

Lecture 2: Energy levels in metal complexes: ligand field theory, spin-orbit coupling, zero-field-splitting, magnetic susceptibility

Ligand Field Theory

The full rotation group of a sphere: R_3 or SU_2

The full rotation group of a sphere has an infinite number of elements. The symmetry operations of R_3 are all rotations about all axes of the sphere. As an exercise you may demonstrate that 2 rotations $C(\phi)$ about 2 different arbitrary axes but of the same angle ϕ belong to the same class.

Recall that any symmetry operations commutes with the hamiltonian of the system that you consider. Hence the wave function associated to each of the terms $2S+1\Gamma$ of the free ion are a basis of the irreducible representations of the full rotation group R_3 of a sphere.

Indeed, a simple formula to determine the characters of a rotation by an angle Φ spanned through the $2l+1$ functions $|l, m\rangle$ is easily obtained (exercise). Consider: $|l, m\rangle = F(r)P_{lm}(\theta)e^{im\phi}$ where $\mathbf{R}(\Phi)$ is a rotation by an angle Φ about the polar axis; we thus obtain:

$$\mathbf{R}(\Phi)|l, m\rangle = \mathbf{R}(\Phi)F(r)P_{lm}(\theta)e^{im\phi} = F(r)P_{lm}(\theta)e^{im(\phi+\Phi)}, \quad m=-l, \dots, 0, \dots, l.$$

It is easily seen that the following diagonal matrix of dimension $(2l+1)$ permits to represent $\mathbf{R}(\Phi)$:

$$\Gamma[\mathbf{R}(\phi)] = \begin{bmatrix} e^{il\phi} & & 0 \\ & \dots & \\ 0 & & e^{-il\phi} \end{bmatrix}$$

and that the characters of this representation becomes

$$\chi(\phi) = e^{il\phi} + e^{i(l-1)\phi} + \dots + e^{-il\phi} = \frac{\sin\left[\left(l+\frac{1}{2}\right)\phi\right]}{\sin\left(\frac{\phi}{2}\right)}$$

If one generalizes for the case of many-electron functions, each irreducible representation Γ has as basis the $2L+1$ spatial functions $|L, M_L\rangle$ i.e. $\Gamma=S$ if $L=0$, $\Gamma=P$ if $L=1$, $\Gamma=D$ if $L=2$, $\Gamma=F$ if $L=3$, $\Gamma=G$ if $L=4$, $\Gamma=H$ if $L=5$, etc. Thus, the character associated to the rotation $C(\phi)$ is:

$$\chi(\phi) = \frac{\sin\left[\left(L+\frac{1}{2}\right)\phi\right]}{\sin\left(\frac{\phi}{2}\right)}$$

The characters of the full rotation group R_3 pour has the identity element $E=C(0)$ and the operations of the class $C(\phi)$ are represented by:

R_3	E	$\infty C(\phi)$
Γ	$2L+1$	$\frac{\sin \left[\left(L + \frac{1}{2} \right) \phi \right]}{\sin \left(\frac{\phi}{2} \right)}$

A complete character table for this group is given below :

R_3	E	$\infty C(\phi)$	
S	1	1	$x^2+y^2+z^2$
P	3	$1+2\cos(\phi)$	$(x,y,z), (R_x,R_y,R_z)$
D	5	$1+2\cos(\phi)+2\cos(2\phi)$	$(2z^2-x^2-y^2, x^2-y^2, xy, xz, yz)$
F	7	$1+2\cos(\phi)+2\cos(2\phi)+2\cos(3\phi)$	
...	

Remember : Terms of all d^n configurations:

configuration	Terms
d^0 et d^{10}	1S
d^1 et d^9	2D
d^2 et d^8	$^1G, ^3F, ^1D, ^3P, ^1S$
d^3 et d^7	$^4F, ^4P, ^2H, ^2G, ^2F, ^2D, ^2D, ^2P$
d^4 et d^6	$^5D, ^3H, ^3G, ^3F, ^3F, ^3D, ^3P, ^3P, ^1I, ^1G, ^1G, ^1F, ^1D, ^1D, ^1S, ^1S$
d^5	$^6S, ^4G, ^4F, ^4D, ^4P, ^2I, ^2H, ^2G, ^2G, ^2F, ^2F, ^2D, ^2D, ^2D, ^2P, ^2S$

Splitting of the energy levels in a chemical environment

Consider the characters of R_3 for $l = 2$

$$\chi(\phi) = \frac{\sin \left[\left(2 + \frac{1}{2} \right) \phi \right]}{\sin \left(\frac{\phi}{2} \right)}$$

For a rotation C_2 $\phi = \pi$ and hence

$$\chi(C_2) = \frac{\sin \left[\left(2 + \frac{1}{2} \right) \pi \right]}{\sin \left(\frac{\pi}{2} \right)} = \frac{\sin \left(\frac{5\pi}{2} \right)}{\sin \left(\frac{\pi}{2} \right)} = \frac{1}{1} = 1$$

And similarly for order 3 and 4 rotations

$$\chi(C_3) = \frac{\sin\left[\left(2+\frac{1}{2}\right)\frac{2\pi}{3}\right]}{\sin\left(\frac{1}{2}\frac{2\pi}{3}\right)} = \frac{\sin\left(\frac{5\pi}{3}\right)}{\sin\left(\frac{\pi}{3}\right)} = \frac{-\sin\left(\frac{\pi}{3}\right)}{\sin\left(\frac{\pi}{3}\right)} = -1$$

$$\chi(C_4) = \frac{\sin\left[\left(2+\frac{1}{2}\right)\frac{\pi}{2}\right]}{\sin\left(\frac{\pi}{4}\right)} = \frac{\sin\left(\frac{5\pi}{4}\right)}{\sin\left(\frac{\pi}{4}\right)} = -1$$

The formula is also valid for the case where $\phi=0$ i.e.

$$\chi(E) = 2l+1 = 5$$

This result can be obtained as follows, that is consider :

$$\chi(\phi=0) = \lim_{\phi \rightarrow 0} \frac{\sin[(l+1/2) \cdot \phi]}{\sin(\phi/2)} = \frac{(l+1/2) \cdot \phi}{\phi/2} = 2 \cdot (l+1/2) = 2l+1$$

In an octahedral (O symmetry point group) environment, using a character table e.g. : P.W. Atkins, M.S. Child, and C.S.P. Phillips; "Tables for Group Theory"; Oxford University Press 1970; the irrep d (l=2) is reducible and the reduction of irrep (short notation for irreducible representations) d (Tables for Group Theory cited above p. 24) yields e + t₂.

Consider a few typical examples:

Example 1: Splitting of the $lL M_L >$ levels in an octahedral environment

Symmetry of level	L	$\chi(E)$	$\chi(C_2)$	$\chi(C_3)$	$\chi(C_4)$	Irreducible representations
S	0	1	1	1	1	A _{1g}
P	1	3	-1	0	1	T _{1u}
D	2	5	1	-1	-1	E _g +T _{2g}
F	3	7	-1	1	-1	A _{2u} +T _{1u} +T _{2u}
G	4	9	1	0	1	A _{1g} +E _g +T _{1g} +T _{2g}
H	5	11	-1	-1	1	E _u +2T _{1u} +T _{2u}
I	6	13	1	1	-1	A _{1g} +A _{2g} +E _g +T _{1g} +2T _{2g}

Example 2: Splitting of the d-orbitals in various symmetries

R ₃	O _h	T _d	D _{4h}	D ₃	D _{2d}
d	e _g +t _{2g}	e+t ₂	a _{1g} +b _{1g} +b _{2g} +e _g	a ₁ +2e	a ₁ +b ₁ +b ₂ +e

Example 3: Splitting of all d² terms in an octahedral environment

There are two procedures.

1st procedure: weak field approach, the terms of the free ion are split by a weak chemical

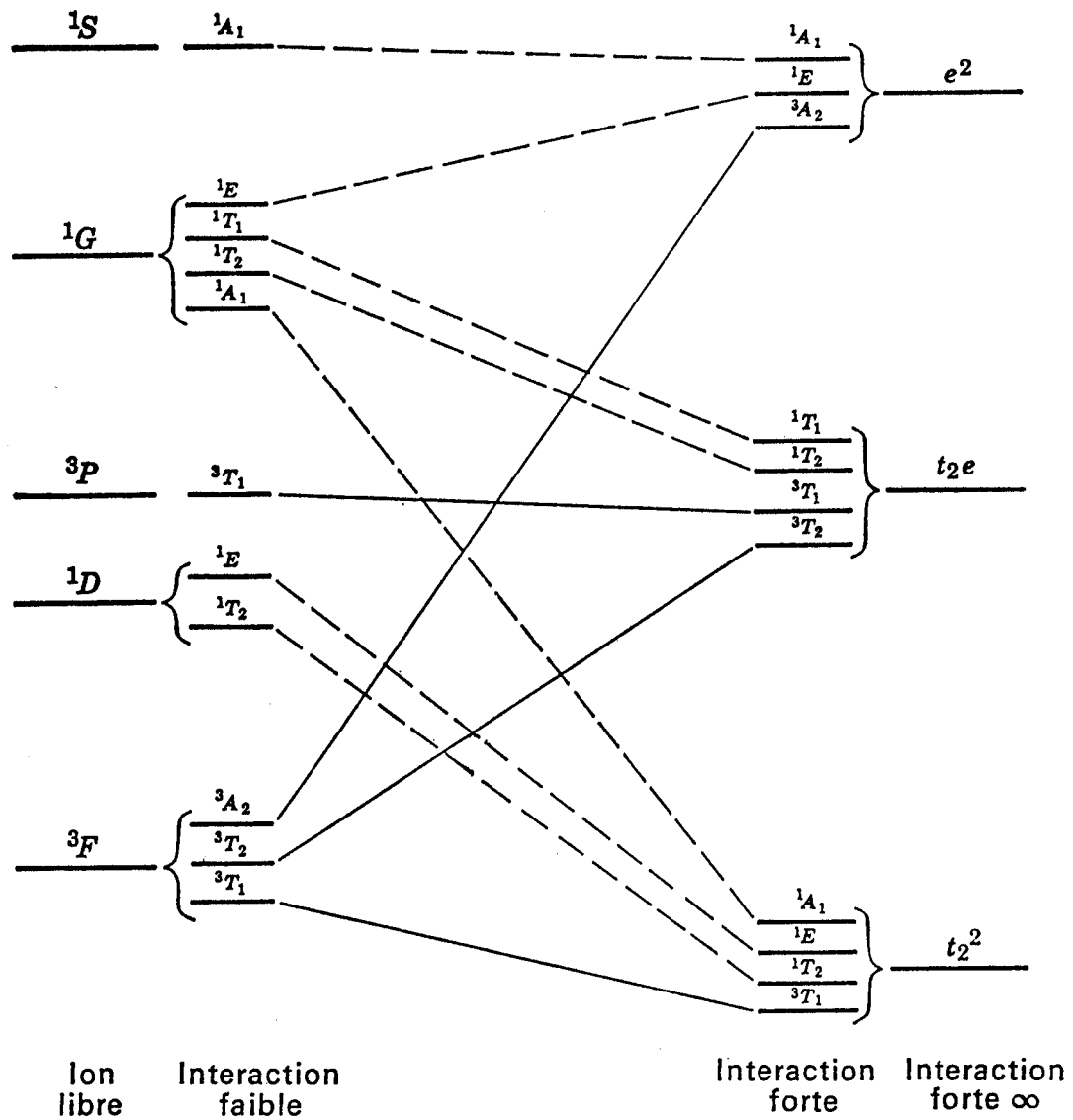
environment (field)

$$\begin{array}{ll}
 {}^1\text{G} & \rightarrow {}^1\text{A}_1 + {}^1\text{E} + {}^1\text{T}_1 + {}^1\text{T}_2 \\
 {}^3\text{F} & \rightarrow {}^3\text{A}_2 + {}^3\text{T}_1 + {}^3\text{T}_2 \\
 {}^1\text{D} & \rightarrow {}^1\text{E} + {}^1\text{T}_2 \\
 {}^3\text{P} & \rightarrow {}^3\text{T}_1 \\
 {}^1\text{S} & \rightarrow {}^1\text{A}_1
 \end{array}$$

