

Crystal field in multielectron ions

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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.

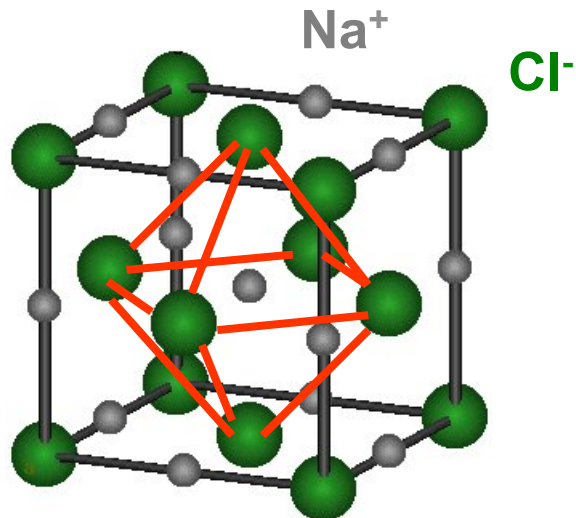
Ions are considered to be undeformable charged spheres and the interaction between them simply results from the electric potential generated by these charges.

(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:

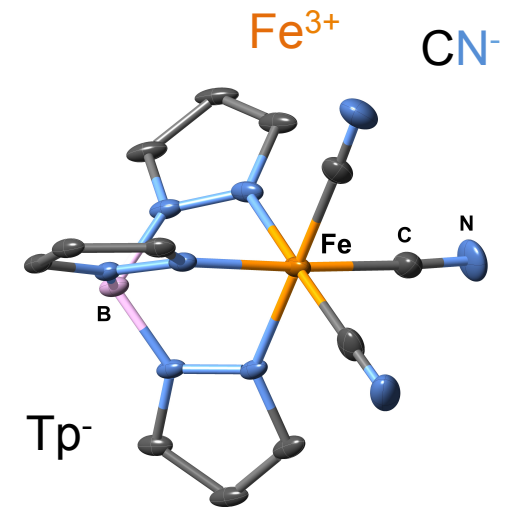
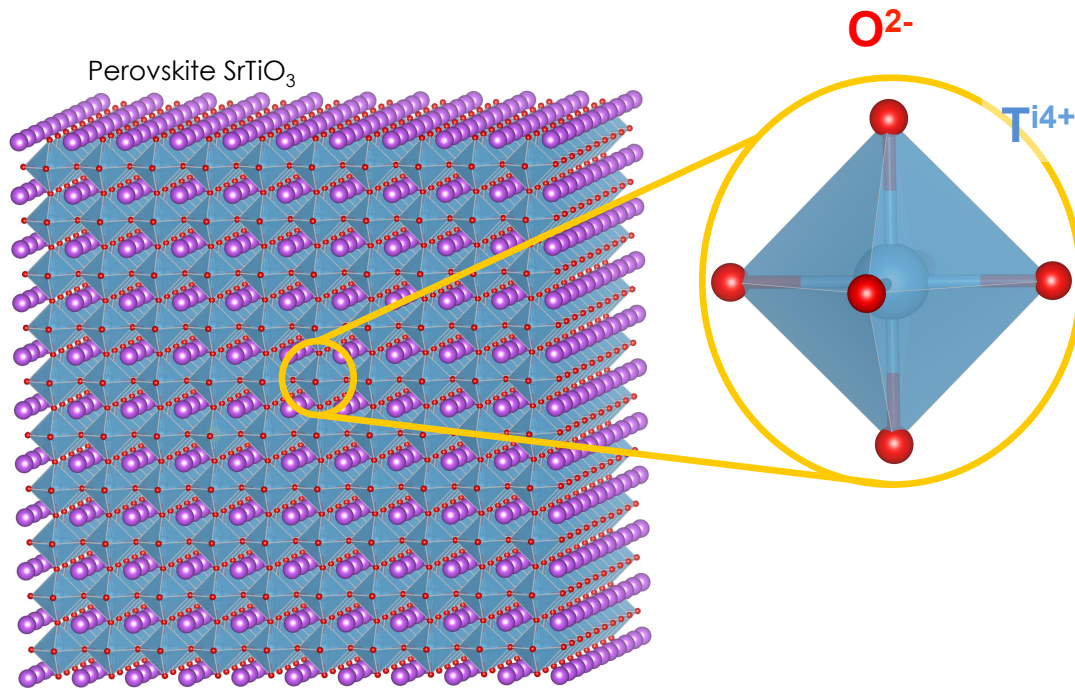
$$V_i = \frac{e}{r}$$

(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
 $\text{Na}^+ \approx \text{metal ion} - \text{Cl}^- \approx \text{ligand}$



Tp =tris-pyrazolyl borate

Symmetries

Symmetry is responsible for many physical and spectroscopic properties of compounds

Group theory is a powerful 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.



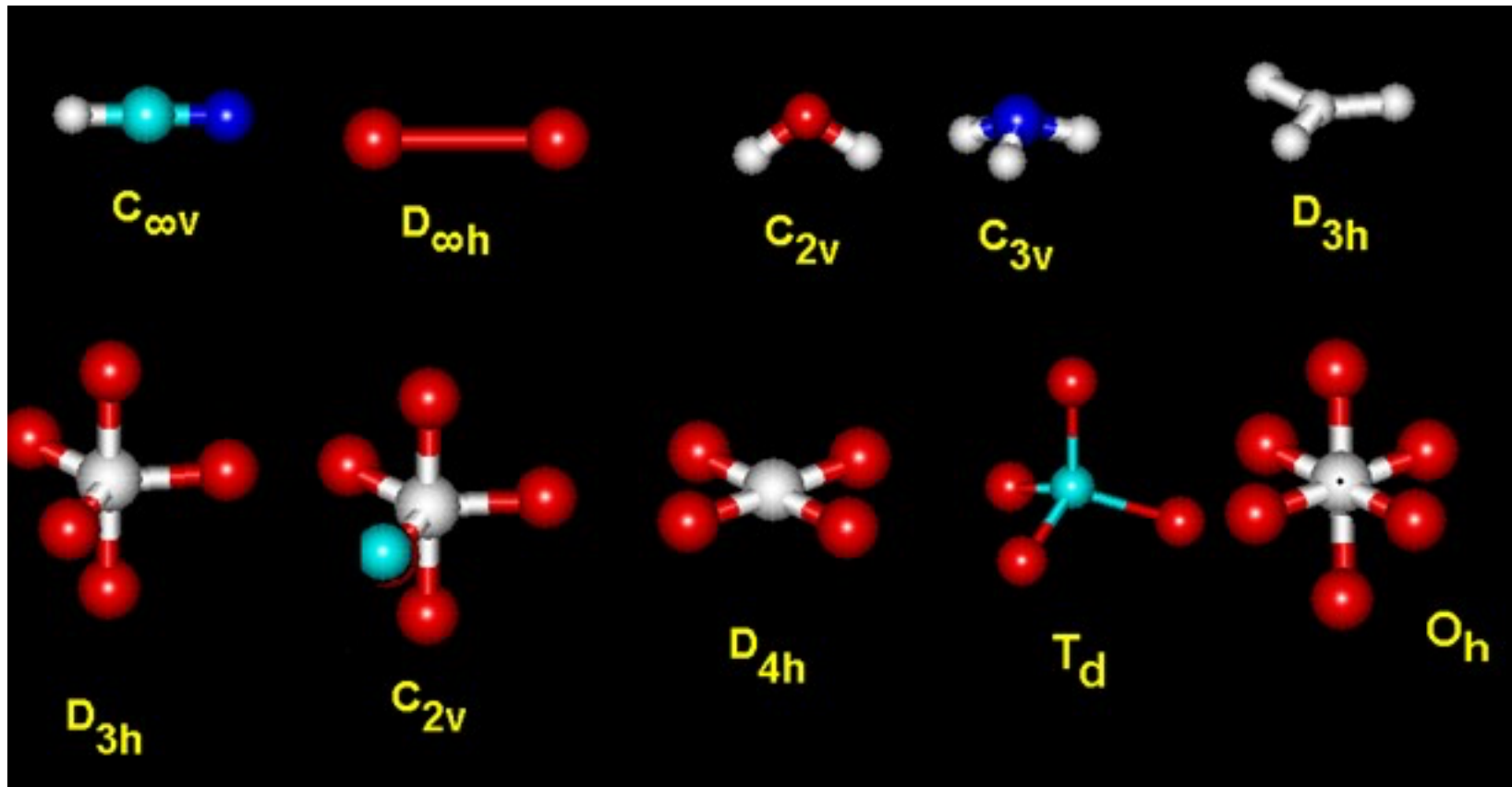
Symmetry operations : some notations to know

- **E**, the identity
- **C_n**, a rotation by an angle $2\pi/n$;
- **σ** reflection in a plane, classified as
 - **σ_h**, reflection through a plane perpendicular to the axis of highest rotational 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 $2\pi/n$
- **I = S₂**, the inversion.



