Crystal field in multielectron ions

Marie-Anne ARRIO

CNRS-Sorbonne Université (Paris)

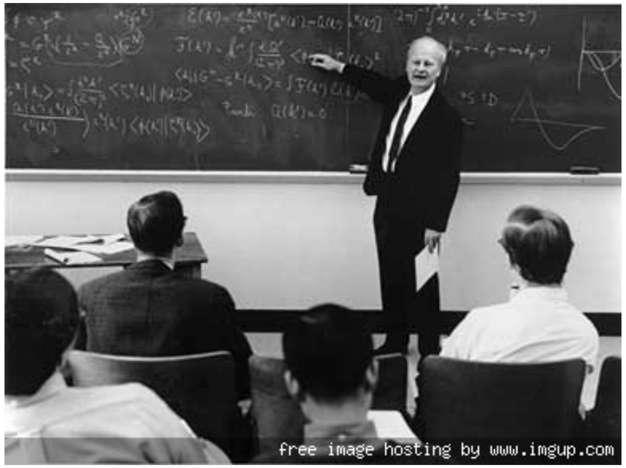
Slides/Figures courtesy of Guillaume Radtke

Crystal field

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

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

Crystal field : origin



Hans Bethe (1906-2005)

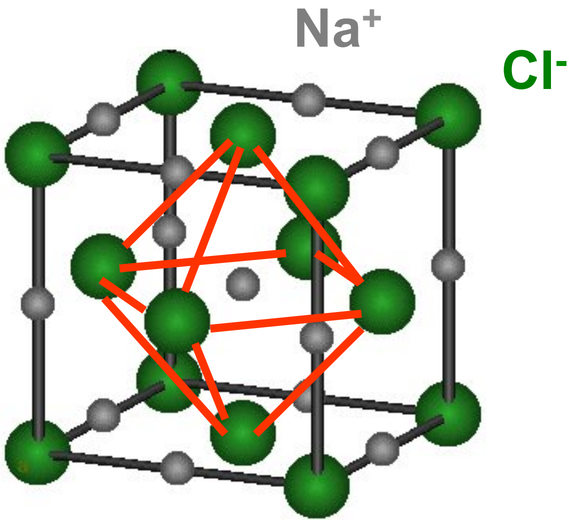
In 1929 (University of Tübingen): Model to explain the properties of NaCl crystal.

Ions are considered to be undeformable charged spheres and the interaction between them simply results from the electric potential generated by these charges.

(Nobel Prize in Physics 1967)

Crystal field : origin

NaCl crystal



Na^+ ion surrounded by 6 Cl^- ions as nearest neighbors

- Ions = indeformable charged spheres
- Interaction results from the created electrostatic potential

Electrostatic potential produced by a negative charge:

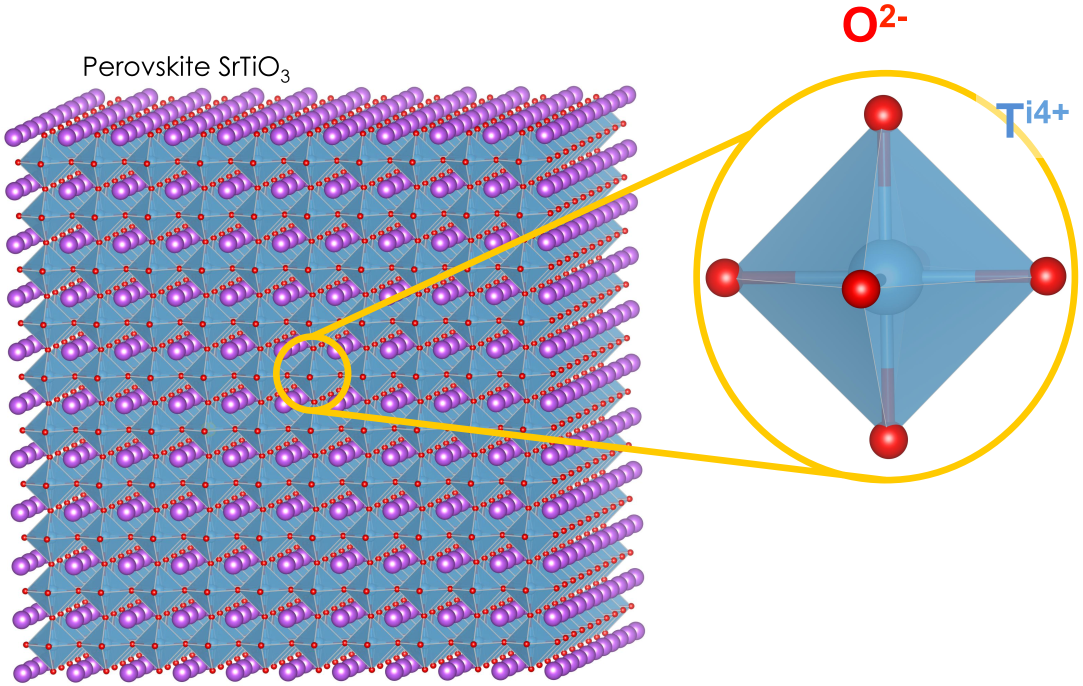
$$V_i = \frac{e}{r}$$

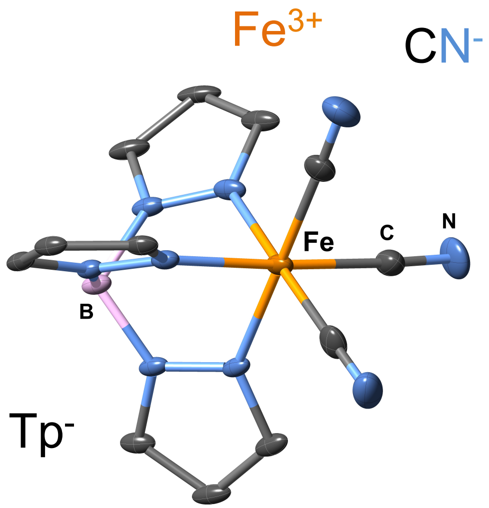
(r = distance between the centered charge and a point i)

Effect of the 6 negative charges: $\sum_{i=1}^{6} V_i$

Crystal field : origin

Analogy for solid-state or complex coordination
Consider the ligands and the metal as charged spheres
Na^+ ≈ metal ion - Cl^- ≈ ligand



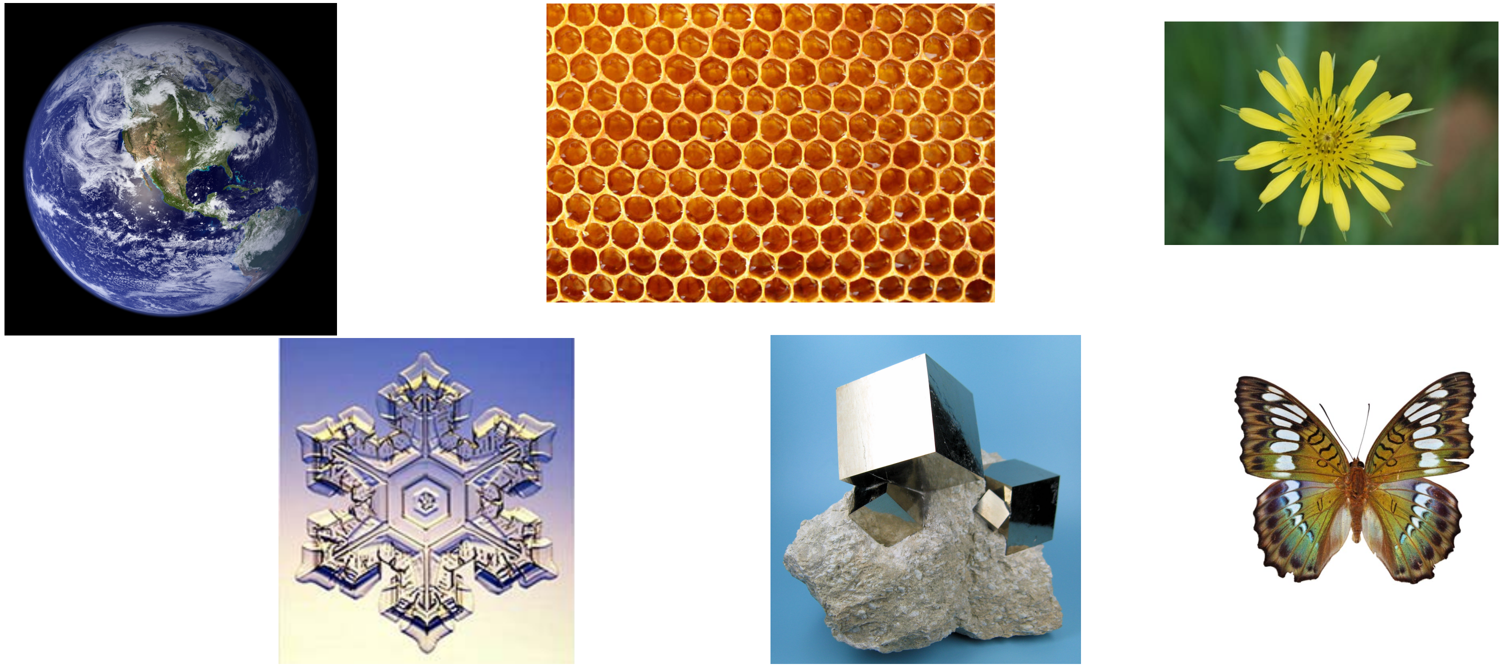


Tp=tris-pyrazolyl borate

Symmetries

Symmetries

Symmetry is responsible for many physical and spectroscopic properties of compounds
Group theory is a powerfull tool, which not only allows one to simplify calculations, but also defines the language of labeling states and can predict without calculations if states couple under certain interactions or if certain transitions are allowed or not.

