

6. Crystal field theory

6.1 Introduction: Crystal field theory is the theory that describes the symmetry lowering of the electrostatic potential of an atom due to its environment. It is relevant for:

- impurities in solids
- intermetallic compounds

In general, aim to the crystal field theory is the analysis of the

- splitting of the energy levels
- symmetry types of the split levels
- choice of the basis function to bring the Hamiltonian into block-diagonal form.

In crystal field theory we write the impurity Hamiltonian in the form:

$$(1) \quad H = \sum_i \left\{ \frac{p_i^2}{2m} - \frac{Ze^2}{r_{in}} + \sum_j \frac{e^2}{r_{ij}} + \sum_j \zeta_{ij} \vec{L}_i \cdot \vec{S}_j + \sum_j J_{ij} \vec{J}_i \cdot \vec{I}_j \right\} + V_{\text{crystal}}$$

$\frac{p_i^2}{2m}$ → free electrons of the impurity
 $-\frac{Ze^2}{r_{in}}$ → Electron in nuclear potential
 $\sum_j \frac{e^2}{r_{ij}}$ → Coulomb between electrons
 $\sum_j \zeta_{ij} \vec{L}_i \cdot \vec{S}_j$ → Spin-orbit
 $\sum_j J_{ij} \vec{J}_i \cdot \vec{I}_j$ → Hyperfine interaction
 V_{crystal} → CRYSTAL FIELD

H_0 is the Hamiltonian of the isolated atom neglecting the spin-orbit interaction. H_0 sets the stage giving the order of magnitude of the energy levels. All other terms in (1) are perturbations. In particular one classifies:

(a) Weak field case if the spin-orbit splittings are stronger than crystal fields \Rightarrow the order of the perturbation is

$$(H_0 + \text{Spin-orbit}) + V_{\text{crystal}}$$

(b) Strong field case

$$(H_0 + V_{\text{crystal}}) + \text{Spin-orbit}$$

We will now concentrate on (b) since (a) requires the knowledge of double-groups.

6.2 Characters of the full rotation group

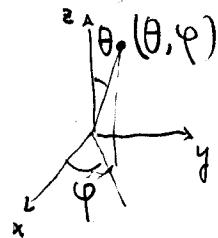
A free atom has full rotational symmetry \Rightarrow the number of symmetry operations commuting with the Hamiltonian (H_0) is ∞ .

C_ϕ around any rotation axis is a symmetry operation.

The spherical harmonics $Y_{lm}(\theta, \varphi)$ generate odd-dimensional irreducible representations of this "full rotational group".

Let us now recall the form of $Y_{lm}(\theta, \varphi)$ and calculate the characters of the rotation and inversion operations for each irreducible representation.

$$Y_{lm}(\theta, \varphi) = \left[\frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!} \right]^{1/2} P_l^m(\cos\theta) e^{im\varphi}$$



$m = -l, \dots, l$. The associated Legendre polynomials $P_l^m(x)$ can be obtained

$$P_l^m(x) = (1-x^2)^{|m|/2} \frac{d^{|m|}}{dx^{|m|}} P_l(x) \quad \left[\text{with } P_l^{-m} = (-1)^m \frac{(l-m)!}{(l+m)!} P_l^m(x) \right]$$

where

$$P_l(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} [(x^2-1)^l]$$

It is also useful in this context to remember that

$$\frac{1}{\sqrt{1-2sx+s^2}} = \sum_{l=0}^{\infty} P_l(x) s^l$$

Examples of spherical harmonics:

$$l=0 \quad P_0(x) = 1 \quad \Rightarrow \quad m=0 \quad P_0^0 = 1 \quad Y_{00} = \frac{1}{\sqrt{4\pi}}$$

$$l=1 \quad P_1(x) = \frac{1}{2} \frac{d}{dx} [(x^2-1)] = x$$

$$P_1^1(x) = (1-x^2)^{1/2} \frac{d}{dx} x = (1-x^2)^{1/2}$$

$$P_1^0(x) = x$$

$$P_1^{-1}(x) = (-1) \cdot \frac{x!}{0!} (1-x^2)^{1/2}$$

$$Y_{11} = \left(\frac{3}{4\pi} \frac{1}{2} \right)^{1/2} \sin\theta e^{i\varphi}$$

$$Y_{10} = \left(\frac{3}{4\pi} \right)^{1/2} \cos\theta$$

$$Y_{1,-1} = -1 \left(\frac{3}{4\pi} \frac{1}{2} \right)^{1/2} \sin\theta e^{-i\varphi}$$

and so on...

