Appendix A

Rotations, Euler Angles and Wigner Rotation Matrices

There are two primary reasons for looking at rotations in NMR of liquid crystals. First, rotational motion of the spin-bearing molecules determines, in part, relaxation behavior of the spin system. Second, one or more r.f. pulse(s) in NMR experiments has the effect of rotating the spin angular momentum of the spin system. Therefore, it is necessary to deal with spatial rotations of the spin system and with spin rotations. The connection between rotations and angular momentum ($\vec{J}$) is expressed by a rotation operator

$$R_n(\theta) = \exp[-i\theta\vec{J} \cdot \hat{n}], \tag{A.1}$$

where $\hat{n}$ is a unit vector directed along an axis n. The operator represents a rotation about the n axis by an angle θ. The derivation of Eq. (A.1) can be found in most quantum mechanics texts. It can be shown that the rotational operator is unitary (i.e., $R^{-1} = R^{\dagger}$). In a coordinate system transformation, a positive rotation of angle θ about an axis n is to rotate the two perpendicular axes by the right-hand rule (i.e., with the thumb pointing along the positive n axis, the perpendicular plane moves in the direction of the fingers wrapped around the axis of rotation). In other words, when looking in the direction of the rotation axis, a positive rotation means that the remaining two axes rotate clockwise. Consider a coordinate system transformation that takes one set of axes (X, Y, Z) into another set (x, y, z), which shares the same origin. This change can always be obtained by three successive rotations, i.e.,

$$R(\alpha, \beta\gamma) = R_z(\gamma)R_N(\beta)R_Z(\alpha), \tag{A.2}$$

where the Euler angles $[\Omega \equiv (\alpha, \beta, \gamma)]$ that produce the coordinate system transformation are given in Fig. A.1. From the figure, it can be seen that first rotation by angle α occurs about the Z axis $[R_Z(\alpha)]$, then rotation by angle β occurs about the nodal line N, and finally, rotation about the z axis by angle γ occurs. An equivalent rotational operator using rotations about the original axis system is

$$R(\alpha, \beta, \gamma) = R_Z(\alpha)R_Y(\beta)R_Z(\gamma). \tag{A.3}$$

Note the order reversal from Eq. (A.2) of the rotations with angles α and γ. The Euler angles and the transformation of coordinate axes according

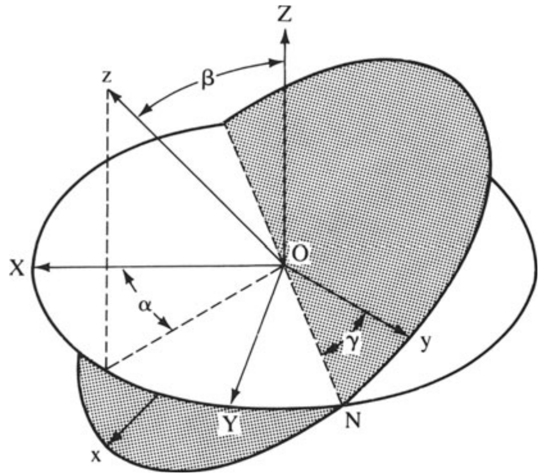

FIGURE A.1. Rotations used in the definition of the Euler angles.

to Eq. (A.2) will be used. For example, our "original X, Y, Z frame" to "final x, y, z frame" can be from the laboratory frame to the principal axes of an interaction tensor (in its principal axis system, $\rho_{J,m}$ is used to denote an irreducible spherical tensor). When a rotation of a coordinate system is performed (by a rotational operator R), the irreducible spherical tensor component $T_{J,m}$ is transformed into a linear combination of the set of $2J + 1$ operators $T_{J,m'}$

$$\begin{aligned}\rho_{J,m} &= R(\alpha,\beta,\gamma)\, T_{J,m} R^{-1}(\alpha,\beta,\gamma) \\ &= \sum_{m'} D^{J}_{m',m}\,(\alpha,\beta,\gamma)\, T_{J,m'}\,, \end{aligned} \tag{A.4}$$

