

The Schrödinger Equation in Three Dimensions

Introduction

In three dimension the Schrödinger equation can be expressed by the equation

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r}, t) + V(\vec{r})\Psi(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}, t) \quad (10.1)$$

Just as we showed in one dimension, the wave function $\Psi(\vec{r}, t)$ can be factored to give

$$\Psi(\vec{r}, t) = \psi(\vec{r})e^{-i\omega t} \quad (10.2)$$

where $\psi(\vec{r})$ is the solution of the three-dimensional time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) = E\psi(\vec{r}) \quad (10.3)$$

We can also express this equation in operator form, by defining the three-dimensional momentum operator (consistent with the one-dimensional definition) by the equation

$$\widehat{\vec{p}} = -i\hbar \widehat{\nabla} = -i\hbar \left(\widehat{e}_x \frac{\partial}{\partial x} + \widehat{e}_y \frac{\partial}{\partial y} + \widehat{e}_z \frac{\partial}{\partial z} \right) \quad (10.4)$$

and the position operator $\widehat{\vec{r}}$ by

$$\widehat{\vec{r}} = \widehat{e}_x x + \widehat{e}_y y + \widehat{e}_z z \quad (10.5)$$

With these definitions the kinetic energy operator is given by

$$\widehat{T} = \frac{\widehat{\vec{p}} \cdot \widehat{\vec{p}}}{2m} = -\frac{\hbar^2}{2m} \widehat{\nabla} \cdot \widehat{\nabla} = -\frac{\hbar^2}{2m} \nabla^2 \quad (10.6)$$

The Free Particle in Three Dimensions

The three-dimensional free particle Schrödinger equation becomes

$$\begin{aligned} -\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) &= E\psi(\vec{r}) \\ \nabla^2 \psi(\vec{r}) &= -\frac{2m}{\hbar^2} E\psi(\vec{r}) = -k^2 \psi(\vec{r}) \end{aligned} \quad (10.7)$$

To solve this last equation, we assume that each dimension is independent so the wave function is factorable into three independent components

$$\psi(\vec{r}) = \psi(x, y, z) = X(x)Y(y)Z(z) \quad (10.8)$$

The Schrödinger equation then becomes

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) X(x)Y(y)Z(z) = -k^2 X(x)Y(y)Z(z) \quad (10.9)$$

or, dividing left and right sides by $X(x)Y(y)Z(z)$ we obtain

$$\frac{1}{X(x)} \frac{\partial^2 X(x)}{\partial x^2} + \frac{1}{Y(y)} \frac{\partial^2 Y(y)}{\partial y^2} + \frac{1}{Z(z)} \frac{\partial^2 Z(z)}{\partial z^2} = -k^2 \quad (10.10)$$

If we let $k^2 = k_x^2 + k_y^2 + k_z^2$ we can write

$$\left[\frac{1}{X(x)} \frac{\partial^2 X(x)}{\partial x^2} + k_x^2 \right] + \left[\frac{1}{Y(y)} \frac{\partial^2 Y(y)}{\partial y^2} + k_y^2 \right] + \left[\frac{1}{Z(z)} \frac{\partial^2 Z(z)}{\partial z^2} + k_z^2 \right] = 0 \quad (10.11)$$

which can be valid for all values of x , y , and z only if each of these brackets are independently zero! This leads to three independent equations of the form

$$\frac{1}{X(x)} \frac{\partial^2 X(x)}{\partial x^2} + k_x^2 = 0 \quad (10.12)$$

with a solution of the form

$$X(x) = Ae^{ik_x x} \quad (10.13)$$

Since a free particle cannot be reflected, the solution is valid for any possible value of k_x , either positive or negative – but not both at the same time. The general three-dimensional solution, then, has the form

$$\psi(\vec{r}) = X(x)Y(y)Z(z) = \mathcal{A}e^{i(k_x x + k_y y + k_z z)} = \mathcal{A}e^{i\vec{k} \cdot \vec{r}} \quad (10.14)$$

where \vec{k} is the wave vector pointed in the direction of propagation of the wave with a magnitude given by

$$|\vec{k}|^2 = k_x^2 + k_y^2 + k_z^2 = \frac{2mE}{\hbar^2} \quad (10.15)$$

The fact that the energy of the system E can be written in terms of three different independent quantities

$$E = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) \quad (10.16)$$

means that there is *degeneracy* in this system. The same value of the energy can be obtained with different combination of quantum numbers associated with the eigenvalues k_x , k_y , and k_z .

From our one-dimensional treatment, we know that $p_x = \hbar k_x$, so we can write

$$\vec{p} = \hbar \vec{k} \quad (10.17)$$

which means that we can write the solution to the free particle in terms of the momentum vector as

$$\psi(\vec{r}) = \mathcal{A}e^{i\vec{p}\cdot\vec{r}/\hbar} \quad (10.18)$$

The time-dependent solution, then, is given by

$$\psi(\vec{r}) = \mathcal{A}e^{i\vec{p}\cdot\vec{r}/\hbar}e^{-i\omega t} \quad (10.19)$$

where $\omega = E/\hbar = p^2/2m\hbar$.

Just as in the one-dimensional case, this wave function is not strictly allowed, since it is not normalizable. We can get around this in some cases by looking at the probability current density, which is now defined in relation to the individual components of the momentum. In general, however, we must form an acceptable solution by utilizing Fourier transforms to obtain

$$\psi(\vec{r}, t) = \frac{1}{(\sqrt{2\pi\hbar})^3} \int \mathcal{A}(\vec{p})e^{i\vec{p}\cdot\vec{r}/\hbar}e^{-i\omega t} d\vec{p} \quad (10.20)$$

The Three-Dimensional Infinite Potential Well

As another simple example of a three-dimensional problem, we will consider the infinite potential well. This problem is similar to the infinite square well. The potential energy within a region defined by

$$\begin{aligned} 0 &\leq x \leq L_x \\ 0 &\leq y \leq L_y \\ 0 &\leq z \leq L_z \end{aligned} \quad (10.21)$$

is zero, while the potential energy outside this region is infinite. This confines a particle to the volume of space described above, so the wave function must go to zero at the boundaries.

