Personal notes on the multipole expansion, see Eq. (6) in Chem. Phys. Lett. **320**, *177 (2000),*
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I. BASICS

A. Angular momentum operators

Angular momentum operators

$$[\hat{J}_i, \hat{J}_j] = i\epsilon_{ijk}\hat{J}_k \tag{1}$$

$$\hat{J}_\pm = \hat{J}_1 \pm i\hat{J}_2 \tag{2}$$
$$\hat{J}^2 = \hat{J}_3(\hat{J}_3 + 1) + \hat{J}_-\hat{J}_+ \tag{3}$$
$$\hat{J}^2 = \hat{J}_3(\hat{J}_3 - 1) + \hat{J}_+\hat{J}_- \tag{4}$$

Angular momentum eigen states

$$\hat{J}^2|jm\rangle = j(j+1)|jm\rangle \tag{5}$$
$$\hat{J}_3|jm\rangle = m|jm\rangle \tag{6}$$
$$\hat{J}_\pm|jm\rangle = C_\pm(j,m)|jm\pm 1\rangle \tag{7}$$
$$C_\pm(j,m) = \sqrt{j(j+1) - m(m\pm 1)} = \sqrt{(j\mp m)(j\pm m+1)}. \tag{8}$$

B. Clebsch-Gordan coefficients and three-jm symbols

Relation three-jm and Clebsch-Gordan coefficients

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \frac{(-1)^{j_1-j_2-m_3}}{\sqrt{2j_3+1}}\langle j_1 m_1 j_2 m_2 | j_3 {-m_3}\rangle \tag{9}$$

and the inverse relation

$$\langle j_1 m_1 j_2 m_2 | j_3 m_3\rangle = (-1)^{j_1-j_2+m_3}\sqrt{2j_3+1}\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & -m_3 \end{pmatrix}. \tag{10}$$

Special case

$$\langle l_1 m_1 l_2 m_2 | 00\rangle = \frac{(-1)^{l_1-m_1}}{\sqrt{2l_1+1}}\delta_{l_1 l_2}\delta_{m_1,-m_2}. \tag{11}$$

$$\langle j_1 m_1 j_2 m_2 | j_3 m_3\rangle = (-1)^{j_1+j_2-j_3}\langle j_1 {-m_1} j_2 {-m_2} | j_3 {-m_3}\rangle \tag{12}$$

C. Wigner-Eckart theorem

Wigner-Eckart theorem

$$\langle jm|T^{(J)}_M|j'm'\rangle = \frac{\langle j||T^{(J)}||j'\rangle}{\sqrt{2j+1}}\langle j'm'JM|jm\rangle(-1)^{2J} \tag{13}$$
$$= (-1)^{j-m}\begin{pmatrix} j & J & j' \\ -m & M & m' \end{pmatrix}\langle j||T^{(J)}||j'\rangle. \tag{14}$$

D. Rotation operator and D-matrices

Active rotation in $(\hat{n}, \phi)$ parameterization

$$\mathcal{U}(\hat{n}) = e^{-i\phi\hat{n}\cdot\hat{\mathbf{J}}} \tag{15}$$

Idem in zyz Euler angles

$$\mathcal{U}(\alpha,\beta,\gamma) = e^{-i\alpha\hat{J}_3}e^{-i\beta\hat{J}_2}e^{-i\gamma\hat{J}_3}. \tag{16}$$

Rotation of $|jk\rangle$

$$\mathcal{U}|jk\rangle = \sum_m |jm\rangle\langle jm|\mathcal{U}|jk\rangle \tag{17}$$

$$= \sum_m |jm\rangle D^{(j)}_{mk}(\mathcal{U}) \tag{18}$$

The $D^{(j)}$-matrices are homomorphic representations

$$D^{(j)}(\mathcal{U}_1\mathcal{U}_2) = D^{(j)}(\mathcal{U}_1)D^{(j)}(\mathcal{U}_2). \tag{19}$$

Unitarity

$$D^{(j)}(\mathcal{U}^{-1}) = D^{(j)}(\mathcal{U})^{-1} = D^{(j)}(\mathcal{U})^{\dagger} \tag{20}$$

