Appendix B
Legendre Polynomials and Related Functions

In this appendix we first summarize formulae for Legendre polynomials, associated Legendre functions and spherical harmonics, which are required in defining the eigenfunctions of the orbital angular momentum operator. We then consider the phase of the spherical harmonics and its relation to the time-reversal operation, and we review two phase conventions that have been used in applications, referred to as the Condon–Shortley and the Fano–Racah phase conventions. Finally, we consider the transformation properties of wave functions under rotations of the axis of quantization in which we introduce and define Euler angles and Wigner rotation matrices. For a detailed discussion of spherical harmonics reference should be made to Hobson [474].

B.1 Legendre Polynomials

Let x be a real variable such that $-1 \leq x \leq 1$. In physical problems the variable x is usually the cosine of an angle θ so that $x = \cos\theta$. Legendre polynomials of degree ℓ are then defined by Rodrigue's formula

$$P_\ell(x) = \frac{1}{2^\ell \ell!}\frac{\mathrm{d}^\ell}{\mathrm{d}x^\ell}(x^2-1)^\ell, \quad \ell = 0, 1, 2, \ldots . \tag{B.1}$$

An equivalent definition of $P_\ell(x)$ is given in terms of a generating function, namely

$$F(x, y) = (1 - 2xy + y^2)^{-1/2} = \sum_{\ell=0}^{\infty} P_\ell(x) y^\ell, \tag{B.2}$$

where this relation has a meaning only when the summation converges, which occurs when $|x| \leq 1$ and $|y| < 1$. By differentiating (B.2) with respect to x we obtain the following useful relation

$$(1 - 2xy + y^2)^{-3/2} = \sum_{\ell=1}^{\infty} P'_\ell(x) y^{\ell-1}, \tag{B.3}$$

P.G. Burke, *R-Matrix Theory of Atomic Collisions*, Springer Series on Atomic, Optical, and Plasma Physics 61, DOI 10.1007/978-3-642-15931-2_14,

where $P'_\ell(x) = \mathrm{d}P_\ell(x)/\mathrm{d}x$.

The Legendre polynomials satisfy the following differential equation

$$\left[(1-x^2)\frac{\mathrm{d}^2}{\mathrm{d}x^2} - 2x\frac{\mathrm{d}}{\mathrm{d}x} + \ell(\ell+1)\right]P_\ell(x) = 0 \tag{B.4}$$

and recurrence relations

$$(\ell+1)P_{\ell+1} - (2\ell+1)xP_\ell + \ell P_{\ell-1} = 0, \tag{B.5}$$

$$P'_{\ell+1} - xP'_\ell = (\ell+1)P_\ell, \tag{B.6}$$

$$P'_{\ell+1} - P'_{\ell-1} = (2\ell+1)P_\ell, \tag{B.7}$$

$$(x^2-1)P'_\ell = \ell xP_\ell - \ell P_{\ell-1}. \tag{B.8}$$

These recurrence relations are valid for the case $\ell = 0$ if we define $P_{-1}(x) = 0$.

The Legendre polynomials also satisfy the orthogonality relation

$$\int_{-1}^{+1} P_\ell(x)P_{\ell'}(x)\mathrm{d}x = \frac{2}{2\ell+1}\delta_{\ell\ell'} \tag{B.9}$$

and the closure relation

$$\frac{1}{2}\sum_{\ell=0}^{\infty}(2\ell+1)P_\ell(x)P_\ell(x') = \delta(x-x'). \tag{B.10}$$

They have parity $(-1)^\ell$ so that

$$P_\ell(-x) = (-1)^\ell P_\ell(x) \tag{B.11}$$

and satisfy the boundary conditions

$$P_\ell(1) = 1, \quad P_\ell(-1) = (-1)^\ell, \tag{B.12}$$

with ℓ zeros in the interval $-1 < x < 1$. Explicit expressions for the first few Legendre polynomials are

$$P_0(x) = 1,$$

$$P_1(x) = x,$$

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

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

$$P_4(x) = \frac{1}{8}(35x^4 - 30x^2 + 3),$$

$$P_5(x) = \frac{1}{8}(63x^5 - 70x^3 + 15x),$$

$$P_6(x) = \frac{1}{16}(231x^6 - 315x^4 + 105x^2 - 5),$$

$$P_7(x) = \frac{1}{16}(429x^7 - 693x^5 + 315x^3 - 35x). \tag{B.13}$$

Explicit values for the higher order polynomials are usually calculated using the recurrence relation (B.5).

B.2 Associated Legendre Functions

The associated Legendre functions $P_\ell^m(x)$ are defined over the interval $-1 \le x \le 1$ by the relation

$$P_\ell^m(x) = (1 - x^2)^{m/2} \frac{\mathrm{d}^m}{\mathrm{d}x^m} P_\ell(x), \quad 0 \le m \le \ell. \tag{B.14}$$

They are seen to be the product of the function $(1 - x^2)^{m/2}$ and a polynomial of degree $(\ell - m)$ and parity $(-1)^{\ell - m}$, having $\ell - m$ zeros in the interval $-1 \le x \le 1$. As with the Legendre polynomials, a generating function can be defined for the associated Legendre functions. It is given by

$$\frac{(2m)!(1 - x^2)^{m/2}}{2^m m!(1 - 2xy + y^2)^{m+1/2}} = \sum_{\ell=0}^{\infty} P_{\ell+m}^m(x) y^\ell. \tag{B.15}$$

The associated Legendre functions satisfy the differential equation

$$\left[(1 - x^2)\frac{\mathrm{d}^2}{\mathrm{d}x^2} - 2x\frac{\mathrm{d}}{\mathrm{d}x} + \ell(\ell + 1) - \frac{m^2}{1 - x^2}\right] P_\ell^m(x) = 0 \tag{B.16}$$

and the recurrence relations

$$(\ell - m + 1)P_{\ell+1}^m - (2\ell + 1)xP_\ell^m + (\ell + m)P_{\ell-1}^m = 0, \quad 0 \le m \le \ell - 1, \tag{B.17}$$

$$P_\ell^{m+1} - \frac{2mx}{(1 - x^2)^{1/2}} P_\ell^m + (\ell + m)(\ell - m + 1)P_\ell^{m-1} = 0, \quad 0 \le m \le \ell - 1, \tag{B.18}$$

$$(2\ell + 1)(1 - x^2)^{1/2} P_\ell^m = P_{\ell+1}^{m+1} - P_{\ell-1}^{m+1}, \quad 0 \le m \le \ell - 2, \tag{B.19}$$

$$(2\ell+1)(1-x^2)^{1/2}P_\ell^m = (\ell+m)(\ell+m-1)P_{\ell-1}^{m-1} - (\ell-m+1) \times (\ell-m+2)P_{\ell+1}^{m-1}, \quad 0 \le m \le \ell, \tag{B.20}$$

$$(1-x^2)\frac{\mathrm{d}P_\ell^m}{\mathrm{d}x} = (\ell+1)xP_\ell^m - (\ell-m+1)P_{\ell+1}^m, \quad 0 \le m \le \ell, \tag{B.21}$$

$$= -\ell x P_\ell^m + (\ell+m)P_{\ell-1}^m, \quad 0 \le m \le \ell-1. \tag{B.22}$$