Inside the “well” Schrödinger's equation is identical to that of the free particle and reduces to

$$\left[\frac{1}{X(x)} \frac{\partial^2 X(x)}{\partial x^2} + k_x^2 \right] + \left[\frac{1}{Y(y)} \frac{\partial^2 Y(y)}{\partial y^2} + k_y^2 \right] + \left[\frac{1}{Z(z)} \frac{\partial^2 Z(z)}{\partial z^2} + k_z^2 \right] = 0 \quad (10.22)$$

or more precisely to three independent equations of the form

$$\frac{1}{X(x)} \frac{\partial^2 X(x)}{\partial x^2} + k_x^2 = 0 \quad (10.23)$$

The only difference between the free particle and the infinite “well” problem is the boundary conditions. The wave function must go to zero at the boundaries of the well. This means that reflection is possible so that the most general solution to the X equation above is given by

$$X(x) = Ae^{ik_x x} + Be^{-ik_x x} \quad (10.24)$$

The boundary condition

$$X(0) = 0 \quad (10.25)$$

requires that

$$A = -B \quad (10.26)$$

so that $X(x)$ is given by

$$X(x) = \mathcal{A} \sin(k_x x) \quad (10.27)$$

where $\mathcal{A} = A/2i$ is complex in general. The additional boundary condition applied at $x = L_x$ gives

$$X(L_x) = \mathcal{A} \sin(k_x L_x) = 0 \quad (10.28)$$

implying that

$$k_x L_x = n_x \pi \Rightarrow k_x = n_x \pi / L_x \quad (10.29)$$

which finally gives

$$X(x) = \mathcal{A} \sin(n_x \pi x / L_x) \quad (10.30)$$

The solution has the same form for each independent coordinate, giving for $\psi(\vec{r})$

$$\psi(\vec{r}) = \mathcal{B} \sin(n_x \pi x / L_x) \sin(n_y \pi y / L_y) \sin(n_z \pi z / L_z) \quad (10.31)$$

with

$$k^2 = k_x^2 + k_y^2 + k_z^2 = \pi^2 [n_x^2 / L_x^2 + n_y^2 / L_y^2 + n_z^2 / L_z^2] = 2mE / \hbar^2 \quad (10.32)$$

or

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m} [n_x^2 / L_x^2 + n_y^2 / L_y^2 + n_z^2 / L_z^2] \quad (10.33)$$

Thus, for the three-dimensional infinite potential well there are three quantum numbers – one associated with each of the degrees of freedom of the system. Notice that the quantum numbers n_x , n_y , and n_z *cannot be zero*! If any of these quantum numbers were zero, the wave function would be zero implying zero probability of finding a particle in the well. This means that the ground state energy cannot be zero! Notice also that the values of the quantum numbers could be positive or negative, but we obtain the same result for $\psi(\vec{r})$ and for E whether the numbers are positive or negative. Thus, we will take the quantum numbers to run from 1 to positive infinity.

One new feature that arises in situations with more than one dimension is the feature of degeneracy. When more than one quantum state has the same energy, those states are said to be degenerate. Consider the case where our three-dimensional infinite

potential well is a cube with $L_x = L_y = L_z = L$. The equation for the energy gives

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2mL^2} [n_x^2 + n_y^2 + n_z^2] = \epsilon [n_x^2 + n_y^2 + n_z^2] \quad (10.34)$$

Table 9.1 lists the first 10 energy levels of the three-dimensional infinite potential well along with the corresponding quantum numbers. Each unique set of quantum numbers gives a unique spacial wave function, corresponding to a unique probability of locating a particle at some point within three-dimensional space. However, several of these unique wave functions have the same total energy. The number of different unique wave functions all having the same total energy is called the *degeneracy* of that particular energy level.

A plot of the first 10 energy levels for the three-dimensional *cubic* infinite potential well is shown in Figure 9.1, along with the degeneracy of each level. Degeneracy is usually associated with symmetry within the system. This particular energy level diagram and its degeneracies arise from the fact that we assumed L_x , L_y , and L_z were all the same. If this were *not* the case, the degeneracy of these individual levels disappears (or at least some of the degeneracy disappears). For example, if L_x , L_y , and L_z are all slightly different, the energy levels are only slightly split – there would generally be three closely spaced energy levels wherever $g = 3$, four where $g = 4$, etc.

Problem 10.1

Use Excel to plot a bar graph of the energies of the 3D infinite potential well, were you can vary L_x , L_y , and L_z . This will give you some idea about how the degeneracy works.

