Spherical harmonics and some of their properties

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Section de chimie et biochimie

Previous knowlegde required

- Group theory
- Quantum mechanics
- Spectroscopy

References

- **Brian L. Silver, « Irreducible Tensor methods An Introduction for chemists » Academic Press 1976**
- D.A. Mc Quarrie, J.D. Simon « Chimie Physique Approche moléculaire » Dunod 2000
- R.McWeeny, « Quantum mechanics: methods and basic applications » Pergamon Press 1973

Angular momentum

- Rotational spectroscopy
- Hydrogen atom
- Spin → NMR, ESR etc
- ee repulsion
- Spin orbit coupling
- Crystal field

Angular momentum operators

$$j^2|jm\rangle = j(j+1)|jm\rangle$$

$$j_z|jm\rangle = m|jm\rangle$$

$$[j_x, j_y] = ij_z$$
$$[j_y, j_z] = ij_x$$
$$[j_z, j_x] = ij_y$$

$$j_+ = j_x + ij_y$$
$$j_- = j_x - ij_y$$

$$j_+|jm\rangle = e^{i\phi}\sqrt{j(j+1) - m(m+1)}\,|j, m+1\rangle$$
$$j_-|jm\rangle = e^{-i\phi}\sqrt{j(j+1) - m(m-1)}\,|j, m-1\rangle$$

ϕ is arbitrary

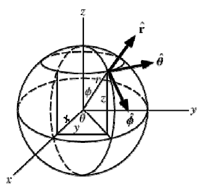
Conventional phase choice (Condon and Shortley) : ϕ=0.

Consequence :

$$Y^*_{l,m} = (-1)^m Y_{l,-m}$$

Angular momentum operators

$$j_x = \frac{1}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) = \frac{1}{i}\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right)$$
$$j_y = \frac{1}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) = \frac{1}{i}\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right)$$
$$j_x = \frac{1}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = \frac{1}{i}\frac{\partial}{\partial\varphi}$$



$$j^2 = j_x^2 + j_y^2 + j_z^2 = -\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) - \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} = -\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}j_z^2$$

Spherical harmonics

$$Y(\theta,\phi)=\Theta(\theta)\cdot\Phi(\phi)$$
$$\Phi(\phi)=A_m\cdot e^{im\phi}$$

Φ is normalized

$$\int_0^{2\pi}\Phi^*(\phi)\cdot\Phi(\phi)d\phi=1$$
$$|A_m|^2\cdot\int_0^{2\pi}d\phi=|A_m|^2\cdot 2\pi=1$$
$$A_m=\frac{1}{\sqrt{2\pi}}$$

$$\Phi_m(\phi)=\frac{1}{\sqrt{2\pi}}e^{im\phi}$$

Spherical harmonics

The function of θ can be expressed as a Legendre polynomial

$$\Theta(\theta)=P(x)$$
$$x=\cos\theta$$
$$0\le\theta\le\pi$$
$$-1\le x\le 1$$

$P_0(x)=1$
$P_1(x)=x$
$P_2(x)=\frac{1}{2}(3x^2-1)$
$P_3(x)=\frac{1}{2}(5x^3-3x)$

Spherical harmonics

$P_0(x)=1$
$P_1(x)=x$
$P_2(x)=\frac{1}{2}(3x^2-1)$
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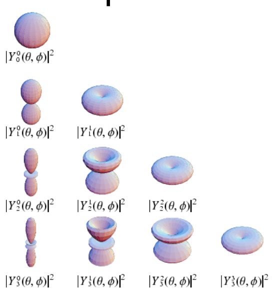


l	m_l	$Y_{l,m}$
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
1	0	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
1	±1	$\mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta\cdot e^{\pm i\phi}$
2	0	$\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1)$
2	±1	$\mp\left(\frac{15}{8\pi}\right)^{1/2}\sin\theta\cdot\cos\theta\cdot e^{\pm i\phi}$
2	±2	$\left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta\cdot e^{\pm 2i\phi}$
3	0	$\left(\frac{7}{16\pi}\right)^{1/2}(5\cos^2\theta-1)\cos\theta$
3	±1	$\mp\left(\frac{21}{64\pi}\right)^{1/2}(5\cos^2\theta-1)\sin\theta\cdot e^{\pm i\phi}$
3	±2	$\left(\frac{105}{32\pi}\right)^{1/2}\sin^2\theta\cdot\cos\theta\cdot e^{\pm 2i\phi}$
3	±3	$\mp\left(\frac{35}{64\pi}\right)^{1/2}\sin^3\theta\cdot e^{\pm 3i\phi}$

