

*Personal notes on the multipole expansion, see Eq. (6) in CPL **320**, 177 (2000), Gerrit C. Groenenboom, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, the Netherlands, 2001, www.theochem.kun.nl/~gerritg, e-mail: gerritg@theochem.kun.nl*

I. BASICS

A. Angular momentum operators

Angular momentum operators

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

$$\hat{J}_{\pm} = \hat{J}_1 \pm i\hat{J}_2. \quad (2)$$

Angular momentum eigen states

$$\hat{J}^2|jm\rangle = j(j+1)|jm\rangle \quad (3)$$

$$\hat{J}_3|jm\rangle = m|jm\rangle \quad (4)$$

$$\hat{J}_{\pm}|jm\rangle = C_{\pm}(j, m)|j, m \pm 1\rangle \quad (5)$$

$$C_{\pm}(j, m) = \sqrt{j(j+1) - m(m \pm 1)} = \sqrt{(j \mp m)(j \pm m + 1)}. \quad (6)$$

B. Clebsch-Gordan coefficients and three- jm symbols

Relation three- jm and Clebsch-Gordan coefficients

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \frac{(-1)^{j_1 - j_2 - m_3}}{\sqrt{2j_3 + 1}} \langle j_1 m_1 j_2 m_2 | j_3 - m_3 \rangle \quad (7)$$

and the inverse relation

$$\langle j_1 m_1 j_2 m_2 | j_3 m_3 \rangle = (-1)^{j_1 - j_2 + m_3} \sqrt{2j_3 + 1} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & -m_3 \end{pmatrix}. \quad (8)$$

Special case

$$\langle l_1 m_1 l_2 m_2 | 00 \rangle = \frac{(-1)^{l_1 - m_1}}{\sqrt{2l_1 + 1}} \delta_{l_1 l_2} \delta_{m_1, -m_2}. \quad (9)$$

$$\langle j_1 m_1 j_2 m_2 | j_3 m_3 \rangle = (-1)^{j_1 + j_2 - j_3} \langle j_1 - m_1 j_2 - m_2 | j_3 - m_3 \rangle \quad (10)$$

C. Wigner-Eckart theorem

Wigner-Eckart theorem

$$\langle jm | T_M^{(J)} | j' m' \rangle = \frac{\langle j || T^{(J)} || j' \rangle}{\sqrt{2j+1}} \langle j' m' JM | jm \rangle (-1)^{2J} \quad (11)$$

$$= (-1)^{j-m} \begin{pmatrix} j & J & j' \\ -m & M & m' \end{pmatrix} \langle j || T^{(J)} || j' \rangle. \quad (12)$$

D. Rotation operator and D -matrices

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

$$\mathcal{U}(\hat{n}) = e^{-i\phi\hat{n}\cdot\hat{\mathbf{J}}} \quad (13)$$

Idem in zyz Euler angles

$$\mathcal{U}(\alpha, \beta, \gamma) = e^{-i\alpha\hat{J}_3} e^{-i\beta\hat{J}_2} e^{-i\gamma\hat{J}_3}. \quad (14)$$

Rotation of $|jk\rangle$

$$\mathcal{U}|jk\rangle = \sum_m |jm\rangle \langle jm|\mathcal{U}|jk\rangle \quad (15)$$

$$= \sum_m |jm\rangle D_{mk}^{(j)}(\mathcal{U}) \quad (16)$$

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

$$D^{(j)}(\mathcal{U}_1\mathcal{U}_2) = D^{(j)}(\mathcal{U}_1)D^{(j)}(\mathcal{U}_2). \quad (17)$$

Unitarity

$$D^{(j)}(\mathcal{U}^{-1}) = D^{(j)}(\mathcal{U})^{-1} = D^{(j)}(\mathcal{U})^\dagger \quad (18)$$

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

$$\mathcal{U}D_{mk}^{(j),*}(\mathcal{U}') \equiv D_{mk}^{(j),*}(\mathcal{U}^{-1}\mathcal{U}') \quad (19)$$

$$= \sum_{m'} D_{mm'}^{(j),*}(\mathcal{U}^{-1})D_{m'k}^{(j),*}(\mathcal{U}') \quad (20)$$

$$= \sum_{m'} D_{m'k}^{(j),*}(\mathcal{U}')D_{m'm}^{(j)}(\mathcal{U}). \quad (21)$$

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

$$D_{mk}^{(j)}(\alpha, \beta, \gamma) = e^{-im\alpha} d_{mk}^{(j)}(\beta) e^{-ik\gamma}. \quad (22)$$

