

Atomic Multiplet theory and Crystal field Multielectron ions

Marie-Anne ARRIO

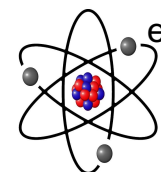
CNRS / Sorbonne Université (Paris)

Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie

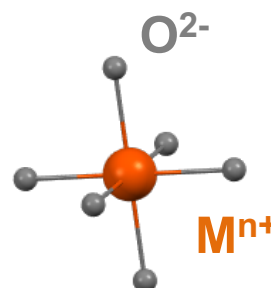


Atomic multiplet theory: N-electrons atom/ion

I. The free atom/ion case (spherical) : N-electrons atom/ion



II. The atom/ion in a crystal field



III. Crystal field and magnetism

N.B : In this lecture, atom/ion will be transition metal (3d series)

Atomic multiplet theory: N-electrons atom/ion

Books

- Free ion (spherical)

R. D. Cowan. The theory of atomic structure and spectra. Los Alamos series in basic and applied sciences. University of California Press, 1981.

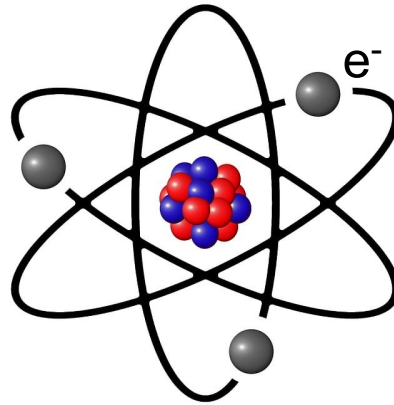
- Free ion (spherical) + crystal field (+magnetism)

M. Weissbluth. Atoms and Molecules. Academic Press, student edition edition, 1978.

C. J. Baulhausen. Introduction to ligand field theory. Series in advanced chemistry. Mc Graw Hill, 1962.

Atomic multiplet theory: N-electrons atom/ion

The free ion case



➤ Electronic configuration:

complete

simplified (open shell)

3d transition metal ions
4f rare earth ions

$1s^2 2s^2 2p^6 3d^n$

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4f^n$

$3d^n$

$4f^n$

Quantum numbers:

n principal

ℓ orbital ($0 \leftrightarrow s, 1 \leftrightarrow p, 2 \leftrightarrow d, \dots$), m_ℓ

s spin, m_s

Orbital level = shell

Partially filled = open shell

Atomic multiplet theory: N-electrons atom/ion

The free ion case

Quantum numbers:

n principal

ℓ orbital ($0 \leftrightarrow s, 1 \leftrightarrow p, 2 \leftrightarrow d, \dots$), m_ℓ

s spin, m_s

1 electron



$\hat{\ell}_i$ orbital angular momentum (operator)

$$\hat{\ell}_i \neq \ell_i$$

ℓ_i and m_{ℓ_i} quantum numbers associated to $\hat{\ell}_i^2$, $\hat{\ell}_{z,i}$

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

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

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

Same definitions for the spin angular momentum $\hat{s}_i$, s_i , m_{s_i}

3dⁿ : Filling n electrons in 3d orbitals ($\ell = 2, s = \frac{1}{2}$):

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

$m_\ell = -2 \quad -1 \quad 0 \quad 1 \quad 2$
 $\uparrow \quad \uparrow\downarrow \quad \text{---} \quad \uparrow \quad \text{---}$
 $m_s = -\frac{1}{2} \quad \frac{1}{2}$

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

Example :

3d² ion (V³⁺, Cr⁴⁺) :

$\binom{10}{2} = 45$ states

degenerate states

Some possibilities:

$m_\ell = -2 \quad -1 \quad 0 \quad 1 \quad 2$

$\uparrow\downarrow$	---	---	---	---	$\uparrow$	$\uparrow$	---	---	---
$\uparrow$	$\downarrow$	---	---	---	$\uparrow$	---	$\uparrow$	---	---
$\uparrow$	---	---	$\downarrow$	---	$\uparrow$	---	---	$\uparrow$	---

Degeneracies => **Multiplets (doublet, triplet,...)**

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

Free ion (spherical)

$$H_{\text{kin}} = \sum_{i=1}^N -\frac{\hbar^2}{2m} \nabla_i^2$$

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

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

Spin-orbit coupling

- One electron (i) $\phi_i(\mathbf{r}, \sigma) = R_{n_i \ell_i}(r) Y_{\ell_i, m_{\ell_i}}(\theta, \phi) \chi_{m_{s_i}}(\sigma)$

Radial
Angular
Spin

- Multi-electron functions for N electrons (configuration) built from the mono-electronic functions**

$$\Psi^H(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_N) \quad \text{with } \mathbf{x} \equiv (\mathbf{r}, \sigma)$$

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \sum \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{x}_1) & \phi_2(\mathbf{x}_1) & \dots & \phi_N(\mathbf{x}_1) \\ \phi_1(\mathbf{x}_2) & \phi_2(\mathbf{x}_2) & \dots & \phi_N(\mathbf{x}_2) \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \phi_1(\mathbf{x}_N) & \phi_2(\mathbf{x}_N) & \dots & \phi_N(\mathbf{x}_N) \end{vmatrix}$$

- Linear combination of Slater determinant**
Anti-symmetric function to satisfy the Pauli principle

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



Contribute to the configuration energy
No degeneracy lifting

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



see also *Lecture* from Maurits Haverkort
haverkort_coulomb_repulsion.pptx

$$\langle \Psi | H_{ee} | \Psi' \rangle$$

I N-electrons atom/ion : Coulomb interaction -Slater integral

Coulomb Hamiltonian:

$$H_{ee} = \sum_{i < j}^{n-1, n} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

(slide from M. Haverkort)

In order to create the Hamiltonian as a matrix we need to evaluate

$$\langle \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n) | H_{ee} | \Psi'(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n) \rangle$$

then the following integral

$$\left\langle \phi_{\tau_1}(\vec{r}_1) \phi_{\tau_2}(\vec{r}_2) \left| \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \right| \phi_{\tau_3}(\vec{r}_1) \phi_{\tau_4}(\vec{r}_2) \right\rangle$$

$\phi_{\tau}(\vec{r})$ One particle orbital
With quantum number τ

The Coulomb Integral is nasty: The integrant diverges at $r_1=r_2$

Solution by Slater: Expand the operator on Spherical Harmonics. Solve the angular part analytical and the Radial integral numerical (Slater Integrals.)

Also works in solids. (Spherical Harmonics are not eigen-states, but still a valid basis set).

Coulomb interaction – Slater Integrals

Expansion on renormalized Spherical Harmonics

(slide from M. Haverkort)

$$\sum_{i < j}^{n-1, n} \frac{1}{|r_i - r_j|} = \sum_{i < j}^{n-1, n} \sum_{k=0}^{\infty} \sum_{m=-k}^{m=k} \frac{\text{Min}[r_i, r_j]^k}{\text{Max}[r_i, r_j]^{k+1}} C_m^{(k)}(\theta_i, \phi_i) C_m^{(k)}(\theta_j, \phi_j)^*$$

with

$$C_m^{(k)}(\theta, \phi) = \sqrt{\frac{4\pi}{2k+1}} Y_m^{(k)}(\theta, \phi)$$

Useful expansion because our basis functions are (close to) spherical

$$\phi_{\tau}(\vec{r}) = R_{n_{\tau}}^{(l_{\tau})}(r) Y_{m_{\tau}}^{(l_{\tau})}(\theta, \phi)$$

Coulomb interaction – Slater Integrals

(slide from M. Haverkort)

Integral to calculate

$$\left\langle \phi_{\tau_1}(\vec{r}_1) \phi_{\tau_2}(\vec{r}_2) \left| \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \right| \phi_{\tau_3}(\vec{r}_1) \phi_{\tau_4}(\vec{r}_2) \right\rangle$$

$$\phi_{\tau}(\vec{r}) = \chi_{\tau} R_{n_{\tau}}^{(l_{\tau})}(r) Y_{m_{\tau}}^{(l_{\tau})}(\theta, \phi)$$

Expansion on renormalized Spherical Harmonics

$$\sum_{k=0}^{\infty} \sum_{m=-k}^{m=k} \left\langle R_{n_{\tau_1}}^{(l_{\tau_1})}(r_1) R_{n_{\tau_2}}^{(l_{\tau_2})}(r_2) \left| \frac{\text{Min}[r_1, r_2]^k}{\text{Max}[r_1, r_2]^{k+1}} \right| R_{n_{\tau_3}}^{(l_{\tau_3})}(r_1) R_{n_{\tau_4}}^{(l_{\tau_4})}(r_2) \right\rangle$$

$$\times \left\langle Y_{m_{\tau_1}}^{(l_{\tau_1})}(\theta_1, \phi_1) \left| C_m^{(k)}(\theta_1, \phi_1) \right| Y_{m_{\tau_3}}^{(l_{\tau_3})}(\theta_1, \phi_1) \right\rangle$$

$$\times \left\langle Y_{m_{\tau_2}}^{(l_{\tau_2})}(\theta_2, \phi_2) \left| C_m^{(k)}(\theta_2, \phi_2)^* \right| Y_{m_{\tau_4}}^{(l_{\tau_4})}(\theta_2, \phi_2) \right\rangle$$

$$\times \langle \chi_{\sigma_{\tau_1}} || \chi_{\sigma_{\tau_3}} \rangle \langle \chi_{\sigma_{\tau_2}} || \chi_{\sigma_{\tau_4}} \rangle = \delta_{\sigma_{\tau_1} \sigma_{\tau_3}} \delta_{\sigma_{\tau_2} \sigma_{\tau_4}}$$

Radial

Angular

Coulomb interaction – Slater Integrals

(slide from M. Haverkort)

Radial part: Slater integrals

$$R_{\tau_1, \tau_2, \tau_3, \tau_4}^{(k)} = \left\langle R_{n_{\tau_1}}^{(l_{\tau_1})}(r_1) R_{n_{\tau_2}}^{(l_{\tau_2})}(r_2) \left| \frac{\text{Min}[r_1, r_2]^k}{\text{Max}[r_1, r_2]^{k+1}} \right| R_{n_{\tau_3}}^{(l_{\tau_3})}(r_1) R_{n_{\tau_4}}^{(l_{\tau_4})}(r_2) \right\rangle$$

Angular part: Analytical solution

$$\begin{aligned} & \left\langle Y_{m_{\tau_1}}^{(l_{\tau_1})}(\theta_1, \phi_1) \left| C_m^{(k)}(\theta_1, \phi_1) \right| Y_{m_{\tau_3}}^{(l_{\tau_3})}(\theta_1, \phi_1) \right\rangle \\ & \times \left\langle Y_{m_{\tau_2}}^{(l_{\tau_2})}(\theta_2, \phi_2) \left| C_m^{(k)}(\theta_2, \phi_2)^* \right| Y_{m_{\tau_4}}^{(l_{\tau_4})}(\theta_2, \phi_2) \right\rangle \\ & \times \langle \chi_{\sigma_{\tau_1}} || \chi_{\sigma_{\tau_3}} \rangle \langle \chi_{\sigma_{\tau_2}} || \chi_{\sigma_{\tau_4}} \rangle \end{aligned}$$

Angular part: Analytical solution

$$\begin{aligned} & \left\langle Y_{m_{\tau_1}}^{(l_{\tau_1})}(\theta_1, \phi_1) \left| C_m^{(k)}(\theta_1, \phi_1) \right| Y_{m_{\tau_3}}^{(l_{\tau_3})}(\theta_1, \phi_1) \right\rangle \\ & \times \left\langle Y_{m_{\tau_2}}^{(l_{\tau_2})}(\theta_2, \phi_2) \left| C_m^{(k)}(\theta_2, \phi_2)^* \right| Y_{m_{\tau_4}}^{(l_{\tau_4})}(\theta_2, \phi_2) \right\rangle \end{aligned}$$

Coupling coefficients (Clebsch-Gordan or 3-j symbols)

The restrictions over k are deduced from the properties of the 3-j symbols

Clebsch-Gordan coefficients related to 3-j symbols

$$\langle \ell_1 \ell_2 m_1 m_2 | \ell_1 \ell_2 \ell_3 m_{\ell_3} \rangle = (-1)^{\ell_2 - \ell_1 - m_{\ell_3}} \sqrt{2\ell_3 + 1} \begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ m_1 & m_2 & -m_{\ell_3} \end{pmatrix}$$

$$\begin{aligned} \langle Y_{l_i}^{m_i}(\theta, \phi) | C_k^m(\theta, \phi) | Y_{l_j}^{m_j}(\theta, \phi) \rangle = \\ (-1)^{m_i} \sqrt{(2l_i + 1)(2l_j + 1)} \begin{pmatrix} l_i & k & l_j \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_i & k & l_j \\ -m_i & m & m_j \end{pmatrix} \end{aligned}$$

$$\neq 0 \text{ if } \begin{array}{l} \ell_i + k + \ell_j \text{ even} \\ |\ell_i - \ell_j| \leq k \leq \ell_i + \ell_j \end{array}$$

Coulomb interaction – Slater Integrals

d – electrons (3dⁿ)

(slide from M. Haverkort)

$$l_1 = l_2 = l_3 = l_4 = 2$$

$$\begin{aligned} & \left\langle Y_{m_{\tau_1}}^{(l_{\tau_1})}(\theta_1, \phi_1) \left| C_m^{(k)}(\theta_1, \phi_1) \right| Y_{m_{\tau_3}}^{(l_{\tau_3})}(\theta_1, \phi_1) \right\rangle \\ & \times \left\langle Y_{m_{\tau_2}}^{(l_{\tau_2})}(\theta_2, \phi_2) \left| C_m^{(k)}(\theta_2, \phi_2)^* \right| Y_{m_{\tau_4}}^{(l_{\tau_4})}(\theta_2, \phi_2) \right\rangle \end{aligned}$$

$$\propto \begin{pmatrix} \ell_i & k & \ell_i \\ 0 & 0 & 0 \end{pmatrix}$$

$$\neq 0 \text{ if } \begin{aligned} & k + 2\ell_i \text{ even} \Rightarrow k \text{ even} \\ & |\ell_i - \ell_j| \leq k \leq \ell_i + \ell_j \Rightarrow 0 \leq k \leq 4 \end{aligned}$$

$$k = 0, 2, 4$$

$$R_{2,2,2,2}^{(0,2,4)} = F^{(0,2,4)} \quad \text{Direct Slater integrals}$$

Coulomb interaction – Slater Integrals

Core (p) valence (d) interaction – direct term

(slide from M. Haverkort)

$$l_1 = l_3 = 2, l_2 = l_4 = 1$$

$$\begin{aligned} & \left\langle Y_{m_{\tau_1}}^{(l_{\tau_1})}(\theta_1, \phi_1) \middle| C_m^{(k)}(\theta_1, \phi_1) \middle| Y_{m_{\tau_3}}^{(l_{\tau_3})}(\theta_1, \phi_1) \right\rangle \\ & \times \left\langle Y_{m_{\tau_2}}^{(l_{\tau_2})}(\theta_2, \phi_2) \middle| C_m^{(k)}(\theta_2, \phi_2)^* \middle| Y_{m_{\tau_4}}^{(l_{\tau_4})}(\theta_2, \phi_2) \right\rangle \end{aligned}$$

$$\propto \begin{pmatrix} l_i & k & l_i \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_j & k & l_j \\ 0 & 0 & 0 \end{pmatrix} \neq 0 \text{ if } \begin{aligned} & k + 2l_i \text{ even} \Rightarrow k \text{ even} \\ & (0 \leq k \leq 2 \text{ and } 0 \leq k \leq 4) \Rightarrow 0 \leq k \leq 2 \end{aligned}$$

$$k = 0, 2$$

$$R_{2,1,2,1}^{(0,2)} = F(0,2) \quad \text{Direct Slater integrals between inequivalent e}^-$$

