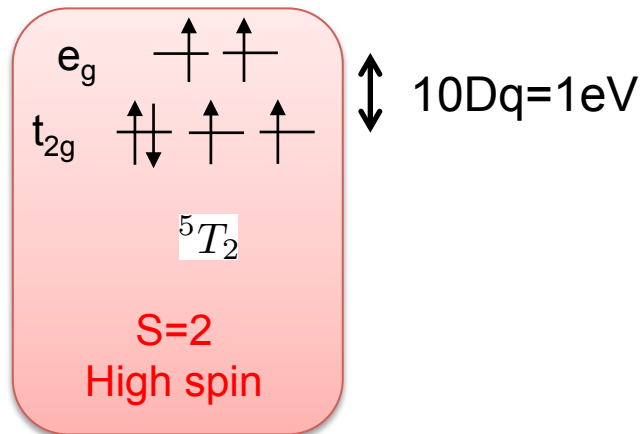- couple to surface (insulating or conducting)
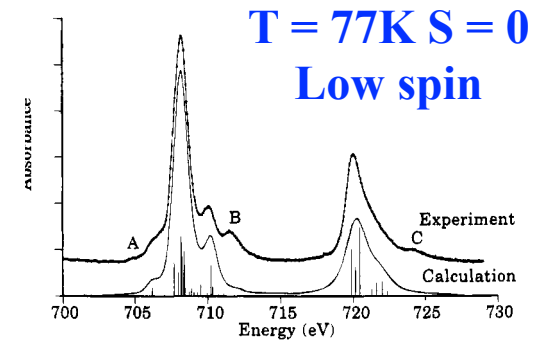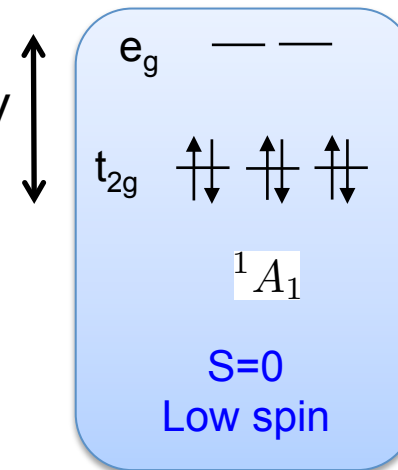 for **molecular spintronic**

Crystal field : spin crossover

Fe^{2+} ion ($3d^6$) in O_h symmetry

Temperature ↘

Fe-N distance
(observed by DRX)

CF strength ↗
(10Dq)

➢ Magnetic properties goes from paramagnetic to non-magnetic

Crystal field effect : spin crossover
XAS at Fe $L_{2,3}$ edges (2p->3d)

T = 300K S = 2
High spin

T = 77K S = 0
Low spin

CFM calculation
Fe^{2+} (3d^6)
O_h symmetry

Left diagram:

e_g ↑ ↑

t_{2g} ↑↓ ↑ ↑

10Dq=1eV

$^5T_2$

S=2
High spin

Right diagram:

10Dq=2.2eV

e_g — —

t_{2g} ↑↓ ↑↓ ↑↓

$^1A_1$

S=0
Low spin

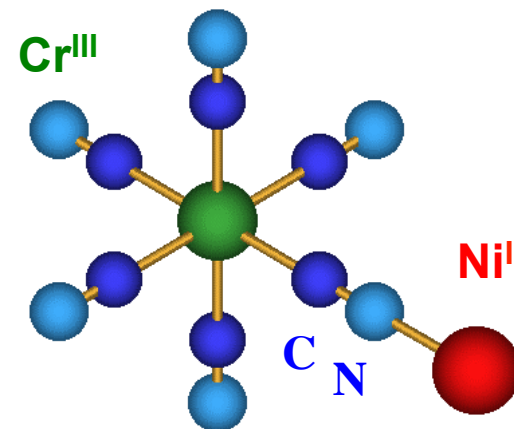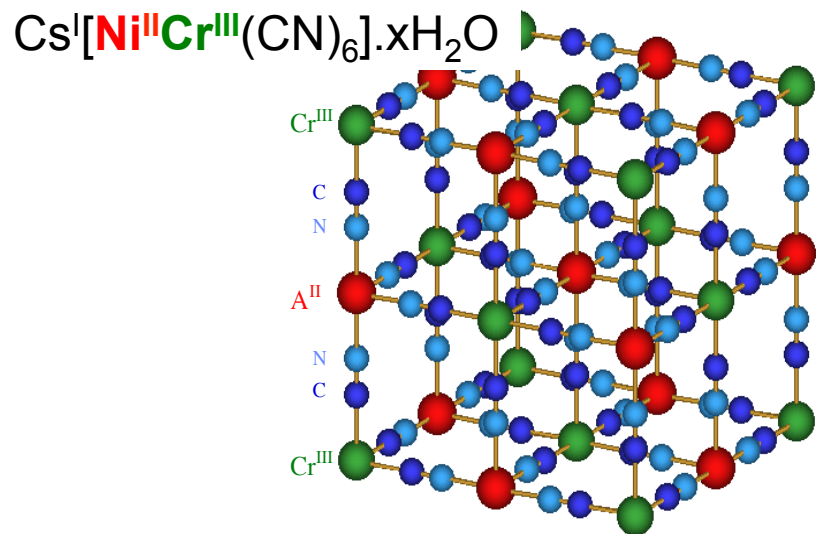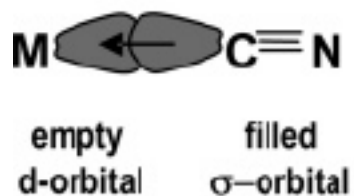*From Briois V., J. Am. Chem. Soc., 117 (1995)*

