APAS 5110. Internal Processes in Gases. Fall 1999.

Angular Momentum

1. Angular Momentum Operator

The definitive reference to angular momentum in quantum mechanics is A. R. Edmonds (1960) "Angular Momentum in Quantum Mechanics", Princeton University Press. Landau & Lifshitz (1977) "Quantum Mechanics" is as always singularly enlightening.

For a single particle, the angular momentum operator $\boldsymbol{L}$ is defined to be

$$\boldsymbol{L} \equiv \boldsymbol{r} \times \boldsymbol{p} \tag{1.1}$$

where $\boldsymbol{p} \equiv -i\hbar\nabla \equiv -i\hbar\partial/\partial\boldsymbol{r}$ is the momentum operator. More generally, for a system of particles a, the total angular momentum operator $\boldsymbol{L}$ is the sum over angular momenta of the particles,

$$\boldsymbol{L} = \sum_{\text{ptles } a} \boldsymbol{r}_a \times \boldsymbol{p}_a \ . \tag{1.2}$$

For simplicity, formulae below are written down for a single particle.

The properties of the angular momentum operator $\boldsymbol{L}$ are often conveniently expressed in terms of its chiral components L_z, L_+, L_-, which are defined in terms of the Cartesian components L_x, L_y, L_z in the same way as the chiral components of any vector quantity

$$L_+ \equiv L_x + iL_y \ , \quad L_- \equiv L_x - iL_y \ . \tag{1.3}$$

Expressions for the chiral components of the angular momentum $\boldsymbol{L}$ of a particle in terms of its spherical coordinates θ, ϕ are

$$L_z = -i\hbar\frac{\partial}{\partial\phi} \ , \tag{1.4a}$$

$$L_\pm = \hbar\, e^{\pm i\phi}\left(\pm\frac{\partial}{\partial\theta} + \cot\theta\frac{\partial}{\partial\phi}\right) \ . \tag{1.4b}$$

The square $L^2 \equiv L_x^2 + L_y^2 + L_z^2$ of the angular momentum operator is, in terms of its chiral components,

$$L^2 = L_z^2 + \frac{1}{2}\left(L_+L_- + L_-L_+\right) \ , \tag{1.5}$$

or, in terms of spherical coordinates θ, ϕ,

$$L^2 = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) \ . \tag{1.6}$$

It is evident from (1.4a) that the z-component L_z of the angular momentum operator will commute with an operator A if and only if A is independent of the azimuthal angle ϕ, that is, if and only if A has rotational symmetry about the z-axis. More generally, all components of the angular momentum operator $\boldsymbol{L}$ will commute with an operator A if and only if A is spherically symmetric. Thus it is apparent that conservation of angular momentum is associated with rotational symmetry, as it should be.

2. Commutation Relations

It is straightforward to check that the commutators of the Cartesian components L_i of the angular momentum operator $\boldsymbol{L}$ with the Cartesian components r_i and p_i of the position and momentum operators $\boldsymbol{r}$ and $\boldsymbol{p}$ are

$$[L_i, r_j] = i\hbar\epsilon_{ijk} r_k \ , \tag{2.1a}$$

$$[L_i, p_j] = i\hbar\epsilon_{ijk} p_k \ , \tag{2.1b}$$

from which it can also be concluded that

$$[L_i, L_j] = i\hbar\epsilon_{ijk} L_k \ . \tag{2.2}$$

Equations (2.1)–(2.2) are examples of the more general result that for any vector $\boldsymbol{A}$,

$$[L_i, A_j] = i\hbar\epsilon_{ijk} A_k \ , \tag{2.3}$$

which follows from the transformation properties of vectors and the fact that $\boldsymbol{L}/\hbar$ is the generator of infinitesimal rotations, equation (9.3).