The associated Legendre functions also satisfy the orthogonality relations

$$\int_{-1}^{+1} P_\ell^m(x)P_{\ell'}^m(x)\mathrm{d}x = \frac{2(\ell+m)!}{(2\ell+1)(\ell-m)!}\delta_{\ell\ell'} \tag{B.23}$$

and have the values

$$P_\ell^m(1) = P_\ell^m(-1) = 0, \quad m \neq 0, \tag{B.24}$$

and

$$P_\ell^m(0) = (-1)^s \frac{(2s+2m)!}{2^\ell s!(s+m)!}, \quad \ell - m = 2s,$$
$$= 0, \quad \ell - m = 2s+1. \tag{B.25}$$

Explicit expressions for the first few associated Legendre functions are

$$P_1^1(x) = (1-x^2)^{1/2},$$
$$P_2^1(x) = 3x(1-x^2)^{1/2},$$
$$P_2^2(x) = 3(1-x^2),$$
$$P_3^1(x) = \frac{3}{2}(5x^2-1)(1-x^2)^{1/2},$$
$$P_3^2(x) = 15x(1-x^2),$$
$$P_3^3(x) = 15(1-x^2)^{3/2},$$
$$P_4^1(x) = \frac{5}{2}(7x^3-3x)(1-x^2)^{1/2},$$
$$P_4^2(x) = \frac{15}{2}(7x^2-1)(1-x^2),$$
$$P_4^3(x) = 105x(1-x^2)^{3/2},$$
$$P_4^4(x) = 105(1-x^2)^2. \tag{B.26}$$

B.3 Spherical Harmonics

The spherical harmonics $Y_{\ell m}(\theta, \phi)$ are simultaneous eigenfunctions of $\boldsymbol{\ell}^2$ and ℓ_z, where in quantum theory $\boldsymbol{\ell} = -\mathrm{i}(\mathbf{r} \times \nabla)$ (with $\hbar = 1$) is the orbital angular momentum operator of a particle and ℓ_z is its z-component. Thus

$$\boldsymbol{\ell}^2 Y_{\ell m}(\theta, \phi) = \ell(\ell+1) Y_{\ell m}(\theta, \phi), \quad \ell = 0, 1, 2, \ldots, \tag{B.27}$$

$$\ell_z Y_{\ell m}(\theta, \phi) = m Y_{\ell m}(\theta, \phi), \quad m = -\ell, -\ell+1, \ldots, \ell, \tag{B.28}$$

where, using spherical polar coordinates θ and ϕ,

$$\boldsymbol{\ell}^2 = -\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \tag{B.29}$$

and

$$\ell_z = -\mathrm{i}\frac{\partial}{\partial\phi}. \tag{B.30}$$

The Laplacian ∇^2 can be written in terms of $\boldsymbol{\ell}^2$ as follows

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{1}{r^2}\boldsymbol{\ell}^2, \tag{B.31}$$

where the kinetic energy of a particle of unit mass is $-\frac{1}{2}\nabla^2$.

The spherical harmonics are defined in terms of the associated Legendre functions by

$$Y_{\ell m}(\theta, \phi) = (-1)^m \left[\frac{(2\ell+1)(\ell-m)!}{4\pi(\ell+m)!}\right]^{1/2} P_\ell^m(\cos\theta)\exp(\mathrm{i}m\phi), \quad m \geq 0, \tag{B.32}$$

where those with $m < 0$ can be obtained from the following important property

$$Y_{\ell m}^*(\theta, \phi) = (-1)^m Y_{\ell -m}(\theta, \phi). \tag{B.33}$$

In these and later equations $*$ corresponds to complex conjugation, and we have adopted the phase convention of Condon and Shortley [227] here and in the rest of this section. It follows from (B.32) and (B.33) that the spherical harmonics $Y_{\ell m}(\theta, \phi)$ have parity $(-1)^\ell$, so that under a reflection in the origin, such that $(\theta, \phi) \to (\pi - \theta, \phi + \pi)$, we have

$$Y_{\ell m}(\pi - \theta, \phi + \pi) = (-1)^\ell Y_{\ell m}(\theta, \phi). \tag{B.34}$$

The spherical harmonics satisfy the orthonormality relation

$$\int_0^{2\pi}\int_0^{\pi} Y^*_{\ell' m'}(\theta,\phi)Y_{\ell m}(\theta,\phi)\sin\theta \mathrm{d}\theta \mathrm{d}\phi = \delta_{\ell\ell'}\delta_{mm'} \tag{B.35}$$

and the closure relation

$$\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{+\ell} Y^*_{\ell m}(\theta,\phi)Y_{\ell m}(\theta',\phi') = \delta(\Omega-\Omega'), \tag{B.36}$$

where

$$\delta(\Omega-\Omega') = \frac{\delta(\theta-\theta')\delta(\phi-\phi')}{\sin\theta}. \tag{B.37}$$

They also satisfy the following product relation

$$Y_{\ell_1 m_1}(\theta,\phi)Y_{\ell_2 m_2}(\theta,\phi) = \sum_{\ell=|\ell_1-\ell_2|}^{\ell_1+\ell_2}\left[\frac{(2\ell_1+1)(2\ell_2+1)}{4\pi(2\ell+1)}\right]^{1/2}(\ell_1 m_1 \ell_2 m_2|\ell m_1+m_2)$$

$$\times\,(\ell_1 0 \ell_2 0|\ell 0)Y_{\ell m_1+m_2}(\theta,\phi), \tag{B.38}$$

where $(\ell_1 m_1 \ell_2 m_2|\ell m_1+m_2)$ are Clebsch–Gordan coefficients defined in Appendix A. Using the result that $Y_{10}(\theta,\phi) = (3/4\pi)^{1/2}\cos\theta$, (B.38) yields the recurrence relation

$$\cos\theta\; Y_{\ell m}(\theta,\phi) = \left[\frac{(\ell+m+1)(\ell-m+1)}{(2\ell+1)(2\ell+3)}\right]^{1/2} Y_{\ell+1 m}(\theta,\phi)$$

$$+\left[\frac{(\ell+m)(\ell-m)}{(2\ell-1)(2\ell+1)}\right]^{1/2} Y_{\ell-1 m}(\theta,\phi). \tag{B.39}$$