Symmetry

$$d_{-m,-m'}^{(j)}(\beta) = d_{m'm}^{(j)}(\beta) = (-1)^{m'-m} d_{-m',-m}^{(j)}(\beta) \quad (23)$$

$$d_{m',m}^{(j)}(\pi - \beta) = (-1)^{j+m'} d_{m,-m'}^{(j)}(\beta). \quad (24)$$

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

$$d^{(0)}(\beta) = 1 \quad (25)$$

$$d^{(\frac{1}{2})}(\beta) = \begin{pmatrix} \cos \frac{\beta}{2} & -\sin \frac{\beta}{2} \\ \sin \frac{\beta}{2} & \cos \frac{\beta}{2} \end{pmatrix} \quad (26)$$

$$d^{(1)}(\beta) = \begin{pmatrix} \frac{1+\cos\beta}{2} & -\frac{\sin\beta}{\sqrt{2}} & \frac{1-\cos\beta}{2} \\ \frac{\sin\beta}{\sqrt{2}} & \cos\beta & -\frac{\sin\beta}{\sqrt{2}} \\ \frac{1-\cos\beta}{2} & \frac{\sin\beta}{\sqrt{2}} & \frac{1+\cos\beta}{2} \end{pmatrix}. \quad (27)$$

For j and j' both either integer or half integer

$$\int_0^{2\pi} d\alpha \int_0^\pi \sin \beta d\beta \int_0^{2\pi} d\gamma D_{mk}^{(j),*}(\alpha, \beta, \gamma) D_{m'k'}^{(j')}(\alpha, \beta, \gamma) = \frac{8\pi^2}{2j+1} \delta_{mm'} \delta_{kk'} \delta_{jj'}. \quad (28)$$

Clebsch-Gordan series

$$D_{m_1 k_1}^{(j_1)}(\mathcal{U}) D_{m_2 k_2}^{(j_2)}(\mathcal{U}) = \sum_{j_3 m_3 k_3} \langle j_1 m_1 j_2 m_2 | j_3 m_3 \rangle \langle j_1 k_1 j_2 k_2 | j_3 k_3 \rangle D_{m_3 k_3}^{(j_3)}(\mathcal{U}). \quad (29)$$

E. Spherical harmonics and Legendre Polynomials

Setting k to zero gives spherical harmonics in the Racah normalization

$$D_{m0}^{(l),*}(\phi, \theta, \gamma) = C_{lm}(\theta, \phi) \quad (30)$$

Normalization

$$\int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi C_{lm}^*(\theta, \phi) C_{l'm'}(\theta, \phi) = \frac{4\pi}{2l+1} \delta_{mm'} \delta_{ll'}. \quad (31)$$

The usual spherical harmonics are normalized to unity

$$Y_{lm}(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi}} C_{lm}(\theta, \phi). \quad (32)$$

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

$$\hat{i}C_{lm}(\theta, \phi) = (-1)^l C_{lm}(\theta, \phi) \quad (33)$$

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

$$\hat{\sigma}_v(xz)C_{lm}(\theta, \phi) = (-1)^m C_{l-m}(\theta, \phi) \quad (34)$$

and furthermore

$$C_{lm}^*(\theta, \phi) = (-1)^m C_{l-m}(\theta, \phi) \quad (35)$$

Also setting m to zero gives Legendre polynomials

$$C_{l0}(\theta, \phi) = P_l(\cos \theta) = d_{00}^{(l)}(\theta). \quad (36)$$

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

$$C_{lm}(0, \phi) = \delta_{m0}. \quad (37)$$

The normalization of the Legendre polynomials

$$\int_0^\pi \sin \theta d\theta P_l(\cos \theta) P_{l'}(\cos \theta) = \frac{2}{2l+1} \delta_{ll'}. \quad (38)$$

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

$$P_0(z) = 1 \quad (39)$$

$$P_1(z) = z \quad (40)$$

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

$$P_1(z)P_l(z) = \sum_L \langle 10l0|L0 \rangle^2 P_L(z) \quad (41)$$

$$= \langle 10l0|l+10 \rangle^2 P_{l+1}(z) + \langle 10l0|l-10 \rangle^2 P_{l-1}(z) \quad (42)$$

$$= \frac{l+1}{2l+1} P_{l+1}(z) + \frac{l}{2l+1} P_{l-1}(z) \quad (43)$$

i.e.

