Atomic Multiplet theory and Crystal fied Multielectron ions

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EXPOSITION

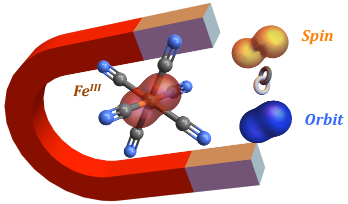
Physique des minéraux une histoire de découvertes

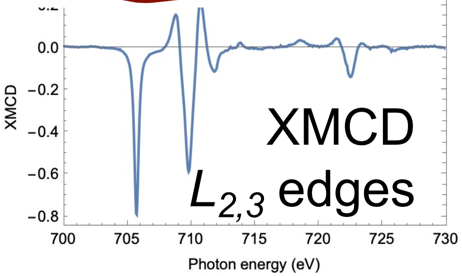
Jusqu'au 30 novembre 2024
à la Collection de minéraux
de Sorbonne Université

Campus pierre et Marie Curie
Patio 14-25, 4 place Jussieu
75005 Paris

Ouvert du mardi au samedi
de 13h à 18h hors jours fériés
https://mineraux.sorbonne-universite.fr/

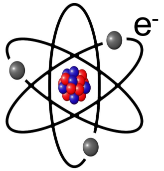
Molecular magnetism



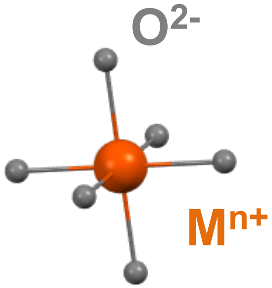


Atomic multiplet theory: N-electrons atom/ion

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.

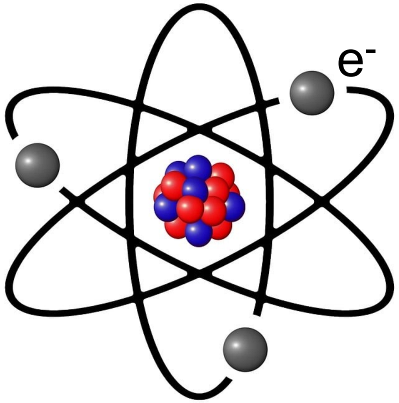
- *Free ion (spherical) + crystal field (+magnetism)*

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

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

I

Atomic multiplet theory: N-electrons atom/ion
The free ion case



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

	complete	simplified (open shell)
3d transition metal ions	$1s^2 2s^2 2p^6$ **$3d^n$**	**$3d^n$**
4f rare earth ions	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ **$4f^n$**	**$4f^n$**

Orbital level = shell
Partially filled = open shell

Quantum numbers:

n principal
ℓ orbital $(0 \leftrightarrow \mathrm{s}, 1 \leftrightarrow \mathrm{p}, 2 \leftrightarrow d, \dots), m_\ell$
s spin, m_s

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Atomic multiplet theory: N-electrons atom/ion
The free ion case

Quantum numbers:

n $principal$
ℓ $orbital$ $(0 \leftrightarrow \mathrm{s}, 1 \leftrightarrow \mathrm{p}, 2 \leftrightarrow d, \dots), m_\ell$
s $spin$, m_s

1 electron

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

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

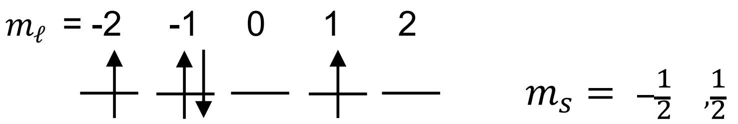
ℓ_i and m_{ℓ_i} quantum numbers associated to $\hat{\ell}_i^2$, $\hat{\ell}_{z,i}$

$$\hat{\ell}_i^2|\ell_i m_{\ell_i}\rangle = \ell_i(\ell_i+1)|\ell_i m_{\ell_i}\rangle$$
$$\hat{\ell}_{z,i}|\ell_i m_{\ell_i}\rangle = m_{\ell_i}|\ell_i m_{\ell_i}\rangle$$
$$-\ell_i \leqslant m_{\ell_i} \leqslant \ell_i$$

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

I N-electrons atom/ion : the free ion case

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

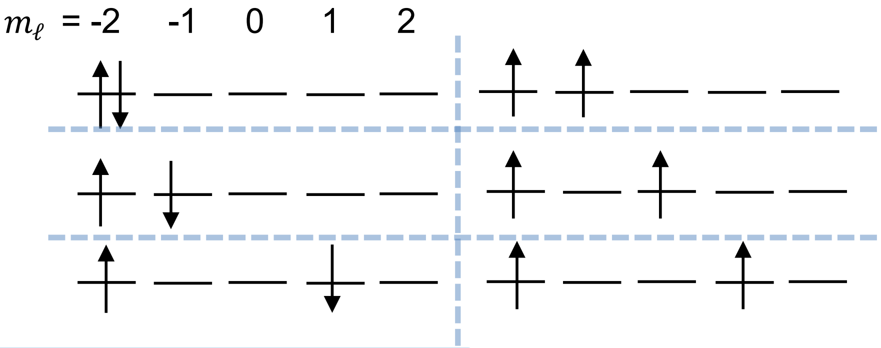


x $2\ell+1=5$ $|\ell, m_\ell\rangle$ angular functions
$2s+1=2$ $|s m_s\rangle$ spin functions } 10 functions

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

Example :

Some possibilites:



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

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

degenerate states

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

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N-electrons atom/ion : Hamilitonian

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

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

Total kinetic energy

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

Coulomb attraction nuclei-electrons

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

Electron-electron Coulomb repulsions

$$H_{s-o} = \sum_{i=1}^{N} \xi(r_i)\hat{\ell}_{\mathbf{i}}.\hat{\mathrm{s}}_{\mathbf{i}}$$

Spin-orbit coupling

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N-electrons atom/ion : *Basis functions* |Ψ>

- 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**

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

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

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

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N-electrons atom/ion
Coulomb interaction -Slater intergral

$$H_{ion} = \underbrace{H_{kin} + H_{e-n}}_{} + H_{e-e} + \cancel{H_{s-o}}$$

Contribute to the configuration energy
No degeneracy lifting

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

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

⇨ see also *Lecture* from Maurits Haverkort
haverkort_coulomb_repulsion.pptx

N-electrons atom/ion : Coulomb interaction -Slater intergral

(slide from M. Haverkort)

Coulomb Hamiltonian:

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

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

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

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

(slide from M. Haverkort)

Expansion on renormalized Spherical Harmonics

$$\sum_{i<j}^{n-1,n} \frac{1}{|r_i - r_j|} =$$

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

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

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

Radial

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

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

Angular

$$\times \left\langle \chi_{\sigma_{\tau_1}} \| \chi_{\sigma_{\tau_3}} \right\rangle \left\langle \chi_{\sigma_{\tau_2}} \| \chi_{\sigma_{\tau_4}} \right\rangle$$

$$= \delta_{\sigma_{\tau_1}\sigma_{\tau_3}} \delta_{\sigma_{\tau_2}\sigma_{\tau_4}}$$

Coulomb interaction – Slater Integrals

(slide from M. Haverkort)

Radial part: Slater integrals

$$R^{(k)}_{\tau_1,\tau_2,\tau_3,\tau_4} =$$

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

Angular part: Analytical solution

$$\left\langle Y^{(l_{\tau_1})}_{m_{\tau_1}}(\theta_1, \phi_1) \left| C^{(k)}_{m}(\theta_1, \phi_1) \right| Y^{(l_{\tau_3})}_{m_{\tau_3}}(\theta_1, \phi_1) \right\rangle$$

$$\times \left\langle Y^{(l_{\tau_2})}_{m_{\tau_2}}(\theta_2, \phi_2) \left| C^{(k)}_{m}(\theta_2, \phi_2)^* \right| Y^{(l_{\tau_4})}_{m_{\tau_4}}(\theta_2, \phi_2) \right\rangle$$

$$\times \left\langle \chi_{\sigma_{\tau_1}} \| \chi_{\sigma_{\tau_3}} \right\rangle \left\langle \chi_{\sigma_{\tau_2}} \| \chi_{\sigma_{\tau_4}} \right\rangle$$

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Coulomb interaction -Slater intergral

Angular part: Analytical solution

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

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

Coupling coefficients (Glebsch-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

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

$$\langle Y_{l_i}^{m_i}(\theta,\phi)\mid C_k^m(\theta,\phi)\mid Y_{l_j}^{m_j}(\theta,\phi)\rangle=$$

$$(-1)^{m_i}\sqrt{(2l_i+1)(2l_j+1)}\underbrace{\begin{pmatrix}l_i & k & l_j\\ 0 & 0 & 0\end{pmatrix}}\begin{pmatrix}l_i & k & l_j\\ -m_i & m & m_j\end{pmatrix}$$

$\neq 0$ if
$\ell_i+k+\ell_j$ even
$|\ell_i-\ell_j]\leqslant k\leqslant \ell_i+\ell_j$

Coulomb interaction – Slater Integrals

(slide from M. Haverkort)

d – electrons (3d^n)

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

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

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

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

≠ 0 if

$$k + 2\ell_i \text{ even} \Rightarrow k \text{ even}$$

$$|\ell_i - \ell_j] \leqslant k \leqslant \ell_i + \ell_j \Rightarrow 0 \leqslant k \leqslant 4$$

$$k = 0, 2, 4$$

$$R_{2,2,2,2}^{(0,2,4)} = F^{(0,2,4)}$$

Direct Slater integrals

Coulomb interaction – Slater Integrals

(slide from M. Haverkort)

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

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

$$\left\langle Y^{(l_{\tau_1})}_{m_{\tau_1}}(\theta_1,\phi_1) \middle| C^{(k)}_{m}(\theta_1,\phi_1) \middle| Y^{(l_{\tau_3})}_{m_{\tau_3}}(\theta_1,\phi_1) \right\rangle$$

$$\times \left\langle Y^{(l_{\tau_2})}_{m_{\tau_2}}(\theta_2,\phi_2) \middle| C^{(k)}_{m}(\theta_2,\phi_2)^{*} \middle| Y^{(l_{\tau_4})}_{m_{\tau_4}}(\theta_2,\phi_2) \right\rangle$$

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

$\neq 0$ if

$$k + 2\ell_i \text{ even} \quad \Rightarrow \quad k \text{ even}$$

$$(0 \leqslant k \leqslant 2 \text{ and } 0 \leqslant k \leqslant 4) \Rightarrow 0 \leqslant k \leqslant 2$$

$$k = 0, 2$$

$$R^{(0,2)}_{2,1,2,1} = F^{(0,2)}$$

Direct Slater integrals between inequivalent e$^-$

Coulomb interaction – Slater Integrals

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

(slide from M. Haverkort)

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

$$\left\langle Y^{(l_{\tau_1})}_{m_{\tau_1}}(\theta_1, \phi_1) \middle| C^{(k)}_{m}(\theta_1, \phi_1) \middle| Y^{(l_{\tau_3})}_{m_{\tau_3}}(\theta_1, \phi_1) \right\rangle$$
$$\times \left\langle Y^{(l_{\tau_2})}_{m_{\tau_2}}(\theta_2, \phi_2) \middle| C^{(k)}_{m}(\theta_2, \phi_2)^{*} \middle| Y^{(l_{\tau_4})}_{m_{\tau_4}}(\theta_2, \phi_2) \right\rangle$$

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

≠ 0 if

$$k + 3 \text{ even} \;\Rightarrow\; k \text{ odd}$$
$$|\ell_i - \ell_j] \leqslant k \leqslant \ell_i + \ell_j \Rightarrow 1 \leqslant k \leqslant 3$$

$$k = 1, 3$$

$$R^{(1,3)}_{2,1,1,2} = G^{(1,3)}$$

Exchange Slater integrals between inequivalent e^-

Coulomb interaction – Slater Integrals

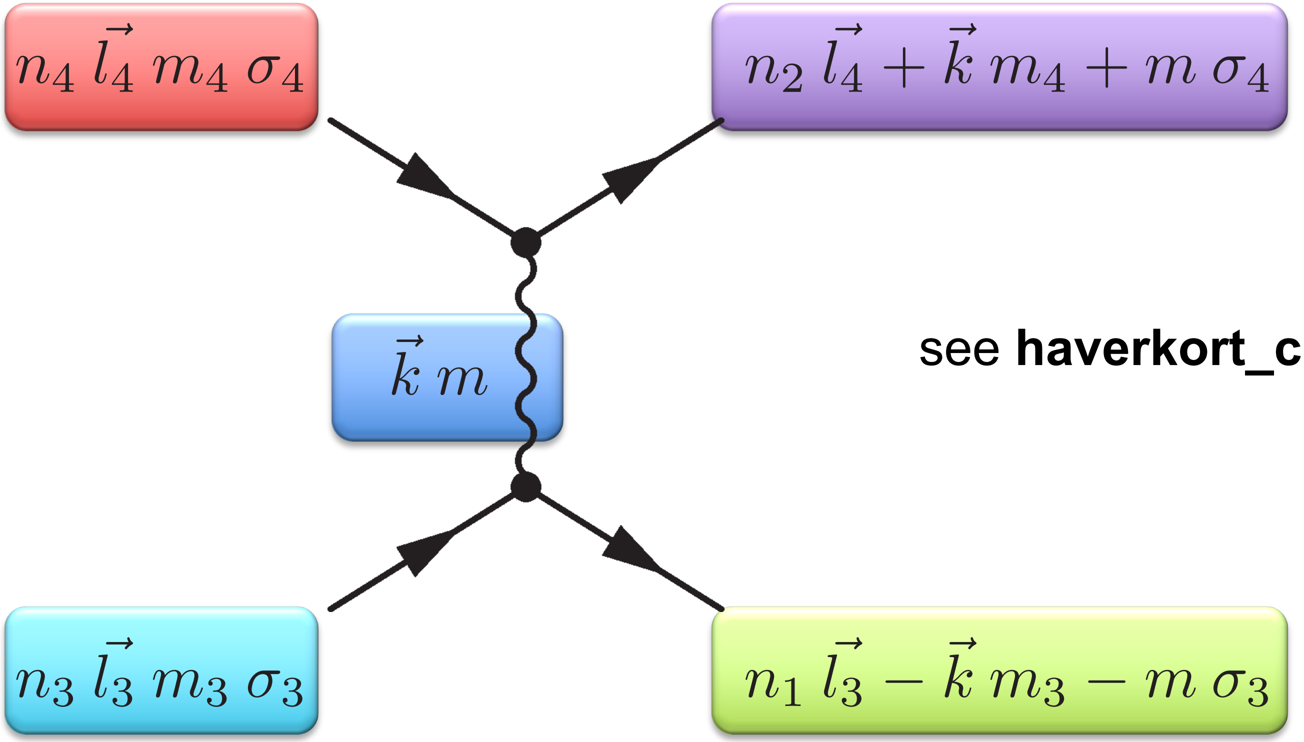
Graphical representation

$$\left\langle Y^{(l_{\tau_1})}_{m_{\tau_1}}(\theta_1,\phi_1)\middle| C^{(k)}_{m}(\theta_1,\phi_1)\middle| Y^{(l_{\tau_3})}_{m_{\tau_3}}(\theta_1,\phi_1)\right\rangle$$

$$\times\left\langle Y^{(l_{\tau_2})}_{m_{\tau_2}}(\theta_2,\phi_2)\middle| C^{(k)}_{m}(\theta_2,\phi_2)^{*}\middle| Y^{(l_{\tau_4})}_{m_{\tau_4}}(\theta_2,\phi_2)\right\rangle$$

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

(slide from M. Haverkort)



see **haverkort_coulomb_repulsion.pptx**

Coulomb interaction -Slater intergral

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

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

$$\sum_{k=0}^{2\ell_j}\sum_{j}^{shells} f_k(\ell_j,\ell_j)\,F^k(\ell_j,\ell_j)$$

radial integrals
“Slater-Condon”

angular integrals
Depend on orbital momentum
and electron filling of the shells

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

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

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

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

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

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

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

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

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

Coulomb interaction - Slater intergral

Core hole ⇒ 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

I

Coulomb interaction : *Basis functions* |L,S,M$_L$,M$_S$>

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

- Basis function for N-electrons $|LSM_LM_S\rangle$

$$\hat{L} = \sum_{i=1}^{N} \hat{\ell}_i$$ is the total electronic orbital momentum of the atom

⚠ $\sum$ means $\oplus$: coupling of angular momentum

$$\hat{S} = \sum_{i=1}^{N} \hat{s}_i$$ is the total electronic spin momentum of the atom

- **H$_{ion}$ and $\widehat{L}^2, \widehat{S}^2$ have common eigenfunctions**

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

I

Coulomb interaction : *Basis functions* |L,S,M_L ,M_S>

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

Basis function for N-electrons $|LSM_LM_S\rangle$

$$\hat{L} = \sum_{i=1}^{N} \hat{\ell}_i$$ is the total orbital momentum of the atom

$$\hat{S} = \sum_{i=1}^{N} \hat{s}_i$$ is the total spin momentum of the atom

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Exemple : 2-electrons

Coupling of angular momentum

$$|\ell_1\ell_2LM_L\rangle = \sum_{m_1=-\ell_1}^{\ell_1}\sum_{m_2=-\ell_2}^{\ell_2} \underbrace{\langle \ell_1\ell_2m_1m_2|\ell_1\ell_2LM_L\rangle}|\ell_1m_1\rangle|\ell_2m_2\rangle$$

Clebsch-Gordan coefficients related to 3-j symbols

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

$$\langle \ell_1\ell_2m_1m_2|\ell_1\ell_2LM_L\rangle = (-1)^{\ell_2-\ell_1-M_L}\sqrt{2L+1}\overbrace{\begin{pmatrix} \ell_1 & \ell_2 & L \\ m_1 & m_2 & -M_L \end{pmatrix}}$$