Coulomb interaction – Slater Integrals

Core (p) valence (d) interaction – exchange term

(slide from M. Haverkort)

$$l_1 = l_4 = 2, l_2 = l_3 = 1$$

$$\begin{aligned} & \left\langle Y_{m_{\tau_1}}^{(l_{\tau_1})}(\theta_1, \phi_1) \middle| C_m^{(k)}(\theta_1, \phi_1) \middle| Y_{m_{\tau_3}}^{(l_{\tau_3})}(\theta_1, \phi_1) \right\rangle \\ & \times \left\langle Y_{m_{\tau_2}}^{(l_{\tau_2})}(\theta_2, \phi_2) \middle| C_m^{(k)}(\theta_2, \phi_2)^* \middle| Y_{m_{\tau_4}}^{(l_{\tau_4})}(\theta_2, \phi_2) \right\rangle \end{aligned}$$

$$\propto \begin{pmatrix} \ell_i & k & \ell_j \\ 0 & 0 & 0 \end{pmatrix} \neq 0 \text{ if } \begin{aligned} & k + 3 \text{ even} \Rightarrow k \text{ odd} \\ & |\ell_i - \ell_j| \leq k \leq \ell_i + \ell_j \Rightarrow 1 \leq k \leq 3 \end{aligned}$$

$$k = 1, 3$$

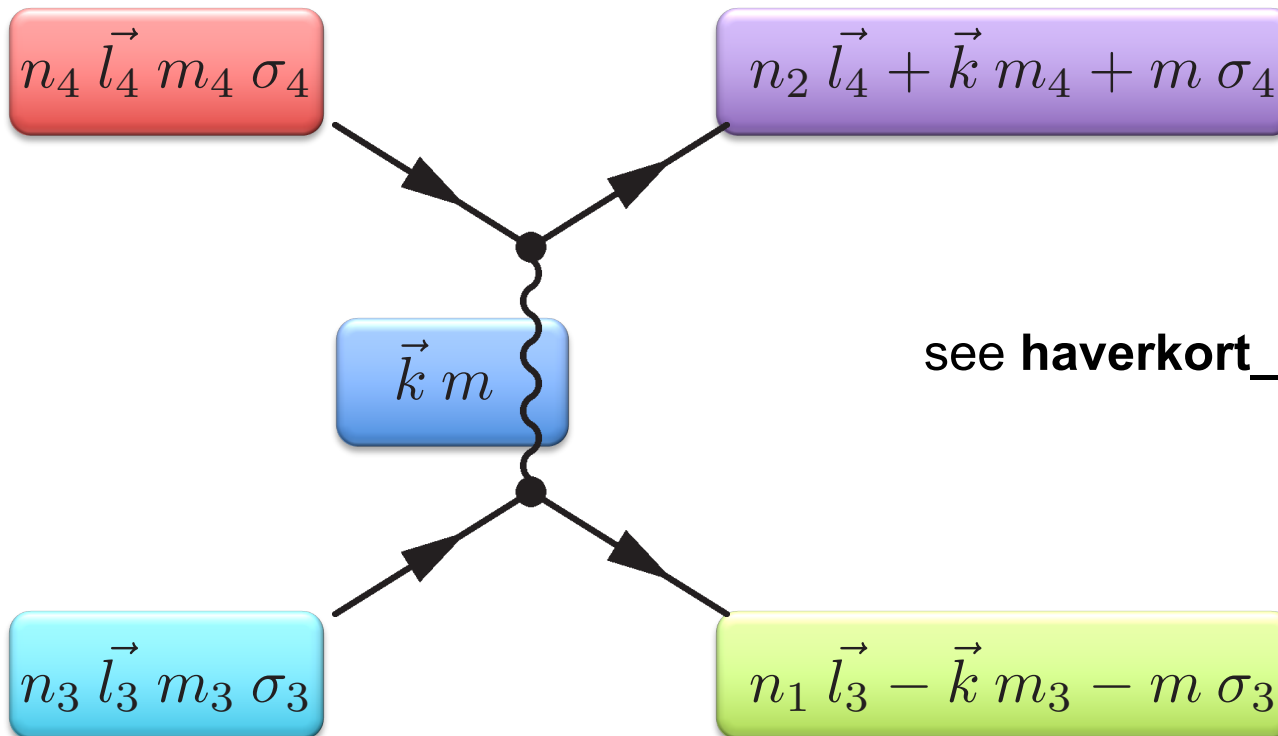
$$R_{2,1,1,2}^{(1,3)} = G^{(1,3)} \quad \text{Exchange Slater integrals between inequivalent e}^-$$

Coulomb interaction – Slater Integrals

Graphical
representation

$$\begin{aligned}
 & \left\langle Y_{m_{\tau_1}}^{(l_{\tau_1})}(\theta_1, \phi_1) \left| C_m^{(k)}(\theta_1, \phi_1) \right| Y_{m_{\tau_3}}^{(l_{\tau_3})}(\theta_1, \phi_1) \right\rangle \\
 & \times \left\langle Y_{m_{\tau_2}}^{(l_{\tau_2})}(\theta_2, \phi_2) \left| C_m^{(k)}(\theta_2, \phi_2)^* \right| Y_{m_{\tau_4}}^{(l_{\tau_4})}(\theta_2, \phi_2) \right\rangle \\
 & \times \left\langle \chi_{\sigma_{\tau_1}} \left| \chi_{\sigma_{\tau_3}} \right\rangle \left\langle \chi_{\sigma_{\tau_2}} \left| \chi_{\sigma_{\tau_4}} \right\rangle \right.
 \end{aligned}$$

(slide from M. Haverkort)



see `haverkort_coulomb_repulsion.pptx`

I Coulomb interaction -Slater integral

The general expression for the electron-electron interaction matrix element is

$$\langle \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n) | H_{ee} | \Psi'(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n) \rangle =$$

$$\sum_{k=0}^{2\ell_j} \sum_j^{\text{shells}} \left[\underbrace{f_k(\ell_j, \ell_j)}_{\text{angular integrals}} \underbrace{F^k(\ell_j, \ell_j)}_{\text{radial integrals "Slater-Condon"}} \right]$$

Depend on orbital momentum and electron filling of the shells

Direct term

Between **equivalent electrons** (belonging to different shells)

$$+ \sum_{k=0}^{\text{Min}(2\ell_i, 2\ell_j)} \sum_{\substack{i,j \\ i \neq j}}^{\text{shells}} f_k(\ell_i, \ell_j) F^k(\ell_i, \ell_j)$$

Direct term

Between **inequivalent electrons** (belonging to different shells)

$$+ \sum_{k=0}^{\ell_i + \ell_j} \sum_{\substack{i,j \\ i \neq j}}^{\text{shells}} g_k(\ell_i, \ell_j) G^k(\ell_i, \ell_j)$$

Exchange term

Between **inequivalent electrons** (belonging to different shells)

Radial integrals calculated numerically from Hartree-Fock atomic spin-orbitals

$$F^k(\ell_i, \ell_j) = \int_0^\infty \int_0^\infty \frac{r_{\leq}^k}{r_{>}^{k+1}} |P_{n_i \ell_i}(r)|^2 |P_{n_j \ell_j}(r')|^2 dr dr'$$

$$G^k(\ell_i, \ell_j) = \int_0^\infty \int_0^\infty \frac{r_{\leq}^k}{r_{>}^{k+1}} P_{n_i \ell_i}^*(r) P_{n_j \ell_j}^*(r') P_{n_j \ell_j}(r) P_{n_i \ell_i}(r') dr dr'$$

Can be scaled to account for covalency, i.e. delocalization = Adjustable parameters

Core hole $\Rightarrow$ Two (or more) open shells

Example : $L_{2,3}$ edges of a $3d^n$ ion

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

$F^2(3d,3d)$, $F^4(3d,3d)$
Electronic repulsion between 3d e^-



Final (excited) configuration $2p^5 3d^{n+1}$

$F^2(3d,3d)$, $F^4(3d,3d)$ e^- 3d

$F^2(2p,3d)$ direct repulsions e^- 3d-2p
 $G^1(2p,3d)$, $G^3(2p,3d)$ exchange repulsions e^- 3d-2p

Radial integrals calculated numerically from Hartree-Fock atomic spin-orbitals (codes: RCN from R. Cowan, FPLO,...). They are included in the Crispy interface (M. Retegan) - Lecture Friday

No spin-orbit $\mathbf{H_{ion} = H_{kin} + H_{e-n} + H_{e-e} + H_{s-o}}$

→ Basis function for N-electrons $|LSM_L M_S\rangle$
 L and M_L quantum numbers associated to $\hat{L}^2, \hat{L}_z$

$$\begin{aligned}\hat{L}^2 |LM_L\rangle &= L(L+1) |LM_L\rangle \\ \hat{L}_z |LM_L\rangle &= M_L |LM_L\rangle\end{aligned}\quad \hat{L} = \sum_{i=1}^N \hat{\ell}_i \quad \triangle ! \quad \sum \text{ means } \oplus \text{ (coupling)}$$

Same definitions for the spin angular momentum S, M_S

→ $\mathbf{H_{ion}}$ and $\hat{L}^2, \hat{S}^2$ have common eigenfunctions

since $H_{kin} + H_{e-n} + H_{e-e}$ commutes with $\hat{L}^2, \hat{L}_z, \hat{S}^2, \hat{S}_z$

→ Basis function for N-electrons $|LSM_L M_S\rangle$

→ Operators $\hat{L}^2, \hat{L}_z, \hat{S}^2, \hat{S}_z$

One electron/orbitals

small letters

$$\hat{l}_i, \hat{l}_{z_i}$$

$$l_i, m_{l_i}$$

$$\hat{s}_i, \hat{s}_{z_i}$$

$$s_i, m_{s_i}$$

Multi-electron ions

CAPITAL LETTERS

$$\hat{L}_i, \hat{L}_{z_i}$$

$$L_i, M_{L_i}$$

$$\hat{S}_i, \hat{S}_{z_i}$$

$$S_i, M_{S_i}$$

I Coulomb interaction : *Basis functions* $|L, S, M_L, M_S\rangle$

No spin-orbit $H_{\text{ion}} = H_{\text{kin}} + H_{\text{e-n}} + H_{\text{e-e}} + H_{\text{s-o}}$

→ Basis function for N-electrons $|LSM_L M_S\rangle$

→ Example : 2-electrons

Coupling of angular momentum

$$|\ell_1 \ell_2 L M_L\rangle = \sum_{m_1=-\ell_1}^{\ell_1} \sum_{m_2=-\ell_2}^{\ell_2} \underbrace{\langle \ell_1 \ell_2 m_1 m_2 | \ell_1 \ell_2 L M_L \rangle}_{\text{Clebsch-Gordan coefficients related to 3-j symbols}} |\ell_1 m_1\rangle |\ell_2 m_2\rangle$$

Clebsch-Gordan coefficients related to 3-j symbols

$$\begin{aligned} |\ell_1 - \ell_2| &\leq L \leq \ell_1 + \ell_2 \\ M_L &= m_1 + m_2 \end{aligned}$$

$$\langle \ell_1 \ell_2 m_1 m_2 | \ell_1 \ell_2 L M_L \rangle = (-1)^{\ell_2 - \ell_1 - M_L} \sqrt{2L + 1} \begin{pmatrix} \ell_1 & \ell_2 & L \\ m_1 & m_2 & -M_L \end{pmatrix}$$

Example : d^2 configuration $\ell_1 = \ell_2$
 $0 \leq L \leq 4$ ie $L = 0, 1, 2, 3, 4$
 $M_L = m_1 + m_2$

I Coulomb interaction : *Basis functions* $|L, S, M_L, M_S\rangle$

No spin-orbit $H_{\text{ion}} = H_{\text{kin}} + H_{\text{e-n}} + H_{\text{e-e}} + H_{\text{s-o}}$

→ Basis function for N-electrons $|LSM_L M_S\rangle$

→ Exemple : 2-electrons

$$|\ell_1 \ell_2 LM_L\rangle = \sum_{m_1=-\ell_1}^{\ell_1} \sum_{m_2=-\ell_2}^{\ell_2} \langle \ell_1 \ell_2 m_1 m_2 | \ell_1 \ell_2 LM_L \rangle |\ell_1 m_1\rangle |\ell_2 m_2\rangle$$

$$|\ell_1 - \ell_2| \leq L \leq \ell_1 + \ell_2$$
$$M_L = m_1 + m_2$$

$$|s_1 s_2 SM_S\rangle = \sum_{m_{s_1}=-s_1}^{s_1} \sum_{m_{s_2}=-s_2}^{s_2} \langle s_1 s_2 m_{s_1} m_{s_2} | s_1 s_2 SM_S \rangle |s_1 m_{s_1}\rangle |s_2 m_{s_2}\rangle$$

$$|s_1 - s_2| \leq S \leq s_1 + s_2$$
$$M_S = m_{s_1} + m_{s_2}$$

$|LSM_L M_S\rangle$ antisymmetric combination of $|\ell_1 \ell_2 LM_L\rangle$ and $|s_1 s_2 SM_S\rangle$
(Pauli exclusion principle)

Coulomb interaction

Basis functions $|L, S, M_L, M_S\rangle$ - Spectroscopic terms

No spin-orbit $H_{\text{ion}} = H_{\text{kin}} + H_{\text{e-n}} + H_{\text{e-e}} + H_{\text{s-o}}$

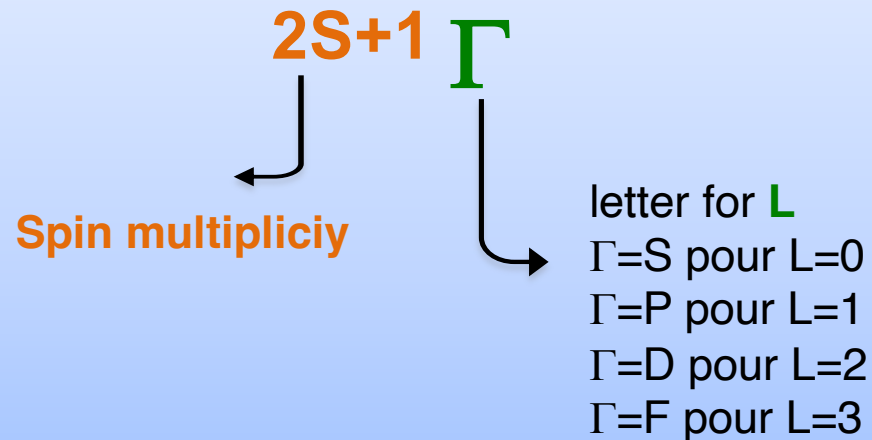
→ Basis function for N-electrons $|LSM_L M_S\rangle$

- ✓ The energy of $|LSM_L M_S\rangle$ does not depend on M_L , M_S
- ✓ Degeneracy (multiplicity) = $(2L + 1)(2S + 1)$

Multiplet state

Orbital degeneracy Spin degeneracy

Spectroscopic term $|L S M_L M_S\rangle$



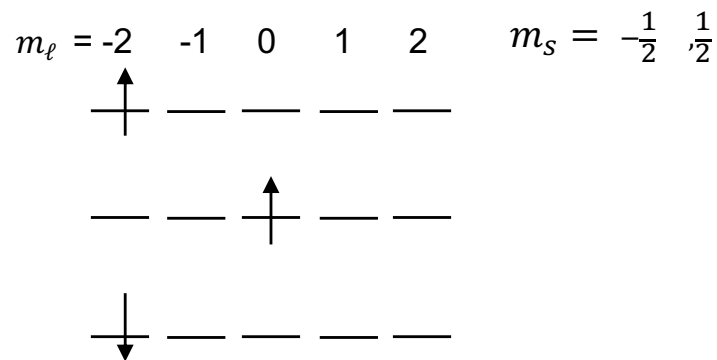
Coulomb interaction

Basis functions $|L, S, M_L, M_S\rangle$ - Spectroscopic terms

No spin-orbit $\mathbf{H_{ion} = H_{kin} + H_{e-n} + H_{e-e} + H_{s-o}}$

Example: d^1

$\binom{10}{1} = 10$ states



$$\hat{L} = \sum_{i=1}^1 \hat{\ell}_i = \hat{\ell}$$

$L = \ell = 2 \rightarrow \text{D term}$

$$\hat{S} = \sum_{i=1}^1 \hat{s}_i = \hat{s}$$

$$S = s = \frac{1}{2}$$

d^1

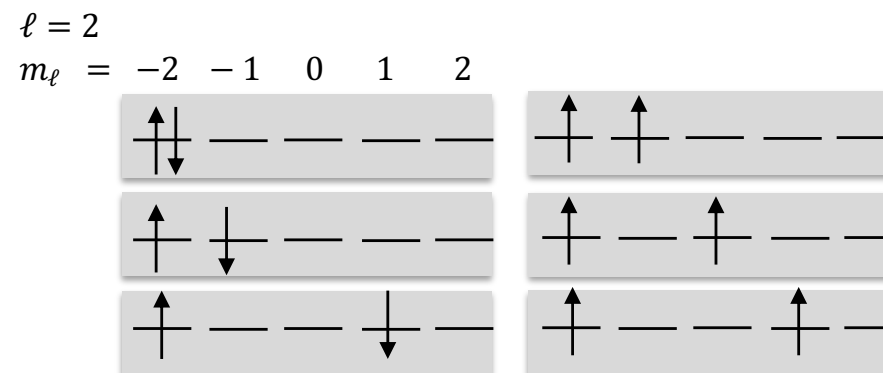
— ^2D

1 Degenerate state
Multiplicity = 10
Spin doublet

Coulomb interaction States/Spectroscopic terms for $3d^2$ ion

$3d^2$

$$\text{Nb states} = \binom{10}{2} = \frac{10!}{2!(10-2)!} = 45$$



$$\hat{L} = \hat{\ell} \oplus \hat{\ell} \quad 0 \leq L \leq 2\ell = 4 \quad L = 0, 1, 2, 3, 4$$

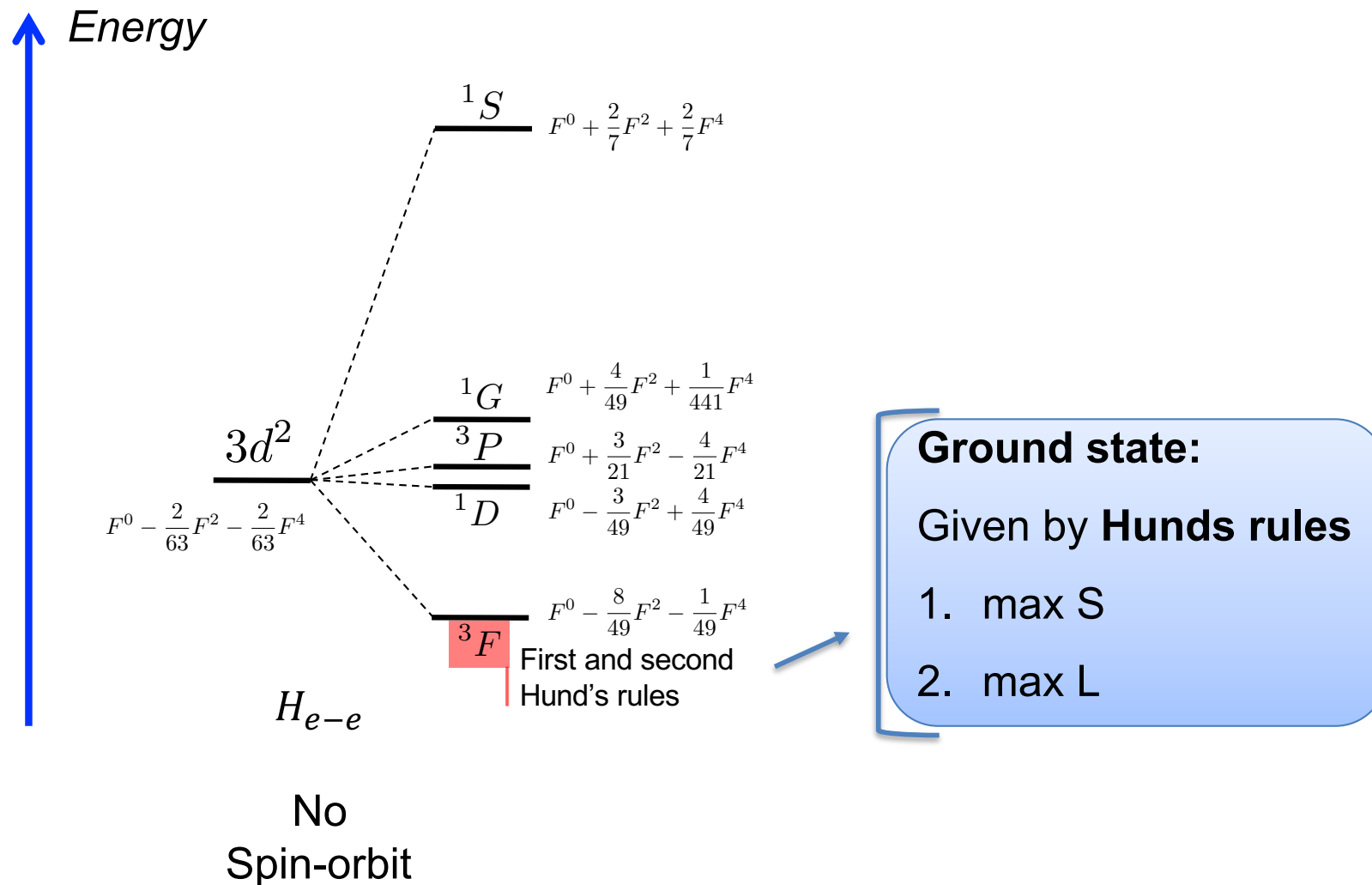
(by step 1) S, P, D, F, G terms

$$\hat{S} = \hat{s} \oplus \hat{s} \quad 0 \leq S \leq 2s = 1 \quad \text{Spin doublet or triplet}$$