2nd procedure: strong field approach, the d-orbitals are first split by a strong chemical environment (field) in e_g et t_{2g} and the inter-electronic repulsion acts as a perturbation. We shall consider all configurations $e_g^x t_{2g}^{n-x}$ ($x = 0, 1, \dots, n$) and determine through the direct product all states stemming from each of those configurations. Our example yields

$$\begin{array}{llll}
 e_g^2: & e_g \otimes e_g = A_{1g} + [A_{2g}] + E_g & \rightarrow & {}^1A_{1g} + {}^3A_{2g} + {}^1E_g \\
 t_{2g}e_g: & t_{2g} \otimes e_g = T_{1g} + T_{2g} & \rightarrow & {}^1T_{1g} + {}^3T_{1g} + {}^1T_{2g} + {}^3T_{2g} \\
 t_{2g}^2: & t_{2g} \otimes t_{2g} = A_{1g} + E_g + [T_{1g}] + T_{2g} & \rightarrow & {}^1A_{1g} + {}^1E_g + {}^3T_{1g} + {}^1T_{2g}
 \end{array}$$

Both procedure are obviously equivalent as illustrated in the correlation diagram below:



Double Groups

The relation

$$\chi(\phi) = \frac{\sin\left[\left(L+\frac{1}{2}\right)\phi\right]}{\sin\left(\frac{\phi}{2}\right)}$$

was obtained neglecting the coupling between the orbital momentum \vec{L} and the spin \vec{S} . However, if one does consider this coupling the resulting momentum

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$$

has to be considered. The relation of $\chi(\phi)$ for the functions associated to a $(2J+1)$ -fold degenerate state reads

$$\chi(\phi) = \frac{\sin\left[\left(J+\frac{1}{2}\right)\phi\right]}{\sin\left(\frac{\phi}{2}\right)}$$

where J is the quantum number associated to \hat{J} .

The possible values for L are all integers, whereas J can also take half integer values. Let's now consider a rotation by an angle ϕ followed by a rotation of 2π about the same axis; if J is integer, the equation above becomes:

$$\chi(\phi+2\pi) = \chi(\phi)$$

However if J is half-integer we get :

$$\chi(\phi+2\pi) = -\chi(\phi)$$

Hence a rotation of 2π can no longer be considered as the identity operation. However a rotation of 4π corresponds to the identity.

To circumvent this difficulty, Bethe proposed note a rotation of 2π by **R** and to associate to each symmetry group G a new one labelled G^* containing all elements of G plus the direct product **R** by G

$$G^* = \{G, \mathbf{R} \otimes G\}$$

Example 1: Irreducible representation spanned by a spin doublet: $\begin{pmatrix} \alpha \\ \beta \end{pmatrix}$

Let's apply the relation for $\chi(\phi)$ with $J=1/2$, we get:

O*	E	R	$4C_3$ $4C_3^2R$ $= 8C_3$	$4C_3R$ $4C_3^2$ $= 8C_3R$	$3C_2$ $3C_2R$ $= 6C_2$	$3C_4$ $3C_4^3R$ $= 6C_4$	$3C_4R$ $3C_4^3$ $= 6C_4R$	$6C_2'$ $6C_2'R$ $= 12C_2'$
$\Gamma\left(\begin{smallmatrix} \alpha \\ \beta \end{smallmatrix}\right)$	2	-2	1	-1	0	$\sqrt{2}$	$-\sqrt{2}$	0

verifying in: P.W. Atkins, M.S. Child, and C.S.P. Phillips; "Tables for Group Theory"; Oxford University Press 1970, we notice:

$$\Gamma\left(\begin{smallmatrix} \alpha \\ \beta \end{smallmatrix}\right) = E_{1/2}$$

Example 2: Irreducible representation spanned by a spin doublet triplet

$J=1$ is integer and yields:

$$\Gamma_{\text{triplet}} = T_1$$

Exemple 3: Determine all spin-orbit components for the ground state 3T_1 of d^2 ion in an octahedral ligand field:

All we have to do is to get the direct product between the irrep of the space part i.e. T_1 and the irrep of the spin part $\Gamma_{\text{triplet}} = T_1$. One obtains :

$$T_1 \otimes T_1 = A_1 + E + T_1 + T_2$$

Hence, the term considered splits under the spin-orbit coupling according to the following scheme:

$$^3T_1 \rightarrow A_1 + E + T_1 + T_2$$

Angular Overlap Model (AOM) and ligand field model

a) Ligand field model

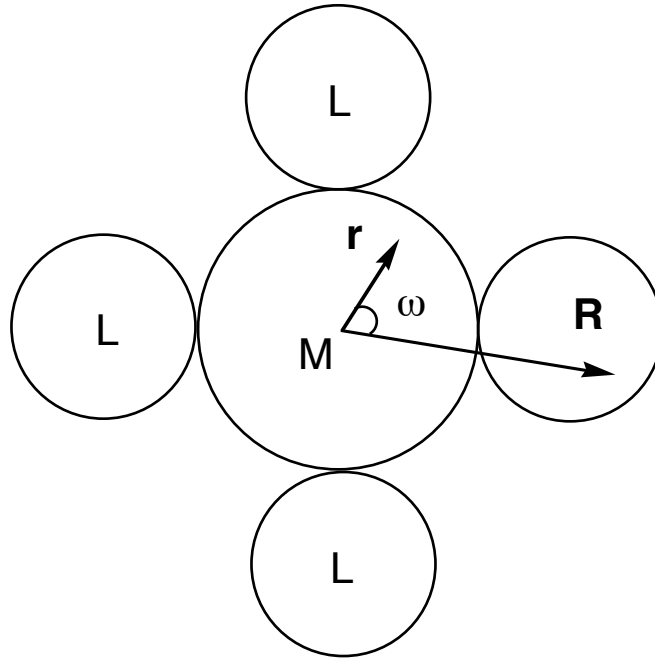
We want to represent the action of the chemical environment through an electrostatic perturbation

$$\mathbf{h} = \mathbf{h}_0 + \mathbf{v}_{\text{LF}}$$

where \mathbf{h}_0 is the hamiltonien of the free ion and \mathbf{v}_{LF} the electrostatic potential of ligand charge density at the metallic centre. If $\rho(\mathbf{r})$ the charge density due to the ligands one obtains for the electrostatic potential

$$v(\mathbf{r}) = -e \int \frac{\rho(\mathbf{R})}{|\mathbf{R} - \mathbf{r}|} d\mathbf{R}$$

The symbols used are defined in the fig. below and e represents the charge of the electron.



Expand $1/|\mathbf{r}-\mathbf{R}|$ to obtain

$$\frac{1}{|\mathbf{R}-\mathbf{r}|} = \frac{1}{r_{<}} \sum_{k=0}^{\infty} \left(\frac{r_{<}}{r_{>}}\right)^k P_k(\cos \omega)$$

where $r_{<} = \min\{r, R\}$, $r_{>} = \max\{r, R\}$ and $P_k(x)$ is a Legendre polynomial of order k .

We suppose (van Vleck and Bethe, 1928) that

$$r < R$$

With this hypothesis, we get:

$$\frac{1}{|\mathbf{R}-\mathbf{r}|} = \frac{1}{R} \sum_{k=0}^{\infty} \left(\frac{r}{R}\right)^k P_k(\cos \omega)$$

Moreover the Legendre polynomial may be expressed in term of spherical harmonics Y_{km} :

$$P_k(\cos \omega) = \frac{4\pi}{2k+1} \sum_{m=-k}^{+k} Y_{km}(\theta, \phi) Y_{km}^*(\Theta, \Phi)$$

where $\mathbf{r} = (r, \theta, \phi)$ and $\mathbf{R} = (R, \Theta, \Phi)$. Thus, one obtains:

$$\mathbf{v}_{\mathbf{LF}} = \sum_{k=0}^{2l} \sum_{q=-k}^{+k} h_{kq} Y_{kq}$$

$l=2$ for d-electrons and $=3$ for f-electrons; the parameters h_{kq} are adjustable and describe the ligand field.