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

Spherical harmonics

Orbital angular momentum : l and m are integers

Normalisation and orthogonality $\int_0^{\pi}\int_0^{2\pi}Y^*_{l',m'_l}Y_{l,m_l}\sin\theta\cdot d\theta d\phi=\delta_{l'l}\delta_{m'_l m_l}$

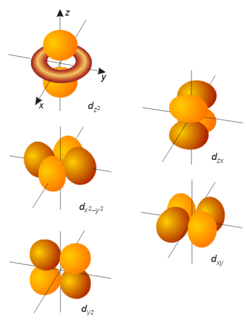
Complex conjugate $Y^*_{l,m}=(-1)^m Y_{l,-m}$

Spherical harmonics

- Symmetry properties
- The 2j+1 states |jm> of fixed j span an irreducible representation $\mathcal{D}^j$ of the infinite rotation group R_3.
- This implies that if one applies an arbitrary rotation D(αβγ) to the state |jm>, one obtains a linear combination of the complete set of 2j+1 states |jm'> with the same j.

Spherical harmonics

$$d_{x^2-y^2}=\frac{1}{\sqrt{2}}[Y_{2,2}+Y_{2,-2}]\cdot R_{n2}$$
$$d_{z^2}=Y_{2,0}\cdot R_{n2}$$
$$d_{yz}=\frac{-i}{\sqrt{2}}[Y_{2,1}+Y_{2,-1}]\cdot R_{n2}$$
$$d_{xz}=\frac{1}{\sqrt{2}}[Y_{2,1}-Y_{2,-1}]\cdot R_{n2}$$
$$d_{xy}=\frac{-i}{\sqrt{2}}[Y_{2,2}-Y_{2,-2}]\cdot R_{n2}$$



http://www.geo.arizona.edu/xtal/geos306/d-orbitals.gif

Coupling of two angular momenta

- Example : 1 atom with 2 electrons, one in a 2 p orbital, one in a 3 p orbital
- Note : no spin-orbit coupling !
- 2p orbital : l_1m_1
- 3p orbital : l_2m_2 $l_1 = l_2 = 1$ $m_{1,2} = -1, 0, 1$
- → 9 possible product states of the form :

$$|l_1m_1\rangle|l_2m_2\rangle = |11\rangle|11\rangle, |11\rangle|10\rangle, |11\rangle|1-1\rangle, etc$$

- Spherical symmetry (R_3) → wavefunctions are eigenfunctions of L^2 (= $(l_1+l_2)^2$) and $L_z=l_{1z}+l_{2z}$

Coupling of two angular momenta

- Symmetry property: 2p, 3p transform as $\mathcal{D}^{(1)}$, product state transforms as $\mathcal{D}^{(1)} \otimes \mathcal{D}^{(1)}$.
- General rule: $\mathcal{D}^{(j1)} \otimes \mathcal{D}^{(j2)} = \mathcal{D}^{(j1+j2)} + \mathcal{D}^{(j1+j2-1)} + \ldots + \mathcal{D}^{(|j1-j2|)}$
- → $\mathcal{D}^{(1)} \otimes \mathcal{D}^{(1)} = \mathcal{D}^{(2)} + \mathcal{D}^{(1)} + \mathcal{D}^{(0)}$
- → 9 (=5+3+1) orthonormal functions LM which are linear combinations

$$|LM\rangle = \sum_{m_1m_2} C^{l_1l_2L}_{m_1m_2M} |l_1m_1\rangle|l_2m_2\rangle$$

Coupling of two angular momenta

$$|LM\rangle = \sum_{m_1m_2} C^{l_1l_2L}_{m_1m_2M} |l_1m_1\rangle|l_2m_2\rangle$$