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Coulomb interaction : *Basis functions* |L,S,M$_L$,M$_S$>

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

➡ Basis function for N-electrons

➡ Exemple : 2-electrons

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

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

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

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

$|L S M_L M_S\rangle$ antisymmetric combination of $|\ell_1 \ell_2 L M_L$ and $|s_1 s_2 S M_S\rangle$

I

Coulomb interaction
Basis functions |L,S,M$_L$,M$_S$> - Spectroscopic terms

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

➡ Basis function for N-electrons $|LSM_LM_S\rangle$

- ✓ The energy of $|LSM_LM_S\rangle$ 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$_S$>

$^{2S+1}\Gamma$

Spin multipliciy

letter for **L**

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

I

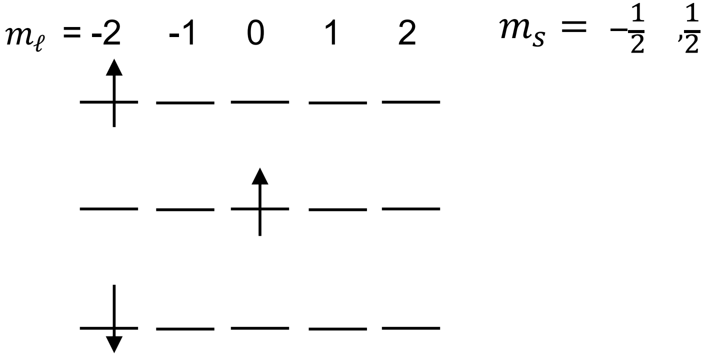
Coulomb interaction

Basis functions |L,S,M_L ,M_S> - Spectroscopic terms

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

Exemple: *d*^{1}

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



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

$L = \ell = 2$ → D term

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

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

d^1

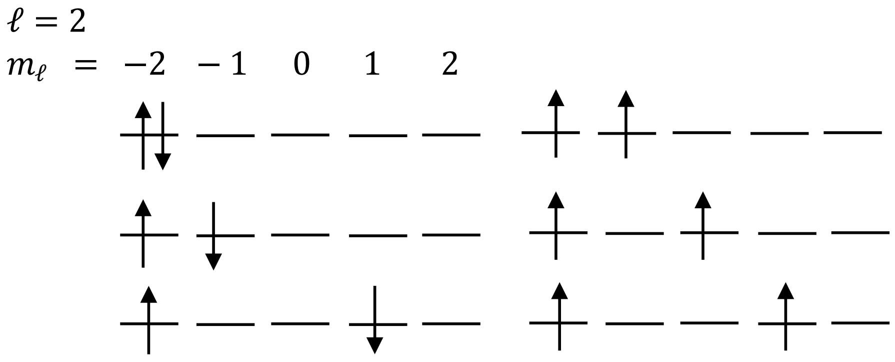
1 Degenerate state
Multiplicity =10
Spin doublet

I

Coulomb interaction
States/*Spectroscopic terms for 3d² ion*

3d²

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



$$\hat{L} = \hat{\ell} \oplus \hat{\ell} \qquad 0 \leqslant L \leqslant 2\ell = 4 \qquad L = 0, 1, 2, 3, 4$$

(by step 1)

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

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

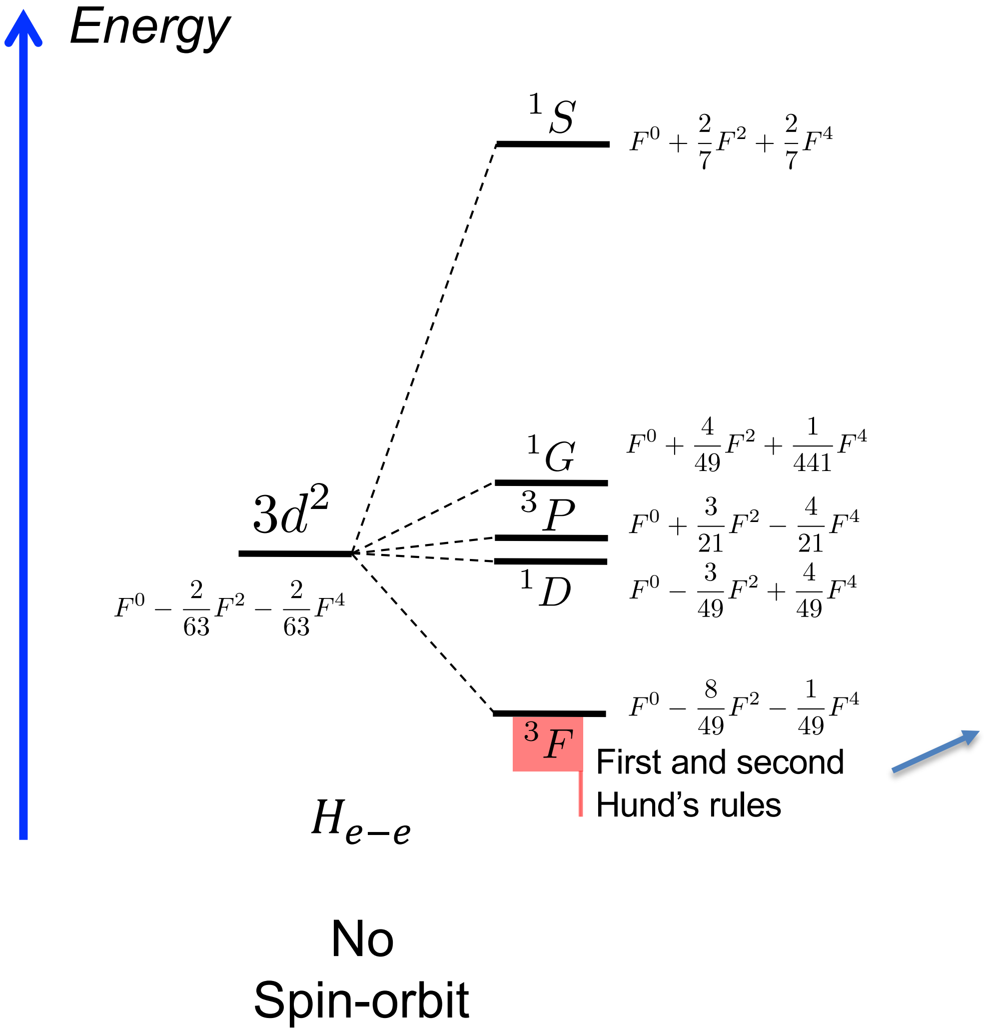
Antisymmetric states
5 terms/states

$$\boxed{{}^1S,\ {}^3P,\ {}^1D,\ {}^3F,\ {}^1G}$$

I

Coulomb interaction

States/*Spectroscopic terms for 3d² ion*



Ground state:

Given by **Hunds rules**

1. max S
2. max L

N-electrons atom/ion : the free ion case

Spin-orbit coupling

$$\mathbf{H_{ion}} = \underbrace{H_{kin} + H_{e\text{-}n} + \mathbf{H_{e\text{-}e}} + \mathbf{H_{s\text{-}o}}}_{\text{Free ion (spherical)}}$$

$$H_{s-o} = \sum_{i=1}^{N} \xi(r_i)\hat{\ell}_{\mathbf{i}}.\hat{\mathbf{s}}_{\mathbf{i}}$$ Spin-orbit coupling

N-electrons atom/ion : the free ion case

Spin-orbit coupling : basis function

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

- Basis functions for N-electrons $|(LS)JM_J>$

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

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

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

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

- The energy of $|(LS)JM_J>$ does not depend on M_J

  Degeneracy = 2J+1

I

N-electrons atom/ion : the free ion case

Spin-orbit coupling : spectroscopic terms

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

Basis function for N-electrons $|(LS)JM_J>$

Spectroscopic terms $|(LS)JM_J>$

$^{2S+1}\Gamma_J$

J value

Spin multipiicity

letter for **L**

Γ=S pour L=0

Γ=P pour L=1

Γ=D pour L=2

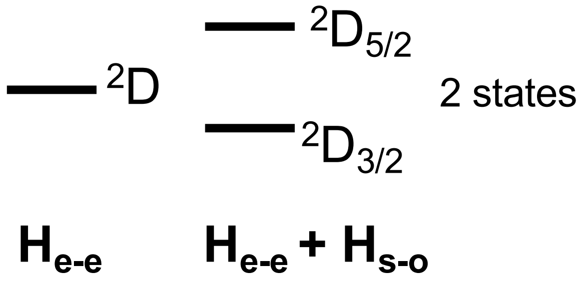
Γ=F pour L=3

Example: d^1

L=2, S=1/2

|L-S| ≤ J ≤ L+S

J=3/2,5/2



I

N-electrons atom/ion : the free ion case

Spin-orbit coupling : matrix elements

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

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

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

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

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

$$\langle \alpha LSJM_J | H_{\text{so}} | \alpha' L' S' J' M'_J \rangle = \sum_{j}^{shells} d_j \, \zeta_j$$

radial integrals
Numerical from HF calculations

angular integrals
Depend on the electron
configuration (analytical)

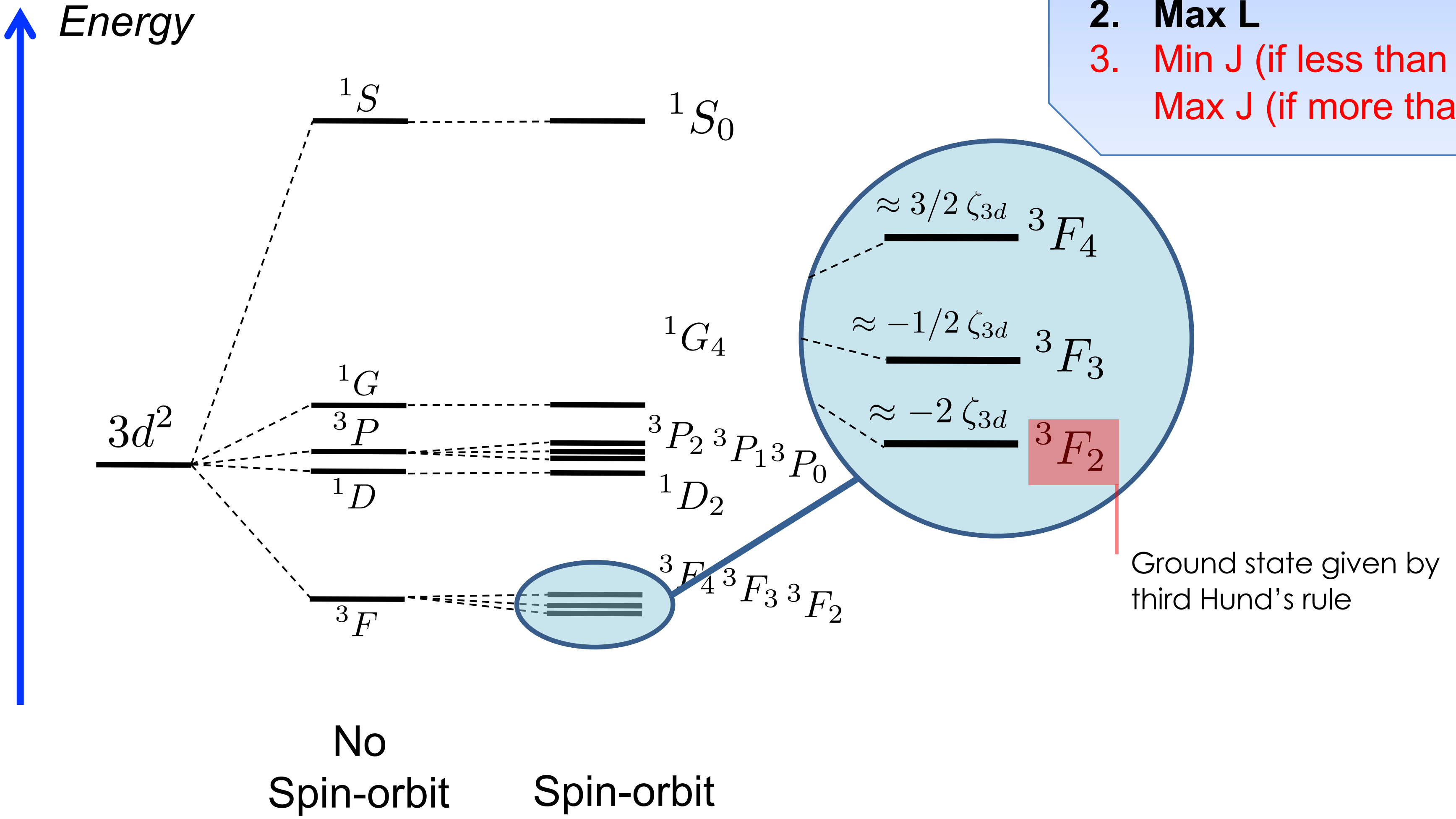
$$\zeta_j = \int_0^\infty \xi_i(r_i) |P_{n_j \ell_j}(r)|^2 dr$$

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 3d² ion*

Ground state:
Given by **Hunds rules**
1. **Max S**
2. **Max L**
3. Min J (if less than half full)
   Max J (if more than half full)



Ground state given by third Hund's rule

I

Coulomb interaction + spin-orbit

Core hole ⇒ 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}

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

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

⇩

Final (excited) configuration $2p^53d^{n+1}$

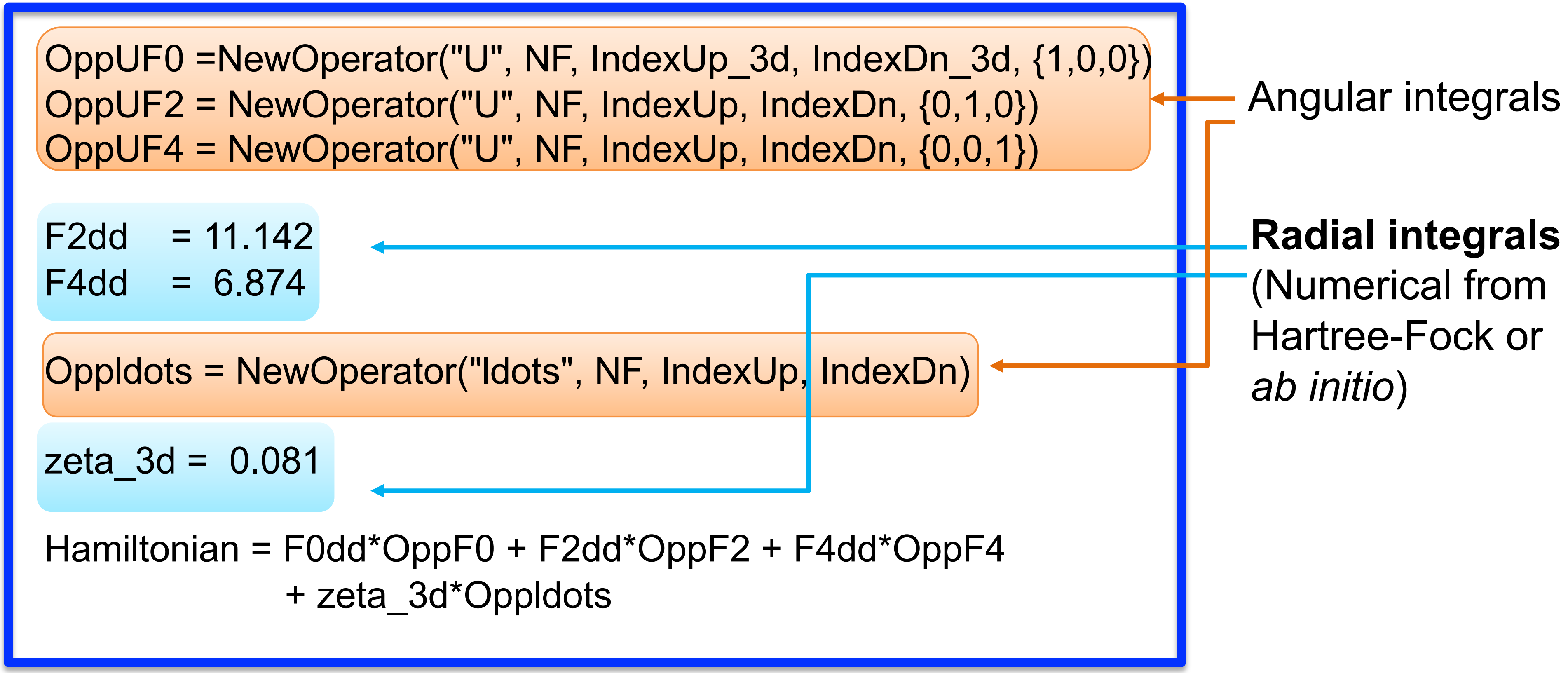
$F^2(3d,3d)$, $F^4(3d,3d)$ e^- 3d

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

+ ζ_{3d}, ζ_{2p}

Coulomb interaction + spin-orbit Quanty

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

Oppldots = NewOperator("ldots", NF, IndexUp, IndexDn)

zeta_3d =  0.081

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

Angular integrals

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

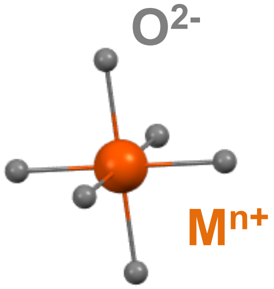
II

Atomic multiplet theory: N-electrons atom/ion

Crystal field

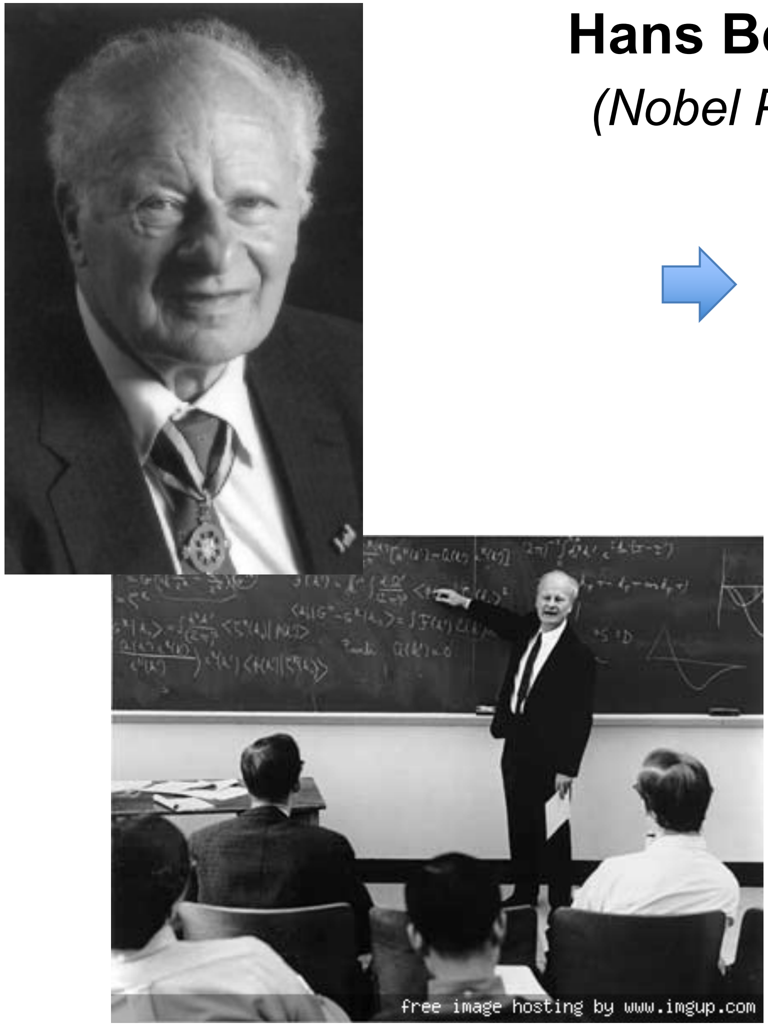
I. The free atom/ion case (spherical) : N-electrons atom/ion

