4.5 The Radial Equation

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}[V(r) - E]R = l(l+1)R \tag{4.76}$$

The equation is simpler with the following change:

$$u(r) = rR(r) \tag{4.77}$$

$$\frac{dR}{dr} = \frac{1}{r}\frac{du}{dr} - \frac{1}{r^2}u(r)$$

$$r^2\frac{dR}{dr} = r\frac{du}{dr} - u(r)$$

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = \frac{d}{dr}\left(r\frac{du}{dr} - u(r)\right) = r\frac{d^2u}{dr^2}$$

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u = Eu \tag{4.78}$$

The normalization condition also simplifies:

$$1 = \int_0^\infty |R(r)|^2\ r^2 dr = \int_0^\infty |u(r)|^2\ dr \tag{4.79}$$

The equation and its normalization condition now have the same form as the one-dimensional Schrödinger Equation , but with an additional term that acts like an effective potential. The extra term arises exactly as it does in the Kepler problem in classical mechanics, where it is called the centrifugal term (for the fictitious centrifugal force). We see that its strength depends on the quantum number of the total angular momentum, and tends to push the wave-function to larger values of r, where the fictitious potential is lower.

From the differential equation we see that the solutions for u, (and R), do not depend on the quantum number, m. Thus the allowed values of E will not depend on m. The eigenfunctions of the central force problem are degenerate in m, so that for every value of l there are $2l+1$ states of the same energy. This degeneracy is a consequence of the symmetry of the system (its potential energy) under rotations. Moreover, we shall encounter cases where the quantum number associated with the radial solution will conspire with the angular momentum in such a way that more than one value of l can be associated with a given energy.

4.5.1 Infinite Well in Three-dimensions

As a simple example, consider a spherical region where $V = 0$ surrounded by an infinite region where the potential is infinite:

$$V(r) = 0, \quad r \leq R, \qquad\qquad V(r) = \infty, \quad r > R \tag{4.80}$$

The infinite potential forces the wave-function to vanish for $r > R$. This means that:

$$R(a) = u(a)/a = 0, \qquad u(a) = 0 \tag{4.81}$$

There is no boundary condition on the derivative at $r = a$ because the infinite step in potential means that the derivative can be discontinuous. Since $R = u/r$, we have to be careful about the behavior of $u(r)$ at the origin.

For $r < R$ $u(r)$ must satisfy the equation:

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}u = Eu \tag{4.82}$$

$$\frac{d^2u}{dr^2} - \frac{l(l+1)}{r^2}u = -\frac{2mE}{\hbar^2}u \equiv -k^2 \ u \tag{4.83}$$

$$\frac{d^2u}{dr^2} = \left[\frac{l(l+1)}{r^2} - k^2\right]u \tag{4.84}$$

Solutions for $l = 0$

The solutions are easily obtained for $l = 0$, but otherwise they are functions that may be unfamiliar to you. For $l = 0$:

$$u = A\sin(kr) + B\cos(kr) \tag{4.85}$$

In order to keep the wave-function finite at the origin, we must set $B = 0$. Sometimes the reason given for this is the normalization requirement. In fact, the solution can be normalized even if it is singular at the origin. A better reason is a physical argument. Imagine the sphere were distorted into a cube, such as we solved in rectangular coordinates. Nothing unusual happens at the center of the cube, so it seems unlikely that there would be a singularity at the center of the sphere. The rigorous argument is that the function $\cos(kr)/r \approx 1/r$ does not satisfy the Schrödinger Equation at the origin. The reason is that $\nabla^2(1/r) = -4\pi\delta^3(\mathbf{r})$, so unless the potential has a delta function at the origin, we must discard the irregular solution that goes like $1/r$ at the origin.

At the boundary $r = R$, the wave-function must vanish, so:

$$kR = n\pi, \qquad n = 1, 2, 3 \cdots \tag{4.86}$$

Thus, the energy is quantized:

$$k = \frac{\sqrt{2mE}}{\hbar} = \frac{n\pi}{a} \tag{4.87}$$

The allowed energies are:

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2} \tag{4.88}$$

The normalization constant is:

$$A = \sqrt{\frac{2}{a}} \tag{4.89}$$

The angular part of the wave function is $Y_0^0 = \frac{1}{\sqrt{4\pi}}$, so the complete wave function is:

$$\psi_{n00} = \frac{1}{\sqrt{2\pi a}} \sin\left(\frac{n\pi r}{a}\right) \tag{4.90}$$

where we are labeling the states ψ_{nlm} according to the values of the three quantum numbers. In this notation, the energy levels, which do not depend on m_l, should be labeled as:

$$E_{n0} = \frac{n^2\pi^2\hbar^2}{2ma^2} \tag{4.91}$$

With $l = 0$ there is no angular dependence.