where $D^{J}_{m',m}(\Omega)$ denote Wigner rotation matrices of rank J. The subscripts of the Wigner functions are projection indices and denote components of the angular momentum $\vec{J}$. The elements of the Wigner matrix are given according to Eq. (A.3),

$$D^{J}_{m',m}(\alpha,\beta,\gamma) = \exp[-i\,m'\alpha] d^{J}_{m',m}(\beta)\ \exp\left[-i\,m\,\gamma\right], \tag{A.5}$$

where $d^{J}_{m',m}(\beta)$ are the corresponding reduced Wigner matrices. In the tables, Wigner matrix elements are listed for rank one and rank two.

Some basic properties of the Wigner matrices are summarized as follows:

1. Symmetry

$$D^{L*}_{m',m}(\alpha,\beta,\gamma) = (-1)^{m'-m} D^{L}_{-m',-m}(\alpha,\beta,\gamma) = D^{L}_{m',m}(-\gamma,-\beta,-\alpha). \tag{A.6}$$

2. The product of two Wigner matrices of different ranks can be expressed in terms of the Clebsch-Gordon series:

$$\begin{aligned} D^{L_1}_{m_1',m_1}(\Omega) D^{L_2}_{m_2',m_2}(\Omega) = \sum_{L,m,m'} & c(L_1 L_2 L; m_1' m_2' m') , \\ & \times c(L_1 L_2 L; m_1 m_2 m) D^{L}_{m',m}(\Omega) \end{aligned} \tag{A.7}$$

where $c(L_1 L_2 L; m_1 m_2 m) \equiv c(L_1 L_2 L; m_1 m_2)$ denote the Clebsch-Gordon coefficients with $m = m_1 + m_2$.

3. The Wigner matrices are orthogonal due to

$$\begin{aligned} \frac{1}{8\pi^2} \int_0^{2\pi} \int_0^{2\pi} \int_0^{\pi} & D^{L_1*}_{m_1',m_1}(\alpha,\beta,\gamma) D^{L_2}_{m_2',m_2}(\alpha,\beta,\gamma) d\alpha \sin\beta d\beta d\gamma \\ & = \frac{1}{2L_1+1}\, \delta_{m_1' m_2'}\, \delta_{m_1 m_2}\, \delta_{L_1 L_2} . \end{aligned} \tag{A.8}$$

4. Closure

$$\sum_n D^{L}_{m,n}(\alpha_1,\beta_1,\gamma_1) D^{L}_{n,m'}(\alpha_2,\beta_2,\gamma_2) = D^{L}_{m,m'}(\alpha,\beta,\gamma) , \tag{A.9}$$

where the Euler angles (α,β,γ) are the resultant of two successive rotations by angles $(\alpha_1,\beta_1,\gamma_1)$ followed by angles $(\alpha_2,\beta_2,\gamma_2)$.

Finally, from properties 2 and 3, the following is found:

$$\begin{aligned} & \frac{1}{8\pi^2} \int_0^{2\pi} \int_0^{2\pi} \int_0^{\pi} D^{L_1}_{m_1',m_1}(\Omega) D^{L_2}_{m_2',m_2}(\Omega) D^{L_3}_{m_3',m_3}(\Omega) d\Omega \\ & = \frac{1}{2L_3+1} \delta_{m_1',m_1}\, \delta_{m_1+m_2,m_3} \\ & \times C(L_1 L_2 L_3; m_1', m_2') C(L_1 L_2 L_3; m_1 m_2) . \end{aligned} \tag{A.10}$$

The Wigner rotation matrix elements are related to the modified (or normalized) spherical harmonics by

$$\begin{aligned} D^{J}_{m,0}(\alpha,\beta,\gamma) &= C_{J,-m}(\beta,\alpha) \\ &= \sqrt{\frac{4\pi}{2J+1}} Y_{J,-m} , \end{aligned} \tag{A.11}$$

$$D^{J}_{0,m}(\alpha,\beta,\gamma) = C_{J,-m}(\beta,\gamma) . \tag{A.12}$$

Table A.1. The Wigner rotation matrices $D^1_{m',m}(\alpha,\beta,\gamma)$.