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** “

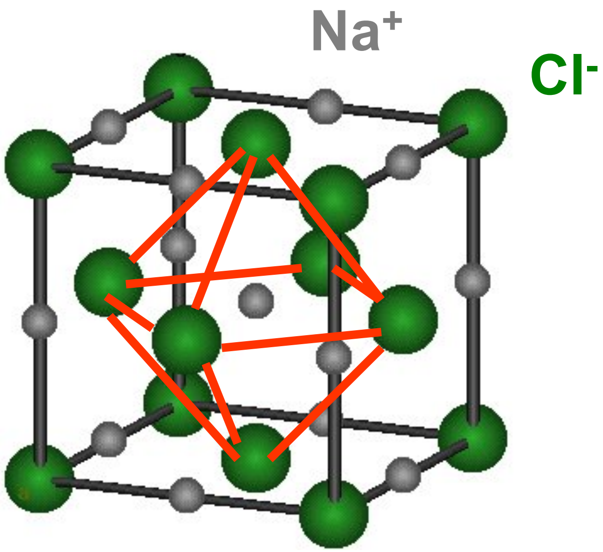
“the atom in the crystal is influenced by the other atoms by an **electric field** of certain symmetry“ = **Crystal field**

[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.

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:

$$V_{CF} = \sum_{i=1}^{6} \frac{e}{r_i}$$

(r_i = Na-Cl distance)

- Depends on the local symmetry

H. Bethe, Annalen der Physik, 1929

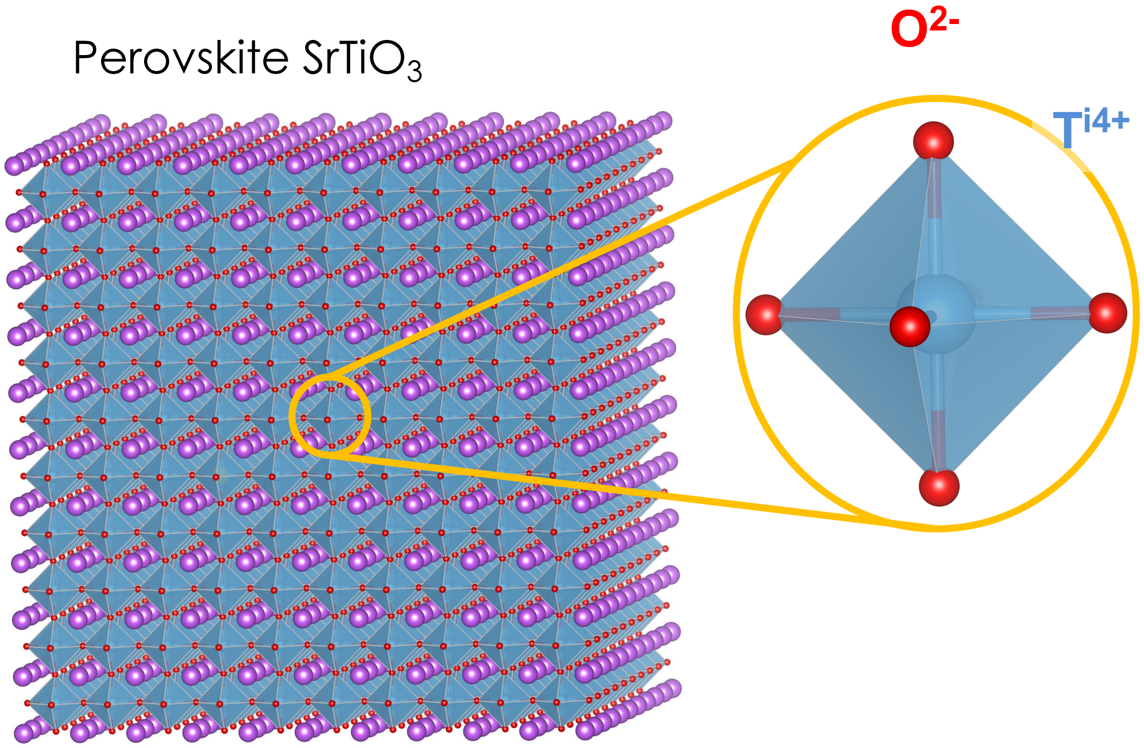
II

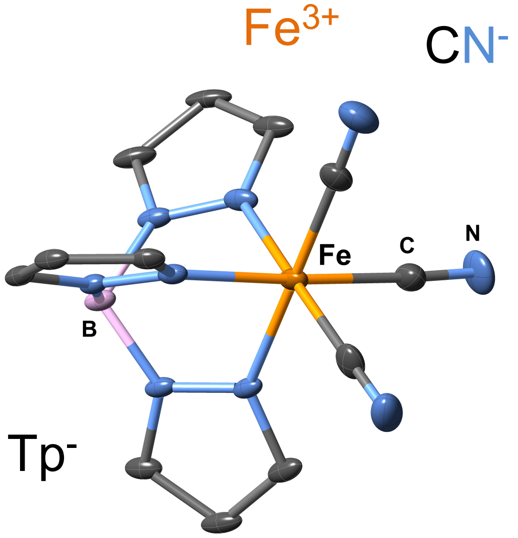
Crystal field : generalization

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

Local model (restricted to the first neighbors /ligands)

Perovskite $SrTiO_3$





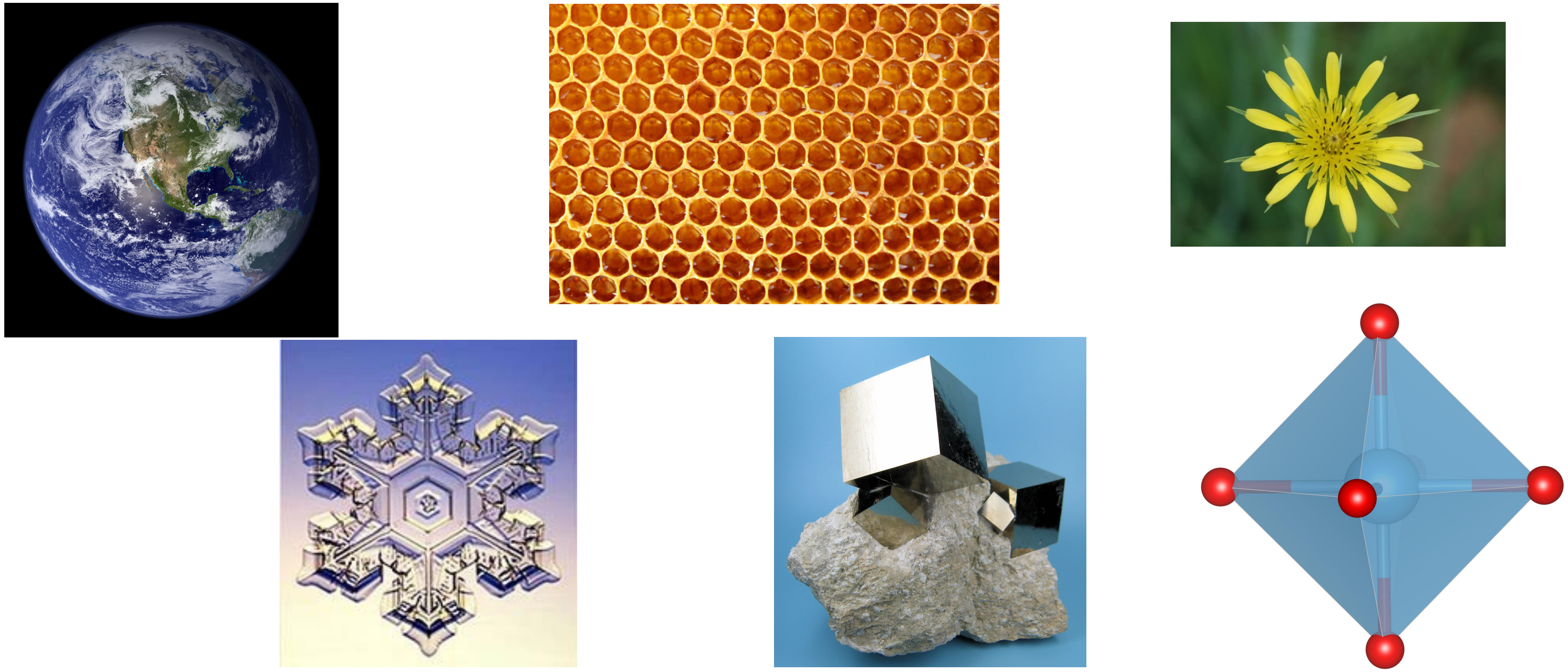
Tp=tris-pyrazolyl borate

II Crystal field Symmetry

Symmetry : responsible for many physical and spectroscopic properties of compounds

Group theory : powerful tool

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



II Crystal field Symmetry

Symmetry operations : some notations to know

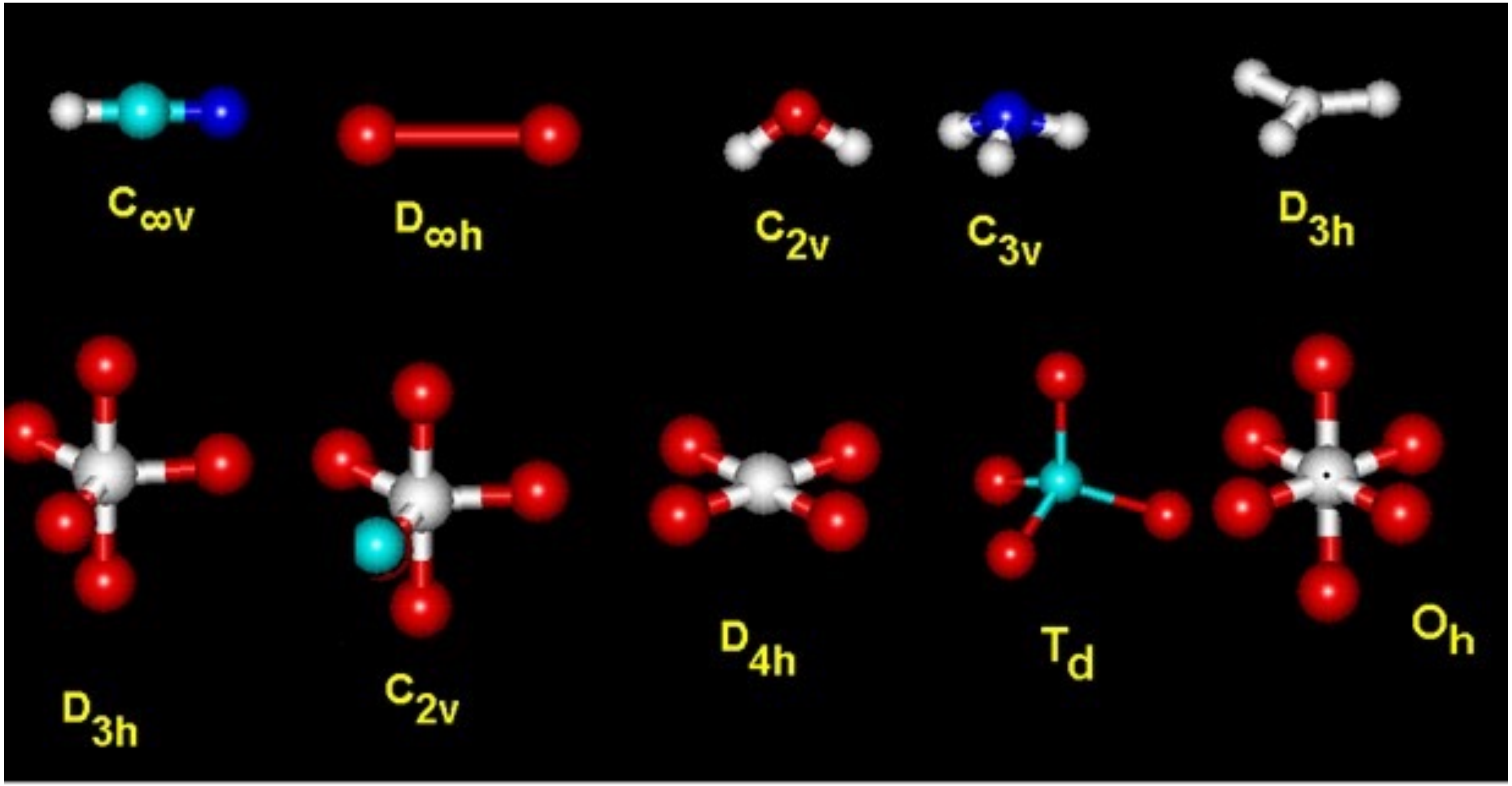
- **E**, the identity
- **C_n**, a rotation by an angle 2π/n;
- **σ** reflection in a plane, classified as
  - **σ_h**, reflection through a plane perpendicular to the axis of highest rotation symmetry, called *principal axis*
  - **σ_v,** reflection through a plane to which the principal axis belongs
  - **σ_d**, reflection through a plane to which the principal axis belongs, and bisecting the angle between the two-fold axes perpendicular to the principal axis.
- **$S_n = \sigma_h \otimes C_n$**, improper rotation of an angle 2π/n
- **$I = S_2$**, the inversion.

⇨ Quanty

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

Crystal field Symmetry – Point groups

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

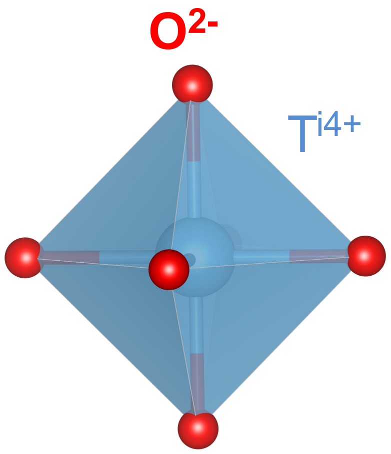


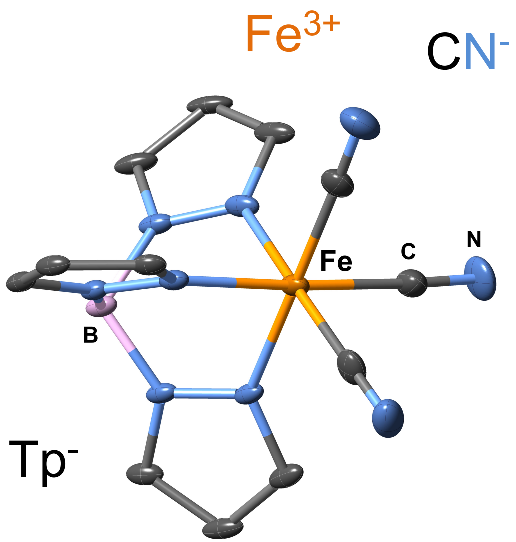
- Each group has a table of representations