The rotation of the function $D^{(j),*}_{mk}(\mathcal{U}')$ is defined by Wigners convention to make it transform like $|jm\rangle$

$$\mathcal{U}D^{(j),*}_{mk}(\mathcal{U}') \equiv D^{(j),*}_{mk}(\mathcal{U}^{-1}\mathcal{U}') \tag{21}$$

$$= \sum_{m'} D^{(j),*}_{mm'}(\mathcal{U}^{-1})D^{(j),*}_{m'k}(\mathcal{U}') \tag{22}$$

$$= \sum_{m'} D^{(j),*}_{m'k}(\mathcal{U}')D^{(j)}_{m'm}(\mathcal{U}). \tag{23}$$

The $d^{(j)}$-matrix is real

$$D^{(j)}_{mk}(\alpha,\beta,\gamma) = e^{-im\alpha}d^{(j)}_{mk}(\beta)e^{-ik\gamma}. \tag{24}$$

Symmetry

$$d^{(j)}_{-m,-m'}(\beta) = d^{(j)}_{m'm}(\beta) = (-1)^{m'-m}d^{(j)}_{-m',-m}(\beta) \tag{25}$$

$$d^{(j)}_{m',m}(\pi-\beta) = (-1)^{j-m}d^{(j)}_{-m',m}(\beta) = (-1)^{j+m'}d^{(j)}_{m,-m'}(\beta). \tag{26}$$

Explicit formulae with $m = j, j-1, \ldots, -j$, i.e., $d^{(j)}_{jj}$ upper left

$$d^{(0)}(\beta) = 1 \tag{27}$$

$$d^{(\frac{1}{2})}(\beta) = \begin{pmatrix} \cos\frac{\beta}{2} & -\sin\frac{\beta}{2} \\ \sin\frac{\beta}{2} & \cos\frac{\beta}{2} \end{pmatrix} \tag{28}$$

$$d^{(1)}(\beta) = \begin{pmatrix} \frac{1+\cos\beta}{2} & -\frac{\sin\beta}{\sqrt{2}} & \frac{1-\cos\beta}{2} \\ \frac{\sin\beta}{\sqrt{2}} & \cos\beta & -\frac{\sin\beta}{\sqrt{2}} \\ \frac{1-\cos\beta}{2} & \frac{\sin\beta}{\sqrt{2}} & \frac{1+\cos\beta}{2} \end{pmatrix}. \tag{29}$$

For j and j' both either integer of half integer

$$\int_0^{2\pi} d\alpha \int_0^{\pi} \sin\beta d\beta \int_0^{2\pi} d\gamma\, D^{(j),*}_{mk}(\alpha,\beta,\gamma)D^{(j')}_{m'k'}(\alpha,\beta,\gamma) = \frac{8\pi^2}{2j+1}\delta_{mm'}\delta_{kk'}\delta_{jj'}. \tag{30}$$

Clebsch-Gordan series

$$D^{(j_1)}_{m_1k_1}(\mathcal{U})D^{(j_2)}_{m_2k_2}(\mathcal{U}) = \sum_{j_3m_3k_3} \langle j_1m_1j_2m_2|j_3m_3\rangle\langle j_1k_1j_2k_2|j_3k_3\rangle D^{(j_3)}_{m_3k_3}(\mathcal{U}). \quad (31)$$

Symmetric top wave function, not parity adapted:

$$\langle \alpha,\beta,\gamma|jmk\rangle \equiv D^{(j),*}_{mk}(\alpha,\beta,\gamma)\sqrt{\frac{2j+1}{8\pi^2}} \quad (32)$$

Matrix elements

$$\langle j_1m_1k_1|D^{(L),*}_{MK}(\alpha,\beta,\gamma)|j_2m_2k_2\rangle = (-1)^{m_1-k_1}\sqrt{(2j_1+1)(2j_2+1)}\begin{pmatrix} j_1 & L & j_2 \\ -m_1 & M & m_2 \end{pmatrix}\begin{pmatrix} j_1 & L & j_2 \\ -k_1 & K & k_2 \end{pmatrix}. \quad (33)$$

If the wave function does not depend on γ and in this equation the integral over gamma is dropped, it still holds if in Eq. (32) the $8\pi^2$ is replaced bye 4π and $\gamma = 0$.