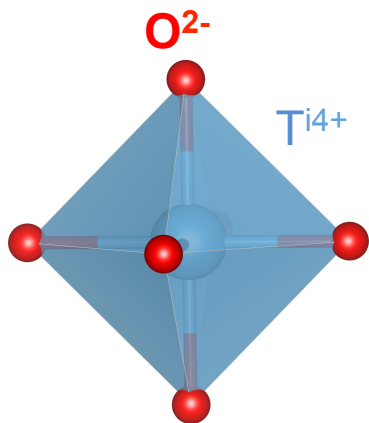
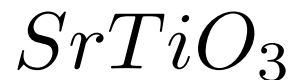
Quanyt mathematica : [Quanyt/guide/PointGroupSymmetry](#)

Symmetries : some point groups

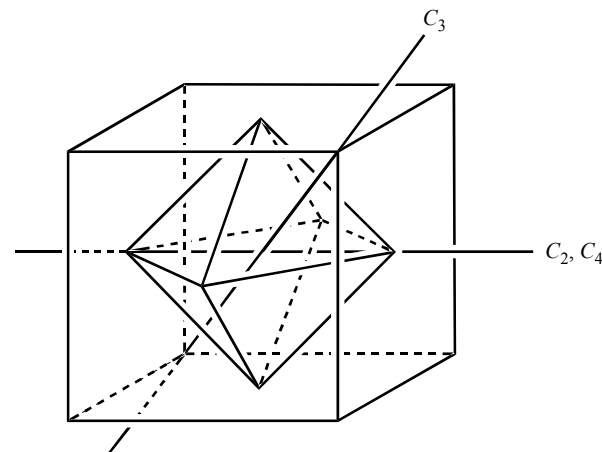


Each group has a table of representations

Symmetries : O_h



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	3σ _h	6σ _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

All you need is in the web page [Quany.org](http://quany.org)
http://quany.org/physics_chemistry/point_groups

The screenshot shows a Firefox browser window with the URL quany.org/physics_chemistry/point_groups. The page content includes:

- Navigation sidebar:**
 - Quanty
 - Documentation
 - Physics and Chemistry
 - Register
 - Download area
 - Copyright
 - Authors
 - How to cite
 - User publications
 - Questions and answers
 - Forum
 - Workshops
 - Calendar
 - Heidelberg
 - Alba
 - Script versions
 - Quanty.nb
 - Quanty.m
 - Quanty.py
 - External programs
 - CTM4
 - Crispy
- Main content area:**
 - Article [Talk](#)
 - Read [Show pagesource](#) [History](#)
 - ## Point groups
 - Table of Contents:**
 - Point groups
 - Different orientations
 - Symmetry operations
 - Irreducible representations
 - Acknowledgements
 - Table of several point groups
 - Table of contents
 - | Nonaxial groups | C₁ - 1 | C_s - m | C_i - $\bar{1}$ | | | | |
|------------------------------|---|---|---|--|--|--|--|
| C_n groups | C₂ - 2 | C₃ - 3 | C₄ - 4 | C₅ - 5 | C₆ - 6 | C₇ - 7 | C₈ - 8 |
| D_n groups | D₂ - 222 | D₃ - 32 | D₄ - 422 | D₅ - 52 | D₆ - 622 | D₇ - 722 | D₈ - 822 |
| C_{nv} groups | C_{2v} - mm2 | C_{3v} - 3m | C_{4v} - 4mm | C_{5v} - 5m | C_{6v} - 6mm | C_{7v} - 7m | C_{8v} - 8mm |
| C_{nh} groups | C_{2h} - 2/m | C_{3h} - $\bar{6}$ | C_{4h} - 4/m | C_{5h} - $\bar{10}$ | C_{6h} - 6/m | | |
| D_{nh} groups | D_{2h} - mmm | D_{3h} - $\bar{6}m2$ | D_{4h} - 4/mmm | D_{5h} - $\bar{10}m2$ | D_{6h} - 6/mmm | D_{7h} - $\bar{14}m2$ | D_{8h} - 8/mmm |
| D_{nd} groups | D_{2d} - $\bar{4}2m$ | D_{3d} - $\bar{3}m$ | D_{4d} - $\bar{8}2m$ | D_{5d} - $\bar{5}m$ | D_{6d} - $\bar{12}2m$ | D_{7d} - $\bar{7}m$ | D_{8d} - $\bar{16}2m$ |
| S_n groups | S₂ - $\bar{2}$ | S₄ - $\bar{4}$ | S₆ - $\bar{6}$ | S₈ - $\bar{8}$ | S₁₀ - $\bar{10}$ | S₁₂ - $\bar{12}$ | |
| Cubic groups | T - 23 | T_h - $m\bar{3}$ | T_d - $\bar{4}3m$ | O - 432 | O_h - $m\bar{3}m$ | I - 532 | I_h - $\bar{5}3m$ |
| Linear groups | C_{∞v} | D_{∞h} | | | | | |
- The following set of pages list properties of the different point groups and their irreducible representations. The table above links to the main page of each of the different point group. For each group we list the character and product table. Often one needs to answer the question how a potential in a given point group looks like and what the eigen-states of that potential are. The eigen states can be grouped according to the irreducible representations of the group and for each of these representations one can give representing functions. The form of these functions and the potential however do depend on the orientation of the point group. We therefor list for each point group different orientations.
- ### Different orientations
- As we are interested in explicit representations we do need to specify the orientation of the symmetry operators. This results in several tables for the same point group but with different choices for the symmetry operations. For example the cubic O_h point group can be represented with the C_4 axes in the x , y and z direction, or with a C_3 axis in the z direction. We list several orientations of the different point-groups available.
- ### Symmetry operations

Crystal field hamiltonian and symmetry

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

Article [Talk](#) [Read](#) [Show pagesource](#) [History](#)

Orientation XYZ

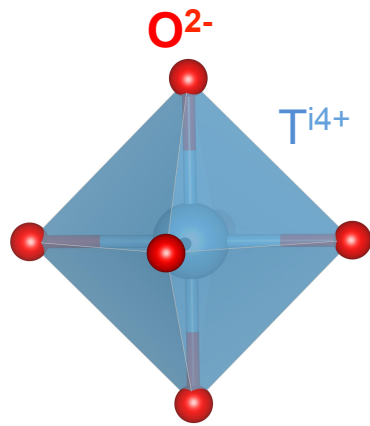
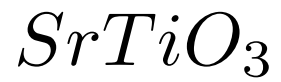
[Table of Contents](#)

Symmetry Operations

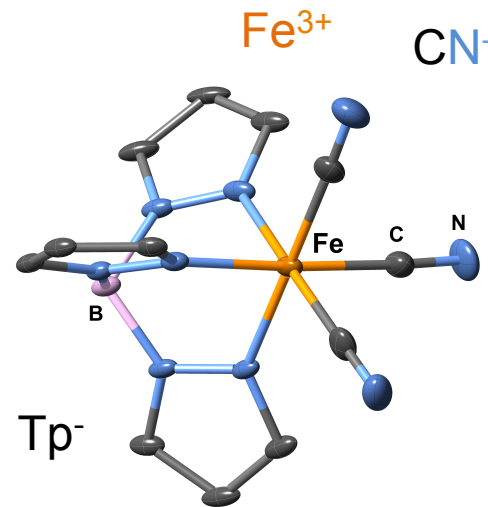
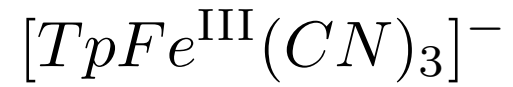
In the Oh Point Group, with orientation XYZ there are the following symmetry operations

Operator	Orientation
E	{0, 0, 0} ,
C_3	{1, 1, 1} , {1, 1, -1} , {1, -1, 1} , {-1, 1, 1} , {-1, -1, 1} , {-1, 1, -1} , {1, -1, -1} , {-1, -1, -1} ,
C_2	{1, 1, 0} , {1, -1, 0} , {1, 0, -1} , {1, 0, 1} , {0, 1, 1} , {0, 1, -1} ,
C_4	{0, 0, 1} , {0, 1, 0} , {1, 0, 0} , {0, 0, -1} , {0, -1, 0} , {-1, 0, 0} ,
C_2	{0, 0, 1} , {0, 1, 0} , {1, 0, 0} ,
i	{0, 0, 0} ,
S_4	{0, 0, 1} , {0, 1, 0} , {1, 0, 0} , {0, 0, -1} , {0, -1, 0} , {-1, 0, 0} ,
S_6	{1, 1, 1} , {1, 1, -1} , {1, -1, 1} , {-1, 1, 1} , {-1, -1, 1} , {-1, 1, -1} , {1, -1, -1} , {-1, -1, -1} ,
σ_h	{1, 0, 0} , {0, 1, 0} , {0, 0, 1} ,

Symmetries



Octahedral
Group : O_h



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 :

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

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

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

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

The crystal fields Hamiltonian thus writes

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

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

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

Crystal field hamiltonian and symmetry

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

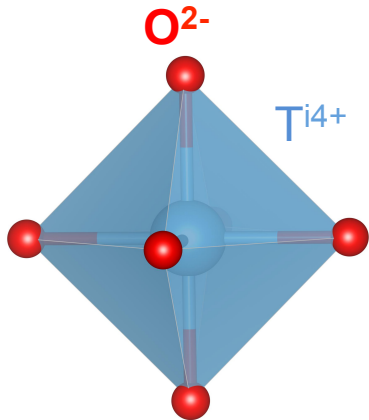
Not all values of A_{km} are allowed : many are zero due to the symmetry around the ion

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

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

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

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

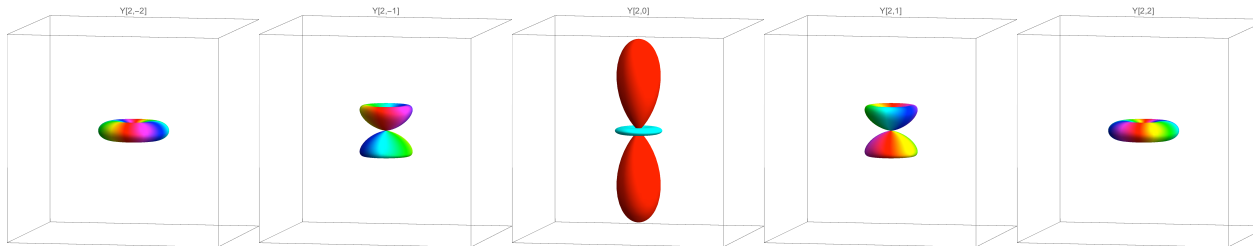
$$\phi_i(\mathbf{r}, \sigma) = \underbrace{\frac{1}{r} P_{n_i l_i}(r)}_{\text{Radial part}} \underbrace{Y_{\ell, m}(\theta, \phi)}_{\substack{\text{Angular part} \\ \text{Spherical harmonics}}} \underbrace{\chi_{m_{s_i}}(\sigma)}_{\text{Spin part}}$$
$$R_{n_i l_i}(r) = \frac{1}{r} P_{n_i l_i}(r)$$