Problem:

calculate the coefficients C

(vector coupling or Clebsch-Gordan coefficients)

$$|00\rangle = \frac{1}{\sqrt{3}}\left(|11\rangle_1|1-1\rangle_2 - |10\rangle_1|10\rangle_2 + |1-1\rangle_1|11\rangle_2\right)$$

$$|11\rangle = \frac{1}{\sqrt{2}}\left(|11\rangle_1|10\rangle_2 - |10\rangle_1|11\rangle_2\right)$$

$$|10\rangle = \frac{1}{\sqrt{2}}\left(|11\rangle_1|1-1\rangle_2 - |1-1\rangle_1|11\rangle_2\right)$$

$$|1-1\rangle = \frac{1}{\sqrt{2}}\left(|10\rangle_1|1-1\rangle_2 - |1-1\rangle_1|10\rangle_2\right)$$

$$|22\rangle = |11\rangle_1|11\rangle_2$$

$$|21\rangle = \frac{1}{\sqrt{2}}\left(|11\rangle_1|10\rangle_2 + |10\rangle_1|11\rangle_2\right)$$

$$|20\rangle = \frac{1}{\sqrt{6}}\left(|11\rangle_1|1-1\rangle_2 + 2|10\rangle_1|10\rangle_2 + |1-1\rangle_1|11\rangle_2\right)$$

$$|2-1\rangle = \frac{1}{\sqrt{2}}\left(|10\rangle_1|1-1\rangle_2 + |1-1\rangle_1|10\rangle_2\right)$$

$$|2-2\rangle = |1-1\rangle_1|1-1\rangle_2$$

Coupling of two angular momenta

- In the case of 2 equivalent 2p electrons, we note that the permutation of the labels 1 and 2 leave the states of L=0 and L=2 unchanged, while they change sign for L=1. For L=0 and L=2 we need a singlet spin function (antisymmetric), and for L=1 a triplet spin function (symmetric):
- → terms ^1A, ^3P, ^1D for the configuration p^2.

Coupling of two angular momenta

$$\begin{pmatrix} |22\rangle \\ |21\rangle \\ |11\rangle \\ |20\rangle \\ |10\rangle \\ |00\rangle \\ |2-1\rangle \\ |1-1\rangle \\ |2-2\rangle \end{pmatrix} = \begin{pmatrix} 1 & & & & & & & & \\ & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & & & & & & \\ & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & & & & & & \\ & & & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \sqrt{2/3} & & & \\ & & & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 & & & \\ & & & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{3}} & & & \\ & & & & & & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & \\ & & & & & & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & \\ & & & & & & & & 1 \end{pmatrix} \begin{pmatrix} |11\rangle_1|11\rangle_2 \\ |11\rangle_1|10\rangle_2 \\ |10\rangle_1|11\rangle_2 \\ |11\rangle_1|1-1\rangle_2 \\ |1-1\rangle_1|11\rangle_2 \\ |10\rangle_1|10\rangle_2 \\ |10\rangle_1|1-1\rangle_2 \\ |1-1\rangle_1|10\rangle_2 \\ |1-1\rangle_1|1-1\rangle_2 \end{pmatrix}$$

Coupling of two angular momenta

Vector coupling coefficients

$$|LM\rangle = \sum_{m_1m_2} C^{l_1l_2L}_{m_1m_2M} |l_1m_1\rangle|l_2m_2\rangle =$$

$$|l_1l_2LM\rangle = \sum_{m_1m_2} C^{l_1l_2L}_{m_1m_2M} |l_1m_1l_2m_2\rangle$$

The angular momentum eigenfunctions form an orthonormal set. Multiplying both sides of the equation above by $|l_1m_1l_2m_2\rangle$ and integrating one obtains :

$$C^{l_1l_2L}_{m_1m_2M} = \langle l_1m_1l_2m_2 | l_1l_2LM\rangle$$

scalar product (real value)

Coupling of two angular momenta

$$C^{l_1 l_2 L}_{m_1 m_2 M} = \langle l_1 m_1 l_2 m_2 | l_1 l_2 LM \rangle$$

$$|l_1 l_2 LM\rangle = \sum_{m_1 m_2} C^{l_1 l_2 L}_{m_1 m_2 M} |l_1 m_1 l_2 m_2\rangle = \sum_{m_1 m_2} |l_1 m_1 l_2 m_2\rangle \langle l_1 m_1 l_2 m_2 | l_1 l_2 LM\rangle$$