Crystal field Symmetry – Point groups

$SrTiO_3$

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



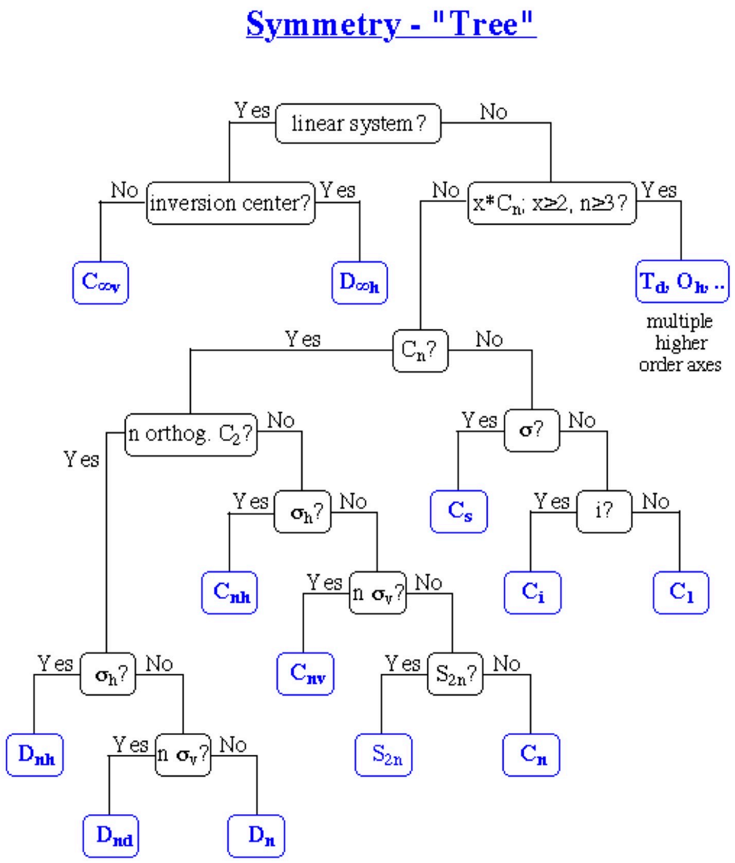


Octahedral
Group : O_h

Approximative
Trigonal group :
C_{3v}

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

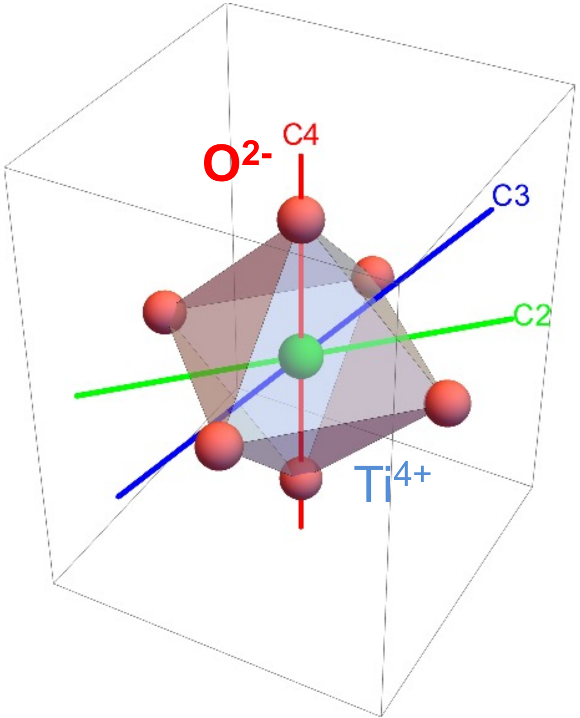
II Crystal field Symmetry – Point groups -tree


Symmetry - "Tree"

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

Crystal field Symmetry: *Octahedral O_h*

$SrTiO_3$



Group : O_h

Character table

Symmetry elements

Basis functions

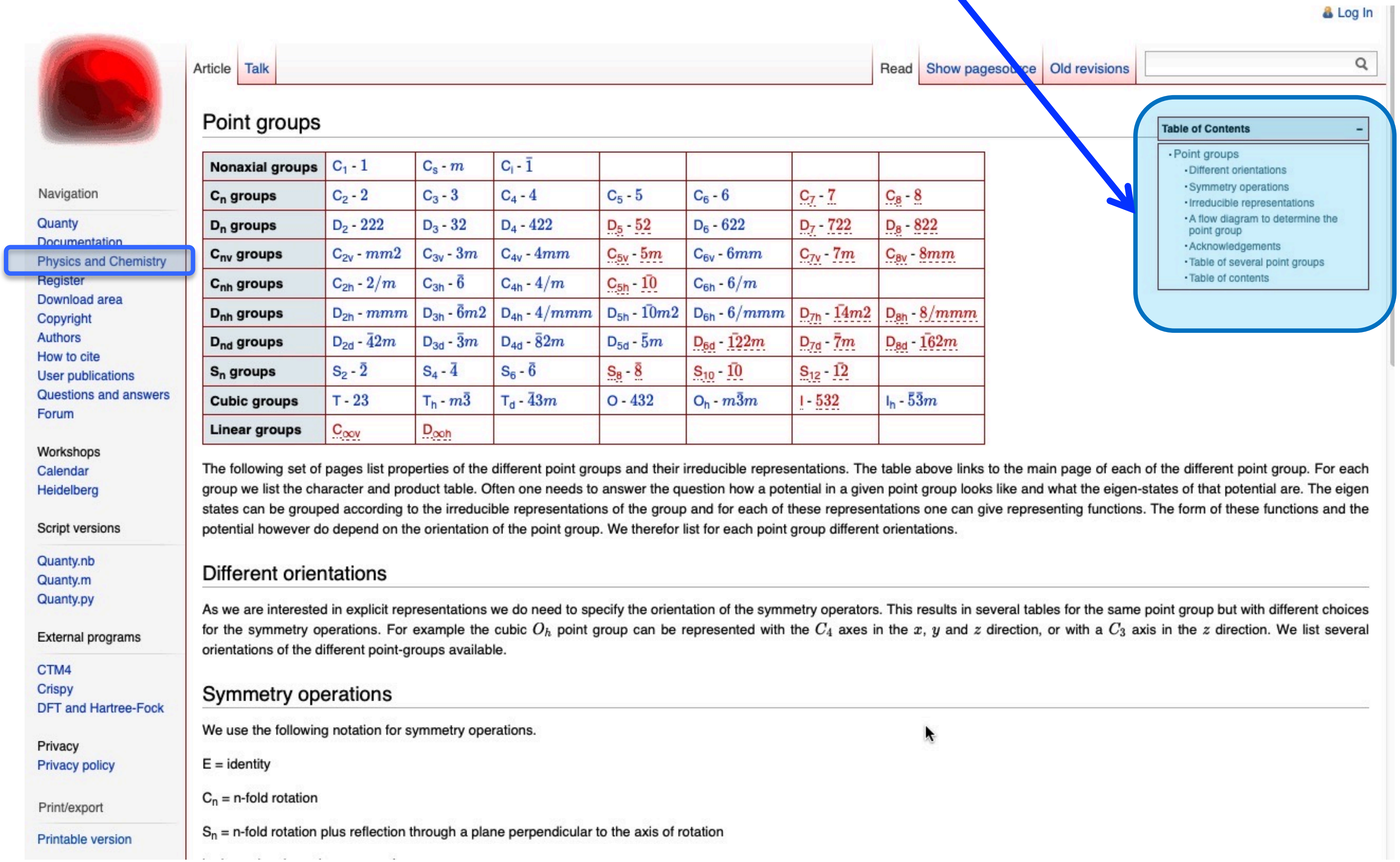
	E	$8C_3$	$6C_2$	$6C_4$	$3C_2 = (C_4)^2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	linear, rotations	quadratic
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1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

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

II

Crystal field *Point groups: Quanty website*

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



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} - $\overline{10}$	C_{6h} - $6/m$		
D_{nh} groups	D_{2h} - mmm	D_{3h} - $\bar{6}m2$	D_{4h} - $4/mmm$	D_{5h} - $\overline{10}m2$	D_{6h} - $6/mmm$	D_{7h} - $\overline{14}m2$	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} - $\overline{12}2m$	D_{7d} - $\bar{7}m$	D_{8d} - $\overline{16}2m$
S_n groups	S_2 - $\bar{2}$	S_4 - $\bar{4}$	S_6 - $\bar{6}$	S_8 - $\bar{8}$	S_{10} - $\overline{10}$	S_{12} - $\overline{12}$	
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 - $\bar{5}\bar{3}m$
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 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

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

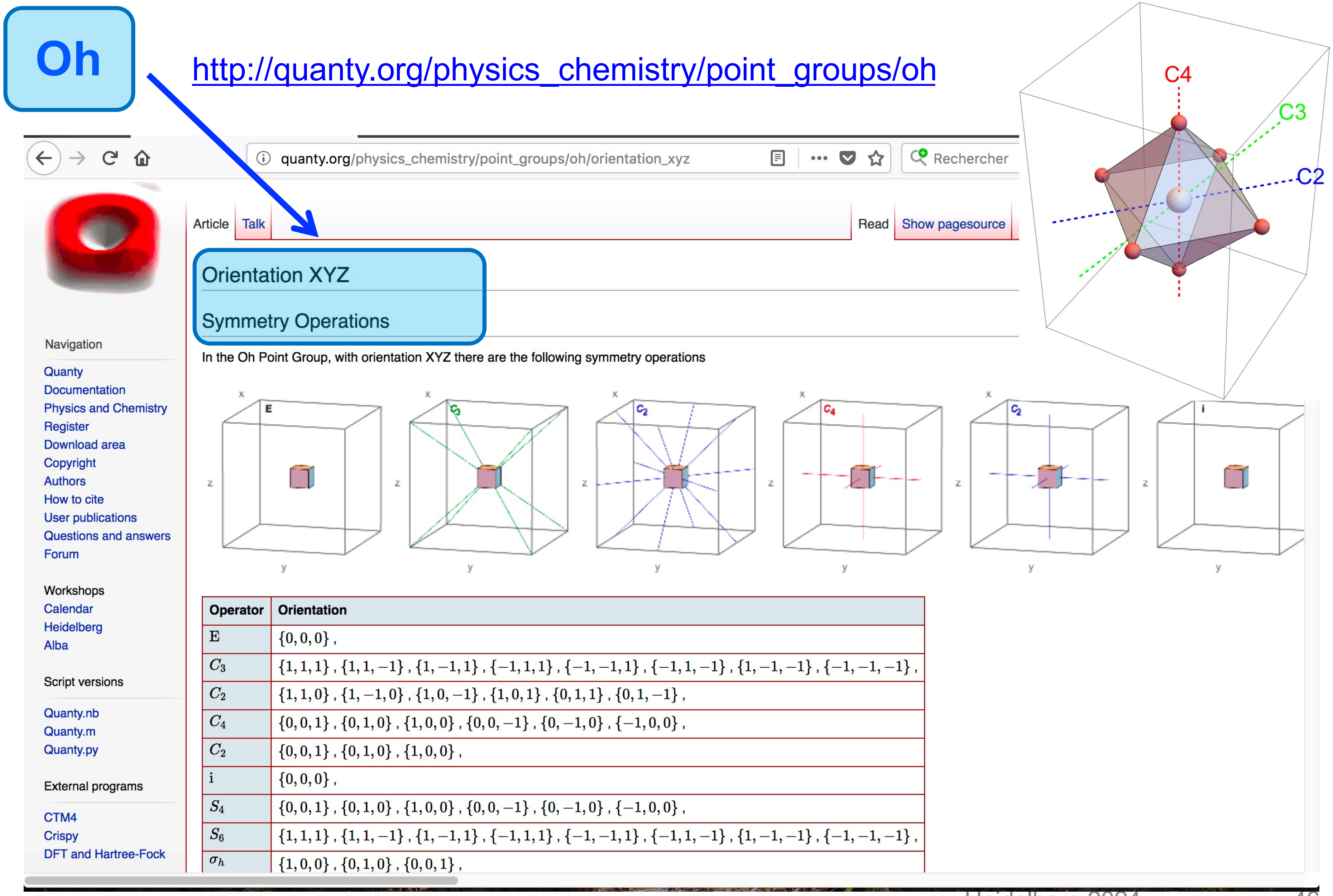
Table of Contents

- 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

Crystal field *Point groups: Quanty website orientations*

Oh

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



Orientation XYZ

Symmetry Operations

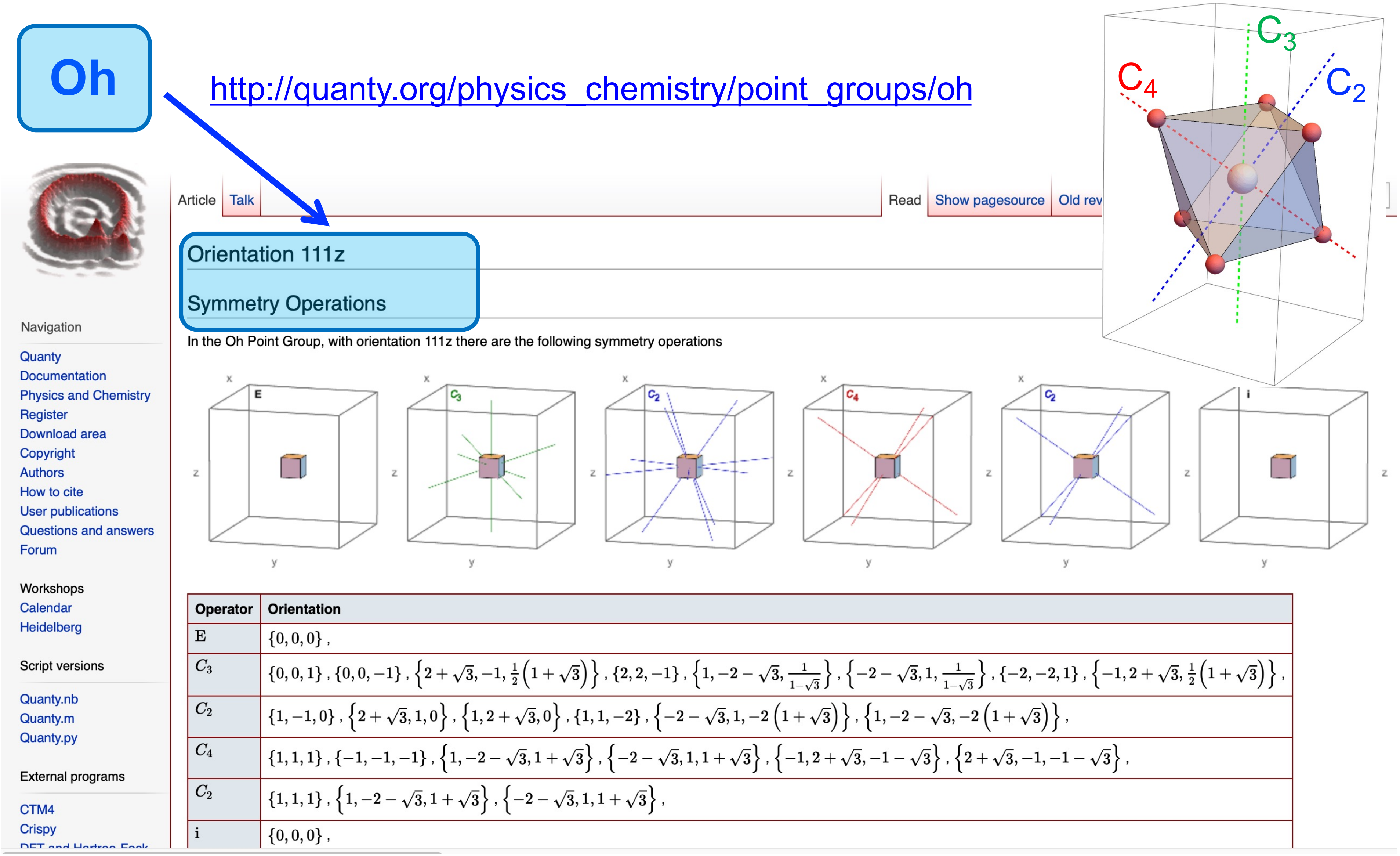
In the Oh Point Group, with orientation XYZ there are the following symmetry operations

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

Crystal field *Point groups: Quanty website orientations*

Oh

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



Navigation

- Quanty
- Documentation
- Physics and Chemistry
- Register
- Download area
- Copyright
- Authors
- How to cite
- User publications
- Questions and answers
- Forum

Workshops

- Calendar
- Heidelberg

Script versions

- Quanty.nb
- Quanty.m
- Quanty.py

External programs

- CTM4
- Crispy
- DFT and Hartree Fock

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

Crystal field Hamiltonian

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

II

Crystal field Hamiltonian

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

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

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

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

The infinite sum is limited by 2ℓ

(from CF matrix element calculation)

II

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)

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

Angular

Spherical harmonics

For an electron in orbital ℓ

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

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

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

II

Crystal field Hamiltonian

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

$$\downarrow$$

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

Hermitian Matrix

Exemples

3d ion $\ell = 2$

$$k = 0, 2, 4$$

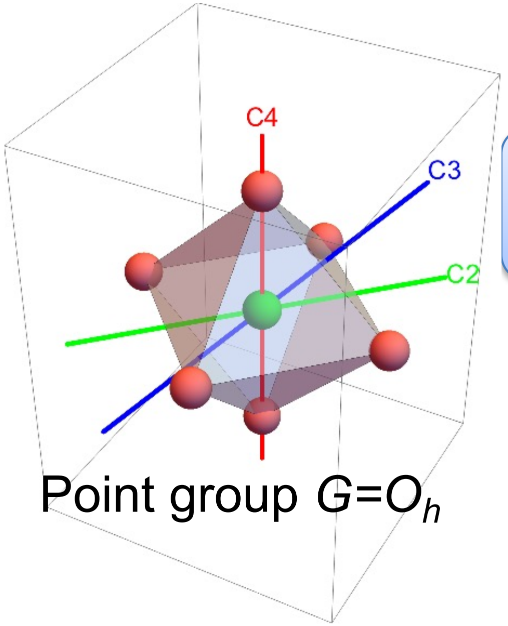
4f ion $\ell = 3$

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

Crystal field Hamiltonian and symmetry

The sum over k is reduced by symmetry properties

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



Point group $G=O_h$

CF Hamiltonian belongs to the point group symmetry ***G***
→ is invariant under all symmetry operation O_i of ***G***