The fact that Y_{lm} generate irreducible representation is due to the addition theorem for spherical harmonics

$$\hat{P}_R Y_{lm}(\theta', \varphi') = \sum_{m'} \Delta^{(l)}(R)_{m'm} Y_{lm'}(\theta, \varphi)$$

In order to find the trace of a rotation of α with respect to a generic rotation axis, we exploit the fact that within the irreducible representation Γ we can choose arbitrarily the z axis, \Rightarrow

$$\hat{P}_\alpha Y_{lm}(\theta, \varphi) = Y_{lm}(\theta, \varphi - \alpha) = e^{-im\alpha} Y_{lm}(\theta, \varphi)$$

$$\Rightarrow \Delta^{(l)}(\alpha)_{m'm} = e^{-im\alpha} \delta_{m'm}, \text{ where } -l \leq m \leq l \Rightarrow$$

$$\begin{aligned} \chi^{(l)}(\alpha) &= \text{Tr} \Delta^{(l)}(\alpha) = \sum_{m=-l}^l e^{-im\alpha} = e^{-il\alpha} [1 + e^{i\alpha} + \dots + e^{2il\alpha}] \\ &= e^{-il\alpha} \left[\frac{e^{i(2l+1)\alpha} - 1}{e^{i\alpha} - 1} \right] = \frac{\sin[(l + \frac{1}{2})\alpha]}{\sin(\frac{\alpha}{2})} \end{aligned}$$

In order to obtain the character of the inversion operation

$$\epsilon Y_{lm}(\theta, \varphi) = Y_{lm}(\pi - \theta, \pi + \varphi) = (-1)^l Y_{lm}(\theta, \varphi)$$

therefore

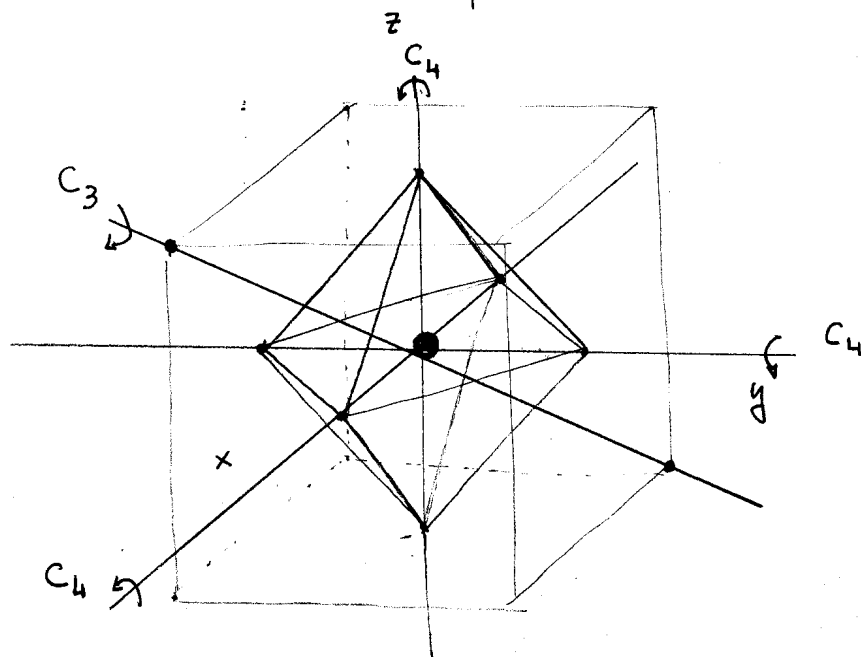
$$\chi^{(l)}(\epsilon) = \sum_{m=-l}^l (-1)^l = (-1)^l (2l+1)$$

Notice that in this way the character of all point group operations can be calculated. for example:

$$\chi^{(l)}(S_n) = \chi^{(l)}(C_{n/2} \otimes \epsilon) = (-1)^l (2l+1) \frac{\sin[(l + \frac{1}{2})\frac{2\pi}{n}]}{\sin(\frac{2\pi}{2n})}$$

Since the full rotation group contains all operation of point groups $\Rightarrow \Delta^{(l)}(\alpha)$ is a representation of the crystal group. In general, though, it will be REDUCIBLE.