Solutions for arbitrary l

The solutions of the radial equation for arbitrary l are the spherical Bessel functions and the spherical Neumann functions. These functions are closely related to the sines and cosines. They are called $j_l(kr)$ and $n_l(kr)$. The general solution is:

$$u(r) = Ar\ j_l(kr) + Br\ n_l(kr) \tag{4.92}$$

and:

$$R(r) = A\ j_l(kr) + B\ n_l(kr) \tag{4.93}$$

The functions can be represented as:

$$j_l(x) = (-x)^l \left(\frac{1}{x}\frac{d}{dx}\right)^l \frac{\sin\ x}{x} \tag{4.94}$$

$$n_l(x) = -(-x)^l \left(\frac{1}{x}\frac{d}{dx}\right)^l \frac{\cos\ x}{x} \tag{4.95}$$

Some specific examples are:

$$j_0(x) = \frac{\sin\ x}{x}, \qquad n_0(x) = -\frac{\cos\ x}{x} \tag{4.96}$$

$$j_1(x) = (-x)\frac{1}{x}\frac{d}{dx}\left(\frac{\sin\ x}{x}\right) = -\frac{d}{dx}\frac{\sin\ x}{x} = \frac{\sin\ x}{x^2} - \frac{\cos\ x}{x} \tag{4.97}$$

$$n_1(x) = -(-x)\left(\frac{1}{x}\frac{d}{dx}\right)\frac{\cos\ x}{x} = \frac{d}{dx}\frac{\cos\ x}{x} = -\frac{\cos\ x}{x^2} - \frac{\sin\ x}{x} \tag{4.98}$$

$$j_2(x) = (-x)^2\left(\frac{1}{x}\frac{d}{dx}\right)\left(\frac{1}{x}\frac{d}{dx}\right)\frac{\sin\ x}{x} = \left(\frac{3}{x^3} - \frac{1}{x}\right)\sin\ x - 3\frac{\cos\ x}{x^2} \tag{4.99}$$

We can make some general observations about the nature of the functions:

1. As $x \to 0$, $j_0(x) \to 1$ and $j_l(x) \to 0$ for $l > 0$, whereas $n_l(x)$ is singular at the origin. Therefore, we cannot use the Neumann solutions in the wave function.

2. The spherical Bessel functions oscillate an infinite number of times as x runs from 0 to ∞, just like the sine function. However, the zeros are not regularly spaced and their positions depend on l. We can label the n^{th} zero of $j_l(x)$ by β_{nl}. That is, $j_l(\beta_{nl}) = 0$. As an example, let us find the zeros of $j_1(x)$:

$$j_1(x) = \frac{\sin x}{x^2} - \frac{\cos x}{x} = 0$$

or:

$$\cos x = \frac{\sin x}{x}$$

so the zeros of $j_1(x)$ are the solutions of the transcendental equation:

$$\tan x = x$$

For large x, we see that the equation for the zeros can be approximated by:

$$\cos x \approx 0$$

so that for large x the zeros of j_1 are approximately at $x = (n + \frac{1}{2})\pi$, where n is a positive integer.

These properties allow us to finish the problem. We must drop the Neumann functions because of their singular behavior at the origin, so:

$$u_l(r) = A\ r\ j_l(kr) \tag{4.100}$$

To satisfy the B.C. at $r = a$, we require that ka be one of the zeros of the function $j_l(x)$. Label the zeros of $j_l(x)$ by $x = \beta_{nl}$ where $n = 1, 2, 3, \cdots$ and where β_{nl} increases with increasing n. To satisfy the boundary condition at $r = a$:

$$ka = \beta_{nl}, \quad n = 1, 2, 3, \cdots \tag{4.101}$$

For each value of l the location of the zeros is different. Since k specifies the energy, this condition quantizes the energy:

$$E_{nl} = \frac{\beta_{nl}^2 \hbar^2}{2ma^2} \tag{4.102}$$

where $n = 1, 2, \cdots$ and independently, $l = 0, 1, 2, \cdots$. The complete wave-function is:

$$\psi_{nlm} = A_{nl}\ j_l(\beta_{nl} r/a)\ Y_{lm}(\theta, \phi), \quad n > 0, \ \ l \geq 0 \tag{4.103}$$

where A_{nl} must be chosen to normalize the wave function.

