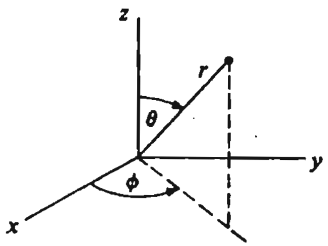


FIGURE 5.7 Spherical polar coordinates.

three components has a definite value. In quantum mechanics when angular momentum is conserved, only its magnitude and one of its components are specifiable.

We could now attempt to find the eigenvalues and common eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$ by using the forms for these operators in Cartesian coordinates. However, we would find that the partial differential equations obtained would not be separable. For this reason, we carry out a transformation to spherical polar coordinates. Figure 5.7 illustrates these coordinates. The coordinate r is the distance from the origin to the point (x, y, z). The angle θ is the angle the vector $\mathbf{r}$ makes with the positive z axis. The angle that the projection of $\mathbf{r}$ in the xy plane makes with the positive x axis is denoted φ. (Mathematics texts often interchange θ and φ. Most physics texts use the designations of Fig. 5.7.) A little trigonometry gives:

$$x = r \sin\theta \cos\varphi \tag{5.79}$$

$$y = r \sin\theta \sin\varphi \tag{5.80}$$

$$z = r\cos\theta \tag{5.81}$$

$$r^2 = x^2 + y^2 + z^2 \tag{5.82}$$

$$\cos\theta = \frac{z}{(x^2 + y^2 + z^2)^{1/2}} \tag{5.83}$$

$$\tan\varphi = y/x \tag{5.84}$$

To transform the angular-momentum operators to spherical polar coordinates, we must transform $\partial/\partial x$, $\partial/\partial y$, and $\partial/\partial z$ into these coordinates. [This transformation may be skimmed if desired. Begin reading again after Eq. (5.111).]

To perform this transformation, we use the *chain rule*. Suppose we have a function of r, θ, and φ: $f(r, \theta, \varphi)$. If we carry out a change of independent variables by substituting

$$r = r(x, y, z) \qquad \theta = \theta(x, y, z) \qquad \varphi = \varphi(x, y, z) \tag{5.85}$$

into f, we transform it into a function of x, y, and z:

$$f[r(x, y, z),\ \theta(x, y, z),\ \varphi(x, y, z)] = g(x, y, z) \tag{5.86}$$

For example, suppose that

$$f(r, \theta, \varphi) = 3r\cos\theta + 2\tan^2\varphi \tag{5.87}$$

Using (5.82), (5.83), and (5.84), we have

$$g(x, y, z) = 3z + 2y^2x^{-2} \tag{5.88}$$

The chain rule tells us how the partial derivatives of $g(x, y, z)$ are related to those of $f(r, \theta, \varphi)$. In fact

$$dg = \left.\frac{\partial f}{\partial r}\right)_{\theta,\varphi} dr + \left.\frac{\partial f}{\partial \theta}\right)_{r,\varphi} d\theta + \left.\frac{\partial f}{\partial \varphi}\right)_{r,\theta} d\phi$$

$$\left.\frac{\partial g}{\partial x}\right)_{y,z} = \left.\frac{\partial f}{\partial r}\right)_{\theta,\varphi} \left.\frac{\partial r}{\partial x}\right)_{y,z} + \left.\frac{\partial f}{\partial \theta}\right)_{r,\varphi} \left.\frac{\partial \theta}{\partial x}\right)_{y,z} + \left.\frac{\partial f}{\partial \varphi}\right)_{r,\theta} \left.\frac{\partial \varphi}{\partial x}\right)_{y,z}$$

$$\left(\frac{\partial g}{\partial x}\right)_{y,z} = \left(\frac{\partial f}{\partial r}\right)_{\theta,\varphi}\left(\frac{\partial r}{\partial x}\right)_{y,z} + \left(\frac{\partial f}{\partial \theta}\right)_{r,\varphi}\left(\frac{\partial \theta}{\partial x}\right)_{y,z} + \left(\frac{\partial f}{\partial \varphi}\right)_{r,\theta}\left(\frac{\partial \varphi}{\partial x}\right)_{y,z} \tag{5.89}$$

$$\left(\frac{\partial g}{\partial y}\right)_{x,z} = \left(\frac{\partial f}{\partial r}\right)_{\theta,\varphi}\left(\frac{\partial r}{\partial y}\right)_{x,z} + \left(\frac{\partial f}{\partial \theta}\right)_{r,\varphi}\left(\frac{\partial \theta}{\partial y}\right)_{x,z} + \left(\frac{\partial f}{\partial \varphi}\right)_{r,\theta}\left(\frac{\partial \varphi}{\partial y}\right)_{x,z} \tag{5.90}$$

$$\left(\frac{\partial g}{\partial z}\right)_{x,y} = \left(\frac{\partial f}{\partial r}\right)_{\theta,\varphi}\left(\frac{\partial r}{\partial z}\right)_{x,y} + \left(\frac{\partial f}{\partial \theta}\right)_{r,\varphi}\left(\frac{\partial \theta}{\partial z}\right)_{x,y} + \left(\frac{\partial f}{\partial \varphi}\right)_{r,\theta}\left(\frac{\partial \varphi}{\partial z}\right)_{x,y} \tag{5.91}$$

To convert these equations to operator equations, we delete f and g. However, it would not do to write, for example,

$$\frac{\partial}{\partial r}\left(\frac{\partial r}{\partial x}\right)_{y,z}$$

for the first term on the right side of the operator equation corresponding to (5.89), because this would imply that $\partial/\partial r$ was to operate on

$$\left[\left(\frac{\partial r}{\partial x}\right)_{y,z} f\right]$$

whereas, according to (5.89), it should operate only on f. For the operator equation corresponding to (5.89) we thus write

$$\frac{\partial}{\partial x} = \left(\frac{\partial r}{\partial x}\right)_{y,z}\frac{\partial}{\partial r} + \left(\frac{\partial \theta}{\partial x}\right)_{y,z}\frac{\partial}{\partial \theta} + \left(\frac{\partial \varphi}{\partial x}\right)_{y,z}\frac{\partial}{\partial \varphi} \tag{5.92}$$

with similar equations for $\partial/\partial y$ and $\partial/\partial z$. The task now is to evaluate the partial derivatives such as $(\partial r/\partial x)_{y,z}$. Taking the partial derivative of (5.82) with respect to x, at constant y and z, we have

$$2r\left(\frac{\partial r}{\partial x}\right)_{y,z} = 2x = 2r\sin\theta\cos\varphi \tag{5.93}$$

$$\left(\frac{\partial r}{\partial x}\right)_{y,z} = \sin\theta\cos\varphi \tag{5.94}$$