Another useful relation which follows from (B.21) and (B.22) is

$$\sin\theta\frac{\partial}{\partial\theta}Y_{\ell m}(\theta,\phi) = \ell\left[\frac{(\ell+m+1)(\ell-m+1)}{(2\ell+1)(2\ell+3)}\right]^{1/2} Y_{\ell+1 m}(\theta,\phi)$$

$$-(\ell+1)\left[\frac{(\ell+m)(\ell-m)}{(2\ell-1)(2\ell+1)}\right]^{1/2} Y_{\ell-1 m}(\theta,\phi). \tag{B.40}$$

Other recurrence relations can be obtained by introducing the shift operators

$$\ell_\pm = \ell_x \pm \mathrm{i}\ell_y = \exp(\pm\mathrm{i}\phi)\left(\pm\frac{\partial}{\partial\theta}+\mathrm{i}\cot\theta\frac{\partial}{\partial\phi}\right). \tag{B.41}$$

We find that

$$\ell_{\pm} Y_{\ell m}(\theta, \phi) = [(\ell \mp m)(\ell \pm m + 1)]^{1/2} Y_{\ell m \pm 1}(\theta, \phi), \tag{B.42}$$

$$\ell_{+} Y_{\ell\ell}(\theta, \phi) = 0, \tag{B.43}$$

$$\ell_{-} Y_{\ell -\ell}(\theta, \phi) = 0. \tag{B.44}$$

The orthonormality relation (B.35) and the product relation (B.38) enable the following integral over three spherical harmonics to be evaluated

$$\int_0^{2\pi}\int_0^{\pi} Y^*_{\ell_3 m_3}(\theta,\phi) Y_{\ell_1 m_1}(\theta,\phi) Y_{\ell_2 m_2}(\theta,\phi) \sin\theta \mathrm{d}\theta \mathrm{d}\phi$$
$$= \left[\frac{(2\ell_1+1)(2\ell_2+1)}{4\pi(2\ell_3+1)}\right]^{1/2} (\ell_1 m_1 \ell_2 m_2|\ell_3 m_3)(\ell_1 0 \ell_2 0|\ell_3 0). \tag{B.45}$$

Another important relation is the spherical harmonic addition theorem

$$Y_{\ell 0}(\theta, 0) = \left(\frac{4\pi}{2\ell+1}\right)^{1/2} \sum_{m=-\ell}^{+\ell} Y^*_{\ell m}(\theta_1, \phi_1) Y_{\ell m}(\theta_2, \phi_2), \tag{B.46}$$

where (θ_1, ϕ_1) and (θ_2, ϕ_2) are the spherical polar angles of two vectors $\mathbf{r_1}$ and $\mathbf{r_2}$ and θ is the angle between these vectors. Using the result that

$$Y_{\ell 0}(\theta, \phi) = \left(\frac{2\ell+1}{4\pi}\right)^{1/2} P_\ell(\cos\theta), \tag{B.47}$$

the addition theorem can be written as

$$P_\ell(\cos\theta) = \frac{4\pi}{2\ell+1} \sum_{m=-\ell}^{+\ell} Y^*_{\ell m}(\theta_1, \phi_1) Y_{\ell m}(\theta_2, \phi_2). \tag{B.48}$$

A further useful formula can be derived from the generating function satisfied by the Legendre polynomials, (B.2), which we write here as

$$\frac{1}{|\mathbf{r_1} - \mathbf{r_2}|} = \sum_{\ell=0}^{\infty} \frac{r_<^\ell}{r_>^{\ell+1}} P_\ell(\cos\theta), \tag{B.49}$$

where θ is the angle between the vectors $\mathbf{r_1}$ and $\mathbf{r_2}$ and $r_<$ is the smaller and $r_>$ is the larger of r_1 and r_2. Using (B.48) we can write (B.49) as

$$\frac{1}{|\mathbf{r_1} - \mathbf{r_2}|} = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} \frac{4\pi}{2\ell+1} \frac{r_<^\ell}{r_>^{\ell+1}} Y^*_{\ell m}(\theta_1, \phi_1) Y_{\ell m}(\theta_2, \phi_2). \tag{B.50}$$

Also we have

$$\frac{\exp(\mathrm{i}k|\mathbf{r_1}-\mathbf{r_2}|)}{|\mathbf{r_1}-\mathbf{r_2}|}=\mathrm{i}k\sum_{\ell=0}^{\infty}(2\ell+1)j_\ell(kr_<)h_\ell^{(1)}(kr_>)P_\ell(\cos\theta), \tag{B.51}$$

where j_ℓ and $h_\ell^{(1)}$ are, respectively, spherical Bessel and spherical Hankel functions of the first kind (see Appendix C). Finally, the plane wave $\exp(\mathrm{i}\mathbf{k}\cdot\mathbf{r})$ can be expanded in spherical harmonics as

$$\exp(\mathrm{i}\mathbf{k}\cdot\mathbf{r})=4\pi\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{+\ell}\mathrm{i}^\ell j_\ell(kr)Y^*_{\ell m}(\theta_k,\phi_k)Y_{\ell m}(\theta,\phi), \tag{B.52}$$

where (θ_k,ϕ_k) and (θ,ϕ) are the spherical polar angles of the two vectors $\mathbf{k}$ and $\mathbf{r}$, respectively. If we use the addition theorem (B.48) and choose the z-axis to coincide with the direction of $\mathbf{k}$ then (B.52) reduces to the partial wave expansion

$$\exp(\mathrm{i}\mathbf{k}\cdot\mathbf{r})=\sum_{\ell=0}^{\infty}(2\ell+1)\mathrm{i}^\ell j_\ell(kr)P_\ell(\cos\theta). \tag{B.53}$$