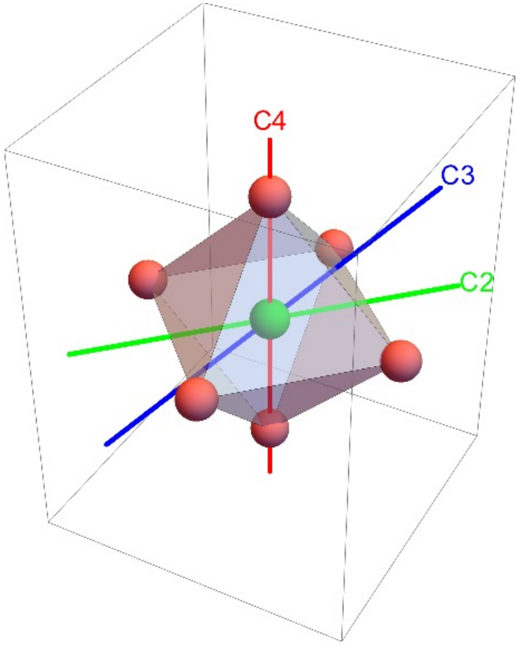
$$O_i H_{CF} = H_{CF}$$

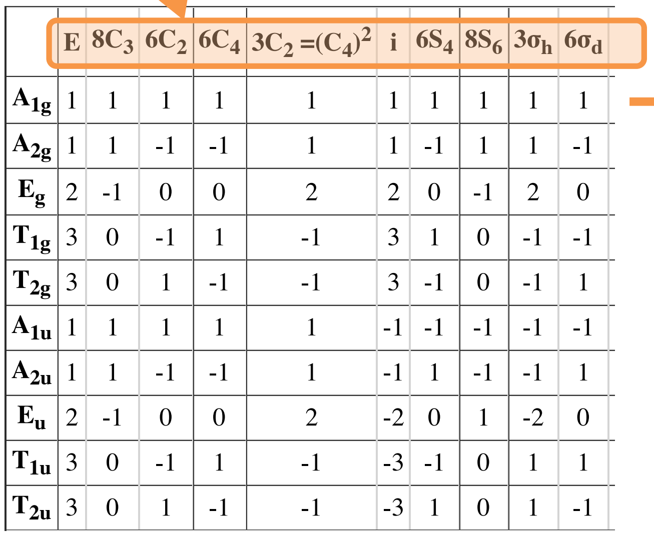
Some A_{km} = 0 due to symmetry

II Crystal field Hamiltonian and symmetry

Example : O_h symmetry

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





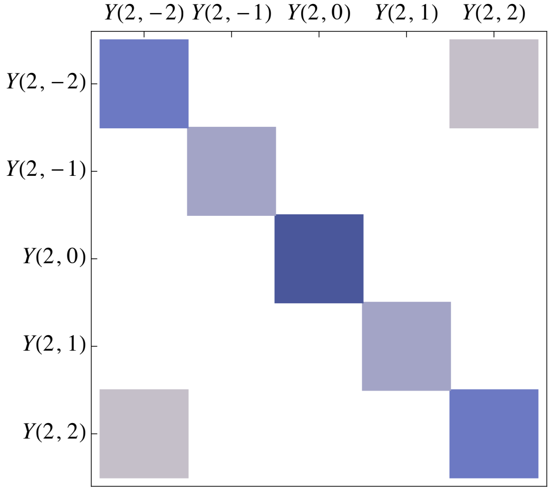
	E	$8C_3$	$6C_2$	$6C_4$	$3C_2 = (C_4)^2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1
E_g	2	-1	0	0	2	2	0	-1	2	0
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1
E_u	2	-1	0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

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

Fully symmetric representation

$$A_{1g} = \Gamma_1$$

CF matrix



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

(A_{00} spherical term)

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

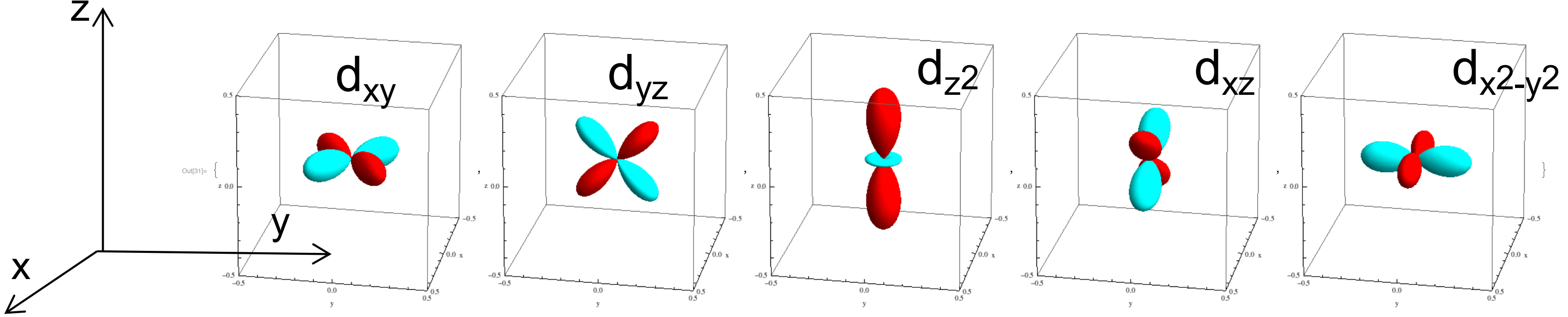
Crystal field *3d* atomic orbitals

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

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

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

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



II

Crystal field 3*d* splitting in O_h symmetry

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

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

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

Not diagonal

2) Diagonalization

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

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

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

II

Crystal field

3d splitting in O_h symmetry
Use of group symmetry

Character table for O_h point group

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

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

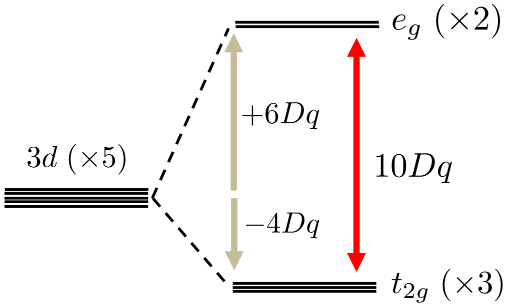
$$\{d_{yz}, d_{xz}, d_{xy}\} \in t_{2g}$$

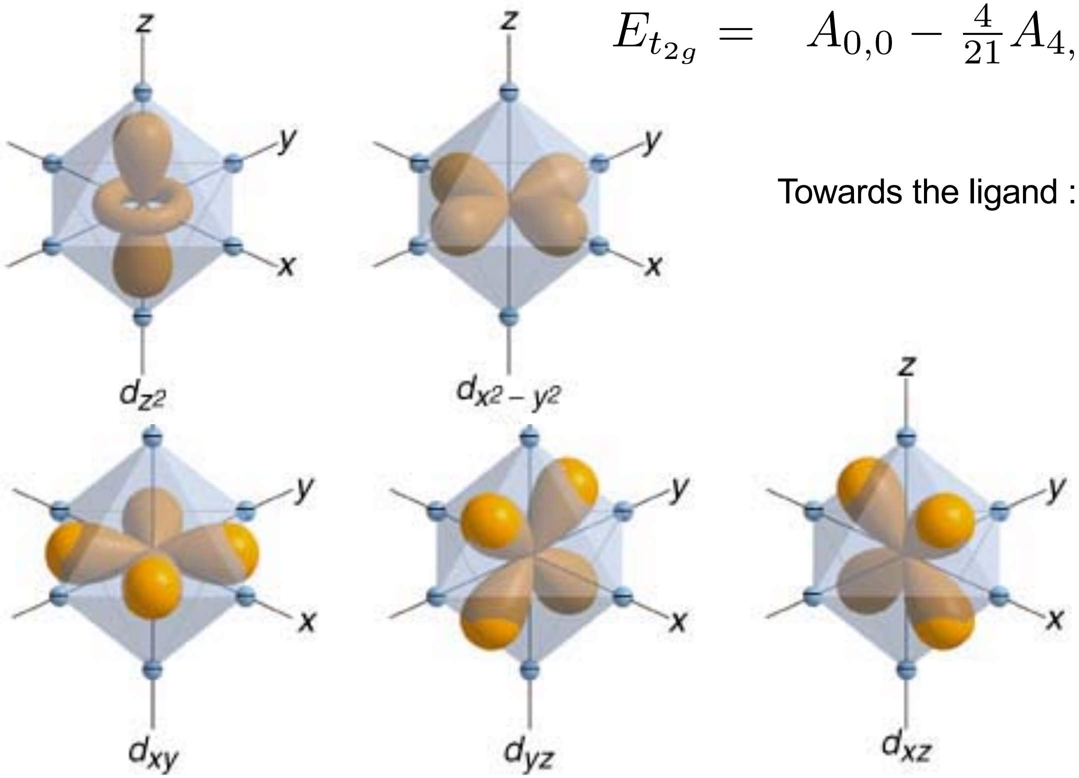
- From the *Oh* group properties, one can guess the splitting of the d orbitals
- d orbitals are called e_g and t_{2g} *

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

3d splitting in O_h symmetry

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



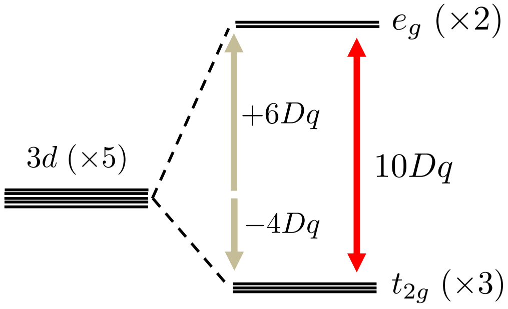


Towards the ligand : destabilized

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

(parameter)

Crystal field O_h Crystal field parameters



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

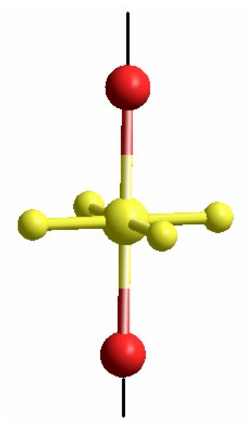
Quanty : $A_{k,m}$ defined in function the orbital energies

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

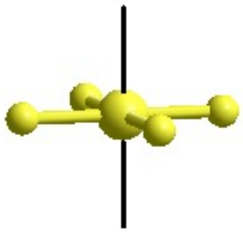
II

Crystal field — *Tetragonal (D_{4h}) crystal field*

D_{4h}



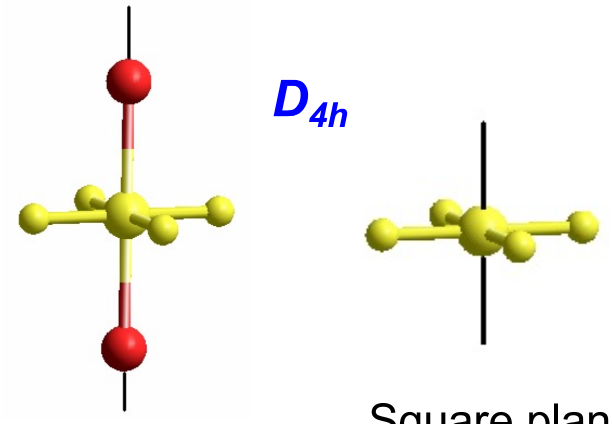
Elongated
or compressed O_h
along C_4 axis



Square planar

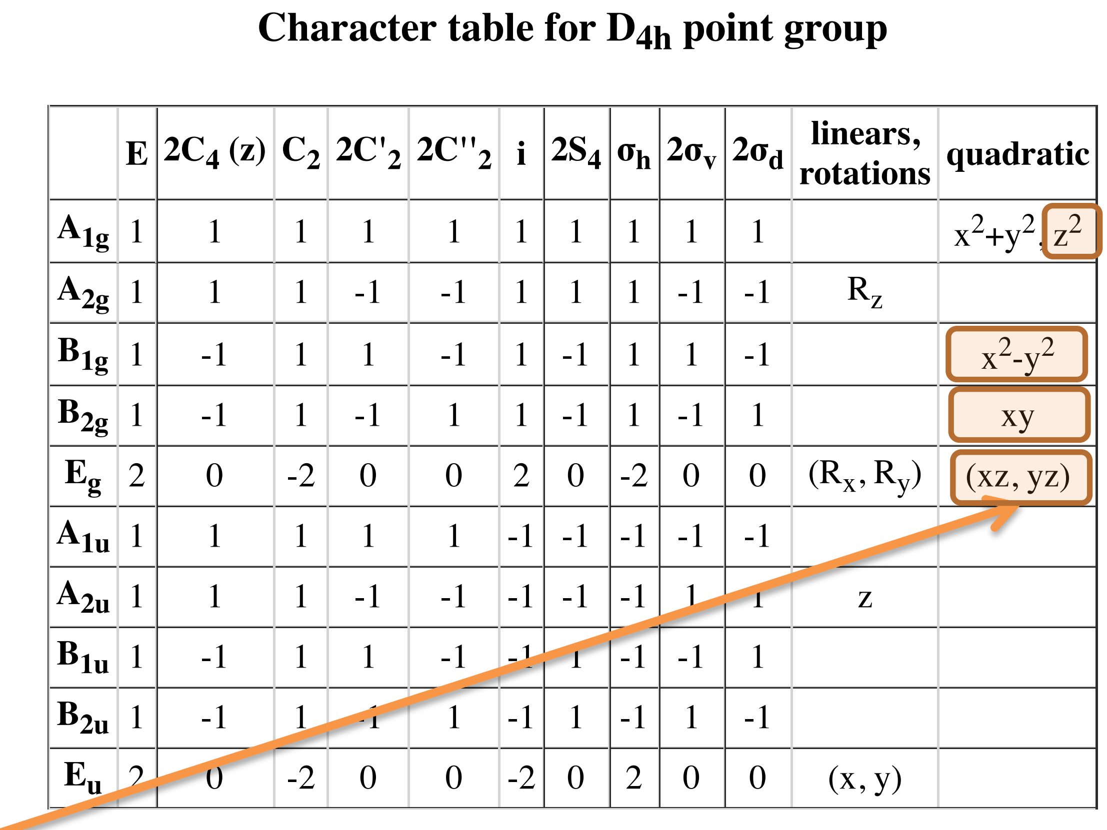
II

Crystal field *Tetragonal (D_{4h}) crystal field*



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$_h$	2σ$_v$	2σ$_d$	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

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

Crystal field *Tetragonal (D_{4h}) crystal field*

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

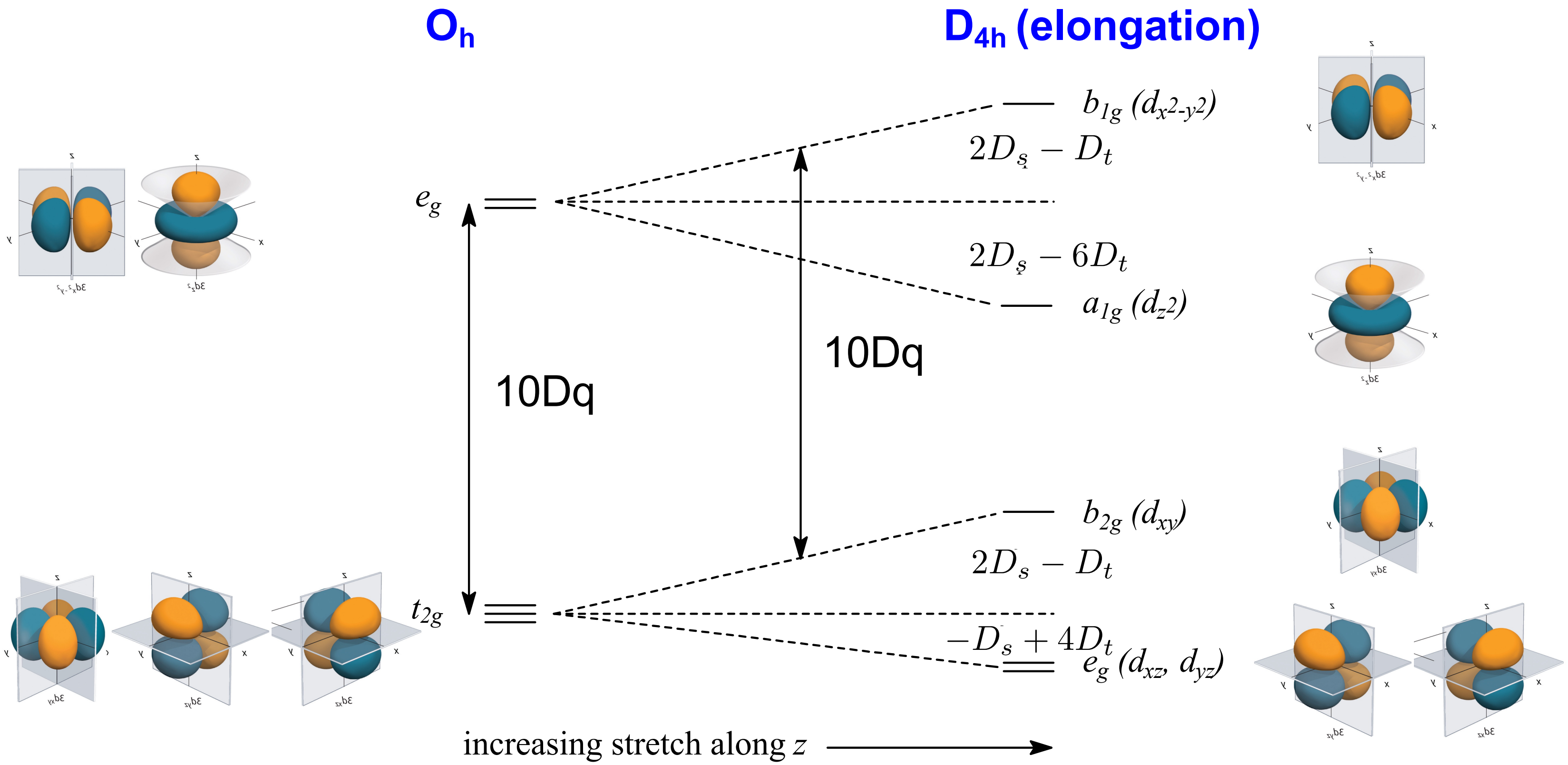
- CF matrix diagonal in the {*d*} basis

$$\begin{array}{c} \begin{matrix} d_{x^2-y^2} & d_{z^2} & d_{yz} & d_{xz} & d_{xy} \end{matrix} \\ \begin{pmatrix} E_{a_{1g}} & 0 & 0 & 0 & 0 \\ 0 & E_{b_{1g}} & 0 & 0 & 0 \\ 0 & 0 & E_{e_g} & 0 & 0 \\ 0 & 0 & 0 & E_{e_g} & 0 \\ 0 & 0 & 0 & 0 & E_{b_{2g}} \end{pmatrix} \end{array}$$