The chiral components of $\boldsymbol{L}$ satisfy the commutation relations

$$[L_z, L_\pm] = \pm\hbar L_\pm \ , \quad [L_+, L_-] = 2\hbar L_z \ . \tag{2.4}$$

Equation (2.4) is a particular case of the more general result that the commutator of the chiral components of $\boldsymbol{L}$ with those of any three-dimensional vector $\boldsymbol{A}$, such as the position operator $\boldsymbol{r}$ or the momentum operator $\boldsymbol{p}$, are

$$[L_z, A_\pm] = -[L_\pm, A_z] = \pm\hbar A_\pm \ , \quad [L_+, A_-] = -[L_-, A_+] = 2\hbar A_z \ . \tag{2.5}$$

Although the components of the angular momentum operator $\boldsymbol{L}$ do not commute with each other, they do all commute with its square L^2

$$[L^2, L_i] = 0 \ . \tag{2.6}$$

3. Spherical Harmonics

Since the components of L_i of the angular momentum operator $\boldsymbol{L}$ do not commute with each other, simultaneous eigenfunctions of all three components of $\boldsymbol{L}$ do not exist. However, the square L^2 of the angular momentum operator commutes with each component, so simultaneous eigenfunctions of L^2 and the component of $\boldsymbol{L}$ along any one axis, say L_z, exist.

The complete orthonormal set of simultaneous eigenfunctions of L^2 and L_z defines the spherical harmonics $Y_{lm}(\theta, \phi)$. The eigenvalues are

$$L^2 Y_{lm} = l(l+1)\,\hbar^2\, Y_{lm} \quad , \quad L_z Y_{lm} = m\,\hbar\, Y_{lm} \ , \tag{3.1}$$

with $l = 0, 1, ...$ ranging over all positive integral values, and $m = -l, -l+1, ..., l$ ranging over the $2l+1$ integral values in the interval $[-l, +l]$. Orthonormality of the Y_{lm} means

$$\int Y^*_{l'm'}(\hat{\boldsymbol{r}}) Y_{lm}(\hat{\boldsymbol{r}})\, do = \delta_{ll'}\delta_{mm'} \ , \tag{3.2}$$

where the integration over solid angle do is over the entire sphere.

An explicit formula for the spherical harmonics $Y_{lm}(\theta,\phi)$ in terms of associate Legendre polynomials P_l^m is

$$Y_{lm}(\theta,\phi) = (-)^{(m+|m|)/2} \left[\frac{(2l+1)}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l^{|m|}(\cos\theta) e^{im\phi} \ . \tag{3.3}$$

Note that

$$Y_{l,-m} = (-)^m Y_{lm}^* \ . \tag{3.4}$$

The spherical harmonics $Y_{lm}(\theta,\phi)$ satisfy many recurrence relations. The computationally useful one, stable in all cases, is the one which follows from applying the dipole operator $\hat{r}_z = \cos\theta$, equation (5.2a):

$$\left[\frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)}\right]^{1/2} Y_{l+1,m} = \cos\theta\, Y_{lm} - \left[\frac{(l+m)(l-m)}{(2l-1)(2l+1)}\right]^{1/2} Y_{l-1,m} \ , \tag{3.5}$$

starting from

$$Y_{ll} = (-)^l Y_{l,-l}^* = (-)^l \left[\frac{(2l+1)!}{4\pi}\right]^{1/2} \frac{\sin^l\theta}{l!\,2^l}\, e^{il\phi} \ . \tag{3.6}$$

For stability, the recurrence (3.5) should always be applied in the direction of increasing l.

4. Effect of Angular Momentum Operator $\boldsymbol{L}$ on Spherical Harmonics

The action of the angular momentum operator $\boldsymbol{L}$ on the spherical harmonics Y_{lm} is especially relevant to the magnetic dipole selection rules for radiative transitions. The relations are most conveniently given in chiral components:

$$L_z\, Y_{l,m} = m\,\hbar\, Y_{l,m} \tag{4.1a}$$

$$L_+\, Y_{l,m} = [(l+m+1)(l-m)]^{1/2}\ \hbar\, Y_{l,m+1} \tag{4.1b}$$

$$L_-\, Y_{l,m} = [(l-m+1)(l+m)]^{1/2}\ \hbar\, Y_{l,m-1} \ . \tag{4.1c}$$

The relations (4.1) can be derived entirely from the commutation relations (2.4) for the chiral components of $\boldsymbol{L}$, without invoking any explicit formula for the spherical harmonics. Equations (4.1b) and (4.1c) show that $L_\pm$ act as 'raising' and 'lowering' operators, respectively increasing and decreasing m by 1 while leaving l unchanged. A precisely analogous set of formulae hold for the spin operator $\boldsymbol{S}$ acting on spin wavefunctions, equations (6.6).