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 : $n=3, \ell=2$ $2\ell+1=5$ basis functions ($-2 \leq \ell \leq 2$)

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)

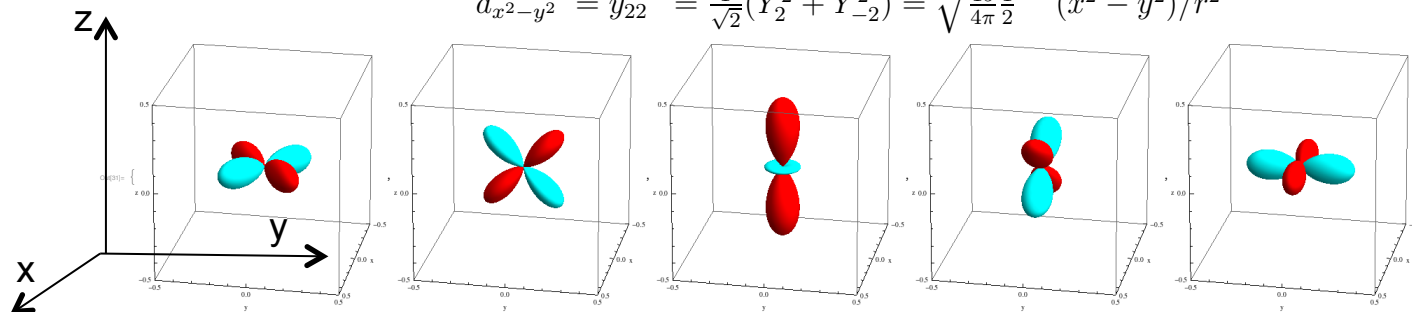
$$d_{xy} = y_{2-2} = \frac{i}{\sqrt{2}}(Y_2^2 - Y_{-2}^2) = \sqrt{\frac{15}{4\pi}} \quad xy/r^2$$

$$d_{yz} = y_{2-1} = \frac{i}{\sqrt{2}}(Y_1^2 + Y_{-1}^2) = \sqrt{\frac{15}{4\pi}} \quad yz/r^2$$

$$d_{3z^2-r^2} = y_{20} = Y_2^0 = \sqrt{\frac{15}{4\pi}} \frac{1}{2\sqrt{3}} (3z^2 - r^2)/r^2$$

$$d_{xz} = y_{21} = \frac{1}{\sqrt{2}}(Y_1^2 - Y_{-1}^2) = \sqrt{\frac{15}{4\pi}} \quad xz/r^2$$

$$d_{x^2-y^2} = y_{22} = \frac{1}{\sqrt{2}}(Y_2^2 + Y_{-2}^2) = \sqrt{\frac{15}{4\pi}} \frac{1}{2} (x^2 - y^2)/r^2$$



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

$$\langle Y_{\ell_1, m_1} | C_{k, m} | Y_{\ell_2, m_2} \rangle = (-1)^{m_1} (2\ell_1 + 1) \begin{pmatrix} \ell_1 & k & \ell_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_1 & k & \ell_1 \\ -m_1 & m & m_2 \end{pmatrix} = (-1)^{m_1} \sqrt{10/7} \begin{pmatrix} 2 & k & 2 \\ -m_1 & m & m_2 \end{pmatrix}$$

$$\text{CF matrix in } \{Y_{2, m}\} \text{ basis} = \begin{matrix} | \ell m \rangle \equiv & | 2 - 2 \rangle & | 2 - 1 \rangle & | 2 0 \rangle & | 2 1 \rangle & | 2 2 \rangle \\ \begin{pmatrix} A_{0,0} + \frac{1}{21}A_{4,0} & 0 & 0 & 0 & \frac{5}{21}A_{4,0} \\ 0 & A_{0,0} - \frac{4}{21}A_{4,0} & 0 & 0 & 0 \\ 0 & 0 & A_{0,0} + \frac{2}{7}A_{4,0} & 0 & 0 \\ 0 & 0 & 0 & A_{0,0} - \frac{4}{21}A_{4,0} & 0 \\ \frac{5}{21}A_{4,0} & 0 & 0 & 0 & A_{0,0} + \frac{1}{21}A_{4,0} \end{pmatrix} \end{matrix}$$

2) Diagonalization

$$\begin{matrix} d_{x^2-y^2} & d_{z^2} & d_{yz} & d_{xz} & d_{xy} \\ \begin{pmatrix} A_{0,0} + \frac{2}{7}A_{4,0} & 0 & 0 & 0 & 0 \\ 0 & A_{0,0} + \frac{2}{7}A_{4,0} & 0 & 0 & 0 \\ 0 & 0 & A_{0,0} - \frac{4}{21}A_{4,0} & 0 & 0 \\ 0 & 0 & 0 & A_{0,0} - \frac{4}{21}A_{4,0} & 0 \\ 0 & 0 & 0 & 0 & A_{0,0} - \frac{4}{21}A_{4,0} \end{pmatrix} \end{matrix}$$

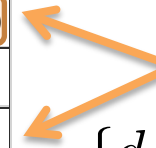
→ The O_h crystal field split the d orbitals in two groups of orbitals
 $\{d_{x^2-y^2}, d_{z^2}\}$ and $\{d_{yz}, d_{xz}, d_{xy}\}$

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		



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

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

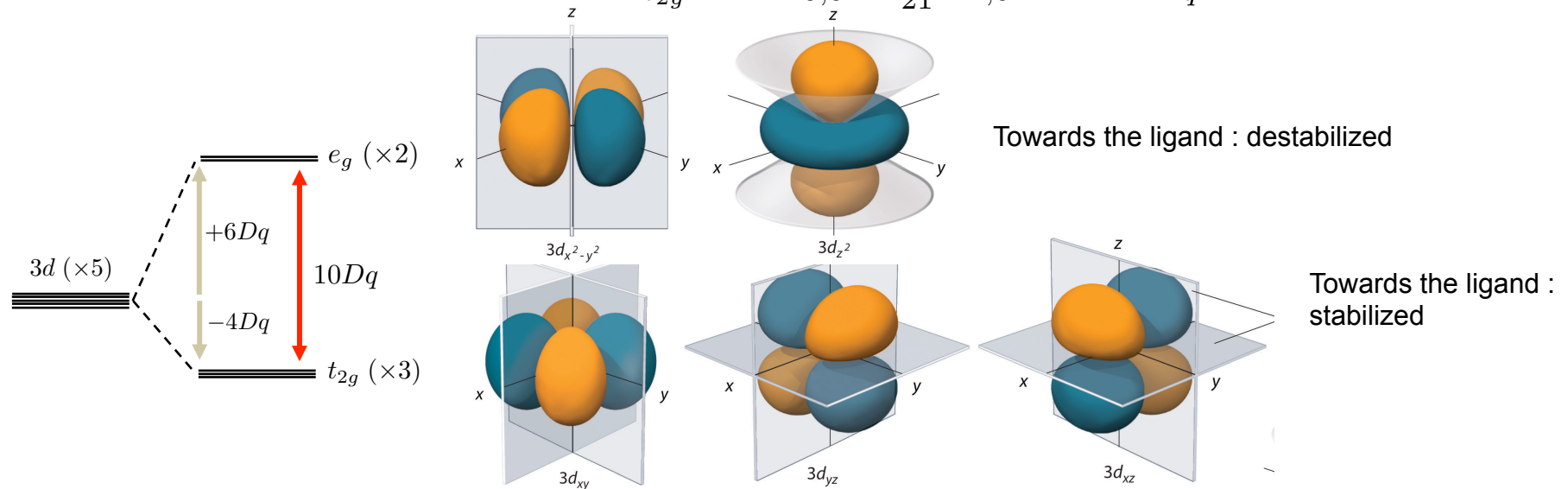
- From the O_h group properties, one could have guessed the splitting of the d orbitals
- d orbitals are called e_g and t_{2g} *

(*)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 $E_{e_g} = A_{0,0} + \frac{2}{7}A_{4,0} = +6D_q$

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

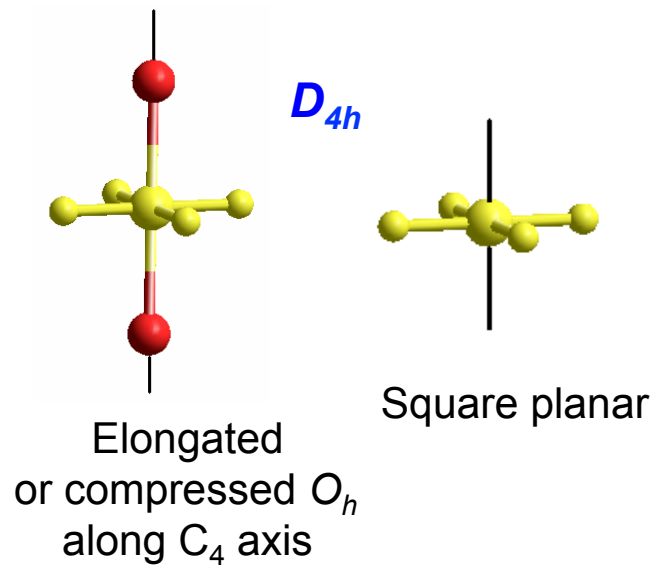


$10Dq \equiv$ adjustable parameter

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



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 D_{4h} 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