Explicit expressions for the first few spherical harmonics are

$$Y_{00}(\theta,\phi)=\left(\frac{1}{4\pi}\right)^{1/2},$$

$$Y_{10}(\theta,\phi)=\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta,$$

$$Y_{1\pm1}(\theta,\phi)=\mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta\exp(\pm\mathrm{i}\phi),$$

$$Y_{20}(\theta,\phi)=\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1),$$

$$Y_{2\pm1}(\theta,\phi)=\mp\left(\frac{15}{8\pi}\right)^{1/2}\sin\theta\cos\theta\exp(\pm\mathrm{i}\phi),$$

$$Y_{2\pm2}(\theta,\phi)=\left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta\exp(\pm2\mathrm{i}\phi),$$

$$Y_{30}(\theta,\phi)=\left(\frac{7}{16\pi}\right)^{1/2}(5\cos^3\theta-3\cos\theta),$$

$$Y_{3\pm1}(\theta,\phi)=\mp\left(\frac{21}{64\pi}\right)^{1/2}\sin\theta(5\cos^2\theta-1)\exp(\pm\mathrm{i}\phi),$$

$$Y_{3\pm 2}(\theta,\phi) = \left(\frac{105}{32\pi}\right)^{1/2} \sin^2\theta \cos\theta \exp(\pm 2\mathrm{i}\phi),$$

$$Y_{3\pm 3}(\theta,\phi) = \mp\left(\frac{35}{64\pi}\right)^{1/2} \sin^3\theta \exp(\pm 3\mathrm{i}\phi). \tag{B.54}$$

It follows that we can write the first-order ($\ell = 1$) spherical harmonics in terms of the Cartesian coordinates x, y and z as

$$Y_{1m}(\theta,\phi) = \left(\frac{3}{4\pi}\right)^{1/2} \frac{1}{r} \begin{cases} -\frac{1}{\sqrt{2}}(x + \mathrm{i}y), & m = 1, \\ z, \quad m = 0, \\ -\frac{1}{\sqrt{2}}(x - \mathrm{i}y), & m = -1. \end{cases} \tag{B.55}$$

Finally, we find it convenient to define two-particle angular functions $Y_{\ell_1\ell_2 LM_L}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2)$ which are simultaneous eigenfunctions of the square of the total orbital angular momentum operator $\mathbf{L}^2$ and its z-component L_z of two particles labelled 1 and 2, where

$$\mathbf{L} = \boldsymbol{\ell}_1 + \boldsymbol{\ell}_2 \quad \text{and} \quad L_z = \ell_{1z} + \ell_{2z}. \tag{B.56}$$

It follows from (A.15) that these eigenfunctions are defined by

$$Y_{\ell_1\ell_2 LM_L}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) = \sum_{m_1 m_2} (\ell_1 m_1 \ell_2 m_2 | L M_L) Y_{\ell_1 m_1}(\theta_1, \phi_1) Y_{\ell_2 m_2}(\theta_2, \phi_2), \tag{B.57}$$

which can be inverted using (A.19) giving

$$Y_{\ell_1 m_1}(\theta_1, \phi_1) Y_{\ell_2 m_2}(\theta_2, \phi_2) = \sum_{L} (\ell_1 m_1 \ell_2 m_2 | L M_L) Y_{\ell_1\ell_2 LM_L}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2). \tag{B.58}$$

Also, it follows from the symmetry relation (A.22) satisfied by the Clebsch–Gordan coefficient in (B.57) that these eigenfunctions satisfy

$$Y_{\ell_1\ell_2 LM_L}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) = (-1)^{\ell_1 + \ell_2 - L} Y_{\ell_2\ell_1 LM_L}(\hat{\mathbf{r}}_2, \hat{\mathbf{r}}_1). \tag{B.59}$$

In addition, it follows from the orthonormality relation (B.35) satisfied by the spherical harmonics that

$$\int\int Y^*_{\ell_1\ell_2 LM_L}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) Y_{\ell_1'\ell_2' L' M_{L'}}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) \mathrm{d}\hat{\mathbf{r}}_1 \mathrm{d}\hat{\mathbf{r}}_2 = \delta_{\ell_1\ell_1'} \delta_{\ell_2\ell_2'} \delta_{LL'} \delta_{M_L M_{L'}}, \tag{B.60}$$

where in this and the above equations we have written $\hat{\mathbf{r}}_1 \equiv (\theta_1, \phi_1)$ and $\hat{\mathbf{r}}_2 \equiv (\theta_2, \phi_2)$ for notational simplicity. These two-particle angular functions are important in the quantum theory of two-electron systems, such as electron collisions with atomic hydrogen or with atoms containing one active electron as in the alkali metal atoms.

B.4 Phase of Spherical Harmonics

The phase of the spherical harmonics $Y_{\ell m}(\theta, \phi)$, defined by (B.32) and (B.33), corresponds to that adopted by Condon and Shortley [227] and is referred to in this monograph as the "Condon–Shortley phase convention". However, it was pointed out by Huby [477] that a careful choice of this phase has to be made in proving the equality of a matrix element to its complex conjugate by means of the time-reversal operation. In particular, the functions used in the vector addition of angular momenta must be defined in such a way that the operation of time reversal gives the same form of the result before and after vector addition. Although the principles involved are well known, an inconsistency in the choice of phase has led to discrepancies in some results. This was discussed by Breit [134] in the context of the Wigner and Eisenbud [972] R-matrix theory of nuclear reactions.

Let us consider the application of the time-reversal operator K (Wigner [966]) on an angular momentum eigenstate ψ_{jm}. We have

$$K\psi_{jm} = \alpha(j)\mathrm{i}^{2m}\psi_{j\,-m}, \tag{B.61}$$

where $\alpha(j)$ can be varied by multiplying the eigenstates by an arbitrary phase factor which is independent of m. It is desirable to choose $\alpha(j)$ so that the form of (B.61) is invariant under the vector addition of angular momenta defined by (A.15). Hence we require that if $\psi_{j_1 m_1}(1)$ and $\psi_{j_2 m_2}(2)$ in (A.15) conform to (B.61) then $\psi_{j_1 j_2 jm}(1, 2)$ should do likewise. It is found that when we use the conventional real representation of the Clebsch–Gordan coefficients $(j_1 m_1 j_2 m_2 | jm)$, this requirement is satisfied by taking

$$\alpha(j) = \mathrm{i}^{-2j} \tag{B.62}$$

so that (B.61) becomes

$$K\psi_{jm} = (-1)^{j-m}\psi_{j\,-m}. \tag{B.63}$$

In the case when ψ_{jm} represents a spherical harmonic, we must adopt a new definition for the phase of this quantity defined by

$$\mathcal{Y}_{\ell m}(\theta, \phi) = \mathrm{i}^{\ell} Y_{\ell m}(\theta, \phi), \tag{B.64}$$

where $Y_{\ell m}(\theta, \phi)$ is the spherical harmonic defined by (B.32) and (B.33). It then follows from (B.33) and (B.64) that

$$\mathcal{Y}^*_{\ell m}(\theta, \phi) = (-1)^{\ell+m}\mathcal{Y}_{\ell -m}(\theta, \phi). \tag{B.65}$$

This modified phase convention for the spherical harmonics $\mathcal{Y}_{\ell m}(\theta, \phi)$ was adopted by Fano and Racah [308], and it was used by Fano [302] in his analysis of the interaction between configurations with several open shells. Following this work, this convention was adopted by Hibbert [462, 464] in a general computer program for atomic structure calculations and by Burke et al. [178], Berrington et al. [95, 98, 102] and Scott and Taylor [844] in their general computer program for atomic continuum calculations using the R-matrix method. In this monograph this phase convention will be referred to as the "Fano–Racah phase convention".