Limit of the crystal field model: towards ligand field model

Example : prussian blue analogues

$Cs^{I}[\mathbf{Ni^{II}Cr^{III}}(CN)_6].xH_2O$

Cr^{III}
C
N
A^{II}
N
C
Cr^{III}

Cr^{III}

Ni^{II}

C
N

(covalent) $\mathbf{Cr^{III}}$-C≡N-$\mathbf{Ni^{II}}$ (ionic)

M ← C≡N
empty   filled
d-orbital   σ−orbital

(i) σ donation

M   C≡N
filled   empty
d-orbital   π*-orbital
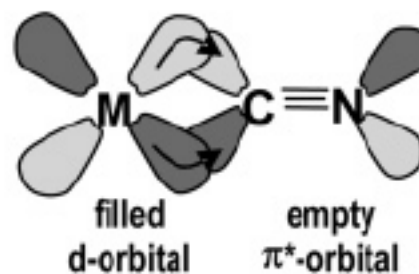
(ii) π back-donation

Weak covalent bond
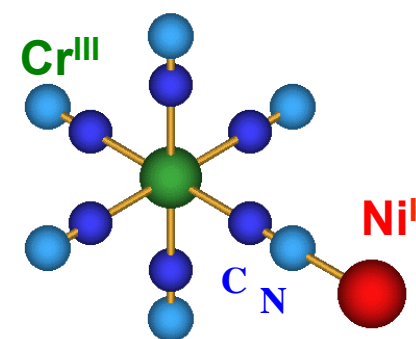
CN-Ni^{II} in Cs[NiCr(CN)$_6$]