Figure 10.1

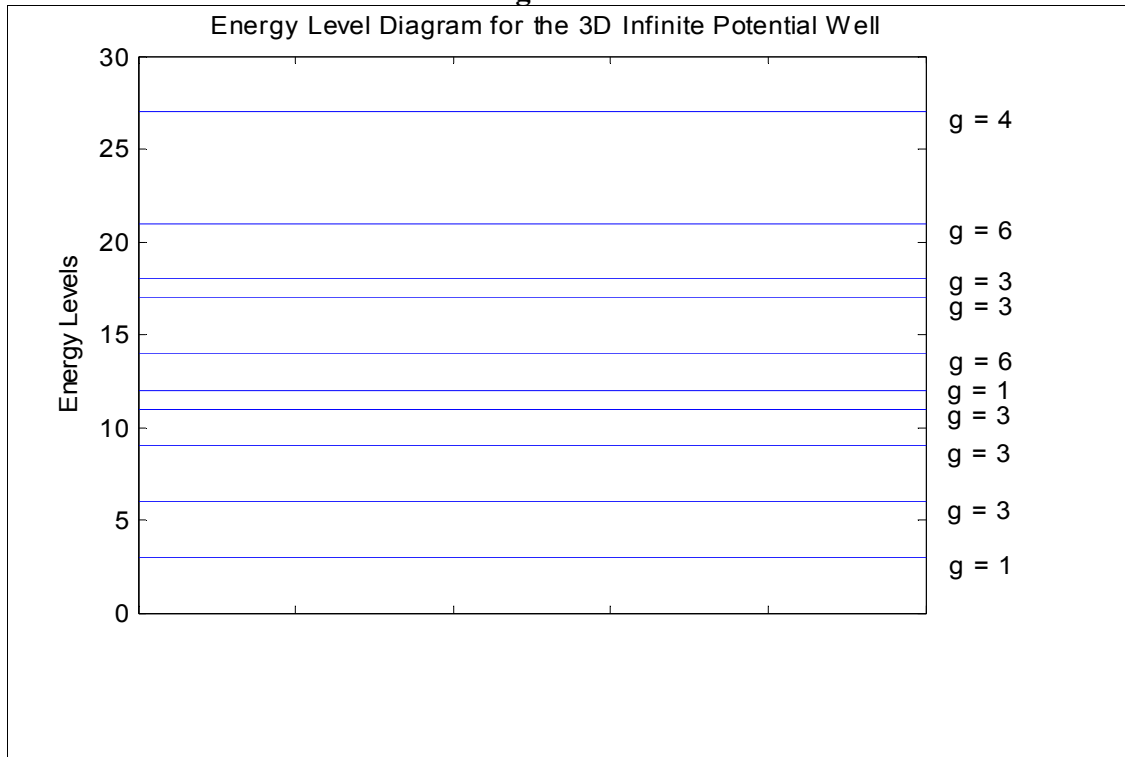


Table 10.1 Energy Values for Different Quantum Numbers

n_x	n_y	n_z	E/ϵ
1	1	1	3
2	1	1	6
1	2	1	6
1	1	2	6
1	2	2	9
2	1	2	9
2	2	1	9
3	1	1	11
1	3	1	11
1	1	3	11
2	2	2	12
1	2	3	14
2	1	3	14
1	3	2	14
2	3	1	14
3	1	2	14
3	2	1	14
3	2	2	17
2	3	2	17
2	2	3	17
4	1	1	18
1	4	1	18
1	1	4	18
4	1	2	21
4	2	1	21
1	4	2	21
2	4	1	21
1	2	4	21
2	1	4	21
3	3	3	27
5	1	1	27
1	5	1	27
1	1	5	27

Angular Momentum

Introduction

In three dimensions, we often encounter forces and potentials which are a function only of the distance from the force center. To take advantage of this fact, the Schrödinger equation for these so-called central forces can be written in spherical coordinates. The three-dimensional Schrödinger equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) = E\psi(\vec{r}) \quad (10.35)$$

can be expressed in terms of r , θ , and ϕ by writing the Laplacian in terms of spherical coordinates:

$$\begin{aligned} \nabla^2 &= \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \left[\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right] \\ \nabla^2 &= \nabla_r^2 + \frac{1}{r^2} \nabla_{\theta,\phi}^2 \end{aligned} \quad (10.36)$$

where, in this last equation, we have expressed the Laplacian in terms of radial and angular operators. The Schrödinger equation, therefore, becomes

$$-\frac{\hbar^2}{2m} \left[\nabla_r^2 + \frac{1}{r^2} \nabla_{\theta,\phi}^2 \right] \psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) = E\psi(\vec{r}) \quad (10.37)$$

which we can express as

$$\left[\left(\frac{-\hbar^2 \nabla_r^2}{2m} \right) + \left(\frac{-\hbar^2 \nabla_{\theta,\phi}^2}{2mr^2} \right) \right] \psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) = E\psi(\vec{r}) \quad (10.38)$$

or

$$\left[\left(\frac{\hat{p}_r^2}{2m} \right) + \left(\frac{\hat{L}^2}{2mr^2} \right) \right] \psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) = E\psi(\vec{r}) \quad (10.39)$$

where the first term is the kinetic energy due to radial momentum, and the second term is the kinetic energy due to angular momentum. For a system in which the radius is *fixed*, the radial term is zero and the only remaining term is the one dependent upon the angular momentum. Such would be the case for a frictionless particle moving on a circular wire of fixed radius, or for a rigid rotator (an example is a diatomic molecule of fixed radius).

Since the Laplacian can be separated into a radial part and an angular part, and since the potential energy function is only a function of the radius, we should be able to separate the wave function into a radial part times an angular part, such as

$$\psi(\vec{r}) = R(r)Y(\theta, \phi) \quad (10.40)$$

Substituting this into the last equation, and dividing by the wave function gives

$$\left[\left(\frac{1}{R(r)} \frac{\hat{p}_r^2 R(r)}{2m} \right) + \left(\frac{1}{Y(\theta, \phi)} \frac{\hat{L}^2 Y(\theta, \phi)}{2mr^2} \right) \right] + V(\vec{r}) = E \quad (10.41)$$

If we multiply through by $2mr^2$ and move terms that are only a function of the radius to one side of the equation, we have

$$\frac{\hat{L}^2 Y(\theta, \phi)}{Y(\theta, \phi)} = - \frac{r^2 \hat{p}_r^2 R(r)}{R(r)} + 2mr^2 [E - V(\vec{r})] \quad (10.42)$$

where

$$\begin{aligned} \hat{p}_r^2 &= -\hbar^2 \nabla_r^2 \\ \hat{L}^2 &= -\hbar^2 \nabla_{\theta, \phi}^2 \end{aligned} \quad (10.43)$$

Since the Schrödinger equation must be valid for all possible values of r , θ , and ϕ the right-hand-side and the left-hand-side of this equation must always be equal to the same constant which we will call λ . Thus, we are left with two differential equations which we must solve

$$\frac{\hat{L}^2 Y(\theta, \phi)}{Y(\theta, \phi)} = \lambda \quad \Rightarrow \quad \hat{L}^2 Y(\theta, \phi) = \lambda Y(\theta, \phi) \quad (10.44)$$

an eigenvalue equation for the square of the angular momentum operator, and

$$- \frac{r^2 \hat{p}_r^2 R(r)}{R(r)} + 2mr^2 [E - V(r)] = \lambda \quad (10.45)$$

or

$$\begin{aligned} \left\{ \frac{\hat{p}_r^2}{2m} + \left[\frac{\lambda}{2mr^2} + V(r) \right] \right\} R(r) &= E R(r) \\ \left\{ \frac{\hat{p}_r^2}{2m} + \left[\frac{\ell^2}{2mr^2} + V(r) \right] \right\} R(r) &= E R(r) \end{aligned} \quad (10.46)$$

which is the Schrödinger equation expressed in terms of a rotating coordinate system where r is the radial distance from the origin and where $\lambda = \ell^2$ is the square of the magnitude of the angular momentum vector.