Differentiating (5.82) with respect to y and with respect to z, we find

$$\left(\frac{\partial r}{\partial y}\right)_{x,z} = \sin\theta\sin\varphi \tag{5.95}$$

$$\left(\frac{\partial r}{\partial z}\right)_{x,y} = \cos\theta \tag{5.96}$$

Suppose we had differentiated (5.79) with respect to r to get

$$\frac{\partial x}{\partial r} = \sin\theta\cos\varphi \tag{5.97}$$

Then, since

$$\frac{\partial r}{\partial x} = \frac{1}{\partial x/\partial r} \tag{5.98}$$

we conclude from (5.97) that

$$\left(\frac{\partial r}{\partial x}\right)_{y,z} = \frac{1}{\sin\theta\cos\varphi} \;(?) \tag{5.99}$$

which disagrees with (5.94). In fact, (5.99) is wrong. To obtain (5.97), we differentiated (5.79) with respect to r, keeping θ and φ constant. Hence (5.97) is more fully written as

$$\left(\frac{\partial x}{\partial r}\right)_{\theta,\varphi} = \sin\theta\cos\varphi \tag{5.100}$$

Moreover, we can only use an equation like (5.98) when the variables kept constant are the same on each side of the equation. Thus

$$\left(\frac{\partial r}{\partial x}\right)_{y,z} = \frac{1}{(\partial x/\partial r)_{y,z}} \tag{5.101}$$

$$\left(\frac{\partial r}{\partial x}\right)_{y,z} \neq \frac{1}{(\partial x/\partial r)_{\theta,\varphi}} \tag{5.102}$$

By not paying proper attention to what variables were being kept constant during the partial differentiation, we obtained the erroneous equation (5.99). (Thermodynamics offers rich opportunities for committing such errors.)

From (5.83) we find

$$-\sin\theta\left(\frac{\partial\theta}{\partial x}\right)_{y,z} = -\frac{xz}{r^3} \tag{5.103}$$

$$\left(\frac{\partial\theta}{\partial x}\right)_{y,z} = \frac{\cos\theta\cos\varphi}{r} \tag{5.104}$$

Also

$$\left(\frac{\partial\theta}{\partial y}\right)_{x,z} = \frac{\cos\theta\sin\varphi}{r} \qquad \left(\frac{\partial\theta}{\partial z}\right)_{x,y} = -\frac{\sin\theta}{r} \tag{5.105}$$

From (5.84), we have

$$\left(\frac{\partial\varphi}{\partial x}\right)_{y,z} = -\frac{\sin\varphi}{r\sin\theta} \tag{5.106}$$

$$\left(\frac{\partial\varphi}{\partial y}\right)_{x,z} = \frac{\cos\varphi}{r\sin\theta} \tag{5.107}$$

$$\left(\frac{\partial\varphi}{\partial z}\right)_{x,y} = 0 \tag{5.108}$$

Substituting (5.94), (5.104), and (5.106) into (5.92), we find

$$\frac{\partial}{\partial x} = \sin\theta\cos\varphi\frac{\partial}{\partial r} + \frac{\cos\theta\cos\varphi}{r}\frac{\partial}{\partial\theta} - \frac{\sin\varphi}{r\sin\theta}\frac{\partial}{\partial\varphi} \tag{5.109}$$

Similarly

$$\frac{\partial}{\partial y} = \sin\theta\sin\varphi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\varphi}{r}\frac{\partial}{\partial\theta} + \frac{\cos\varphi}{r\sin\theta}\frac{\partial}{\partial\varphi} \tag{5.110}$$

$$\frac{\partial}{\partial z} = \cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta} \tag{5.111}$$

At long last, we are ready to express the angular-momentum components in spherical polar coordinates. Substituting (5.80), (5.81), (5.110), and (5.111) into (5.63), we have

$$\hat{L}_x = -i\hbar\Big[r\sin\theta\sin\varphi\Big(\cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\Big)$$

$$-r\cos\theta\Big(\sin\theta\sin\varphi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\varphi}{r}\frac{\partial}{\partial\theta} + \frac{\cos\varphi}{r\sin\theta}\frac{\partial}{\partial\varphi}\Big)\Big]$$

$$\hat{L}_x = i\hbar\Big(\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\Big) \tag{5.112}$$

Also

$$\hat{L}_y = -i\hbar\Big(\cos\varphi\frac{\partial}{\partial\theta} - \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\Big) \tag{5.113}$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi} \tag{5.114}$$

By squaring each of $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$, and then adding their squares, we can construct $\hat{L}^2$ [Eq. (5.66)]. The result is (Problem 5.10):

$$\hat{L}^2 = -\hbar^2\Big(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\Big) \tag{5.115}$$

Occasionally $\hat{L}^2$ is written in the form

$$\hat{L}^2 = -\hbar^2\Big[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\Big] \tag{5.116}$$

Using the definition of the product of operators, we readily verify the equivalence of (5.116) and (5.115). Although the angular-momentum operators depend on all three Cartesian coordinates, x, y, and z, they involve only the two spherical polar coordinates θ and φ.

We now find the common eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$, which we denote by Y. Since these operators involve θ and φ only, Y will be a function of these two coordinates: $Y = Y(\theta, \varphi)$. (Of course, since the operators

For $m = -l, (l-1), \dots l$

$$\Phi = e^{\pm i l \phi}$$ l ~~integer~~ non-negative integer.

$$0 < \phi < 2\pi$$

so Φ is single valued

CHAPTER 7

SPHERICALLY SYMMETRIC SYSTEMS

7-1 The Schrödinger equation for spherically symmetric potentials. The potential energy of a particle which moves in a central, spherically symmetric field of force depends only upon the distance r between the particle and the center of force. The Schrödinger equation for the energy states of such a system is therefore

$$\nabla^2\psi + \frac{2m}{\hbar^2}[E - V(r)]\psi = 0. \tag{7-1}$$

Spherical polar coordinates (Fig. 7-1),

$$\begin{aligned} x &= r\sin\theta\cos\phi, \\ y &= r\sin\theta\sin\phi, \\ z &= r\cos\theta, \end{aligned} \tag{7-2}$$

are appropriate to the symmetry of the problem, since the potential function $V(r)$ is independent of the angular variables θ and ϕ. The Schrödinger equation (7-1), expressed in these coordinates, is

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] + \frac{2m}{\hbar^2}[E - V(r)]\psi = 0. \tag{7-3}$$

The energy states of the system are determined by those solutions of this equation which are continuous, have continuous derivatives in r, θ, and ϕ, and are, for bound states, quadratically integrable.