The two following relation are useful:

$$h_{kq} = -\frac{4\pi e}{2k+1} \langle r^k \rangle \int \frac{\rho(R) Y_{kq}^*(\Theta, \Phi)}{R^{k+1}} dR$$

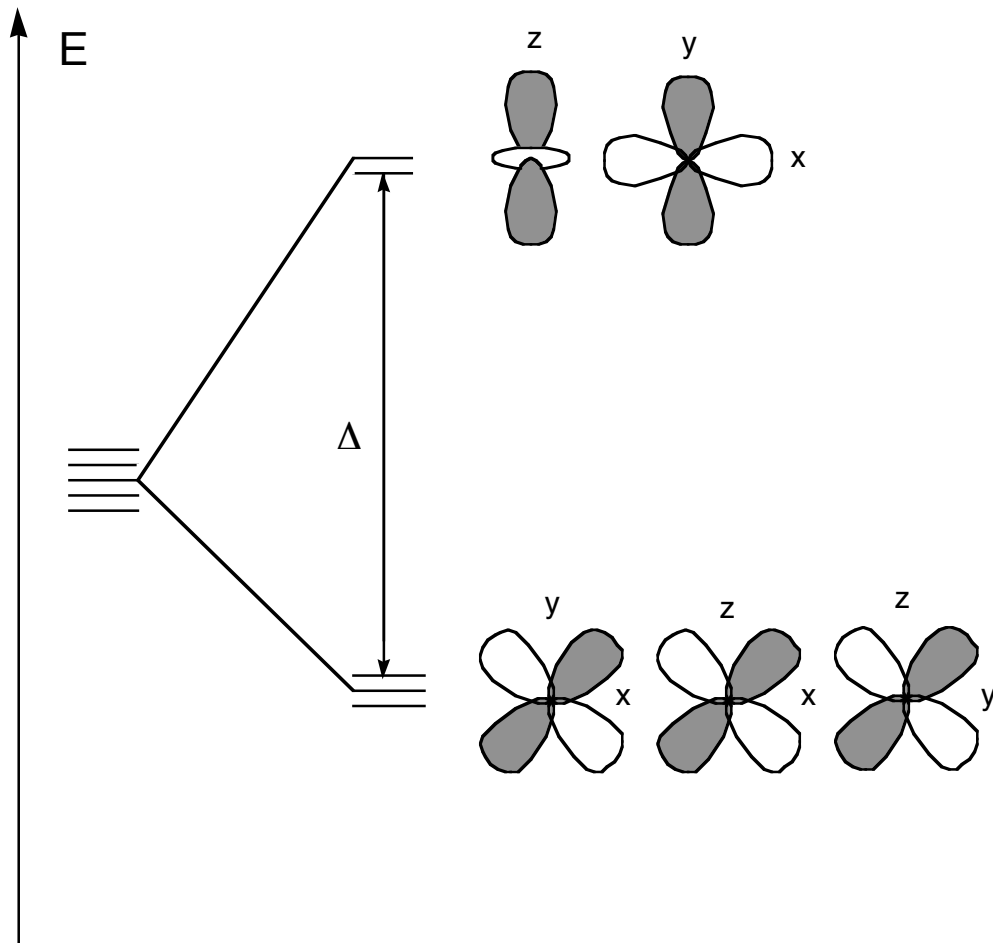
$$= \sum_{m, m'} (-1)^m (2k+1) \begin{pmatrix} l & l & k \\ -m & m' & q \end{pmatrix} \langle l m | \mathbf{v}_{LF} | l m' \rangle$$

$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$ are the well-known 3-j symbols of Wigner. The matrix $\langle l m | \mathbf{v}_{LF} | l m' \rangle$ has the dimension $(2l+1) \times (2l+1)$ and represents the operator \mathbf{v}_{LF} in the basis of the d-, or f-orbitals. The same result can be obtained with the AOM discussed in the following section.

E.g. for an octahedral d complex we get :

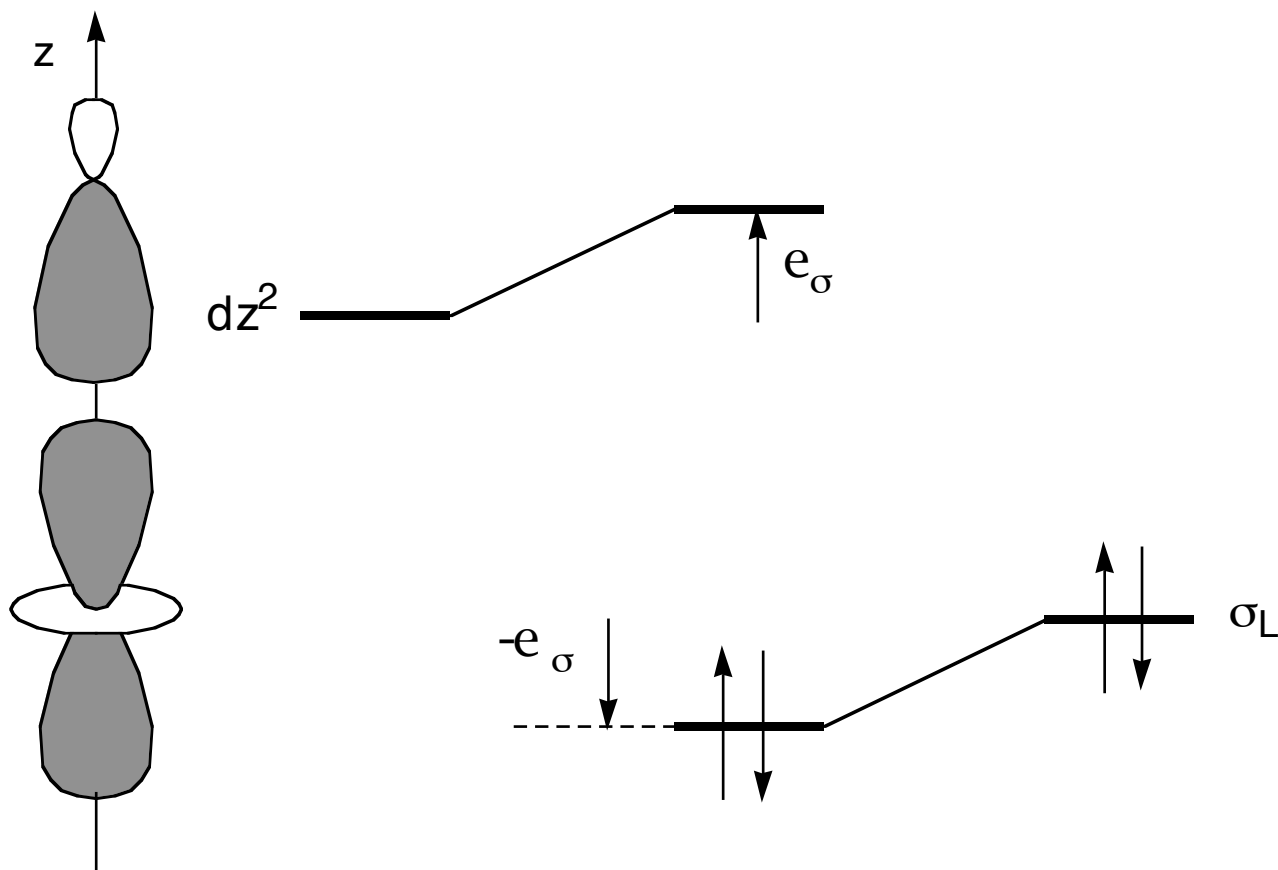
$$\mathbf{v}_{Oh} = -\frac{3}{2} \Delta Y_{4-4} - \frac{5}{2} \Delta Y_{40} - \frac{3}{2} \Delta Y_{44}$$

Thus the action of an octahedral ligand field has the following splitting scheme:



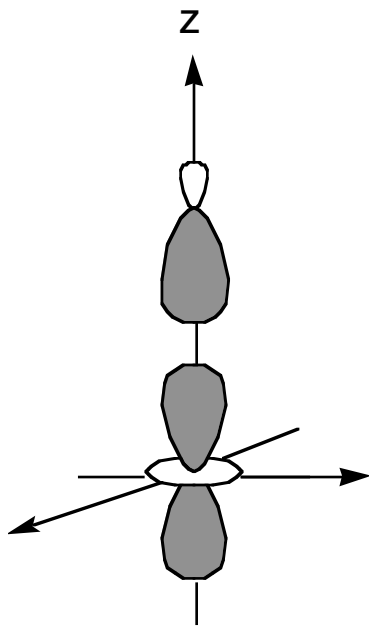
b) Angular Overlap Model (AOM)

Consider:

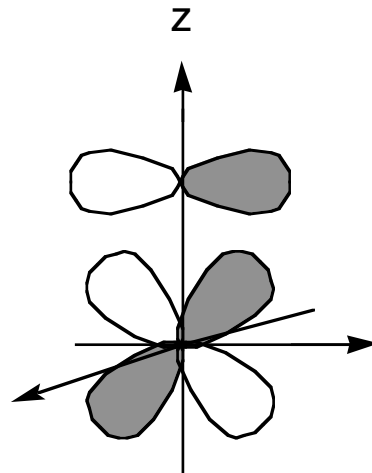


Consider now other possible types of M-L interactions:

- | | | |
|-------------------|----------|------------------|
| no nodal plane: | σ | |
| one nodal plane: | π | |
| two nodal planes: | δ | (never observed) |

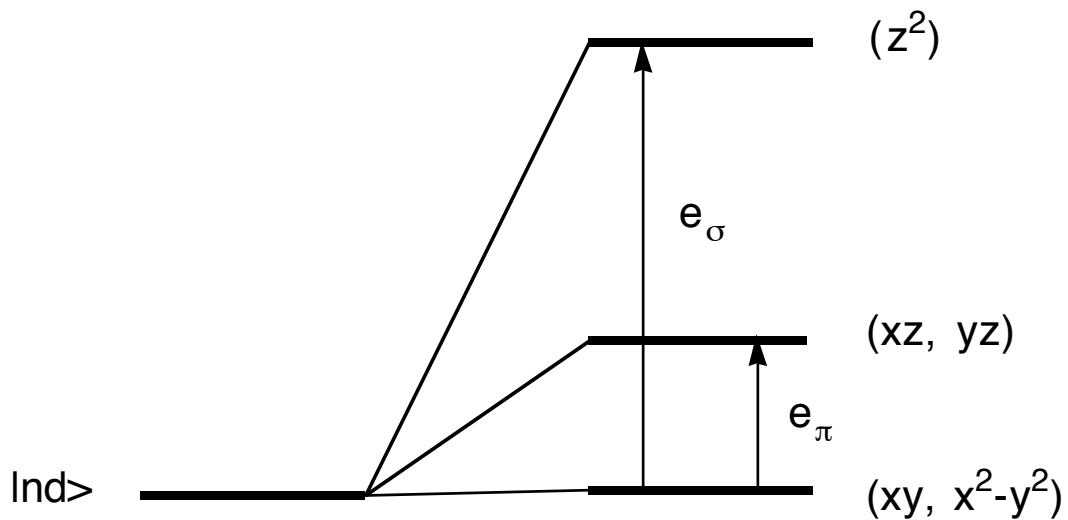


Définition de e_{σ}



Définition de e_{π}

Consider the splitting of the 5 d-orbitals due to a local M-L interaction:



A semi-quantitative physical interpretation of the parameters e_{σ} et e_{π} can be estimated as follows:

$$e_k \approx \frac{\langle \psi_M | \mathbf{h} | \psi_{L_k} \rangle^2}{\langle \psi_M | \mathbf{h} | \psi_M \rangle - \langle \psi_{L_k} | \mathbf{h} | \psi_{L_k} \rangle} \approx \text{const.} \cdot \langle \psi_M | \psi_L \rangle^2$$

where \mathbf{h} is an effective hamiltonian for the M-L entity and ψ represents respectively the orbitals of the metal M and of the ligand L, i.e. σ or π .