Analytical Approach

One way to make further progress in the treatment of angular momentum is to follow the analytic approach where we need to solve the eigenfunction equation for the

square of the angular momentum

$$\begin{aligned}\widehat{L}^2 Y(\theta, \phi) &= \lambda Y(\theta, \phi) & (10.47) \\ -\hbar^2 \nabla_{\theta, \phi}^2 Y(\theta, \phi) &= \lambda Y(\theta, \phi) \\ -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] Y(\theta, \phi) &= \lambda Y(\theta, \phi)\end{aligned}$$

Now this last equation is a function of the two angles θ and ϕ , and is separable into two independent equations. We can demonstrate this by assuming the function $Y(\theta, \phi)$ is separable so that $Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$, and then multiplying through by $\sin^2\theta$, and dividing by $\Theta(\theta)\Phi(\phi)$ to obtain

$$\frac{-\hbar^2}{\Theta(\theta)} \left[\sin\theta \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Theta(\theta)}{\partial\theta} \right) \right] + \frac{-\hbar^2}{\Phi(\phi)} \frac{\partial^2\Phi(\phi)}{\partial\phi^2} = \lambda \sin^2\theta \quad (10.48)$$

Moving all the terms that are functions only of ϕ to one side of the equation gives

$$\frac{-\hbar^2}{\Phi(\phi)} \frac{\partial^2\Phi(\phi)}{\partial\phi^2} = \lambda \sin^2\theta - \frac{-\hbar^2}{\Theta(\theta)} \left[\sin\theta \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Theta(\theta)}{\partial\theta} \right) \right] \quad (10.49)$$

Now, one can show that the z -component of the angular momentum vector, expressed in terms of spherical coordinates is

$$\widehat{L}_z = -i\hbar \frac{\partial}{\partial\phi} \quad (10.50)$$

so that this last equation can be written

$$\frac{\widehat{L}_z^2 \Phi(\phi)}{\Phi(\phi)} = \lambda \sin^2\theta - \frac{-\hbar^2}{\Theta(\theta)} \left[\sin\theta \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Theta(\theta)}{\partial\theta} \right) \right] \quad (10.51)$$

Again, if this equation is to be valid for all possible combinations of θ and ϕ , then both sides must be set equal to the same constant, μ . Thus, we are left with two differential equations which we must solve

$$\frac{\widehat{L}_z^2 \Phi(\phi)}{\Phi(\phi)} = \mu \quad \Rightarrow \quad \widehat{L}_z^2 \Phi(\phi) = \mu \Phi(\phi) \quad (10.52)$$

an eigenvalue equation for the square of the z -component of the angular momentum operator, and

$$\lambda \sin^2\theta - \frac{-\hbar^2}{\Theta(\theta)} \left[\sin\theta \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Theta(\theta)}{\partial\theta} \right) \right] = \mu \quad (10.53)$$

Dividing this last equation by $\sin^2(\theta)$, multiplying by $\Theta(\theta)$, and regrouping, we obtain the differential equation for the $\Theta(\theta)$ function:

$$-\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Theta(\theta)}{\partial\theta} \right) \right] + \frac{\mu}{\sin^2\theta} \Theta(\theta) = \lambda \Theta(\theta) \quad (10.54)$$

We first solve the eigenvalue equation for square of the z -component of the angular momentum

$$\begin{aligned} \hat{L}_z^2 \Phi(\phi) &= \mu \Phi(\phi) & (10.55) \\ \left(-i\hbar \frac{\partial}{\partial\phi} \right)^2 \Phi(\phi) &= \mu \Phi(\phi) \\ \frac{\partial^2 \Phi(\phi)}{\partial\phi^2} &= -\frac{\mu}{\hbar^2} \Phi(\phi) \end{aligned}$$

The function $\Phi(\phi)$ must be of the form

$$\Phi(\phi) = Ae^{\alpha\phi} \quad (10.56)$$

from which we obtain

$$\alpha^2 Ae^{\alpha\phi} = -\frac{\mu}{\hbar^2} Ae^{\alpha\phi} \quad (10.57)$$

or

$$\alpha^2 = -\frac{\mu}{\hbar^2} \Rightarrow \alpha = \pm i \frac{\sqrt{\mu}}{\hbar} = \pm im \quad (10.58)$$

where $m = \sqrt{\mu}/\hbar$. This gives, for the $\Phi(\phi)$ solution

$$\Phi(\phi) = Ae^{+im\phi} + Be^{-im\phi} \quad (10.59)$$

Consider the time-dependence of this solution, which would be of the form

$$\Phi(\phi, t) = Ae^{+i(m\phi - \omega t)} + Be^{-i(m\phi + \omega t)} \quad (10.60)$$

The terms on the right-hand-side represent wave functions with a phase velocity of $\pm \omega/m$, respectively. A single particle can not move in both directions at the *same* time, so each of these solutions must be eigensolutions for the problem. The superposition simply indicates the uncertainty of knowing the direction of motion.

We require the eigenfunctions to be single valued, so that $\Phi(\phi \pm 2\pi) = \Phi(\phi)$, or

$$Ae^{+im\phi} = Ae^{+im(\phi \pm 2\pi)} = Ae^{+im\phi} e^{\pm im2\pi} \quad (10.61)$$

which is valid as long as

$$e^{\pm im2\pi} = 1 \quad (10.62)$$

which requires that m be an integer. In fact, we can absorb the \pm into the constant so that

m must be a positive or a negative integer and the eigenfunction be expressed as

$$\Phi(\phi) = Ae^{im\phi} \quad (10.63)$$

where

$$m = \sqrt{\mu}/\hbar \quad \text{where } m = 0, \pm 1, \pm 2, \dots (10.64)$$

or

$$\mu = \hbar^2 m^2 \quad (10.65)$$

The eigenfunction equation for \hat{L}_z^2 then becomes

$$\hat{L}_z^2 \Phi(\phi) = \hbar^2 m^2 \Phi(\phi) \quad (10.66)$$

or

$$\hat{L}_z \Phi(\phi) = \hbar m \Phi(\phi) \quad \text{where } m = 0, \pm 1, \dots (10.67)$$

The $\Theta(\theta)$ function now must satisfy the equation

$$-\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Theta(\theta)}{\partial\theta} \right) \right] + \frac{\hbar^2 m^2}{\sin^2\theta} \Theta(\theta) = \lambda \Theta(\theta) \quad (10.68)$$

or

$$-\left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Theta(\theta)}{\partial\theta} \right) \right] - \frac{\lambda}{\hbar^2} \Theta(\theta) + \frac{m^2}{\sin^2\theta} \Theta(\theta) = 0 \quad (10.69)$$