Ni^{II} L$_{2,3}$ edges (2p to 3d)
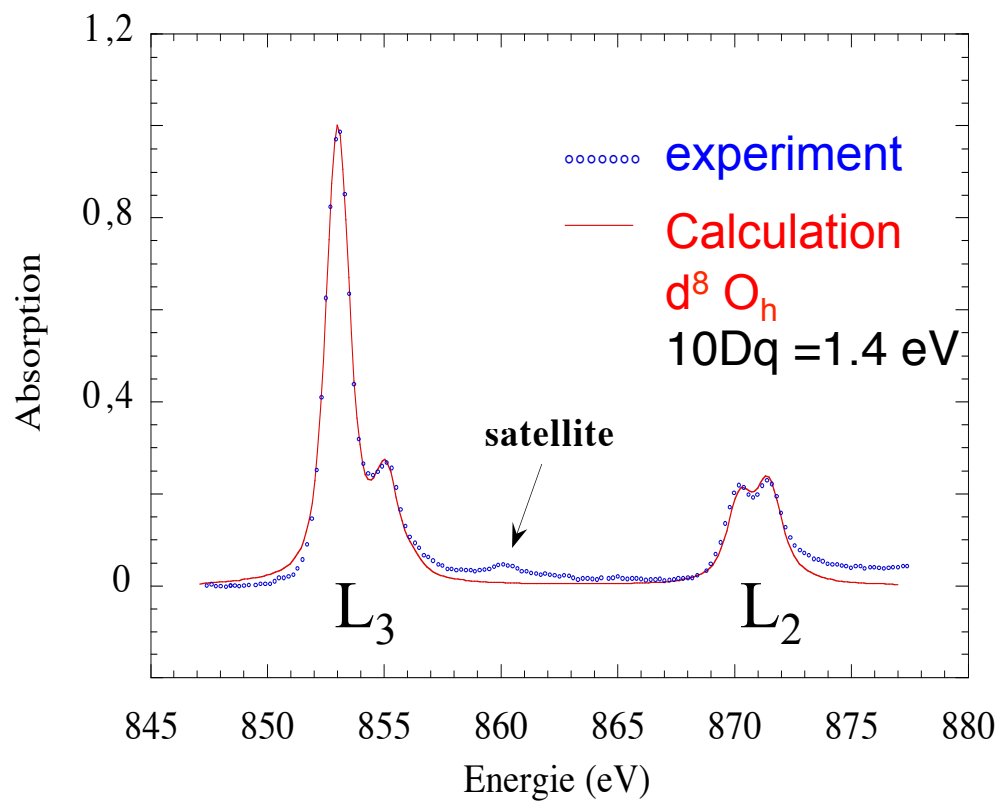
Weakness of crystal field theory
Strong crystal field
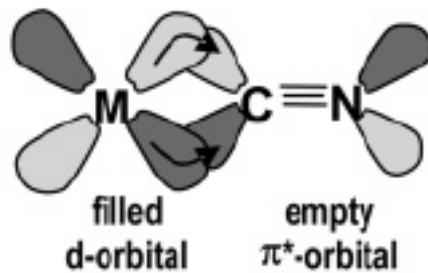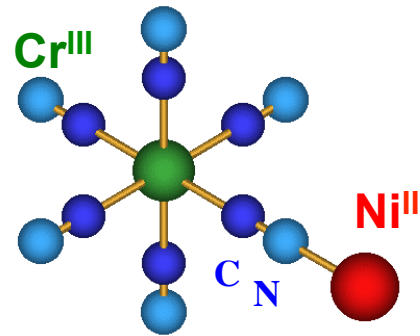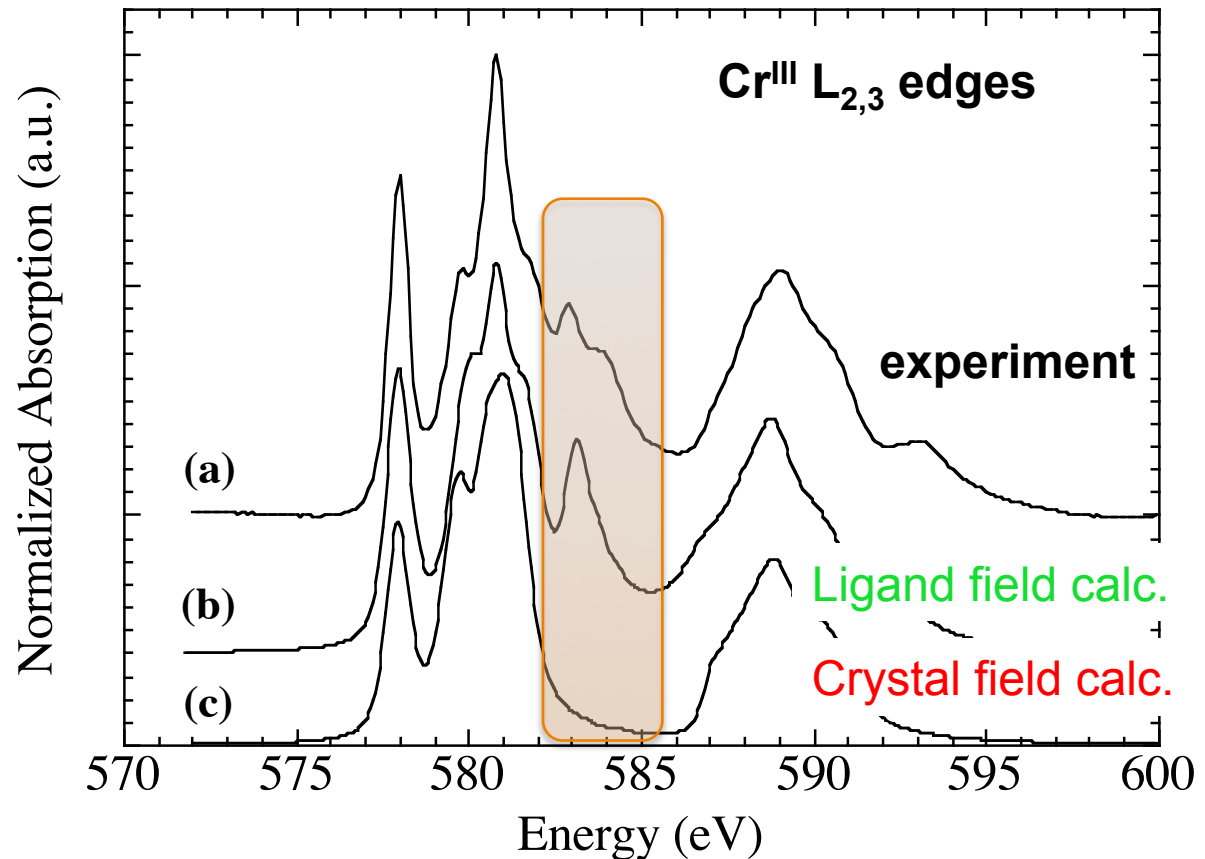
❑ **Crystal field** : Oh, large 10Dq (=3.5eV) + strong slater reduction (50%)
   Incomplete model due to the strong metal to ligand charge transfer
❑ **Ligand field** : metal to ligand charge transfer
   $d^3d^0 + d^2d^1$

Ligand field multiplets

- To account for electron coming from ligands or neighbor metal

- **Multi-configurations** approach
  also called cluster model
               charge transfer model (CT)

- Two types of **charge transfer** (**CT**):