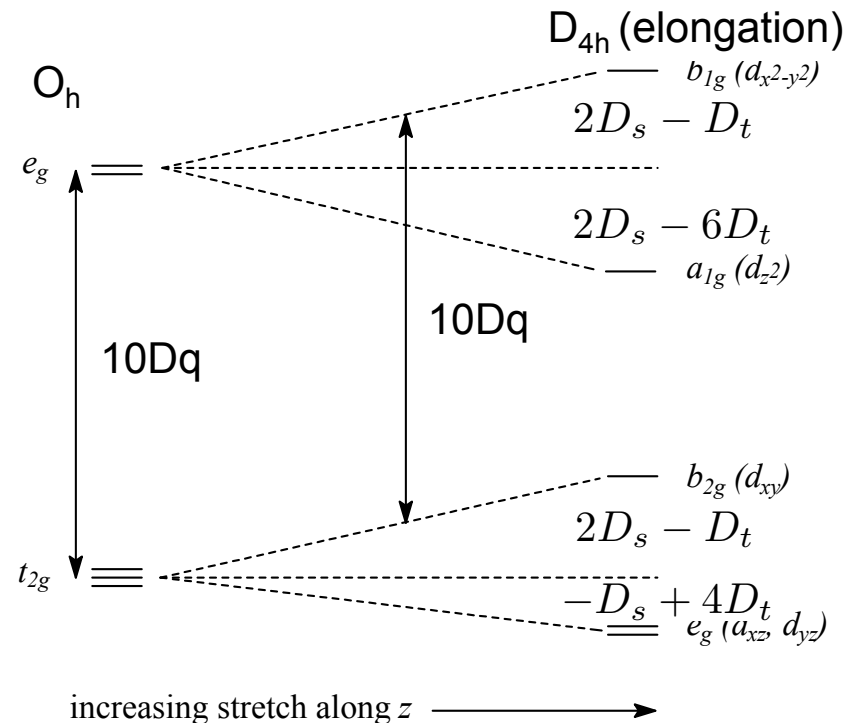
$$H_{CF}^{D_{4h}} = A_{0,0}C_{0,0} + A_{2,0}C_{2,0} + A_{4,0}C_{4,0} + A_{4,4}(C_{4,-4} + C_{4,4})$$

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

$E_{a_{1g}} = 6D_q - 2D_s - 6D_t \quad (d_{z^2})$	$A_{0,0} = 1/5(E_{a_1} + E_{b_1} + E_{b_2} + 2E_e)$
$E_{b_{1g}} = 6D_q + 2D_s - D_t \quad (d_{x^2-y^2})$	$A_{2,0} = E_{a_1} - E_{b_1} - E_{b_2} + E_e$
$E_{b_{2g}} = -4D_q + 2D_s - D_t \quad (d_{xy})$	$A_{4,0} = 3/10(6E_{a_1} + E_{b_1} + E_{b_2} - 8E_e)$
$E_{e_g} = -4D_q - D_s + 4D_t \quad (d_{xz}, d_{yz})$	$A_{4,4} = A_{4,-4} = 3/20(\sqrt{70}E_{b_1} - \sqrt{70}E_{b_2})$

with

The relation with D_q, D_s, D_t can be found in the book of König&Kremer « Ligand field. Energy diagram »



Crystal field hamiltonian in QUANTY

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

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:

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

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

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

The parameter is $10D_q$ and the hamiltonian writes $H_{CF} = 10D_q * OpptenDq$

→ In this *Oh* case, the hamiltonian is similar but it can be different for lower symmetries ($E_i(d)$ vs $10D_q, D_s, D_t, \dots$). 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 Fe²⁺

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

$2l+1=5$	$ \ell, m_\ell\rangle$	angular functions	}	10 functions
$2s+1=5$	$ sm_s\rangle$	spin functions		

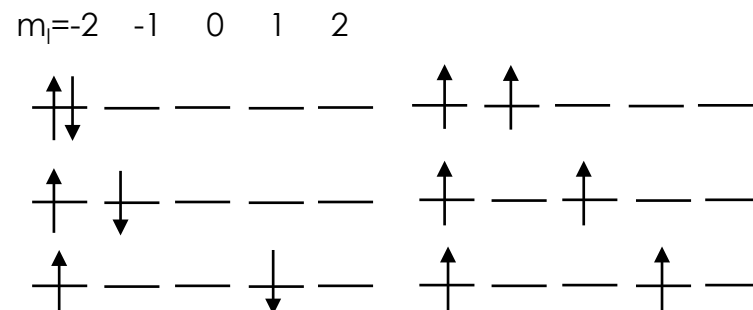
$$\text{Nb states} = C_{10}^n = \frac{10!}{n!(10-n)!}$$

Degeneracy = **multiplets**

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

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

Some possibilites:




Multi-electrons ions configuration and symmetry

d² ion in O_h symmetry

	e_g — — — — \uparrow — \downarrow —
	t_{2g} $\uparrow\downarrow$ — — \uparrow — \downarrow — \uparrow — — — \uparrow — — —
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

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

 Free ion (spherical) **Crystal field**

$$H_{\text{cin}} = \sum_{i=1}^N -\frac{\hbar^2}{2m} \nabla_{r_i}^2$$

Total kinetic energy

$$H_{\text{e-n}} = \sum_{i=1}^N -\frac{Ze^2}{4\pi\epsilon_0 r_i}$$

Coulomb attraction nuclei-electrons

$$H_{\text{e-e}} = \sum_{i<j=1}^N \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

Electron-electron Coulomb repulsions

$$H_{\text{s-o}} = \sum_{i=1}^N \xi_i(r_i) \mathbf{l}_i \cdot \mathbf{s}_i$$

Spin-orbit coupling

Hamiltonian of the ion with N electrons

Basis functions $|\Psi\rangle$


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

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

- **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

$$\hat{\ell}_{z,i} |l_i m_{\ell_i}\rangle = m_{\ell_i} |l_i m_{\ell_i}\rangle$$

$$\hat{\ell}_i^2 |l_i m_{\ell_i}\rangle = l_i(l_i + 1) |l_i m_{\ell_i}\rangle$$

$$-l_i \leq m_{\ell_i} \leq l_i$$

- ✓ Same definitions for \hat{S} and \hat{J}
- ✓ $\hat{J} = \hat{L} \oplus \hat{S}$ operator associated with the spin-orbit coupling
 $L - S \leq J \leq |L + S|$

Free ion with N electrons : basis functions

➤ **Fonctions $|\alpha(L,S)JM_J\rangle$**

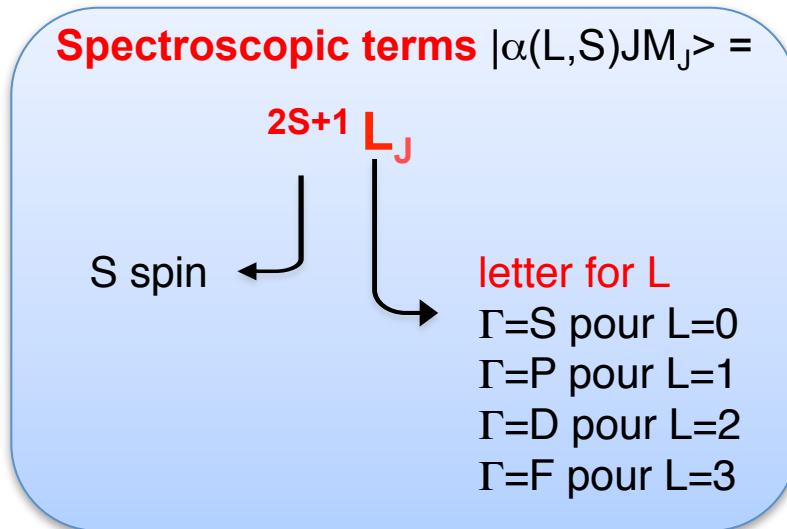
Common eigenfunctions with $\hat{J}^2, \hat{J}_z, \hat{L}^2, \hat{S}^2$

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

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

➤ The energy of $|\alpha(L,S)\rangle$ does not depend on M_L, M_S
 Degeneracy of $|\alpha(L,S)\rangle = (2L+1)(2S+1)$

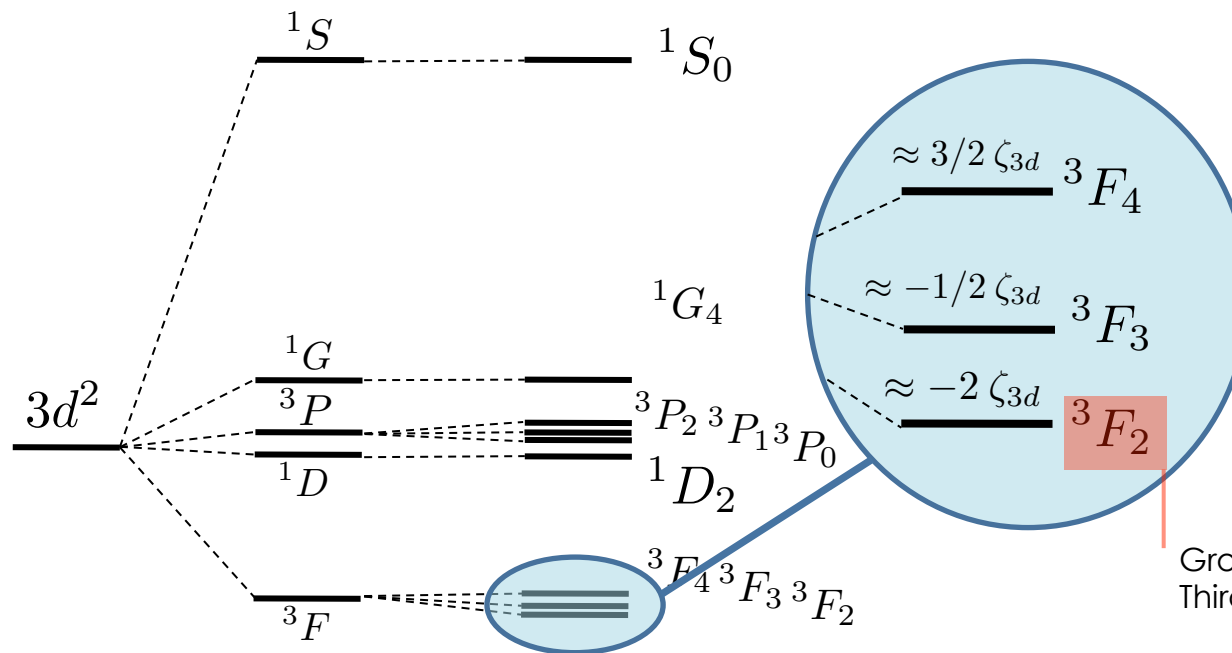
➤ The energy of $|\alpha(L,S)JM_J\rangle$ does not depend on M_J
 Degeneracy of $|\alpha(L,S)JM_J\rangle = 2J+1$