Properties: C=0 unless $m_1+m_2=M$ and $l_1+l_2 \geq L \geq |l_1-l_2|$ (triangle rule)

Real scalar product implies that $\langle a | b \rangle = \langle b | a \rangle$

$$\langle l_1 m_1 l_2 m_2 | l_1 l_2 LM \rangle = \langle l_1 l_2 LM | l_1 m_1 l_2 m_2 \rangle$$

Coupling of two angular momenta

$$|l_1 l_2 LM\rangle = \sum_{m_1 m_2} |l_1 m_1 l_2 m_2\rangle \langle l_1 m_1 l_2 m_2 | l_1 l_2 LM\rangle$$

$$|l_1 m_1 l_2 m_2\rangle = \sum_{LM} |l_1 l_2 LM\rangle \langle l_1 l_2 LM | l_1 m_1 l_2 m_2\rangle$$

The orthogonality of the vector-coupling matrix implies

$$\sum_{m_1 m_2} \langle l_1 m_1 l_2 m_2 | l_1 l_2 LM\rangle \langle l_1 m_1 l_2 m_2 | l_1 l_2 L'M'\rangle = \delta_{L'L}\delta_{M'M}\Delta(l_1 l_2 L)$$

3-j symbol

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1-j_2-m_3} \frac{1}{\sqrt{2j_3+1}} \langle j_1 m_1 j_2 m_2 | j_1 j_2 j_3 - m_3 \rangle$$

The 3-j symbols can be calculated exactly.

In the past, tables of these symbols have been published, today one finds 3-j symbol calculators on the web

eg http://www.gleet.org.uk/cleb/tjjava.html

or in mathematica.

Note the change of sign of m_3 between the vector coupling coefficient and the 3–j symbol.

3-j symbol

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ 0 & 0 & 0 \end{pmatrix} = (-1)^{\frac{J}{2}} \sqrt{\frac{(j_1+j_2-j_3)!(j_1+j_3-j_2)!(j_2+j_3-j_1)!}{(j_1+j_2+j_3+1)!}} \cdot \frac{(J/2)!}{(J/2-j_1)!(J/2-j_2)!(J/2-j_3)!}$$

$$J = j_1 + j_2 + j_3$$

$$\begin{pmatrix} 1 & 1 & 2 \\ 0 & 0 & 0 \end{pmatrix} = \sqrt{\frac{1\cdot 2\cdot 2}{5!}} \cdot \frac{2}{1} = \sqrt{\frac{4}{5\cdot 4\cdot 3\cdot 2}} \cdot 2 = \sqrt{\frac{2}{15}}$$

$$\begin{pmatrix} j_1 & j_2 & 0 \\ m_1 & -m_2 & 0 \end{pmatrix} = \frac{(-1)^{j_1-m_1}}{\sqrt{2j_1-1}} \delta_{j_1 j_2} \delta_{m_1 m_2}$$

3-j symbol

$$\begin{pmatrix} j & j & 1 \\ m & -m & 0 \end{pmatrix} = \frac{(-1)^{j-m} m}{\sqrt{(2j+1)(j+1)j}}$$

$$\begin{pmatrix} 1 & 1 & 1 \\ 1 & -1 & 0 \end{pmatrix} = \frac{1}{\sqrt{3\cdot 2\cdot 1}} = \frac{1}{\sqrt{6}}$$