Solutions of Eq. (7-3) can be constructed by the method of separation of variables. To apply this method, we attempt to find a solution of the form

$$\psi = R(r)Y(\theta, \phi), \tag{7-4}$$

in which $R(r)$ is independent of the angles, and $Y(\theta, \phi)$ is independent

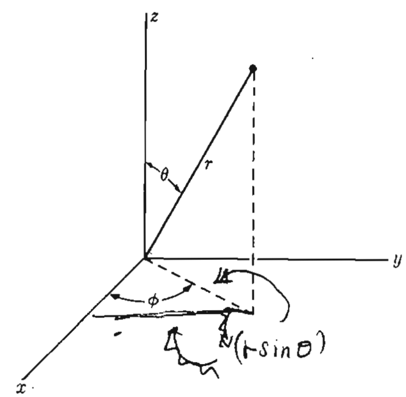


FIG. 7-1. Spherical polar coordinate system.

$\times r^2$

of r. Substituting Eq. (7-4) into Eq. (7-3) and rearranging, we obtain

$$\frac{1}{R}\left[\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2m}{\hbar^2}[E - V(r)]r^2R\right] = -\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]. \tag{7-5}$$

In this equation, the left-hand member depends, by hypothesis, only upon the variable r, while the right-hand member is independent of r. Consequently, the equation can be satisfied identically only if each member is a constant, C. The energy is determined by the equation for the *radial wave function* $R(r)$,

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left\{\frac{2m}{\hbar^2}[E - V(r)] - \frac{C}{r^2}\right\}R = 0, \tag{7-6}$$

whereas the angular part of the solution, $Y(\theta, \phi)$, satisfies

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} = -CY. \tag{7-7}$$

Equation (7-7) is independent of the energy E and of the potential energy $V(r)$. Therefore, the angular dependence of the wave functions is determined solely by the property of spherical symmetry, and admissible solutions of Eq. (7-7) are valid for every spherically symmetric system regardless of the special form of the potential function. We shall first give attention to the solutions of the angular equation and return to the radial equation in the discussion of specific examples. // Say this.

Equation (7-7) for the functions Y can be separated again by the substitution

$$Y(\theta, \phi) = \mathrm{P}(\theta)\Phi(\phi). \tag{7-8}$$

We obtain

$$\frac{1}{P}\left[\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{dP}{d\theta}\right)\right] + C\sin^2\theta = -\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = m^2, \tag{7-9}$$

in which the separation constant is written as m^2. The second of Eqs. (7-9) is

$$\frac{d^2\Phi}{d\phi^2} + m^2\Phi = 0, \tag{7-10}$$

which has the solutions

$$\Phi = e^{\pm im\phi}. \tag{7-11}$$

By the substitution $\mu = \cos\theta$, the first of Eqs. (7–9) is reduced to

$$\frac{d}{d\mu}\left[(1-\mu^2)\frac{dP}{d\mu}\right] + \left(C - \frac{m^2}{1-\mu^2}\right)P = 0, \tag{7–12}$$

which is the differential equation defining the *associated Legendre functions*.[1]

It is possible to solve this equation by the method of series, that is, by a procedure similar to that used for the harmonic oscillator (Section 5–9). This is done in detail in mathematical works devoted to the subject of spherical harmonics, and it is found that bounded, differentiable solutions of Eq. (7–12) exist if and only if the constant C is

$$C = l(l+1), \tag{7–13}$$

where l is a non-negative integer, and m has one of the integer values $-l$, $-l+1, \ldots, l-1, l$. These are therefore the only admissible values of C and m if ψ is to be the wave function for a physical system. Note that the functions defined by Eq. (7–11) are therefore *single-valued* functions of ϕ. In other subjects, such as electrostatics, the functions $Y(\theta, \phi)$ must represent physical quantities known in advance to be single-valued, so that the requirement that m be an integer follows immediately from Eq. (7–11). The wave function ψ, however, is interpreted physically through the product $\psi^*\psi$ which is independent of m (provided m is real); hence the condition of single-valuedness of $\psi^*\psi$ cannot be applied directly. The requirement that m be an integer arises, rather, from the condition of boundedness of ψ and $\nabla\psi$, for if m is not an integer, the solutions of Eq. (7–12) are irregular at the poles $\mu = \pm 1$.[2]

made this word

7–2 Spherical harmonics. We shall now construct the functions $Y(\theta, \phi)$ by a method (due to Kramers)[3] which is more direct than the method of series. We have already remarked that the angular functions Y are independent of E and $V(r)$; therefore, no generality is lost in this

skip

[1] E. T. Whittaker and G. N. Watson, *A Course of Modern Analysis.* 4th ed., Cambridge: Cambridge University Press, 1927, Section 15.5 ff.

[2] W. Pauli, *Die Allgemeinen Prinzipien der Wellenmechanik.* Ann Arbor: J. W. Edwards, Publisher, 1947, p. 126.

[3] H. A. Kramers, *Quantum Mechanics.* Amsterdam: North-Holland Publishing Co., 1957, §45, p. 168. H. C. Brinkman, *Applications of Spinor Invariants in Atomic Physics.* Amsterdam: North-Holland Publishing Co., 1956. Cf. also R. Courant and D. Hilbert, *Methods of Mathematical Physics.* New York: Interscience Publishers, Inc., 1953, Vol. I, Appendix to Chapter VII.

part of the problem if Eq. (7–1) is replaced by Laplace's equation

$$\nabla^2\psi = 0. \tag{7–14}$$

Solutions of this equation are called harmonic functions. A single-valued harmonic function which is continuous in a neighborhood of the origin can be approximated arbitrarily well by a polynomial in x, y, z. If such a polynomial is to have the form of Eq. (7–4), it must be homogeneous in these variables, i.e., it must have the form

$$\psi_l = \sum_{p+q+r=l} a_{pqr}x^p y^q z^r, \tag{7–15}$$

in which the numbers a_{pqr} must be chosen so that Eq. (7–14) is satisfied. The integer l is, of course, the degree of the polynomial. The number of terms in the sum (7–15) is $(\frac{1}{2})(l+1)(l+2)$: For a given value of p, the index q can have the $l-p+1$ values $0, 1, \ldots, l-p$, while p can have any of the $l+1$ values $0, 1, 2, \ldots, l$; thus the total number of combinations,

$$(l+1) + (l) + (l-1) + \cdots + 1 = \tfrac{1}{2}(l+1)(l+2),$$

is the number of linearly independent polynomials of degree l. Now the Laplacian of the function (7–15) is a polynomial of degree $l-2$; hence, the requirement that Laplace's equation be satisfied imposes $(\frac{1}{2})(l-1)l$ conditions on the coefficients a_{pqr}. There remain, therefore,

$$\tfrac{1}{2}(l+1)(l+2) - \tfrac{1}{2}(l-1)l = 2l+1$$

linearly independent harmonic polynomials of degree l. Explicitly, these may be taken to be

$$\begin{aligned}
l &= 0: \quad 1; \\
l &= 1: \quad x, y, z; \\
l &= 2: \quad xy, yz, zx, x^2 - y^2, 2z^2 - x^2 - y^2; \\
l &= 3: \quad x(x^2 - 3z^2), x(x^2 - 3y^2), y(y^2 - 3x^2), y(y^2 - 3z^2), \\
&\qquad\quad z(z^2 - 3x^2), z(z^2 - 3y^2), xyz;
\end{aligned} \tag{7–16}$$

and so on.