4 energy levels

Tetragonal (D_{4h}) crystal field

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



O_h

D_{4h} (elongation)

e_g

t_{2g}

10Dq

10Dq

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

$2D_s - D_t$

$2D_s - 6D_t$

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

$b_{2g}\ (d_{xy})$

$2D_s - D_t$

$-D_s + 4D_t$

$e_g\ (d_{xz},\ d_{yz})$

increasing stretch along z →

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

Crystal field Hamiltonians in Quanty

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

1) Pre-defined CF potential

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

The Oh potential is defined by:

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

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

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

3) Hamiltonian

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

Tutorials today

II

Crystal field Crystal fied parameters : Notations

Vary from an author to the other

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

(Haverkort/Quanty)

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

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 Quanty : 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 !!!)*

II

Crystal field *Lower symmetries*

$\boldsymbol{O_h}$	1 parameter (10Dq or $A_{4,0}$)	2 energies	$E_{e_g}, \; E_{t_{2g}}$
$\boldsymbol{D_{4h}}$	3 parameters (10Dq,Ds,Dt or $A_{2,0}$,$A_{4,0}$,$A_{4,4}$)	4 energies	$E_{a_{1g}}, E_{b_{1g}}, E_{e_g}, E_{b_{2g}}$
$\boldsymbol{D_{3d}}$	3-4 parameters (10Dq,Dσ,Dτ or $A_{2,0}$,$A_{4,0}$,$A_{4,3}$,$A_{4,-3}$)	3 energies	$E_{a_{1g}}, E_{e_g}, E_{e_g}$
$\boldsymbol{C_{2v}}$	9 parameters 😵	5 energies (5 orbtials)	

II

Crystal field *Multi-electrons ions 3d^n*

II

Crystal field *Multi-electrons ions $3d^n$*

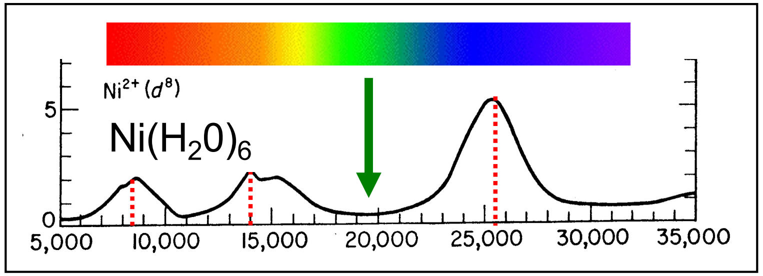
A lot of physical-chemical properties are due to the crystal field

For example

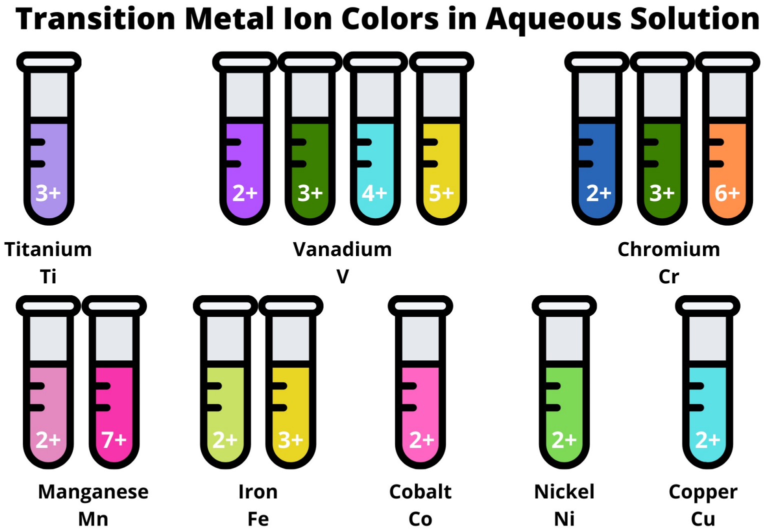
- **Color**
- Magnetic properties

→

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



UV-visible Absorption spectroscopy



Hamiltion for N-electrons ions *(3dⁿ)*

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

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

Total kinetic energy

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

Coulomb attraction nuclei-electrons

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

Electron-electron Coulomb repulsions

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

Spin-orbit coupling

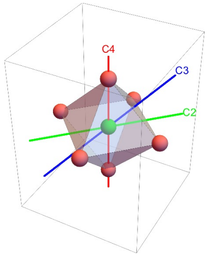
Crystal field *N-electrons ions : basis functions*

- **Basis functions**

Spherical symmetry:

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

Local symmetry around the ion → point group *G*:



Basis functions of the representations of group G

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

Γ irreducible representation of G

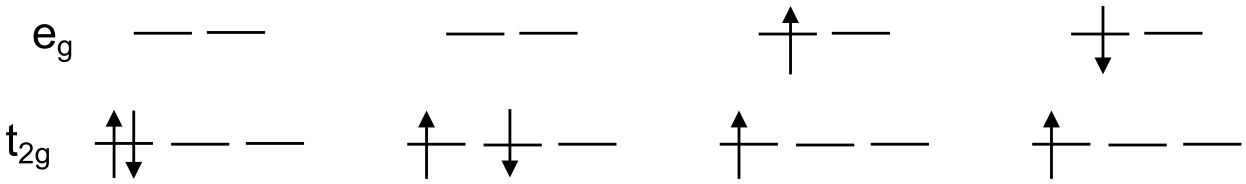
$\Gamma\gamma$ basis function of G

- 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)

N-electrons ions $3d^n$ Configuration and symmetry

d^2 ion in O_h symmetry



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

II

Crystal field

N-electrons ions $3d^n$
Spectroscopic terms

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

Spectroscopic terms

Free ion (spherical)

$$|(LS)JM_J>$$

$$^{2S+1}\Gamma_J$$

Spin multipiicity

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

Crystal field

$$|(LS)J\,\mathbf{\Gamma}\gamma>$$

$$^{2S+1}\Gamma$$

Spin multipiicity

Irreducible representation
of the point group
(local symmetry)

II

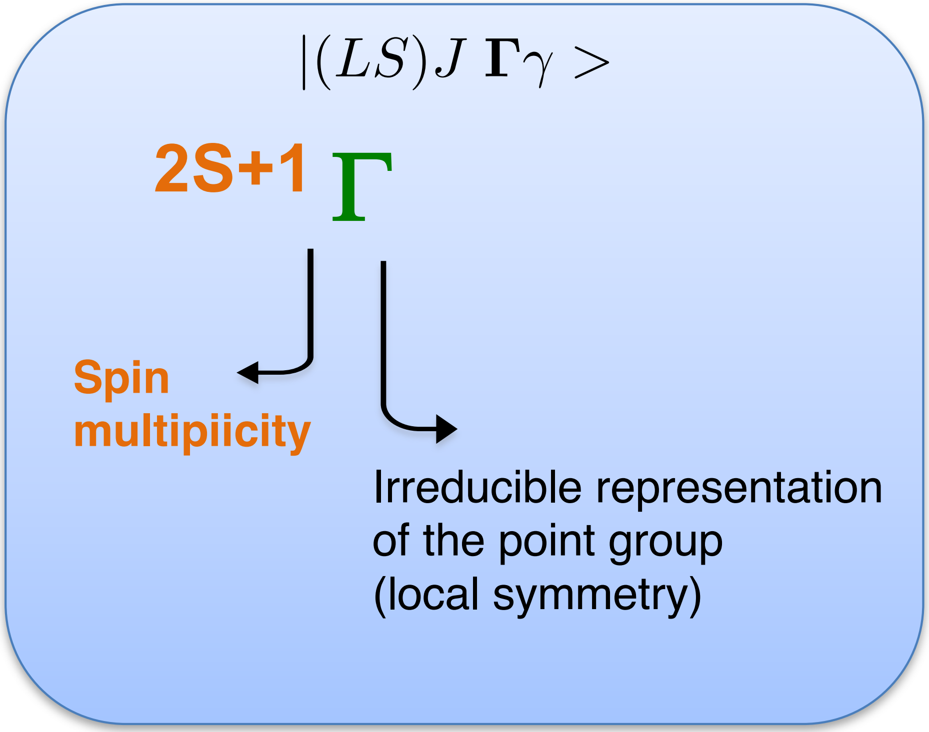
Crystal field N-electrons ions $3d^n$

Spectroscopic terms

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

Spectroscopic terms

Crystal field



$$|(LS)J\,\boldsymbol{\Gamma}\gamma >$$

$$^{2S+1}\Gamma$$

Spin multipiicity

Irreducible representation of the point group (local symmetry)

Crystal field + Spin-orbit

$$|(LS)J\,\boldsymbol{\Gamma}\gamma >$$

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

II

Crystal field — N-electrons ions *3dⁿ*

Matrix elements / group theory

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

* *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)

II

Crystal field N-electrons ions *3dⁿ*

Matrix elements / group theory

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

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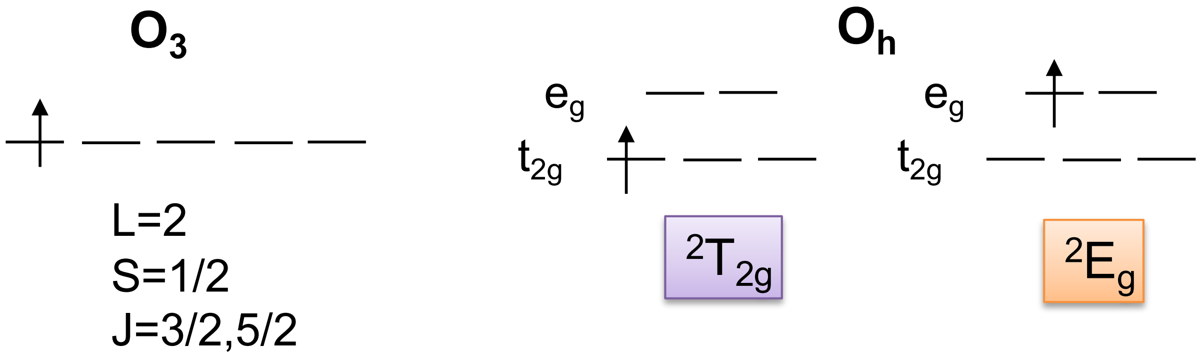
⇨ Crystal field mixes J states if $\Gamma_i \otimes \Gamma_j \ni A_{1(g)}$

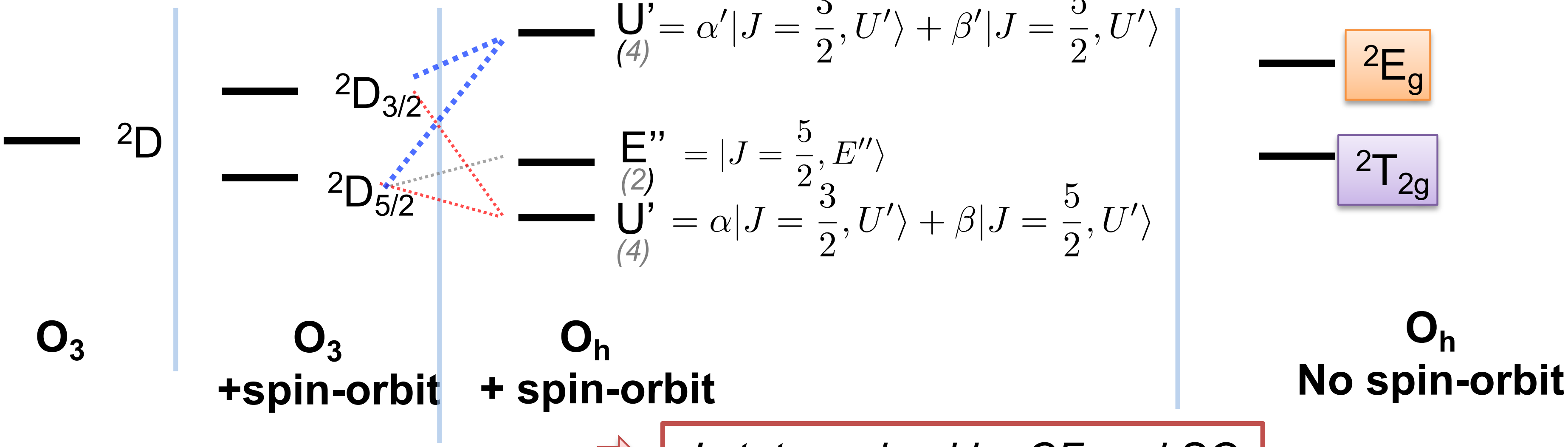
(group multiplication table)

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

Orbitals



States (spectroscopic terms) d^9



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

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

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

J states mixed by CF and SO

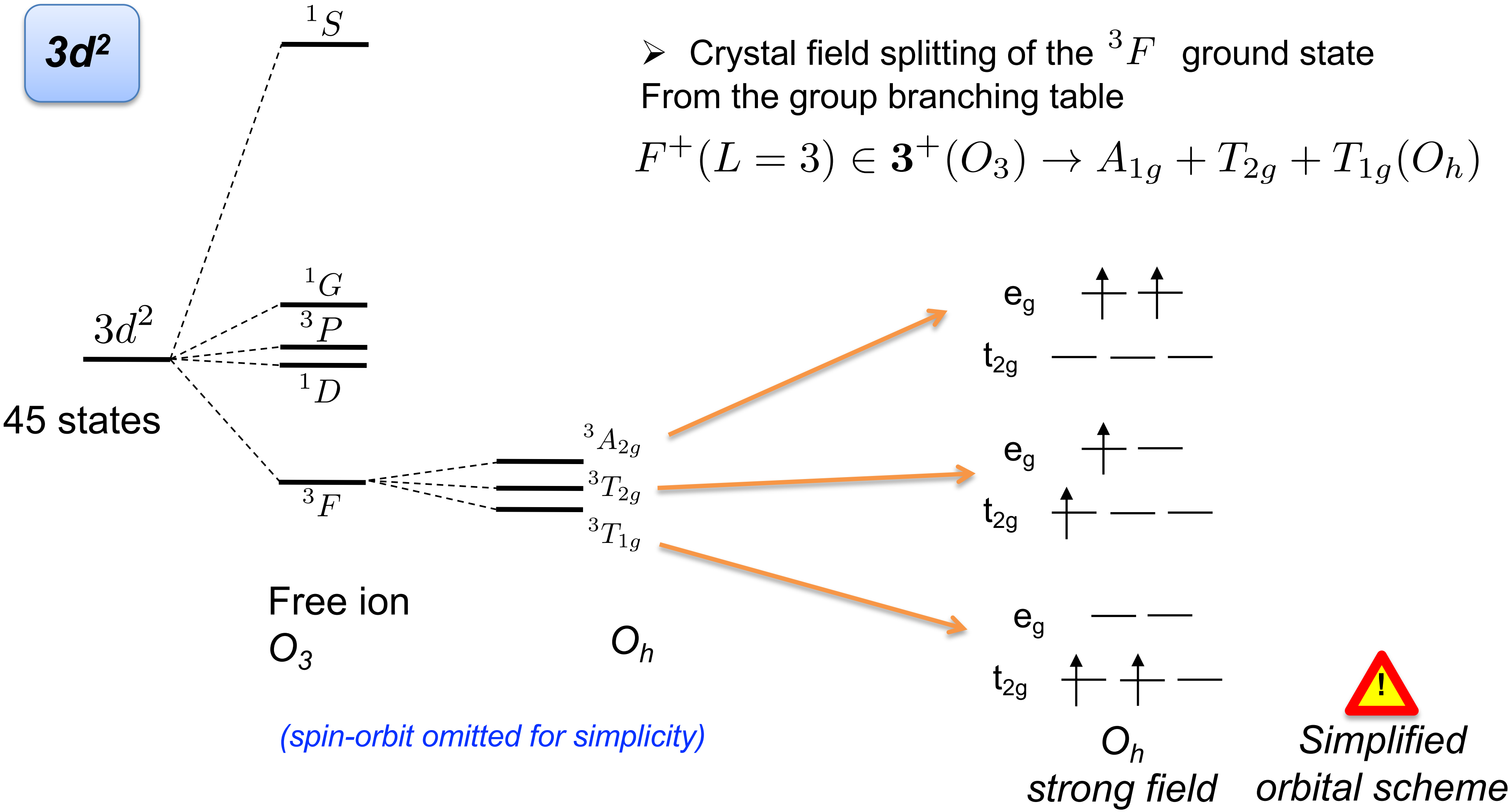
II

Crystal field Energy levels for *3d²* ion (Oh)

- ➢ Crystal field splitting of the ^3F ground state

From the group branching table

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



(spin-orbit omitted for simplicity)