3-j symbol

Calculation of some of the vector coupling elements in the matrix above

$$\langle 1111 | 1122 \rangle = \sqrt{2\cdot 2+1} \cdot (-1)^{1-1-(-2)} \cdot \begin{pmatrix} 1 & 1 & 2 \\ 1 & 1 & -2 \end{pmatrix} = \sqrt{5} \cdot \sqrt{\frac{1}{5}} = 1$$

$$\langle 1011 | 1111 \rangle = \sqrt{2\cdot 1+1} \cdot (-1)^{1-1-(-1)} \cdot \begin{pmatrix} 1 & 1 & 1 \\ 0 & 1 & -1 \end{pmatrix} = -\sqrt{3} \cdot \sqrt{\frac{1}{6}} = -\sqrt{\frac{1}{2}}$$

$$\langle 1010 | 1120 \rangle = \sqrt{2\cdot 2+1} \cdot (-1)^{1-1-0} \cdot \begin{pmatrix} 1 & 1 & 2 \\ 0 & 0 & 0 \end{pmatrix} = \sqrt{5} \cdot \sqrt{\frac{2}{15}} = \sqrt{\frac{2}{3}}$$

$$\langle 1110 | 1121 \rangle = \sqrt{2\cdot 2+1} \cdot (-1)^{1-1-(-1)} \cdot \begin{pmatrix} 1 & 1 & 2 \\ 1 & 0 & -1 \end{pmatrix} = \sqrt{5} \cdot \left(-\frac{1}{2}\sqrt{\frac{2}{5}}\right) = -\sqrt{\frac{1}{2}}$$

3-j symbol

Some symmetry properties of the 3-j symbols:

Even permutation → same sign

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \begin{pmatrix} j_2 & j_3 & j_1 \\ m_2 & m_3 & m_1 \end{pmatrix} = \begin{pmatrix} j_3 & j_1 & j_2 \\ m_3 & m_1 & m_2 \end{pmatrix}$$

Odd permutation:

$$(-1)^{j_1+j_2+j_3}\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \begin{pmatrix} j_2 & j_1 & j_3 \\ m_2 & m_1 & m_3 \end{pmatrix} = \begin{pmatrix} j_1 & j_3 & j_2 \\ m_1 & m_3 & m_2 \end{pmatrix} = \begin{pmatrix} j_3 & j_2 & j_1 \\ m_3 & m_2 & m_1 \end{pmatrix}$$

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3}\begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix}$$

→ if m_i=0 J must be even

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = 0$$ if $m_1 + m_2 + m_3 \neq 0$

3-j symbol

Integral of 3 spherical harmonics

$$\int_0^{\pi}\int_0^{2\pi} Y_{m_1}^{l_1} Y_{m_2}^{l_2} Y_{m_3}^{l_3} \sin\theta \cdot d\theta d\phi = \sqrt{\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}}\begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

Note: no complex conjugate in this expression

The Wigner-Eckart Theorem

In spectroscopy, we use the following symmetry property:

The matrix element $\langle \psi_a^i | O_q^k | \psi_b^j \rangle = 0$ unless $\Gamma^i \otimes \Gamma^j \supset \Gamma^k$

However, this theorem does not exploit all symmetry properties.
The Wigner-Eckart Theorem relates matrix elements to coupling coefficients

$$\langle jm | T_{m_2}^{j_2} | j_1 m_1 \rangle = K \langle j_1 m_1 j_2 m_2 | j_1 j_2 jm \rangle$$

K is a constant independent of m_i

If the vector coupling coefficient is replaced by a 3-j symbol, one obtains

$$\langle \alpha' j' m' | T_q^k | \alpha j m \rangle = (-1)^{j'-m'}\begin{pmatrix} j' & k & j \\ m' & q & m \end{pmatrix}\langle \alpha' j' \| T^k \| \alpha j \rangle$$

The Wigner-Eckart Theorem

$$\langle \alpha' j' m' | T_q^k | \alpha j m \rangle = (-1)^{j'-m'}\begin{pmatrix} j' & k & j \\ m' & q & m \end{pmatrix}\langle \alpha' j' \| T^k \| \alpha j \rangle$$

The last term is called a **reduced matrix element.**

α represents any additional quantum number necessary to specify the state.