It is evident that each term in the polynomial (7–15) is proportional to r^l. Hence, ψ_l can be written

$$\psi_l = r^l Y_l(\theta, \phi), \tag{7–17}$$

in which $Y_l(\theta, \phi)$ is a *spherical harmonic of order l*. The separation constant

Legendre Solution – Power series

$$P(\mu) = \sum_{k=0}^{\infty} a_k \mu^k \qquad \text{try a power series}$$

$(\mu = \cos\theta)$

sub. in

$$\frac{d}{d\mu}\left[(1-\mu^2) \frac{dP}{d\mu} \right] + cP = 0 \qquad (1)$$

get by equating same power of μ^k

a recursion relation

$$a_{k+2} = \frac{k(k+1) - c}{(k+1)(k+2)} a_k \qquad (2)$$

Note from (1) that it doesn't change under $\mu \to -\mu$ (Same as for HO)

So solutions are either "even" or "odd".

Here, it means symmetric or antisymmetric with respect to x, y plane because the substitution $\mu \to -\mu$ means $\theta \to \pi - \theta$.

Thus from (2) $a_{-2} = 0$ for the even and $a_{-1} = 0$ for the odd solution.

For large k $\quad \frac{a_{k+2}}{a_k} \sim \frac{k}{k+2} \sim$ constant

This means $P(\mu) \sim \mu^k/k$ and

series diverges for $\mu \to 1$ (or -1).

Thus, reject infinite series.

To terminate series then,

set $\quad C = \ell(\ell+1)$

And this is quantization again.

Here, it is quantization of angular momentum - we will see that the eigenvector/value problem solved here is of the operator L^2

So, the orbital angular momentum can only be $\hbar^2 \ell(\ell+1)$

So, $\quad 0, 2\hbar^2, 6\hbar^2, \ldots$

$\quad\quad S \quad P, \quad D, \ldots$

Set $m=0$ to get

$$\frac{d}{d\mu}\left[(1-\mu^2)\frac{dP}{d\mu}\right] + CP = 0$$

Legendre's differential equation.

Solutions are

$$P_\ell(\mu) = \frac{1}{2^\ell \ell!}\frac{d^\ell}{d\mu^\ell}(\mu^2-1)^\ell$$

These are the Legendre polynomials.

$$P_0(\mu) = 1, \quad P_1(\mu) = \mu, \quad P_2(\mu) = \tfrac{1}{2}(3\mu^2-1), \ldots$$

(Remember $-1<\mu<1$ since $\mu = \cos\theta$ $0<\theta<\pi$)

For $m \neq 0$ have associated Legendre

$$P_\ell^m(\mu) = (1-\mu^2)^{m/2}\frac{d^m P_\ell(\mu)}{d\mu^m}$$

for $0<m\leq \ell$.

$$P_\ell^0(\mu) = P_\ell(\mu).$$

Orthogonality

$$\int_{-1}^{+1} P_\ell^m(\mu)\, P_{\ell'}^m(\mu)\, d\mu = 0 \qquad \ell \neq \ell'$$

The integral in this expression can be evaluated most easily by substituting the expression (7–28) for one of the P_l^m and (7–31) for the other; thus

$$\int_{-1}^{1} [P_l^m(\mu)]^2\, d\mu = (-)^m \frac{(l+m)!}{(l-m)!} \frac{1}{2^{2l}(l!)^2} \times \int_{-1}^{1} \left[\frac{d^{l+m}}{d\mu^{l+m}} (\mu^2-1)^l\right]\left[\frac{d^{l-m}}{d\mu^{l-m}} (\mu^2-1)^l\right] d\mu. \tag{7–40}$$

The function $(\mu^2 - 1)^l$ has a zero of order l at each of the points $\mu = \pm 1$, whence, if (7–40) is integrated by parts $l - m$ times, the integrated part will vanish each time. The result is

$$\int_{-1}^{1} [P_l^m(\mu)]^2\, d\mu = (-)^m \frac{(l+m)!}{(l-m)!} \frac{(-)^{l-m}}{2^{2l}(l!)^2} \times \int_{-1}^{1} \left[\frac{d^{2l}}{d\mu^{2l}} (\mu^2-1)^l\right] (\mu^2-1)^l\, d\mu$$
$$= \frac{(l+m)!}{(l-m)!} \frac{(2l)!}{2^{2l}(l!)^2} \int_{-1}^{1} (1-\mu^2)^l\, d\mu. \tag{7–41}$$

The integral in this equation is (Problem 7–6)

$$\int_{-1}^{1} (1-\mu^2)^l\, d\mu = 2^{2l+1} \frac{(l!)^2}{(2l+1)!},$$

whence

$$\int_{-1}^{1} [P_l^m(\mu)]^2\, d\mu = \frac{2}{2l+1} \frac{(l+m)!}{(l-m)!}, \tag{7–42}$$

and Eq. (7–39) becomes

$$|A_l^m|^2 \cdot 2\pi \cdot \frac{2}{2l+1} \frac{(l+m)!}{(l-m)!} = 1. \tag{7–43}$$

The orthonormal functions Y_l^m are therefore

$$Y_l^m(\theta, \phi) = (-)^m \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}}\, e^{im\phi} P_l^m(\cos\theta), \tag{7–44}$$

in which the phase factor $(-)^m$ has been chosen to agree with that most commonly used in the literature.[1] The function Y_l^{-m} is related to Y_l^m

[1] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra*. Cambridge: Cambridge University Press, 1953, Chapter III, Section 4. J. M. Blatt and V. F. Weisskopf, *Theoretical Nuclear Physics*. New York: John Wiley and Sons, 1952, Appendix A, Section 2.

through the identity (7–32):

$$Y_l^{-m} = (-)^m Y_l^{m*}. \tag{7–45}$$

The functions P_l^m can be computed from the *Legendre polynomials*,

$$P_l = P_l^0 = \frac{1}{2^l l!} \frac{d^l}{d\mu^l} (\mu^2 - 1)^l, \tag{7–46}$$

by means of the relation

$$P_l^m = \sin^m\theta \frac{d^m}{d\mu^m} P_l. \tag{7–47}$$

In this way, one can construct the table

$$\begin{aligned}
&Y_0^0 = \frac{1}{\sqrt{4\pi}} \\
&Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos\theta, && Y_1^1 = -\sqrt{\frac{3}{8\pi}}\, e^{i\phi} \sin\theta, \\
&Y_2^0 = \sqrt{\frac{5}{16\pi}} (3\cos^2\theta - 1), && Y_2^1 = -\sqrt{\frac{15}{8\pi}}\, e^{i\phi} \sin\theta\cos\theta, \\
& && Y_2^2 = \sqrt{\frac{15}{32\pi}}\, e^{2i\phi} \sin^2\theta,
\end{aligned} \tag{7–48}$$

. . .