The solution to this differential equation can be determined using a power series solution if we make use of the change of variable

$$\zeta = \cos\theta \quad (10.70)$$

since

$$\frac{\partial f}{\partial\theta} = \frac{\partial f}{\partial(\cos\theta)} \cdot \frac{\partial(\cos\theta)}{\partial\theta} = \sin\theta \frac{\partial f}{\partial(\cos\theta)} \Rightarrow \frac{1}{\sin\theta} \frac{\partial f}{\partial\theta} = \frac{\partial f}{\partial(\cos\theta)} \quad (10.71)$$

Writing the differential equation in the form

$$-\left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\frac{\sin^2\theta}{\sin\theta} \frac{\partial\Theta(\theta)}{\partial\theta} \right) \right] - \frac{\lambda}{\hbar^2} \Theta(\theta) + \frac{m^2}{\sin^2\theta} \Theta(\theta) = 0 \quad (10.72)$$

we make the change of variables to obtain

$$\left[\frac{\partial}{\partial\zeta} \left((1-\zeta^2) \frac{\partial P(\zeta)}{\partial\zeta} \right) \right] + \left(\frac{\lambda}{\hbar^2} - \frac{m^2}{(1-\zeta^2)} \right) P(\zeta) = 0 \quad (10.73)$$

The solution to this differential equation must be continuous, square-integrable, and single-valued throughout the domain of ζ , which is from -1 to $+1$. We will make the further simplification at this point of setting $m = 0$, and attempt a solution to the equation

$$\left[\frac{\partial^2 P(\zeta)}{\partial \zeta^2} - 2\zeta \frac{\partial P(\zeta)}{\partial \zeta} - \zeta^2 \frac{\partial^2 P(\zeta)}{\partial \zeta^2} \right] + \frac{\lambda}{\hbar^2} P(\zeta) = 0 \quad (10.74)$$

of the form

$$P(\zeta) = \sum_{n=0} c_n \zeta^n \quad (10.75)$$

where

$$\begin{aligned} \frac{\partial^2 P(\zeta)}{\partial \zeta^2} &= \sum_{n=0} n(n-1) c_n \zeta^{n-2} = \sum_{n'=0} (n'+2)(n'+1) c_{n'+2} \zeta^{n'} \quad (10.76) \\ -2\zeta \frac{\partial P(\zeta)}{\partial \zeta} &= -2\zeta \sum_{n=0} n c_n \zeta^{n-1} = -2 \sum_{n=0} n c_n \zeta^n \\ -\zeta^2 \frac{\partial^2 P(\zeta)}{\partial \zeta^2} &= -\zeta^2 \sum_{n=0} n(n-1) c_n \zeta^{n-2} = - \sum_{n=0} n(n-1) c_n \zeta^n \end{aligned}$$

giving

$$\sum_{n=0} \left\{ (n+2)(n+1) c_{n+2} - \left[2n + n(n-1) - \frac{\lambda}{\hbar^2} \right] c_n \right\} \zeta^n = 0 \quad (10.77)$$

In order for this equation to be valid for all possible values of ζ , the coefficients of each power must be zero, giving

$$(n+2)(n+1) c_{n+2} - \left[2n + n(n-1) - \frac{\lambda}{\hbar^2} \right] c_n = 0 \quad (10.78)$$

or

$$c_{n+2} = \frac{2n + n(n-1) - (\lambda/\hbar^2)}{(n+2)(n+1)} c_n = \frac{n(n+1) - (\lambda/\hbar^2)}{(n+1)(n+2)} c_n \quad (10.79)$$

Notice that as $n \rightarrow \infty$, $c_{n+2}/c_n \rightarrow 1$ so that the infinite sum would blow up. This means that we must terminate the infinite series at some point. Thus, for a particular value of n , say ℓ , we must have that $c_{\ell+2} = 0$, or

$$\ell(\ell+1) - (\lambda/\hbar^2) = 0 \quad (10.80)$$

giving

$$\lambda = \hbar^2 \ell(\ell + 1) \quad (10.81)$$

Development of Legendre Polynomials

The Associated Legendre Polynomials

Operator Method

We showed above that the Schrödinger equation can be written as

$$\left[\left(\frac{\widehat{p}_r^2}{2m} \right) + \left(\frac{\widehat{L}^2}{2mr^2} \right) \right] \psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) = E\psi(\vec{r}) \quad (10.82)$$

For the central force problem, the potential energy term is a function only of $|\vec{r}|$ and the torque is zero, which means that the angular momentum is a constant of the motion. We know that for any quantum mechanical operator,

$$\frac{d}{dt} \langle \psi(t) | \widehat{A} | \psi(t) \rangle = \langle \psi(t) | \frac{\partial}{\partial t} \widehat{A} | \psi(t) \rangle + \frac{i}{\hbar} \langle \psi(t) | [\widehat{H}, \widehat{A}] | \psi(t) \rangle \quad (10.83)$$

This equation tells us that for the expectation value of the angular momentum operator to be zero, that operator must *not* explicitly depend upon the time, and *must* commute with the Hamiltonian. We therefore need to define the angular momentum operator and verify that it is time independent and that it commutes with the Hamiltonian.

We begin with the classical definition of the angular momentum

$$\vec{L} = \vec{r} \times \vec{p} \quad (10.84)$$

The three components of the *operator* corresponding to this vector we expect to be of the form

$$\begin{aligned} \widehat{L}_x &= \widehat{y}\widehat{p}_z - \widehat{z}\widehat{p}_y \\ \widehat{L}_y &= \widehat{z}\widehat{p}_x - \widehat{x}\widehat{p}_z \\ \widehat{L}_z &= \widehat{x}\widehat{p}_y - \widehat{y}\widehat{p}_x \end{aligned} \quad (10.85)$$

In one dimension, we found that the commutator

$$[\widehat{x}, \widehat{p}_x] = i\hbar \quad (10.86)$$

Here we have products of position operators in one dimension with momentum operators in another dimension. How do these commute? To determine this we examine the

commutator in position representation as follows:

$$\begin{aligned} [\widehat{y}, \widehat{p}_z]f(x, y, z) &= y \left(-i\hbar \frac{\partial}{\partial z} \right) f(x, y, z) - \left(-i\hbar \frac{\partial}{\partial z} \right) y f(x, y, z) \quad (10.87) \\ &= -i\hbar \left(y \frac{\partial f}{\partial z} - y \frac{\partial f}{\partial z} \right) = 0 \end{aligned}$$

so we find, in general,

$$\begin{aligned} [\widehat{x}_i, \widehat{x}_j] &= 0 \quad (10.88) \\ [\widehat{p}_i, \widehat{p}_j] &= 0 \\ [\widehat{x}_i, \widehat{p}_j] &= i\hbar \delta_{ij} \end{aligned}$$