In practice, the modifications which have to be made to the formulae given in Appendix B.3 due to the adoption of the Fano–Racah phase convention are small. However, care has to be taken to ensure that the same phase convention is used consistently throughout the analysis and calculation of any given process. As an example, we derive in Appendix D.1 explicit expressions for the long-range multipole potential coefficients in non-relativistic electron collisions with atoms and ions using both the Fano–Racah and the Condon–Shortley phase conventions. We give below formulae obtained using spherical harmonics satisfying the Fano–Racah phase convention.

We observe first that the spherical harmonics defined by (B.64) satisfy the usual orthonormality relation given by (B.35), which can be written as

$$\int_0^{2\pi} \int_0^{\pi} \mathcal{Y}^*_{\ell' m'}(\theta, \phi) \mathcal{Y}_{\ell m}(\theta, \phi) \sin\theta \mathrm{d}\theta \mathrm{d}\phi = \delta_{\ell\ell'} \delta_{mm'}. \tag{B.66}$$

However, the expression for the product of two spherical harmonics given by (B.38) now becomes

$$\begin{aligned} \mathcal{Y}_{\ell_1 m_1}(\theta, \phi) \mathcal{Y}_{\ell_2 m_2}(\theta, \phi) = \sum_{\ell} & \mathrm{i}^{\ell_1 + \ell_2 - \ell} \left[\frac{(2\ell_1 + 1)(2\ell_2 + 1)}{4\pi(2\ell + 1)} \right]^{1/2} \\ & \times (\ell_1 m_1 \ell_2 m_2 | \ell m_1 + m_2) \\ & \times (\ell_1 0 \ell_2 0 | \ell 0) \mathcal{Y}_{\ell m_1 + m_2}(\theta, \phi). \end{aligned} \tag{B.67}$$

Using the result that $\mathcal{Y}_{10}(\theta, \phi) = \mathrm{i}(3/4\pi)^{1/2} \cos\theta$, (B.67) then reduces to

$$\cos\theta \mathcal{Y}_{\ell m}(\theta, \phi) = \sum_{\ell'} \mathrm{i}^{\ell - \ell'} \left[\frac{2\ell + 1}{2\ell' + 1} \right]^{1/2} (10\ell m | \ell' m)(10\ell 0 | \ell' 0) \mathcal{Y}_{\ell' m}(\theta, \phi). \tag{B.68}$$

In addition it follows from (B.40), by comparing with (B.39) and after using (B.68), that

$$\begin{aligned} \sin\theta \frac{\partial}{\partial\theta} \mathcal{Y}_{\ell m}(\theta, \phi) = \sum_{\ell'} & \mathrm{i}^{\ell - \ell'} f(\ell, \ell') \left[\frac{2\ell + 1}{2\ell' + 1} \right]^{1/2} (10\ell m | \ell' m) \\ & \times (10\ell 0 | \ell' 0) \mathcal{Y}_{\ell' m}(\theta, \phi), \end{aligned} \tag{B.69}$$

where

$$f(\ell,\ell') = \begin{cases} \ell, & \ell' = \ell+1 \\ -\ell-1, & \ell' = \ell-1. \end{cases} \tag{B.70}$$

Also we find that the integral over three spherical harmonics given by (B.45) reduces to

$$\int_0^{2\pi}\int_0^{\pi} \mathcal{Y}^*_{\ell_3 m_3}(\theta,\phi)\mathcal{Y}_{\ell_1 m_1}(\theta,\phi)\mathcal{Y}_{\ell_2 m_2}(\theta,\phi)\sin\theta \mathrm{d}\theta\mathrm{d}\phi$$
$$= \mathrm{i}^{\ell_1+\ell_2-\ell_3}\left[\frac{(2\ell_1+1)(2\ell_2+1)}{4\pi(2\ell_3+1)}\right]^{1/2}(\ell_1 m_1 \ell_2 m_2|\ell_3 m_3)(\ell_1 0 \ell_2 0|\ell_3 0), \tag{B.71}$$

where the factor $\mathrm{i}^{\ell_1+\ell_2-\ell_3}$ is real since, from (A.27), the Clebsch–Gordan coefficient $(\ell_1 0 \ell_2 0|\ell_3 0)$ vanishes unless $\ell_1+\ell_2-\ell_3$ is even.

The matrix element of the momentum operator $\hat{\boldsymbol{\epsilon}}\cdot\mathbf{p}$, which occurs in our discussion of multiphoton processes in intense laser fields in Chaps. 9 and 10, can be obtained from (B.68) and (B.69). If we take the z-axis to lie along the laser polarization direction $\hat{\boldsymbol{\epsilon}}$ then

$$\hat{\boldsymbol{\epsilon}}\cdot\mathbf{p} = -\mathrm{i}\frac{\partial}{\partial z} = -\mathrm{i}\left(\cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\right). \tag{B.72}$$

Using (B.68) and (B.69) we then obtain the following expression for the matrix elements

$$\langle\mathcal{Y}_{\ell m}(\theta,\phi)|\hat{\boldsymbol{\epsilon}}\cdot\mathbf{p}|\mathcal{Y}_{\ell' m'}(\theta,\phi)\rangle = \mathrm{i}^{\ell'-\ell-1}\left[\frac{2\ell'+1}{2\ell+1}\right]^{1/2}(10\ell' m'|\ell m)$$
$$\times (10\ell' 0|\ell 0)\left(\frac{\mathrm{d}}{\mathrm{d}r} - \frac{f(\ell',\ell)}{r}\right)\delta_{mm'}, \tag{B.73}$$

where $f(\ell',\ell)$ is defined by (B.70), with ℓ and ℓ' interchanged. Also, in our evaluation of the matrix elements which occur in multiphoton processes, discussed in Chaps. 9 and 10 and Appendix D, see, for example, (9.44) and (D.40), it is necessary to determine the angular integrals which arise in the following matrix element

$$M = \langle r^{-1}f(r)\mathcal{Y}_{\ell m}(\theta,\phi)|\hat{\boldsymbol{\epsilon}}\cdot\mathbf{p}|r^{-1}g(r)\mathcal{Y}_{\ell' m'}(\theta,\phi)\rangle. \tag{B.74}$$