The spherical harmonics $Y_l^m(\theta, \phi)$ are a complete orthonormal set of functions, i.e.,

$$(Y_{l'}^{m'}, Y_l^m) = \delta_{ll'}\, \delta_{mm'}, \tag{7–49}$$

and any function $f(\theta, \phi)$ which is continuous and has continuous first and second derivatives can be expanded in the form

$$f(\theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} f_l^m Y_l^m(\theta, \phi). \tag{7–50}$$

The coefficients f_l^m are given by

$$f_l^m = (Y_l^m, f), \tag{7–51}$$

and the value of $f(\theta, \phi)$ at the pole ($\theta = 0$) is (Problem 7–11)

$$f(0, \phi) = \sum_{l=0}^{\infty} f_l^0 Y_l^0(0, \phi) = \sum_{l=0}^{\infty} \sqrt{\frac{2l+1}{4\pi}}\, f_l^0. \tag{7–52}$$

In the particular case that $f(\theta, \phi)$ is a spherical harmonic Y_l, we have $f_{l'}^m = (Y_{l'}^m, Y_l)$, which is zero unless $l' = l$. Consequently, Eq. (7–52)

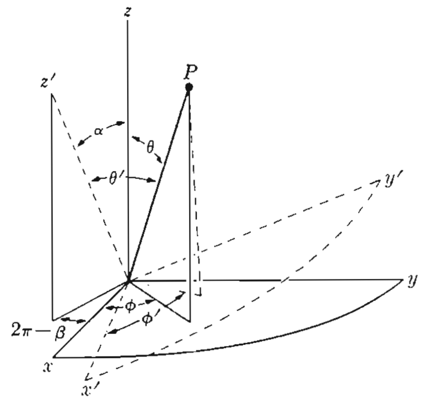


FIG. 7-2. Coordinate systems for the proof of the addition theorem.

becomes (cf. Problem 7-10)

$$Y_l(0, \phi) = \sqrt{\frac{2l+1}{4\pi}}\,(Y_l^0,\ Y_l) = \frac{2l+1}{4\pi}\,\big(P_l\,(\cos\theta),\ Y_l\big). \tag{7-53}$$

This relation can be used to prove an important formula, called the *addition theorem for spherical harmonics*, which establishes the relation between spherical harmonics referred to two differently oriented systems of axes.

Let the point P on the unit sphere be defined by the coordinates θ and ϕ with respect to the axes x, y, z and by θ' and ϕ' with respect to x', y', z' (Fig. 7-2). The rectangular coordinates of P in the two coordinate systems are related linearly by means of the table of direction cosines of the angles between the primed and unprimed axes.[1] Consequently, a homogeneous polynomial of degree l in x, y, z becomes, after transformation to the primed coordinates, a homogeneous polynomial of degree l in x', y', z'. Also, the Laplace equation

$$\nabla^2\psi = \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = 0 \tag{7-54}$$

is invariant to this change of variables (Problem 7-12), i.e., it becomes

$$\nabla'^2\psi = \frac{\partial^2\psi}{\partial x'^2} + \frac{\partial^2\psi}{\partial y'^2} + \frac{\partial^2\psi}{\partial z'^2} = 0. \tag{7-55}$$

[1] G. Joos, *Theoretical Physics*. New York: G. E. Stechert and Co., 1934, Chapter I.

It follows that a spherical harmonic of degree l in x', y', z' is also a spherical harmonic of degree l (although one of different form[1]) in x, y, z.

The meaning of these considerations is clear: The physical system is spherically symmetric, and the direction chosen for the coordinate axes is of no significance for the mathematical description of the system. The angular dependence of the wave functions has been shown to be given by the functions $Y_l^m(\theta, \phi)$, which are a complete set of $2l+1$ harmonics of degree l. Consequently, it must be possible to express the spherical harmonics of the same degree, $Y_l^m(\theta', \phi')$, with respect to any other system of axes as linear combinations of the $Y_l^m(\theta, \phi)$. This *invariance to rotation of the coordinate system* characterizes the symmetry. It is the fundamental property upon which the entire theory of spherical harmonics depends.

In particular, the function $P_l\,(\cos\theta')$ is a spherical harmonic of degree l, and therefore

$$P_l\,(\cos\theta') = \sum_{m=-l}^{l} a_m Y_l^m(\theta, \phi), \tag{7-56}$$

in which the coefficients a_m are

$$a_m = \big(Y_l^m(\theta, \phi), P_l\,(\cos\theta')\big) = \big(P_l\,(\cos\theta'), Y_l^{m*}(\theta, \phi)\big). \tag{7-57}$$

The last equation follows from the fact that the Legendre polynomial is a real function. Substituting θ', ϕ' for θ, ϕ in Eq. (7-53), we obtain

$$\big(P_l\,(\cos\theta'),\ Y_l^{m*}(\theta, \phi)\big) = \frac{4\pi}{2l+1}\,Y_l^{m*}(\theta, \phi)\big|_{\theta'=0}. \tag{7-58}$$

Now at $\theta' = 0$, the angles θ and ϕ are equal to the angles α and β which are the polar coordinates of the z'-axis with respect to the x, y, z-system (Fig. 7-2). Hence,

$$a_m = \frac{4\pi}{2l+1}\,Y_l^{m*}(\alpha, \beta), \tag{7-59}$$

and

$$P_l\,(\cos\theta') = \frac{4\pi}{2l+1}\sum_{m=-l}^{l} Y_l^{m*}(\alpha, \beta)\,Y_l^m(\theta, \phi). \tag{7-60}$$

The relation between θ' and the angles θ, ϕ is determined from the geometry of Fig. 7-2:

$$\cos\theta' = \cos\alpha\cos\theta + \sin\alpha\sin\theta\cos(\phi - \beta). \tag{7-61}$$

[1] The two polynomials have different coefficients a_{pqr}.