E. Spherical harmonics and Legendre Polynomials

Setting k to zero gives spherical harmonics in the Racah normalization

$$D^{(l),*}_{m0}(\phi,\theta,\gamma) = C_{lm}(\theta,\phi) \quad (34)$$

Normalization

$$\int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi\, C^*_{lm}(\theta,\phi)C_{l'm'}(\theta,\phi) = \frac{4\pi}{2l+1}\delta_{mm'}\delta_{ll'}. \quad (35)$$

The usual spherical harmonics are normalized to unity

$$Y_{lm}(\theta,\phi) = \sqrt{\frac{2l+1}{4\pi}}C_{lm}(\theta,\phi). \quad (36)$$

Inversion $\hat{i}(\theta,\phi) = (\pi-\theta,\phi+\pi)$

$$\hat{i}C_{lm}(\theta,\phi) = (-1)^l C_{lm}(\theta,\phi) \quad (37)$$

and reflection in the xz-plane $\hat{\sigma}_v(xz)(\theta,\phi) = (\theta,-\phi)$

$$\hat{\sigma}_v(xz)C_{lm}(\theta,\phi) = (-1)^m C_{l-m}(\theta,\phi) \quad (38)$$

and furthermore

$$C^*_{lm}(\theta,\phi) = (-1)^m C_{l-m}(\theta,\phi) \quad (39)$$

Also setting m to zero gives Legendre polynomials

$$C_{l0}(\theta,\phi) = P_l(\cos\theta) = d^{(l)}_{00}(\theta). \quad (40)$$

Since $d^{(l)}(0)$ is a unit matrix we have $d^l_{m0}(0) = \delta_{m0}$ and

$$C_{lm}(0,\phi) = \delta_{m0}. \quad (41)$$

The normalization of the Legendre polynomials

$$\int_0^\pi \sin\theta d\theta\, P_l(\cos\theta)P_{l'}(\cos\theta) = \frac{2}{2l+1}\delta_{ll'}. \quad (42)$$

From the explicit expressions for $d^{(j)}$ with $z \equiv \cos\beta$

$$P_0(z) = 1 \quad (43)$$

$$P_1(z) = z \quad (44)$$

From the Clebsch-Gordan series with $m = k = 0$ and $j_1 = 1$ and $j_2 = l$ we derive a recursion relation for the Legendre polynomials

$$P_1(z)P_l(z) = \sum_L \langle 10l0|L0\rangle^2 P_L(z) \tag{45}$$

$$= \langle 10l0|l+10\rangle^2 P_{l+1}(z) + \langle 10l0|l-10\rangle^2 P_{l-1}(z) \tag{46}$$

$$= \frac{l+1}{2l+1}P_{l+1}(z) + \frac{l}{2l+1}P_{l-1}(z) \tag{47}$$

i.e.

$$P_{l+1}(z) = \frac{z(2l+1)P_l(z) - lP_{l-1}(z)}{l+1} \tag{48}$$

$$P_2(z) = \frac{3z^2-1}{2}. \tag{49}$$

For the spherical harmonics we again use the explicit expressions for $d^{(j)}$

$$C_{0,0}(\theta,\phi) = 1 \tag{50}$$

$$C_{1,1}(\theta,\phi) = -\frac{1}{\sqrt{2}}(\cos\phi + i\sin\phi)\sin\theta \tag{51}$$

$$C_{1,0}(\theta,\phi) = \cos\theta \tag{52}$$

$$C_{1,-1}(\theta,\phi) = \frac{1}{\sqrt{2}}(\cos\phi - i\sin\phi)\sin\theta. \tag{53}$$

The Clebsch-Gordan series gives

$$C_{1\mu}(\theta,\phi)C_{lm}(\theta,\phi) = \sum_{LM} \langle 1\mu lm|LM\rangle\langle 10l0|L0\rangle C_{LM}(\theta,\phi). \tag{54}$$

For $\mu = 1$ and $m = l$ only one term remains

$$C_{1,1}(\theta,\phi)C_{ll}(\theta,\phi) = \sqrt{\frac{l+1}{2l+1}}C_{l+1,l+1}(\theta,\phi). \tag{55}$$

Thus

$$C_{ll}(\theta,\phi) = \sqrt{\frac{(2l-1)!!}{l!}}[C_{1,1}(\theta,\phi)]^l. \tag{56}$$

Other C_{lm} are obtained using the $\hat{L}_-$ operator. With the notation

$$[C^{(l_1)} \times C^{(l_2)}]^{(L)}_M = \sum_{m_1m_2} C_{l_1,m_1}C_{l_2,m_2}\langle l_1m_1l_2m_2|LM\rangle, \tag{57}$$

we have the explicit formula

$$C_{lm} = \sqrt{\frac{(2l-1)!!}{l!}}\left[[C^{(1)} \times C^{(1)}]^{(2)} \times \ldots\right]^{(l)}_m \tag{58}$$