After separating the radial and angular integrals in (B.74) we can rewrite this equation as

$$M = \langle r^{-2}f(r)|M_{\mathrm{ang}}|g(r)\rangle, \tag{B.75}$$

where the angular matrix element M_{ang} is defined by

$$M_{\mathrm{ang}} = \mathrm{i}^{\ell'-\ell-1}\left[\frac{2\ell'+1}{2\ell+1}\right]^{1/2}(10\ell'm'|\ell m)(10\ell'0|\ell 0)$$
$$\times\left(\frac{\mathrm{d}}{\mathrm{d}r} - \frac{f(\ell',\ell)}{r} - \frac{1}{r}\right)\delta_{mm'}. \qquad \text{(B.76)}$$

Comparing (B.76) with the angular matrix element defined by (B.73), we see that the additional factor $-1/r$, which occurs in (B.76), arises from the operation of $\hat{\boldsymbol{\epsilon}} \cdot \mathbf{p}$ on the radial wave function $r^{-1}g(r)$ in (B.74). The angular matrix element M_{ang} then operates on the reduced radial wave function $g(r)$ in (B.75).

Finally, we note that the expansions of the Legendre polynomial and the plane wave, given by (B.48) and (B.52), respectively, can be rewritten in terms of spherical harmonics, defined using the Fano–Racah phase convention as

$$P_\ell(\cos\theta) = \frac{4\pi}{2\ell+1}\sum_{m=-\ell}^{+\ell}\mathcal{Y}^*_{\ell m}(\theta_1,\phi_1)\mathcal{Y}_{\ell m}(\theta_2,\phi_2) \qquad \text{(B.77)}$$

and

$$\exp(\mathrm{i}\mathbf{k}\cdot\mathbf{r}) = 4\pi\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{+\ell}\mathrm{i}^\ell j_\ell(kr)\mathcal{Y}^*_{\ell m}(\theta_k,\phi_k)\mathcal{Y}_{\ell m}(\theta,\phi). \qquad \text{(B.78)}$$

Also, the simultaneous eigenfunctions of the square of the total orbital angular momentum operator $\mathbf{L}^2$ and its z-component L_z of two particles labelled 1 and 2, defined earlier by (B.57), are now given by

$$\mathcal{Y}_{\ell_1\ell_2LM_L}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2) = \sum_{m_1m_2}(\ell_1m_1\ell_2m_2|LM_L)\mathcal{Y}_{\ell_1m_1}(\theta_1,\phi_1)\mathcal{Y}_{\ell_2m_2}(\theta_2,\phi_2), \qquad \text{(B.79)}$$

where, as before, these eigenfunctions satisfy the symmetry relation

$$\mathcal{Y}_{\ell_1\ell_2LM_L}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2) = (-1)^{\ell_1+\ell_2-L}\mathcal{Y}_{\ell_2\ell_1LM_L}(\hat{\mathbf{r}}_2,\hat{\mathbf{r}}_1) \qquad \text{(B.80)}$$

and the orthogonality relation

$$\int\int\mathcal{Y}^*_{\ell_1\ell_2LM_L}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)\mathcal{Y}_{\ell'_1\ell'_2L'M_{L'}}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)\mathrm{d}\hat{\mathbf{r}}_1\mathrm{d}\hat{\mathbf{r}}_2 = \delta_{\ell_1\ell'_1}\delta_{\ell_2\ell'_2}\delta_{LL'}\delta_{M_LM_{L'}}. \qquad \text{(B.81)}$$

B.5 Transformation Under Rotations

In Appendix A.1 we considered a quantum system described by a set of wave functions ψ_{jm} which were simultaneous eigenfunctions of the total angular momentum operator squared $\mathbf{J}^2$ and its z-component J_z belonging to the eigenvalues $j(j+1)$ and m, respectively. In this appendix we consider how these functions transform under rotations of the axis of quantization with the physical system fixed in space. An important example of the need for this development arises in electron–molecule collisions, which we consider in Chap. 11, where the transformation of the collision wave function from the molecular to the laboratory frame of reference is required in the calculation of the scattering amplitudes and cross sections.

We specify a general rotation by three Euler angles α, β and γ. We adopt a right-handed coordinate system, as used by Rose [797], Edmonds [284] and Fano and Racah [308]. The Euler angles are defined by the following three rotations which are performed successively, as illustrated in Fig. B.1:

i. A rotation about the z-axis through an angle α $(0 \leq \alpha < 2\pi)$ giving the new coordinate axes x', y', z', as illustrated in Fig. B.1 (i).
ii. A rotation about the new y'-axis through an angle β $(0 \leq \beta < \pi)$ giving the new coordinate axes x'', y'', z'', as illustrated in Fig. B.1 (ii).
iii. A rotation about the new z''-axis through an angle γ $(0 \leq \gamma < 2\pi)$ giving the final coordinate axes x''', y''', z''', as illustrated in Fig. B.1 (iii).

The Euler angles α, β, γ are each defined by a positive or zero right-hand screw rotation.

We now consider the effect on the wave function of a particle due to a rotation of the coordinate system through the Euler angles α, β, γ. The wave function $\psi(x, y, z)$ in the original coordinate system is related to the wave function

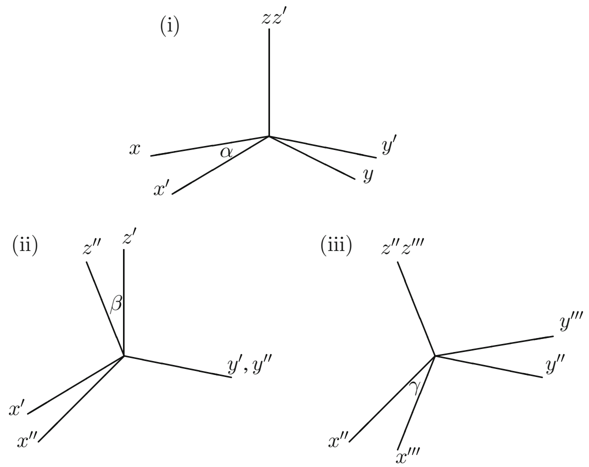

Fig. B.1 Right-handed coordinate system showing the Euler angles α, β, γ

$\psi'(x', y', z')$ in the rotated coordinate system by the product of three unitary operators as follows:

$$\psi' = R(\alpha, \beta, \gamma)\psi = R_\gamma R_\beta R_\alpha \psi, \tag{B.82}$$

where the operators R_α, R_β and R_γ correspond to successive rotations about the z-, y'- and z''-axes, respectively. For an infinitesimal rotation $\mathrm{d}\theta$ about the z-axis we find that

$$R\psi(x, y, z) = (1 - \mathrm{i}\mathrm{d}\theta J_z)\psi(x, y, z), \tag{B.83}$$

where the angular momentum operator J_z, introduced in this equation, and the corresponding angular momentum operators J_x and J_y, obtained by infinitesimal rotations about the x- and y-axes, respectively, are defined by

$$J_x = -\mathrm{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right), \tag{B.84}$$

$$J_y = -\mathrm{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right), \tag{B.85}$$

$$J_z = -\mathrm{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right). \tag{B.86}$$