The angles θ and ϕ are determined by the direction of the unit vector $\hat{\mathbf{r}}$ pointing from the origin toward P, and it is often convenient to use the notation

$$Y_l^m(\theta, \phi) = Y_l^m(\hat{\mathbf{r}}). \tag{7–62}$$

Thus if $\hat{\mathbf{r}}'$ is a vector in the direction of the z'-axis, we have

$$\cos \theta' = \hat{\mathbf{r}}' \cdot \hat{\mathbf{r}},$$

and Eq. (7–60) becomes

$$P_l(\hat{\mathbf{r}}' \cdot \hat{\mathbf{r}}) = \frac{4\pi}{2l+1} \sum_{m=-l}^{l} Y_l^{m*}(\hat{\mathbf{r}}') Y_l^m(\hat{\mathbf{r}}). \tag{7–63}$$

Equation (7–60) or Eq. (7–63) is the addition theorem.

7–3 Degeneracy; angular momentum. The energies of the stationary states of a spherically symmetric system are those values of E for which the radial wave equation (7–6) has solutions which are admissible as wave functions. This equation is equivalent to

$$\frac{d^2u}{dr^2} + \left\{\frac{2m}{\hbar^2}[E - V(r)] - \frac{l(l+1)}{r^2}\right\} u = 0, \tag{7–64}$$

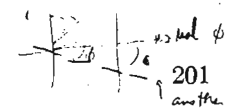
where $rR = u$. Except for a change in the range of the independent variable ($r \geq 0$), this equation is of the same form as the one-dimensional Schrödinger equation (5–3) provided the function

$$`V' = V(r) - \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2} \tag{7–65}$$

is regarded as an "equivalent one-dimensional potential-energy function." The solutions of Eq. (7–64) are similar in character to those of Eq. (5–3), in that there is, in general, a partly continuous and partly discrete spectrum of allowed values of E. It is clear that the energy eigenvalues depend, in general, upon the quantum number l, but that they are independent of m. Therefore, each of the functions $RY_l^m (m = -l, \ldots, l)$ is a solution of the Schrödinger equation (7–1) for the same value of E, and since these functions are linearly independent, *the states of energy E are $(2l+1)$-fold degenerate.* The reason for this degeneracy is the rotational symmetry of the system.

In order to see this more clearly, let $\psi(r, \theta, \phi)$ be an eigenfunction belonging to the energy E, i.e.,

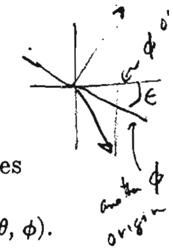
$$H\psi(r, \theta, \phi) = E\psi(r, \theta, \phi). \tag{7–66}$$



Since the angle ϕ can be measured with respect to any direction perpendicular to the z-axis, the function $\psi(r, \theta, \phi + \epsilon)$ must also be an eigenfunction for the same value of E, i.e.,

$$H\psi(r, \theta, \phi + \epsilon) = E\psi(r, \theta, \phi + \epsilon), \tag{7–67}$$

where ϵ is an arbitrary angle. Now if ϵ is small, we have



$$\psi(r, \theta, \phi + \epsilon) = \psi(r, \theta, \phi) + \epsilon \frac{\partial}{\partial \phi} \psi(r, \theta, \phi);$$

hence, introducing the operator $D = \partial/\partial\phi$, Eq. (7–67) becomes

$$H\psi(r, \theta, \phi) + \epsilon HD\psi(r, \theta, \phi) = E\psi(r, \theta, \phi) + \epsilon DE\psi(r, \theta, \phi).$$

By Eq. (7–66), this reduces to

$$(HD - DH)\psi(r, \theta, \phi) = 0. \tag{7–68}$$

This equation is true for all eigenfunctions of the Hamiltonian, and since these are, by hypothesis, a complete set of states of the system, we have

$$[H, D] = 0, \tag{7–69}$$

i.e., the operator $D = \partial/\partial\phi$ commutes with the Hamiltonian (cf. Section 6–9). The relation (7–69), which can be verified by writing out the Schrödinger equation in the form (7–3) (Problem 7–18), states in quantum-mechanical terms that H describes a system invariant to rotation about the z-axis.

According to the general theory of Chapter 6, the operators H and D must have simultaneous eigenfunctions. The functions Y_l^m contain the angle ϕ only in the factor $e^{im\phi}$, whence

$$De^{im\phi} = ime^{im\phi}.$$

The eigenvalues of D are purely imaginary, and hence D is not Hermitian. The operator

$$L_z = \frac{\hbar}{i} D = \frac{\hbar}{i}\frac{\partial}{\partial\phi}, \tag{7–70}$$

however, satisfies the eigenvalue equation

$$L_z e^{im\phi} = m\hbar e^{im\phi} \tag{7–71}$$

m integer so boundary term vanishes

and is Hermitian. Explicitly, if ψ is any single-valued function of ϕ, we have

$$(\psi, L_z\psi) = \int_0^{2\pi} \psi^* \frac{\hbar}{i}\frac{\partial\psi}{\partial\phi}\,d\phi = \int_0^{2\pi}\left(-\frac{\hbar}{i}\frac{\partial\psi^*}{\partial\phi}\right)\psi\,d\phi = (L_z\psi, \psi),$$

where the second integral is obtained from the first by integration by parts.

The physical interpretation of the operator L_z follows immediately from the rules (6–83). Thus, we have

no t dependence

$$D\psi = \frac{\partial\psi}{\partial\phi} = \frac{\partial\psi}{\partial x}\frac{\partial x}{\partial\phi} + \frac{\partial\psi}{\partial y}\frac{\partial y}{\partial\phi} = x\frac{\partial\psi}{\partial y} - y\frac{\partial\psi}{\partial x},$$

$x = \sin\theta\cos\phi$
$y = \sin\theta\sin\phi$

whence

$$L_z = x\left(\frac{\hbar}{i}\frac{\partial}{\partial y}\right) - y\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right) = xp_y - yp_x. \tag{7–72}$$

The operator L_z therefore corresponds to the z-component of the angular momentum of the particle. The classical angular-momentum vector is defined to be

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}.$$

The corresponding vector operator

$$\mathbf{L}_{\text{op}} = \mathbf{r}_{\text{op}} \times \mathbf{p}_{\text{op}} \tag{7–73}$$

has the components L_z [Eq. (7–72)] and

$$L_x = yp_z - zp_y, \qquad L_y = zp_x - xp_z. \tag{7–74}$$

Note that $[x, p_y] = 0$, etc., so that the order of the factors in the terms of Eq. (7–72) and Eq. (7–74) can be changed if desired:

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} = -\mathbf{p} \times \mathbf{r}. \tag{7–75}$$

The negative sign in this equation results, of course, from the definition of the vector product.