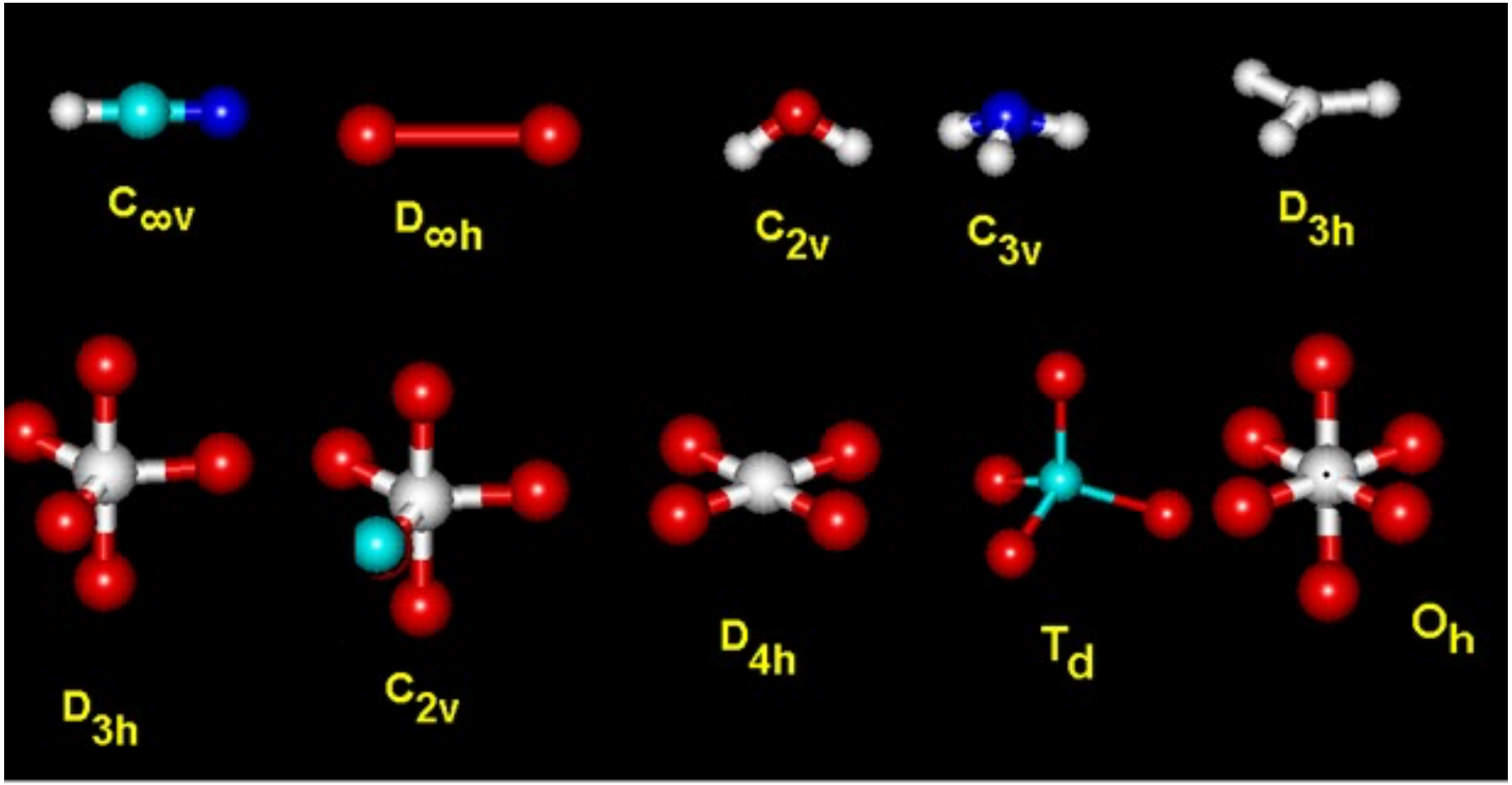


Symmetry operations : some notations to know

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

⇨ Quanty mathematica : Quanty/guide/PointGroupSymmetry

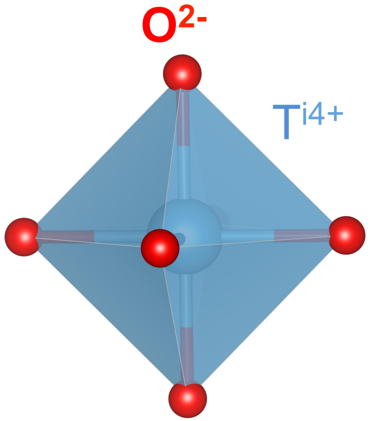
Symmetries : some point groups



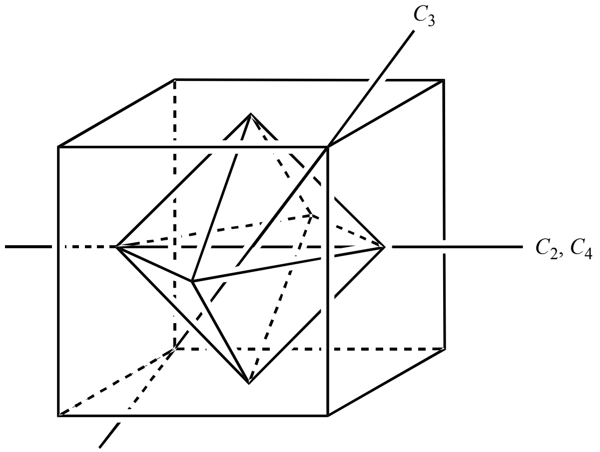
Each group has a table of representations

Symmetries : O_h

$SrTiO_3$



Octahedral
Group : O_h

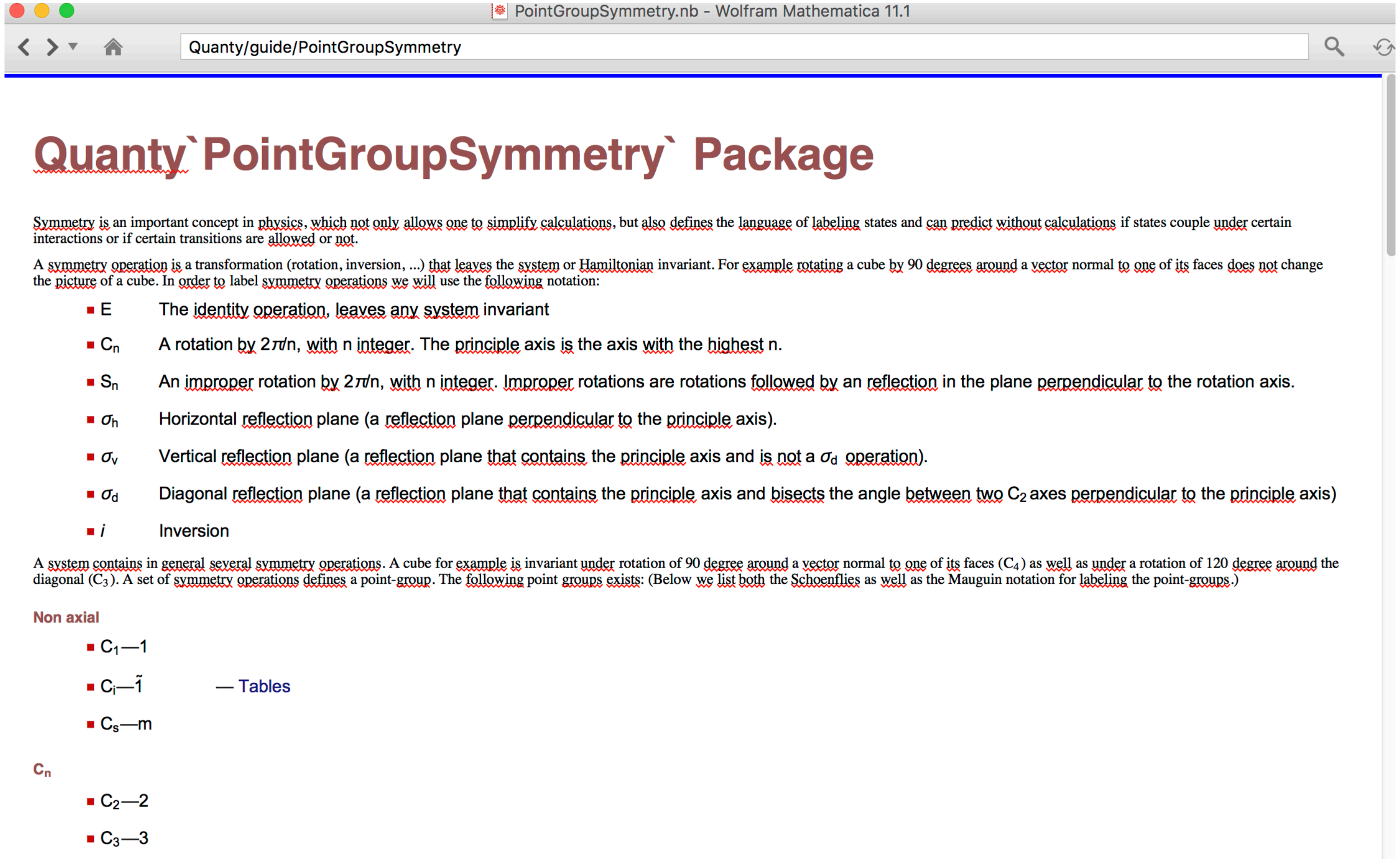


Character table for O_h point group

	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		

Crystal field hamiltonian and symmetry

(Almost) All you need is in Quanty-mathematica !!!!



Quanty`PointGroupSymmetry` Package

Symmetry is an important concept in physics, which not only allows one to simplify calculations, but also defines the language of labeling states and can predict without calculations if states couple under certain interactions or if certain transitions are allowed or not.

A symmetry operation is a transformation (rotation, inversion, ...) that leaves the system or Hamiltonian invariant. For example rotating a cube by 90 degrees around a vector normal to one of its faces does not change the picture of a cube. In order to label symmetry operations we will use the following notation:

- E — The identity operation, leaves any system invariant
- C_n — A rotation by $2\pi/n$, with n integer. The principle axis is the axis with the highest n.
- S_n — An improper rotation by $2\pi/n$, with n integer. Improper rotations are rotations followed by an reflection in the plane perpendicular to the rotation axis.
- σ_h — Horizontal reflection plane (a reflection plane perpendicular to the principle axis).
- σ_v — Vertical reflection plane (a reflection plane that contains the principle axis and is not a σ_d operation).
- σ_d — Diagonal reflection plane (a reflection plane that contains the principle axis and bisects the angle between two C_2 axes perpendicular to the principle axis)
- *i* — Inversion

A system contains in general several symmetry operations. A cube for example is invariant under rotation of 90 degree around a vector normal to one of its faces (C_4) as well as under a rotation of 120 degree around the diagonal (C_3). A set of symmetry operations defines a point-group. The following point groups exists: (Below we list both the Schoenflies as well as the Mauguin notation for labeling the point-groups.)