    Metal to ligand : **MLCT**
    Ligand to Metal : **LMCT**

Ligand to metal charge transfer LMCT

$$2p^6 3d^{n+1}\underline{L}$$

Δ

$$2p^6 3d^n$$

$\underline{L} = 3d^9$ «ligand hole»

$$|i\rangle = \alpha\, |2p^6 3d^n\rangle + \beta\, |2p^6 3d^{n+1}\underline{L}\rangle$$
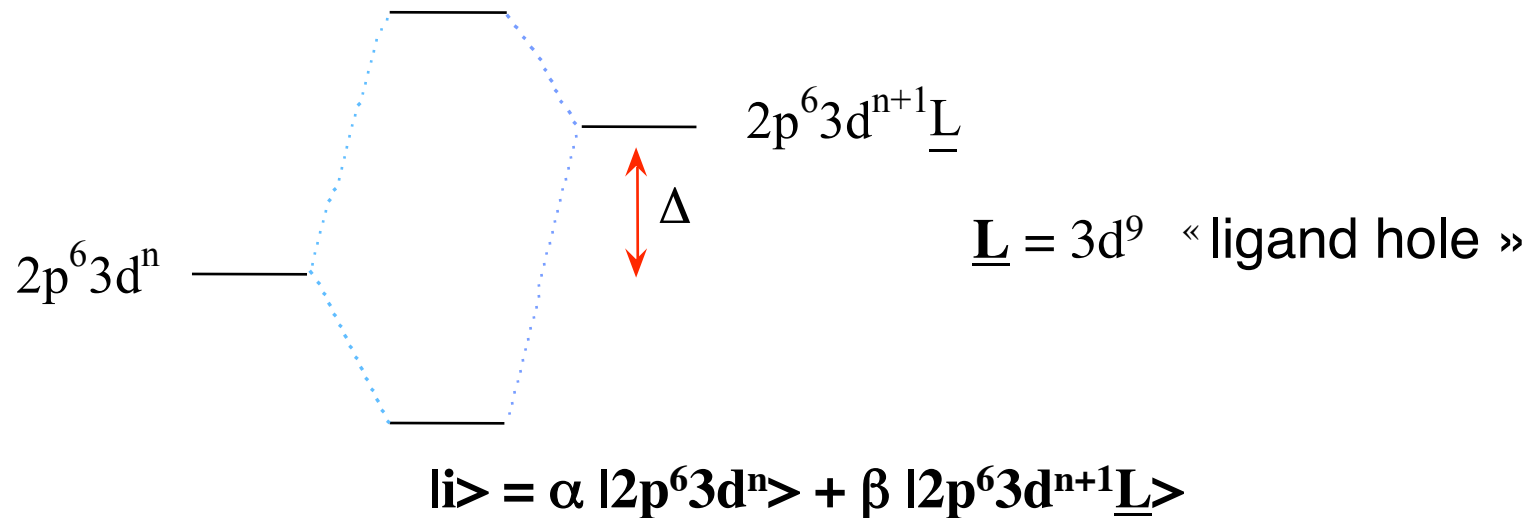
Parameters

Δ **energy (eV)**

Charge transfer integral (symmetry dependent)

$V = \langle 3d^n | H | 3d^{n+1}\underline{L} \rangle$ (also called T)

In O_h symmetry: V_{t2g} et V_{eg}

Ligand to metal charge transfer LMCT

Core spectroscopies : excited state   2p for $L_{2,3}$ edges
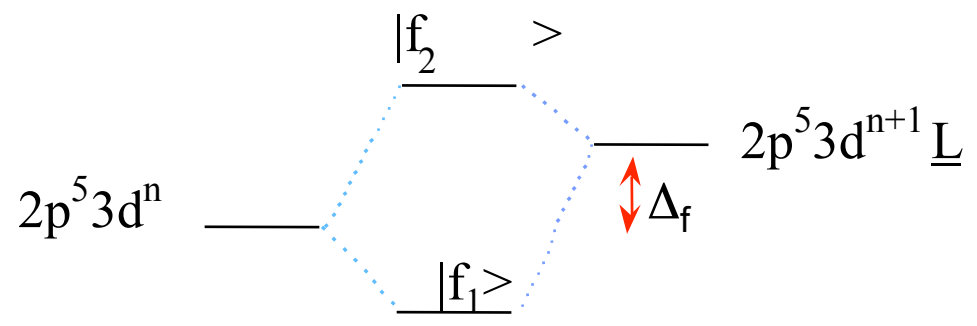1s for K edge