Equation (7–69), which is equivalent to

$$[H, L_z] = 0, \tag{7–76}$$

expresses the fact that the z-component of $\mathbf{L}$ is a constant of the motion for any spherically symmetric system. Hence, the law of conservation of angular momentum holds in quantum as well as in classical mechanics, as it must, since it is a direct consequence of the geometrical symmetry of the system. Furthermore, since

$$[H, L_x] = [H, L_y] = 0, \tag{7–77}$$

$\frac{\partial\langle L_z\rangle}{\partial t} = \langle [H, L_z]\rangle = 0$ $\qquad$ $[x_i, p_j] = i\hbar\delta_{ij}$

or, in general,

$$[H, \mathbf{L}] = 0, \tag{7–78}$$

an eigenfunction of H can be simultaneously an eigenfunction of L_x, or L_y, or L_z, or of any linear combination of these operators. The function RY_l^m is now seen to be a simultaneous eigenfunction of H and L_z; the $(2l + 1)$-fold degeneracy has been resolved by means of the commuting operator L_z, according to the general procedure described in Section 6–8. (1)

The rotational degeneracy of the states does not occur, of course, for a system which is not spherically symmetric. If forces are introduced which destroy the spherical symmetry, then the energy will depend, in general, upon m as well as l. Such forces are represented by additional terms in the Hamiltonian, which do not commute with $\mathbf{L}$, so that Eq. (7–78) is no longer true. The introduction of such forces *removes* the degeneracy. We shall show in Section 10–5 that, for a charged particle, the degeneracy is completely removed by the application of an external magnetic field, which defines a special direction in space.

The functions RY_l^m are eigenfunctions of the z-component of angular momentum and represent states which are *quantized with respect to the z-axis*. We have seen that any direction in space can be chosen as the axis of quantization since every component of $\mathbf{L}$ commutes with H. However, *the components of* $\mathbf{L}$ *are not commuting operators;* hence it is usually impossible to form a simultaneous eigenfunction of two different components of $\mathbf{L}$. It is a matter of algebra to show (Problem 7–19) that the operators L_x, L_y, L_z satisfy the commutation rules

$$[L_x, L_y] = i\hbar L_z, \qquad [L_y, L_z] = i\hbar L_x, \qquad [L_z, L_x] = i\hbar L_y, \tag{7–79}$$

or, in vector form (Problem 7–20),

$$\mathbf{L} \times \mathbf{L} = i\hbar\mathbf{L}. \tag{7–80}$$

The equations (7–79) are the fundamental relations among the components of any angular-momentum vector. They express, in precise form, that successive rotations of the coordinate frame about axes in two different directions are not commutable operations.[1] We shall show in Chapter 9 that a complete characterization of the angular-momentum operators can be obtained from the relations (7–79). Some of the consequences of these relations, which result from the definitions (7–72), (7–74) and the commutation rules (6–83), are listed in Problems 7–21 and 7–22.

[1] Cf., e.g., L. Page, *Introduction to Theoretical Physics*. 2nd ed. New York: D. Van Nostrand Co., Inc., 1935, p. 101. G. Joos, *Theoretical Physics*. New York: G. E. Stechert and Co., 1934, p. 132.

① eq. 7.64 is m-ind. This is for 'E' the energy. ② its (2l+1) fold deg.
③ Since $[H, L_z] = 0$ can choose simultaneous eigenfunctions. For fixed l,
... ④ Those of L_z are not - these eigenvalues are distinct.

The square of the angular-momentum operator $\mathbf{L}$ is

$$\mathbf{L}^2 = \mathbf{L}\cdot\mathbf{L} = L_x^2 + L_y^2 + L_z^2. \tag{7-81}$$

The operator $\mathbf{L}^2$ *commutes with every component of* $\mathbf{L}$, i.e.,

you show in homework

$$[\mathbf{L}^2, L_x] = [\mathbf{L}^2, L_y] = [\mathbf{L}^2, L_z] = 0, \tag{7-82}$$

for it follows from Eqs. (7-81) and (7-79) that, for example,

$$\begin{aligned}[\mathbf{L}^2, L_x] &= [L_x^2, L_x] + [L_y^2, L_x] + [L_z^2, L_x]\\ &= L_y[L_y, L_x] + [L_y, L_x]L_y + L_z[L_z, L_x] + [L_z, L_x]L_z\\ &= i\hbar(-L_yL_z - L_zL_y + L_zL_y + L_yL_z) = 0.\end{aligned}$$

Furthermore, because of the relations (7-76) and (7-77), $\mathbf{L}^2$ commutes with the Hamiltonian for a spherically symmetric system:

$$[H, \mathbf{L}^2] = 0. \tag{7-83}$$

The operators H, L_z and $\mathbf{L}^2$ are commuting operators, and the energy states of our problem can therefore be written as simultaneous eigenfunctions of these operators (cf. Section 6-8). We have already seen that the functions $RY_l^m(\theta, \phi)$ are eigenfunctions of H and L_z, and it will now be shown that

$$\mathbf{L}^2 Y_l^m(\theta, \phi) = l(l+1)\hbar^2 Y_l^m(\theta, \phi), \tag{7-84}$$

i.e., the spherical harmonic of degree l is an eigenfunction of the square of the total angular momentum, belonging to the eigenvalue $l(l+1)\hbar^2$.

The spherical harmonics are functions of the angles θ and ϕ, and the operator $\mathbf{L}$ has been defined in terms of the rectangular coordinates x, y, z. A change of variables is therefore required, which can be carried out by straightforward substitution [Eqs. (7-2); Problem 7-25]. Alternatively, using vector methods, we can proceed directly from the definition

$$\mathbf{L} = \frac{\hbar}{i}\,\mathbf{r}\times\nabla \tag{7-85}$$

to arrive at

$$\begin{aligned}\mathbf{L}^2\psi &= -\hbar^2\mathbf{r}\times\nabla\cdot(\mathbf{r}\times\nabla\psi) = -\hbar^2\mathbf{r}\cdot\nabla\times(\mathbf{r}\times\nabla\psi)\\ &= -\hbar^2\mathbf{r}\cdot[\mathbf{r}\nabla^2\psi + (\nabla\psi\cdot\nabla)\mathbf{r} - (\nabla\cdot\mathbf{r})\nabla\psi - (\mathbf{r}\cdot\nabla)\nabla\psi].\end{aligned} \tag{7-86}$$