Non axial

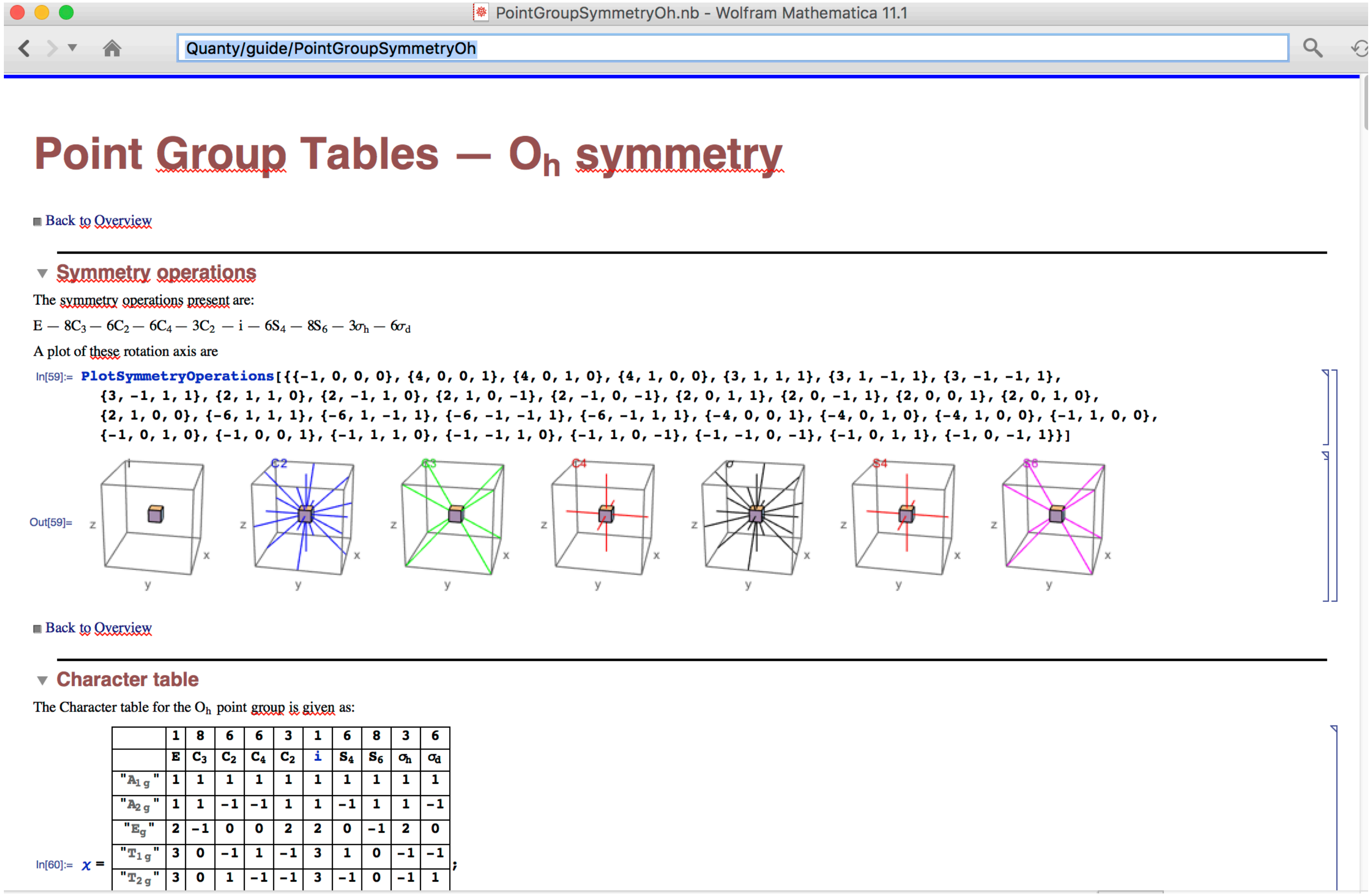
- C_1—1
- C_i—$\bar{1}$ — Tables
- C_s—m

C_n

- C_2—2
- C_3—3

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

Crystal field hamiltonian and symmetry



Point Group Tables — O$_h$ symmetry

■ Back to Overview

Symmetry operations

The symmetry operations present are:

E — 8C$_3$ — 6C$_2$ — 6C$_4$ — 3C$_2$ — i — 6S$_4$ — 8S$_6$ — 3σ_h — 6σ_d

A plot of these rotation axis are

```
In[59]:= PlotSymmetryOperations[{{-1, 0, 0, 0}, {4, 0, 0, 1}, {4, 0, 1, 0}, {4, 1, 0, 0}, {3, 1, 1, 1}, {3, 1, -1, 1}, {3, -1, -1, 1},
   {3, -1, 1, 1}, {2, 1, 1, 0}, {2, -1, 1, 0}, {2, 1, 0, -1}, {2, -1, 0, -1}, {2, 0, 1, 1}, {2, 0, -1, 1}, {2, 0, 0, 1}, {2, 0, 1, 0},
   {2, 1, 0, 0}, {-6, 1, 1, 1}, {-6, 1, -1, 1}, {-6, -1, -1, 1}, {-6, -1, 1, 1}, {-4, 0, 0, 1}, {-4, 0, 1, 0}, {-4, 1, 0, 0}, {-1, 1, 0, 0},
   {-1, 0, 1, 0}, {-1, 0, 0, 1}, {-1, 1, 1, 0}, {-1, -1, 1, 0}, {-1, 1, 0, -1}, {-1, -1, 0, -1}, {-1, 0, 1, 1}, {-1, 0, -1, 1}}]
```

Out[59]=

■ Back to Overview

Character table

The Character table for the O$_h$ point group is given as:

In[60]:= χ =

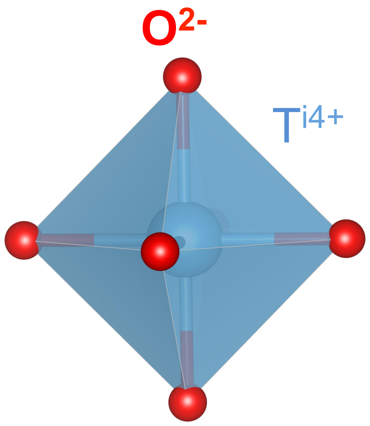
	1	8	6	6	3	1	6	8	3	6
	E	C$_3$	C$_2$	C$_4$	C$_2$	i	S$_4$	S$_6$	σ_h	σ_d
"A$_{1g}$"	1	1	1	1	1	1	1	1	1	1
"A$_{2g}$"	1	1	-1	-1	1	1	-1	1	1	-1
"E$_g$"	2	-1	0	0	2	2	0	-1	2	0
"T$_{1g}$"	3	0	-1	1	-1	3	1	0	-1	-1
"T$_{2g}$"	3	0	1	-1	-1	3	-1	0	-1	1

;

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

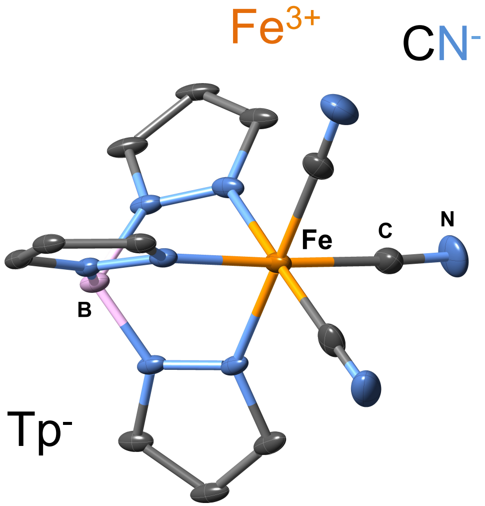
Symmetries

$SrTiO_3$



Octahedral
Group : O_h

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



Trigonal
Group : C_{3v}

Crystal field hamiltonian

Crystal field hamiltonian

The crystal field potential can be expanded on the normalized spherical harmonics

$$H_{CF}=\sum_{k=0}^{\infty}\sum_{m=-k}^{k}A_{k,m}C_k^m(\theta,\phi)\quad\text{with } C_{k,m}(\theta,\phi)=\left(\frac{4\pi}{2k+1}\right)^{1/2}Y_{k,m}(\theta,\phi)$$

Where to stop the expansion ?

➔Writing the CF matrix element on the basis functions. Depends on :

$$\langle Y_{\ell_1,m_1}|C_{k,m}|Y_{\ell_1,m_2}\rangle=(-1)^{m_1}(2\ell_1+1)\begin{pmatrix}\ell_1 & k & \ell_1\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\ell_1 & k & \ell_1\\ -m_1 & m & m_2\end{pmatrix}$$

$$\boxed{\neq 0 \text{ if } k \text{ even } (2\ell_1+k \text{ even}),\ 0\leq k\leq 2\ell_1}$$

$$\langle Y_{\ell_1,m_1}|C_{k,m}|Y_{\ell_2,m_2}\rangle=(-1)^{m_1}\sqrt{(2\ell_1+1)(2\ell_2+1)}\begin{pmatrix}\ell_1 & k & \ell_2\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\ell_1 & k & \ell_2\\ -m_1 & m & m_2\end{pmatrix}$$

$$\neq 0 \text{ if } \ell_1+k+\ell_2 \text{ even},\ |\ell_1-\ell_2|\leq k\leq|\ell_1+\ell_2| \text{ and } -m_1+m+m_2=0$$

The crystal fields Hamiltonian thus writes

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

with ℓ the orbital momentum of the shell (2 for 3d ions, 3 for 4f ions)

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

Crystal field hamiltonian and symmetry

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

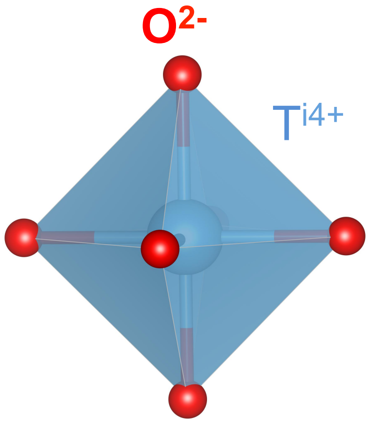
Not all values of A_{km} are allowed : many are zero due to the symmetry around the ion

Symmetry related:

For all symmetry operation (O_i) of the point-group G, we have

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

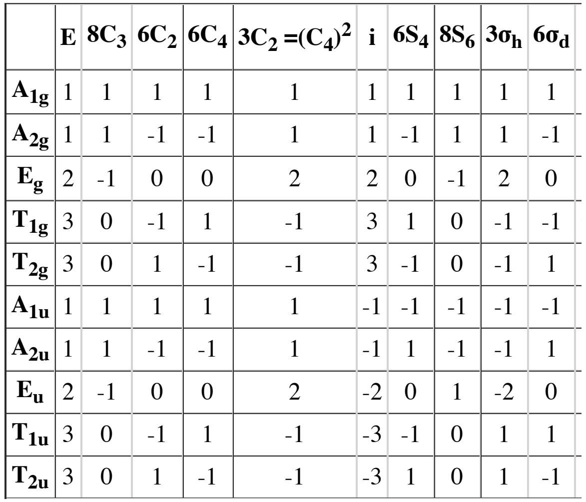
Example of the cubic case



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

Only one nonzero A_{km} : A_{40}

O_i



	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

Notations for crystal field parameters

The notations vary a lot from an author to the other

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

(Haverkort/QUANTY)

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

And symmetry dependent parameters like (Balhausen, König, Kremer,..)

10Dq for cubic

{10Dq, Ds, Dt} for tetragonal symmetry D4h

…. etc.