Since the different components of the position operator commute, we designate a three-dimensional state vector for position with the notation

$$|\vec{r}\rangle = |x, y, z\rangle = |x_1, x_2, x_3\rangle \quad (10.89)$$

because all of these position measurements are *compatible*. Likewise we can designate the three-dimensional state vector for momentum by the equation

$$|\vec{p}\rangle = |p_x, p_y, p_z\rangle = |p_1, p_2, p_3\rangle \quad (10.90)$$

When we examine the commutator relationships of the components of \widehat{L} with each other, with \widehat{L}^2 and with the Hamiltonian, we find the following relationships

$$[\widehat{L}_x, \widehat{L}_y] = i\hbar \widehat{L}_z \quad xyz \text{ cyclic} \quad (10.91)$$

$$[\widehat{L}^2, \widehat{L}_i] = 0 \quad i = x, y, \text{ or } z \quad (10.92)$$

and

$$[\widehat{L}, \widehat{H}] = 0 \quad (10.93)$$

where we define

$$\widehat{L}^2 = \widehat{L}_x^2 + \widehat{L}_y^2 + \widehat{L}_z^2 \quad (10.94)$$

Since both \widehat{L}^2 and any of the other components commute, we know that we can define an eigenvector of \widehat{L}^2 which is simultaneously an eigenvector of one of the other components of \widehat{L} . It is conventional to choose the z -component and write the eigenvalue equations

$$\begin{aligned} \widehat{L}^2 |\lambda, m\rangle &= \lambda |\lambda, m\rangle \quad (10.95) \\ \widehat{L}_z |\lambda, m\rangle &= \hbar m |\lambda, m\rangle \end{aligned}$$

where λ and m are to be determined.

Since the angular momentum operator commutes with the Hamiltonian operator, we can also write this last equation in the form

$$\begin{aligned}\widehat{L}^2 |E, \lambda, m\rangle &= \lambda |E, \lambda, m\rangle \\ \widehat{L}_z |E, \lambda, m\rangle &= \hbar m |E, \lambda, m\rangle\end{aligned}\quad (10.96)$$

In what follows, however, we will *not* include the notation for the total energy to keep the notation simpler.

Problem 10.2

Beginning with the defining relationships for the components of the angular momentum operator, show that

$$[\widehat{L}_x, \widehat{L}_y] = i\hbar \widehat{L}_z \quad xyz \text{ cyclic}$$

Problem 10.3

Show that

$$[\widehat{L}^2, \widehat{L}_i] = 0 \quad i = x, y, \text{ or } z$$

Problem 10.4

Show that

$$[\widehat{L}, \widehat{H}] = 0$$

As we have already seen, quantum mechanical commutator relationships are very fundamental, since these relationships are independent of a particular representation (position, momentum, etc.). Although the commutator relationships we developed above were based upon the classically defined angular momentum operator, there are *other*, similar operators which obey these same commutator relationships. These other operators must, therefore, correspond to different types of angular momentum operators.

It is conventional to designate *any arbitrary angular momentum operator* which satisfies the commutator relationships above by the notation \widehat{J} and to reserve the designation of \widehat{L} for the *orbital* angular momentum operator. Thus, we rewrite the commutator relationships in terms of the generic angular momentum operator \widehat{J}

$$[\widehat{J}_x, \widehat{J}_y] = i\hbar \widehat{J}_z \quad xyz \text{ cyclic} \quad (10.97)$$

$$[\widehat{J}^2, \widehat{J}_i] = 0 \quad i = x, y, \text{ or } z \quad (10.98)$$

where we define

$$\widehat{J}^2 = \widehat{J}_x^2 + \widehat{J}_y^2 + \widehat{J}_z^2 \quad (10.99)$$

Again, since both \widehat{J}^2 and any of the other components commute, we know that we can define an eigenvector of \widehat{J}^2 which is simultaneously an eigenvector of one of the other components of \widehat{J} . We choose the z -component and write the eigenvalue equations

$$\begin{aligned} \widehat{J}^2 |\lambda, m\rangle &= \lambda |\lambda, m\rangle \\ \widehat{J}_z |\lambda, m\rangle &= \hbar m |\lambda, m\rangle \end{aligned} \quad (10.100)$$

where λ and m are to be determined.

Step-up and Step-down Operators

In order to determine the eigenvalues of these equations we will make use of the non-Hermitian operators

$$\begin{aligned} \widehat{J}_+ &= \widehat{J}_x + i\widehat{J}_y \\ \widehat{J}_- &= \widehat{J}_x - i\widehat{J}_y \end{aligned} \quad (10.101)$$

We find that the commutator relationships between these operators and with \widehat{J}_z are given by

$$\begin{aligned} [\widehat{J}_z, \widehat{J}_+] &= +\hbar\widehat{J}_+ \\ [\widehat{J}_z, \widehat{J}_-] &= -\hbar\widehat{J}_- \\ [\widehat{J}_+, \widehat{J}_-] &= +2\hbar\widehat{J}_z \end{aligned} \quad (10.102)$$

In addition, we notice that

$$\begin{aligned} \widehat{J}_+\widehat{J}_- &= (\widehat{J}_x + i\widehat{J}_y)(\widehat{J}_x - i\widehat{J}_y) = \widehat{J}_x^2 + \widehat{J}_y^2 + i[\widehat{J}_y, \widehat{J}_x] \\ &= \widehat{J}^2 - \widehat{J}_z^2 + \hbar\widehat{J}_z \end{aligned} \quad (10.103)$$

and, similarly,

$$\widehat{J}_-\widehat{J}_+ = \widehat{J}^2 - \widehat{J}_z^2 - \hbar\widehat{J}_z \quad (10.104)$$