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

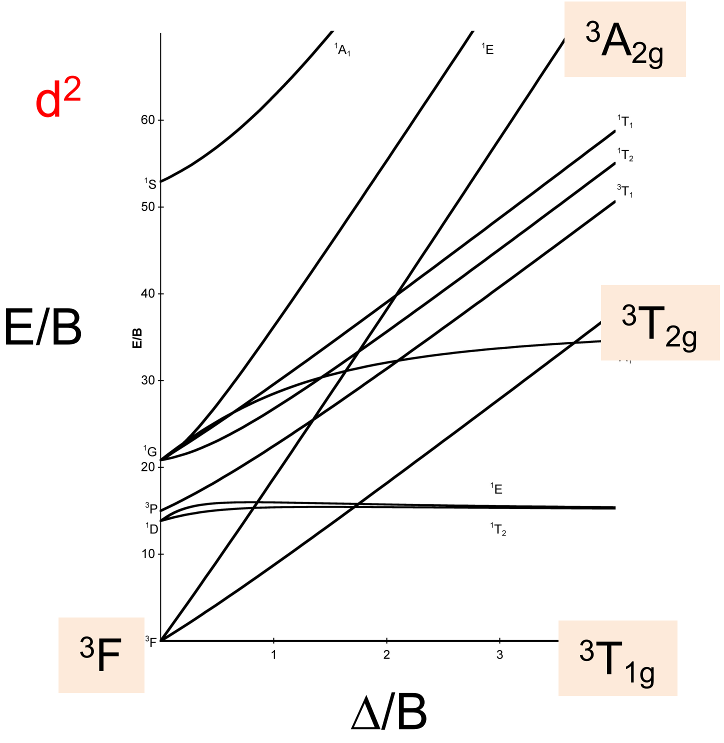
Crystal field Energy level diagram / Tanabe-Sugano

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

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

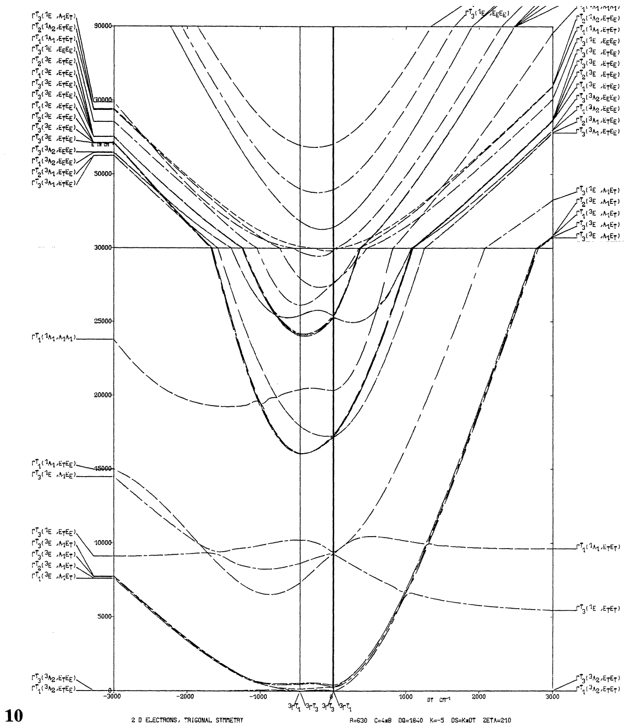
- **Tanabe-Sugano diagram (1954)**

$O_h(T_d)$, no spin-orbit



- **König&Kremer (1970)**

Low symmetries+spin-orbit



(*)B Racah parameters related to the slater integrals

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

II

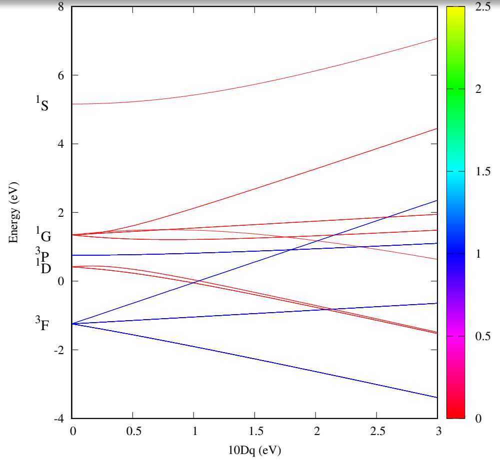
Crystal field Energy level diagram / Tanabe-Sugano

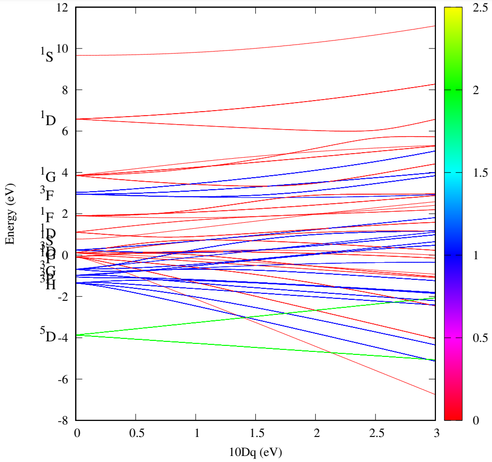
- **Tanabe-Sugano diagram (1954)**
  $O_h(T_d)$, no spin-orbit
- **König&Kremer (≈1970)**
  Low symmetries+spin-orbit
- 2024 : special conference

70 years of the
Tanabe-Sugano
diagrams

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

Quanty Tutorial :
02_Energy_Level_Diagram_Tanabe-Sugano.Quanty





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.

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

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:

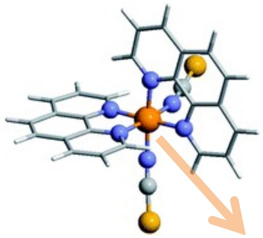
$$\langle \Gamma_i | \hat{O} | \Gamma_i \rangle$$
$$\text{with } \hat{O} = L_z, S_z, \ldots$$

Example of crystal field effect

Spin crossover

Crystal field Example : spin crossover

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

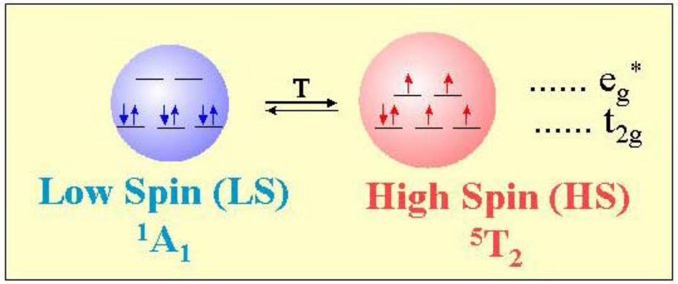


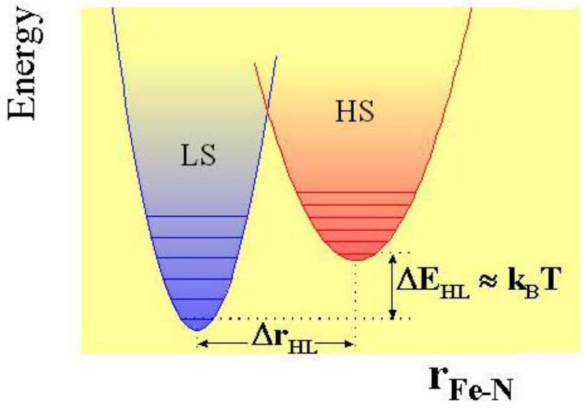
Color change thermochromism

T = 77 K
Low spin S = 0

Fe^{2+} d^6

T = 300 K
High spin S = 2





Fe-N distance
⇩
CF strength
⇩
Color change

Ex of application: thermochromic painting

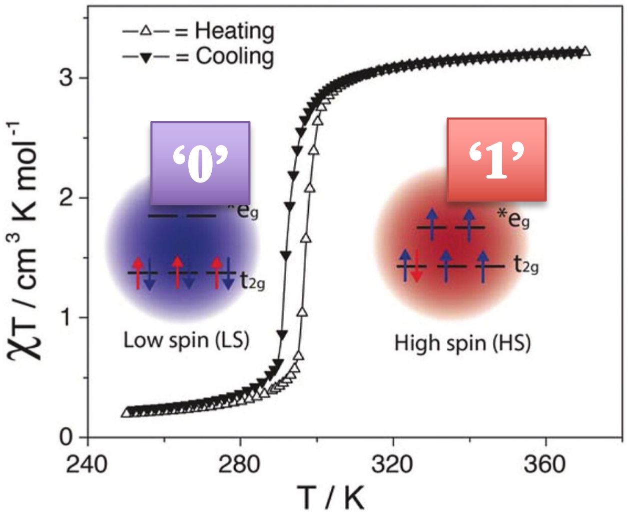
II

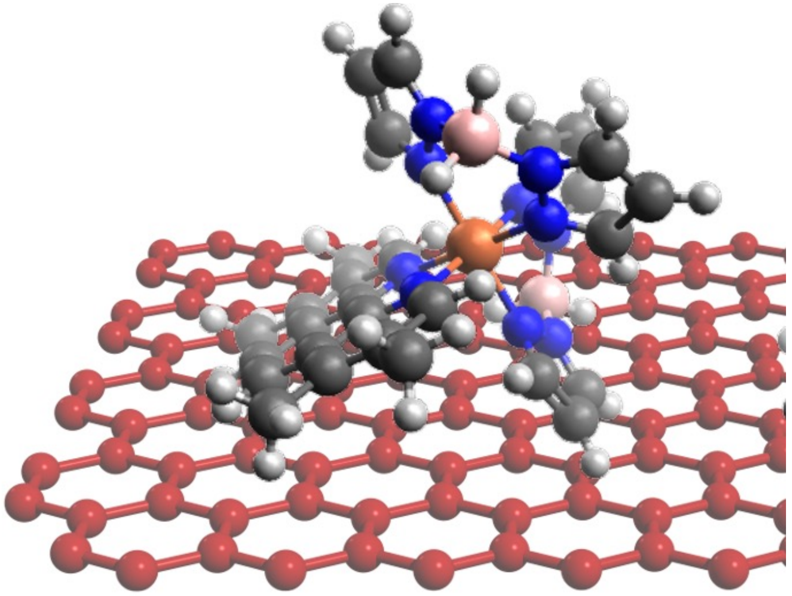
Crystal field Example : spin crossover

Magnetism:

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

  for **molecular spintronic**





II

Crystal field Example : spin crossover

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

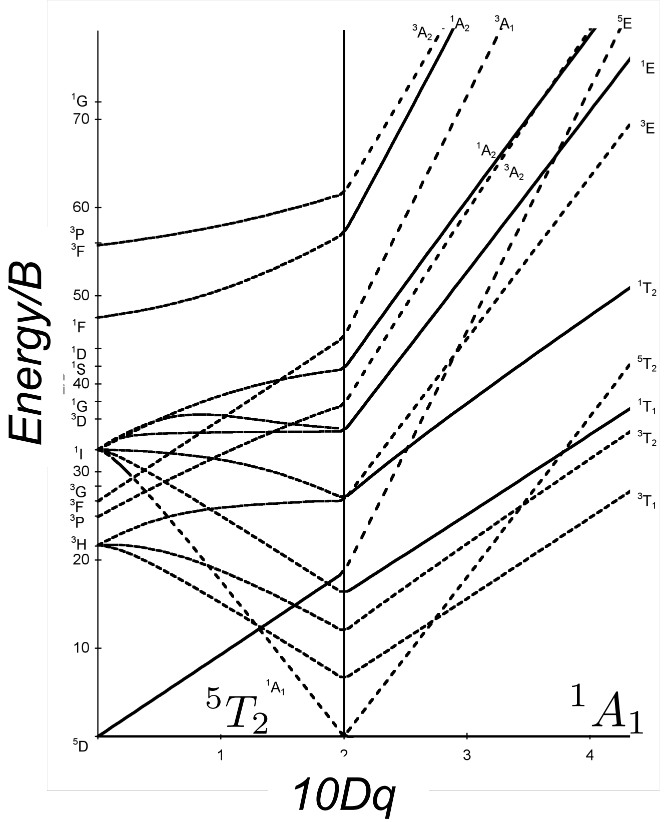
Temperature ↘

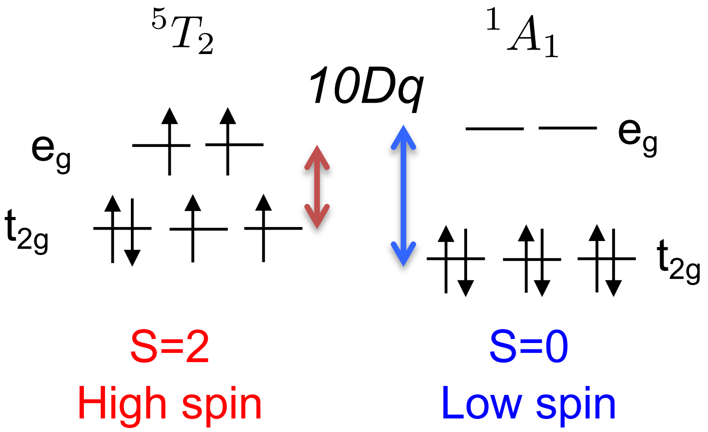
⇩

Fe-N distance (observed by DRX)

⇩

CF strength ↗ *(10Dq)*





S=2
High spin

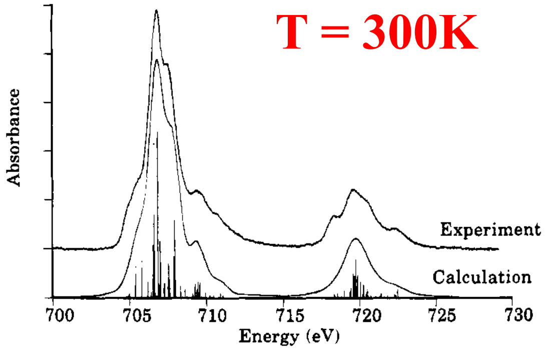
S=0
Low spin

- ➢ Magnetic properties goes from paramagnetic to non-magnetic

Example : spin crossover

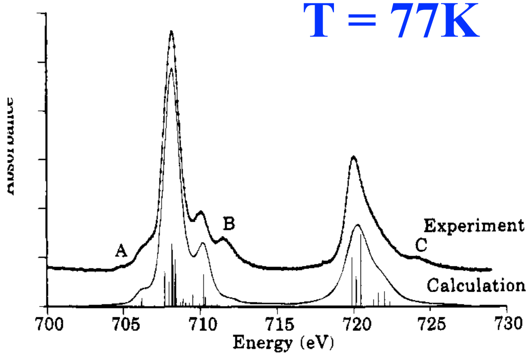
XAS at Fe $L_{2,3}$ edges (2p->3d)

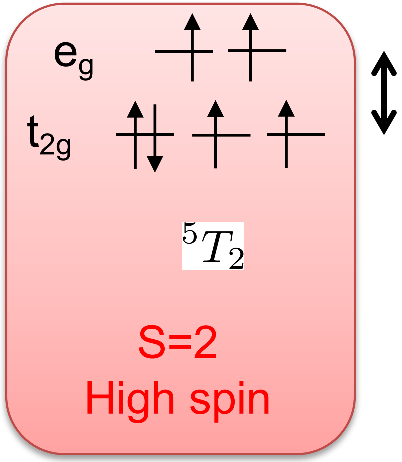
T = 300K



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

T = 77K

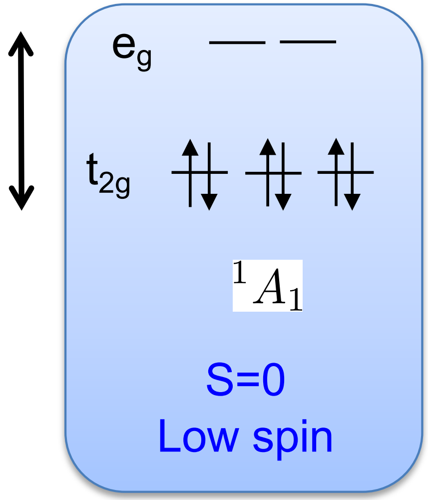




$^5T_2$

10Dq=1eV

S=2
High spin



10Dq=2.2eV

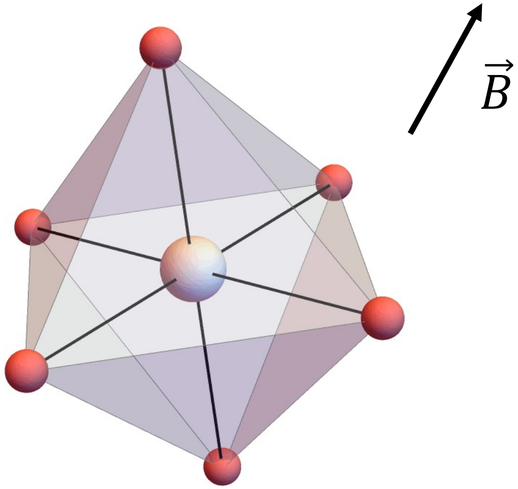
$^1A_1$

S=0
Low spin

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

III

Crystal field and magnetim



III Crystal field and magnetim

Hamiltonian

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

Free ion (spherical)

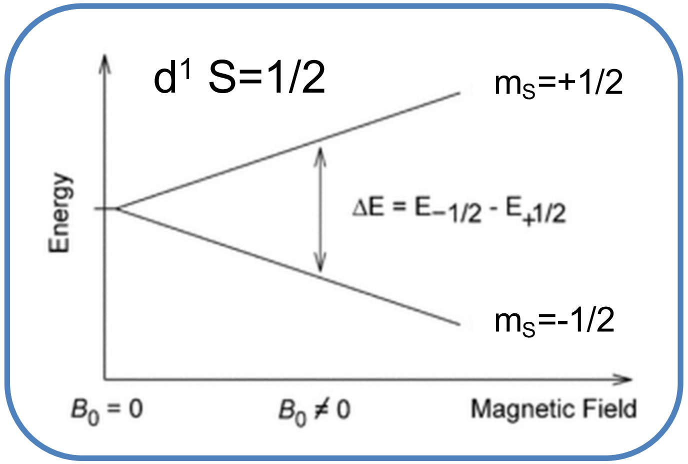
Crystal field

External Magnetic field

Magnetic coupling
With neighbours
(ferro/antiferro-magnetism)