It follows from (B.83) that a finite rotation about the z-axis can be written as

$$R\psi = \exp(-\mathrm{i}\theta J_z)\psi. \tag{B.87}$$

Hence, the sequence of rotations defined by the Euler angles α, β, γ in (B.82) are represented by the operator

$$R(\alpha, \beta, \gamma) = \exp(-\mathrm{i}\gamma J_{z''})\ \exp(-\mathrm{i}\beta J_{y'})\ \exp(-\mathrm{i}\alpha J_z), \tag{B.88}$$

where J_z, $J_{y'}$ and $J_{z''}$ are the components of $\mathbf{J}$ along the z-, y'- and z''-axes, respectively, in Fig. B.1. We can also show that the operator $R(\alpha, \beta, \gamma)$ in (B.88) can be expressed in terms of rotations made in the *original* coordinate system by the equation

$$R(\alpha, \beta, \gamma) = \exp(-\mathrm{i}\alpha J_z)\ \exp(-\mathrm{i}\beta J_y)\ \exp(-\mathrm{i}\gamma J_z), \tag{B.89}$$

which correspond to a rotation γ about the z-axis, followed by a rotation β about the y-axis and finally a rotation α about the z-axis. We observe that since the above equations have been obtained using the commutation relations satisfied by the orbital angular momentum operators, defined by (B.84), (B.85) and (B.86), they are valid for general angular momentum operators satisfying these commutation relations.

The matrix elements of the rotation operator $R(\alpha, \beta, \gamma)$ in (B.82) are defined by the equation

$$D^j_{m'm}(\alpha, \beta, \gamma) = \langle \psi_{jm'} | R(\alpha, \beta, \gamma) | \psi_{jm} \rangle, \tag{B.90}$$

where j is a conserved quantum number since $\mathbf{J}^2$ commutes with each term in the expression for $R(\alpha, \beta, \gamma)$ defined by (B.89). Also when ψ in (B.82) is taken to be ψ_{jm} we obtain

$$R(\alpha, \beta, \gamma)\psi_{jm} = \sum_{m'} D^j_{m'm}(\alpha, \beta, \gamma)\psi_{jm'}. \tag{B.91}$$

The quantities $D^j_{m'm}(\alpha, \beta, \gamma)$ in (B.90) and (B.91) are known as Wigner rotation matrices.

In order to obtain an explicit expression for $D^j_{m'm}(\alpha, \beta, \gamma)$ we substitute (B.89) into (B.90) giving

$$D^j_{m'm}(\alpha, \beta, \gamma) = \langle \psi_{jm'} | \exp(-\mathrm{i}\alpha J_z)\ \exp(-\mathrm{i}\beta J_y)\ \exp(-\mathrm{i}\gamma J_z) | \psi_{jm} \rangle. \tag{B.92}$$

It follows from (A.6) that $J_z \psi_{jm} = m\psi_{jm}$, and hence (B.92) can be written as

$$D^j_{m'm}(\alpha, \beta, \gamma) = \exp(-\mathrm{i}m'\alpha)\ d^j_{m'm}(\beta)\ \exp(-\mathrm{i}m\gamma), \tag{B.93}$$

where the reduced rotation matrix $d^j_{m'm}(\beta)$ is defined by

$$d^j_{m'm}(\beta) = \langle \psi_{jm'} | \exp(-\mathrm{i}\beta J_y) | \psi_{jm} \rangle. \tag{B.94}$$

Using the Condon–Shortley phase convention, discussed in Appendix B.4, the reduced rotation matrices are real and are defined by

$$d^j_{m'm}(\beta) = \sum_t (-1)^{t+m'-m} \frac{[(j+m)!(j-m)!(j+m')!(j-m')!]^{1/2}}{(j-m'-t)!(j+m-t)!(t+m'-m)!t!} \times \left(\cos\tfrac{1}{2}\beta\right)^{2j+m-m'-2t} \left(\sin\tfrac{1}{2}\beta\right)^{m'-m+2t}, \tag{B.95}$$

where the summation is over all integer values of t such that the arguments of the factorials are greater than or equal to zero.

We can show that the reduced rotation matrix satisfies the following symmetry relations:

$$d^j_{m'm}(\beta) = d^j_{mm'}(-\beta), \tag{B.96}$$

$$d^j_{m'm}(\beta) = (-1)^{m'-m} d^j_{mm'}(\beta), \tag{B.97}$$

$$d^j_{m'm}(\beta) = (-1)^{m'-m} d^j_{-m'\,-m}(\beta). \tag{B.98}$$

We can also show that the rotation matrices satisfy the following symmetry relations:

$$D^j_{m'm}(-\gamma, -\beta, -\alpha) = D^{j*}_{mm'}(\alpha, \beta, \gamma), \tag{B.99}$$

$$D^j_{m'm}(\alpha, \beta, \gamma) = (-1)^{m'-m} D^{j*}_{-m'\,-m}(\alpha, \beta, \gamma). \tag{B.100}$$

They also satisfy the orthonormality relations

$$\sum_m D^{j*}_{m'm}(\alpha, \beta, \gamma) D^j_{m''m}(\alpha, \beta, \gamma) = \delta_{m'm''}, \tag{B.101}$$

$$\sum_m D^j_{mm'}(\alpha, \beta, \gamma) D^j_{mm''}(\alpha, \beta, \gamma) = \delta_{m'm''}. \tag{B.102}$$

These equations follow from (B.91), which corresponds to a unitary transformation from one set of orthogonal eigenfunctions ψ_{jm} to another set of orthogonal eigenfunctions $R(\alpha, \beta, \gamma)\psi_{jm}$, obtained by rotating the coordinate axes. Explicit values for the reduced rotation matrices $d^j_{m'm}$ are given in Tables B.1, B.2 and B.3 for $j = 1/2$, 1 and $3/2$, respectively.