3d transitions metal ions

In material made of 3d transitions metal ions, a lot of physico-chemical properties are due to the crystal field,

For example

- *Color*
- *Magnetic properties*

Ni^{2+}

3d orbitals

- Basis of atomic orbitals

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

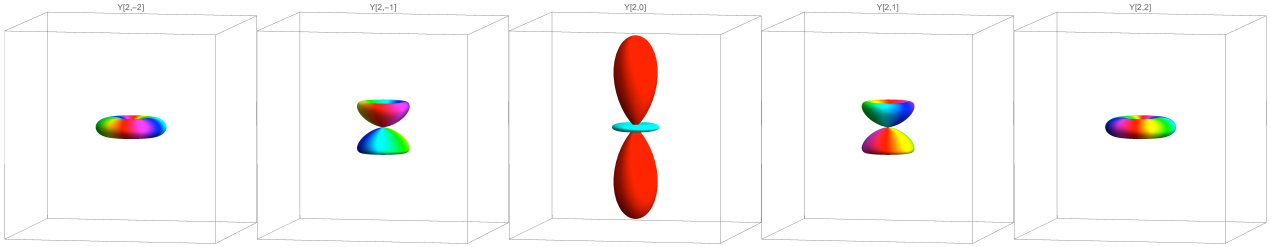
$$R_{n_i\ell_i}(r) = \frac{1}{r}P_{n_i\ell_i}(r)$$

3d atomic orbitals

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

- 3d levels : n=2, ℓ=2 2ℓ+1=5 basis functions (-2 ≤ ℓ ≤ 2)

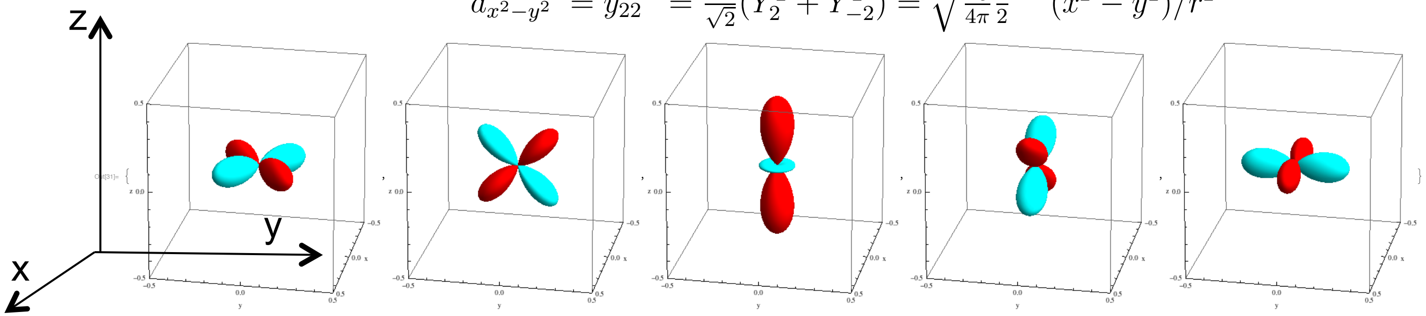
See Quanty/tutorial/hydrogen_wavefunctions



- 3d orbitals are linear combination of $Y_{2,m}(\theta,\phi)\ with\ m=-2,-1,0,1,2$

(real harmonics = tesseral harmonics Z)

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



O_h crystal field splitting of 3d electron

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

1) Matrix elements

$$\langle Y_{\ell_1,m_1}|C_{k,m}|Y_{\ell_1,m_2}\rangle = (-1)^{m_1}(2\ell_1+1)\begin{pmatrix}\ell_1 & k & \ell_1\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\ell_1 & k & \ell_1\\ -m_1 & m & m_2\end{pmatrix} = (-1)^{m_1}\sqrt{10/7}\begin{pmatrix}2 & k & 2\\ -m_1 & m & m_2\end{pmatrix}$$

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

$$\begin{array}{c}
\begin{array}{ccccc}
|\ell\ m\rangle \equiv |2\,-2\rangle & |2\,-1\rangle & |2\ 0\rangle & |2\ 1\rangle & |2\ 2\rangle
\end{array}\\
\left(\begin{array}{ccccc}
A_{0,0}+\frac{1}{21}A_{4,0} & 0 & 0 & 0 & \frac{5}{21}A_{4,0}\\
0 & A_{0,0}-\frac{4}{21}A_{4,0} & 0 & 0 & 0\\
0 & 0 & A_{0,0}+\frac{2}{7}A_{4,0} & 0 & 0\\
0 & 0 & 0 & A_{0,0}-\frac{4}{21}A_{4,0} & 0\\
\frac{5}{21}A_{4,0} & 0 & 0 & 0 & A_{0,0}+\frac{1}{21}A_{4,0}
\end{array}\right)
\end{array}$$

2) Diagonalization

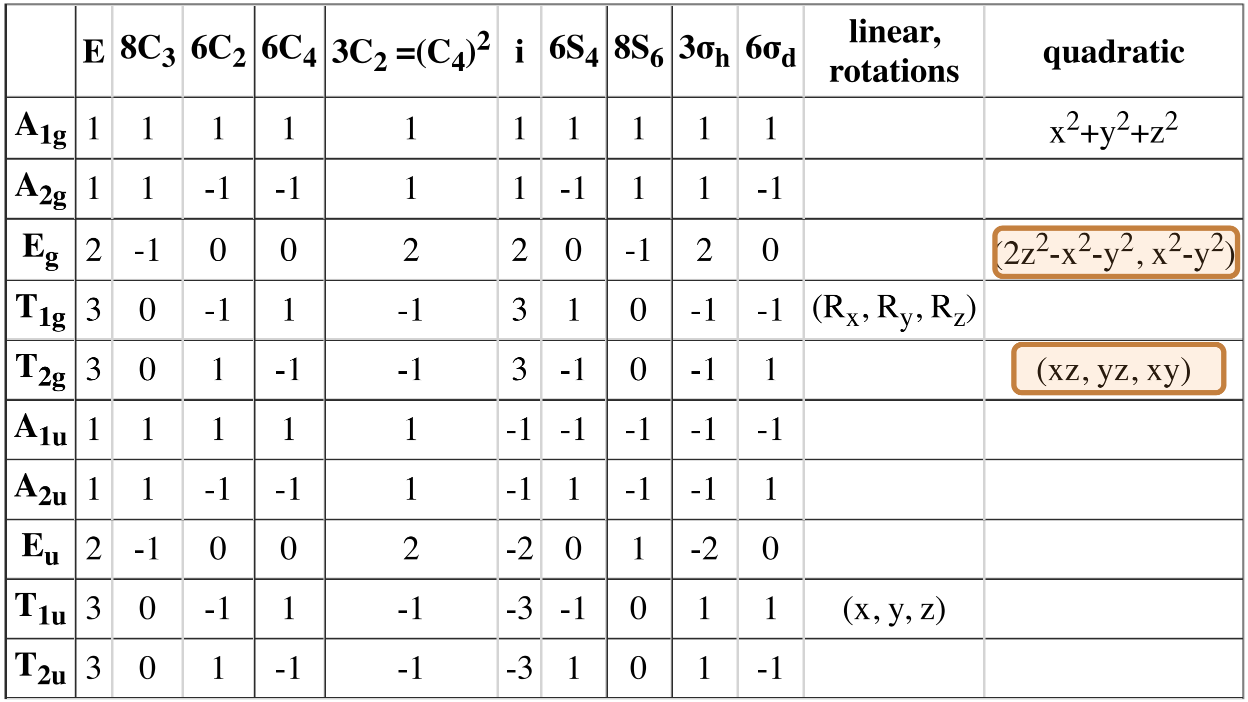
$$\begin{array}{c}
\begin{array}{ccccc}
d_{x^2-y^2} & d_{z^2} & d_{yz} & d_{xz} & d_{xy}
\end{array}\\
\left(\begin{array}{ccccc}
A_{0,0}+\frac{2}{7}A_{4,0} & 0 & 0 & 0 & 0\\
0 & A_{0,0}+\frac{2}{7}A_{4,0} & 0 & 0 & 0\\
0 & 0 & A_{0,0}-\frac{4}{21}A_{4,0} & 0 & 0\\
0 & 0 & 0 & A_{0,0}-\frac{4}{21}A_{4,0} & 0\\
0 & 0 & 0 & 0 & A_{0,0}-\frac{4}{21}A_{4,0}
\end{array}\right)
\end{array}$$

➔The O_h crystal field split the *d* orbitals in two groups of orbitals

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

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		

$$\{d_{x^2-y^2}, d_{z^2}\} \in e_g$$

$$\{d_{yz}, d_{xz}, d_{xy}\} \in t_{2g}$$

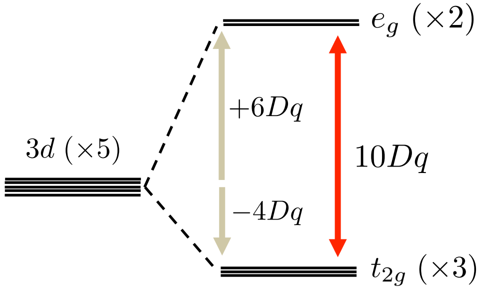
- From the *Oh* group properties, one could have guessed the splitting of the d orbitals
- d orbitals are called e_g and t_{2g} *

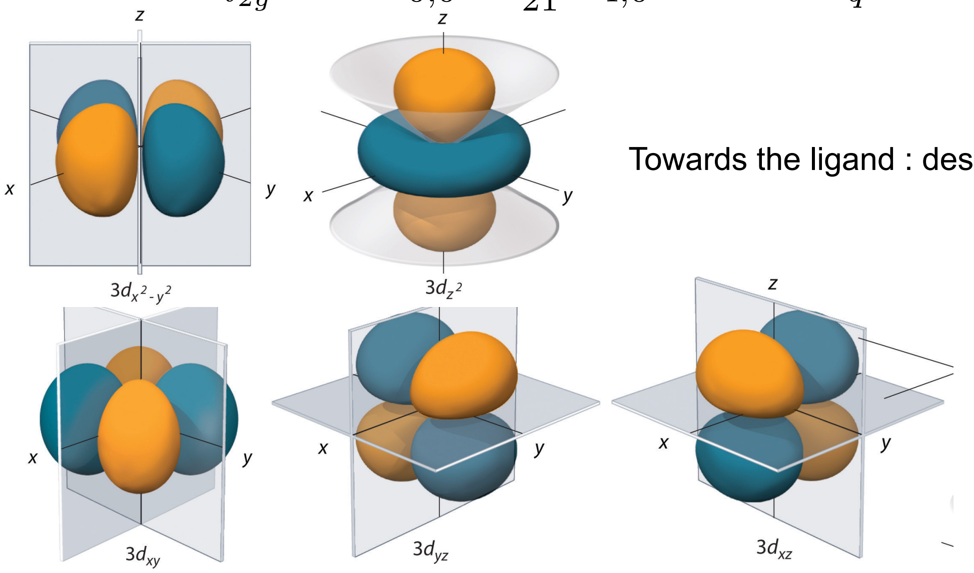
(*)N.B. : lower case letter (e_g and t_{2g}) for one electron

O_h Crystal field splitting of 3d electron Parameters

From the diagonalization, one get

$$\begin{aligned} E_{e_g} &= & A_{0,0} + \tfrac{2}{7} A_{4,0} &= & +6D_q \\ E_{t_{2g}} &= & A_{0,0} - \tfrac{4}{21} A_{4,0} &= & -4D_q \end{aligned}$$





Towards the ligand : destabilized

Towards the ligand : stabilized

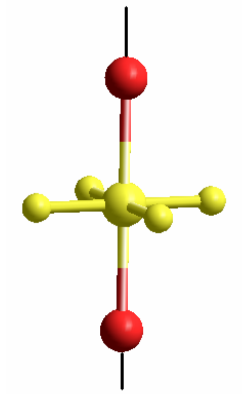
$10Dq \equiv$ adjustable parameter

In QUANTY, the $A_{k,m}$ are defined in function the orbital energies (this choice can be modified)