We will now use these raising and lowering operators to determine the eigenvalues of the eigenvalue equations for \widehat{J}^2 and \widehat{J}_z . First, from the commutation relationship between \widehat{J}_z and \widehat{J}_+ , we find

$$[\widehat{J}_z, \widehat{J}_+] = +\hbar\widehat{J}_+ \quad (10.105)$$

or

$$\widehat{J}_z \widehat{J}_+ - \widehat{J}_+ \widehat{J}_z = \hbar \widehat{J}_+ \Rightarrow \widehat{J}_z \widehat{J}_+ = \widehat{J}_+ (\widehat{J}_z + \hbar) \quad (10.106)$$

Operating on an eigenvector with this operator gives

$$\begin{aligned} \widehat{J}_z \widehat{J}_+ |\lambda, m\rangle &= \widehat{J}_+ (\widehat{J}_z + \hbar) |\lambda, m\rangle \\ \widehat{J}_+ (\hbar m + \hbar) |\lambda, m\rangle &= \hbar(m+1) \widehat{J}_+ |\lambda, m\rangle \end{aligned} \quad (10.107)$$

which demonstrates that $\widehat{J}_+ |\lambda, m\rangle$ must be an eigenvector whose m -value is one greater than the eigenvector $|\lambda, m\rangle$! Similarly,

$$\widehat{J}_z \widehat{J}_- |\lambda, m\rangle = \hbar(m-1) \widehat{J}_- |\lambda, m\rangle \quad (10.108)$$

which likewise demonstrates that $\widehat{J}_- |\lambda, m\rangle$ must be an eigenvector whose m -value is one less than the eigenvector $|\lambda, m\rangle$! This means that the step-up and step-down operators have the property

$$\begin{aligned} \widehat{J}_+ |\lambda, m\rangle &= c_+ |\lambda, m+1\rangle \\ \widehat{J}_- |\lambda, m\rangle &= c_- |\lambda, m-1\rangle \end{aligned} \quad (10.109)$$

where c_{\pm} are constants as yet to be determined.

Problem 10.5

Using the definition of \widehat{J}_+ and \widehat{J}_- and the commutator relationships for angular momentum, show that

$$\begin{aligned} [\widehat{J}_z, \widehat{J}_+] &= +\hbar \widehat{J}_+ \\ [\widehat{J}_z, \widehat{J}_-] &= -\hbar \widehat{J}_- \\ [\widehat{J}_+, \widehat{J}_-] &= +2\hbar \widehat{J}_z \end{aligned}$$

Determination of the Eigenvalues of \widehat{J}^2 and \widehat{J}_z

But now that we know the properties of the \widehat{J}_+ and \widehat{J}_- operators, we can use them to determine the eigenvalues λ and m . In addition, we know that the z -component of the angular momentum can never be larger than the magnitude of the angular momentum. This means that

$$\langle \widehat{J}_z^2 \rangle \leq \langle \widehat{J}^2 \rangle \quad (10.110)$$

or, in terms of the eigenvectors

$$\langle \lambda, m | (\widehat{J}^2 - \widehat{J}_z^2) | \lambda, m \rangle \geq 0 \quad (10.111)$$

But the result of this equation is obvious, since $|\lambda, m\rangle$ are eigenvectors of both \widehat{J}^2 and \widehat{J}_z . It is just

$$\lambda - \hbar^2 m^2 \geq 0 \quad (10.112)$$

or

$$\hbar^2 m^2 \leq \lambda \quad (10.113)$$

This means that m may be positive or negative, but cannot be greater in magnitude than a certain value determined by λ . Thus, m has a maximum value, m_{max} , and a minimum value, m_{min} . Since the step-up operator will always increase the value of the m quantum number by one, if we operate on the ket $|\lambda, m_{max}\rangle$ with the step-up operator, we cannot get another eigenvector, so we must have

$$\widehat{J}_+ |\lambda, m_{max}\rangle = 0 \quad (10.114)$$

Likewise, the \widehat{J}_- operator operating on the ket $|\lambda, m_{min}\rangle$ must also give

$$\widehat{J}_- |\lambda, m_{min}\rangle = 0 \quad (10.115)$$

Now we can use a clever “trick” to determine the value of m_{max} and m_{min} . We operate on the maximum and minimum kets with the combined operators $\widehat{J}_+ \widehat{J}_-$ and $\widehat{J}_- \widehat{J}_+$. Since

$$\widehat{J}_+ |\lambda, m_{max}\rangle = 0 \quad (10.116)$$

we also have

$$\widehat{J}_- \widehat{J}_+ |\lambda, m_{max}\rangle = 0 \quad (10.117)$$

but

$$\begin{aligned} \widehat{J}_- \widehat{J}_+ |\lambda, m_{max}\rangle &= (\widehat{J}^2 - \widehat{J}_z^2 - \hbar \widehat{J}_z) |\lambda, m_{max}\rangle = 0 \\ &= (\lambda - \hbar^2 m_{max}^2 - \hbar^2 m_{max}) |\lambda, m_{max}\rangle = 0 \\ &= [\lambda - \hbar^2 m_{max} (m_{max} + 1)] |\lambda, m_{max}\rangle = 0 \end{aligned} \quad (10.118)$$

Now the ket cannot be zero, so that the coefficients out front must satisfy the equation

$$\lambda - \hbar^2 m_{max} (m_{max} + 1) = 0 \quad (10.119)$$

Similarly, for the \widehat{J}_- operator operating on the minimum ket, we have

$$\widehat{J}_- |\lambda, m_{min}\rangle = 0 \quad (10.120)$$

Again we operate on this vector with the \widehat{J}_+ operator to obtain

$$\widehat{J}_+\widehat{J}_-|\lambda, m_{min}\rangle = 0 \quad (10.121)$$

but

$$\begin{aligned} \widehat{J}_+\widehat{J}_-|\lambda, m_{min}\rangle &= \left(\widehat{J}^2 - \widehat{J}_z^2 + \hbar\widehat{J}_z\right)|\lambda, m_{min}\rangle = 0 \\ &= (\lambda - \hbar^2 m_{min}^2 + \hbar^2 m_{min})|\lambda, m_{min}\rangle = 0 \\ &= [\lambda - \hbar^2 m_{min}(m_{min} - 1)]|\lambda, m_{min}\rangle = 0 \end{aligned} \quad (10.122)$$