5. Effect of Dipole Operator $\hat{\boldsymbol{r}}$ on Spherical Harmonics

The action of the dipole operator on spherical harmonics is especially relevant to the electric dipole selection rules for radiative transitions. The dipole operator $\hat{\boldsymbol{r}}$ is the unit vector in the radial direction. The Cartesian components of the vector are $\hat{r}_x$, $\hat{r}_y$, $\hat{r}_z$. The chiral components of the vector are $\hat{r}_z$, $\hat{r}_+$, $\hat{r}_-$

$$\hat{r}_z = \cos\theta \ , \tag{5.1a}$$

$$\hat{r}_\pm \equiv \hat{r}_x \pm i\hat{r}_y = e^{\pm i\phi}\sin\theta \ . \tag{5.1b}$$

The action of the dipole operator $\hat{\boldsymbol{r}}$ on the spherical harmonics is most conveniently given again in chiral components:

$$\hat{r}_z\, Y_{l,m} = \cos\theta\, Y_{l,m} \tag{5.2a}$$
$$= \left[\frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)}\right]^{1/2} Y_{l+1,m} + \left[\frac{(l+m)(l-m)}{(2l-1)(2l+1)}\right]^{1/2} Y_{l-1,m}\ ,$$
$$\hat{r}_+\, Y_{l,m} = e^{i\phi}\sin\theta\, Y_{l,m} \tag{5.2b}$$
$$= -\left[\frac{(l+m+1)(l+m+2)}{(2l+1)(2l+3)}\right]^{1/2} Y_{l+1,m+1} + \left[\frac{(l-m)(l-m\ -1)}{(2l-1)(2l+1)}\right]^{1/2} Y_{l-1,m+1}\ ,$$
$$\hat{r}_-\, Y_{l,m} = e^{-i\phi}\sin\theta\, Y_{l,m} \tag{5.2c}$$
$$= \left[\frac{(l-m+1)(l-m+2)}{(2l+1)(2l+3)}\right]^{1/2} Y_{l+1,m-1}\ - \left[\frac{(l+m)(l+m\ -1)}{(2l-1)(2l+1)}\right]^{1/2} Y_{l-1,m-1}\ .$$

And one more useful little relation:

$$\sin\theta\frac{\partial}{\partial\theta}\, Y_{l,m} = \frac{1}{2}\left(\hat{r}_- L_+ - \hat{r}_+ L_-\right) Y_{l,m} \tag{5.3}$$
$$= l\left[\frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)}\right]^{1/2} Y_{l+1,m} - (l+1)\left[\frac{(l+m)(l-m)}{(2l-1)(2l+1)}\right]^{1/2} Y_{l-1,m}\ .$$

6. Spin

The commutation properties (2.2) of the angular momentum operator are intimately related to the properties of the three-dimensional orthogonal rotation group $O(3)$. Indeed, the commutation properties (2.2) essentially define the local properties of $O(3)$. The quantities L_i (or rather $L_i/\hbar$) are the **generators** of the group; their fundamental role in generating rotations will be seen in §9. However, the global topological properties of the rotation group $O(3)$ are *not* uniquely defined by the commutation relations (2.2), and in fact $O(3)$ does not have the simplest topological structure consistent with the commutation relations. Specifically, a rotation by 360° about any axis defines a closed loop in $O(3)$ which is not continously deformable to a point — one says that $O(3)$ is not simply-connected. However, a rotation by two turns, 720°, about any axis defines a loop which is continuously deformable to a point. The group which results from covering $O(3)$ twice is simply-connected, and is isomorphic to the special unitary group $SU(2)$, the group of two-dimensional complex unitary matrices of unit determinant. The group cannot be enlarged any further given the commutation rules (2.2).

The enlarged group $SU(2)$ admits eigenfunctions whose angular momentum quantum numbers l and m take half-integral as well as integral values. Remarkably, nature seems to know about this. Whereas orbital angular momentum appears always quantized in integral units, the fundamental particles of nature also possess their own private intrinsic angular momenta, called spin. Among the fundamental particles, electrons, neutrinos, and quarks all have spin half, the smallest possible nonzero spin. Photons, vector bosons, and gluons, which mediate the forces between the spin half particles, have spin one, while the graviton, which mediates the force between particles' energy-momenta — a vector, or spin one property — alone has spin two. No other spins are observed in the fundamental particles, although

Higgs bosons are conjectured (for simplicity) to have zero spin, and supersymmetry predicts particles with spin $\frac{3}{2}$. It is thought that no fundamental particle can have spin higher than two.