The Wigner-Eckart Theorem

If the operator is a spherical harmonic operating on states │lm>, the reduced matrix elements can be calculated as follows:

Using the general integration of 3 spherical harmonics

$$\langle Y_0^{l_1} | Y_0^{l_2} | Y_0^{l_3} \rangle = \sqrt{\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}}\begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix}^2$$

Using the Wigner Eckart theorem

$$\langle Y_0^{l_1} | Y_0^{l_2} | Y_0^{l_3} \rangle = \langle l_1 0 | Y_0^{l_2} | l_3 0 \rangle = (-1)^{l_1}\begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix}\langle l_1 \| Y^{l_2} \| l_3 \rangle$$

$$\langle l_1 \| Y^{l_2} \| l_3 \rangle = (-1)^{l_1}\sqrt{\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}}\begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix}$$

The Wigner-Eckart Theorem

If one uses Racah's normalised spherical harmonics:

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

$$\langle l_1 \| C^k \| l_3 \rangle = (-1)^{l_1}\sqrt{(2l_1+1)(2l_3+1)}\begin{pmatrix} l_1 & k & l_3 \\ 0 & 0 & 0 \end{pmatrix}$$

$$\langle 3 \| C^2 \| 3 \rangle = -\frac{14}{\sqrt{105}} \approx -1.37$$

$$\langle 3 \| C^4 \| 3 \rangle = \frac{\sqrt{14}}{\sqrt{11}} \approx 1.13$$

$$\langle 3 \| C^6 \| 3 \rangle = -\frac{70}{\sqrt{3003}} \approx -1.28$$

CF Matrix elements

$$\left\langle Y_m^l \middle| C_q^k \middle| Y_{m_1}^{l_1} \right\rangle = \int_0^{\pi}\int_0^{2\pi} Y_m^{l^*} C_q^k Y_{m_1}^{l_1} \sin\theta \cdot d\theta d\phi = (-1)^m \int_0^{\pi}\int_0^{2\pi} Y_{-m}^{l} C_q^k Y_{m_1}^{l_1} \sin\theta \cdot d\theta d\phi =$$

$$(-1)^m \sqrt{(2l+1)(2l_1+1)} \begin{pmatrix} l & k & l_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & k & l_1 \\ -m & q & m_1 \end{pmatrix}$$

$$\left\langle Y_2^3 \middle| C_0^4 \middle| Y_2^3 \right\rangle = (2\cdot 3+1) \begin{pmatrix} 3 & 4 & 3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 3 & 4 & 3 \\ -2 & 0 & 2 \end{pmatrix} = 7 \cdot \left(-\sqrt{\frac{2}{77}}\right) \cdot \left(\frac{7}{6}\sqrt{\frac{2}{77}}\right) = -\frac{7}{33}$$

$$\left\langle Y_2^3 \middle| C_4^4 \middle| Y_{-2}^3 \right\rangle = (2\cdot 3+1) \begin{pmatrix} 3 & 4 & 3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 3 & 4 & 3 \\ -2 & 4 & -2 \end{pmatrix} = 7 \cdot \left(-\sqrt{\frac{2}{77}}\right) \cdot \left(-\frac{1}{3}\sqrt{\frac{5}{11}}\right) = \frac{\sqrt{70}}{33}$$

A table of these values can be found in:
S.Sugano, Y.Tanabe and H.Kamimura, Multiplets of Transition-Metal Ions in Crystals,
Academic Press, 1970, New York and London, p.13.

6-j symbols

Introduced to describe the coupling of 3 angular momenta. It can be expressed in terms of 3-j symbols:

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{Bmatrix} = \sum_{all(n,m_1,m_2)} (-1)^{j_4+j_5+j_6+n_1+n_2+n_3} (2j_3+1) \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_5 & j_6 \\ m_1 & n_5 & -n_6 \end{pmatrix} \begin{pmatrix} j_4 & j_2 & j_6 \\ -n_4 & m_2 & n_6 \end{pmatrix} \begin{pmatrix} j_4 & j_5 & j_3 \\ n_4 & -n_5 & m_3 \end{pmatrix}$$

The Wigner 6j -symbols are returned by the *Mathematica* function SixJSymbol[*j1*, *j2*, *j3* , *j4*, *j5*, *j6*].