Antisymmetric states
5 terms/states

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

Coulomb interaction States/Spectroscopic terms for $3d^2$ ion



N-electrons atom/ion : the free ion case

Spin-orbit coupling

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

Free ion (spherical)

$$H_{s-o} = \sum_{i=1}^N \xi(r_i) \hat{\ell}_i \cdot \hat{s}_i \quad \text{Spin-orbit coupling}$$

N-electrons atom/ion : the free ion case

Spin-orbit coupling : basis function

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

➔ Basis functions for N-electrons $|(LS)JM_J\rangle$

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

➔ **Common eigenfunctions** with $\hat{J}^2, \hat{J}_z, \hat{L}^2, \hat{S}^2$
 $H_{\text{cin}} + H_{\text{e-n}} + H_{\text{e-e}} + H_{\text{s-o}}$ commutes with $\hat{J}^2, \hat{J}_z, \hat{L}^2, \hat{S}^2$
 $(H_{\text{cin}} + H_{\text{e-n}} + H_{\text{e-e}})$ commutes with $\hat{L}^2, \hat{L}_z, \hat{S}^2, \hat{S}_z$

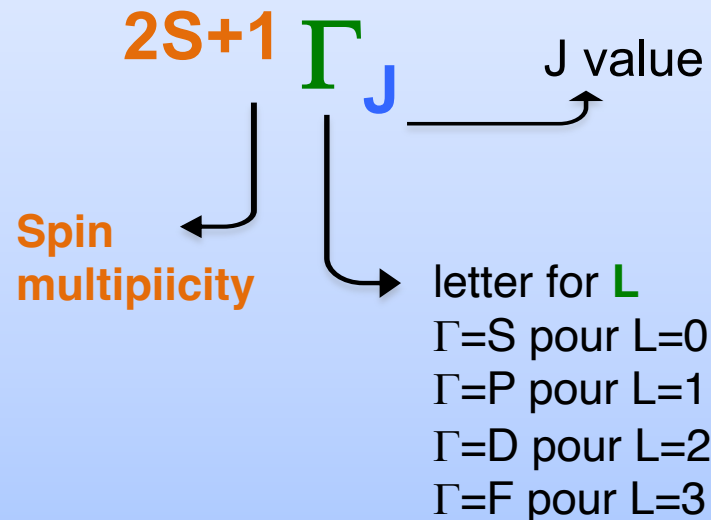
➔ The energy of $|(LS)JM_J\rangle$ does not depend on M_J
 Degeneracy = $2J+1$

Spin-orbit coupling : spectroscopic terms

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

➔ Basis function for N-electrons $|(LS)JM_J\rangle$

Spectroscopic terms $|(LS)JM_J\rangle$



Example: d^1

$$L=2, S=1/2$$

$$|L-S| \leq J \leq L+S$$

$$J=3/2, 5/2$$

$$\begin{array}{rcl}
 & \text{---} & {}^2D_{5/2} \\
 \text{---} & {}^2D & \text{---} & {}^2D_{3/2} & \text{2 states} \\
 H_{\text{e-e}} & & H_{\text{e-e}} + H_{\text{s-o}}
 \end{array}$$

Spin-orbit coupling : matrix elements

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

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

$$\xi_i(r_i) = \frac{\alpha^2}{2} \frac{1}{r} \frac{dV_i(r_i)}{dr_i}$$

V_i central-field potential
for an electron i the spin-orbital i

The general expression for the spin-orbit interaction matrix element is :

$$\langle \alpha L S J M_J | H_{\text{so}} | \alpha' L' S' J' M_J' \rangle = \sum_j^{\text{shells}} d_j \zeta_j$$

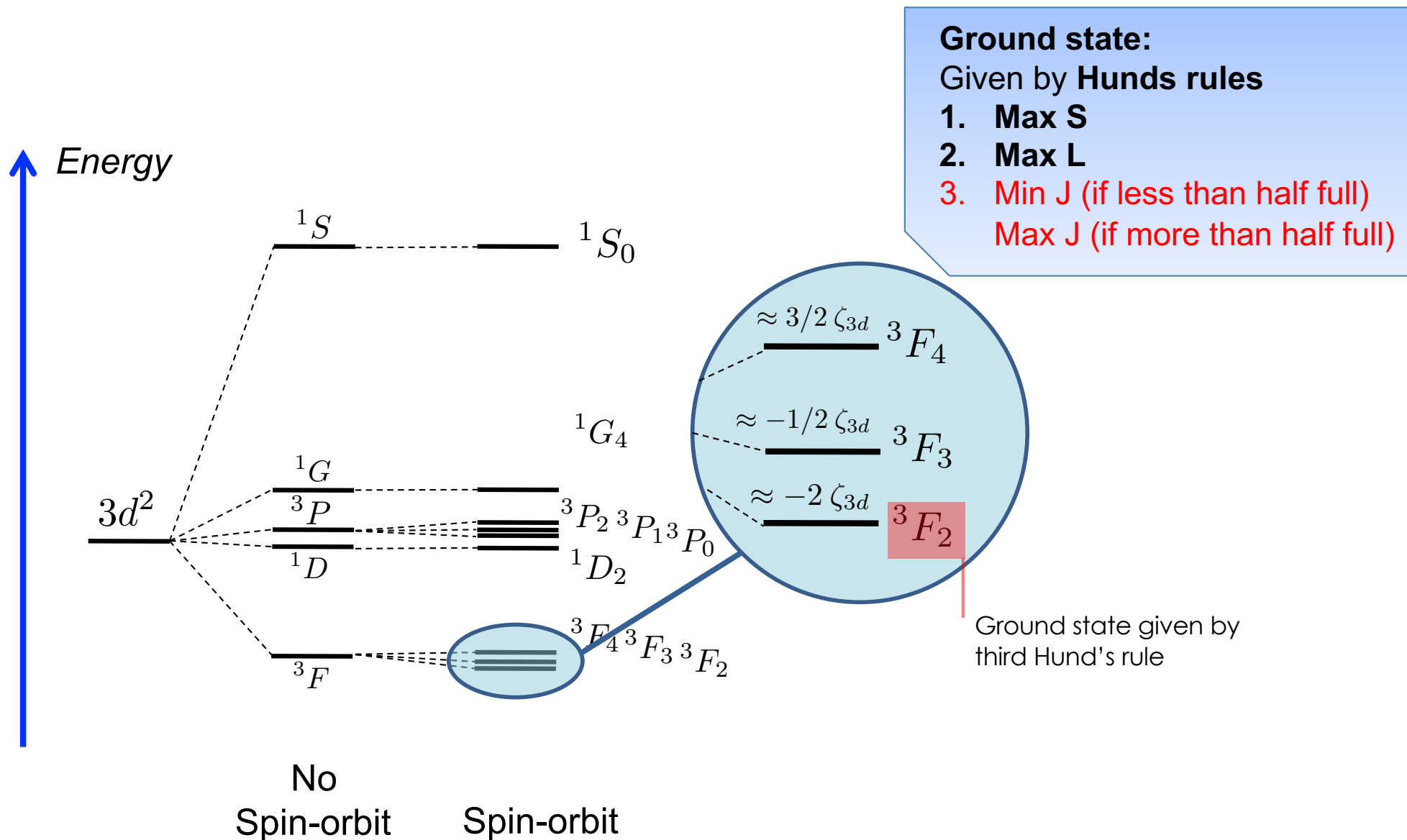
angular integrals
Depend on the electron
configuration (analytical)

radial integrals
Numerical from HF calculations

$$\zeta_j = \int_0^\infty \xi_i(r_i) |P_{n_j \ell_j}(r)|^2 dr$$

ζ_j **Radial integrals calculated numerically** from Hartree-Fock atomic spin-orbitals (codes: RCN from R. Cowan, FPLO,...). They are included in the **Crispy** interface (M. Retegan) - Lecture Friday

Coulomb interaction + spin-orbit States/Spectroscopic terms for $3d^2$ ion



Core hole $\Rightarrow$ Two (or more) open shells

Example : $L_{2,3}$ edges of a $3d^n$ ion *Radial integrals*

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

$F^2(3d,3d), F^4(3d,3d)$
Electronic repulsion between $3d$ e^- + ζ_{3d}

$$0.02 \text{ eV} \leq \zeta_{3d} \leq 0.1 \text{ eV}$$

$$10 \text{ eV} \leq \zeta_{2p} \leq 20 \text{ eV}$$



Final (excited) configuration $2p^5 3d^{n+1}$

$F^2(3d,3d), F^4(3d,3d)$ $e^- 3d$

$F^2(2p,3d)$ direct

$G^1(2p,3d), G^3(2p,3d)$ exchange

+ ζ_{3d}, ζ_{2p}

Quanty script



Next tutorial

```
OppUF0 = NewOperator("U", NF, IndexUp_3d, IndexDn_3d, {1,0,0})  
OppUF2 = NewOperator("U", NF, IndexUp, IndexDn, {0,1,0})  
OppUF4 = NewOperator("U", NF, IndexUp, IndexDn, {0,0,1})
```

```
F2dd = 11.142  
F4dd = 6.874
```

```
OppIdots = NewOperator("Idots", NF, IndexUp, IndexDn)
```

```
zeta_3d = 0.081
```

```
Hamiltonian = F0dd*OppF0 + F2dd*OppF2 + F4dd*OppF4  
              + zeta_3d*OppIdots
```

Angular integrals

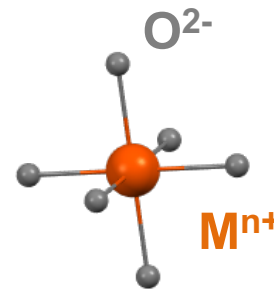
Radial integrals
(Numerical from
Hartree-Fock or
ab initio)

Atomic multiplet theory: N-electrons atom/ion

Crystal field

I. The free atom/ion case (spherical) : N-electrons atom/ion

II. The atom/ion in a crystal field



III. Crystal field and magnetism

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**

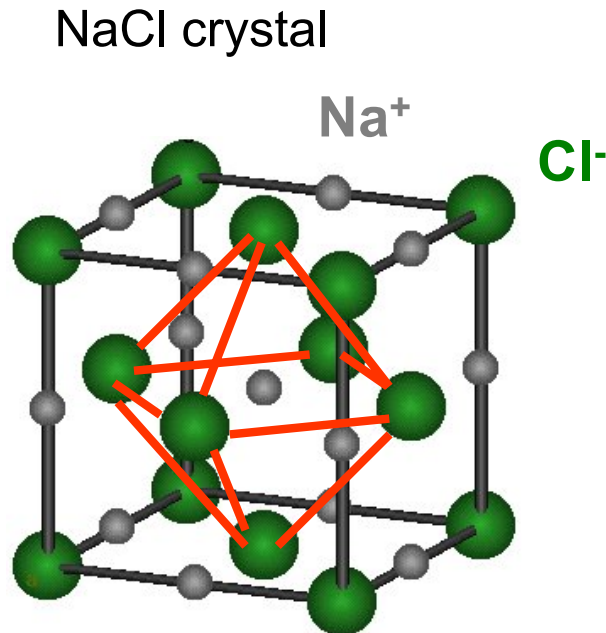


[1] H. Bethe, Annalen der Physik, 1929

[2] W. Kutzelnigg, Angew. Chem. 44, 25 (2005)

Crystal field : origin

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



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:

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

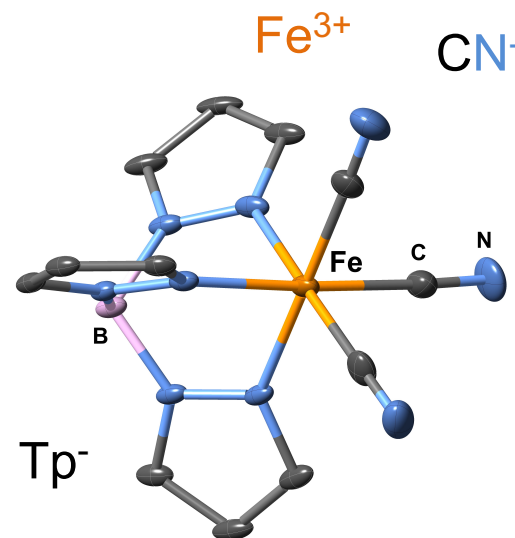
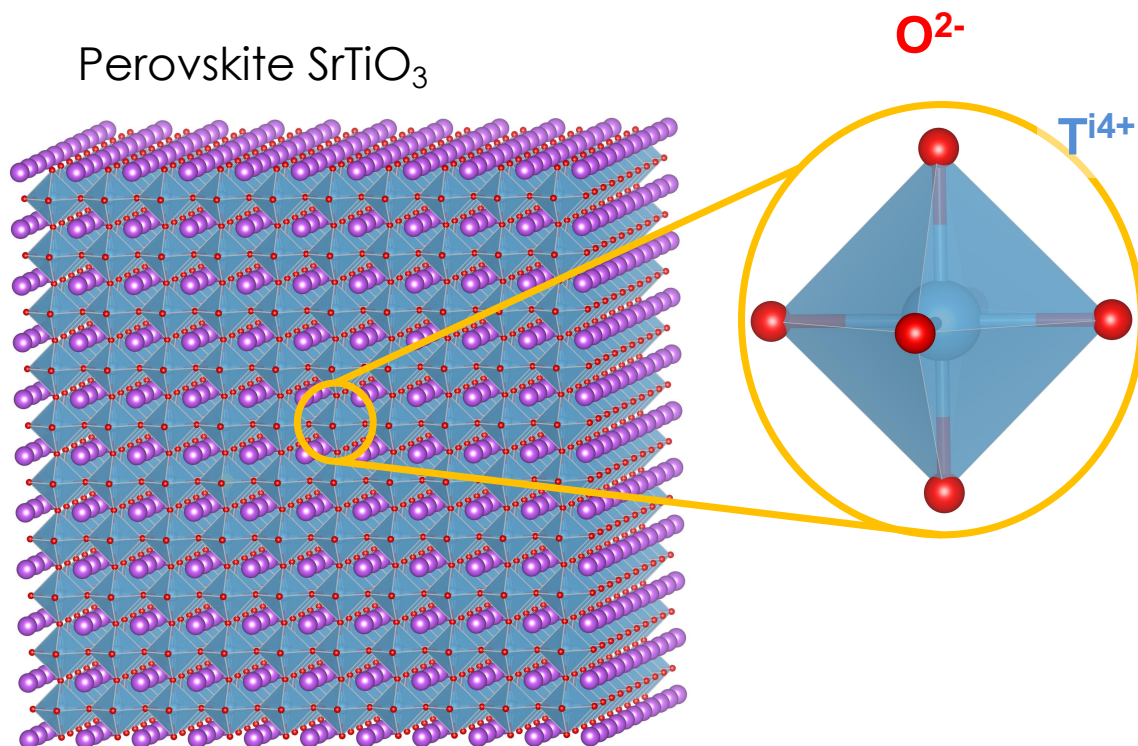
➤ Depends on the local symmetry

II Crystal field : generalization

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

Local model (restricted to the first neighbors or ligands)

Perovskite SrTiO_3

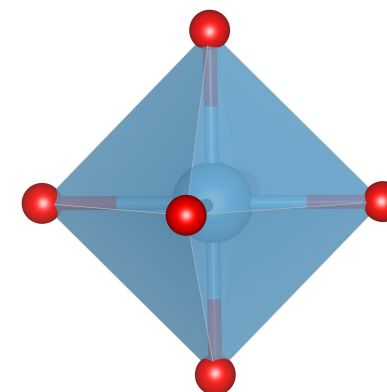
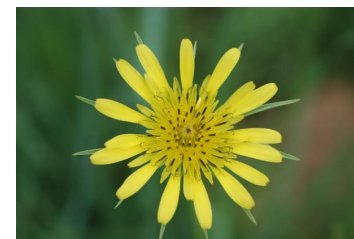
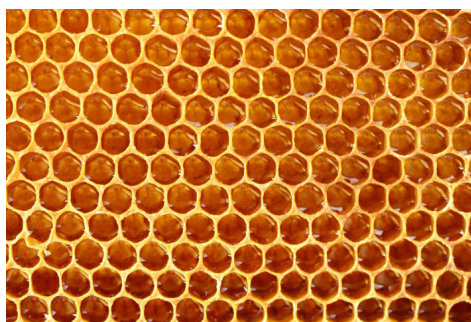