$$|f_2 \quad >$$

$2p^5 3d^n$ _____

_____ $2p^5 3d^{n+1} \underline{L}$

$\updownarrow \Delta_f$

$|f_1>$

Metal to ligand charge transfer MLCT

$$2p^6 3d^{n-1} L^-$$

$$\Delta$$

$$L^- = 3d^1$$

$$2p^6 3d^n$$

$$|i\rangle = \alpha\, |2p^6 3d^n\rangle + \beta\, |2p^6 3d^{n-1} L^-\rangle$$
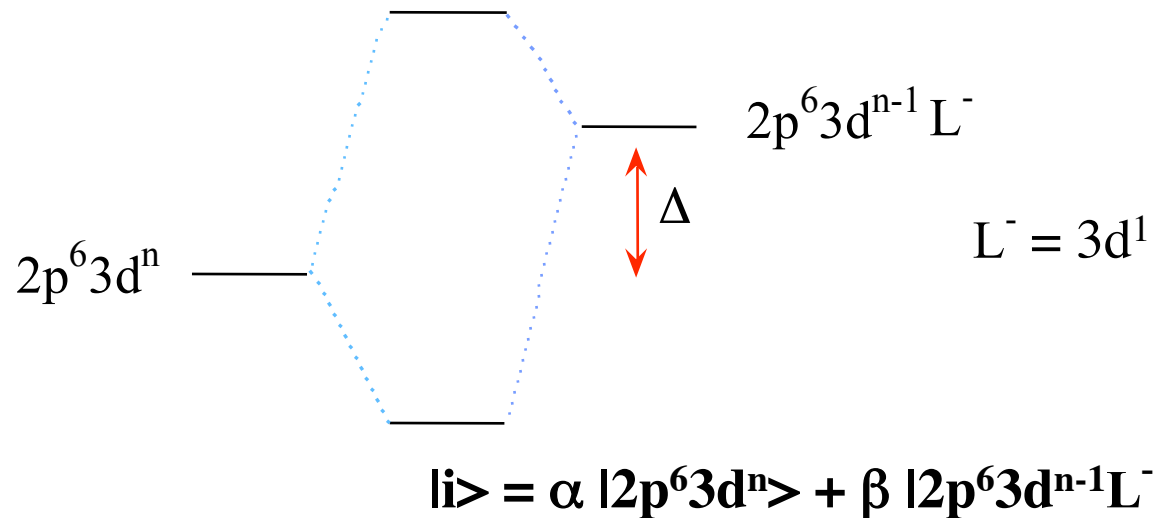
Parameters

Δ **energy (eV)**

Charge transfer integral (symmetry dependent)
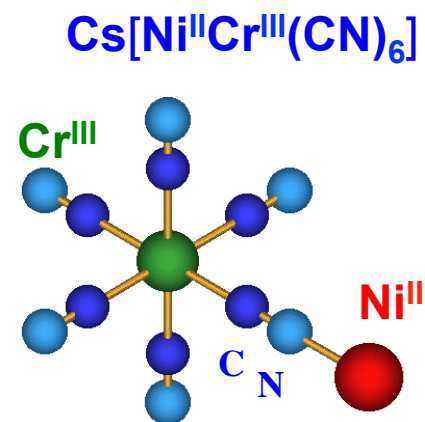
$$V = \langle 3d^n | H | 3d^{n-1} L^- \rangle$$

In O_h symmetry: V_{t2g} et V_{eg}

LMCT
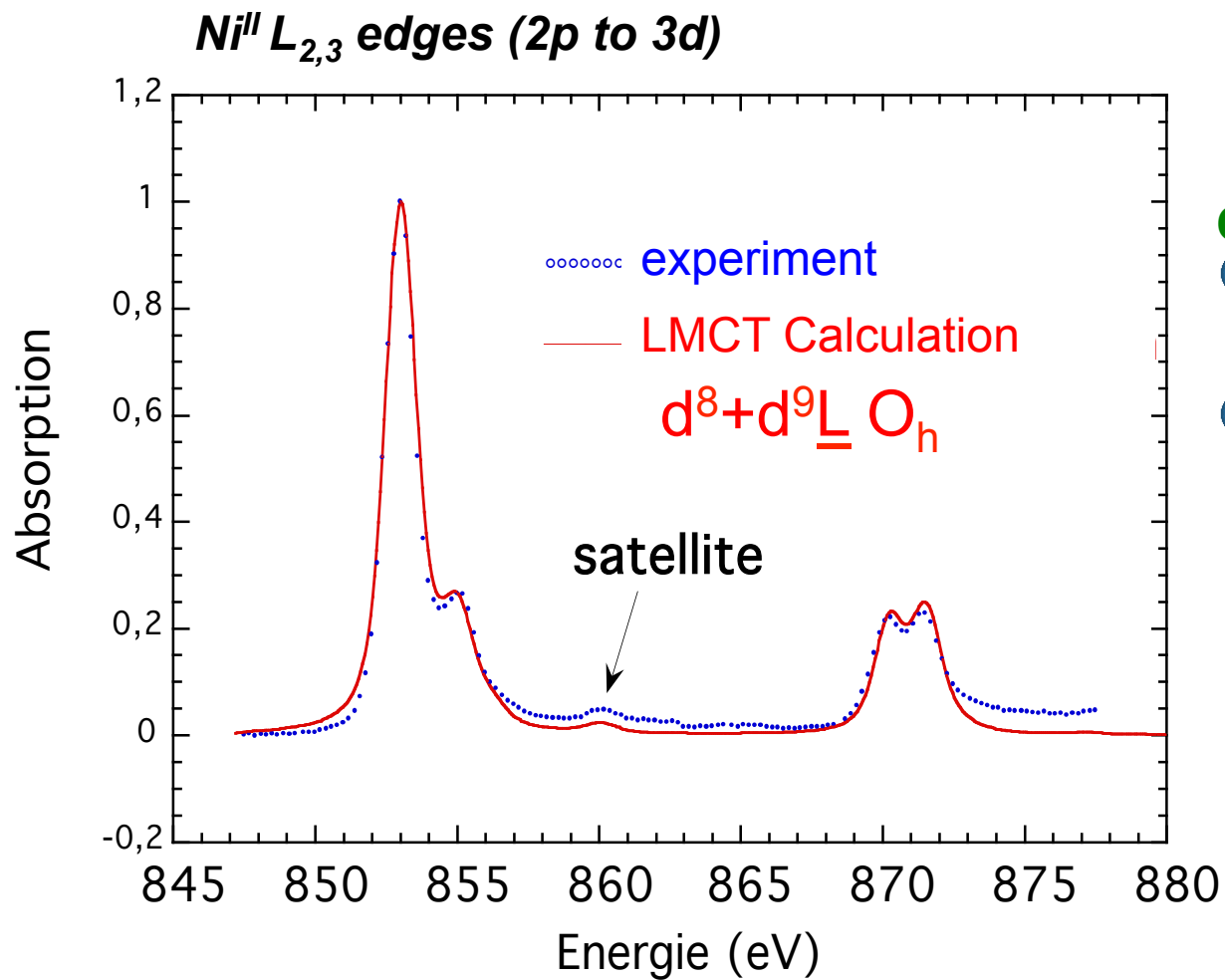
Ni^{II} L$_{2,3}$ edges (2p to 3d)