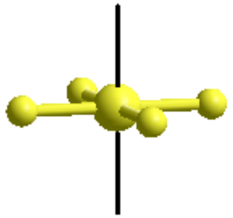
$$A_{k,m} = \begin{cases} \frac{2}{5} E_{e_g} + \frac{3}{5} E_{t_{2g}} & k = 0 \quad m = 0 \\ \frac{21}{10} (E_{e_g} - E_{t_{2g}}) & k = 4 \quad m = 0 \\ \frac{21}{10} \sqrt{\frac{5}{14}} (E_{e_g} - E_{t_{2g}}) & k = 4 \quad m = \pm 4 \\ 0 & \text{True} \end{cases}$$

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

D_{4h}



Elongated
or compressed O_h
along C_4 axis



Square planar

Character table for D_{4h} point group

	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 the D4h table, one can predict the 3d splitting in 4 groups

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

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

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

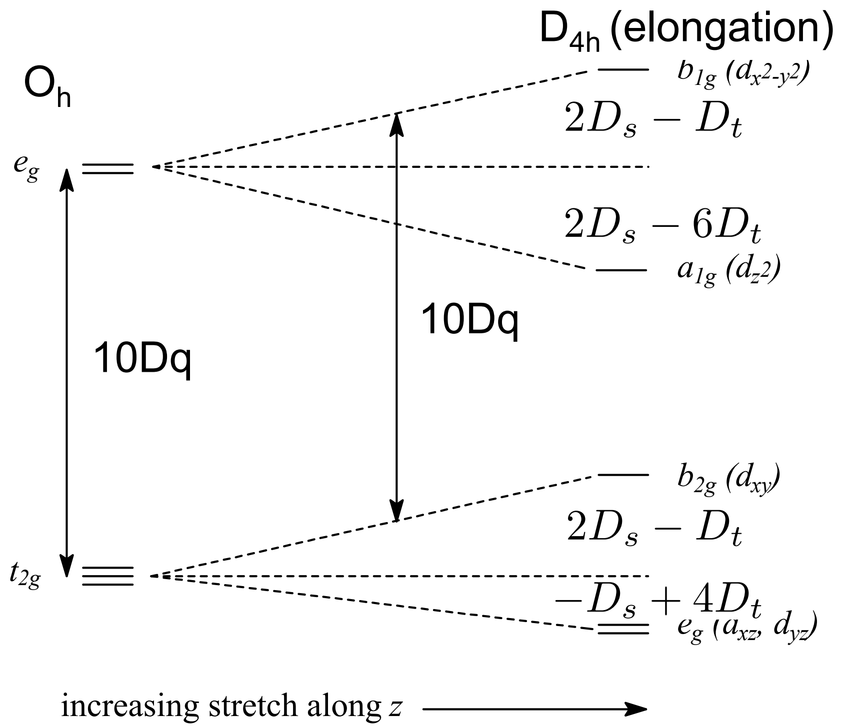
The CF matrix is diagonal in the {d} basis and the energies are :

$$\begin{aligned} E_{a_{1g}} &= 6D_q - 2D_s - 6D_t \quad (d_{z^2}) \\ E_{b_{1g}} &= 6D_q + 2D_s - D_t \quad (d_{x^2-y^2}) \\ E_{b_{2g}} &= -4D_q + 2D_s - D_t \quad (d_{xy}) \\ E_{e_g} &= -4D_q - D_s + 4D_t \quad (d_{xz}, d_{yz}) \end{aligned}$$

with

$$\begin{aligned} A_{0,0} &= 1/5(E_{a_1} + E_{b_1} + E_{b_2} + 2E_e) \\ A_{2,0} &= E_{a_1} - E_{b_1} - E_{b_2} + E_e \\ A_{4,0} &= 3/10(6E_{a_1} + E_{b_1} + E_{b_2} - 8E_e) \\ A_{4,4} &= A_{4,-4} = 3/20(\sqrt{70}E_{b_1} - \sqrt{70}E_{b_2}) \end{aligned}$$

The relation with Dq,Ds,Dt can be found in the book of 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 $H_{CF} = 10Dq * OpptenDq$

→ In this *Oh* case, the hamiltonian is similar but it can be different for lower symmetries (E_i(d) vs 10Dq,Ds,Dt,…). Anyway, the results should be the same.

Multi-electrons ions

1. Configuration : simple picture
2. The spherical ion : L,S,J basis function
3. Crystal field : basis functions and matrix element
4. Energy diagram (Tanabe-Sugano)
5. Spectroscopic terms and orbitals

6. Example of LS/HS FeII

Multi-electrons ions : configuration

Electronic configuration:	complete	reduced to open shell
3d transition metal ions	$1s^2 2s^2 2p^6$ **3d^n**	**3d^n**
4f rare earth ions	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ **4f^n**	**4f^n**

- Many possibility of filling of the 3d orbitals

$$\left.\begin{array}{l} 2\ell+1=5\ |\ell,m_\ell> \text{ angular functions} \\ 2s+1=5\ |sm_s> \text{ spin functions} \end{array}\right\} \text{10 functions}$$

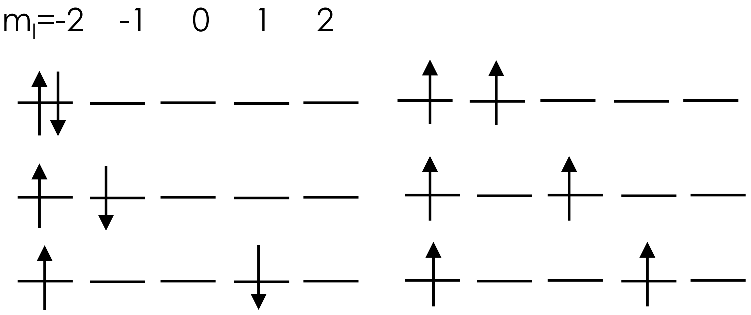
Nb states = $C^n_{10} = \frac{10!}{n!(10-n)!}$

Degeneracy = **multiplets**

Example of a d^2 system (V^{3+}, Cr^{4+}) :

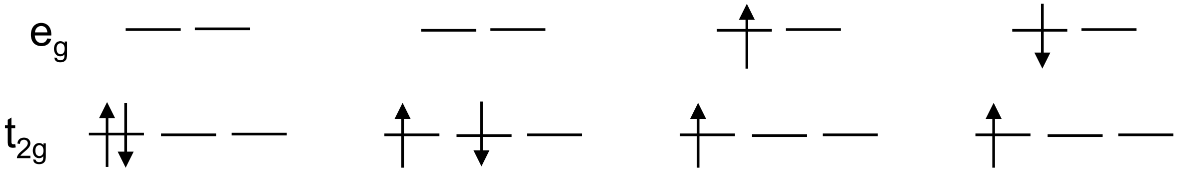
degenerate states : $C^2_{10} = 45$

Some possibilites:



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

$$\mathbf{H}_{\mathbf{ion}} = \underbrace{\mathbf{H}_{\mathbf{cin}} + \mathbf{H}_{\mathbf{e\text{-}n}} + \mathbf{H}_{\mathbf{e\text{-}e}} + \mathbf{H}_{\mathbf{s\text{-}o}}}_{\text{Free ion (spherical)}} \underbrace{+\ \mathbf{H}_{\mathbf{CF}}}_{\text{Crystal field}}$$

$$H_{cin} = \sum_{i=1}^{N} -\frac{h^2}{2m}\nabla^2_{r_i}$$

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

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

Spin-orbit coupling

Hamiltonian of the ion with N electrons

Basis functions |Ψ>

- **Multi-electron functions for N electrons**

  $\Psi(r_1, r_2, \ldots, r_N)$

- **Linear combination of Slater determinant built from the mono-electronic functions**
- **Anti-symmetric function to satisfy the Pauli principle**

Ion with N electrons : operators

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

⚠ 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 ion with N electrons : basis functions

- **Fonctions |α(L,S)JM$_J$>**

Eigenfunctions of $\widehat{J}^2, \widehat{J}_z, \widehat{L}^2, \widehat{S}^2$

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

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

- The energy of |α(L,S) > does not depend on $M_{L,}$ M_S
  Degeneracy of |α(L,S)> = (2L+1)(2S+1)

- The energy of |α(L,S)JM$_J$> does not depend on M_J
  Degeneracy of |α(L,S)JM$_J$> = 2J+1

Spectroscopic terms |α(L,S)JM$_J$> =

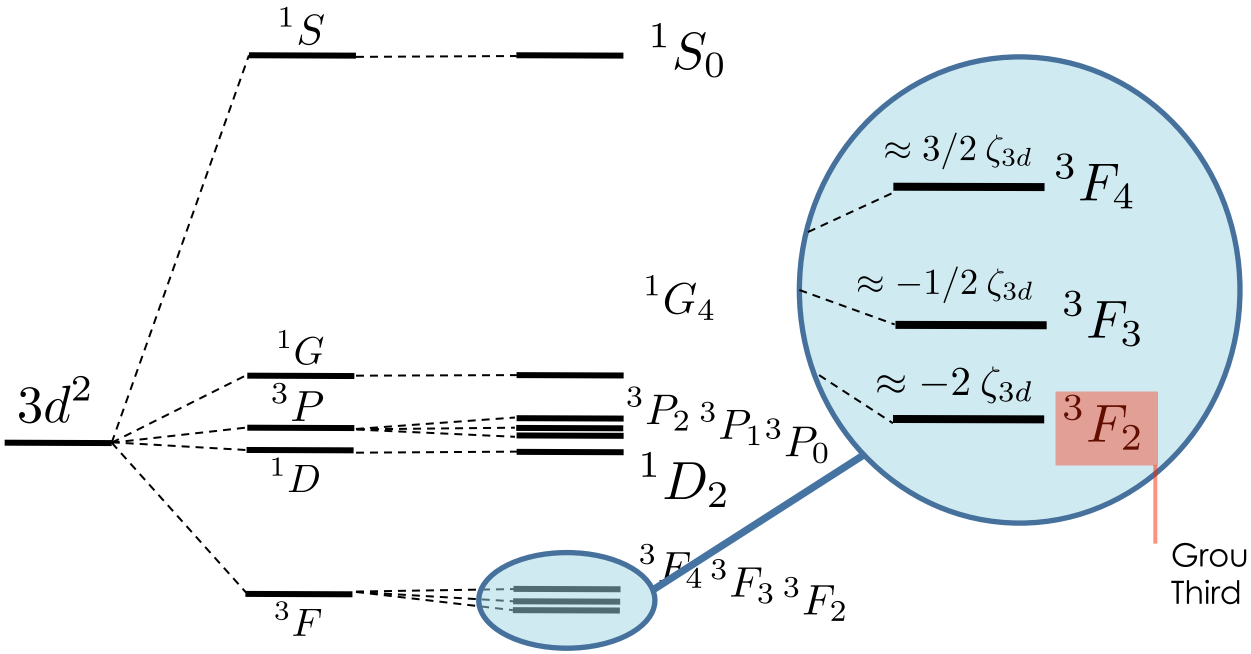
$^{2S+1}L_J$

S spin

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

Free ion : spectroscopic terms for 3d² ion

Split the 5 LS terms into 9 (L,S)J terms : $^1G_4,\ ^3F_4,\ ^3F_3,\ ^3F_2,\ ^1D_2,\ ^3P_2,\ ^3P_1,\ ^3P_0,\ ^1S_0$