Tp=tris-pyrazolyl borate

Symmetry : responsible for many physical and spectroscopic properties of compounds

Group theory : powerful tool

- simplify calculations,
- predict some properties
- defines the language of labeling



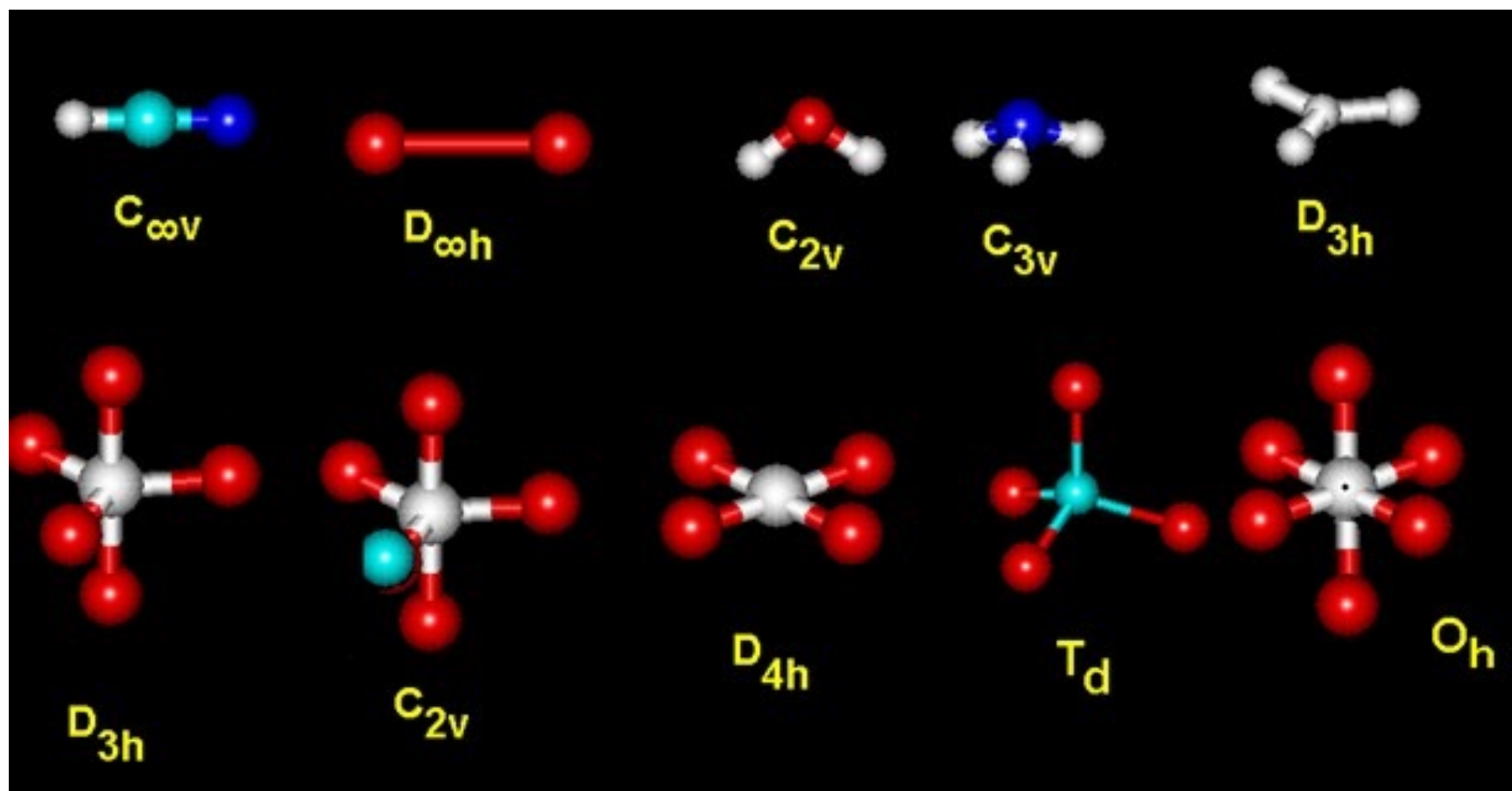
Symmetry operations : some notations to know

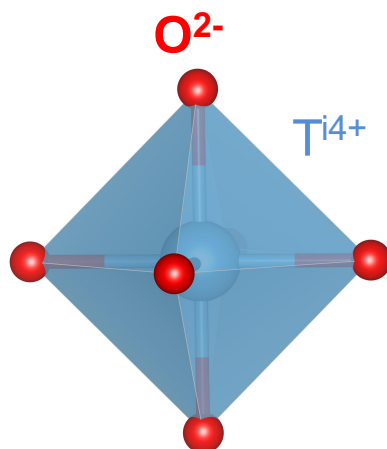
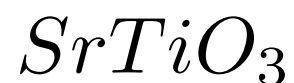
- **E**, the identity
- **C_n**, a rotation by an angle $2\pi/n$;
- **σ** reflection in a plane, classified as
 - **σ_h**, reflection through a plane perpendicular to the axis of highest rotation symmetry, called *principal axis*
 - **σ_v**, reflection through a plane to which the principal axis belongs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

 **Quanty**

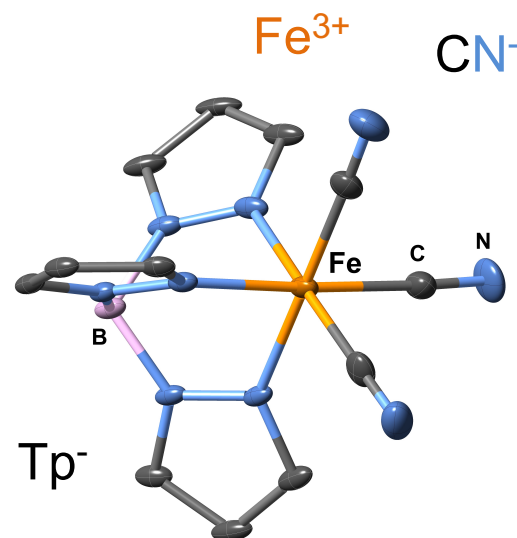
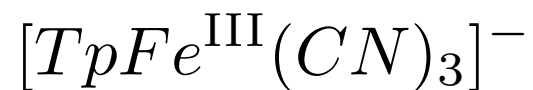
https://www.quanty.org/physics_chemistry/point_groups#symmetry_operations

- ◆ A group of symmetry is an ensemble of symmetry operations (group theory)
- ◆ Each group is labeled (here in Schönflies notation)
- ◆ Each group has a table of representations





Octahedral
Group : O_h



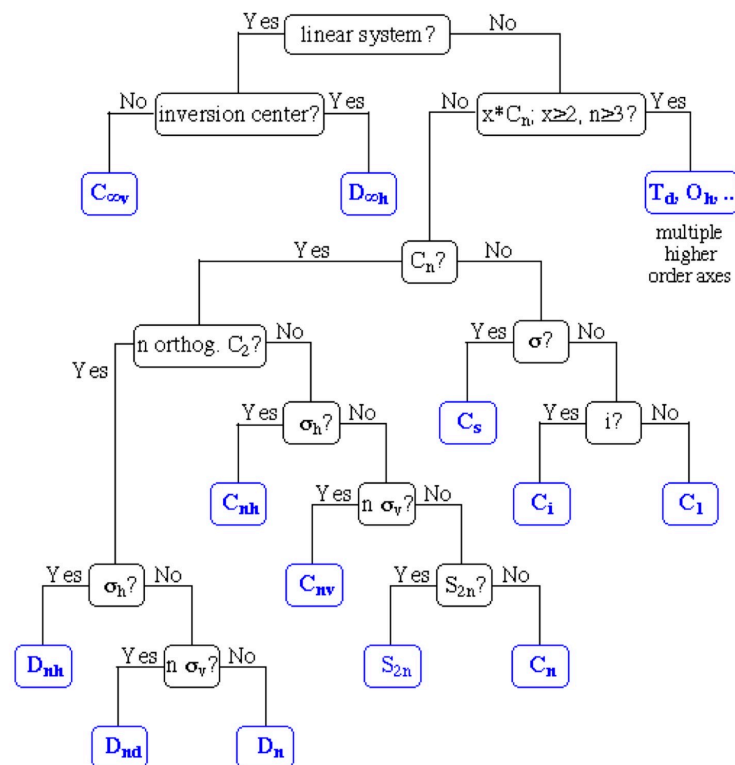
Approximative
Trigonal group :
 C_{3v}



Local point group deduced from crystallography data (.cif or other) or approximation

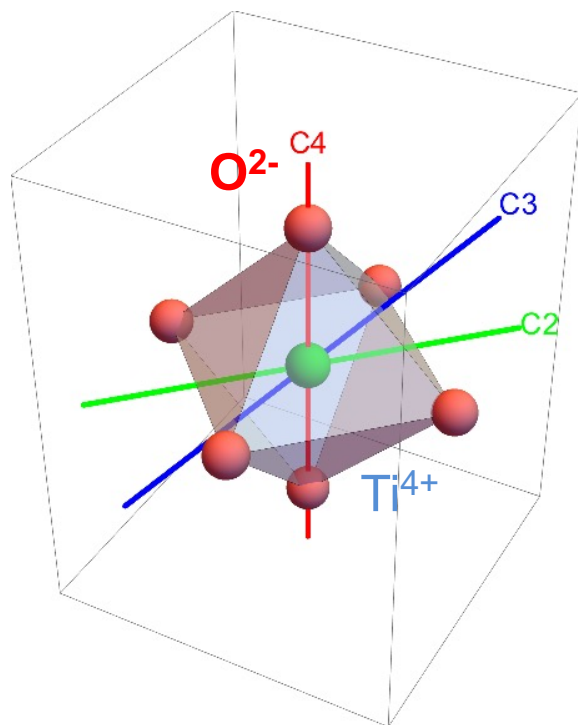
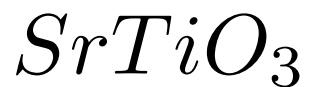
II Crystal field Symmetry – Point groups -tree

Symmetry - "Tree"



Quanty :

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



Group : O_h

Character table

Symmetry elements

Basis functions

	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		

Irreducible representation :

labeled the symmetry properties of a state in the group

II Crystal field Point groups: Quanty website

All you need is in the web page Quanty.org

http://quany.org/physics_chemistry/point_groups



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Point groups

Nonaxial groups	$C_1 - 1$	$C_s - m$	$C_i - \bar{1}$				
C_n groups	$C_2 - 2$	$C_3 - 3$	$C_4 - 4$	$C_5 - 5$	$C_6 - 6$	$C_7 - 7$	$C_8 - 8$
D_n groups	$D_2 - 222$	$D_3 - 32$	$D_4 - 422$	$D_5 - 52$	$D_6 - 622$	$D_7 - 722$	$D_8 - 822$
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	$S_2 - \bar{2}$	$S_4 - \bar{4}$	$S_6 - \bar{6}$	$S_8 - \bar{8}$	$S_{10} - \bar{10}$	$S_{12} - \bar{12}$	
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	$C_{\infty v}$	$D_{\infty h}$					

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 therefore 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

We use the following notation for symmetry operations.

E = identity

C_n = n-fold rotation

S_n = n-fold rotation plus reflection through a plane perpendicular to the axis of rotation

Log In

Table of Contents

- Point groups
- Different orientations
- Symmetry operations
- Irreducible representations
- A flow diagram to determine the point group
- Acknowledgements
- Table of several point groups
- Table of contents

Oh

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

← → ↻ 🏠 quany.org/physics_chemistry/point_groups/oh/orientation_xyz ⓘ ⋮ 📧 ☆ 🔍 Rechercher

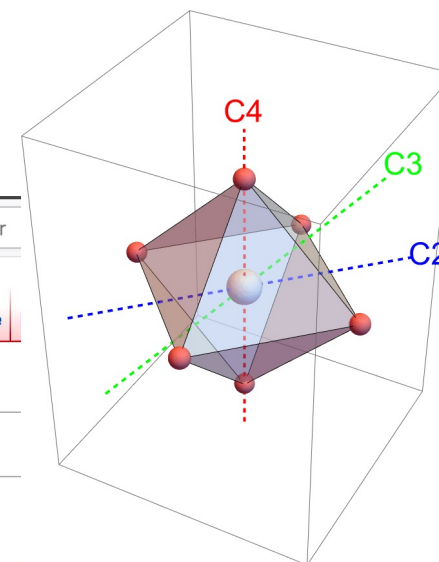
Article **Talk** Read Show pagesource

Orientation XYZ

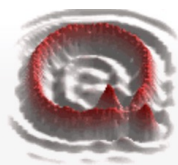
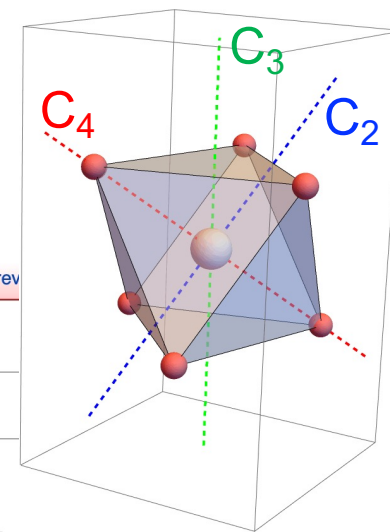
Symmetry Operations

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	$\{1, 0, 0\}, \{0, 1, 0\}, \{0, 0, 1\}$,



Oh

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

Article

Talk

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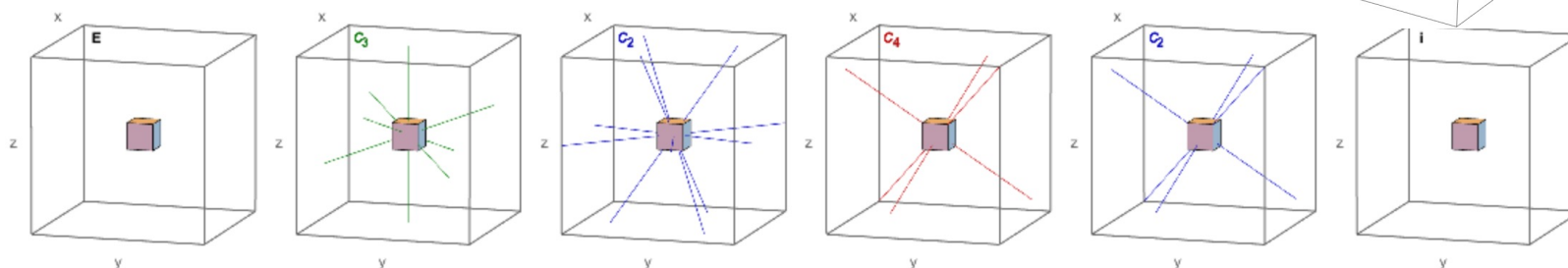
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Old rev

Orientation 111z

Symmetry Operations

In the Oh Point Group, with orientation 111z there are the following symmetry operations



Operator	Orientation
E	$\{0, 0, 0\}$,
C_3	$\{0, 0, 1\}, \{0, 0, -1\}, \left\{2 + \sqrt{3}, -1, \frac{1}{2}(1 + \sqrt{3})\right\}, \{2, 2, -1\}, \left\{1, -2 - \sqrt{3}, \frac{1}{1 - \sqrt{3}}\right\}, \left\{-2 - \sqrt{3}, 1, \frac{1}{1 - \sqrt{3}}\right\}, \{-2, -2, 1\}, \left\{-1, 2 + \sqrt{3}, \frac{1}{2}(1 + \sqrt{3})\right\}$,
C_2	$\{1, -1, 0\}, \{2 + \sqrt{3}, 1, 0\}, \{1, 2 + \sqrt{3}, 0\}, \{1, 1, -2\}, \{-2 - \sqrt{3}, 1, -2(1 + \sqrt{3})\}, \{1, -2 - \sqrt{3}, -2(1 + \sqrt{3})\}$,
C_4	$\{1, 1, 1\}, \{-1, -1, -1\}, \{1, -2 - \sqrt{3}, 1 + \sqrt{3}\}, \{-2 - \sqrt{3}, 1, 1 + \sqrt{3}\}, \{-1, 2 + \sqrt{3}, -1 - \sqrt{3}\}, \{2 + \sqrt{3}, -1, -1 - \sqrt{3}\}$,
C_2	$\{1, 1, 1\}, \{1, -2 - \sqrt{3}, 1 + \sqrt{3}\}, \{-2 - \sqrt{3}, 1, 1 + \sqrt{3}\}$,
i	$\{0, 0, 0\}$,

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Crystal-field theory

Approximate the solid by a single atom in an effective potential

$$V(\vec{r})$$

!!!! WARNING !!!!

Crystal-field potentials do not exist.

They are effective Hamiltonians introduced to mimic covalent bonding.