In nonrelativistic quantum mechanics, spin is introduced phenomenologically. A spin operator $\boldsymbol{S}$ is defined, which operates only on the spin part of the wavefunction, not on the spatial part, and which commutes with all spatial operators. Conversely, spatial operators operate only on the spatial part of the wavefunction, not on the spin part. The spin operator is itself a vector quantity, with Cartesian components S_x, S_y, S_z. The spin operator $\boldsymbol{S}$ satisfies the same commutation rules (2.2) as the angular momentum operator $\boldsymbol{L}$, namely

$$[S_i, S_j] = i\hbar\epsilon_{ijk}S_k \ . \tag{6.1}$$

Its eigenfunctions χ_σ satisfy, in complete analogy to the spherical harmonics (3.1),

$$S^2\chi_\sigma = s(s+1)\,\hbar^2 \ , \quad S_z\chi_\sigma = \sigma\,\hbar \ , \tag{6.2}$$

with s taking integral or half-integral values, and $\sigma = -s, -s+1, ..., s$ running over all $2s+1$ integral (if s is integral) or half-integral (if s is half-integral) values in the interval $[-s, s]$.

The wavefunction of a particle with spin s is a $(2s+1)$-component spinor, which can be written

$$|\psi\rangle = \sum_{\sigma=-s}^{s} \psi(\sigma, \boldsymbol{x}, t)\chi_\sigma \ . \tag{6.3}$$

The spinor components $\psi(\sigma, \boldsymbol{x}, t)$ comprise a set of $2s+1$ complex numbers, one for each component σ. In the case of a spin half particle, $s = 1/2$, the eigenfunctions χ_σ are spin up $|\uparrow\rangle$ or spin down or $|\downarrow\rangle$, with eigenvalues $\sigma = \pm 1/2$, and the wavefunction is a two-component spinor

$$|\psi(t, \boldsymbol{x})\rangle = \psi\left(t, \boldsymbol{x}, +\tfrac{1}{2}\right)|\uparrow\rangle + \psi\left(t, \boldsymbol{x}, -\tfrac{1}{2}\right)|\downarrow\rangle \ . \tag{6.4}$$

The chiral components S_z, S_+, S_- of the spin operator are defined in the usual way by

$$S_+ \equiv S_x + iS_y \ , \quad S_- \equiv S_x - iS_y \ , \tag{6.5}$$

in precise analogy to the chiral components of the angular momentum operator $\boldsymbol{L}$, equation (1.3). Naturally, since the commutation rules of the spin operator $\boldsymbol{S}$ are by construction the same as those of the orbital angular momentum operator $\boldsymbol{L}$, the commutation rules of the chiral components of $\boldsymbol{S}$ are the same as those, equation (2.4), for $\boldsymbol{L}$. The matrix elements of the chiral components of $\boldsymbol{S}$, acting on the eigenfunctions $\chi_{s\sigma}$ are the same as those, equations (4.1a)–(4.1c), for the angular momentum acting on the spherical harmonics:

$$S_z\,\chi_{s,\sigma} = \sigma\,\hbar\,\chi_{s\sigma} \tag{6.6a}$$

$$S_+\,\chi_{s,\sigma} = [(s+\sigma+1)(s-\sigma)]^{1/2}\ \hbar\,\chi_{s,\sigma+1} \tag{6.6b}$$

$$S_-\,\chi_{s,\sigma} = [(s-\sigma+1)(s+\sigma)]^{1/2}\ \hbar\,\chi_{s,\sigma-1} \ . \tag{6.6c}$$

7. Pauli Matrices

For some purposes it is convenient to represent the components of the spin operator $\boldsymbol{S}$ in terms of an explicit set of matrices. In particular, for spin half particles, it can be convenient to represent the spin operator $\boldsymbol{S}$ by a vector of **Pauli matrices** $\boldsymbol{\sigma}$ in $SU(2)$

$$\boldsymbol{S} = \frac{\hbar}{2}\boldsymbol{\sigma} \tag{7.1}$$

whose three components are 2×2 complex matrices which are Hermitian, unitary, and traceless:

$$\sigma_x \equiv \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} , \quad \sigma_y \equiv \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} , \quad \sigma_z \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} . \tag{7.2}$$

Particularly useful formulae are

$$\boldsymbol{\sigma}^2 = 3 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} , \quad (\boldsymbol{a}.\boldsymbol{\sigma})(\boldsymbol{b}.\boldsymbol{\sigma}) = \boldsymbol{a}.\boldsymbol{b} + i\, \boldsymbol{a} \times \boldsymbol{b}\,.\,\boldsymbol{\sigma} , \tag{7.3}$$

where $\boldsymbol{a}$ and $\boldsymbol{b}$ are any vectors. By means of equations (7.3), any scalar function of $\boldsymbol{\sigma}$ can be reduced to a constant plus a function linear in $\boldsymbol{\sigma}$.