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

1 electron (S=1/2)
spherical



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

III

Crystal field and magnetim
Magnetic moments

- **Magnetic moments : Definitions**

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

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

$$(\text{in } \hbar \text{ unit}, g_0 \approx 2)$$

⚠ *z is the direction of the external magnetic field*

- **Crystal field effect**

$|i >= |(L,S)J\Gamma\gamma\rangle$ 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}+$H_{e\text{-}n}$+$H_{e\text{-}e}$+$H_{s\text{-}o}$ commute with $\widehat{J}^2, \widehat{J}_z, \widehat{L}^2, \widehat{S}^2$

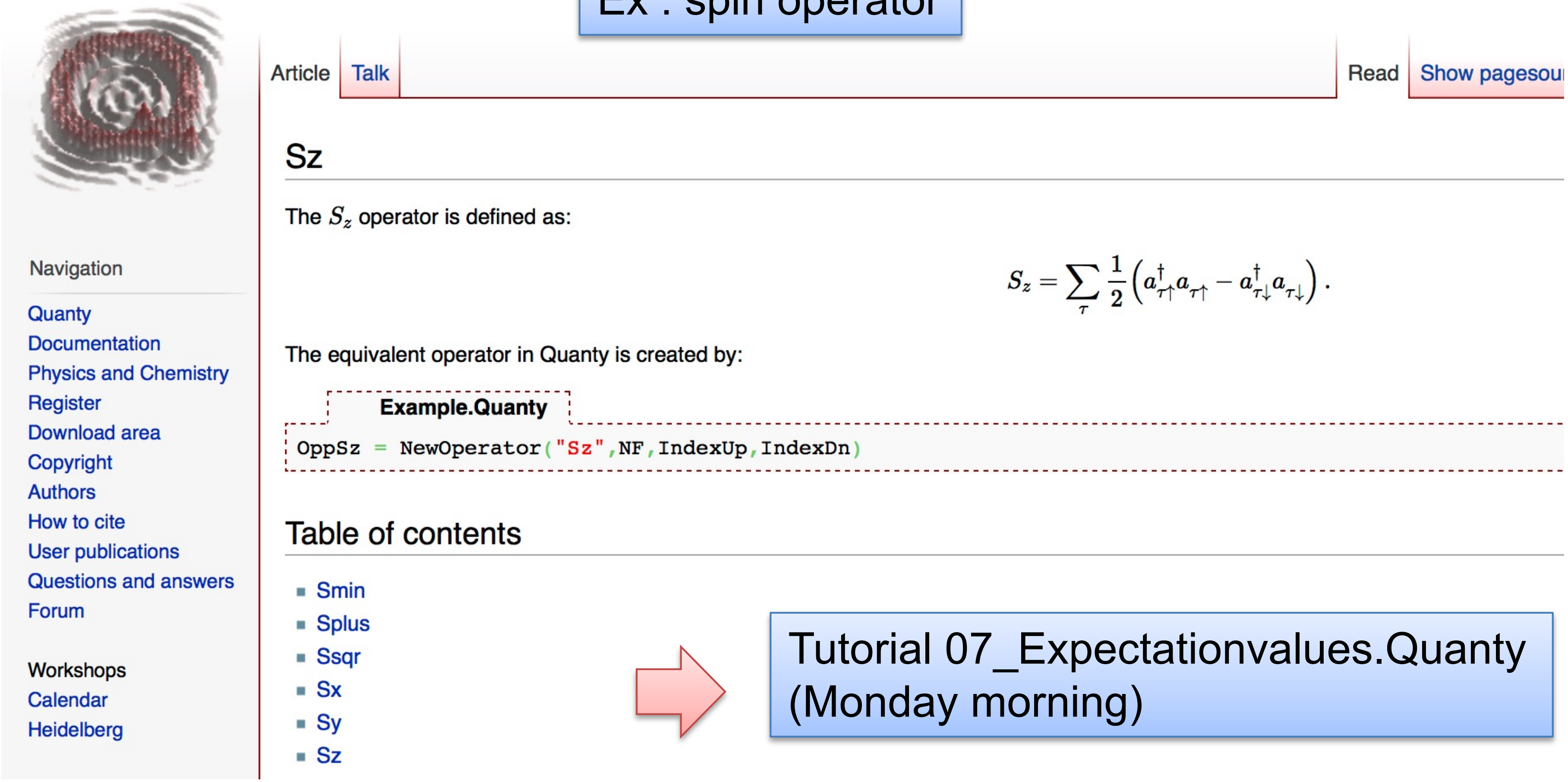
(H_{cin}+$H_{e\text{-}n}$+$H_{e\text{-}e}$ commute with $\hat{L}^2, \hat{L}_z, \hat{S}^2, \hat{S}_z$)

Magnetic moments with Quanty

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

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

Ex : spin operator



Sz

The S_z operator is defined as:

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

The equivalent operator in Quanty is created by:

Example.Quanty

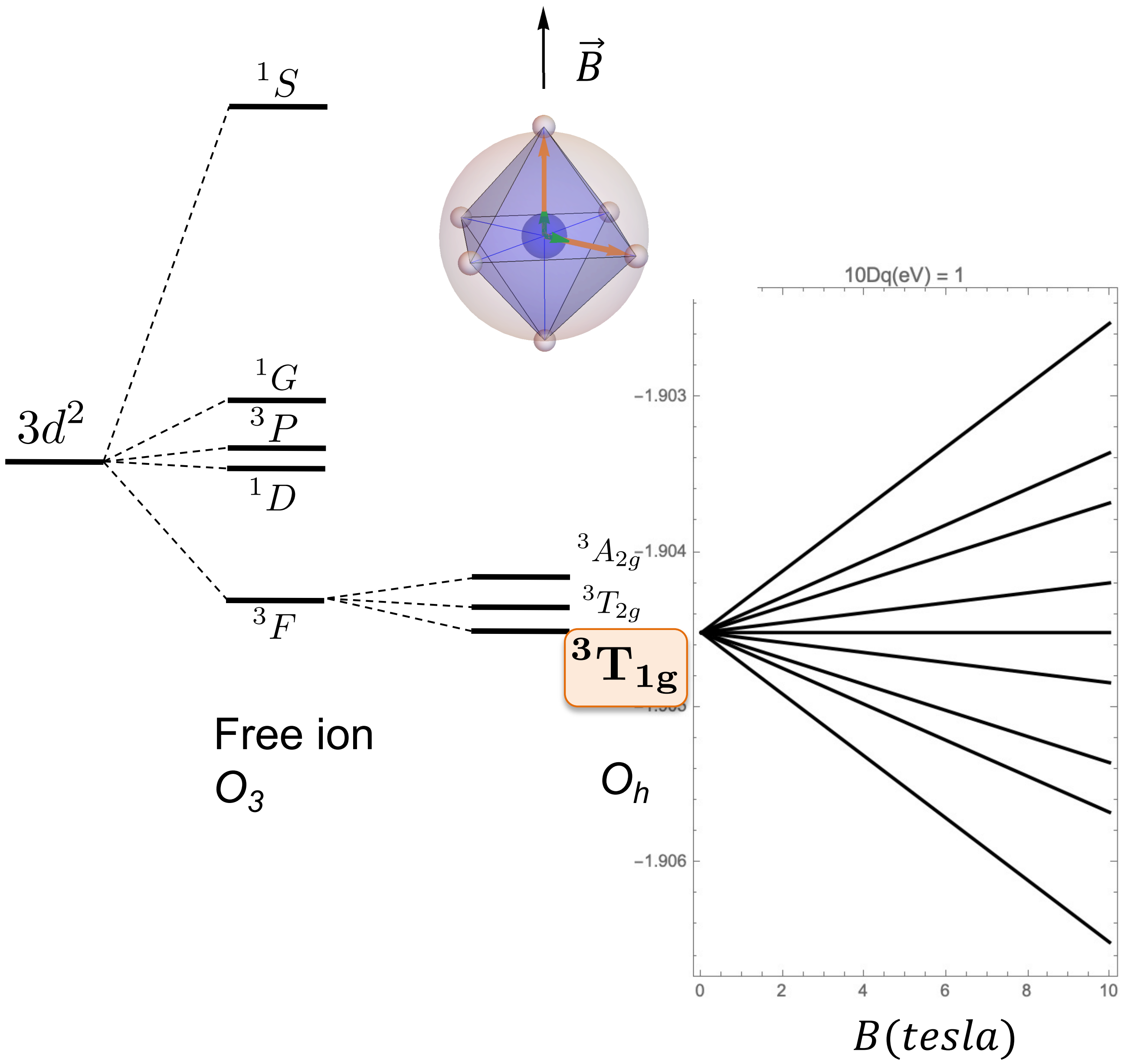
```
OppSz = NewOperator("Sz",NF,IndexUp,IndexDn)
```

Table of contents

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

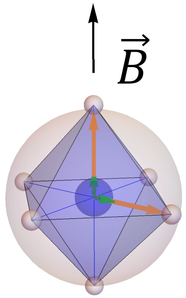
Tutorial 07_Expectationvalues.Quanty (Monday morning)

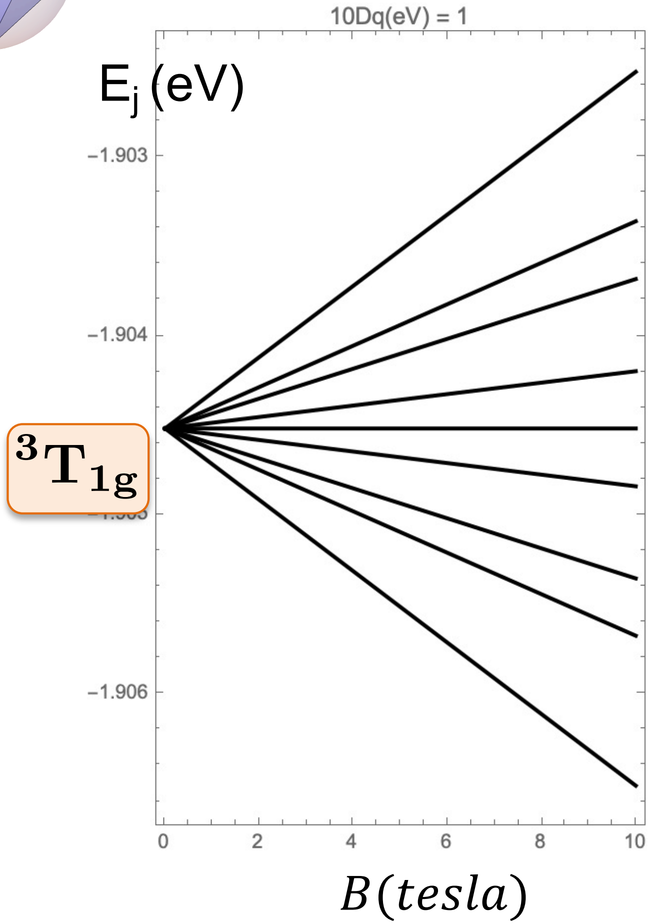
III Crystal field and magnetism Paramagnetic d^2 ion



$\langle j\|S_z\|j\rangle$	$\langle j\|L_z\|j\rangle$
1	1.44
1	0
0	1.44
1	-1.45
0	0
-1	1.44
0	-1.45
-1	0
-1	-1.45

Paramagnetic d^2 ion





Magnetization at temperature T

Boltzmann distribution

- The j^{th} state contribution is

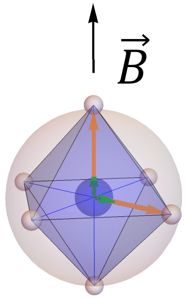
$$\frac{\exp\left(\frac{E_j - E_0}{k_B T}\right)}{\sum_{j=1}^{Nb\ states} \exp\left(\frac{E_j - E_0}{k_B T}\right)}$$

- $<S_z>$ value at T is

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

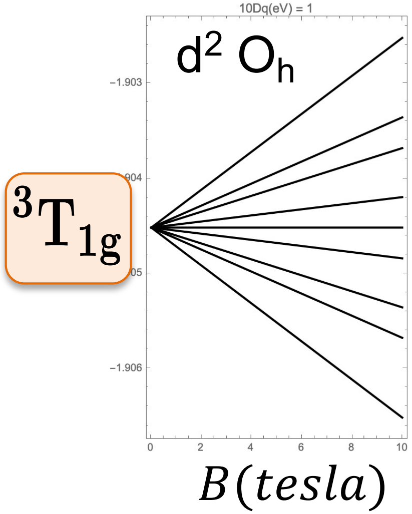
- *Same expression for* $<L_z>$ value at T

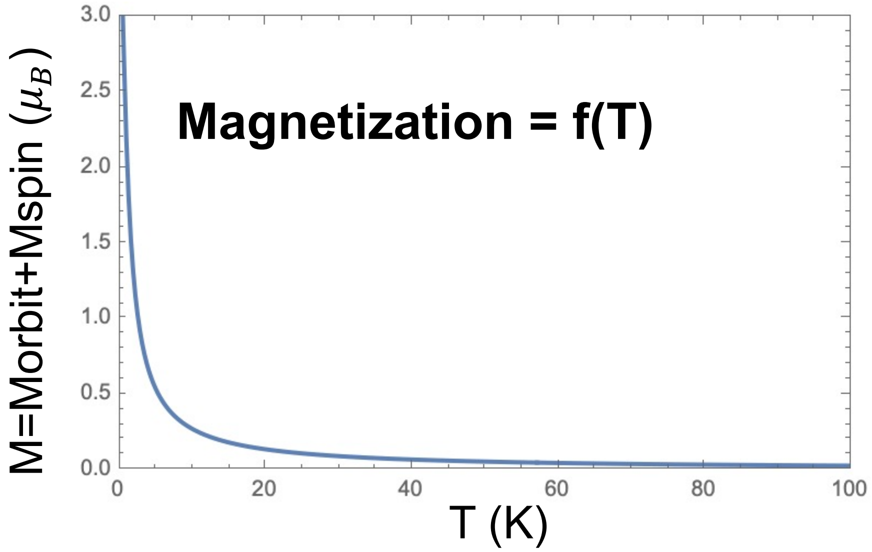
III Crystal field and magnetism Paramagnetic d^2 ion



Magnetization at temperature T

Boltzmann distribution





More in next tutorials

Temperature_and_Bolzmann_statistics.Quanty

Paramagnetic_Susceptibility_NiO.Quanty

Magneticsusceptibility_NiO.Quanty

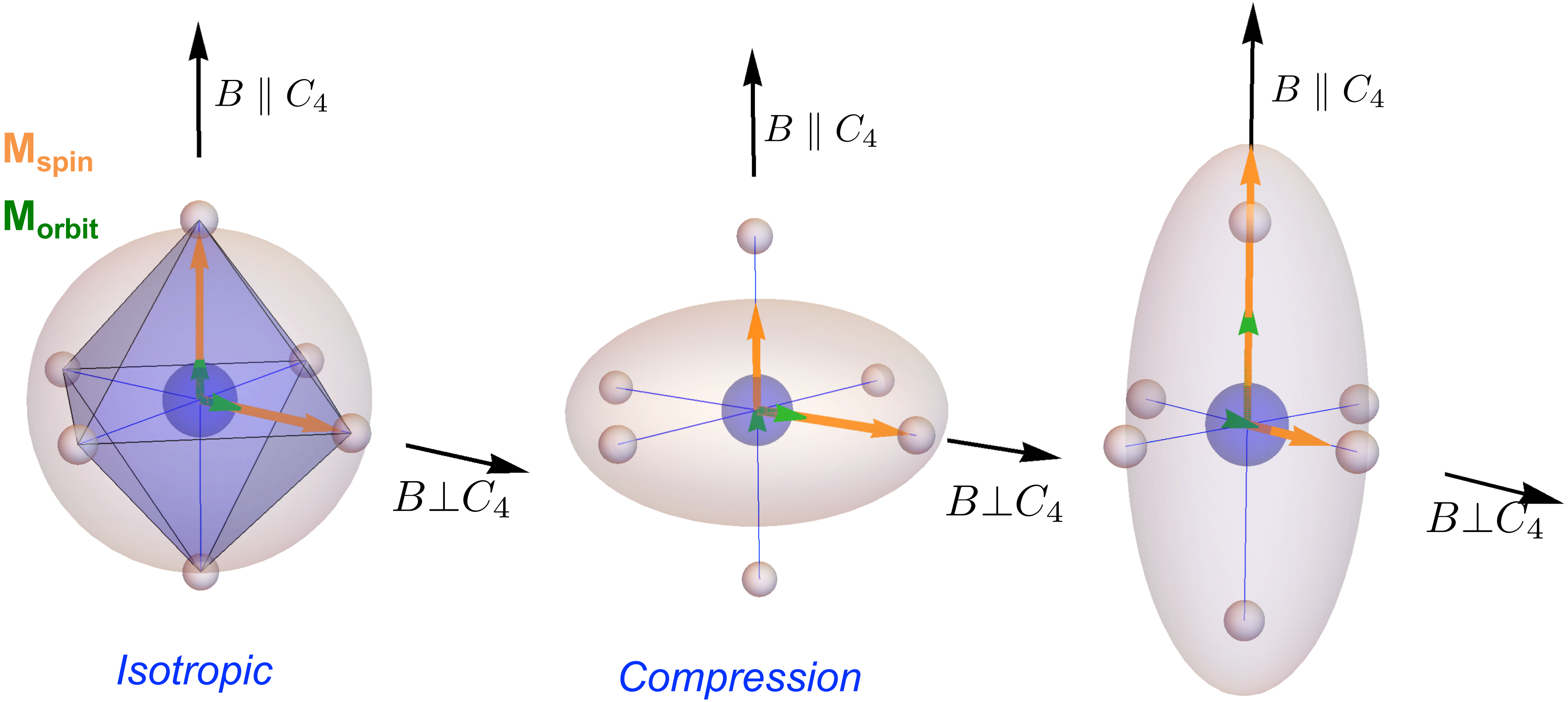
III

Crystal field and magnetism

Paramagnetism
Natural Anisotropies

Tetragonal distortion : D_{4h}

Oh



Isotropic

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

Spin operator of the ion

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

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, DTMFT…)
- 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…