Cs[Ni^{II}Cr^{III}(CN)$_6$]

ooooooo experiment

—— LMCT Calculation

d^8+d^9$\underline{L}$ O$_h$

satellite

Weakness of crystal field theory
Strong crystal field
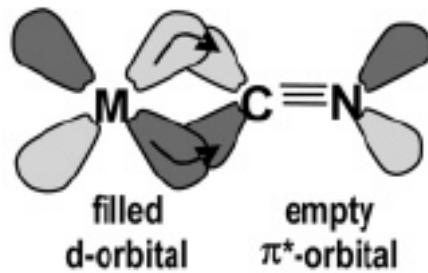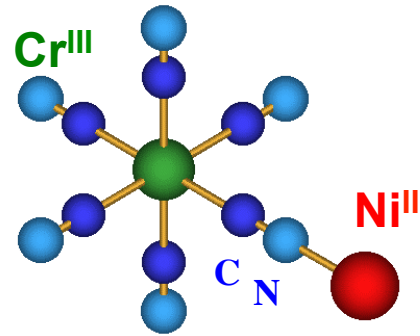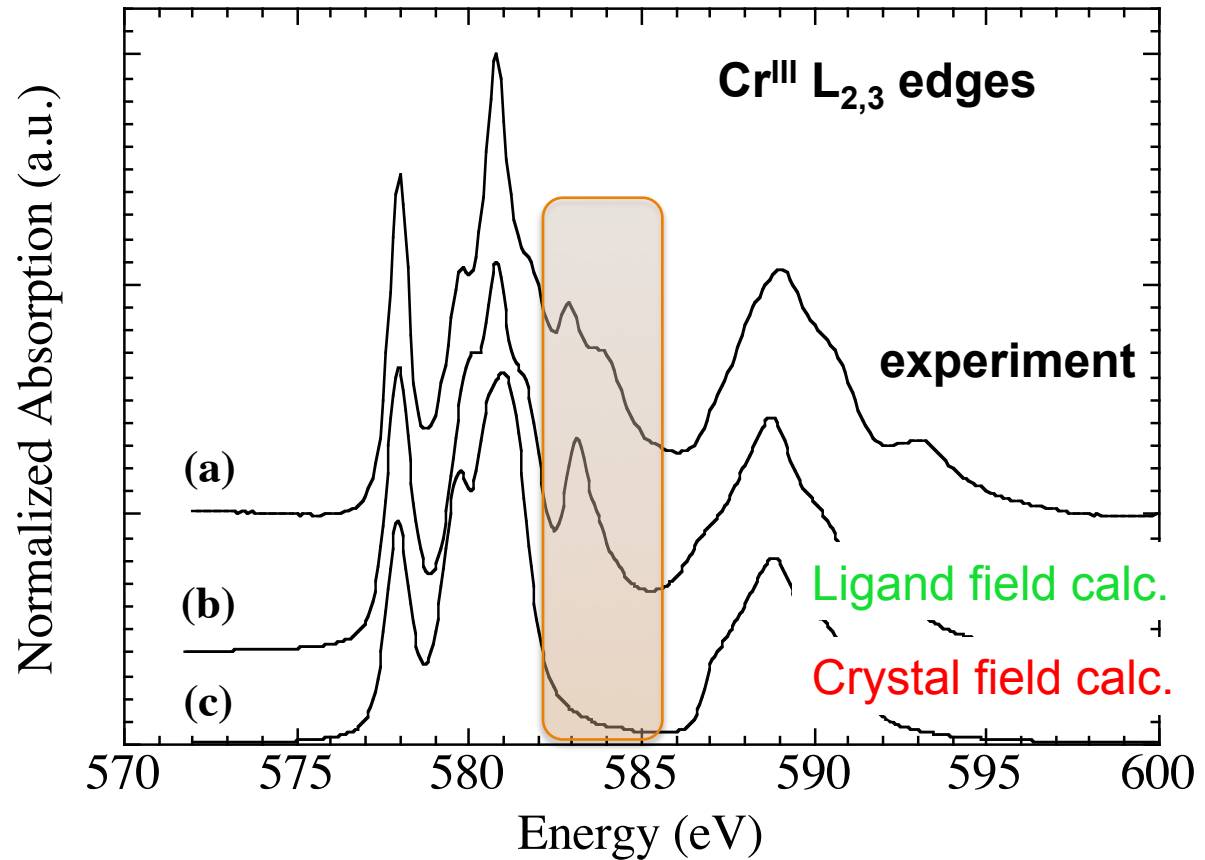
Crystal field : Oh, large 10Dq (=3.5eV) + strong slater reduction (50%)