Covalent bonds are stronger than ionic bonds

Crystal Field (CF) potential :
expanded on the normalized spherical harmonics

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

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

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

The infinite sum is limited by 2ℓ

(from CF matrix element calculation)

Crystal field Hamiltonian – 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)

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

For an electron in orbital ℓ

$$\begin{aligned} \langle \phi_i | H_{CF} | \phi_j \rangle &\propto \langle Y_{\ell, m_i} | C_{k, m} | Y_{\ell, m_j} \rangle \\ &\propto \begin{pmatrix} \ell & k & \ell \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell & k & \ell \\ -m_i & m & m_j \end{pmatrix} \end{aligned}$$

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

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

$\downarrow$
 $A_{k,m} = (-1)^m A_{k,-m}^*$
 Hermitian Matrix

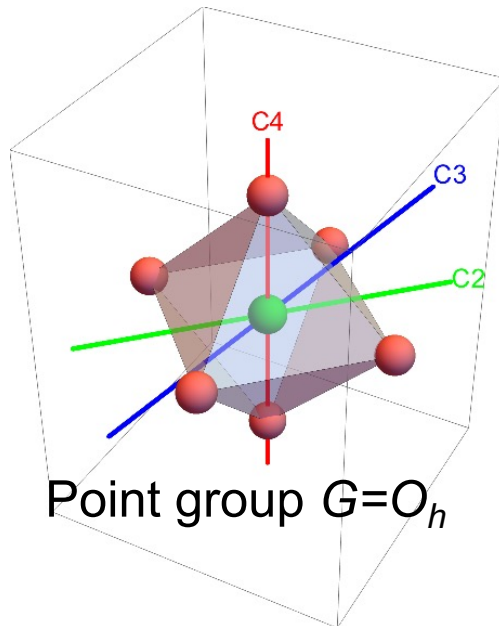
Exemples

3d ion $\ell = 2$
 $k = 0, 2, 4$

4f ion $\ell = 3$
 $k = 0, 2, 4, 6$

The sum over k is reduced by symmetry properties

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



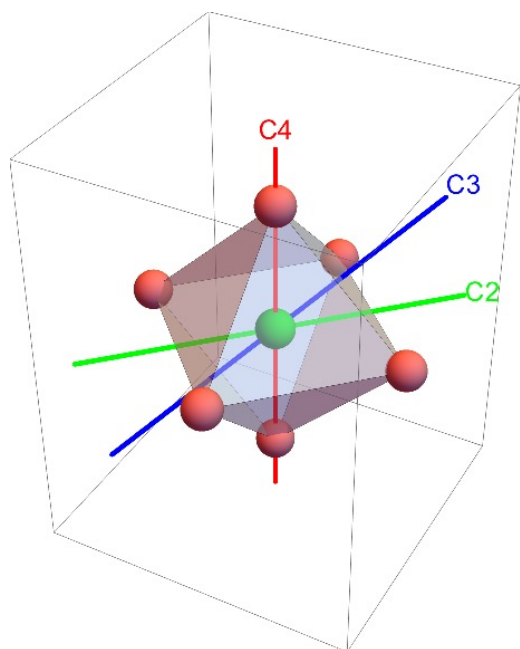
CF Hamiltonian belongs to the point group symmetry $\mathbf{G}$
 $\rightarrow$ is invariant under all symmetry operation O_i of $\mathbf{G}$

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

Some $A_{km} = 0$ due to 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	3σ _h	6σ _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

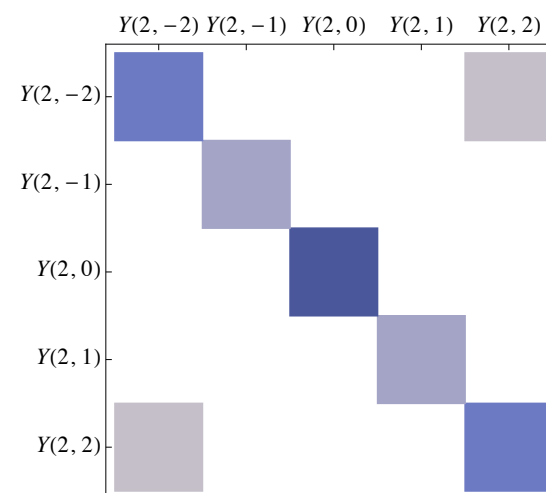
$$H_{CF} \in A_{1g}$$

Fully symmetric representation
 $A_{1g} = \Gamma_1$

Only 2 non-zero A_{km} : A_{00} , A_{40}
 (A_{00} spherical term)

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

CF matrix

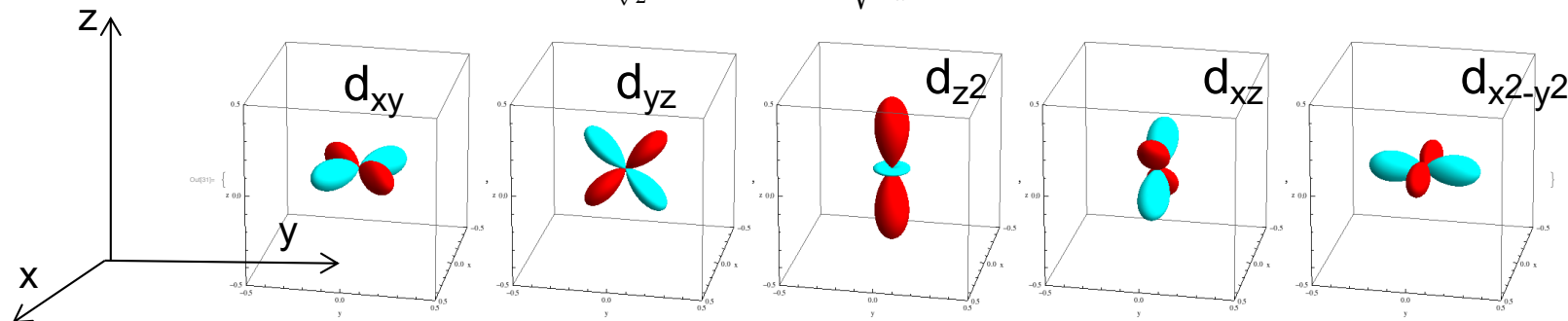


- Basis of atomic orbitals $\phi_i(\mathbf{r}, \sigma) = \frac{1}{r} P_{n_i l_i}(r) Y_{\ell, m}(\theta, \phi) \chi_{m_{s_i}}(\sigma)$
- 3d shell : $n=3, \ell=2$ $2\ell+1=5$ basis functions ($-2 \leq m_\ell \leq 2$)

$$Y_{2, m_\ell}(\theta, \phi) \text{ with } m_\ell = -2, -1, 0, 1, 2$$

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

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



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

1) CF matrix in $\{Y_{2,m}\}$ basis (see quanty.org)

$$\begin{array}{ccccc}
 |\ell m\rangle \equiv |2 - 2\rangle & |2 - 1\rangle & |2 0\rangle & |2 1\rangle & |2 2\rangle \\
 \begin{pmatrix}
 A_{0,0} + \frac{1}{21}A_{4,0} & 0 & 0 & 0 & \frac{5}{21}A_{4,0} \\
 0 & A_{0,0} - \frac{4}{21}A_{4,0} & 0 & 0 & 0 \\
 0 & 0 & A_{0,0} + \frac{2}{7}A_{4,0} & 0 & 0 \\
 0 & 0 & 0 & A_{0,0} - \frac{4}{21}A_{4,0} & 0 \\
 \frac{5}{21}A_{4,0} & 0 & 0 & 0 & A_{0,0} + \frac{1}{21}A_{4,0}
 \end{pmatrix} & \text{Not diagonal}
 \end{array}$$

2) Diagonalization

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



O_h crystal field splits the d orbitals in two groups

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

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		

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

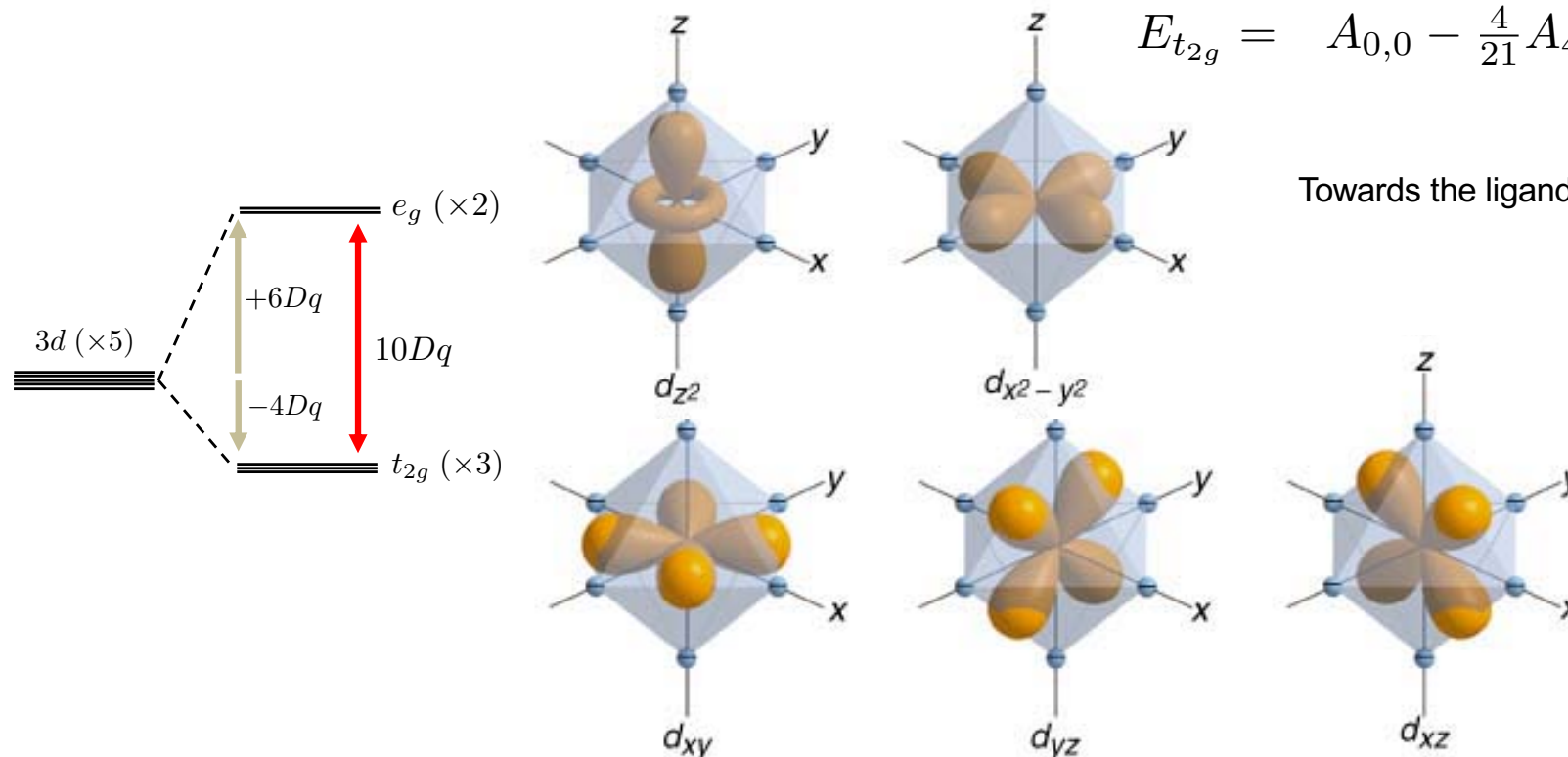
- From the O_h group properties, one can guess the splitting of the d orbitals
- d orbitals are called e_g and t_{2g} *

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

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

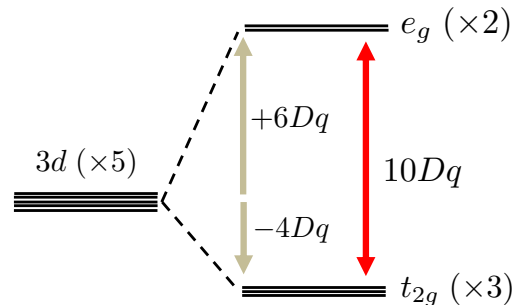
$$E_{t_{2g}} = A_{0,0} - \frac{4}{21}A_{4,0} = -4D_q$$

Towards the ligand : destabilized



$$10D_q = E_{e_g} - E_{t_{2g}} \text{ Crystal field strength}$$

(parameter)

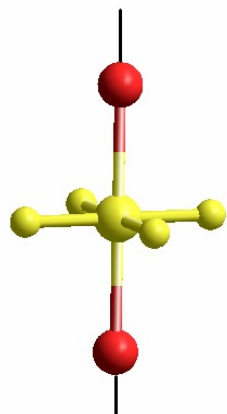


$$E_{e_g} = A_{0,0} + \frac{2}{7}A_{4,0} = +6Dq$$

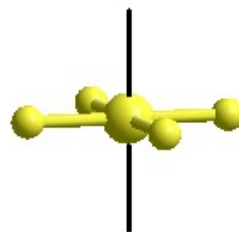
$$E_{t_{2g}} = A_{0,0} - \frac{4}{21}A_{4,0} = -4Dq$$

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

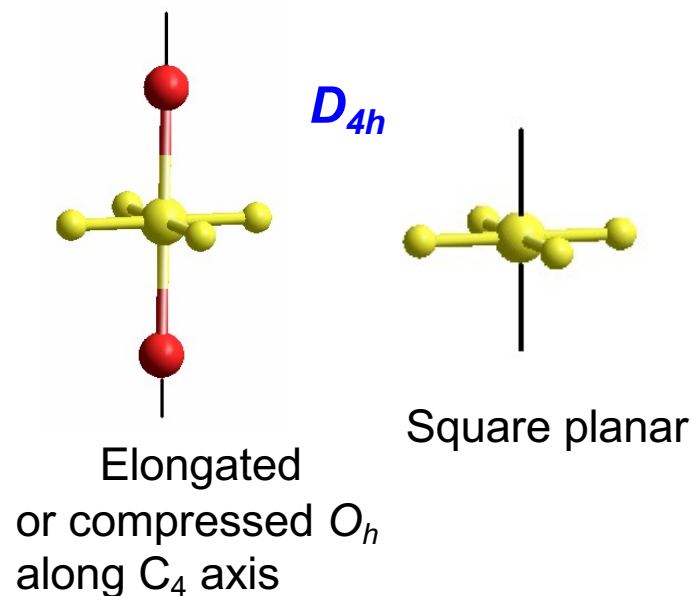
$$A_{k,m} = \begin{cases} \frac{2}{5}E_{e_g} + \frac{3}{5}E_{t_{2g}} & k=0 \quad m=0 \\ \frac{21}{10}(E_{e_g} - E_{t_{2g}}) & k=4 \quad m=0 \\ \frac{21}{10}\sqrt{\frac{5}{14}}(E_{e_g} - E_{t_{2g}}) & k=4 \quad m=\pm 4 \\ 0 & \text{True} \end{cases}$$

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

$$\{d_{z^2}\} \in a_{1g}$$

$$\{d_{x^2-y^2}\} \in b_{1g}$$

$$\{d_{xy}\} \in b_{2g}$$

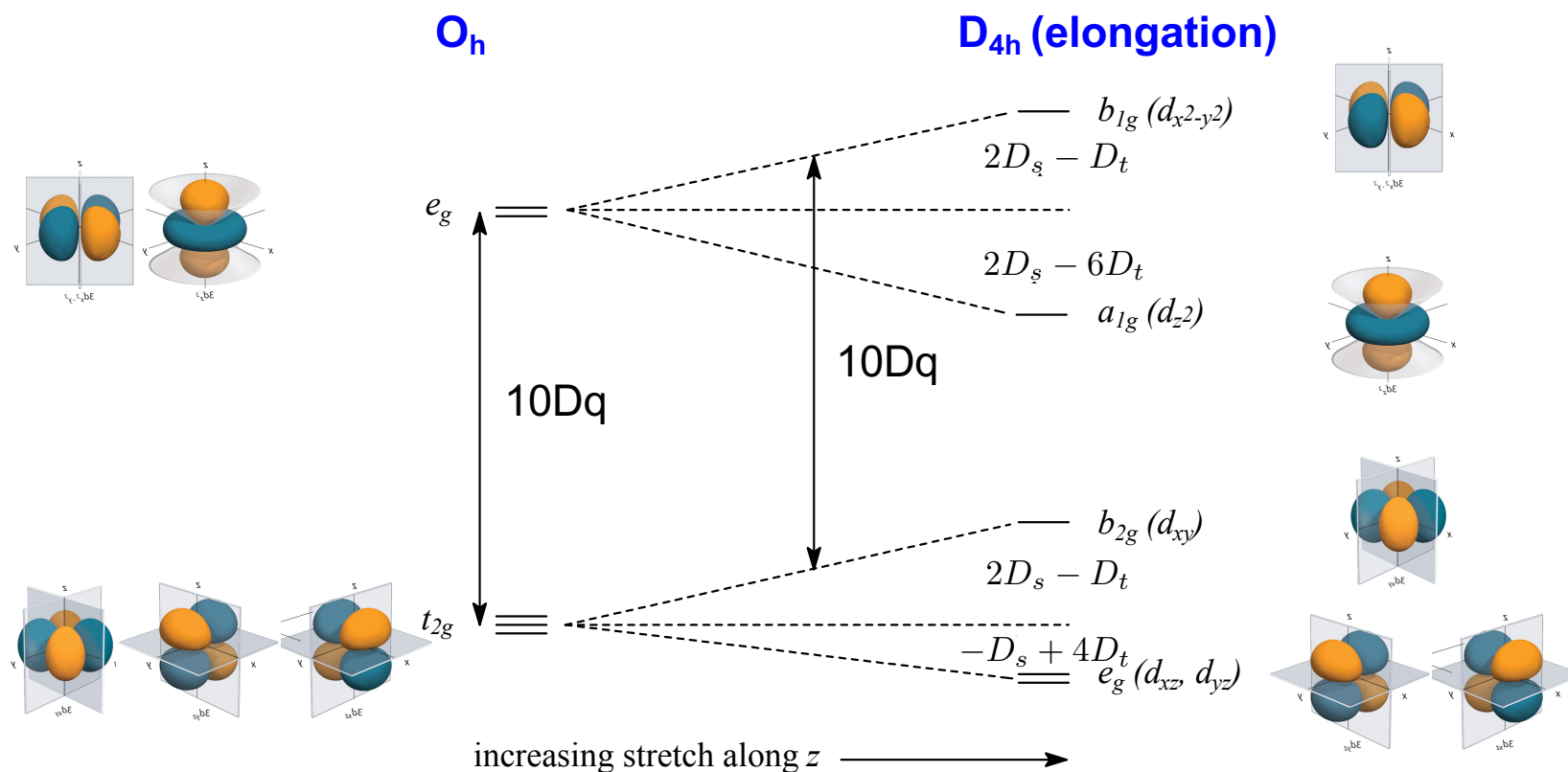
$$\{d_{xz}, d_{yz}\} \in e_g$$

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

➤ CF matrix diagonal in the $\{d\}$ basis

$$\begin{array}{ccccc}
 d_{x^2-y^2} & d_{z^2} & d_{yz} & d_{xz} & d_{xy} \\
 \left(\begin{array}{ccccc}
 E_{a_{1g}} & 0 & 0 & 0 & 0 \\
 0 & E_{b_{1g}} & 0 & 0 & 0 \\
 0 & 0 & E_{e_g} & 0 & 0 \\
 0 & 0 & 0 & E_{e_g} & 0 \\
 0 & 0 & 0 & 0 & E_{b_{2g}}
 \end{array} \right) & & 4 \text{ energy levels}
 \end{array}$$