If we suppose additivity and transferability of the AOM parameters we obtain for the ligand field

$$\mathbf{v} = \sum_{\mathbf{L}} \mathbf{v}_{\mathbf{L}}$$

The calculation of the elements $\langle d_i | \mathbf{v} | d_j \rangle$ in the basis of d-orbitals:

$$\begin{aligned} d_1 = dz^2 &= R(r) (3z^2 - r^2) / (2\sqrt{3}) \\ d_2 = dyz &= R(r) yz \\ d_3 = dxz &= R(r) xz \\ d_4 = dxy &= R(r) xy \\ d_5 = dx^2 - y^2 &= R(r) (x^2 - y^2) / 2 \end{aligned}$$

is illustrated below.

Let us first consider the interaction of a ligand L in axial z position with the d-orbitals, i.e.

$$\langle d_i | \mathbf{v}^z_{\mathbf{L}} | d_j \rangle = v^z_{ij,L}$$

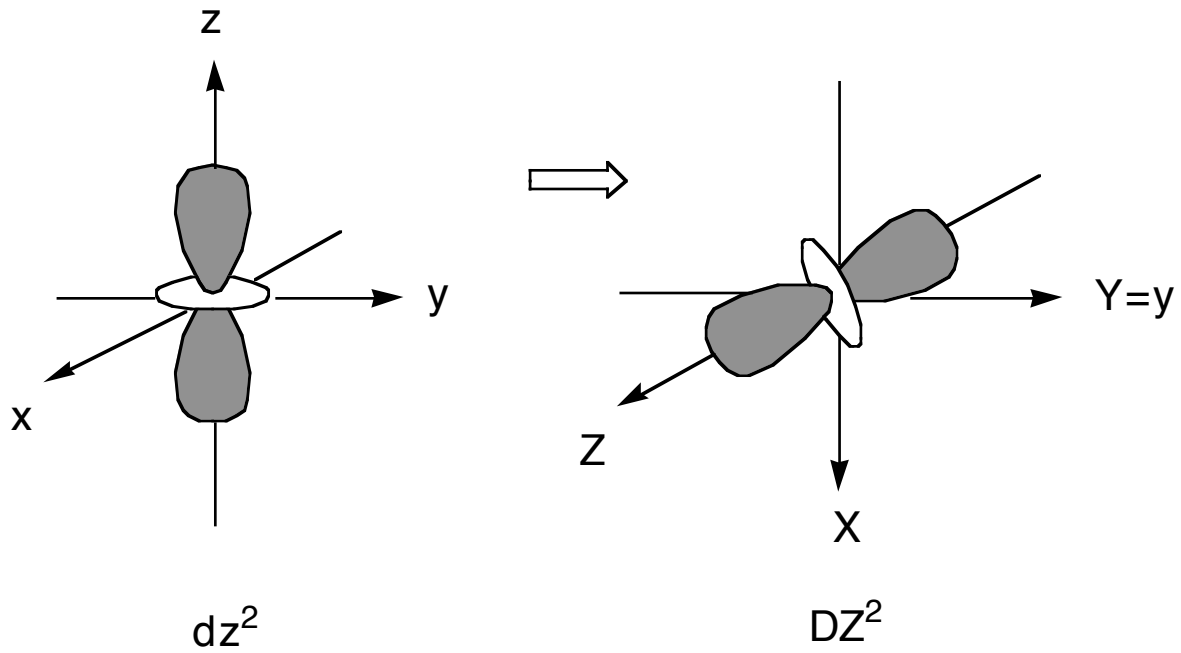
$\mathbf{v}^z_{\mathbf{L}}$	z^2	yz	xz	xy	$x^2 - y^2$
z^2	σ_L				
yz		π_L			
xz			π_L		
xy				0	
$x^2 - y^2$					0

Next consider the interaction of ligand L on the x-axis with the d-orbitals, i.e. $\langle d_i | \mathbf{v}^x_{\mathbf{L}} | d_j \rangle = v^x_{ij,L} =$

?. we have to carry out the following axis transformation:

$$\begin{aligned} x &\rightarrow Z \\ y &\rightarrow Y \\ z &\rightarrow -X \end{aligned}$$

and let us apply this transformation to the previous system



we obviously get

$$v_L^x = v_L^z$$

and

$$\begin{aligned} dz^2 &\cong \frac{1}{2\sqrt{3}} (3z^2 - r^2) = \frac{1}{2\sqrt{3}} (3X^2 - R^2) = \\ &= -\frac{1}{2} \left[\frac{1}{2\sqrt{3}} (3Z^2 - R^2) \right] + \frac{\sqrt{3}}{2} \left[\frac{1}{2} (X^2 - Y^2) \right] = \\ &= -\frac{1}{2} DZ^2 + \frac{\sqrt{3}}{2} DX^2 - Y^2 \end{aligned}$$

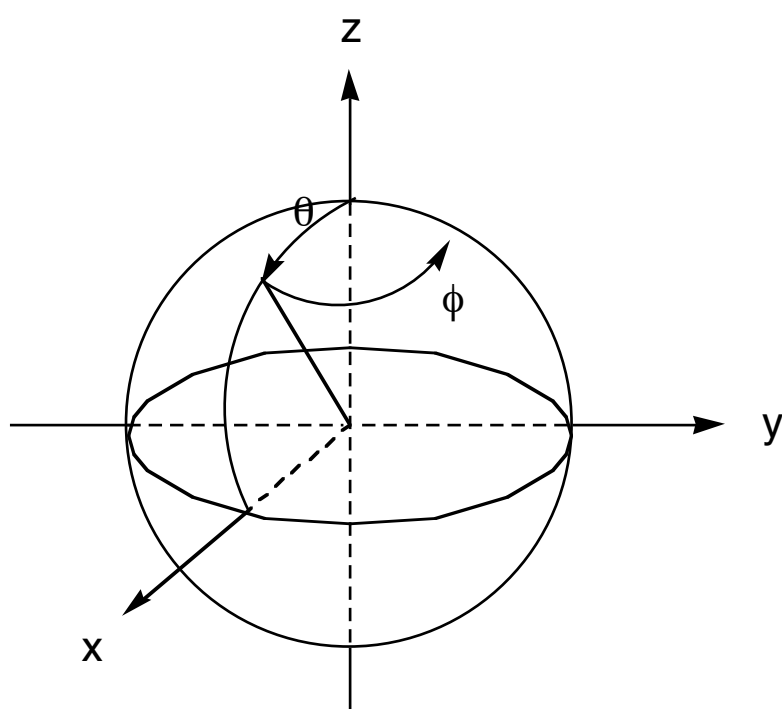
Hence

$$\begin{aligned} \langle dz^2 | v_L^x | dz^2 \rangle &= \langle -\frac{1}{2} DZ^2 + \frac{\sqrt{3}}{2} DX^2 - Y^2 | v_L^z | -\frac{1}{2} DZ^2 + \frac{\sqrt{3}}{2} DX^2 - Y^2 \rangle = \\ \frac{1}{4} \langle DZ^2 | v_L^z | DZ^2 \rangle &- \frac{\sqrt{3}}{4} \langle DZ^2 | v_L^z | DX^2 - Y^2 \rangle - \frac{\sqrt{3}}{4} \langle DX^2 - Y^2 | v_L^z | DZ^2 \rangle + \frac{3}{4} \langle DX^2 - Y^2 | v_L^z | DX^2 - Y^2 \rangle \\ &= \frac{1}{4} \langle DZ^2 | v_L^z | DZ^2 \rangle = \frac{1}{4} \sigma_L \end{aligned}$$

If we apply the same calculation to all elements $\langle d_i | v_{L}^x | d_j \rangle = v_{ij,L}^x$ we get

v^x_L	z^2	yz	xz	xy	x^2-y^2
z^2	$\frac{1}{4} \sigma_L$				$-\frac{\sqrt{3}}{4} \sigma_L$
yz					
xz			π_L		
xy				π_L	
x^2-y^2	$-\frac{\sqrt{3}}{4} \sigma_L$				$\frac{1}{4} \sigma_L$

Finally consider an arbitrary position where the ligand L is located on an axis (θ, ϕ)



$$(x, y, z) \rightarrow (X, Y, Z)$$

If one applies this transformation to the whole set of d-orbitals we obtain

$$\mathbf{T} \mathbf{D} = \mathbf{d}$$

where the elements of \mathbf{T} are given in the table below:

T	Z²	YZ	XZ	XY	X²-Y²
z²	$\frac{1}{4}(1 + 3\cos 2\theta)$	0	$-\frac{\sqrt{3}}{2} \sin 2\theta$	0	0
Yz	$\frac{\sqrt{3}}{2} \sin 2\theta \sin \phi$	$\cos \theta \cos \phi$	$\cos 2\theta \sin \phi$	0	0
Xz	$\frac{\sqrt{3}}{2} \sin 2\theta \cos \phi$	$-\cos \theta \sin \phi$	$\cos 2\theta \cos \phi$	0	0
xy	$\frac{\sqrt{3}}{2} \sin^2 \theta \sin 2\phi$	$\sin \theta \cos 2\phi$	$\frac{1}{2} \sin 2\theta \sin 2\phi$	0	0
x²-y²	$\frac{\sqrt{3}}{2} \sin^2 \theta \cos 2\phi$	$-\sin \theta \sin 2\phi$	$\frac{1}{2} \sin 2\theta \cos 2\phi$	0	0

Whereas the calculation of the elements $\langle d_i | \mathbf{v}_L^{(\theta, \phi)} | d_j \rangle$ are obtained as previously

$$\begin{aligned}
 \langle d_i | \mathbf{v}_L^{(\theta, \phi)} | d_j \rangle &= v_{ij,L}^{(\theta, \phi)} = \langle \sum_k T_{ik} D_k | \mathbf{v}_L^{(\theta, \phi)} | \sum_l T_{jl} D_l \rangle \\
 &= \sum_{k,l} T_{ik} T_{jl} \langle D_k | \mathbf{v}_L^{(\theta, \phi)} | D_l \rangle
 \end{aligned}$$

But

$$\langle D_k | \mathbf{v}_L^{(\theta, \phi)} | D_l \rangle = \langle d_k | \mathbf{v}_L^Z | d_l \rangle$$

where

$$\mathbf{v}_{kk,L}^Z = \begin{cases} \sigma_L \equiv \mathbf{e}_{\sigma,L} & \text{pour } k = 1 \quad (z^2) \\ \pi_L \equiv (\mathbf{e}_{\pi||,L}, \mathbf{e}_{\pi\perp,L}) & \text{pour } k = 2,3 \quad (yz, xz) \\ 0 & \text{pour } k = 4,5 \quad (xy, x^2-y^2) \end{cases}$$

Thus

$$\langle d_i | \mathbf{v}_L^{(\theta, \phi)} | d_j \rangle = v_{ij,L}^{(\theta, \phi)} = \sum_{k=1}^5 T_{ik} T_{jk} \mathbf{v}_{kk,L}^Z$$

To summarize, the calculation of the d-level splitting is as follows:

- (i) Calculate $\mathbf{v}_{ij,L}^{(\theta, \phi)} = \sum_{k=1}^3 T_{ik} T_{jk} \mathbf{e}_{k,L}$, where $k = (\mathbf{e}_{\sigma,L}, \mathbf{e}_{\pi||,L}, \mathbf{e}_{\pi\perp,L})$ for each ligand L.
- (ii) Calculate the full matrix: $\mathbf{v}_{ij} = \sum_L \mathbf{v}_{ij,L}^{(\theta, \phi)}$
- (iii) If needed diagonalize the matrix $\mathbf{v}_{ij} = \mathbf{v}$
- (iv) The eigenvalues thus obtained are energies levels of the d-orbitals in the field of the ligands

To conclude we give below two tables. The 1st one represents the splitting of the d-orbitals for common coordination geometries. The 2nd one lists numerical values of AOM parameters for common cobalt and chrome complexes.