Ligand field : MLCT $d^3 + d^2 L^-$

Crystal field and magnetism

1. Introduction / Definition
2. One electron (3d electron)
    1. Symmetries
    2. Hamiltonian
    3. Crystal field splitting of 3d electron

3. Multi-electrons ion (3d electrons)
    1. Hamiltonian
    2. Configurations/ spectroscopic terms
    3. Symmetry
    4. Examples

4. Crystal field and magnetism
1. Hamiltonian
2. Magnetic moment (spin and orbit)
3. Zeeman effect / paramagnetism

Magnetism

➢ **Hamiltonian**

H$_{ion}$ = H$_{cin}$ + H$_{e-n}$ + H$_{e-e}$ + H$_{s-o}$ + H$_{CF}$ +H$_{Zeeman}$ +H$_{Exchange}$

Free ion (spherical)   Crystal field

$$H_{Zeeman} = -\overrightarrow{m}.\overrightarrow{H} = \mu_B(\hat{L} + g_0\hat{S}).\overrightarrow{H}$$

$$= \mu_B(L_x + 2S_x)H_x + \mu_B(L_y + 2S_y)H_y + \mu_B(L_z + 2S_z)H_z$$

1 electron (S=1/2) spherical

d^1 S=1/2   m$_S$=+1/2

Energy

$\Delta E = E_{-1/2} - E_{+1/2}$

m$_S$=-1/2

$B_0 = 0$ $B_0 \neq 0$ Magnetic Field
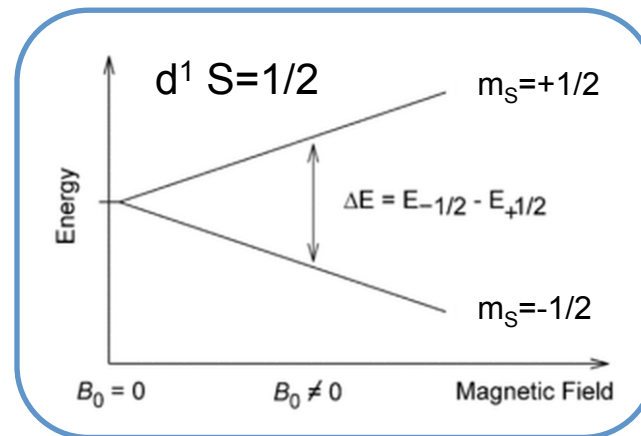
$$H_{Exchange} = S_xH_x + S_yH_y + S_zH_z$$

Magnetic moments

➤ **Definitions**

$$m = m_{orbit} + m_{spin}$$

$$m_{orbit} = -\langle i|\hat{L}_z|i\rangle \mu_B$$

$$m_{spin} = -g_o\langle i|\hat{S}_z|i\rangle \mu_B = -2\langle i|\hat{S}_z|i\rangle \mu_B$$

➤ **Crystal field effect**

$$|i> = |(L,S)J\Gamma\gamma\rangle \text{ are not eigenfunctions of } \hat{L}_z \text{ or } \hat{S}_z$$

$$\langle i|\hat{L}_z|i\rangle \neq m_L$$

$$\langle i|\hat{S}_z|i\rangle \neq m_S$$

$H_{cin}+H_{e-n}+H_{e-e}+H_{s-o}$ commute with $\hat{J}^2, \hat{J}_z, \hat{L}^2, \hat{S}^2$

($H_{cin}+H_{e-n}+H_{e-e}$ commute with $\hat{L}^2, \hat{L}_z, \hat{S}^2, \hat{S}_z$)

Magnetic moments and spectroscopies

> For 3d ions, the orbital magnetic moment is quenched (nul) in most cases.
> Some 3d ions have significant orbital magnetic moment
> $$(Co^{2+}, \text{ low spin } Fe^{3+}, Fe^{2+})$$

→ **magnetic anisotropy**

> **Magnetic core spectroscopies**
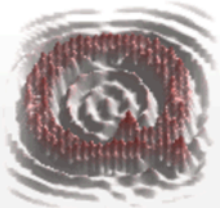> XMCD, RIXS-MCD, XMLD, XMχD

→ access to

Spin and orbit magnetic moment
Anisotropies + Angular dependences

Magnetic moments in Quanty

➢ **Quanty**: any operator ($\hat{O}$) and its expectation values

$$\langle i|\hat{O}|i\rangle$$

Ex : spin operator

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Sz

The S_z operator is defined as:

$$S_z = \sum_\tau \frac{1}{2}\left(a^\dagger_{\tau\uparrow}a_{\tau\uparrow} - a^\dagger_{\tau\downarrow}a_{\tau\downarrow}\right).$$