8. Coupling of Angular Momenta

When two or more electrons are present in an atom, the electrostatic interaction between the electrons destroys the spherical symmetry of the force field, so that the individual angular momenta of electrons are no longer conserved. To the extent that spin-orbit coupling can be neglected, the angular momenta of the individual electrons precess, preserving the absolute values of their angular momenta, but changing in direction. The square L^2 and z-component L_z of the total angular momentum $\boldsymbol{L}$,

$$\boldsymbol{L} \equiv \sum_{\text{electrons } a} \boldsymbol{l}_a , \tag{8.1}$$

remain conserved, and the squares of the individual electronic angular momenta l_a^2 are also conserved, but the z-components $l_{a,z}$ are not conserved. The angular eigenfunction of a two-electron state is thus characterized by quantum numbers l_1, l_2, L, M corresponding to the absolute values l_1 and l_2 of the angular momenta of two electrons, and the absolute value L and z-component M of the total angular momentum.

Similarly, the interaction of electronic spins in a multi-electron atom causes the individual spins to precess, preserving the square S^2 and z-component S_z of the total spin $\boldsymbol{S}$,

$$\boldsymbol{S} \equiv \sum_{\text{electrons } a} \boldsymbol{s}_a , \tag{8.2}$$

but not the z-components $s_{a,z}$ of the individual electron spins (the absolute values $s_a = \frac{1}{2}$ of the individual electron spins, being fundamental properties of electrons, are also conserved).

Consider then a two-particle angular eigenfunction $|j_1 j_2\, JM\rangle$ where particles with specified absolute values j_1 and j_2 of their angular momenta couple to produce a total angular momentum with absolute value J and z-projection M. The angular momenta j and J here could denote either orbital angular momenta, or spin angular momenta, or perhaps their sum; the formulae below are valid in all cases. The eigenfunction $|j_1 j_2\, JM\rangle$ can be

written as a sum of products of 1-particle eigenfunctions $|j_a m_a\rangle$ [if $\boldsymbol{j}$ is an orbital angular momentum, then $|j_a m_a\rangle = Y_{j_a,m_a}(\theta_a, \phi_a)$]

$$|j_1 j_2\, JM\rangle = \sum_{m_1+m_2=M} \langle j_1 m_1\, j_2 m_2 | j_1 j_2\, JM\rangle |j_1 m_1| j_2 m_2\rangle \ . \tag{8.3}$$

The fact that $M = m_1 + m_2$ follows immediately from the equality of operators $J_z = j_{1,z} + j_{2,z}$. The quantities $\langle j_1 m_1\, j_2 m_2 | j_1 j_2\, JM\rangle$, often abbreviated $\langle m_1 m_2 | JM\rangle$, are called **Clebsh-Gordan coefficients**

$$\text{Clebsh-Gordan coefficients:} \quad \langle j_1 m_1\, j_2 m_2 | j_1 j_2\, JM\rangle \ . \tag{8.4}$$

Closely related are the **Wigner $3j$-symbols**

$$\text{Wigner } 3j\text{-symbols:} \quad \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \ . \tag{8.5}$$

Clebsh-Gordan coefficients are related to Wigner $3j$-symbols by

$$\langle j_1 m_1\, j_2 m_2 | j_1 j_2\, JM\rangle = (-)^{j_1 - j_2 + M} (2J+1)^{1/2} \begin{pmatrix} j_1 & j_2 & J \\ m_1 & m_2 & -M \end{pmatrix} \ . \tag{8.6}$$