Table: Splitting of d-orbitals in three common ligand fields

orbital	octahedron	square planar (xy)	tetrahedron
z^2	$3e_{\sigma}$	e_{σ}	$\frac{8}{3} e_{\pi}$
yz	$4e_{\pi}$	$2 (e_{\pi }+e_{\pi\perp})$	$\frac{4}{3} e_{\sigma} + \frac{8}{9} e_{\pi}$
xz	$4e_{\pi}$	$2 e_{\pi }$	$\frac{4}{3} e_{\sigma} + \frac{8}{9} e_{\pi}$
xy	$4e_{\pi}$	$2 e_{\pi }$	$\frac{4}{3} e_{\sigma} + \frac{8}{9} e_{\pi}$
X^2-y^2	$3e_{\sigma}$	$3e_{\sigma}$	$\frac{8}{3} e_{\pi}$

Table: AOM parameters for a few common Cr- and Co-complexes in 10^3cm^{-1} .

M-L	e_{σ}	e_{π}	$\Delta_o (=3e_{\sigma}-4e_{\pi})$
Cr-Br	5.34	1.00	10.02
Cr-Cl	5.56	0.90	13.07
Cr-F	7.63	1.88	15.37
Cr-OH	8.66	2.25	17.00
Cr-NCS	6.41	0.38	17.71
Cr-py	5.80	-0.58	19.71
Cr-NH ₃	7.28	0.00	21.85
Cr-CN	8.48	-0.29	26.50
Co-Cl	6.29	1.29	14.60
Co-OH ₂	6.60	1.08	15.47
Co-OH	9.61	4.54	10.67
Co-NH ₃	7.81	0.00	23.43
Co-CN	12.15	0.39	34.89

Matlab script :

```
% O
data=[0 0 6 1 1;
90 0 6 1 1;
90 90 6 1 1;
90 180 6 1 1;
90 270 6 1 1;
180 0 6 1 1];
% D4
%data=[
```



```

%90 0 6 1 1;
%90 90 6 1 1;
%90 180 6 1 1;
%90 270 6 1 1];
% D3
%data=[ 54.7356    0 1. .0 .0;
%      54.7356 120 1. .0 .0;
%      54.7356 240 1. .0 .0;
%      125.2644  60 1. .0 .0;
%      125.2644 180 1. .0 .0;
%      125.2644 300 1. .0 .0];
% Icosahedron
%data=[
%      0          0 1 0.1 0.1;
%  63.4349    90.0000 1 0.1 0.1;
%  63.4349    18.0000 1 0.1 0.1;
%  63.4349   306.0000 1 0.1 0.1;
%  63.4349   234.0000 1 0.1 0.1;
%  63.4349   162.0000 1 0.1 0.1;
% 116.5651   270.0000 1 0.1 0.1;
% 116.5651   198.0000 1 0.1 0.1;
% 116.5651   126.0000 1 0.1 0.1;
% 116.5651    54.0000 1 0.1 0.1;
% 116.5651   342.0000 1 0.1 0.1;
% 180.0000          0 1 0.1 0.1];
n=size(data);conv=pi/180;
for i=1:5
for j=1:5
v(i,j)=0;
for l=1:n(1)
t=trd(conv*data(l,1:2));
for k=1:3
v(i,j)=v(i,j)+t(i,k)*t(j,k)*data(l,k+2);
end
end
end
end
disp('   Dsigma   Dpi,s   Dpi,c   Ddel,s   Ddel,c')
disp(v)
[c e]=eig(v);
[e iv]=sort(diag(e));
e=e';disp(' ');disp(e)
c=c(:,iv);disp(c)
%v
%[c e]=eig(v);
%[e iv]=sort(diag(e));
%e=e'
%c=c(:,iv)

function t=trd(w)
theta=w(1);phi=w(2);
sq=sin(theta);cq=cos(theta);s2q=sin(theta+theta);
c2q=cos(theta+theta);sq2=sq*sq;
sf=sin(phi);cf=cos(phi);s2f=sin(phi+phi);c2f=cos(phi+phi);
r32=0.5*sqrt(3);
t=[0.25*(1+3*c2q) 0 -r32*s2q;
r32*s2q*sf cq*cf c2q*sf;
r32*s2q*cf -cq*sf c2q*cf;
r32*sq2*s2f sq*c2f 0.5*s2q*s2f;
r32*sq2*c2f -sq*s2f 0.5*s2q*c2f];

```

Density Functional Theory calculation of the Ligand-Field manifold (LFDFT)

Ligand field theory has been used with success to describe ground and excited electronic states originating from d^n transition metals (TM) in their complexes. Both crystal/ligand field theory (LFT) and developments - the angular overlap model (AOM) parameterize the Hamiltonian in terms of one-electron (ligand field) parameters and two-electrons repulsion integrals within the manifold of d-electrons. The latter ones are treated as atomic-like, thus preserving spherical symmetry, while the former take full account for the lowering of symmetry when a spherical TM atom or ion is introduced in a complex. Thus, in cubic symmetry, only one energy parameter $10Dq$ – the energy difference between the σ and π , e_g and t_{2g} for octahedral field (or between the $\sigma+\pi$ and π , t_2 and e orbitals for tetrahedral field) is introduced in addition to Racah's inter-electronic repulsion parameters B and C . These three parameters are usually determined from a fit to electronic absorption spectra in high resolution. From these data, two general observations can be made:

- i) Ligands order in a sequence of increasing values of $10Dq$, called spectrochemical series, where negatively charged ligands such as $I < Br < Cl < F$ possess smaller $10Dq$ values, than neutral molecules $H_2O < NH_3 < \text{pyridine}$, CN^- and CO being the strongest ligand due to their ability for back bonding.
- ii) B and C parameters in complexes are smaller than those for the free ions - the phenomenon being discovered by Schäffer and Jørgensen and rationalized in terms of the electronic cloud expansion of the d-orbitals when going from free TM ions to complexes (nephelauxetic effect). The more reducing and softer ligands show a stronger reduction than the more oxidizing and harder ones.

Description of the model

The LFDFT method, which has been recently proposed by Atanasov and Daul is briefly summarised here. Let us assume that we know the complex geometry, either from a first principle geometry optimisation or from X-ray data. The first step consists in a spin-restricted SCF DFT calculation of the average of the d^n configuration (AOC), providing an equal occupation $n/5$ on each MO dominated by the d-orbitals. The Kohn-Sham orbitals, which are constructed using this AOC are best suited for a treatment in which, interelectronic repulsion is - as is done in LF theory, approximated by atomic-like Racah parameters B and C . The next step consists in a spin-unrestricted calculation of the manifold of all Slater determinants (SD) originating from the d^n shell, i.e. 45, 120, 210 and 252 SD for $d^{2,8}$, $d^{3,7}$, $d^{4,6}$ and d^5 TM ions, respectively. These SD energies are used in the third step to extract the parameters of the one-electron 5×5 LF matrix h_{ab} as well as Racah's parameters B and C in a procedure, which we describe below. Finally, we introduce these parameters as input for a LF program allowing to calculate all the multiplets using CI of the full LF manifold utilizing the symmetry as much as possible. We should note that in classical LF theory, it is only the LF h_{ab} matrix, which carries information about the symmetry and the actual bonding in the complex, thus providing useful chemical information.

For octahedral complexes the LF matrix reduces to one parameter – $10Dq$. We, thus have, for each SD energy the simple linear expression in terms of B , C and $10Dq$:

$$\begin{aligned} E(SD_{\mu}^d) &= E\left(\det|d_{i(\mu,1)}\sigma_{i(\mu,1)}d_{i(\mu,2)}\sigma_{i(\mu,2)}\cdots d_{i(\mu,n)}\sigma_{i(\mu,n)}|\right) = \sum_i \langle d_i | h_{LF} | d_i \rangle + \sum_{i < j} (J_{ij} - K_{ij} \delta_{\sigma_i \sigma_j}) \\ &= \frac{3m_{\mu} - 2n_{\mu}}{5} 10Dq + \beta_{\mu} B + \gamma_{\mu} C + E_0 \end{aligned}$$

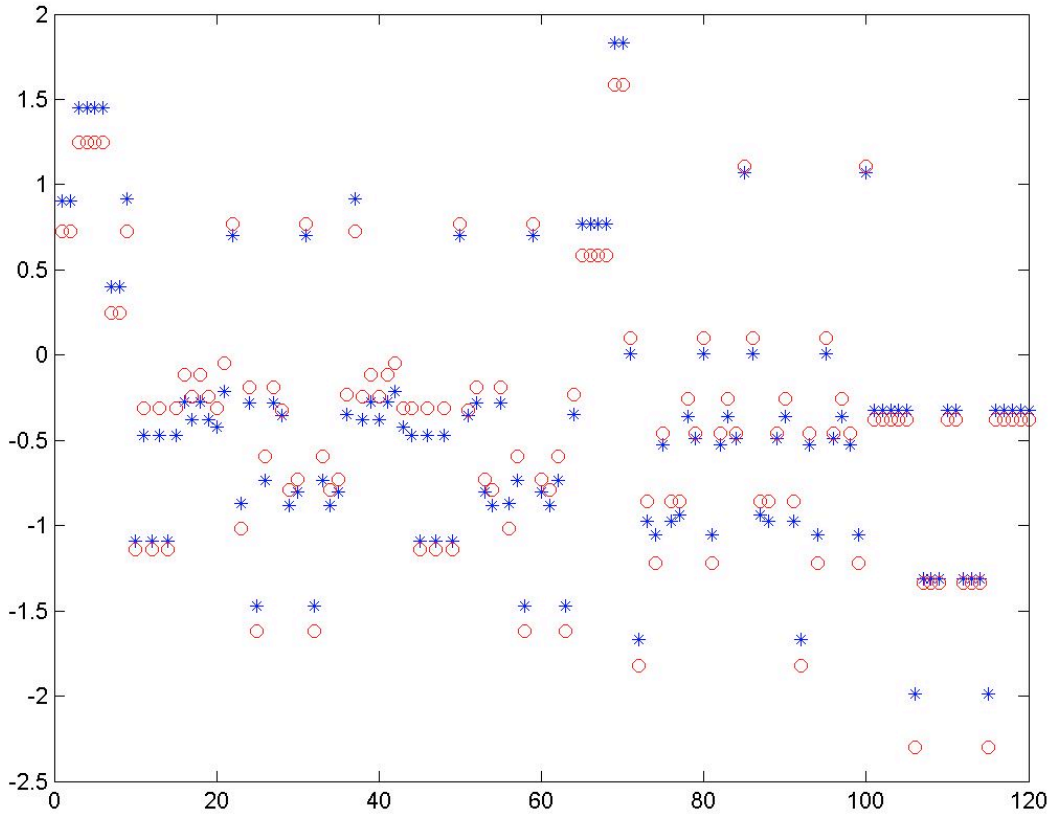
The single determinants SD_{μ}^d are labelled with the subscript $\mu = 1, \dots, \binom{10}{n}$ and with the superscript d to refer to pure d-spinorbitals. The values of m_{μ} and n_{μ} specify the electronic configuration

$t_{2g}^n e_g^m$, while the β_μ and γ_μ are coefficients obtained after substituting standard expressions for the Coulomb J_{ij} and exchange K_{ij} integrals in terms of d-only orbitals d_i and spin functions σ_i . E_0 represents the gauge origin of energy.