*only diagonal energy corrections here (neglect off diagonal coupling with other LS terms)

Landé interval rule

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

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
  does not use the $\{\Gamma\}$ basis for diagonalization but its knowledge is necessary to label the states (spectroscopic terms)

Crystal field and group theory

Free ion

O_3 is the group of the sphere
|α(L,S) J M_J> partners of irrep* J of O_3

$$\mathbf{J}(SO_3) \rightarrow \sum_{M_J=-J}^{J} \mathbf{M_J}(SO_2)$$

Hamiltonian expanded on $C_{k,m}$ <> $T^{k,m}$

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

Ion in solid/molecule

G is the subgroup of the sphere
|a(L,S) J Γ γ > partners of the irrep* Γ of **G**

$$\mathbf{J}(SO_3) \rightarrow \sum_i \mathbf{\Gamma_i}(G)$$

$$ex: \mathbf{2}(SO_3) \rightarrow t_{2g}(O_h) + e_g O_h$$

Hamiltonian expanded on $C_{k,m}$ <> $T^{k,m}$

$$H_{CF} = \sum_{\substack{k=0,\\ k\ even}}^{2\ell} \sum_i A_{J,\Gamma_i} T_{J,\Gamma_i}$$

$$ex: H_{CF}^{O_h} = aT^{4(SO_3),A_{1g}(O_h)}$$

H_{CF} is fully symmetric in O_h
and transforms as $A_{1g}(O_h)$

---

* *irrep=irreducible representation*

Crystal field and group theory
Matrix elements

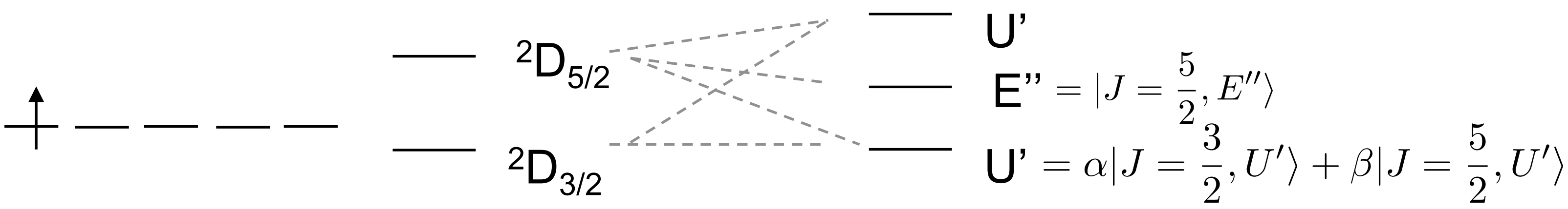
$H_{CF} \in A_{1(g)}$ * (fully symmetric representation of group **G**)

* *g* only for centro-symmetric group

$$\langle (L_i, S_i) J_i \Gamma_i | H_{CF} | (L_j, S_j) J_j \Gamma_j \rangle \neq 0 \text{ if } \Gamma_i \otimes A_{1(g)} \otimes \Gamma_j = \boxed{\Gamma_i \otimes \Gamma_j \ni A_{1(g)}}$$

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

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



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

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

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

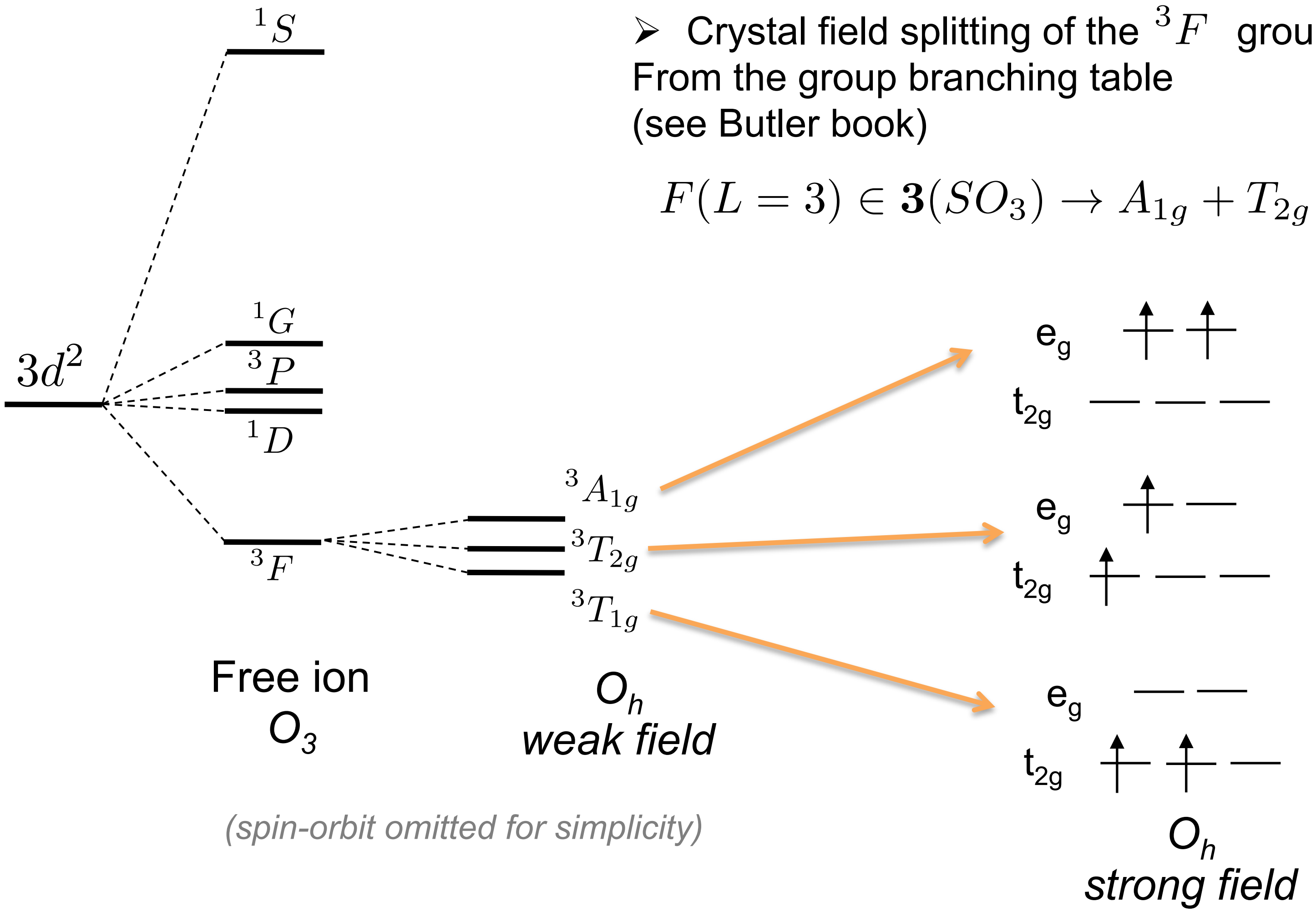
Crystal field and group theory

Example of d^2 ion in O_h symmetry

- Crystal field splitting of the ^3F ground state

From the group branching table
(see Butler book)

$$F(L=3) \in \mathbf{3}(SO_3) \rightarrow A_{1g} + T_{2g} + T_{1g}(O_h)$$



(spin-orbit omitted for simplicity)

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

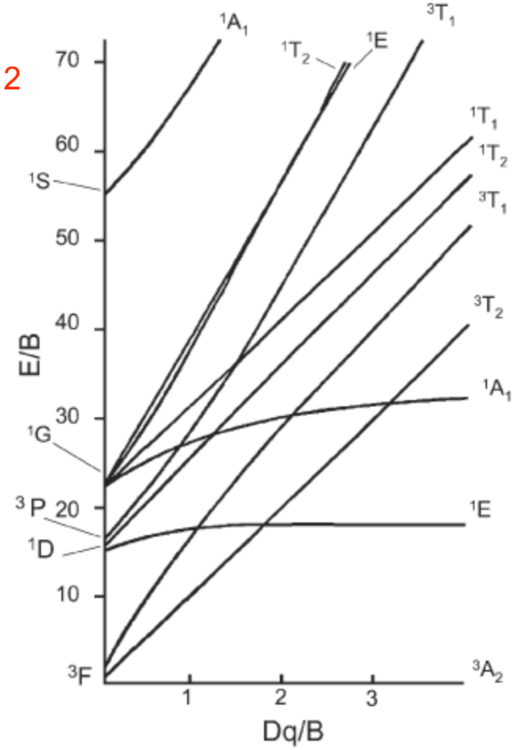
Crystal field : energy diagram

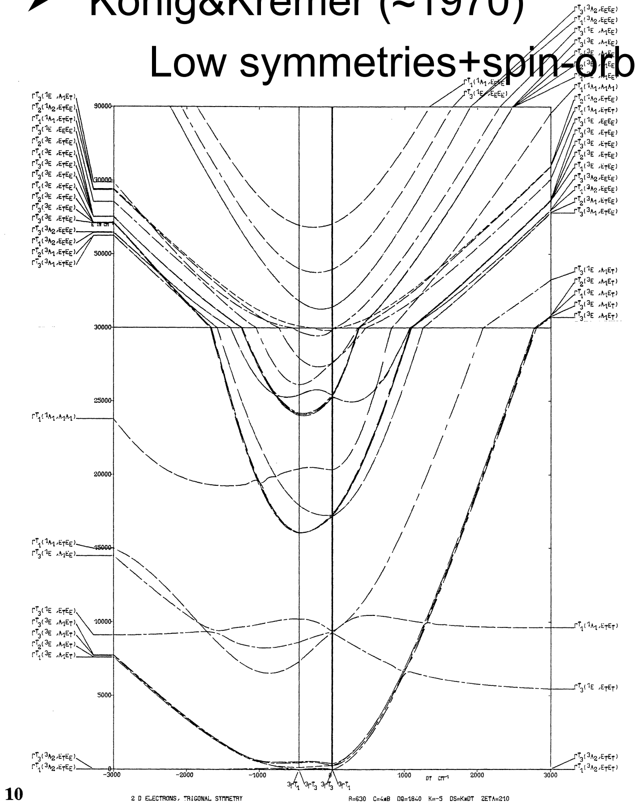
- Plot of the **energy** of spectroscopic terms $\left({}^{2S+1}\Gamma \text{ or } {}^{2S+1}\Gamma_J\right)$ as function of **crystal field parameter (10Dq,Ds,…)** (and B Racah parameter (*))

- Tanabe-Sugano diagram (1954)
  $O_h(T_d)$, no spin-orbit

- König&Kremer (≈1970)
  Low symmetries+spin-orbit

d^2





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

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

Crystal field : multi-electron and orbitals

Multi-electron ions

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

Term written with capital letter in Müliken 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:

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

One electron/orbitals

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

Small letter

ex: a_{1g}, e_2

Multiplet and crystal field today

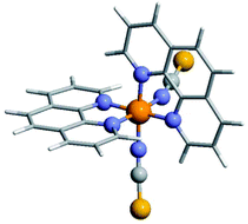
Calculations including the core-hole (ex : $2p^5 3d^{n+1}$, $3d^9 4f^{n+1}$,…) and many kind of transitions (electric dipole, magnetic dipole…)

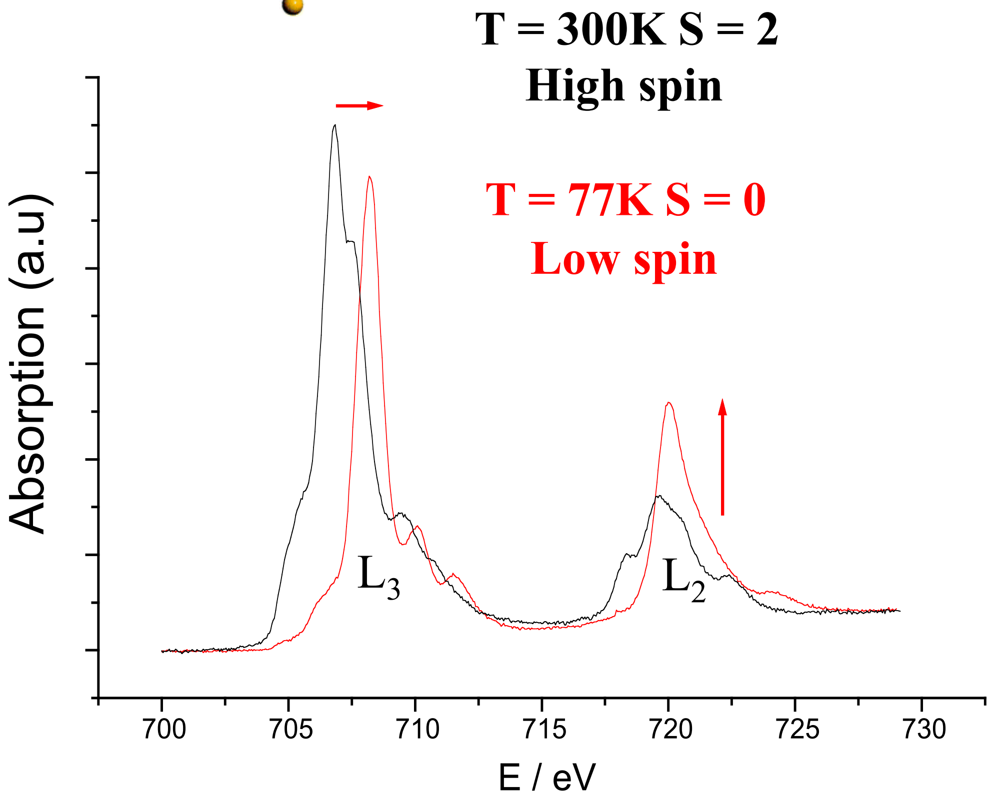
✓ **RACAH/BANDER**, Thole's code (core of CTM4XAS)
Based on group theory (Butler "Point group symmetry applications")
Difficult to modified and adapt to new spectroscopies since Theo Thole died in1996

✓ **QUANTY**, Haverkort's code
Flexible for the need of the new spectroscopies/physical properties

Example of crystal field : spin crossover

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





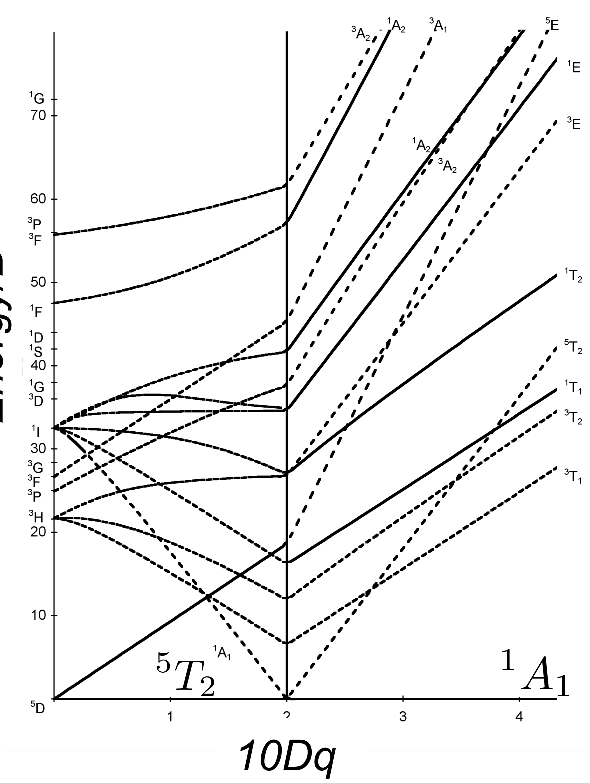
The spin crossover has been intensively studied and observed with many different spectroscopies and magnetic measurements

Ex : XAS at $L_{2,3}$ edges

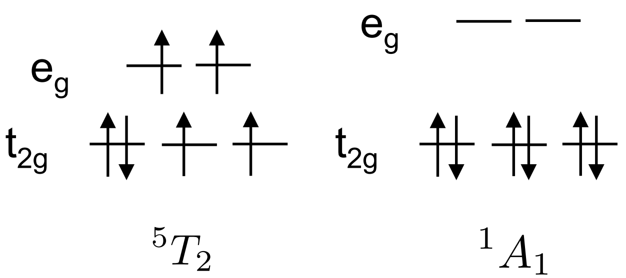
It is a well known crystal field effect named spin crossover

Crystal field effect : spin crossover

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



When 10Dq increases, the ground state changes



S=2
High spin

S=0
Low spin

- The magnetic properties goes from paramagnetic to non-magnetic
- Good candidate for many applications like molecular spintronic

Crystal field and magnetism

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

Magnetic moments

- Definitions

$$
\begin{aligned}
&m = m_{orbit} + m_{spin} \\
&m_{orbit} = -\langle i|\hat{L}_z|i\rangle \mu_B \\
&m_{spin} = -g_o\langle i|\hat{S}_z|i\rangle \mu_B = -2\langle i|\hat{S}_z|i\rangle \mu_B \\
&(\text{in } \hbar \text{ unit, with } \mu_B > 0)
\end{aligned}
$$

- Crystal field effect:

|(L,S)J Γγ> (Γ term) are not eigenfunctions of $\hat{L}_z$

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

Linear combination of m_L

For 3d ions, the orbital magnetic moment is quenched in most cases.
Some 3d ions have significant orbital magnetic moment (Co^{2+}, low spin Fe^{3+}, Fe^{2+})
→ atomic magnetic anisotropy

Magnetic moments

- QUANTY can calculate the expectation values of any operator ($\hat{O}$)

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

Thus one can get the

- Magnetic properties:

  Magnetization for a paramagnetic ion in function of
    the temperature T
    the external magnetic field B

  Susceptibility

External magnetic field effect : Zeeman effect

- **Hamiltonian**

$$H_{ion} = H_{cin} + H_{e\text{-}n} + H_{e\text{-}e} + H_{s\text{-}o} + H_{CF} \qquad + H_{Zeeman}$$

Free ion (spherical) Crystal field

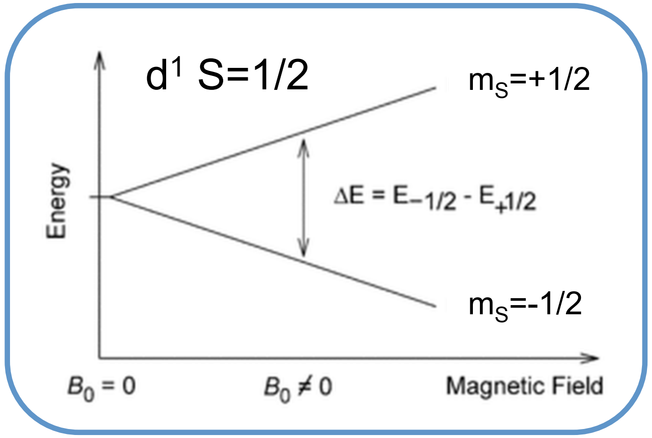
$$\begin{aligned} H_{Zeeman} &= -\vec{m}.\vec{H} = \mu_B(\hat{L} + g_0\hat{S}).\vec{H} \\ &= \mu_B(L_x + 2S_x)H_x + \mu_B(L_y + 2S_y)H_y + \mu_B(L_z + 2S_z)H_z \end{aligned}$$

- **Matrix element** depend on the magnetic moment

$$\langle \Gamma_i | H_{Zeeman} \rangle \Gamma_i \rangle = \mu_B \left(\langle \Gamma_i | L_z | \rangle \Gamma_i \rangle + g_0 \langle \Gamma_i | S_z | \rangle \Gamma_i \rangle \right) H_z$$

➡ Splitting of Γ_i states that depends on (m_L,m_S)

1 electron (S=1/2)
spherical



Magnetization of paramagnetic 3d ion (Zeeman effect)

- Magnetic moment of state Γ_i

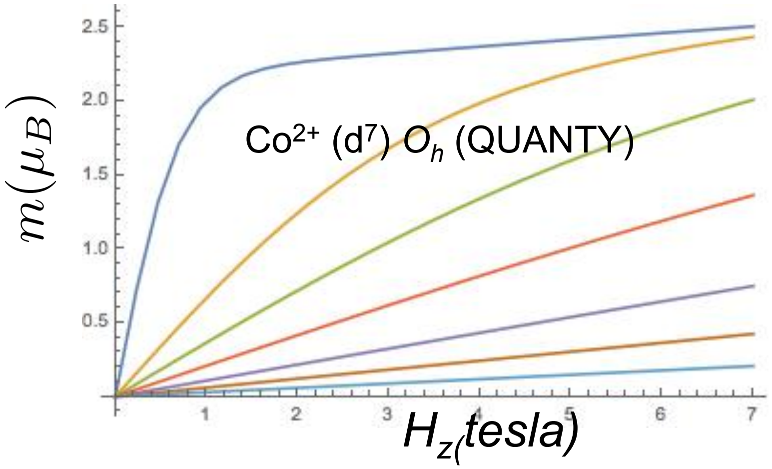
$$m_i = -\langle \Gamma_i | \hat{L_z} + 2\hat{S}_z | \Gamma_i \rangle \mu_B$$

- Magnetic moment at temperature T in the magnetic field H_z

$$m(T, H_z) = \frac{1}{Z} \sum_{i=1}^{Nbstates} m_i e^{-\frac{E_i}{k_B T}}$$

With Z the partition function $Z = \sum_{i=1}^{Nbstates} e^{-\frac{E_i}{k_B T}}$

- Magnetization curve for a paramagnetic ion $m(T, H_z) = f(H_z)$



Conclusion (remarks)