6.3 Cubic crystal field for a paramagnetic transition metal ion



A paramagnetic ion (e.g. an iron impurity) in a cubic host crystal. If the impurity is in a substitutional lattice site, it is surrounded by an octahedron of negative ions. A regular octahedron (thus also a crystal) has a O_h symmetry. To simplify a bit the notation let us first consider O .

	E	$3C_2$	$8C_3$	$6C_4$	$6C_2'$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	2	-1	0	0
T_1	3	-1	0	1	-1
T_2	3	-1	0	-1	1

The next steps are similar to the ones required to calculate the equivalent bond lengths. Let us consider, to fix the ideas, the irreducible representation with $l=2$ of the full rotational group and calculate its character system relative to O .

$$\chi^{(l)}(E) = \lim_{\alpha \rightarrow 0} \frac{\sin[(l+\frac{1}{2})\alpha]}{\sin(\alpha/2)} = \frac{l+\frac{1}{2}}{\frac{1}{2}} = 2l+1 = 5 \quad \text{dimension of the representation!}$$

$$\chi^{(l)}(3C_2) = \frac{\sin[(l+\frac{1}{2})\pi]}{\sin(\frac{\pi}{2})} \stackrel{l=2}{=} \frac{\sqrt{2} \sin \frac{5\pi}{2}}{1} = 1$$

$$\chi^{(l)}(8C_3) = \frac{\sin[(l+\frac{1}{2})\frac{2\pi}{3}]}{\sin(\frac{2\pi}{6})} \stackrel{l=2}{=} \frac{-\sqrt{3}/2}{\sqrt{3}/2} = -1$$

$$\chi^{(l)}(6C_4) = \frac{\sin[\frac{3\pi}{2} \cdot \frac{2\pi}{4}]}{\sin(\frac{\pi}{4})} \stackrel{l=2}{=} -\frac{1}{\sqrt{2}} \cdot \frac{\sqrt{2}}{1} = -1$$

$$\chi^{(l)}(6C_2') = \chi^{(l)}(3C_2) \stackrel{l=2}{=} 1$$

$$\Gamma_0^{(2)} = \{ 5 \ 1 \ -1 \ -1 \ 1 \}$$

The extension to O_h is trivial

$$\Gamma_{O_h}^{(2)} = \left\{ \begin{array}{ccccccccc} E & 3C_2 & 8C_3 & 6C_4 & 6C_2' & i & 3C_2 & 8C_3 & 6C_4 & 6C_2' \\ 5 & 1 & -1 & -1 & 1 & +5 & +1 & -1 & -1 & +1 \end{array} \right\}$$

By application of the reduction formula we then obtain:

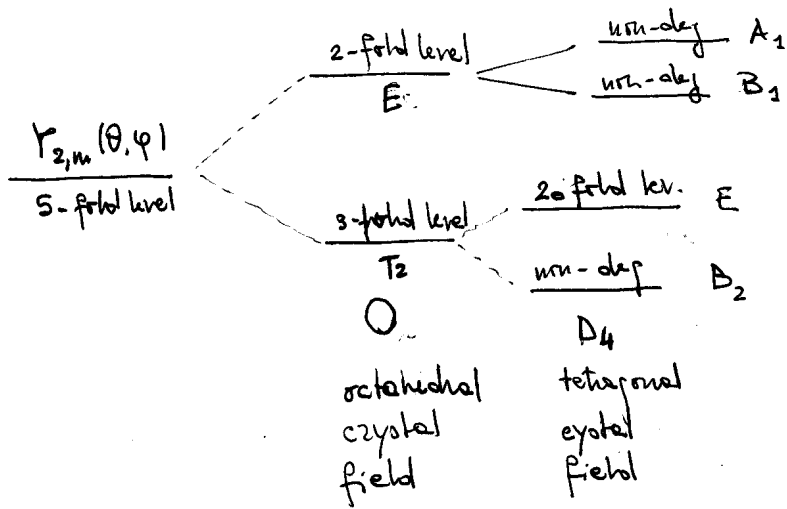
$$\Gamma_0^{(2)} = E \oplus T_2 \quad \text{and} \quad \Gamma_{O_h}^{(2)} = E_g \oplus T_{2g}$$

It is interesting to see what happens if, for example the impurity is introducing strain and the crystal field acquires a

$$D_4 \text{ symmetry: } \Gamma_{D_4}^{(2)} = \left\{ \begin{array}{cccc} E & C_2 & 2C_4 & 2C_2' \\ 5 & 1 & -1 & 1 \end{array} \right\}$$

$\Gamma_{D_4}^{(2)} = A_1 \oplus B_1 \oplus B_2 \oplus E$ and the level of degeneracy is further lowered.