Having obtained energy expressions for each SD_μ^d : 10Dq, B, C and E_0 are estimated using a least-squares procedure. Using matrix notation, we thus obtain an *overdetermined* system of linear equations with the unknown parameters stored in \vec{X} and given below.

$$\vec{E} = \mathbf{A}\vec{X}, \quad \text{i.e.} \quad \vec{X} = (\mathbf{A}^T \mathbf{A})^{-1} \mathbf{A}^T \vec{E}$$

Comparing SD energies from DFT with those calculated using the LF parameter values, we can state for all considered cases, that the LF parameterization scheme is remarkably compatible with SD energies from DFT; standard deviations between DFT-SD energies and their LFDFT values are generally between 0.01 and 0.1 eV as shown in the Fig. Below.



This model can obviously be generalized allowing to treat systems with symmetry lower than cubic or even without any symmetry (C_1). Here we make use of the general observation that the KS orbitals and the set of SD considered in eq.(1) convey all the information needed to setup the LF matrix.

Following the effective Hamiltonian approach, let us consider the KS orbitals dominated by d-functions which result from an AOC d^n DFT-SCF calculation. From the components of the eigenvector matrix built up from such MOs one takes only the components corresponding to the d functions. Let us denote the square matrix composed of the new column vectors by \mathbf{U} and introduce the overlap matrix \mathbf{S} :

$$\mathbf{S} = \mathbf{U}\mathbf{U}^T$$

Since \mathbf{U} is in general not orthogonal, we use Löwdin's symmetric orthogonalisation procedure to obtain an equivalent set of orthogonal eigenvectors (\mathbf{C}):

$$\mathbf{C} = \mathbf{S}^{-\frac{1}{2}}\mathbf{U}$$

We identify now these vectors as the eigenfunctions of the effective LF Hamiltonian $h_{\text{LF}}^{\text{eff}}$ sought, as

$$\varphi_i = \sum_{\mu=1}^5 c_{\mu i} d_{\mu}$$

Thus, the fitting procedure described in the previous section will enable us to estimate $h_{ii} = \langle \varphi_i | h_{\text{LF}}^{\text{eff}} | \varphi_i \rangle$ and hence the full representation matrix of $h_{\text{LF}}^{\text{eff}}$ as

$$h_{\mu\nu} = \langle d_{\mu} | h_{\text{LF}}^{\text{eff}} | d_{\nu} \rangle = \sum_{i=1}^5 c_{\mu i} h_{ii} c_{\nu i}$$

The next step is now to generalize the fitting procedure for the case of no or low symmetry. The energy of a single determinant becomes thus:

$$E(\text{SD}_k^{\varphi}) = E\left(\det\left|\varphi_{i(k,1)}\sigma_{i(k,1)}\varphi_{i(k,2)}\sigma_{i(k,2)}\cdots\varphi_{i(k,n)}\sigma_{i(k,n)}\right|\right) = \sum_i \langle \varphi_i | h_{\text{LF}} | \varphi_i \rangle + \sum_{i<j} (J_{ij} - K_{ij}\delta_{\sigma_i\sigma_j})$$

Where SD_k^{φ} is composed of the spinorbitals mentioned earlier.

In order to calculate the electrostatic contribution, it is useful to consider the transformation from the basis of SD_k^{φ} to the one of SD_{μ}^d . Using basic linear algebra, we get:

$$|\text{SD}_k^{\varphi}\rangle = \sum_{\mu} T_{k\mu} |\text{SD}_{\mu}^d\rangle$$

Where $T_{k\mu} = \det|c_{i(k,1:n),j(\mu,1:n)}|$ i.e. the determinant of a nxn sub-matrix of $\mathbf{C} \otimes \sigma$

$$\begin{vmatrix} c_{i(k,1),j(\mu,1)} & c_{i(k,1),j(\mu,2)} & \cdots & c_{i(k,1:n),j(\mu,n)} \\ c_{i(k,2),j(\mu,1)} & c_{i(k,2),j(\mu,2)} & \cdots & c_{i(k,2),j(\mu,n)} \\ \cdots & \cdots & \cdots & \cdots \\ c_{i(k,n),j(\mu,1)} & c_{i(k,n),j(\mu,2)} & \cdots & c_{i(k,n),j(\mu,n)} \end{vmatrix}$$

With the indices of the spinorbitals $\varphi_{i(k,1)}\sigma_{i(k,1)}, \varphi_{i(k,2)}\sigma_{i(k,2)}, \dots, \varphi_{i(k,n)}\sigma_{i(k,n)}$ and $d_{j(\mu,1)}\sigma_{j(\mu,1)}, d_{j(\mu,2)}\sigma_{j(\mu,2)}, \dots, d_{j(\mu,n)}\sigma_{j(\mu,n)}$ respectively. Note that these indices are in fact a two-dimensional array of (number of SD) x (number of electrons or holes) integers. Finally the energy of a SD can be rewritten as

$$E_k = E(\text{SD}_k^{\varphi}) = \sum_i \langle \varphi_i | h_{\text{LF}} | \varphi_i \rangle + \sum_{\mu,\nu} T_{k\mu} T_{k\nu} \langle \text{SD}_{\mu}^d | G | \text{SD}_{\nu}^d \rangle$$

Where $G = 1/r_{12}$ i.e. the electrostatic repulsion of all electron pairs in the LF manifold.

The matrix elements are readily obtained using Slater's rules and the resulting electrostatic two-electron integrals $\langle abcd \rangle$ in terms of Racah's parameters. Thus the final equation to estimate h_{ii} , ($i = 1, \dots, 5$), B and C from the DFT energies E_k of all the SD within the LF manifold will be of the same shape as eqs.(4) and (5) where $\vec{X} = (h_{11}, \dots, h_{55}, B, C)$ and **A** is calculated as indicated above

Examples

CrCl ₄				CrBr ₄			
Term	LDA	GGA	LF-fit	Exp. ^a	LDA	GGA	Exp. ^a
³ A ₂ (e ²)	0	0	0	0	0	0	0
¹ E(e ²)	6542	7101	6089	-	6373	6832	6666
¹ A ₁ (e ²)	11114	11971	10586	-	10698	11364	10869
³ T ₂ (e ¹ t ₂ ¹)	7008	6524	7010	7250	6163	5605	-
³ T ₁ (e ¹ t ₂ ¹)	10316	10062	10440	10000	9269	8820	-
¹ T ₂ (e ¹ t ₂ ¹)	13454	13489	12991	12000	12434	12295	-
¹ T ₁ (e ¹ t ₂ ¹)	15074	15456	14718	-	14037	14215	-
¹ A ₁ (t ₂ ²)	32099	32891	30599	-	30120	30531	-
¹ E(t ₂ ²)	21121	20878	20716	-	19271	18777	-
³ T ₁ (t ₂ ²)	16033	15795	16229	16666	14424	14043	13258
¹ T ₂ (t ₂ ²)	21217	21014	20822	-	19373	18920	-
R(M-X)	2.104	2.144	-	-	2.264	2.318	-
B	355	419	376	-	347	403	-
C	1903	1952	1579	-	1855	1887	-
10Dq	7008	6524	7250	-	6162	5605	-
SD	0.054	0.070	-	-	0.054	0.067	-
(10Dq) _{orb}	7258	6686	-	-	6371	5726	-

CrCl ₆ ³⁻				CrBr ₆ ³⁻		
Term	LDA	LFT fit to exper.	Exp.	LDA	LFT fit to exper	Exp.
⁴ A _{2g} (t _{2g} ³)	0	0	0	0	0	0
² E _g (t _{2g} ³)	10756	14426	14430 ^b	10333	13900	13900 ^b
² T _{1g} (t _{2g} ³)	11180	14873	-	10694	14348	-
² T _{2g} (t _{2g} ³)	15918	21037	-	15185	20281	-
⁴ T _{2g} (t _{2g} ¹ e _g ¹)	10911	12800	12800 ^b	9816	12400	12400 ^b
⁴ T _{1g} (t _{2g} ¹ e _g ¹)	15618	18198	18200 ^b	13992	17700	17700 ^b
² A _{1g} (t _{2g} ¹ e _g ¹)	20056	25351	-	18709	24459	-
² T _{1g} (t _{2g} ¹ e _g ¹)	21878	27421	-	20316	26503	-
² T _{2g} (t _{2g} ¹ e _g ¹)	21568	27079	-	20047	26159	-
² E _g (t _{2g} ¹ e _g ¹)	23147	29098	-	21530	28126	-
⁴ T _{1g} (t _{2g} ¹ e _g ¹)	24375	28455	-	21861	27643	-
R(M-X)	2.419	-	2.335 ^d	2.588	-	2.47 ^e

Practical calculation of energy levels in metal complexes: Multiplets, Spin-Orbit and Zero-Field-Splitting

The calculation of energy levels within the whole ligand field manifold is now an easy task. All we need is to combine the results of the previous chapters. This, is best achieved using computational methods in the MATLAB environment.