Free ion : spectroscopic terms for $3d^2$ 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

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

Ground state given by Third Hund's rule

Crystal field : basis function

➤ Basis functions

Spherical symmetry:

$$|\alpha(\mathbf{L}, \mathbf{S}) \mathbf{J} M_J\rangle$$

Local symmetry around the ion → point group G:

Basis functions of the representations of group G

$$|\alpha(\mathbf{L}, \mathbf{S}) \mathbf{J} \Gamma \gamma\rangle$$

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
 $|\alpha(L,S) J M_J\rangle$ partners of irrep* J of O_3

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

Hamiltonian expanded on $C_{k,m} \leftrightarrow T^{k,m}$

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

* irrep=irreducible representation

Ion in solid/molecule

G is the subgroup of the sphere
 $|\mathbf{a}(L,S) J \Gamma \gamma\rangle$ partners of the irrep* Γ of G

$$J(SO_3) \rightarrow \sum_i \Gamma_i(G)$$

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

Hamiltonian expanded on $C_{k,m} \leftrightarrow T^{k,m}$

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

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

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

Crystal field and group theory

Matrix elements

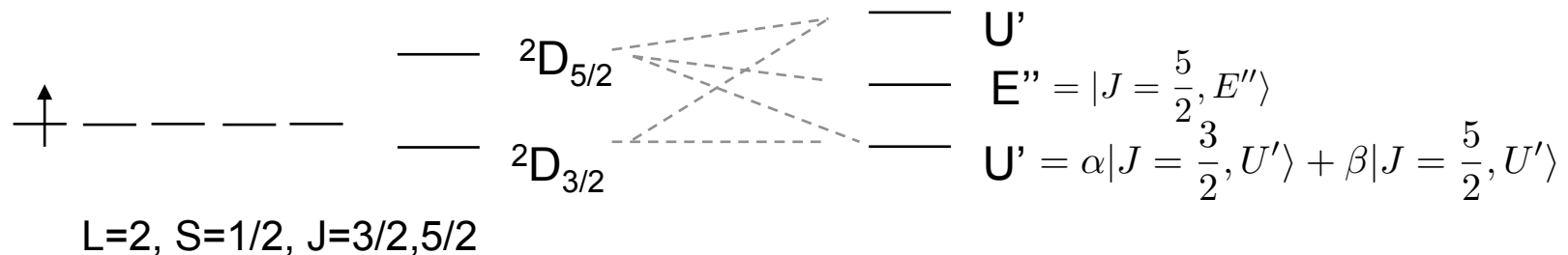
$$H_{CF} \in A_{1(g)}^* \quad (\text{fully symmetric representation of group } \mathbf{G})$$

* g only for centro-symmetric group

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

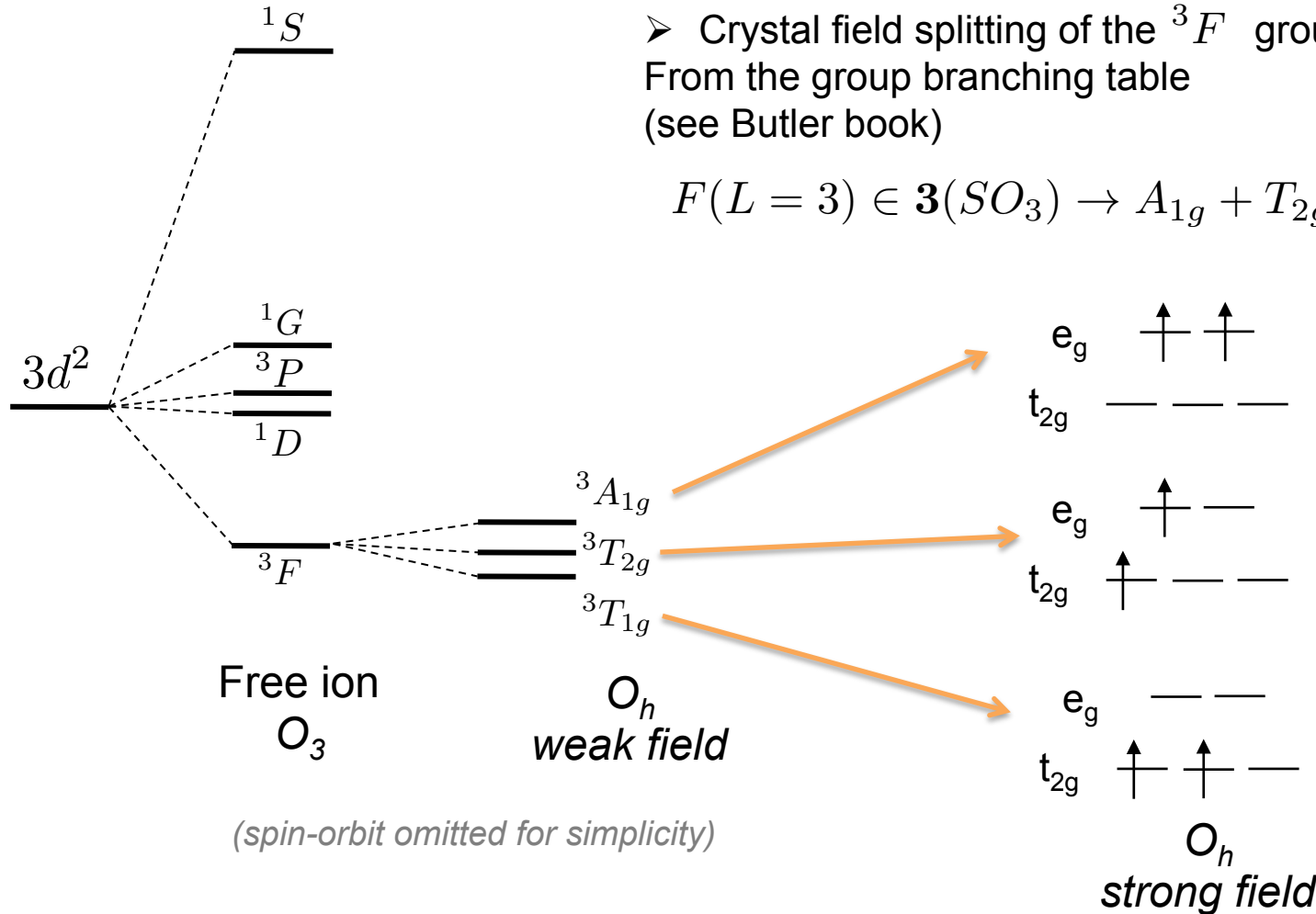
→ Crystal field mixes J states if $\Gamma_i \otimes \Gamma_j \ni A_{1(g)}$

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



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)

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



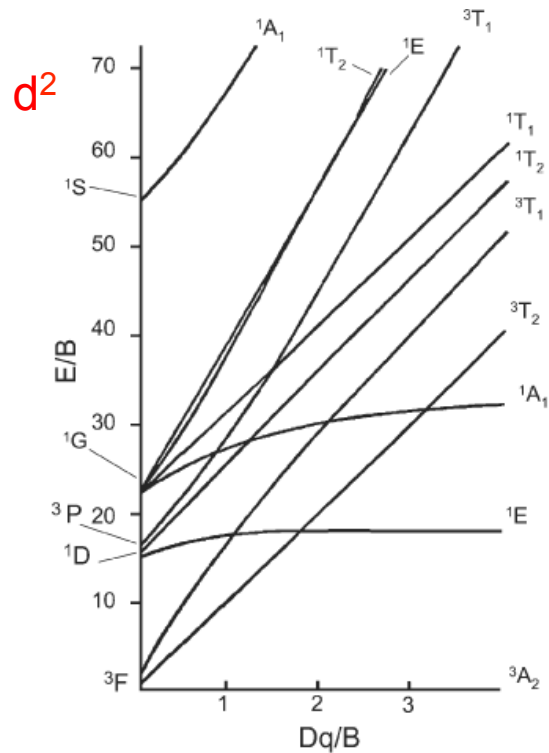
From the multi-electronic state, one can get **the electron density on the orbitals** of the group (it is not necessary integer)

Crystal field : energy diagram

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

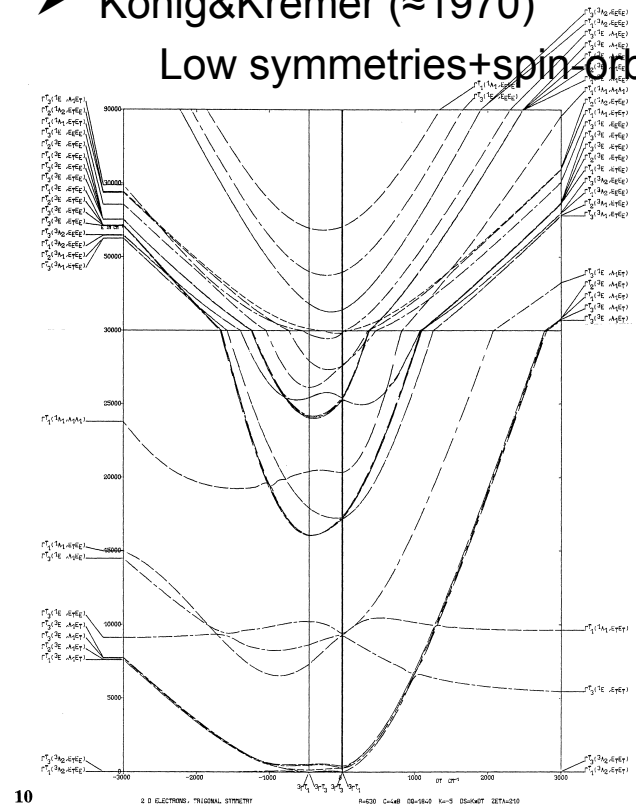
- Tanabe-Sugano diagram (1954)