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



(*)The relation with Dq, D_s, D_t in König&Kremer « Ligand field. Energy diagram »

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

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:

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

2) 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);
```

3) Hamiltonian

$$H_{CF} = 10D_q * OpptenDq$$

Tutorials today

Vary from an author to the other

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

(Haverkort/Quanta)

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

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

$10Dq$ for O_h

$10Dq, Ds, Dt$ for D_{4h}

$10Dq, D\sigma, D\tau$ for D_{3d} or C_{3v}

Parameters used in **Quanta** : A_{km}
Orbital energies + off-diagonal elements
Symmetry-dependent

E_{eg}, E_{t2g} for O_h

$E_{a1g}, E_{eg}, E_{b1g}, E_{b2g}$ for D_{4h}

$\approx E_{a1g}, E_{eg}, E_{eg}$ for D_{3d} (!!! Not general case !!!)

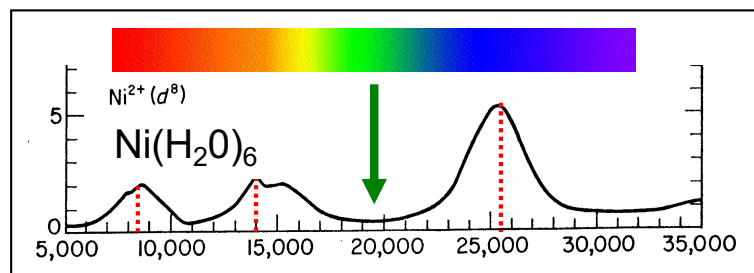
O_h	1 parameter (10Dq or $A_{4,0}$)	2 energies	$E_{e_g}, E_{t_{2g}}$
D_{4h}	3 parameters (10Dq, Ds, Dt or $A_{2,0}, A_{4,0}, A_{4,4}$)	4 energies	$E_{a_{1g}}, E_{b_{1g}}, E_{e_g}, E_{b_{2g}}$
D_{3d}	3-4 parameters (10Dq, D σ , D τ or $A_{2,0}, A_{4,0}, A_{4,3}, A_{4,-3}$)	3 energies	$E_{a_{1g}}, E_{e_g}, E_{e_g}$
C_{2v}	9 parameters 	5 energies (5 orbitals)	

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

For example

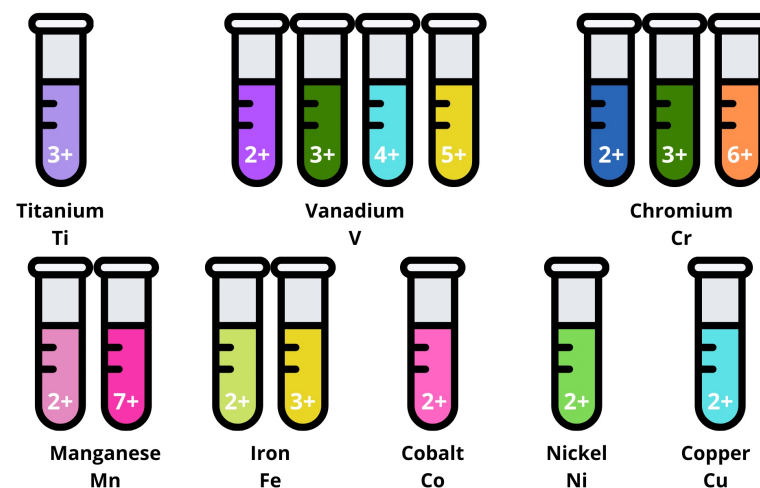
- **Color**
- Magnetic properties

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



UV-visible Absorption spectroscopy

Transition Metal Ion Colors in Aqueous Solution



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


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

➤ **Basis functions**

Spherical symmetry:

$$|(L,S) J M_J\rangle$$

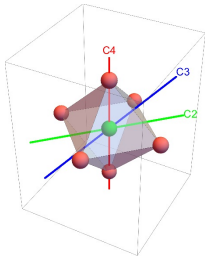
Local symmetry around the ion → point group G :

Basis functions of the representations of group G

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

Γ irreducible representation of G

$\Gamma\gamma$ basis function of G

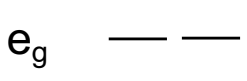
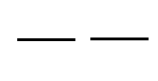
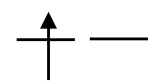
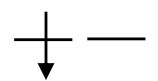
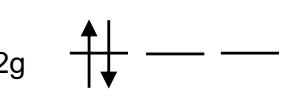
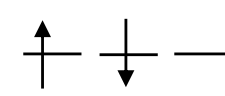
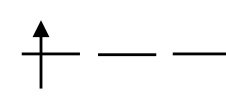
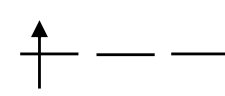


- Thole's code (F.M.F de Groot : **TTMULT**, **CTM4XAS**)
uses group theory and the $\{\Gamma\}$ basis

➤ **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)

d^2 ion in O_h symmetry

	e_g 			
	t_{2g} 			
Orbital degeneracy	3	6	$3 \times 2 = 6$	$3 \times 2 = 6$
Spin degeneracy	1 ($S=0$)	1 ($S=0$)	3 ($S=1$)	1 ($S=0$)

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

Spectroscopic terms

Free ion (spherical)

$$|(LS)JM_J\rangle$$

$$2S+1 \Gamma_J$$

Spin
multiplicityletter for **L** $\Gamma=S$ pour $L=0$ $\Gamma=P$ pour $L=1$ $\Gamma=D$ pour $L=2$ $\Gamma=F$ pour $L=3$

Crystal field

$$|(LS)J \Gamma \gamma\rangle$$

$$2S+1 \Gamma$$

Spin
multiplicityIrreducible representation
of the point group
(local symmetry)

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

Spectroscopic terms

Crystal field

$$|(LS)J \Gamma \gamma >$$

 $2S+1 \Gamma$
Spin
multiplicity

Irreducible representation
of the point group
(local symmetry)
 $A_1, T_2, E \dots$

Crystal field + Spin-orbit

$$|(LS)J \Gamma \gamma >$$

$$\Gamma = \Gamma(S) \otimes \Gamma(L)$$

$$H_{CF} \in A_{1(g)}^* \quad (\text{fully symmetric representation of group } \mathbf{G}) \quad A_{1g} = \Gamma_1$$

* 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 $\Gamma_i \otimes \Gamma_j \ni A_{1(g)}$