$$P_{l+1}(z) = \frac{z(2l+1)P_l(z) - lP_{l-1}(z)}{l+1} \quad (44)$$

$$P_2(z) = \frac{3z^2 - 1}{2}. \quad (45)$$

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

$$C_{0,0}(\theta, \phi) = 1 \quad (46)$$

$$C_{1,1}(\theta, \phi) = -\frac{1}{\sqrt{2}}(\cos \phi + i \sin \phi) \sin \theta \quad (47)$$

$$C_{1,0}(\theta, \phi) = \cos \theta \quad (48)$$

$$C_{1,-1}(\theta, \phi) = \frac{1}{\sqrt{2}}(\cos \phi - i \sin \phi) \sin \theta. \quad (49)$$

The Clebsch-Gordan series gives

$$C_{1\mu}(\theta, \phi)C_{lm}(\theta, \phi) = \sum_{LM} \langle 1\mu lm|LM \rangle \langle 10l0|L0 \rangle C_{LM}(\theta, \phi). \quad (50)$$

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

$$C_{1,1}(\theta, \phi)C_{ll}(\theta, \phi) = \sqrt{\frac{l+1}{2l+1}} C_{l+1,l+1}(\theta, \phi). \quad (51)$$

Thus

$$C_{ll}(\theta, \phi) = \sqrt{\frac{(2l-1)!!}{l!}} [C_{1,1}(\theta, \phi)]^l. \quad (52)$$

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

$$[C^{(l_1)} \times C^{(l_2)}]_M^{(L)} = \sum_{m_1 m_2} C_{l_1, m_1} C_{l_2, m_2} \langle l_1 m_1 l_2 m_2 | LM \rangle, \quad (53)$$

we have the explicit formula

$$C_{lm} = \sqrt{\frac{(2l-1)!!}{l!}} \left[[C^{(1)} \times C^{(1)}]^{(2)} \times \dots \right]_m^{(l)} \quad (54)$$

F. Regular harmonics

The regular harmonics are homogeneous polynomials defined by

$$R_{lm}(\mathbf{r}) = r^l C_{lm}(\hat{r}) \quad (55)$$

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

$$R_{0,0}(\mathbf{r}) = 1 \quad (56)$$

$$R_{1,1}(\mathbf{r}) = -\frac{1}{\sqrt{2}}(x + iy) \equiv r_{+1} \quad (57)$$

$$R_{1,0}(\mathbf{r}) = z \equiv r_0 \quad (58)$$

$$R_{1,-1}(\mathbf{r}) = \frac{1}{\sqrt{2}}(x - iy) \equiv r_{-1} \quad (59)$$

and

$$R_{l,l}(\mathbf{r}) = \sqrt{\frac{(2l-1)!!}{l!}} (r_{+1})^l \quad (60)$$

$$R_{lm}(\mathbf{r}) = \sqrt{\frac{(2l-1)!!}{l!}} [\mathbf{r} \times \mathbf{r}]^{(2)} \times \dots \times \dots \Big|_m^{(l)}. \quad (61)$$

In particular

$$R_{2,\pm 2}(\mathbf{r}) = \frac{1}{2} \sqrt{\frac{3}{2}} [(x^2 - y^2) \pm 2ixy] \quad (62)$$

$$R_{2,\pm 1}(\mathbf{r}) = \mp \sqrt{\frac{3}{2}} (x \pm iy)z \quad (63)$$

$$R_{2,0}(\mathbf{r}) = \frac{1}{2}(3z^2 - r^2) = \frac{1}{2}(2z^2 - x^2 - y^2). \quad (64)$$