$O_h(T_d)$, 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 : 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:

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

with $\hat{O} = L_z, S_z, \dots$

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)

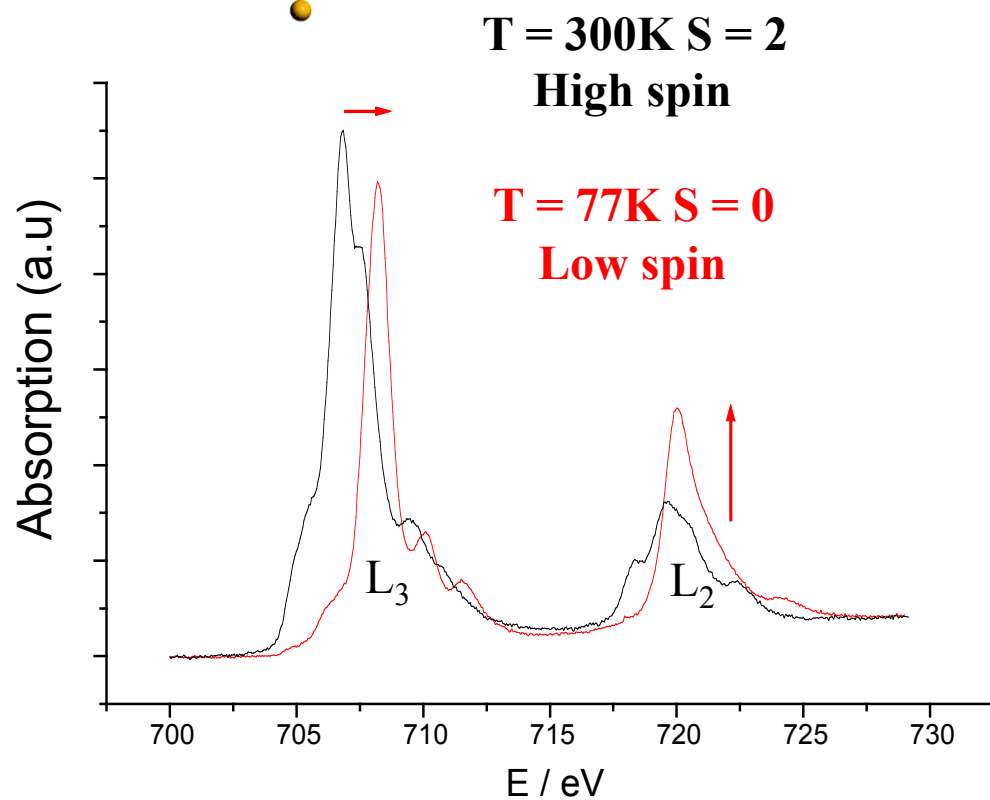
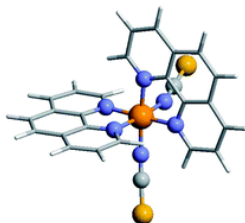
Based on group theory (Butler "Point group symmetry applications")

Difficult to modified and adapt to new spectroscopies since Theo Thole died in 1996

✓ **QUANTY**, Haverkort's code

Flexible for the need of the new spectroscopies/physical properties

Example of crystal field : spin crossover



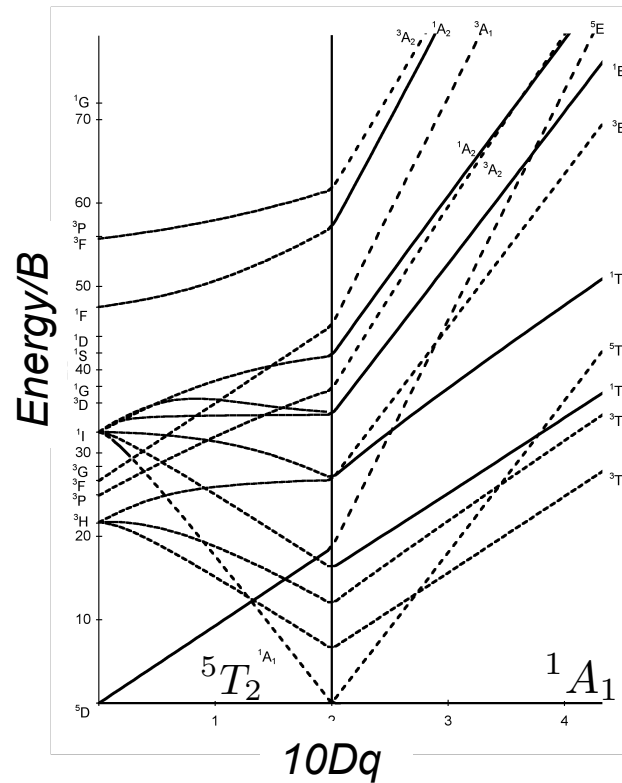
The spin crossover has been intensively studied and observed with many different spectroscopies and magnetic measurements

Ex : XAS at L_{2,3} edges

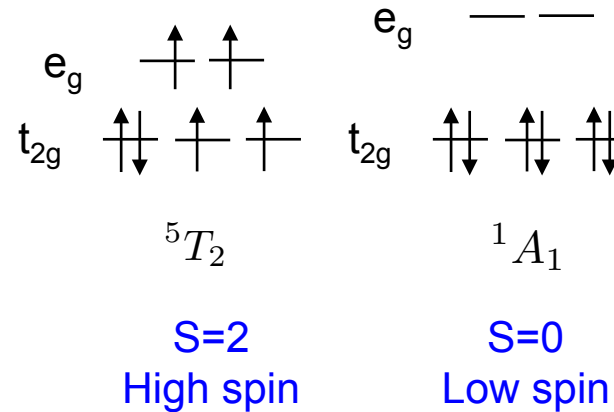
It is a well known crystal field effect named spin crossover

Crystal field effect : spin crossover

Fe²⁺ ion (3d⁶) in O_h symmetry

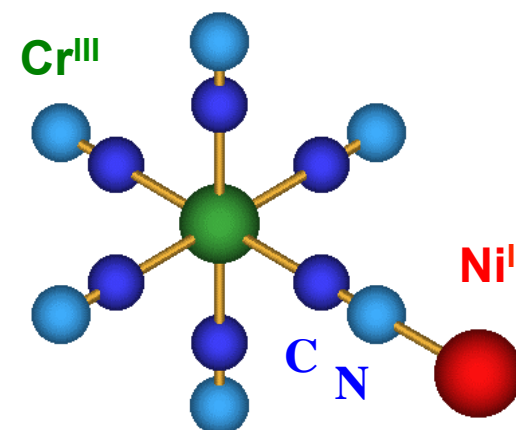
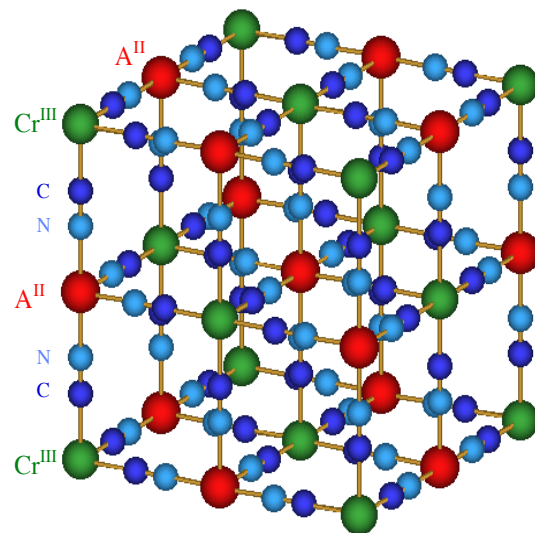


When 10Dq increases, the ground state changes

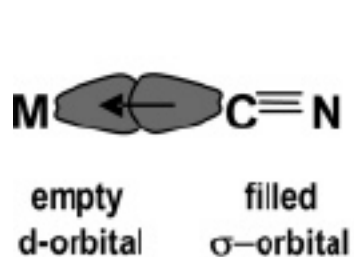


- The magnetic properties goes from paramagnetic to non-magnetic
- Good candidate for many applications like molecular spintronic