(group multiplication table)

$$H_{CF} \in A_{1(g)}^* \quad \text{(fully symmetric representation of group } \mathbf{G} \text{)} \quad A_{1g} = \Gamma_1$$

* g only for centro-symmetric group

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

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

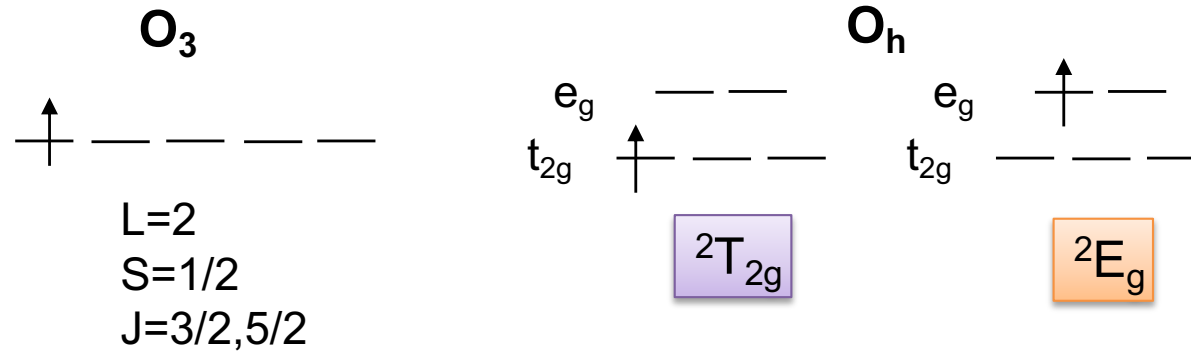
$$\text{if } \Gamma_i \otimes A_{1(g)} \otimes \Gamma_j = \Gamma_i \otimes \Gamma_j \ni A_{1(g)}$$

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

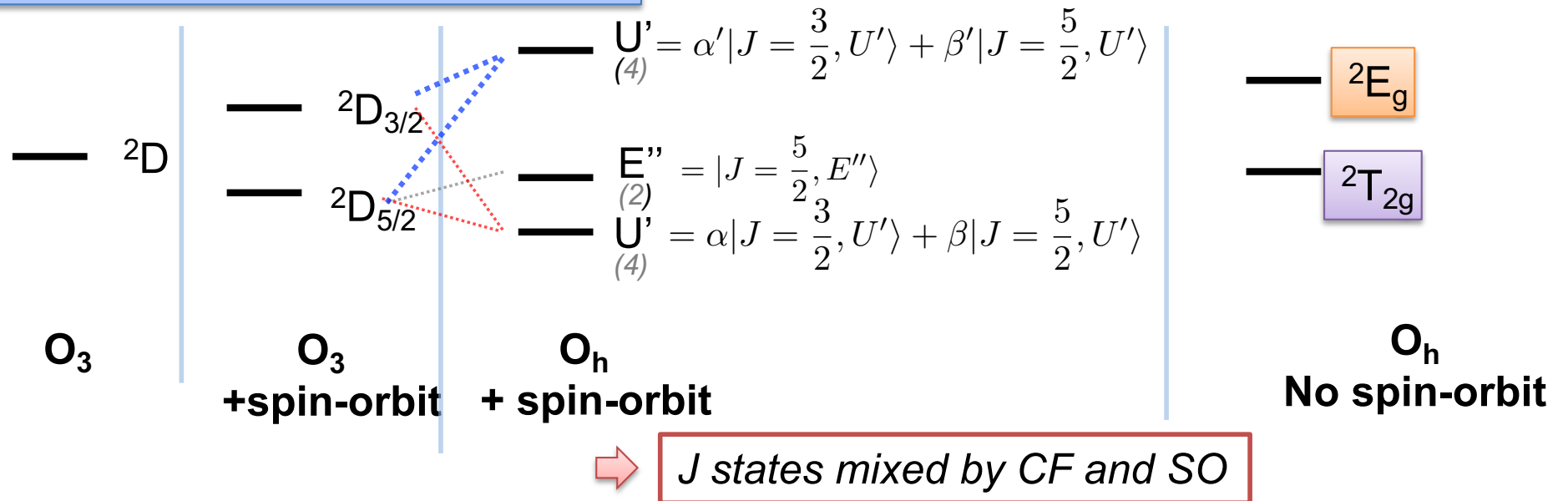
(group multiplication table)

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

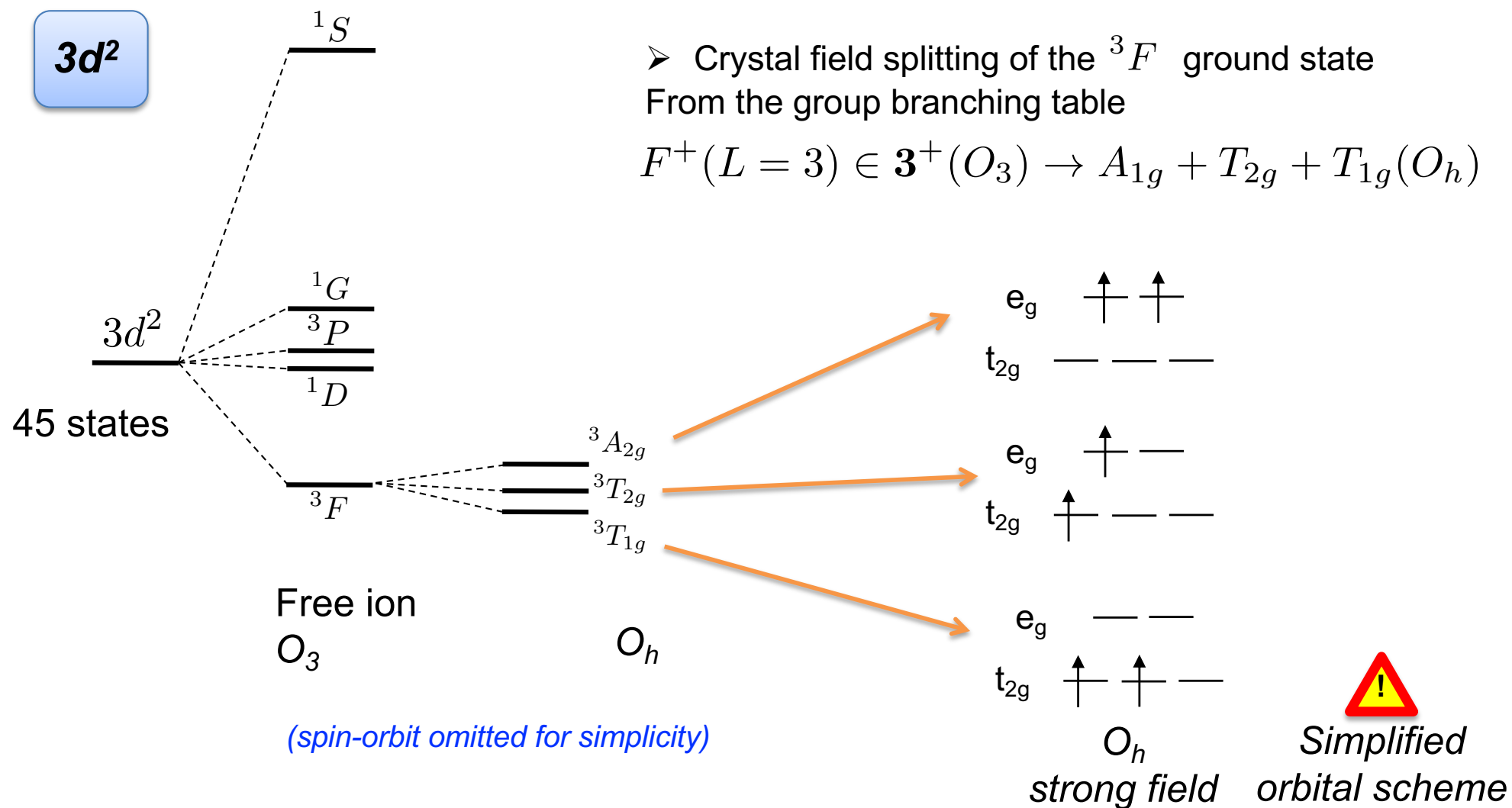
Orbitals



States (spectroscopic terms) d^9



Crystal field Energy levels for $3d^2$ ion (O_h)



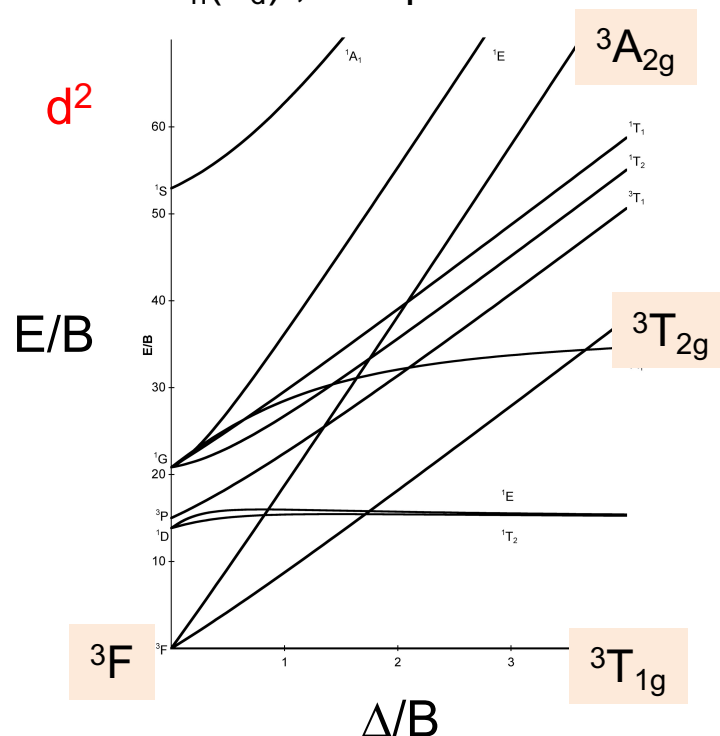
From the multi-electronic state, one can get the electron density on the orbitals of the group (it is not necessary integer)

II Crystal field Energy level diagram / Tanabe-Sugano

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

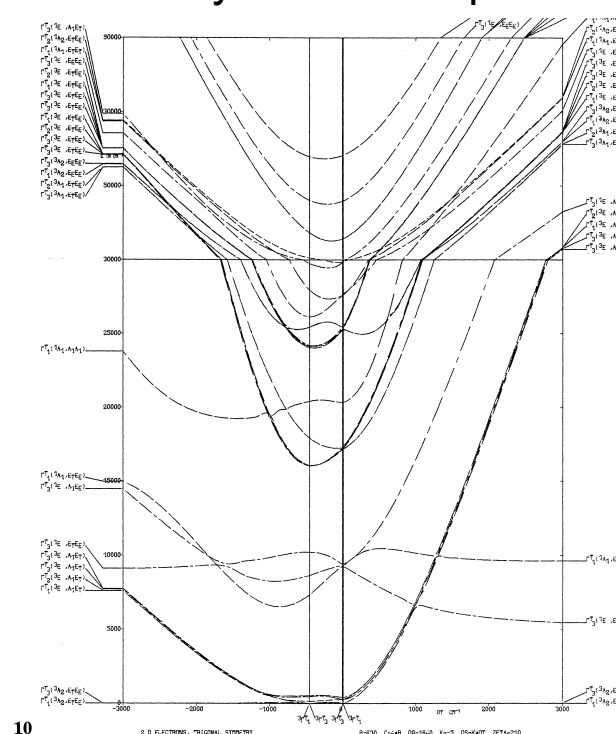
➤ Tanabe-Sugano diagram (1954)

$O_h(T_d)$, no spin-orbit



➤ König&Kremer (1970)

Low symmetries+spin-orbit



(*)B Racah parameters related to the Slater integrals

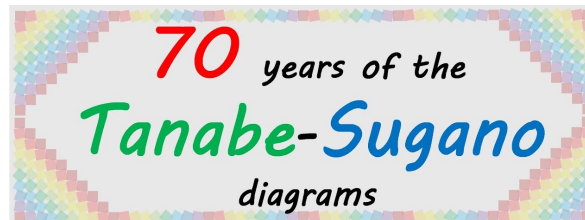
$$A = F^0(3d,3d) - \frac{49}{441}F^4(3d,3d)$$

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

$$C = \frac{35}{441}F^4(3d,3d)$$

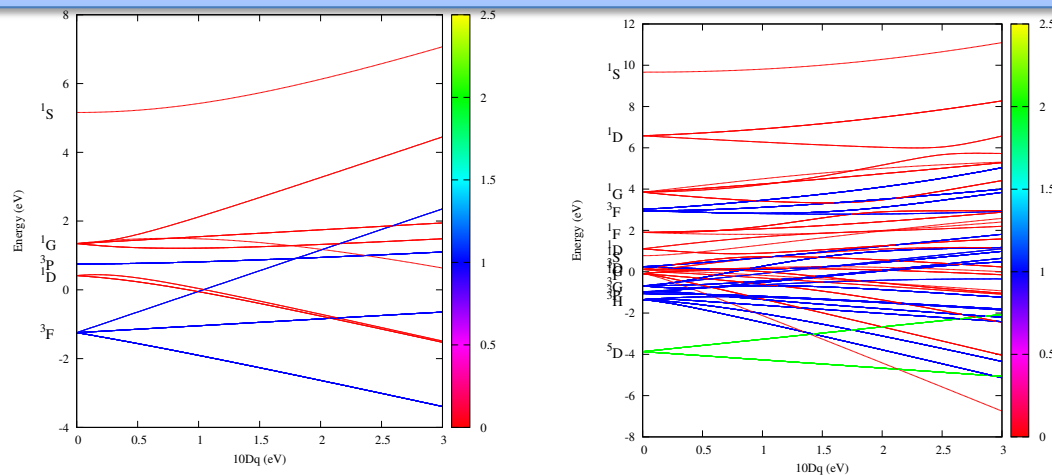
Crystal field Energy level diagram / Tanabe-Sugano

- **Tanabe-Sugano diagram (1954)**
 $O_h(T_d)$, no spin-orbit
- **König&Kremer (≈ 1970)**
Low symmetries+spin-orbit
- **2024 : special conference**



(<https://sites.google.com/view/70years-of-tanabe-sugano/home>)

Quany Tutorial :
02_Energy_Level_Diagram_Tanabe-Sugano.Quany



Crystal field : one electron / multi-electron

One electron/orbitals

- Orbitals : $\gamma_i \in G$

Small letter

ex: e_g, t_{2g}

a_{1g}, e_2

Multi-electron ions

- Spectroscopic terms : $\Gamma_i \in G$

Term written with **CAPITAL LETTER**
in Mulliken notation.

$A_{1g}, T_2, \dots$

or Koster notation : Γ_i

- Electron density / orbital occupation

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

- L, S, J, M_L, M_S, M_J not « good » quantum numbers.**

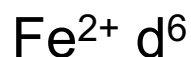
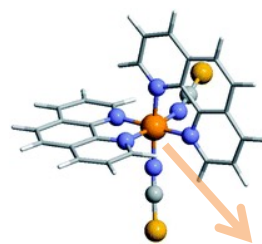
Expectation values:

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

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

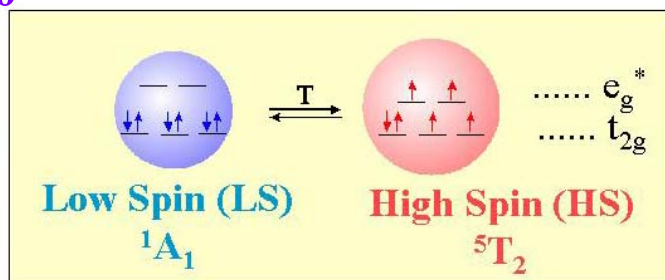
Example of crystal field effect

Spin crossover

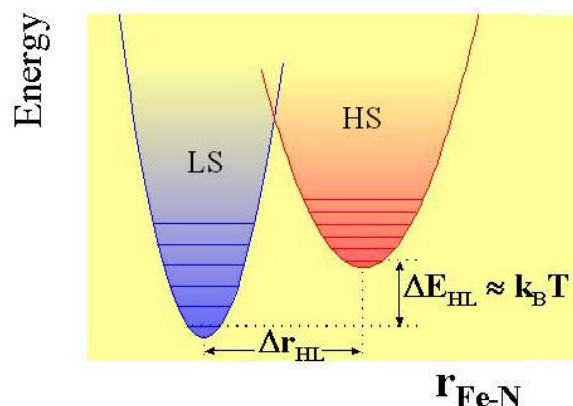


Color change
thermochromism

$T = 77 \text{ K}$
Low spin $S = 0$



$T = 300 \text{ K}$
High spin $S = 2$

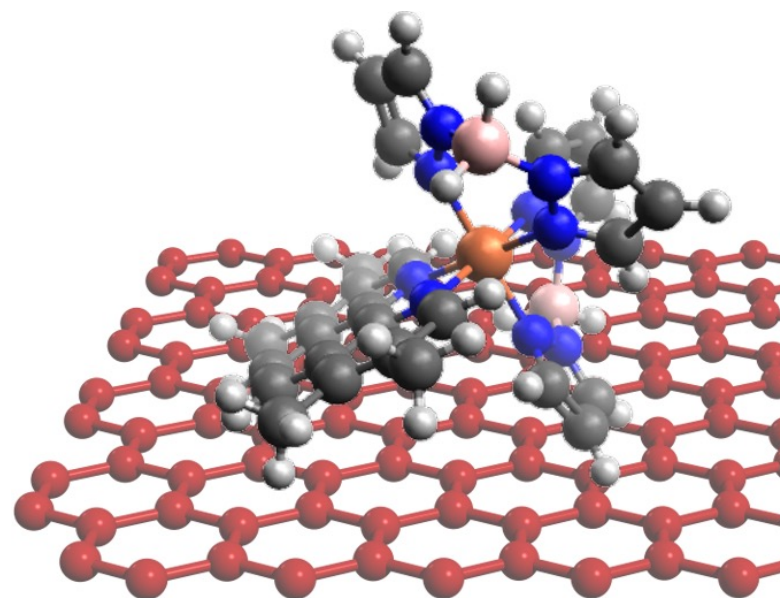
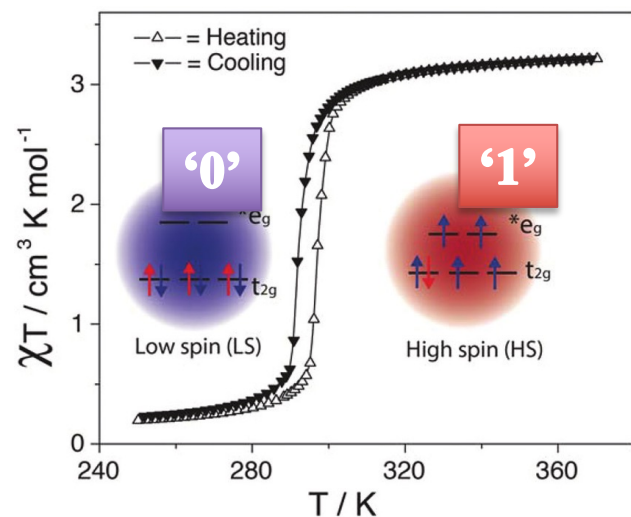


Fe-N distance
↓
CF strength
↓
Color change

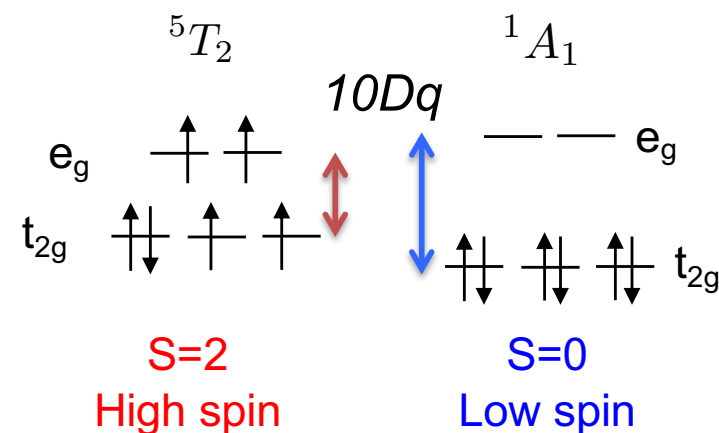
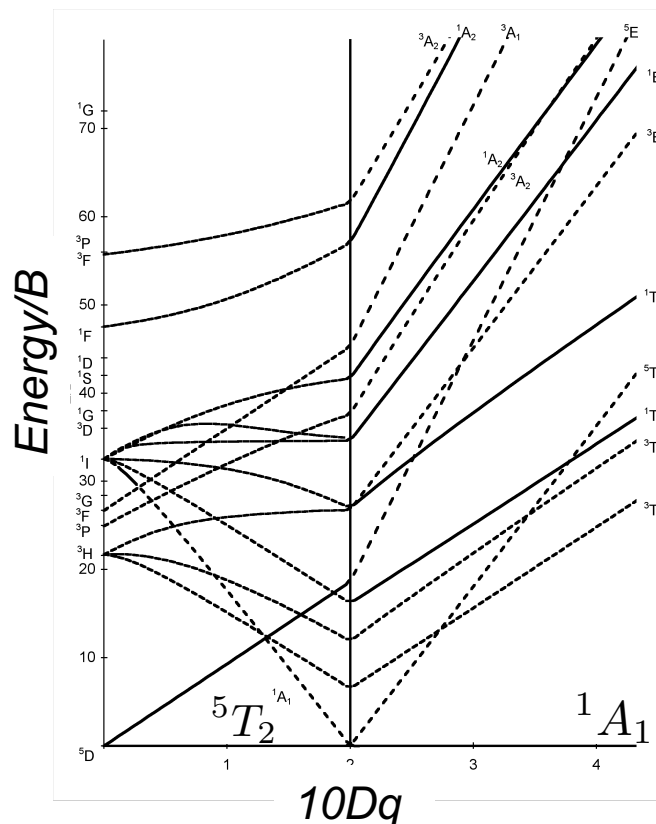
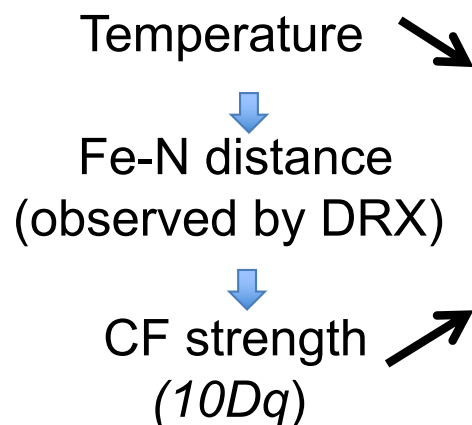
Ex of application: thermochromic painting

Magnetism:

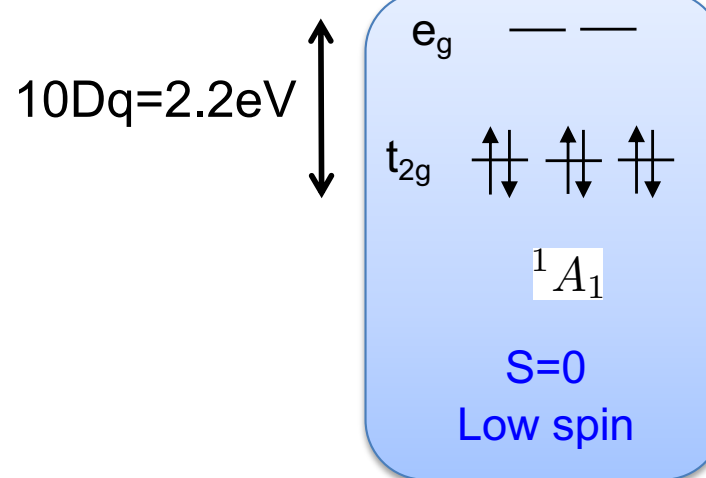
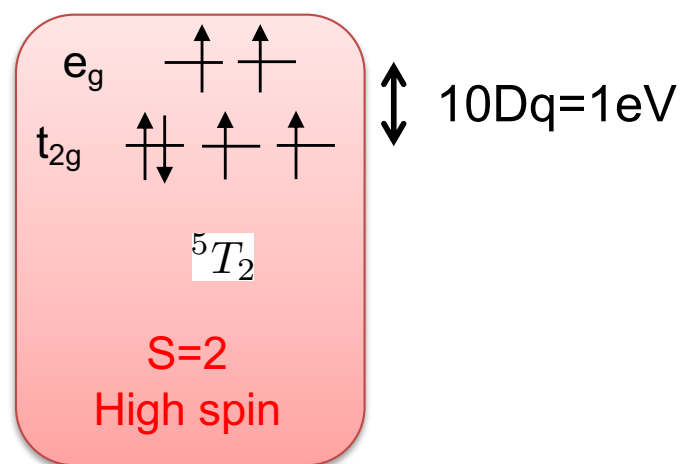
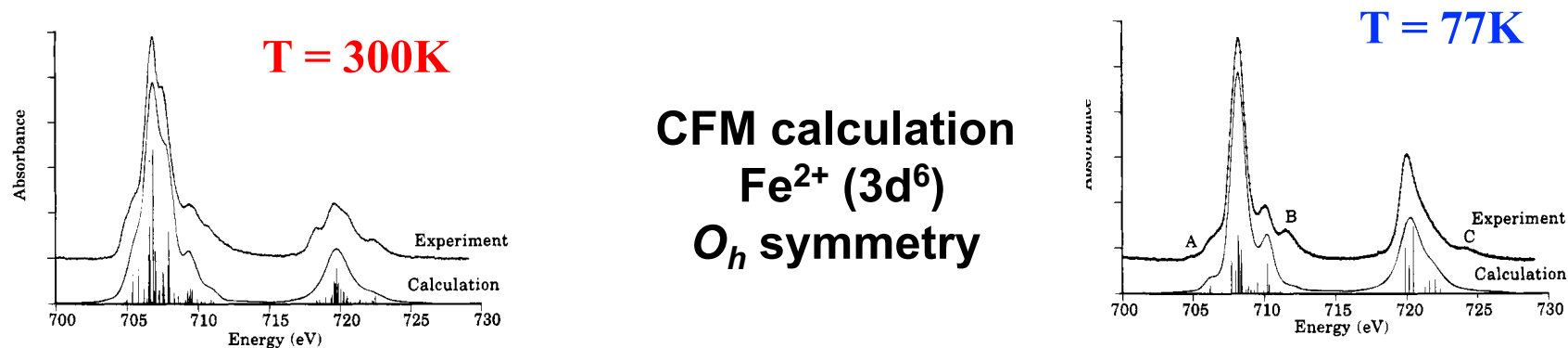
- switch between “0”(LS) and “1”(HS)
- driven by external stimuli (temperature, light, ...)
- couple to surface (insulating or conducting)
for **molecular spintronic**



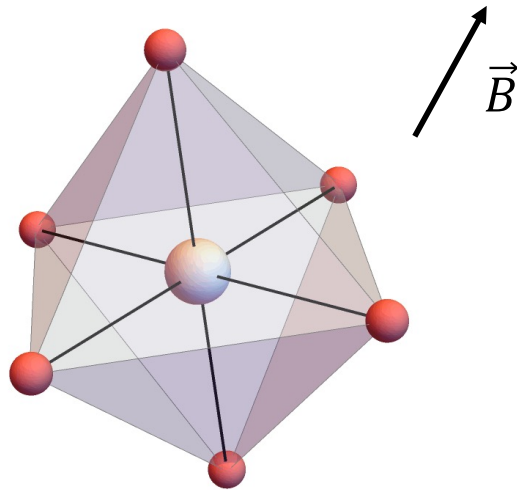
Fe²⁺ ion (3d⁶) in O_h symmetry



- Magnetic properties goes from paramagnetic to non-magnetic

XAS at Fe $L_{2,3}$ edges (2p→3d)

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



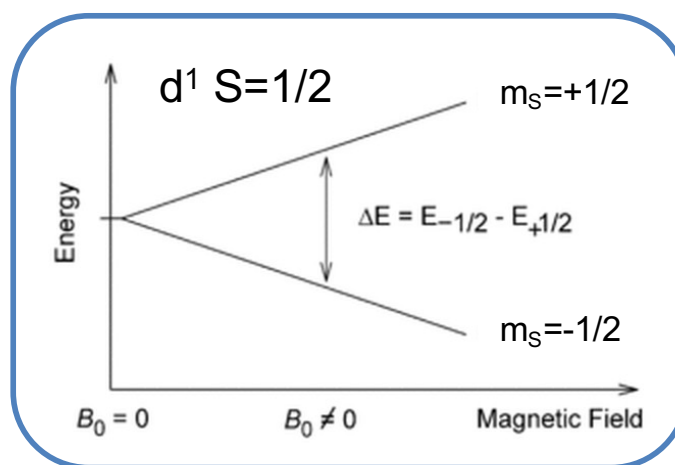
Hamiltonian

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