Again, the ket cannot be zero, so that the coefficients out front must satisfy the equation

$$\lambda - \hbar^2 m_{min}(m_{min} - 1) = 0 \quad (10.123)$$

The two equations relating m_{min} and m_{max} to λ together give

$$m_{min}(m_{min} - 1) = m_{max}(m_{max} + 1) \quad (10.124)$$

This can be written as

$$\begin{aligned} m_{min}^2 - m_{min} - (m_{max}^2 + m_{max}) &= 0 \\ (m_{min}^2 - m_{max}^2) - (m_{min} + m_{max}) &= 0 \\ (m_{min} - m_{max})(m_{min} + m_{max}) - (m_{min} + m_{max}) &= 0 \\ (m_{min} - m_{max} - 1)(m_{min} + m_{max}) &= 0 \end{aligned}$$

which can have two possible solutions:

$$\begin{aligned} m_{min} &= m_{max} + 1 \\ m_{min} &= -m_{max} \end{aligned} \quad (10.125)$$

the first of which obviously leads to a contradiction. Thus, we now know that the maximum and minimum values of the quantum number m are equal in magnitude. Let's call this number j . Thus, $m_{max} = j$ and $m_{min} = -j$, and either of our equations for λ yield

$$\lambda - \hbar^2 j(j + 1) = 0 \quad (10.126)$$

from which we obtain

$$\lambda = \hbar^2 j(j + 1) \quad (10.127)$$

where $j = m_{max}$. We therefore have a relationship between λ and the maximum and minimum values of m (j and $-j$). (From this point on, we will now write our kets in the form $|j, m\rangle$ rather than $|\lambda, m\rangle$, since we know the value of λ .) But we still don't know just what the values of m are. To determine the possibilities, consider operating on the minimum ket $|j, m_{min}\rangle$ multiple times with the \widehat{J}_+ operator. Each time we operate, the value of m increases by one unit (in terms of \hbar). This means we have

$$m_{min} + 1 + 1 + 1 + \cdots = m_{max} \quad (10.128)$$

or

$$m_{max} - m_{min} = n \quad (10.129)$$

where n is an integer, or zero. But $m_{max} = j$ and $m_{min} = -j$ so that this last equation gives

$$\begin{aligned} j - (-j) &= n & (10.130) \\ 2j &= n \\ j &= n/2 \end{aligned}$$

which means that j is either an integer, half-integer, or zero! Thus, we can have the following situations:

$$\begin{aligned} j = 0 & \quad m = 0 & (10.131) \\ j = \frac{1}{2} & \quad m = -\frac{1}{2}, +\frac{1}{2} \\ j = 1 & \quad m = -1, 0, +1 \\ j = \frac{3}{2} & \quad m = -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2} \\ & \quad \vdots \end{aligned}$$

The Significance of Half-Integer Spins

When we examine analytically the solutions for the z -component of the *orbital angular momentum*, L_z , we find that the acceptable values for the m quantum number are integers (or zero). The half-integer solutions, then, do not correspond to *orbital* angular momentum. These solutions correspond to the quantum mechanical *spin* angular momentum (and actually arise when one attempts to solve the Schrödinger equation relativistically). The spin of a system is, therefore, not classical, although there are some classical analogues (for example the relationship between *any* angular momentum and the magnetic moment). We find in nature that different elementary particles (and combinations of elementary particles) have different values of *intrinsic spin*, characteristic of the particle. The intrinsic spin of the particle does not change and is not a function of the coordinates of space. We will examine the special case of half-integer electron spin in the next section.

Evaluating c_{\pm}

We are now in a position to determine the coefficients c_{\pm} , arising from the action of the \widehat{J}_+ and \widehat{J}_- operators. To do this we examine the expectation value of the $\widehat{J}_- \widehat{J}_+$ operator $\langle j, m | \widehat{J}_- \widehat{J}_+ | j, m \rangle$. Notice that \widehat{J}_- is the adjoint of \widehat{J}_+ , or $\widehat{J}_- = \widehat{J}_+^\dagger$. This means we can write

$$\begin{aligned} \langle j, m | \widehat{J}_- \widehat{J}_+ | j, m \rangle &= \langle j, m | \widehat{J}_+^\dagger \widehat{J}_+ | j, m \rangle & (10.132) \\ &= \sum_j \langle j, m | \widehat{J}_+^\dagger | j', m \rangle \langle j', m | \widehat{J}_+ | j, m \rangle \end{aligned}$$

Now, using the definition of the adjoint operation, we can write this last equation as

$$\begin{aligned}
 \langle j, m | \widehat{J}_- \widehat{J}_+ | j, m \rangle &= \sum_{j'} \langle j', m | \widehat{J}_+ | j, m \rangle^* \langle j', m | \widehat{J}_+ | j, m \rangle & (10.133) \\
 &= \sum_{j'} c_+^* \langle j', m | j, m + 1 \rangle^* c_+ \langle j', m | j, m + 1 \rangle \\
 &= \sum_{j'} |c_+|^2 \langle j, m + 1 | j', m \rangle \langle j', m | j, m + 1 \rangle \\
 &= |c_+|^2
 \end{aligned}$$

But we can evaluate the expectation value of $\widehat{J}_- \widehat{J}_+$ easily, just as we did earlier, to obtain

$$\begin{aligned}
 |c_+|^2 &= \langle j, m | \widehat{J}_- \widehat{J}_+ | j, m \rangle & (10.134) \\
 &= \langle j, m | \left(\widehat{J}^2 - \widehat{J}_z^2 - \hbar \widehat{J}_z \right) | j, m \rangle \\
 &= \hbar^2 j(j+1) - \hbar^2 m^2 - \hbar^2 m \\
 &= \hbar^2 [j(j+1) - m(m+1)]
 \end{aligned}$$

Similarly, one can show that

$$|c_-|^2 = \langle j, m | \widehat{J}_+ \widehat{J}_- | j, m \rangle = \hbar^2 [j(j+1) - m(m-1)] \quad (10.135)$$

This gives, assuming that c_+ and c_- are real,

$$\begin{aligned}
 \widehat{J}_+ | j, m \rangle &= \hbar \sqrt{j(j+1) - m(m+1)} | j, m + 1 \rangle & (10.136) \\
 \widehat{J}_- | j, m \rangle &= \hbar \sqrt{j(j+1) - m(m-1)} | j, m - 1 \rangle
 \end{aligned}$$

We have now developed all the equations we need to completely characterize the angular momentum of a system. We now wish to examine half-integer spin systems.