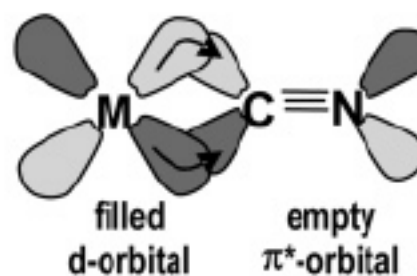
Example : prussian blue analogues



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



(i) σ donation

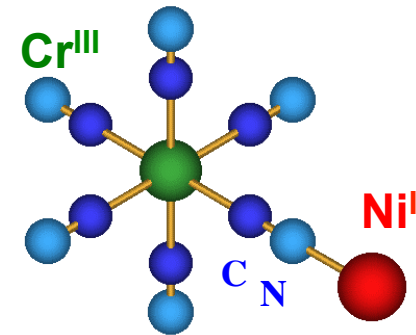
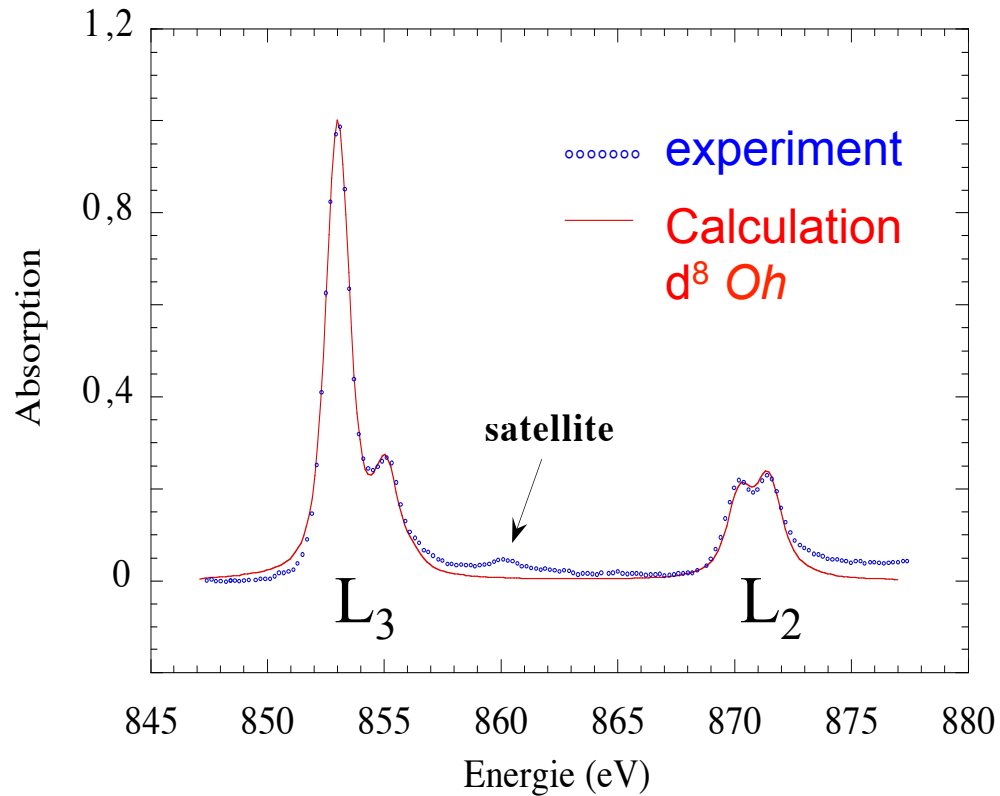


(ii) π back-donation

Weak covalent bond

CN-Ni^{II} in Cs[NiCr(CN)₆]

Ni^{II} L_{2,3} edges (2p to 3d)

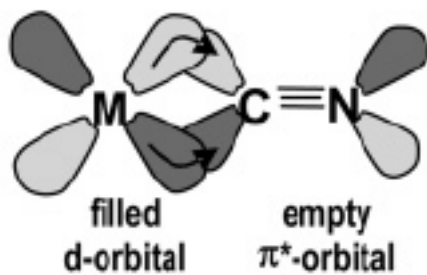
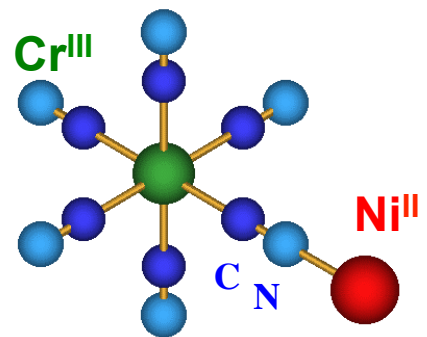


Oh crystal field $10Dq = 1.4 \text{ eV}$
 (= optical spectro.)

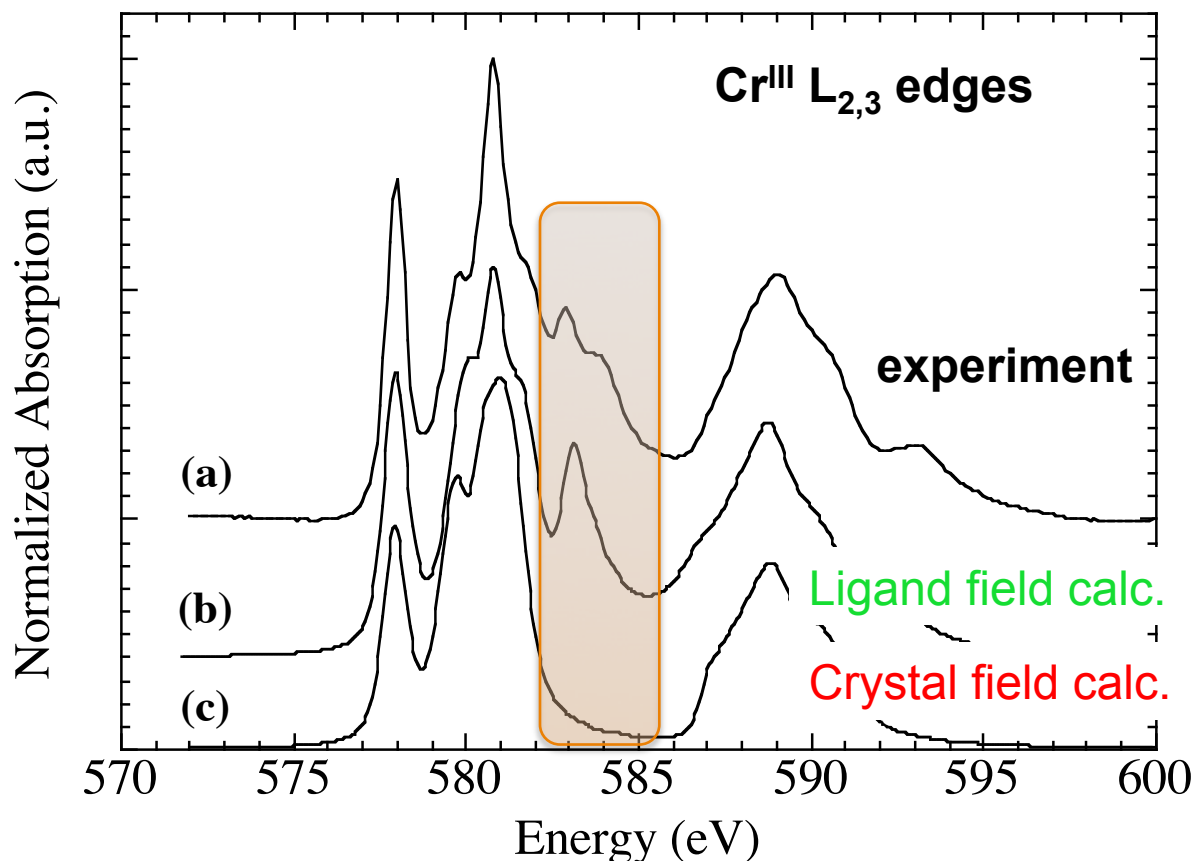
$\kappa = 0.8$ (weak covalent bond)

Weakness of crystal field theory

Strong crystal field



(ii) π back-donation



- ❑ **Crystal field** : Oh, large $10Dq$ ($=3.5\text{eV}$) + strong Slater reduction (50%)
Incomplete model due to the strong metal to ligand charge transfer
- ❑ **Ligand field** : metal to ligand charge transfer
 $d^3d^0 + d^2d^1$

Crystal field and magnetism

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

External magnetic field effect : Zeeman effect

➤ Hamiltonian

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

Free ion (spherical) Crystal field

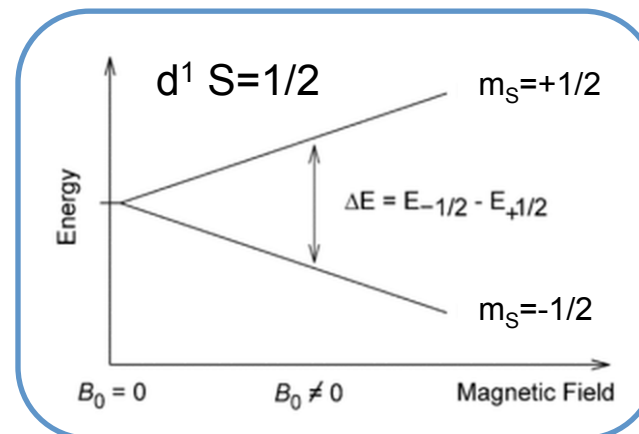
$$\begin{aligned} H_{\text{Zeeman}} &= -\vec{m} \cdot \vec{H} = \mu_B (\hat{L} + g_0 \hat{S}) \cdot \vec{H} \\ &= \mu_B (L_x + 2S_x) H_x + \mu_B (L_y + 2S_y) H_y + \mu_B (L_z + 2S_z) H_z \end{aligned}$$

➤ Matrix element depend on the magnetic moment

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

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

1 electron ($S=1/2$)
spherical



Magnetic moments

➤ Definitions

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

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

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

(in \hbar unit, with $\mu_B > 0$)

➤ Crystal field effect:

$|(L,S)J \Gamma \gamma\rangle$ (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

Magnetization of paramagnetic 3d ion (Zeeman effect)