Table B.1 Reduced rotation matrices $d^j_{m'm}$ for $j = \frac{1}{2}$

m'	$m = \frac{1}{2}$	$m = -\frac{1}{2}$
$\frac{1}{2}$	$\cos \frac{1}{2}\beta$	$-\sin \frac{1}{2}\beta$
$-\frac{1}{2}$	$\sin \frac{1}{2}\beta$	$\cos \frac{1}{2}\beta$

Table B.2 Reduced rotation matrices $d^j_{m'm}$ for $j = 1$

m'	$m = 1$	$m = 0$	$m = -1$
1	$\cos^2 \frac{1}{2}\beta$	$-\frac{1}{\sqrt{2}} \sin \beta$	$\sin^2 \frac{1}{2}\beta$
0	$\frac{1}{\sqrt{2}} \sin \beta$	$\cos \beta$	$-\frac{1}{\sqrt{2}} \sin \beta$
-1	$\sin^2 \frac{1}{2}\beta$	$\frac{1}{\sqrt{2}} \sin \beta$	$\cos^2 \frac{1}{2}\beta$

Table B.3 Reduced rotation matrices $d^j_{m'm}$ for $j = \frac{3}{2}$ where $p = 3\sin^2(\frac{1}{2}\beta) - 2$ and $q = 3\cos^2(\frac{1}{2}\beta) - 2$

m'	$m = \frac{3}{2}$	$m = \frac{1}{2}$	$m = -\frac{1}{2}$	$m = -\frac{3}{2}$
$\frac{3}{2}$	$\cos^3\frac{1}{2}\beta$	$-\sqrt{3}\cos^2\frac{1}{2}\beta\sin\frac{1}{2}\beta$	$\sqrt{3}\cos\frac{1}{2}\beta\sin^2\frac{1}{2}\beta$	$-\sin^3\frac{1}{2}\beta$
$\frac{1}{2}$	$\sqrt{3}\cos^2\frac{1}{2}\beta\sin\frac{1}{2}\beta$	$q\cos\frac{1}{2}\beta$	$p\sin\frac{1}{2}\beta$	$\sqrt{3}\cos\frac{1}{2}\beta\sin^2\frac{1}{2}\beta$
$-\frac{1}{2}$	$\sqrt{3}\cos\frac{1}{2}\beta\sin^2\frac{1}{2}\beta$	$-p\sin\frac{1}{2}\beta$	$q\cos\frac{1}{2}\beta$	$-\sqrt{3}\cos^2\frac{1}{2}\beta\sin\frac{1}{2}\beta$
$-\frac{3}{2}$	$\sin^3\frac{1}{2}\beta$	$\sqrt{3}\cos\frac{1}{2}\beta\sin^2\frac{1}{2}\beta$	$\sqrt{3}\cos^2\frac{1}{2}\beta\sin\frac{1}{2}\beta$	$\cos^3\frac{1}{2}\beta$

The spherical harmonics discussed in Appendix B.3 correspond to a particular example of functions satisfying (B.91). We can write (B.91) in this case as

$$Y_{\ell m}(\theta', \phi') = \sum_{m'} D^{\ell}_{m'm}(\alpha, \beta, \gamma) Y_{\ell m'}(\theta, \phi). \tag{B.103}$$

If $m = 0$ we find, using (B.47) and the spherical harmonic addition theorem (B.48), that

$$D^{\ell}_{m0}(\alpha, \beta, 0) = \left(\frac{4\pi}{2\ell + 1}\right)^{1/2} Y^*_{\ell m}(\beta, \alpha). \tag{B.104}$$

The rotation matrices also satisfy the following orthogonality relation

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi} D^{j'*}_{m'n'}(\alpha, \beta, \gamma) D^{j}_{mn}(\alpha, \beta, \gamma) \mathrm{d}\alpha \sin\beta \mathrm{d}\beta \mathrm{d}\gamma$$
$$= \frac{8\pi^2}{2j+1}\delta_{jj'}\delta_{mm'}\delta_{nn'}, \tag{B.105}$$

which reduces to (B.35) satisfied by the spherical harmonics when $n = n' = 0$.

We conclude this appendix by observing that the Wigner rotation matrices are eigenfunctions of the total angular momentum operator of a rigid body whose orientation is specified by the Euler angles (α, β, γ) and which has two of its principal moments of inertia equal. The rotational kinetic operator of this body, which corresponds to a symmetric top molecule, is given by

$$T_R = \frac{1}{2I_1}(\ell_1^2 + \ell_2^2) + \frac{1}{2I_2}\ell_3^2, \tag{B.106}$$

where ℓ_1^2, ℓ_2^2 and ℓ_3^2 are the squares of the components of the angular momentum operator along the principal axes of inertia which are fixed in the body. The normalized eigenfunctions belonging to this operator are

$$\phi_{LKM}(\alpha, \beta, \gamma) = \left(\frac{2L+1}{8\pi^2}\right)^{1/2} D^{L^*}_{KM}(\alpha, \beta, \gamma), \tag{B.107}$$

where both K and M can assume integral values which go over the range $-L$ to L. The corresponding eigenenergies $E(L, K)$ of the rotational kinetic energy operator can be obtained by writing (B.106) as

$$T_R = \frac{1}{2I_1}\boldsymbol{\ell}^2 + \frac{1}{2}\left(\frac{1}{I_2} - \frac{1}{I_1}\right)\ell_3^2, \tag{B.108}$$

where $\boldsymbol{\ell}^2 = \ell_1^2 + \ell_2^2 + \ell_3^2$. Hence the eigenenergies are given by

$$E(L, K) = \frac{1}{2I_1}L(L+1) + \frac{1}{2}\left(\frac{1}{I_2} - \frac{1}{I_1}\right)K^2. \tag{B.109}$$

The rotational eigenfunctions of a general polyatomic molecule are described by the asymmetric top wave function

$$\psi_{LK\lambda}(\alpha, \beta, \gamma) = \left(\frac{2L+1}{8\pi^2}\right)^{1/2} \sum_M a_{LM\lambda} D^{L^*}_{KM}(\alpha, \beta, \gamma), \tag{B.110}$$

where the coefficients $a_{LM\lambda}$ can be obtained by diagonalizing the rotational kinetic energy operator

$$T_R = \frac{\ell_1^2}{2I_1} + \frac{\ell_2^2}{2I_2} + \frac{\ell_3^2}{2I_3} \tag{B.111}$$

in the basis of the symmetric top eigenfunctions $\phi_{LKM}(\alpha, \beta, \gamma)$ defined by (B.107). These coefficients have been given by King et al. [535, 536] and the rotational eigenfunctions and eigenfunctions of polyatomic molecules have been discussed by Herzberg [457].