The Matlab script below is an extension to the ones presented in Chap. 2. This procedure calls :

- (i) `get2ei4a` : gets all 2-electron integrals for atoms with open [lq(1) lq(2) ...]^{Ne}-shells. The electrostatic matrixelements `<iabcd(:,1) iabcd(:,2) | iabcd(:,3) iabcd(:,4) > = vabcd(:, :)*parameters(:)`. The target transformation following the call to `get2ei4a` re-expresses the abstract Slater-Condon parameters into non-redundant `<ablcld>`.
- (ii) `gensrd` : generates all single determinants for n electrons occupying spinorbitals `k_start` to `k_end`.
- (iii) `getls` : get **l**, **s** and **l.s** one-electron matrices

```
%
% generate g-, lf-, ls-data for lq^ne
%
%global iabcd vabcd
%
global lq
%
global lx ly lz sx sy sz ls
%
% get - electrostatic 2-electron matrix elements
%       - ligandfield 1-electron matrix elements
%       - spin and orbit 1-electron matrix elements
t0=cputime;
%lq=[2,0];
lq=[3];
ne=1;
%
% generate single determinants or microstates for lq^ne
ir=genersd(ne,1,2*sum(lq+lq+1));
%
% get <ab|cd>
%[vabcd,iabcd]=get2ei4a(lq);
%
% get l, s and l*s 1-e matrices: l=2 & s=1/2
[lx,ly,lz,sx,sy,sz,ls]=getls(lq,1/2);
%
% calculate
nsd=length(ir);ij=0;
for i=1:nsd
    for j=1:i
        ij=ij+1;
        lfddata(ij,:)=lfab(ir(i,:),ir(j,:));
        lsdata(ij,:)=zab(ir(i,:),ir(j,:));
%        gdata(ij,:)=gab(ne,ir(i,:),ir(j,:));
    end
end
Elapsed_time=cputime-t0
%save data_d2 ir gdata lfddata lsdata
save data_f1 ir lfddata lsdata
```

```
function lf=lfab(la,lb)
global lq;
% Get <A|lf(1:(lq+lq+1)*(lq+1))|jB>
%
```

```

ne=max(size(la));lf=zeros(1,(lq+lq+1)*(lq+1));
ie=0;id=0;sgn=1;
for k=1:ne
ld=find(la(k)==lb);
if isempty(ld)
id=id+1;kd(id)=la(k); if rem(k,2)==1, sgn=-sgn; end
else
ie=ie+1;ke(ie)=la(k);
end
end
%kd
%ke
if id == 0
% id=0
for k=1:ne
if iwab(ke(k),ke(k))>0, lf(iwab(ke(k),ke(k)))=lf(iwab(ke(k),ke(k)))+1; end
% f=f+wab(ke(k),ke(k));
end
elseif id==1
% id>0
iv=0;
for k=1:ne
ld=find(lb(k)==la);
if isempty(ld)
iv=iv+1;kdp(iv)=lb(k); if rem(k,2)==1, sgn=-sgn; end
end
end
%kdp
% f=sgn*wab(kd(1),kdp(1));
if iwab(kd(1),kdp(1))>0, lf(iwab(kd(1),kdp(1)))=sgn; end
end

```

```

function iw=iwab(i,ip)
% Get iw(<i|f|ip>)
%
ia=fix((i+1)/2);
ib=fix((ip+1)/2);
%
if rem(i,2)~=rem(ip,2)
iw=0;
else
if ia<=ib, iw=ia+ib*(ib-1)/2;end
if ib<=ia, iw=ib+ia*(ia-1)/2;end
end

```

Once the full Electrostatic Repulsion, Ligandfield and Spin-Orbit matrices are generated (this task is needed only once for a given LF-manifold), the following program has to be executed in order to get the full electronic structure.

```

%=====
% erlfls
%=====
load data_d5
%
[nsd ne]=size(ir);ij=0;
%
% input parameters
r=[0; 1; 4];
lfpar=[ 0;
        0;      0;
        0;      0;      20;
        0;      0;      0;      0;

```

```

0;          0;          0;          0;          20];
zeta=0.2;
%
% get electrostatic matrix in basis of microstates
ij=0;
for i=1:nsd
    for j=1:i
        ij=ij+1;
        h(i,j)=gdata(ij,:)*r+lfddata(ij,:)*lfpar+lndata(ij,7)*zeta;
        h(j,i)=conj(h(i,j));
    end
end
% get Eigenvalues and Eigenvectors of h
[c,e]=eig(h);[e,ie]=sort(real(diag(e)));
e=e-e(1)*ones(size(e));c=c(:,ie);
% sort according to multiplicities
i0=1;i1=0;
for i=2:nsd
    if abs(e(i)-e(i-1))>0.001
        i1=i1+1;w(i1)=e(i-1);mul(i1)=i-i0;i0=i;
    end
end
i1=i1+1;w(i1)=e(i0);mul(i1)=nsd-i0+1;
% print result
fprintf(' _____ \n')
fprintf(' Multiplicity          E \n')
fprintf(' _____ \n')
for i=1:i1
    fprintf('          %3i          %12.3f\n',mul(i),w(i))
end
fprintf(' _____ \n')

```

Interaction of paramagnetic electrons in a metal complex with an external magnetic field.

Example : Ground state of d^1

Consider the ground state $^2T_{2g}$ of a d^1 ion in an octahedral ligandfield. We suppose that the excited 2E_g state is sufficiently separated in energy from the ground state. If we neglect 2nd order spin-orbit coupling, the ground state $^2T_{2g}$ will split into a new ground state Γ_8 that is fourfold degenerate and in a doublet Γ_7 higher in energy by an amount of $\frac{3}{2}\lambda$. Next, we consider the interaction with an external magnetic field (Zeeman) to 1st order, i.e. $\left\langle \Gamma_8 \left(^2T_{2g} \right) \left| \vec{H} \cdot \left(\beta \vec{L} + g_e \beta \vec{S} \right) \right| \Gamma_8 \left(^2T_{2g} \right) \right\rangle$. If we diagonalize this matrix a surprising result is obtained, that is, the orbital contribution $\beta \hat{L} \cdot \vec{H}$ compensates exactly the spin contribution $\beta g_e \hat{S} \cdot \vec{H}$ (if we take $g_e = 2$). Thus, Γ_8 is accidentally not influenced to 1st order by the Zeeman perturbation. However, Γ_7 is split into two components by an amount $\pm \beta |\vec{H}|$ versus Γ_7 . To second order the components of Γ_7 and Γ_8 couple. Two components of Γ_8 are lowered by $-\frac{4}{3} \frac{\beta^2 H^2}{\lambda}$, the two others remain unchanged. The components of Γ_7 are both destabilized by $\frac{4}{3} \frac{\beta^2 H^2}{\lambda}$. The whole splitting pattern is represented graphically in figure 1 below. Note that this result is independent of the direction of the magnetic field since the complex is cubic and hence magnetically isotropic.

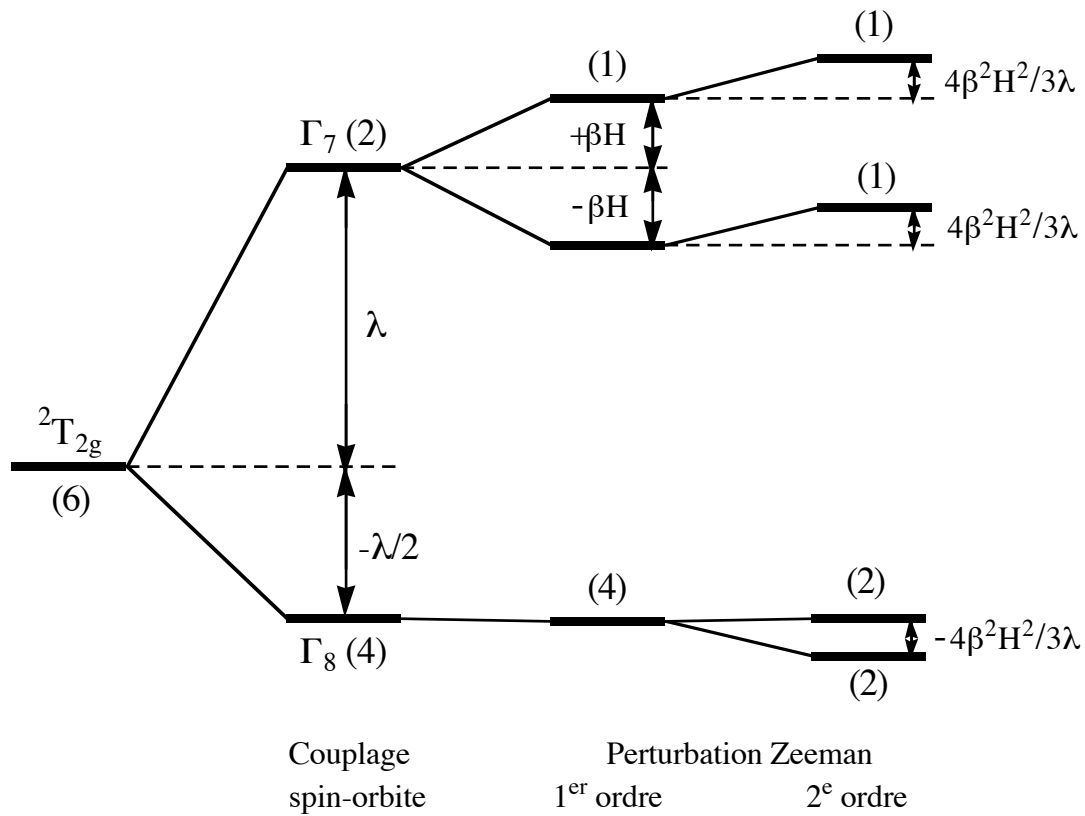


FIG. 1 - Successive action of spin-orbit coupling and Zeeman perturbation onto the ground state of a d^1 ion in an octahedral field.

Note that the Zeeman perturbation acts only to 2nd order because the term we consider is perturbed by spin-orbit-coupling.

Reminder : Van Vleck Formula

Consider E_n the energy the n -th electronic level of a complex molecule or ion in an external magnetic field \vec{H} . Let's expand E_n as:

$$E_n = E_n^{(0)} + E_n^{(1)}H + E_n^{(2)}H^2 + \dots$$

where $E_n^{(0)}$ is the energy without magnetic field and $E_n^{(1)}$ et $E_n^{(2)}$ the first and second order Zeeman coefficients respectively.

Moreover: $\chi = \frac{M}{H}$

This yields the Van Vleck formula:

$$\chi = \frac{N \sum_n \left[\frac{(E_n^{(1)})^2}{kT} - 2 E_n^{(2)} \right] \exp\left(-\frac{E_n^{(0)}}{kT}\right)}{\sum_n \exp\left(-\frac{E_n^{(0)}}{kT}\right)}$$

describing the variation of χ as a function of the temperature. Below 10K this formula may lose its validity. The coefficient $E_n^{(1)}$ and $E_n^{(2)}$ can easily be calculated using ligand field theory.