- Magnetic moment of state Γ_i

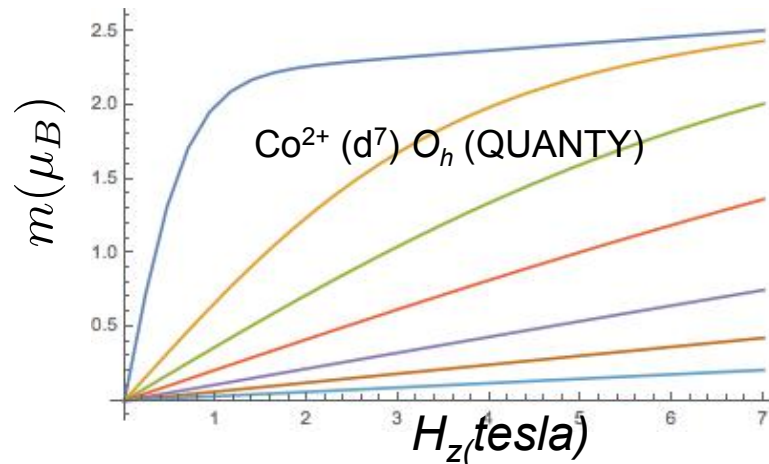
$$m_i = -\langle \Gamma_i | \hat{L}_z + 2\hat{S}_z | \Gamma_i \rangle \mu_B$$

- Magnetic moment at temperature T in the magnetic field H_z

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

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

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



Conclusion (remarks)

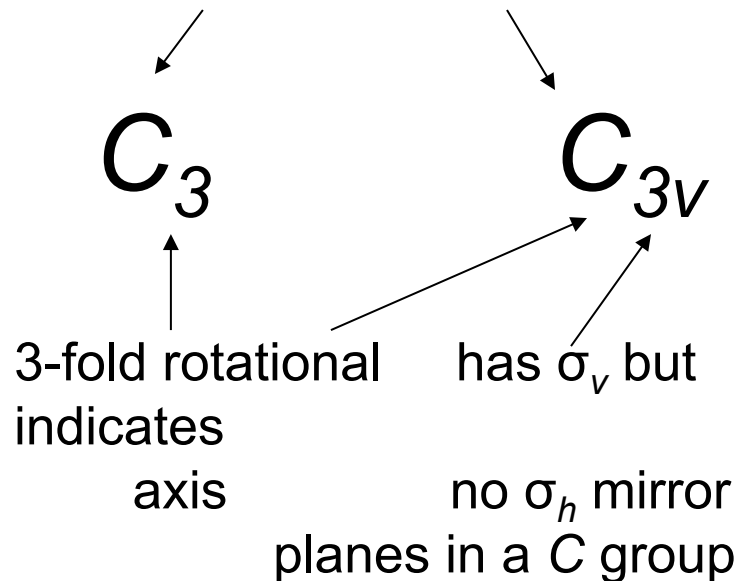
- It can be difficult and sometime false to make a single electron model for the multi-electron ion
- Other $\{d\}$ basis than $\{d_{xy}, d_{xz}, d_{yz}, d_{z^2}, d_{x^2-y^2}\}$ can be chosen for complex symmetries (ex: C_{3v}, D_{5d})
- Crystal field is an empirical model (parameter dependent) but it 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 (not discussed here)

Appendix

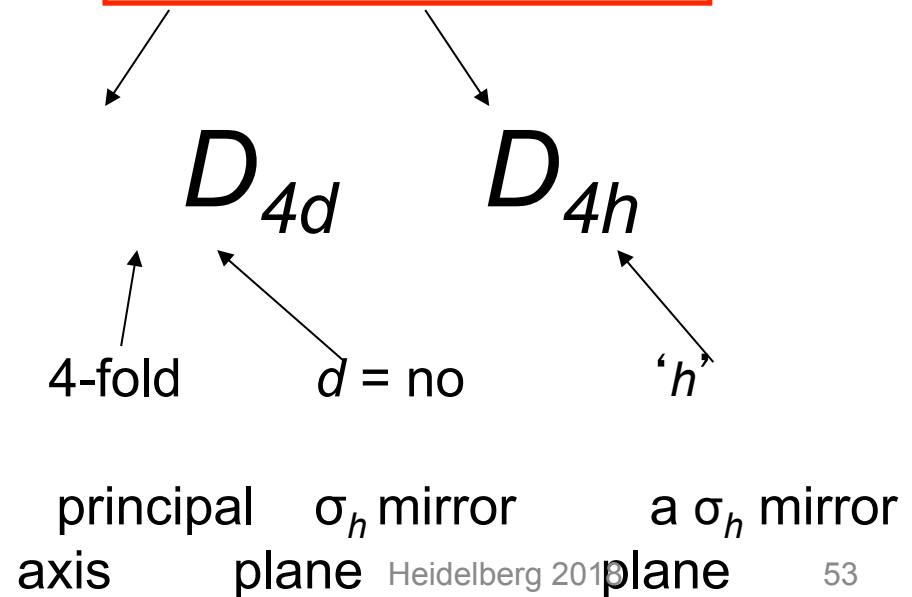
Naming point groups:

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

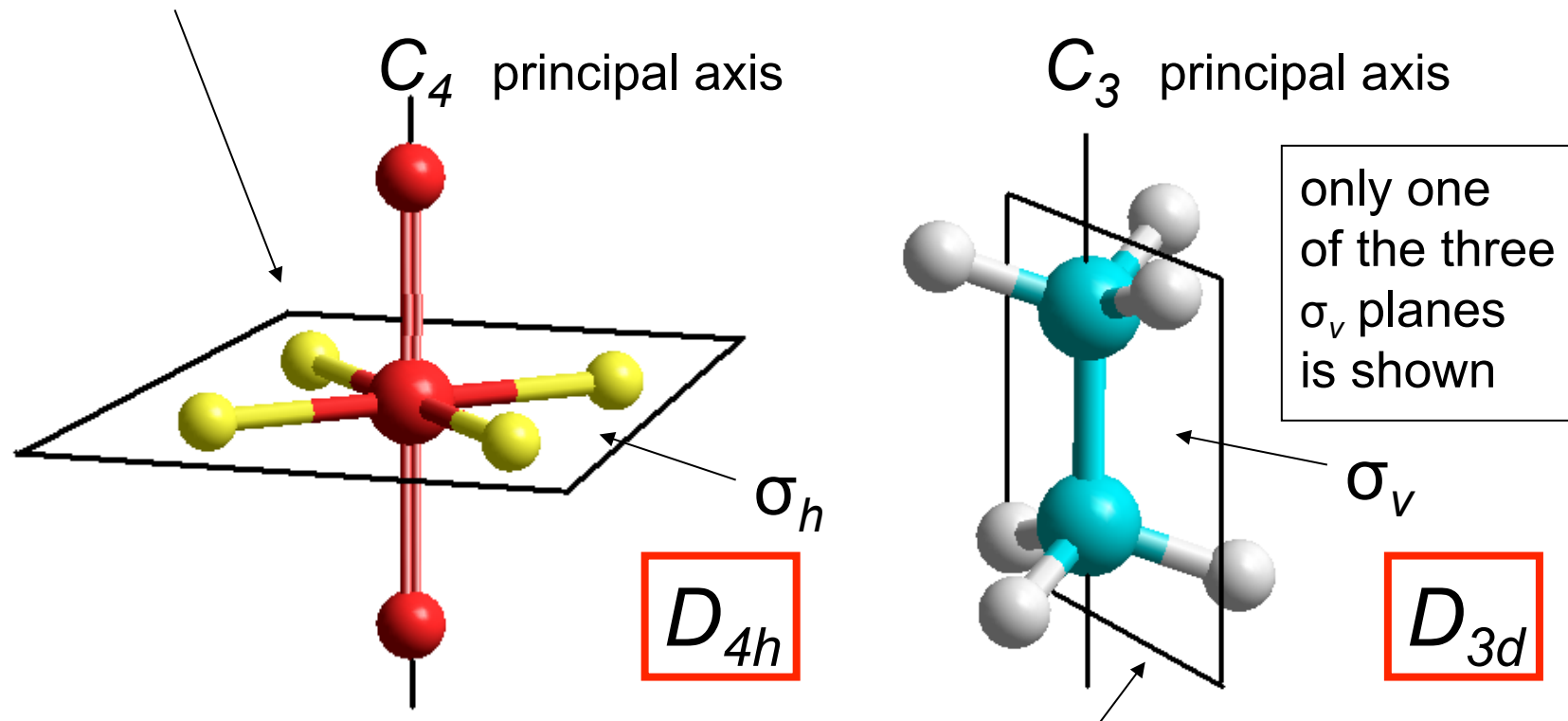


A 'D' indicates an n -fold principal rotation axis plus n 2-fold axes at right angles to it



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.

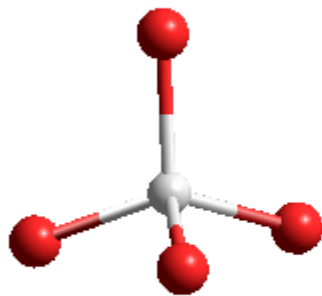
Naming platonic solids:

Platonic solids:

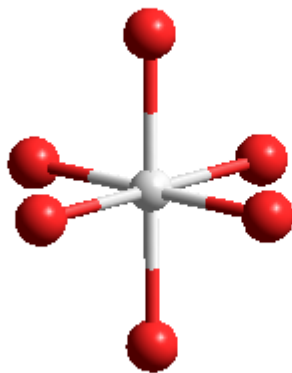
T = tetrahedral = 4 three-fold axes

O = octahedral = 3 four-fold axes

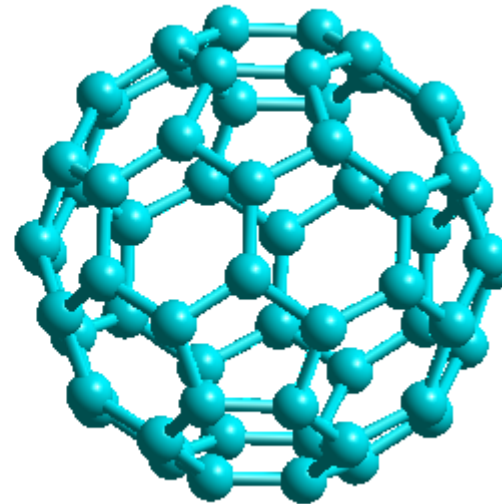
I = icosahedral = 6 five-fold axes



T_d



O_h



I_h

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