Now if $\mathbf{A}$ is any vector and ϕ any scalar function, we have, by the definition of the gradient operator,

$$(\mathbf{A}\cdot\nabla)\mathbf{r} = \mathbf{A}, \qquad (\mathbf{r}\cdot\nabla)\mathbf{A} = r\,\frac{\partial \mathbf{A}}{\partial r}, \qquad (\mathbf{r}\cdot\nabla)\phi = r\,\frac{\partial\phi}{\partial r},$$

and

$$\nabla\cdot\mathbf{r} = 3.$$

Application of these rules in Eq. (7-86) yields

$$\begin{aligned}\mathbf{L}^2\psi &= -\hbar^2r^2\nabla^2\psi - \hbar^2\left[r\,\frac{\partial\psi}{\partial r} - 3r\,\frac{\partial\psi}{\partial r} - \mathbf{r}\cdot\left(r\,\frac{\partial}{\partial r}\,\nabla\psi\right)\right]\\ &= -\hbar^2r^2\nabla^2\psi - \hbar^2\left[-2r\,\frac{\partial\psi}{\partial r} - \frac{\partial}{\partial r}(r\mathbf{r}\cdot\nabla\psi) + \nabla\psi\cdot\frac{\partial}{\partial r}(r\mathbf{r})\right]\\ &= -\hbar^2r^2\nabla^2\psi + \hbar^2\,\frac{\partial}{\partial r}\left(r^2\,\frac{\partial\psi}{\partial r}\right),\end{aligned}$$

or

$$\frac{1}{\hbar^2r^2}\,\mathbf{L}^2\psi = -\nabla^2\psi + \frac{1}{r^2}\,\frac{\partial}{\partial r}\left(r^2\,\frac{\partial\psi}{\partial r}\right).$$

Now, if $\nabla^2\psi$ is expressed in terms of spherical polar coordinates, the preceding equation becomes

$$\mathbf{L}^2\psi = -\hbar^2\left[\frac{1}{\sin\theta}\,\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\,\frac{\partial^2\psi}{\partial\phi^2}\right], \tag{7-87}$$

i.e., the operator $-\mathbf{L}^2/\hbar^2r^2$ is just the "angular part" of the Laplacian operator. The relation (7-84) is therefore equivalent to Eq. (7-7), in which $C = l(l+1)$ [Eq. (7-18)].

The results of this section are summarized in the statement that the spherical harmonics $Y_l^m(\theta, \phi)$ are simultaneous eigenfunctions of the operators L_z and $\mathbf{L}^2$ belonging to the eigenvalues $m\hbar$ and $l(l+1)\hbar^2$, respectively. Since these functions are a complete set with respect to functions of θ and ϕ, L_z and $\mathbf{L}^2$ are a complete set of commuting operators for this class of functions. The Hamiltonian H, representing a spherically symmetric system, commutes with L_z and $\mathbf{L}^2$, and these three operators form a complete set with respect to the quantum states of the system.

7-4 The three-dimensional harmonic oscillator. A particle attracted toward a fixed point by a force proportional to the distance from the point has the potential energy

$$V(r) = \tfrac{1}{2}kr^2 = \tfrac{1}{2}k(x^2 + y^2 + z^2),$$

which is spherically symmetric. The Schrödinger equation for this system is

$$-\frac{\hbar^2}{2m}\,\nabla^2\psi + \tfrac{1}{2}kr^2\psi = E\psi,$$

$L_x = y p_z - z p_y \qquad L_y = z p_x - x p_z$

~~$L_x L_y = (z p_x - x p_z) f$~~

$L_x L_y f = (y p_z - z p_y)(z p_x - x p_z) f$

$= (y p_z z p_x + z p_y x p_z - z p_y z p_x - y p_z x p_z) f$

$= (\overset{O}{y p_x} + \overset{A}{y z p_z p_x} + \overset{C}{z x p_y p_z} - \overset{B}{z z p_y p_x} - \overset{D}{y x p_z p_z}) f$

you work out $L_y L_x f$

$(\overset{A}{z y p_x p_z} - \overset{B}{z z p_x p_y} - \overset{D}{x y p_z p_z} + \overset{O}{x p_y} + \overset{C}{x z p_z p_y}) f$

subtract

$[L_x, L_y] = \cancel{z x p_y p_z - x z p_z p_y} \quad y p_x - x p_y = i\hbar L_z$

Cyclic perm $\qquad [L_y, L_z] = i\hbar L_x \qquad [L_z, L_x] = i\hbar L_y$

or $\quad \underline{L} \times \underline{L} = i\hbar \underline{L} \quad$ note cross product gives commutator.

Also, if we write out $L^2 = L_x^2 + L_y^2 + L_z^2$ explicitly using spherical coords — tedious but easy to do because we obtained as before

$$\frac{\partial}{\partial x} = \frac{\partial}{\partial r}\frac{\partial r}{\partial x} + \frac{\partial}{\partial \theta}\frac{\partial \theta}{\partial x} + \frac{\partial}{\partial \varphi}\frac{\partial \varphi}{\partial x} \qquad \text{etc}$$

and L_x, L_y, L_z involve x, y, z & $\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}$

eventually get

$$L^2 \psi = -\hbar^2 \left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial \psi}{\partial \theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 \psi}{\partial \varphi^2} \right]$$

that is $-\dfrac{L^2}{\hbar^2 r^2}$ is just the angular part of the Laplacian.

Compare 7-3

This means $\hat{H} = \underbrace{\frac{-\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r}\right) + \frac{1}{2mr^2}L^2}_{T} + V(r)$

And the eigenvalue-eigenvector problem is

$$\frac{L^2}{\hbar^2}Y = +CY \qquad C = \ell(\ell+1)$$

so

$$L^2 Y_\ell^m(\theta,\varphi) = \ell(\ell+1)\hbar^2 Y_\ell^m(\theta,\varphi).$$

This is very useful because we now show that

$$[H, L^2] = 0. \qquad = [T, L^2] + [V, L^2]$$

Here $T = -\underbrace{\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r}\right)}_{G(r)} + \frac{1}{2mr^2}L^2$

$$[T, L^2] = [G(r), L^2] + [\tfrac{1}{2mr^2}L^2, L^2]$$

L^2 only is a θ,φ operator, so commutes with $G(r)$

also $[L^2, L^2] = 0$.

$[V, L^2] = 0$ again since L^2 θ,φ operator $V = V(r)$ central potential KE.

$\therefore [H, L^2] = 0.$

Thus we may use eigenfunctions of L^2 also to be simultaneous w H and with L_z.

Summarizing. $[H, L^2]=0$, $[H, L_z]=0$.
So, use eigenfuncts, simultaneous, of H, L_z, L^2 to characterize ang. momentum.

$$H\psi = E\psi \qquad L^2\psi = \ell(\ell+1)\hbar^2\psi \qquad L_z\psi = m\hbar\psi$$

$$\ell = 0, 1, 2, \ldots \quad -\ell \le m \le \ell.$$

$$\psi = R(r)\, Y_\ell^m(\theta,\varphi).$$

L^2, L_z are complete set of commuting ops for functs of θ, φ with eigenfunctions $Y_\ell^m(\theta,\varphi)$.