F. Regular harmonics

The regular harmonics are homogeneous polynomials defined by

$$R_{lm}(\mathbf{r}) = r^l C_{lm}(\hat{r}) \tag{59}$$

with $x = r\cos\phi\sin\theta$, $y = r\sin\phi\sin\theta$, and $z = r\cos\theta$

$$R_{0,0}(\mathbf{r}) = 1 \tag{60}$$

$$R_{1,1}(\mathbf{r}) = -\frac{1}{\sqrt{2}}(x+iy) \equiv r_{+1} \tag{61}$$

$$R_{1,0}(\mathbf{r}) = z \equiv r_0 \tag{62}$$

$$R_{1,-1}(\mathbf{r}) = \frac{1}{\sqrt{2}}(x-iy) \equiv r_{-1} \tag{63}$$

and

$$R_{l,l}(\mathbf{r}) = \sqrt{\frac{(2l-1)!!}{l!}}(r_{+1})^l \tag{64}$$

$$R_{lm}(\mathbf{r}) = \sqrt{\frac{(2l-1)!!}{l!}}\left[[\mathbf{r}\times\mathbf{r}]^{(2)}\times\dots\right]^{(l)}_m . \tag{65}$$

In particular

$$R_{2,\pm2}(\mathbf{r}) = \frac{1}{2}\sqrt{\frac{3}{2}}[(x^2-y^2)\pm 2ixy] \tag{66}$$

$$R_{2,\pm1}(\mathbf{r}) = \mp\sqrt{\frac{3}{2}}(x\pm iy)z \tag{67}$$

$$R_{2,0}(\mathbf{r}) = \frac{1}{2}(3z^2-r^2) = \frac{1}{2}(2z^2-x^2-y^2). \tag{68}$$

Real spherical harmonics are defined for $m \geq 0$ by

$$R_{l0,c} = R_{l,0} \tag{69}$$

$$R_{lm,c} = \frac{1}{\sqrt{2}}[(-1)^m R_{lm} + R_{l-m}] \tag{70}$$

$$iR_{lm,s} = \frac{1}{\sqrt{2}}[(-1)^m R_{lm} - R_{l-m}] \tag{71}$$

so that for $m > 0$

$$R_{lm} = \frac{(-1)^m}{\sqrt{2}}[R_{lm,c} + iR_{lm,s}] \tag{72}$$

$$R_{l-m} = \frac{1}{\sqrt{2}}[R_{lm,c} - iR_{lm,s}] \tag{73}$$

and explicitly

$$R_{1,1,c} = x \tag{74}$$

$$R_{1,1,s} = y \tag{75}$$

$$R_{1,0,c} = z \tag{76}$$

$$R_{2,2,c} = \frac{1}{2}\sqrt{3}(x^2-y^2) \tag{77}$$

$$R_{2,2,s} = \sqrt{3}xy \tag{78}$$

$$R_{2,1,c} = \sqrt{3}xz \tag{79}$$

$$R_{2,1,s} = \sqrt{3}yz \tag{80}$$

$$R_{2,0,c} = z^2 - \frac{1}{2}(x^2+y^2) \tag{81}$$

The multipole operator for n particles at positions $\mathbf{r}_i$ with charges q_i is given by

$$\hat{Q}_{lm} = \sum_i q_i R_{lm}(\mathbf{r}_i) \tag{82}$$

In MOLPRO the following definitions are used for the quadrupole moment

$$Q_{xx} = x^2 - \frac{1}{2}(y^2+z^2) \tag{83}$$

$$Q_{yy} = y^2 - \frac{1}{2}(x^2+z^2) \tag{84}$$

$$Q_{zz} = z^2 - \frac{1}{2}(x^2+y^2) \tag{85}$$

$$Q_{xy} = \frac{3}{2}xy \tag{86}$$

$$Q_{xz} = \frac{3}{2}xz \tag{87}$$

$$Q_{yz} = \frac{3}{2}yz \tag{88}$$

So we have $Q_{20} = Q_{zz}$.