The $3j$-symbols, which are real-valued, are defined up to an overall $\pm$ sign by the symmetrical relation

$$|00\rangle = \sum_{m_1+m_2+m_3=0} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} |j_1 m_1\rangle |j_2 m_2\rangle |j_3 m_3\rangle \ , \tag{8.7}$$

in which three angular momenta with given absolute values j_1, j_2, j_3 combine to produce a total angular momentum of zero. In addition to the constraint $m_1 + m_2 + m_3 = 0$, the three j_a must satisfy **triangle inequalities**, i.e. they should be able to form the sides of a closed triangle, which means that j_1 must satisfy the inequality

$$|j_2 - j_3| \le j_1 \le |j_2 + j_3| \ , \tag{8.8}$$

and similarly j_2 and j_3 must satisfy the inequalities obtained by permuting the indices in (8.8). Exchanging any pair of columns of a $3j$-symbol multiplies it by $(-)^{j_1+j_2+j_3}$,

$$\begin{pmatrix} j_2 & j_1 & j_3 \\ m_2 & m_1 & m_3 \end{pmatrix} = (-)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \ , \quad \text{etc.,} \tag{8.9}$$

which means the $3j$-symbol changes sign under exchange of columns if $j_1 + j_2 + j_3$ is odd.

A classic, but not necessarily numerically stable, way to evaluate Clebsch-Gordon coefficients is to start with the wavefunction $|j_1 j_2\, JJ\rangle$ having the largest value of M, namely $M = J$. The Clebsh-Gordon coefficients for this wavefunction are given by

$$\begin{aligned} &\langle j_1 m_1\, j_2 m_2 | j_1 j_2\, JJ\rangle \\ &= (-)^{j_1 - m_1} \left[\frac{(2J+1)!(j_1+j_2-J)!(j_1+m_1)!(j_2+m_2)!}{(J+j_1+j_2+1)!(J+j_1-j_2)!(J+j_2-j_1)!(j_1-m_1)!(j_2-m_2)!} \right]^{1/2} \ , \end{aligned} \tag{8.10}$$

with the usual constraint $m_1 + m_2 = J$. Operating on the resulting expansion (8.3) of $|j_1 j_2\, JJ\rangle$ in terms of the single particle eigenfunctions $|j_1 m_1| j_2 m_2\rangle$ with the lowering operator

$$J_- = j_{1,-} + j_{2,-} \tag{8.11}$$

then yields $|j_1 j_2\, JM\rangle$ with M reduced by 1 at each operation.

To my knowledge, the best way to compute the Clebsch-Gordon coefficients numerically is from the Wigner $3j$-symbols, equation (8.6), as follows:

(1) The 3-j symbol with all m's zero may be computed by the recursion method described in §3.8 of Edmonds (1960).
(2) The 3-j symbol with nonzero m's may be computed from the recursion formulae (3.7.13) of Edmonds.

One final useful formula: the integral of a product of three Y_{lm}'s over all directions is

$$\int Y_{l_1 m_1}(\hat{\boldsymbol{r}}) Y_{l_2 m_2}(\hat{\boldsymbol{r}}) Y_{l_3 m_3}(\hat{\boldsymbol{r}}) do$$
$$= \left[\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}\right]^{1/2} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} . \quad (8.12)$$

9. Operator of Rotations

Under the action of an infinitesimal rotation $\delta\phi$ about the z-axis, a spatial wavefunction ψ transforms to

$$\psi \to \psi + \delta\phi \frac{\partial \psi}{\partial \phi} = (1 + i\delta\phi\, L_z/\hbar)\, \psi \ . \quad (9.1)$$

More generally, an infinitesimal rotation by $\delta\alpha$ about an arbitrary unit direction $\boldsymbol{n}$ transforms a wavefunction ψ to

$$\psi \to \psi + \delta\alpha \frac{\partial \psi}{\partial \alpha} = (1 + i\delta\alpha\, \boldsymbol{n}.\boldsymbol{L}/\hbar)\, \psi \ . \quad (9.2)$$

Thus the operator

$$1 + i\delta\alpha\, \boldsymbol{n}.\boldsymbol{L}/\hbar \quad (9.3)$$

produces an infinitesimal rotation by angle $\delta\alpha$ about axis $\boldsymbol{n}$. In mathematical group theory, one says that $\boldsymbol{L}/\hbar$ are the generators of the rotation group. Applying the infinitesimal operator (9.3) infinitely many times, one concludes that the operator of a finite rotation by angle α about unit direction $\boldsymbol{n}$ (not necessarily in the $\hat{\boldsymbol{z}}$ direction) is

$$\exp(i\alpha\, \boldsymbol{n}.\boldsymbol{L}/\hbar) \ . \quad (9.4)$$

In the same way, a spin wavefunction χ is transformed by an infinitesimal rotation by $\delta\alpha$ about an arbitrary unit direction $\boldsymbol{n}$ to