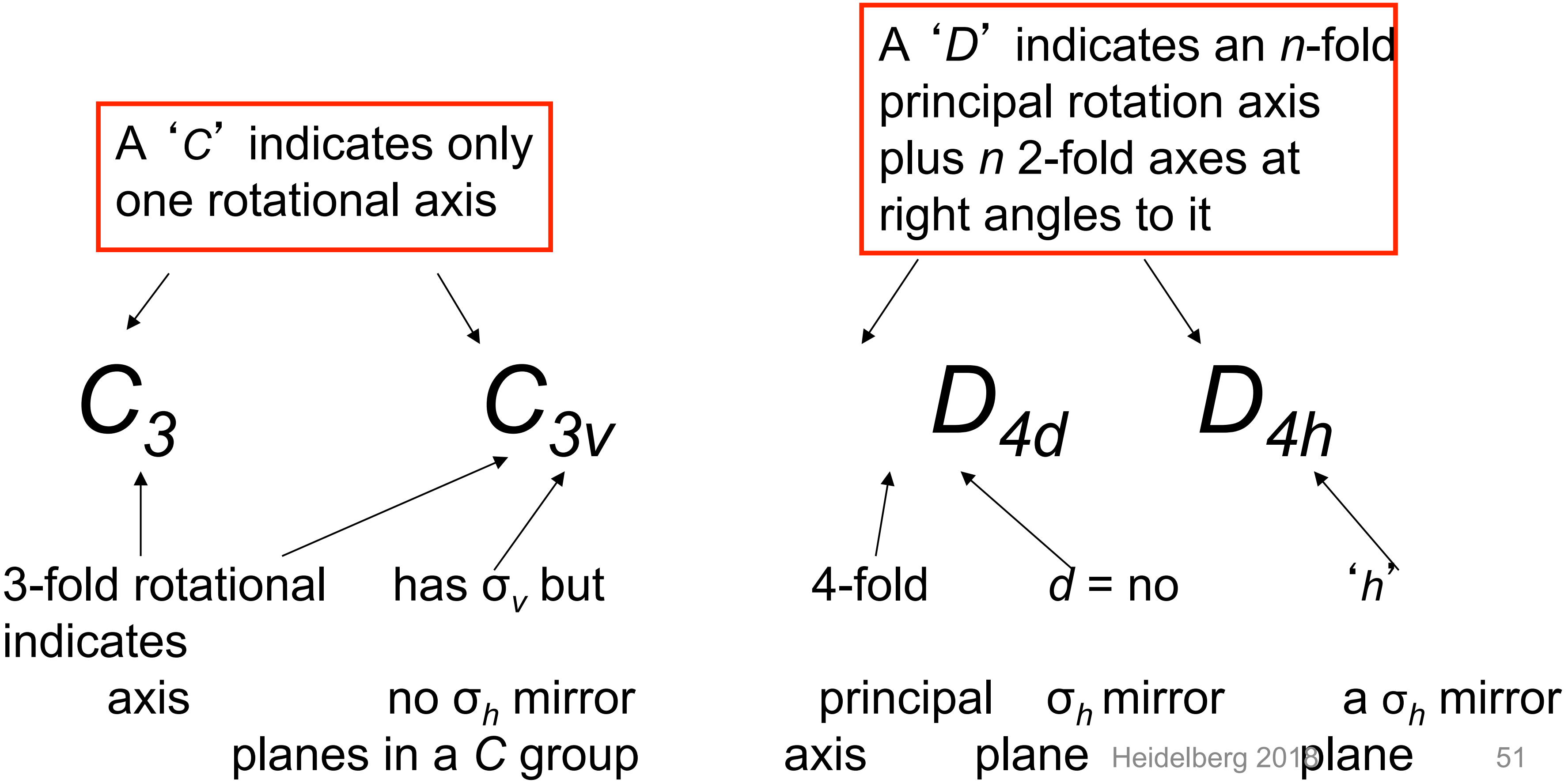
- It can be difficult and sometime false to make a single electron model for t-->he multi-electron ion
- Other {*d*} basis than {d_{xy},d_{xz},d_{yz},d_{z2},d_{x2-y2}} can be chosen for complex symmetries (ex: C_{3v}, D_{5d})
- Crystal field is an empirical model (parameter dependent) but it can be linked to more *ab-initio* methods (tight-binding, DFT, CASSCF,…)
  (Lecture: Maurits Haverkort)
- Crystal field will make angular dependences in transitions (Lecture : Amélie Juhin)
- Crystal field affect the magnetic properties of 4f rare earth ions

Thanks for your attention
and enjoy you next tutorial on crystal field !!!!

Appendix

Naming point groups:

The name of the point group has information about the symmetry elements present. The letter is the rotational group and the subscript number after the letter indicates the order of the principal rotational axis (e.g. 3-fold or 4 fold etc.):



A ‘*C*’ indicates only one rotational axis

A ‘*D*’ indicates an *n*-fold principal rotation axis plus *n* 2-fold axes at right angles to it

C_3 C_{3v} D_{4d} D_{4h}

3-fold rotational
indicates
axis

has σ_v but
no σ_h mirror
planes in a *C* group

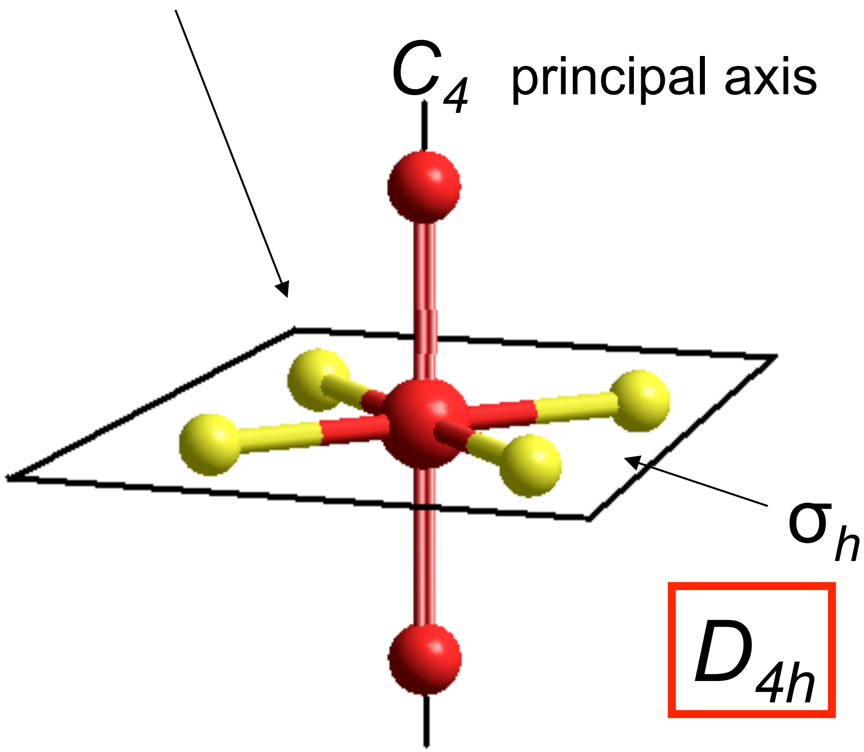
4-fold
principal
axis

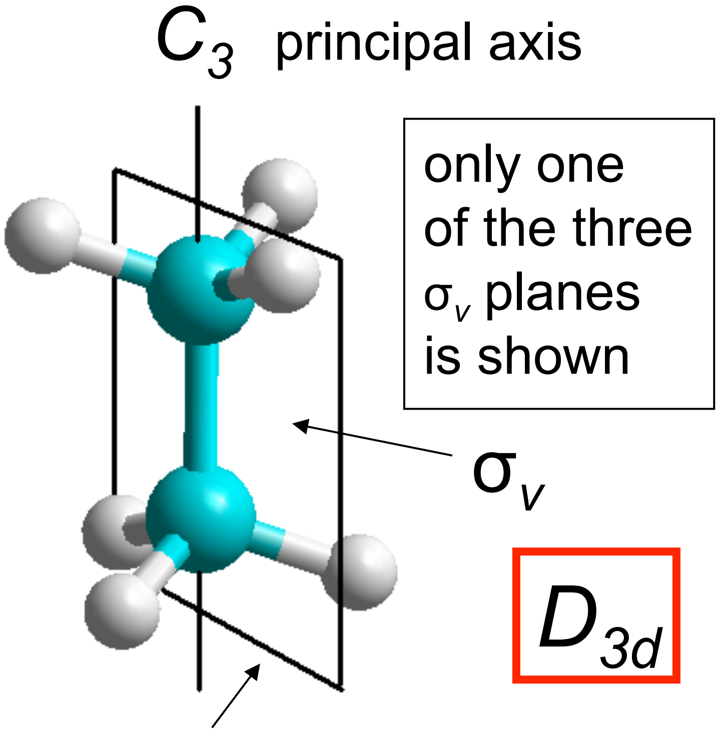
d = no
σ_h mirror
plane

‘*h*’
a σ_h mirror
plane

Naming point groups (contd.):

A subscript '*h*' means that there is a σ_h mirror plane at right angles to the *n*-fold principal axis:

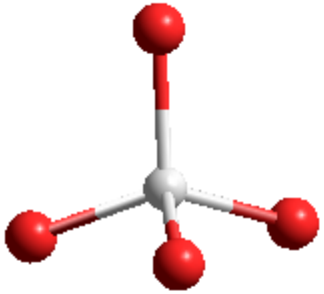




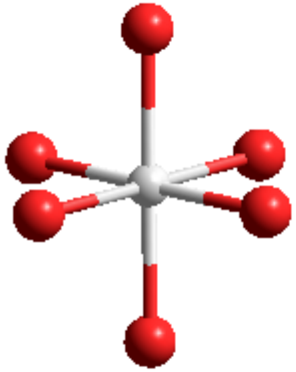
A subscript '*d*' (or *v* for *C* groups) means there is no σ_h mirror plane, but only *n* σ_v mirror planes containing the principal C_n axis.

Naming platonic solids:

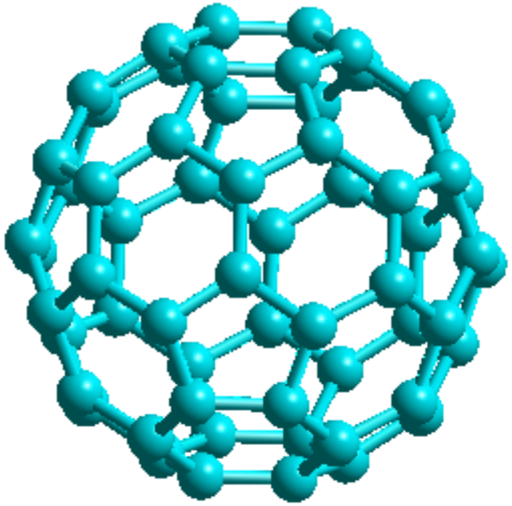
Platonic solids:
T = tetrahedral = 4 three-fold axes
O = octahedral = 3 four-fold axes
I = icosahedral = 6 five-fold axes



T_d



O_h



C_{60}
'bucky-ball'
or 'Fullerene'

I_h