Summarizing



6.4 Comments on basis functions

Group theory tells us how the impurity ion energy levels are split by the crystal field. Not the ordering of the levels. This can though be typically inferred from the form of the basis functions. Let us assume an anionic tetrahedral crystal field: (negative charge at the corners of the tetrahedron introduced in the beginning of 6.3)

$$T_2: \quad xy \quad yz \quad zx \quad \rightarrow \quad \text{only slightly modified}$$

$$E: \quad x^2 - y^2, \quad 3z^2 - r^2 \quad \rightarrow \quad \text{strongly shifts upwards}$$

The T_2 orbitals have densities far from the ions, while E type orbitals point in the direction of the anions \Rightarrow strong repulsive interaction. By further lowering the symmetry to D_4 , the basis functions associated to the irreducible representations

$$E \begin{cases} y^2 \\ zx \end{cases} \quad B_2 \begin{cases} xy \end{cases} \quad B_1 \begin{cases} x^2 - y^2 \end{cases} \quad A_1 \begin{cases} z^2 \end{cases}$$

Then we conclude that E and B_2 come from T_2 B_1 and A_1 from E .

6.5 Comments on the form of crystal fields

The set of spherical harmonics is a complete set \Rightarrow any function can be written in terms of Y_{lm} . Group theory, though, can greatly simplify the problem. V_{cristal} is invariant under all transformations belonging to the point group \Rightarrow it must transform like A_{1g} . If we write a table of the irreducible representations of O_h contained in $Y_{l,m}$ one obtains that $l=0$, and $l=4$ (and $l=6, 8, 10, 12, 14, \dots$) contain A_{1g} .

Let us now prove it explicitly: the potential generated in x, y, z by a charge e in $x = -a$ is

$$V_{x=-a} = \frac{e}{\sqrt{(x+a)^2 + y^2 + z^2}} = \frac{e}{a \sqrt{\left(1 + \frac{x}{a}\right)^2 + \left(\frac{y}{a}\right)^2 + \left(\frac{z}{a}\right)^2}} = \frac{e}{a \sqrt{1 + \varepsilon}}$$

now considering $|x, y, z| \ll a$

$$(1 + \varepsilon)^{-1/2} = 1 - \frac{1}{2} \varepsilon + \frac{3}{8} \varepsilon^2 - \frac{5}{16} \varepsilon^3 + \frac{35}{128} \varepsilon^4 + \dots$$

where $\varepsilon = \frac{x^2}{a^2} + \left(\frac{y}{a}\right)^2 + \left(\frac{z}{a}\right)^2$.

$$V_{x=a} + V_{x=-a} = \frac{2e}{a} \left[1 - \frac{1}{2} \left(\frac{r^2}{a^2}\right) + \frac{3}{2} \left(\frac{x^2}{a^2}\right) + \frac{3}{8} \left(\frac{r^4}{a^4}\right) - \frac{15}{4} \left(\frac{x^2}{a^2}\right) \left(\frac{r^2}{a^2}\right) + \frac{35}{8} \left(\frac{x^4}{a^4}\right) + \dots \right]$$

If now we put a charge e in $x = \pm a, y = \pm a, z = \pm a$ we obtain:

$$V_{\text{total}} = \frac{2e}{a} \left[3 + \frac{35}{8a^4} (x^4 + y^4 + z^4) - \frac{21}{8} \left(\frac{r^4}{a^4}\right) + \dots \right]$$

\Rightarrow the perturbation lifting the degeneracy of the free atom is

$$V_{\text{cubic}} = \frac{35e}{40^3} \left[(x^4 + y^4 + z^4) - \frac{3}{5} r^4 \right] \quad (2)$$

Since the crystal field is generated by point like charges and is interesting far from them, it solves the Laplace equation $\nabla^2 V = 0$ which is of the form $r^l Y_{lm}(\theta, \phi)$. From the group theoretical analysis we already expect $Y_{4,m}$ to participate to V_{cubic} . Comparison with (2) tells us that they will be $Y_{4,4}, Y_{4,-4}$ composing $x^4 + y^4$ and $Y_{4,0}$ associated to z^4 . Interestingly the same form of the potential is obtained if one starts from anions at the vertices of a cube as group theory straightforwardly predicts.