See also: http://mathworld.wolfram.com/Wigner6j-Symbol.html

Electron-electron repulsion

Matrix elements for interelectronic repulsion:

$$\left\langle SLM_S M_L \middle| \frac{e^2}{r_{12}} \middle| S'L'M'_S M'_L \right\rangle$$

Expansion of $1/r_{12}$ using Legendre polynomials:

$$\frac{1}{r_{12}} = \sum_k \left(\frac{r_<^k}{r_>^{k+1}} \right) \cdot P_k(\cos(\omega_{12}))$$

$$P_k(\cos(\omega_{12})) = \frac{4\pi}{2k+1} \sum_{q=-k}^{k} Y_{kq}^*(\theta_1,\varphi_1) Y_{kq}(\theta_2,\varphi_2)$$

Electron-electron repulsion

Let us define the operators:

$$C_{kq} = \left(\frac{4\pi}{2k+1} \right)^{1/2} \cdot Y_{kq}$$

$$P_k(\cos(\omega_{12})) = \sum_q (-1)^q (C_{k-q}(1) \cdot C_{kq}(2)) = C_k(1) \cdot C_k(2)$$

This corresponds to a scalar product of the vectors $C_k(i)$.

$$\left\langle SLM_S M_L \middle| \left(\frac{e^2 r_<^k}{r_>^{k+1}} \right) \cdot C_k(1) \cdot C_k(2) \middle| S'L'M'_S M'_L \right\rangle$$

This treatment allows to separate the **radial contribution** from the **angular part** expressed by the $\mathbf{C_k}$.

Electron-electron repulsion : example $2p^2$

$$\left\langle SLM_S M_L \middle| \frac{e^2}{r_{12}} \middle| SL'M_S M'_L \right\rangle = \sum_k f_k(r) \left\langle SLM_S M_L \middle| C_k(1) \cdot C_k(2) \middle| SL'M_S M'_L \right\rangle =$$

$$= \sum_k f_k(r) \cdot (-1)^{2l+L} \delta_{LL'} \delta_{M_L M_L'} \delta_{SS'} \delta_{M_S M_s'} \cdot \begin{Bmatrix} l & l & k \\ l & l & L \end{Bmatrix} \langle l \| C_k \| l \rangle^2$$

$$= \sum_k f_k(r) \cdot (-1)^L \delta_{LL'} \delta_{M_L M_L'} \delta_{SS'} \delta_{M_S M_s'} \cdot 3^2 \cdot \begin{pmatrix} 1 & k & q \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{Bmatrix} 1 & 1 & k \\ 1 & 1 & L \end{Bmatrix}$$

$$f_k(r) = F^k = e^2 \int \left(\frac{r_<^k}{r_>^{k+1}} \right) \cdot R_{2p}^2(r_1) \cdot R_{2p}^2(r_2) dr_1 dr_2$$

The integrals F^k are called **Slater integrals**.

Coulomb splitting

In this case, k = 0 et k = 2.

We can calculate the relative energy of the terms ^1S (L=0), ^3P (L=1) et ^1D (L=2)

$$E(^1S) = 9\sum_k \begin{Bmatrix} 1 & 1 & k \\ 1 & 1 & 0 \end{Bmatrix} \begin{pmatrix} 1 & k & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 (-1)^0 F^k = 9\left[\frac{1}{3} \cdot \left(\frac{-1}{\sqrt{3}} \right)^2 F^0 + \frac{1}{3} \cdot \left(\sqrt{\frac{2}{15}} \right)^2 \right] = F^0 + \frac{2}{5} F^2$$

$$E(^3P) = 9\sum_k \begin{Bmatrix} 1 & 1 & k \\ 1 & 1 & 1 \end{Bmatrix} \begin{pmatrix} 1 & k & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 (-1)^1 F^k = F^0 - \frac{1}{5} F^2$$

$$E(^1D) = 9\sum_k \begin{Bmatrix} 1 & 1 & k \\ 1 & 1 & 2 \end{Bmatrix} \begin{pmatrix} 1 & k & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 (-1)^2 F^k = F^0 + \frac{1}{25} F^2$$

The **ground state term** is given by **Hund's rule**:

-Maximum spin multiplicity (all N spins are parallel if N<3 in $2p^N$)

-each projection m_l of the orbital momentum is the largest allowed by the exclusion rule. **N = 2 ($2p^2$)** :

L = l + (l-1) = 1 + 0 = 1

S = ½ + ½ = 1 → Etat fondamental L = 1, S = 1 → ^{3}**P**