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

$$R_{l0,c} = R_{l,0} \quad (65)$$

$$R_{lm,c} = \frac{1}{\sqrt{2}} [(-1)^m R_{lm} + R_{l-m}] \quad (66)$$

$$iR_{lm,s} = \frac{1}{\sqrt{2}} [(-1)^m R_{lm} - R_{l-m}] \quad (67)$$

so that for $m > 0$

$$R_{lm} = \frac{(-1)^m}{\sqrt{2}} [R_{lm,c} + iR_{lm,s}] \quad (68)$$

$$R_{l-m} = \frac{1}{\sqrt{2}} [R_{lm,c} - iR_{lm,s}] \quad (69)$$

and explicitly

$$R_{1,1,c} = x \quad (70)$$

$$R_{1,1,s} = y \quad (71)$$

$$R_{1,0,c} = z \quad (72)$$

$$R_{2,2,c} = \frac{1}{2} \sqrt{3} (x^2 - y^2) \quad (73)$$

$$R_{2,2,s} = \sqrt{3}xy \quad (74)$$

$$R_{2,1,c} = \sqrt{3}xz \quad (75)$$

$$R_{2,1,s} = \sqrt{3}yz \quad (76)$$

$$R_{2,0,c} = z^2 - \frac{1}{2}(x^2 + y^2) \quad (77)$$

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

$$\hat{Q}_{lm} = \sum_i q_i R_{lm}(\mathbf{r}_i) \quad (78)$$

In MOLPRO the following definitions are used for the quadrupole moment

$$Q_{xx} = x^2 - \frac{1}{2}(y^2 + z^2) \quad (79)$$

$$Q_{yy} = y^2 - \frac{1}{2}(x^2 + z^2) \quad (80)$$

$$Q_{zz} = z^2 - \frac{1}{2}(x^2 + y^2) \quad (81)$$

$$Q_{xy} = \frac{3}{2}xy \quad (82)$$

$$Q_{xz} = \frac{3}{2}xz \quad (83)$$

$$Q_{yz} = \frac{3}{2}yz \quad (84)$$

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

II. THE MULTIPOLE EXPANSION

Shifting a regular harmonic gives

$$R_{LM}(\mathbf{R} + \mathbf{r}) = \sum_{l_1+l_2=L} \sum_{m_1+m_2=M} \binom{2L}{2l_1}^{\frac{1}{2}} \langle l_1 m_1 l_2 m_2 | LM \rangle R_{l_1 m_1}(\mathbf{R}) R_{l_2 m_2}(\mathbf{r}). \quad (85)$$

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

$$P_l(\hat{R} \cdot \hat{r}) = \sum_{m=-l}^l C_{lm}^*(\hat{R}) C_{lm}(\hat{r}). \quad (86)$$

The multipole expansion for $r < R$

$$\frac{1}{|\mathbf{R} - \mathbf{r}|} = \sum_{l=0}^{\infty} \frac{r^l}{R^{l+1}} P_l(\hat{R} \cdot \hat{r}) \quad (87)$$

$$= \sum_{lm} \frac{C_{lm}^*(\hat{R})}{R^{l+1}} R_{lm}(\mathbf{r}). \quad (88)$$

Combining these equations, using $R_{l_2 m_2}(-\mathbf{r}_b) = (-1)^{l_2} R_{l_2 m_2}(\mathbf{r}_b)$, gives

$$\frac{1}{|\mathbf{R} + \mathbf{r}_b - \mathbf{r}_a|} = \sum_{LM} \frac{C_{LM}^*(\hat{R})}{R^{L+1}} \sum_{l_1+l_2=L} \sum_{m_1+m_2=M} (-1)^{l_2} \binom{2L}{2l_1}^{\frac{1}{2}} \quad (89)$$

$$\times \langle l_1 m_1 l_2 m_2 | LM \rangle R_{l_1 m_1}(\mathbf{r}_a) R_{l_2 m_2}(\mathbf{r}_b). \quad (90)$$

The coulomb interaction operator between monomers A and B is

$$V(\mathbf{R}, \mathbf{r}_a, \mathbf{r}_b) = \frac{q_a q_b}{|\mathbf{R} + \mathbf{r}_b - \mathbf{r}_a|} \quad (91)$$

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

$$\mathbf{r}_a = \hat{R}_y(\theta) \mathbf{r}_a^{BF}. \quad (92)$$

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

$$\langle \chi | \hat{Q}_{l_a m_a}(\mathbf{r}_a) | \chi \rangle = \langle \chi | \hat{Q}_{l_a 0}(\mathbf{r}_a^{BF}) | \chi \rangle C_{l_a m_a}(\theta, 0), \quad (93)$$

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

$$\langle \lambda \mu | \hat{Q}_{l_b m_b}(\mathbf{r}_b) | \lambda \mu' \rangle = (-1)^{\lambda-\mu} \begin{pmatrix} \lambda & l_b & \lambda \\ -\mu & m_b & \mu' \end{pmatrix} \langle \lambda || Q^{(l_b)} || \lambda \rangle. \quad (94)$$

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

$$V_{\mu\mu'}(\theta) = \langle \chi \lambda \mu | \hat{V}(\theta) | \chi \lambda \mu' \rangle \quad (95)$$

$$= \sum_{l_a} \sum_{l_b} \frac{\langle \chi | Q_{l_a 0} | \chi \rangle \langle \lambda || Q^{(l_b)} || \lambda \rangle}{R^{l_a+l_b+1}} (-1)^{l_a+\lambda-\mu} \left[\frac{(2l_a+2l_b+1)!}{(2l_a)!(2l_b)!} \right]^{\frac{1}{2}} \\ \times \sum_{m_a m_b} \begin{pmatrix} l_a & l_b & l_a+l_b \\ m_a & m_b & 0 \end{pmatrix} \begin{pmatrix} \lambda & l_b & \lambda \\ -\mu & m_b & \mu' \end{pmatrix} C_{l_a m_a}(\theta, 0) \quad (96)$$

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