II. THE MULTIPOLE EXPANSION

Shifting a regular harmonic gives

$$R_{LM}(\mathbf{R}+\mathbf{r}) = \sum_{l_1+l_2=L} \sum_{m_1+m_2=M} \begin{pmatrix} 2L \\ 2l_1 \end{pmatrix}^{\frac{1}{2}} \langle l_1 m_1 l_2 m_2 | LM \rangle R_{l_1 m_1}(\mathbf{R}) R_{l_2 m_2}(\mathbf{r}). \tag{89}$$

The spherical harmonics addition theorem, $\hat{R}\cdot\hat{r} = \cos\theta$

$$P_l(\hat{R}\cdot\hat{r}) = \sum_{m=-l}^{l} C^*_{lm}(\hat{R}) C_{lm}(\hat{r}). \tag{90}$$

The multipole expansion for $r < R$

$$\frac{1}{|\mathbf{R}-\mathbf{r}|} = \sum_{l=0}^{\infty} \frac{r^l}{R^{l+1}} P_l(\hat{R}\cdot\hat{r}) \tag{91}$$

$$= \sum_{lm} \frac{C^*_{lm}(\hat{R})}{R^{l+1}} R_{lm}(\mathbf{r}). \tag{92}$$

Combining these equations, using $R_{l_2m_2}(-\mathbf{r}_b) = (-1)^{l_2} R_{l_2m_2}(\mathbf{r}_b)$, gives

$$\frac{1}{|\mathbf{R}+\mathbf{r}_b-\mathbf{r}_a|} = \sum_{LM} \frac{C^*_{LM}(\hat{R})}{R^{L+1}} \sum_{l_1+l_2=L} \sum_{m_1+m_2=M} (-1)^{l_2} \begin{pmatrix} 2L \\ 2l_1 \end{pmatrix}^{\frac{1}{2}} \tag{93}$$

$$\times \langle l_1 m_1 l_2 m_2 | LM \rangle R_{l_1 m_1}(\mathbf{r}_a) R_{l_2 m_2}(\mathbf{r}_b). \tag{94}$$

The coulomb interaction operator between monomers A and B is

$$V(\mathbf{R},\mathbf{r}_a,\mathbf{r}_b) = \frac{q_a q_b}{|\mathbf{R}+\mathbf{r}_b-\mathbf{r}_a|} \tag{95}$$

where the summation over a and b is implicit, and $\mathbf{R}$ connects the centers of mass of A and B. We take $\mathbf{R}$ parallel to the SF z-axis so that we have $C^*_{LM}(\hat{R}) = \delta_{M0}$. Let A be a linear molecule in the xz plane where the molecular axis makes an angle θ with the z axis. Attach a body fixed frame to A so that

$$\mathbf{r}_a = \hat{R}_y(\theta)\mathbf{r}_a^{BF}. \tag{96}$$

If A is in a Σ-state it only has $m_a = 0$ multipole moments and we have

$$\langle \chi | \hat{Q}_{l_a m_a}(\mathbf{r}_a) | \chi \rangle = \langle \chi | \hat{Q}_{l_a 0}(\mathbf{r}_a^{BF}) | \chi \rangle C_{l_a m_a}(\theta, 0), \tag{97}$$

where χ is the wave function for A. Let B be an atom in a degenerate $|\lambda\mu\rangle$ state then from the Wigner-Eckart theorem we have

$$\langle \lambda\mu | \hat{Q}_{l_b m_b}(\mathbf{r}_b) | \lambda\mu' \rangle = (-1)^{\lambda-\mu} \begin{pmatrix} \lambda & l_b & \lambda \\ -\mu & m_b & \mu' \end{pmatrix} \langle \lambda || Q^{(l_b)} || \lambda \rangle. \tag{98}$$

Thus, the interaction matrix in the basis $|\chi\lambda\mu\rangle, \mu = -\lambda, \ldots, \lambda$ is

$$V_{\mu\mu'}(\theta) = \langle \chi\lambda\mu | \hat{V}(\theta) | \chi\lambda\mu' \rangle \tag{99}$$

$$= \sum_{l_a} \sum_{l_b} \frac{\langle \chi | Q_{l_a 0} | \chi \rangle \langle \lambda || Q^{(l_b)} || \lambda \rangle}{R^{l_a+l_b+1}} (-1)^{l_a+\lambda-\mu} \left[\frac{(2l_a+2l_b+1)!}{(2l_a)!(2l_b)!} \right]^{\frac{1}{2}}$$

$$\times \sum_{m_a m_b} \begin{pmatrix} l_a & l_b & l_a+l_b \\ m_a & m_b & 0 \end{pmatrix} \begin{pmatrix} \lambda & l_b & \lambda \\ -\mu & m_b & \mu' \end{pmatrix} C_{l_a m_a}(\theta, 0) \tag{100}$$

Diagonalization of this matrix for a given value of θ yields eigen functions as linear combinations of $|\chi\lambda\mu\rangle$, from which the $|\mu|$-populations are computed.