		m	
m'	1	0	-1
1	$\frac{1+\cos\beta}{2}\, e^{-i(\alpha+\gamma)}$	$-\frac{1}{\sqrt{2}}\sin\beta e^{-i\alpha}$	$\frac{1-\cos\beta}{2} e^{-i(\alpha-\gamma)}$
0	$\frac{1}{\sqrt{2}}\sin\beta e^{-i\gamma}$	$\cos\beta$	$-\frac{1}{\sqrt{2}}\sin\beta e^{i\gamma}$
-1	$\frac{1-\cos\beta}{2}\, e^{i(\alpha-\gamma)}$	$\frac{1}{\sqrt{2}}\sin\beta e^{i\alpha}$	$\frac{1+\cos\beta}{2}\, e^{i(\alpha+\gamma)}$

Table A.2. The Wigner rotation matrices $D^2_{m'm}(\alpha,\beta,\gamma)$.

			m		
m'	2	1	0	-1	-2
2	$(\frac{1+\cos\beta}{2})^2$ $e^{-2i(\alpha+\gamma)}$	$-\frac{1+\cos\beta}{2}\sin\beta$ $e^{-i(2\alpha+\gamma)}$	$\sqrt{\frac{3}{8}}\sin^2\beta$ $e^{-i2\alpha}$	$-\frac{1-\cos\beta}{2}\sin\beta$ $e^{i(-2\alpha+\gamma)}$	$(\frac{1-\cos\beta}{2})^2$ $e^{2i(-\alpha+\gamma)}$
1	$\frac{1+\cos\beta}{2}\sin\beta$ $e^{-i(\alpha+2\gamma)}$	$[\cos^2\beta - \frac{1-\cos\beta}{2}]$ $e^{-i(\alpha+\gamma)}$	$-\sqrt{\frac{3}{8}}\ \sin 2\beta$ $e^{-i\alpha}$	$[\ \frac{1+\cos\beta}{2} - \cos^2\beta]$ $e^{i(-\alpha+\gamma)}$	$-\frac{1-\cos\beta}{2}\sin$ $e^{i(-\alpha+2\gamma)}$
0	$\sqrt{\frac{3}{8}}\sin^2\beta$ $e^{-i2\gamma}$	$\sqrt{\frac{3}{8}}\sin 2\beta$ $e^{-i\gamma}$	$\frac{3\cos^2\beta-1}{2}$	$-\sqrt{\frac{3}{8}}\sin 2\beta$ $e^{i\gamma}$	$\sqrt{\frac{3}{8}}\sin^2\beta$ $e^{i2\gamma}$
-1	$\frac{1-\cos\beta}{2}\sin\beta$ $e^{i(\alpha-2\gamma)}$	$[\frac{1+\cos\beta}{2} - \cos^2\beta]$ $e^{i(\alpha-\gamma)}$	$\sqrt{\frac{3}{8}}\sin^2\beta$ $e^{i\alpha}$	$[\cos^2\beta - \frac{1-\cos\beta}{2}]$ $e^{i(\alpha+\gamma)}$	$-\frac{1+\cos\beta}{2}\sin$ $e^{i(\alpha+2\gamma)}$
-2	$(\frac{1-\cos\beta}{2})^2$ $e^{2i(\alpha-\gamma)}$	$(\frac{1-\cos\beta}{2})\sin\beta$ $e^{i(2\alpha-\gamma)}$	$\sqrt{\frac{3}{8}}\sin^2\beta$ $e^{i2\alpha}$	$(\frac{1+\cos\beta}{2})\sin\beta$ $e^{i(2\alpha+\gamma)}$	$(\frac{1+\cos\beta}{2})^2$ $e^{2i(\alpha+\gamma)}$

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