$$\chi \to (1 + i\delta\alpha\, \boldsymbol{n}.\boldsymbol{S}/\hbar)\, \chi \ , \quad (9.5)$$

and the operator of a finite rotation by α about direction $\boldsymbol{n}$ is

$$\exp(i\alpha\, \boldsymbol{n}.\boldsymbol{S}/\hbar) \ . \quad (9.6)$$

In general, a rotation will affect both spatial and spin parts of a wavefunction at once, so that the operator of a finite rotation by α about direction n becomes

$$\exp(i\alpha \boldsymbol{n}.\boldsymbol{J}/\hbar) \ , \quad (9.7)$$

where the total angular momentum $\boldsymbol{J}$ is the sum of spatial and spin angular momenta

$$\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S} \ . \quad (9.8)$$

Consider then a finite rotation of an angular wavefunction $|jm\rangle$, where j and m are integral or half-integral quantum numbers which could represent either orbital angular momentum, or spin angular momentum, or their sum. A finite rotation transforms $|jm\rangle$ into linear combinations of other angular wavefunctions $|jn\rangle$ with the same j, which follows from the fact that $\boldsymbol{L}$ (or $\boldsymbol{S}$) acting on Y_{lm} (or $\chi_{s\sigma}$) leaves l (or s) fixed, equations (4.1a)–(4.1c) [or (6.6a)–(6.6c)]. The sets of $|jm\rangle$ with constant j, which are transformed into each other by rotations, form the irreducible representations of the rotation group.

Define the rotation matrix D^j_{mn} to be the matrix elements of a finite rotation:

$$\exp(i\alpha\, \boldsymbol{n}.\boldsymbol{J}/\hbar)|jm\rangle = \sum_{n=-j}^{j} D^j_{mn}|jn\rangle \ . \tag{9.9}$$

This rotation matrix can be evaluated explicitly as follows. Any rotation in three-dimensional space can be defined in terms of three Euler angles, a rotation of ϕ about the z-axis, followed by a rotation of θ about the y-axis, followed by another rotation of ϕ' about the z-axis. Thus the finite rotation operator (9.7) can be written

$$\exp(i\alpha \boldsymbol{n}.\boldsymbol{J}/\hbar) = \exp(i\phi' J_z/\hbar)\, \exp(i\theta J_y/\hbar)\, \exp(i\phi J_z/\hbar) \ , \tag{9.10}$$

and the rotation matrix D^j_{mn} becomes

$$D^j_{mn} = e^{i\phi' m}\Theta^j_{mn}(\theta)e^{i\phi n} \ . \tag{9.11}$$

The matrix $\Theta^j_{mn}(\theta)$ of a rotation by angle θ about the y-axis is real, and is given by the stable (for increasing j) recurrence relation

$$\begin{aligned} &l\,[(j+n+1)(j-n+1)(j+m+1)(j-m+1)]^{1/2}\ \Theta^{j+1}_{mn} \\ &= (2j+1)\,[j(j+1)\cos\theta - mn]\ \Theta^j_{mn} - (j+1)\,[(j+n)(j-n)(j+m)(j-m)]^{1/2}\ \Theta^{j-1}_{mn} \ , \end{aligned} \tag{9.12}$$

starting from

$$\Theta^j_{jm} = (-)^{j-m}\Theta^j_{mj} = \left[\frac{(2j)!}{(j+m)!(j-m)!}\right]^{1/2} \cos^{j+m}\frac{\theta}{2}\ \sin^{j-m}\frac{\theta}{2} \ . \tag{9.13}$$

The finite rotation operator (9.7) is unitary, and so therefore also is the rotation matrix D^j_{mn}, and likewise the rotation matrix Θ^j_{mn}. Since Θ^j_{mn} is real as well as unitary, it is an orthogonal matrix, and since its inverse must also be equivalent to a rotation of $-\theta$ about the y-axis, it follows that the inverse of Θ^j_{mn} is

$$\Theta^j_{nm}(-\theta) = \Theta^j_{mn}(\theta) \ . \tag{9.14}$$

The inverse of the rotation matrix D^j_{mn} is its Hermitian conjugate

$$D^{j\dagger}_{nm} = e^{-i\phi n}\Theta^j_{mn}(\theta)e^{-i\phi' m} \ . \tag{9.15}$$