Free ion (spherical) Crystal field External Magnetic field Magnetic coupling With neighbours (ferro/antiferro-magnetism)

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

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



$$\text{➤ } H_{\text{Exchange}} \approx \hat{S} \cdot \hat{B}_{\text{exch}}$$

Crystal field and magnetism

Magnetic moments

➤ Magnetic moments : Definitions

$$M = M_{orbit} + M_{spin}$$

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

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

(in $\hbar$ unit, $g_0 \approx 2$)



z is the direction of the external magnetic field

➤ Crystal field effect

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

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

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



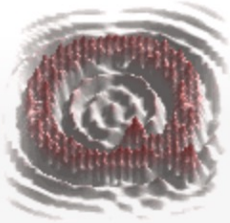
$H_{cin} + H_{e-n} + H_{e-e} + H_{s-o}$ commute with $\hat{J}^2, \hat{J}_z, \hat{L}^2, \hat{S}^2$
 $(H_{cin} + H_{e-n} + H_{e-e})$ commute with $\hat{L}^2, \hat{L}_z, \hat{S}^2, \hat{S}_z$

Magnetic moments with Quanty

- **Quanty**: calculates 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:

$$S_z = \sum_{\tau} \frac{1}{2} (a_{\tau\uparrow}^{\dagger} a_{\tau\uparrow} - a_{\tau\downarrow}^{\dagger} a_{\tau\downarrow}).$$

The equivalent operator in Quanty is created by:

Example.Quanty

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

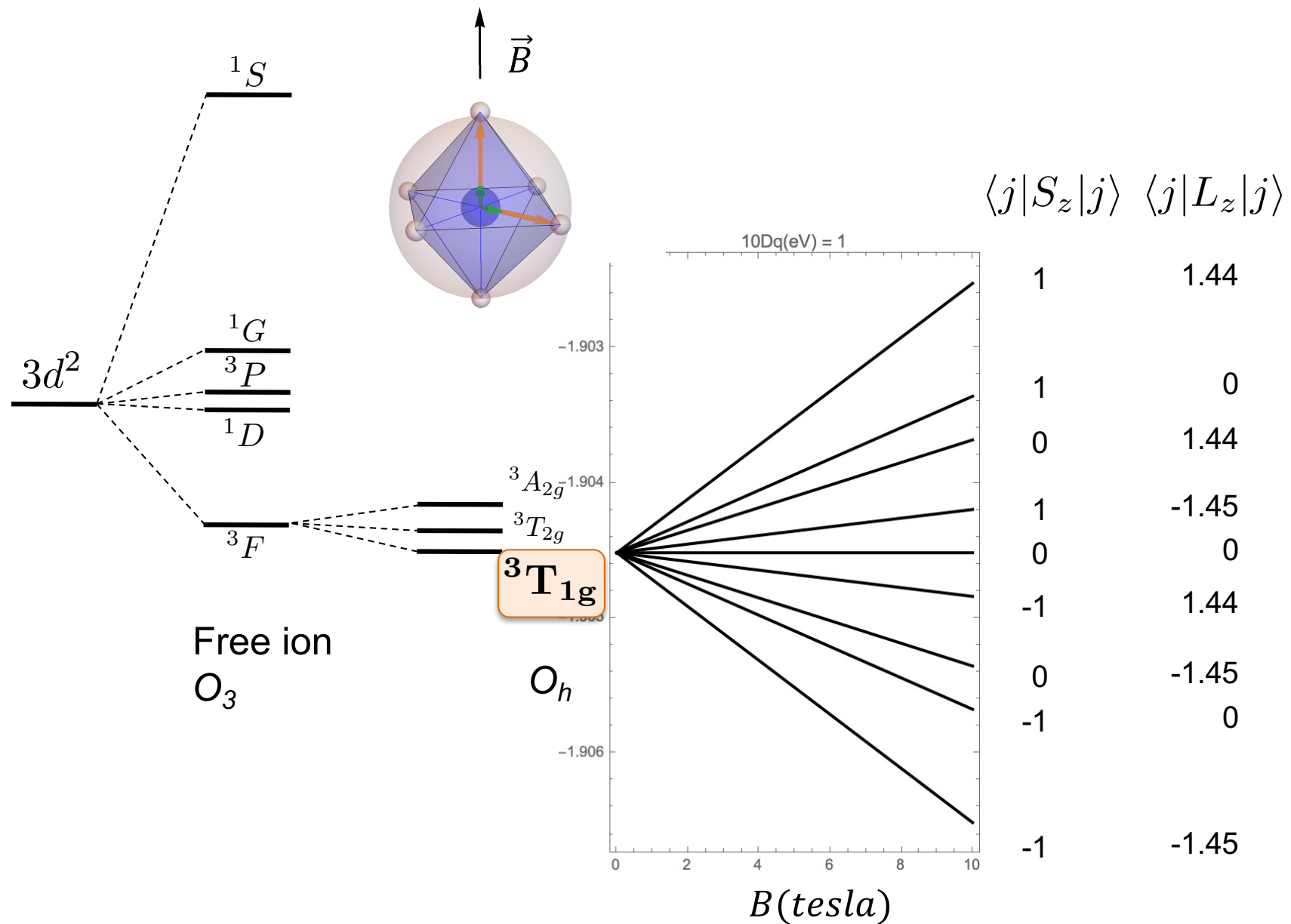
Table of contents

- Smin
- Splus
- Ssq
- Sx
- Sy
- Sz

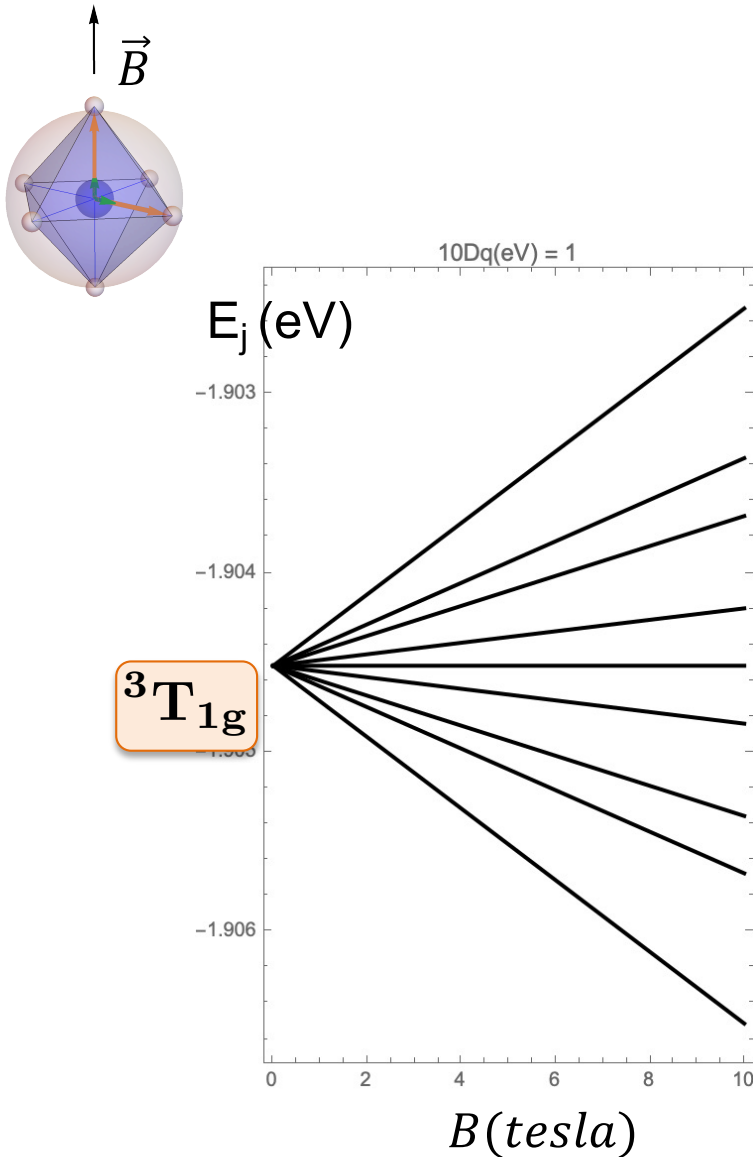


Tutorial 07_Expectationvalues.Quanty
(Monday morning)

III Crystal field and magnetism Paramagnetic d^2 ion



III Crystal field and magnetism Paramagnetic d^2 ion



Magnetization at temperature T

Boltzmann distribution

- The j^{th} state contribution is

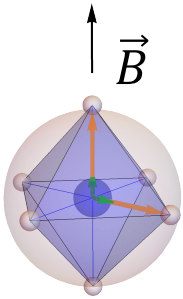
$$\frac{\exp\left(\frac{E_j - E_0}{k_B T}\right)}{\sum_{j=1}^{Nb \text{ states}} \exp\left(\frac{E_j - E_0}{k_B T}\right)}$$

- $\langle S_z \rangle$ value at T is

$$\langle S_z \rangle (T) = \frac{\sum_{j=1}^{Nb \text{ states}} \langle j | S_z | j \rangle \exp\left(\frac{E_j - E_0}{k_B T}\right)}{\sum_{j=1}^{Nb \text{ states}} \exp\left(\frac{E_j - E_0}{k_B T}\right)}$$

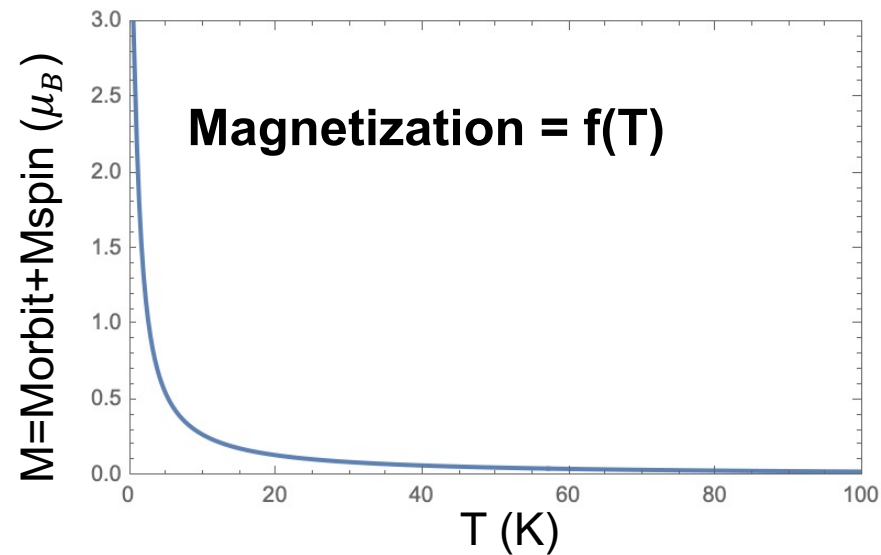
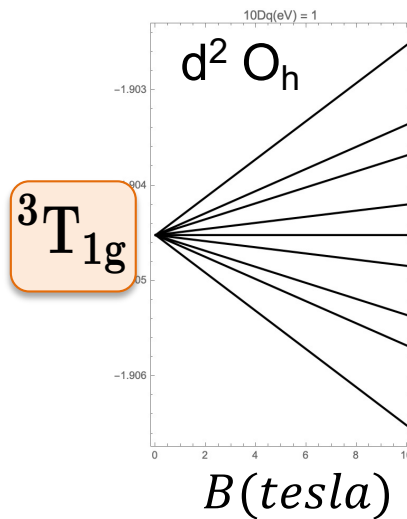
- Same expression for $\langle L_z \rangle$ value at T

III Crystal field and magnetism Paramagnetic d^2 ion



Magnetization at temperature T

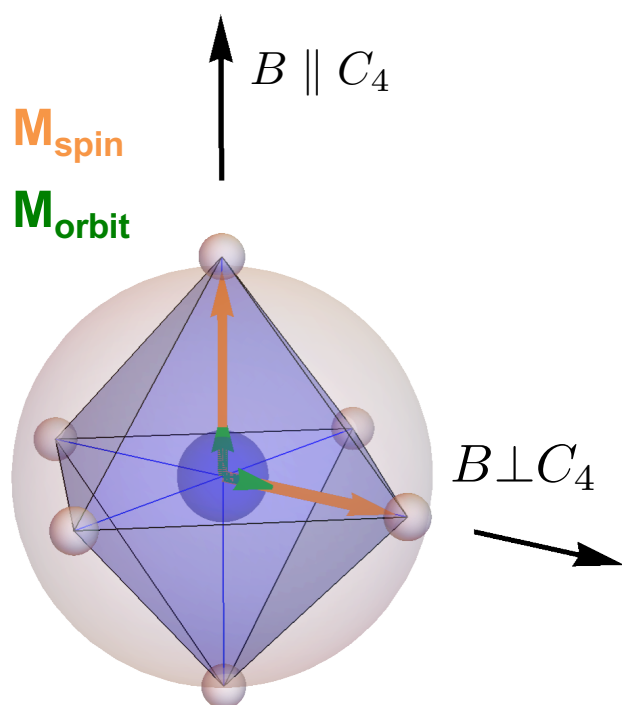
Boltzmann distribution



More in next tutorials

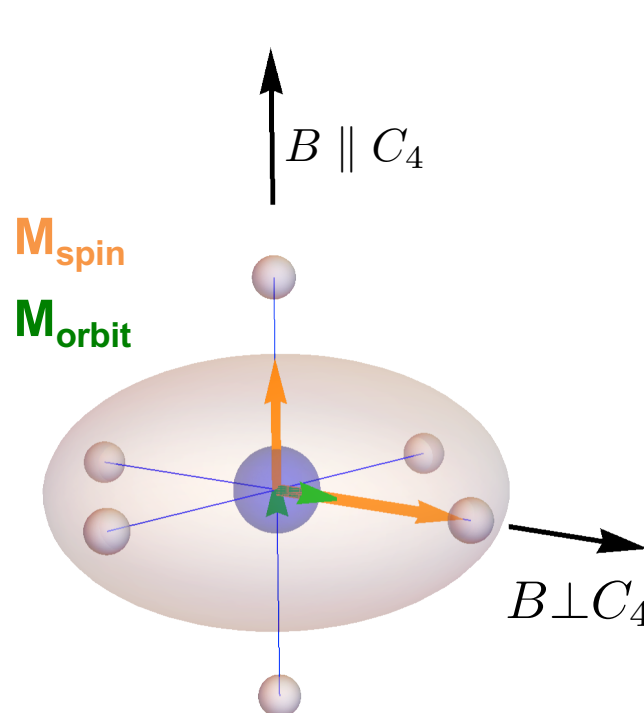
Temperature_and_Boltzmann_statistics.Quanty
Paramagnetic_Susceptibility_NiO.Quanty
Magneticsusceptibility_NiO.Quanty

O_h
Isotropic

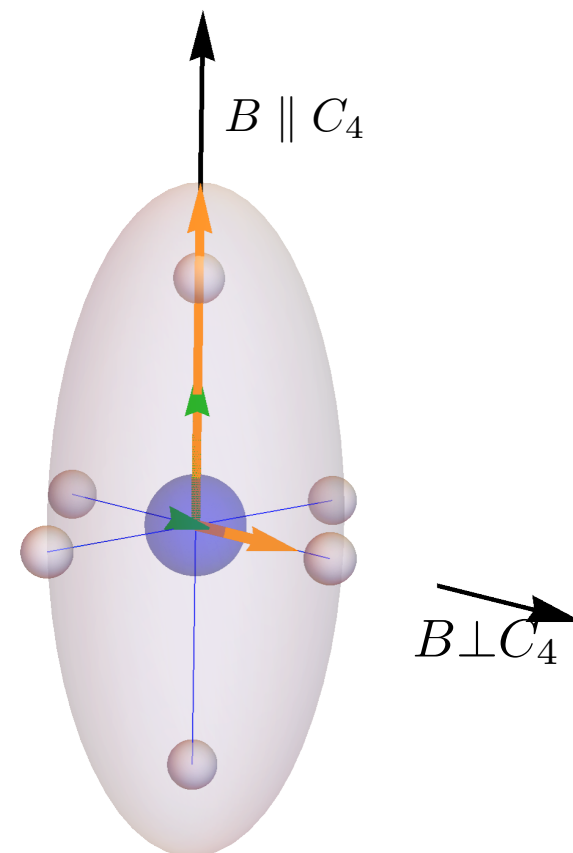


Tetragonal distortion : D_{4h}

Compression
Easy magnetization plane



Elongation
Easy magnetization axis



Crystal field and magnetism

Spin-spin exchange interaction

Heisenberg Hamiltonian

$$H_{Exchange} = - \sum_{i < j} J_{ij} \hat{S}_i \hat{S}_j$$

Simplified Hamiltonian for atomic calculation

$$H_{Exchange} \approx \hat{S} \cdot \hat{B}_{exch}$$

Spin operator
of the ion

Average field resulting from the exchange
with neighbor spins

Conclusion / remarks

- Multiplet theory with crystal field is an **atomic model**
- Crystal/ligand field is a **semi-empirical** model (parameter dependent)
can be linked to more *ab-initio* methods (tight-binding, DFT, CASSCF, DMFT...)
- Crystal field can create **natural and/or magnetic anisotropies**
- Works for ***core hole spectroscopies when excited states are localized (3d,4f ions)***
 - **Calculations including the core-hole** (ex : $2p^5 3d^{n+1}$, $3d^9 4f^{n+1}$,...)
 - **Multipole Transitions** : electric dipole, electric quadrupole, magnetic dipole...