The equivalent operator in Quanty is created by:

```
Example.Quanty
OppSz = NewOperator("Sz",NF,IndexUp,IndexDn)
```

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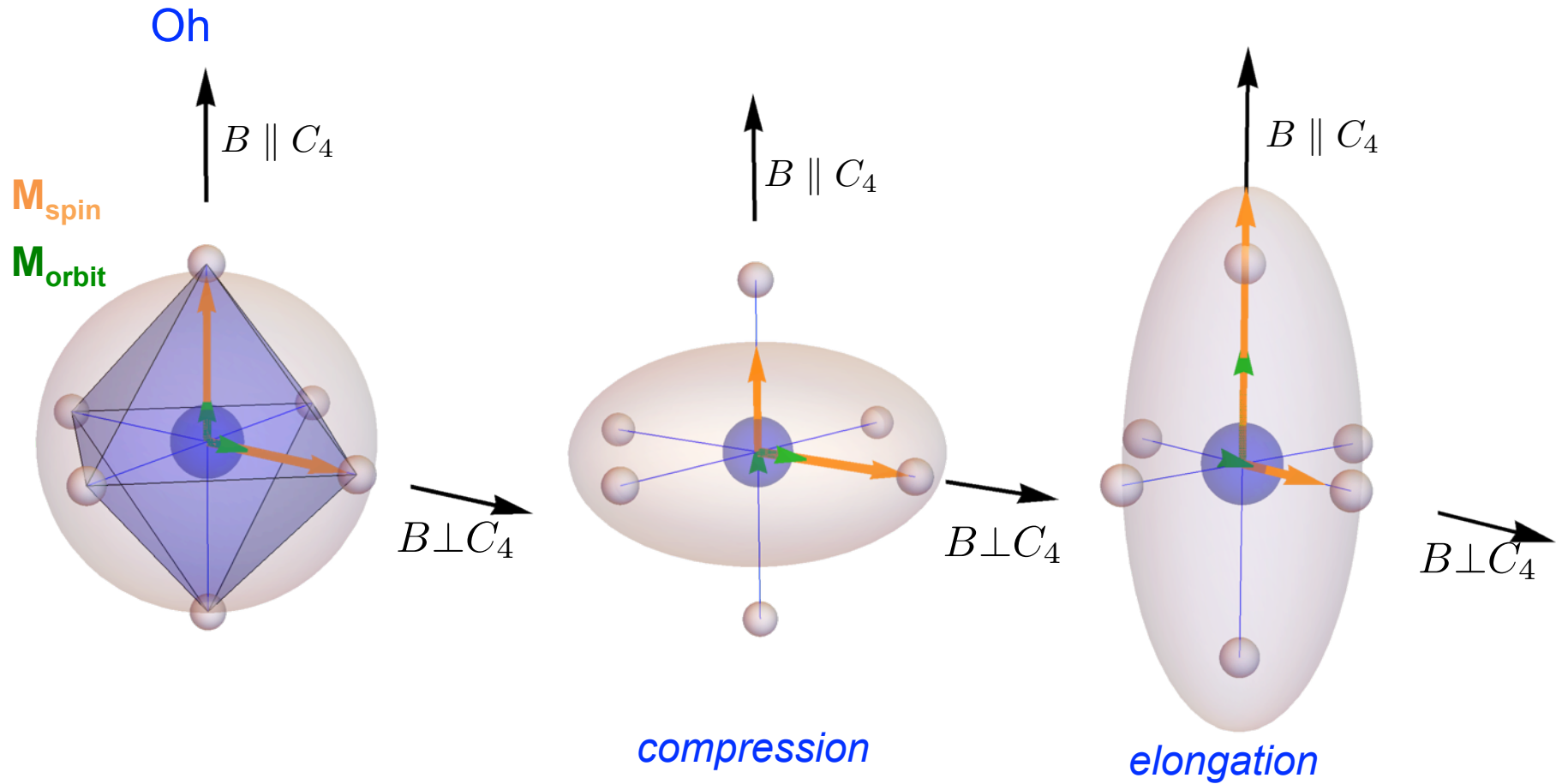Heidelberg

Table of contents

- Smin
- Splus
- Ssqr
- Sx
- Sy
- Sz

Tutorial 07_Expectationvalues.Quanty
(Monday morning)

Crystal field and magnetism

Tetragonal distortion : D_{4h}

Oh

$B \parallel C_4$

M_{spin}
M_{orbit}

$B \perp C_4$

$B \parallel C_4$

$B \perp C_4$

compression

$B \parallel C_4$

$B \perp C_4$

elongation

Conclusion / remarks

- Crystal field and ligand field are atomic models

- Crystal/ligand field are a semi-empirical model (parameter dependent)
  can be linked to more *ab-initio* methods (tight-binding, DFT, CASSCF,…)

- Crystal field can create **natural and/or magnetic anisotropies**
  angular dependences
  measured by core spectroscopies using polarized X-rays (linear or circular)

⇨ **Following Lectures**

- Crystal field affect the properties of **4f rare earth ions** (not discussed here)
  More parameters