Paramagnetism of d^n ions in strong octahedral fields

Combining the results of the two previous sections, the variation of the paramagnetism of a d^1 ion as a function of temperature is easily obtained. The terms $E_n^{(0)}$, $E_n^{(1)}$ et $E_n^{(2)}$ are gathered together below for the various levels n .

n	$E_n^{(0)}$	$E_n^{(1)}$	$E_n^{(2)}$
1	$-\frac{\lambda}{2}$	0	$-\frac{4}{3} \frac{\beta^2}{\lambda}$
2	$-\frac{\lambda}{2}$	0	$-\frac{4}{3} \frac{\beta^2}{\lambda}$
3	$-\frac{\lambda}{2}$	0	0
4	$-\frac{\lambda}{2}$	0	0
5	λ	$-\beta$	$\frac{4}{3} \frac{\beta^2}{\lambda}$
6	λ	β	$\frac{4}{3} \frac{\beta^2}{\lambda}$

Insert into Van Vleck's equation, we obtain:

$$\chi = \frac{N\beta^2}{3kT} \frac{8 + (3x-8) \exp\left(-\frac{3x}{2}\right)}{x \left[2 + \exp\left(-\frac{3x}{2}\right)\right]}$$

where:

$$x = \frac{\lambda}{kT}$$

One frequently expresses this result as the variation in function of temperature of the effective magnetic moment μ_{eff} conventionally related to χ as:

$$\mu_{\text{eff}} = \left(\frac{3k\chi T}{N\beta^2} \right)^{1/2}$$

For the case studied here we get:

$$\mu_{\text{eff}} = \left(\frac{8 + (3x-8) \exp\left(-\frac{3x}{2}\right)}{x \left[2 + \exp\left(-\frac{3x}{2}\right) \right]} \right)^{1/2}$$

If the Curie law is satisfied, μ_{eff} does not depend on temperature. It is seen according to the eq. above that this is not the case. Indeed, μ_{eff} vanishes for $T = 0$ et becomes equal to $\sqrt{5}$ as the temperature increases infinitely. Figure 2 represents the variation of μ_{eff} as a function of $\frac{kT}{\lambda}$.

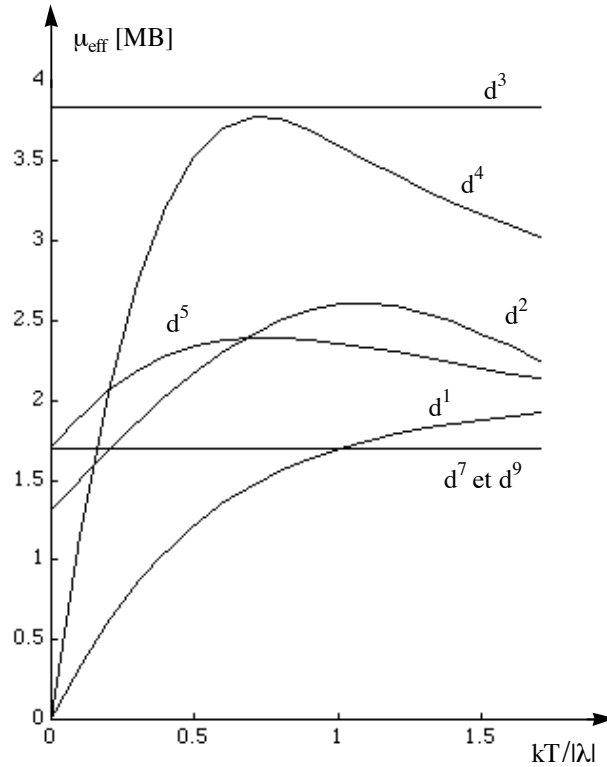


FIG. 2. —Theoretical variation of the effective magnetic moment as a function of temperature for octahedral d^n ions in strong fields.

Let's return to the Van Vleck formula and consider the paramagnetism of a complex whose ground state $2S+1\Gamma$, is well separated from all excited states and does not possess any orbital angular momentum. Hence no spin-orbit coupling needs to be taken into account. If the complex is octahedral, its ground state is necessarily orbital singlet or doublet. Thus, the Zeeman perturbation has second order contribution i.e. all $E_n^{(2)}$ are zero. Moreover, all $E_n^{(0)}$ are identical, and one obtains:

$$\chi = \frac{N}{kT} \sum_n \frac{(E_n^{(1)})^2}{n}$$

The Zeeman perturbation acts only onto to the $2S+1$ spin functions and the terms $E_n^{(1)}$ take the following values: $S, S-1, \dots, -S+1, -S$ in units of $g_e\beta$. The eq. above becomes thus:

$$\chi = \frac{N g_e^2 \beta^2}{kT} \cdot \frac{(-S)^2 + (-S+1)^2 + \dots + (S-1)^2 + S^2}{2S+1}$$

$$\chi = \frac{N g_e^2 \beta^2}{kT} \cdot \frac{S(S+1)}{3}$$

that is:

$$\mu_{\text{eff}} = g_e \sqrt{S(S+1)}$$

Hence the paramagnetism follows Curie's law as a particular case of the more general Van Vleck equation. The eq. above may be rewritten, if we take $g_e = 2$ as:

$$\mu_{\text{eff}} = \sqrt{N(N+2)}$$

where N is the number of unpaired electrons.

As example, Figure 2 represents the theoretical variation of the effective magnetic moment of d^n ($0 < n < 10$) ions in a strong octahedral field as a function of $\frac{kT}{|\lambda|}$. For the ions $d^3(^4A_{2g})$, $d^6(^1A_{1g})$, $d^7(^2E_g)$, $d^8(^3A_{2g})$ et $d^9(^2E_g)$, μ_{eff} does not depend on temperature. For the other configurations $d^1(^2T_{2g})$, $d^2(^3T_{1g})$, $d^4(^3T_{1g})$, $d^5(^2T_{2g})$, μ_{eff} changes as a function of temperature.

A *matlab* script to calculate magnetic susceptibility χ is listed below :

```
%
% lf+er+l+s for d**3
%
% Order of d-orbitals:
%  z2, x2-y2, xy, xz, yz
%
% Order of d-spinorbitals:
%  z2+, z2-, x2-y2+, x2-y2-, xy+, xy-, xz+, xz-, yz+, yz-
%
clear all
%
%=====
% D A T A      I N P U T
%
% Input of Racah's parameter: r=[A B C]
r=[0; 0.53; 2.00];
% Input of LF mat. el. <di|LF|dj>
lfpar=[-9.2;
        0; -9.2;
        0; 0; 0;
        0; 0; 0; 0;
        0; 0; 0; 0; 0];
% spin-orbit coupling constant
zeta=-0.4;
% Orbital Reduction Factor
orf=0.8;
% gyromagnetic value of free electron
ge=2.0023;
% (2S+1)*M(gamma) for g.s. multiplet
% Ex.: g.s. for octahedral [Co(ii)L_6]^q
%      S=3/2 & gamma = T_1, ergo nvv=4*3=12
nvv=12;
%
% Number of quadrature points for spatial orientation (theta,phi) of magnetic
field
```

```

ntheta=10; nphi=20;
%
% kinetic energy k*T in same energy units as Racah's, LF and SO parameters
% kT=0.695cm-1 at 1K
kt=0.2;
%
% magnetic field in users energy units [beta*H]
% h0=0.467cm-1 at 1Tesla=10'000gauss
h0=0.001;
%
%=====
%
% get: - microstates ldata_dn
%       - electrost. rep. gdata_dn
%       - LF matrix lfdata_dn
%       - L&S matrix lsdata_dn
%
load full_d3.mat
nsd=max(size(ldata_d3));kkpmx=max(size(gdata_d3));
%
%
% Calc.
%
% get h = er + lf + so
kkp=0;
for k=1:nsd
for kp=1:k
kkp=kkp+1;
h(k,kp)=lfdata_d3(kkp,:)*lfpar+gdata_d3(kkp,:)*r+zeta*lsdata_d3(kkp,7);
h(kp,k)=conj(h(k,kp));
% get orbital and spin angular momentum matrices (large memory)
lx(k,kp)=lsdata_d3(kkp,1);sx(k,kp)=lsdata_d3(kkp,4);
lx(kp,k)=conj(lx(k,kp));sx(kp,k)=conj(sx(k,kp));
ly(k,kp)=lsdata_d3(kkp,2);sy(k,kp)=lsdata_d3(kkp,5);
ly(kp,k)=conj(ly(k,kp));sy(kp,k)=conj(sy(k,kp));
lz(k,kp)=lsdata_d3(kkp,3);sz(k,kp)=lsdata_d3(kkp,6);
lz(kp,k)=conj(lz(k,kp));sz(kp,k)=conj(sz(k,kp));
end
end
% get Eigenvalues and Eigenvectors of h
[c,e]=eig(h);[e,ie]=sort(real(diag(e)));
e=e-e(1)*ones(size(e));c=c(:,ie);
% sort according to multiplicities
i0=1;i1=0;
for i=2:nsd
if abs(e(i)-e(i-1))>0.001
i1=i1+1;w(i1)=e(i-1);mul(i1)=i-i0;i0=i;
end
end
i1=i1+1;w(i1)=e(i0);mul(i1)=nsd-i0+1;
% print result
fprintf('_____ \n')
fprintf('(2S+1)*M(gamma)          E \n')
fprintf('_____ \n')
for i=1:i1
fprintf('          %3i          %12.3f\n',mul(i),w(i))
end
fprintf('_____ \n')
% Get Zeeman matrices (large memory)
zx=c(:,1:nvv)'.*(orf*lx+ge*sx)*c(:,1:nvv);
zy=c(:,1:nvv)'.*(orf*ly+ge*sy)*c(:,1:nvv);
zz=c(:,1:nvv)'.*(orf*lz+ge*sz)*c(:,1:nvv);
% get van Vleck coefficient
e0=e(1:nvv);
% *** integrate over u=cos(theta) and phi

```

```

% get angular grid (Gauss-Legendre)
% u=cos(theta) , -1<u<1
[u,wu]=gauleg(-1,1,ntheta);
% phi , 0<phi<2*pi
[phi,wf]=gauleg(0,pi+pi,nphi);
%
dh=0.01*h0;
schi=0;
for iu=1:ntheta
for ip=1:nphi
eh=[sqrt(1-u(iu)*u(iu))*cos(phi(ip)) sqrt(1-u(iu)*u(iu))*sin(phi(ip)) u(iu)];
hze=diag(e0)+(zx*eh(1)++zy*eh(2)+zz*eh(3))*dh;
e1=sort(eig(hze));
hze=diag(e0)+(zx*eh(1)++zy*eh(2)+zz*eh(3))*(dh+dh);
e2=sort(eig(hze));
w=inv([dh dh*dh/2;dh+dh 2*dh*dh])*[e1'-e0'; e2'-e0'];
e0;
e1=real(w(1,:));
e2=real(w(2,:));
% magnetic susceptibility from van Vleck formula
x=exp(-e0/kt);
chi=0;
for k=1:nvv
chi=chi+x(k)*(e1(k)*e1(k)/kt-e2(k)-e2(k));
end
chi=chi/sum(x);
schi=schi+chi*wu(iu)*wf(ip);
end
end
chi=schi/sum(wu)/sum(wf);
mu_eff=sqrt(3*kt*chi)

```