The radial wave-function is pushed out to larger r for higher values of l. To see this behavior, calculate $\langle r \rangle$ as a function of l.

4.6 Appendix

4.6.1 Solving the angular equation

The angular part of the Schrödinger Equation is independent of the potential, provided of course that the potential is a central force potential depending only on r. Thus this part of the equation is the same for a large variety of problems, so we investigate its solution first. The angular equation is:

$$\frac{\partial}{\partial \mu}\left((1-\mu^2)\frac{\partial Y}{\partial \mu}\right) + \frac{1}{1-\mu^2}\left(\frac{\partial^2 Y}{\partial \phi^2}\right) = -l(l+1) \tag{4.104}$$

Multiplying by $1-\mu^2$:

$$(1-\mu^2)\frac{\partial}{\partial \mu}\left((1-\mu^2)\frac{\partial Y}{\partial \mu}\right) + l(l+1)(1-\mu^2)Y + \left(\frac{\partial^2 Y}{\partial \phi^2}\right) = 0 \tag{4.105}$$

which we can write in operator form as:

$$\hat{L}(\mu)Y + \hat{M}(\phi)Y = 0 \tag{4.106}$$

where:

$$\hat{L} \equiv (1-\mu^2)\frac{\partial}{\partial \mu}\left((1-\mu^2)\frac{\partial}{\partial \mu}\right) + l(l+1)(1-\mu^2)$$

and:

$$\hat{M} \equiv \frac{\partial^2 Y}{\partial \phi^2}$$

We can now write $Y = \Theta(\mu)\Phi(\phi)$ to obtain:

$$\frac{1}{\Theta}\hat{L}\Theta + \frac{1}{\Phi}\hat{M}\Phi = 0$$

Each term must separately be constant:

$$\frac{1}{\Phi}\hat{M}\Phi = C = -\frac{1}{\Theta}\hat{L}\Theta$$

Solutions for $\Phi(\phi)$

The solution for Φ is immediate. The differential equation is:

$$\frac{\partial^2 \Phi}{\partial \phi^2} = C\Phi \tag{4.107}$$

so that:

$$\Phi = e^{\pm\sqrt{C}\phi} \tag{4.108}$$

There is a special boundary condition associated with the variable ϕ, namely that $\phi + 2\pi$ is the same as ϕ. Therefore:

$$e^{\pm\sqrt{C}\phi+2\pi} = e^{\pm\sqrt{C}\phi}$$

$$e^{\pm\sqrt{C}2\pi} = 1 = e^{\pm 2m\pi i}, \qquad m = 0, 1, 2, \cdots$$

so $\sqrt(C) = im$, and $C = -m^2$. We can eliminate the $\pm$ symbol in the solution for Φ by allowing m to be any integer from $-\infty$ to ∞. The final result is:

$$\Phi = e^{im\phi}, \quad m = 0, \pm 1, \pm 2, \cdots \tag{4.109}$$

Solutions for $\Theta(\mu)$

Substituting $C = -m^2$ into the equation for Θ:

$$\left[\frac{\partial}{\partial\mu}\left((1-\mu^2)\frac{\partial\Theta}{\partial\mu}\right)\right] + \left[l(l+1) - \frac{m^2}{1-\mu^2}\right]\Theta = 0 \tag{4.110}$$

$$(1-\mu^2)\frac{\partial^2\Theta}{\partial\mu^2} - 2\mu\frac{\partial\Theta}{\partial\mu} + \left[l(l+1) - \frac{m^2}{1-\mu^2}\right]\Theta = 0 \tag{4.111}$$

Since this equation depends only on m^2, its solution for negative and positive values of m will be the same. In the following we will take $m \geq 0$.

Solution for $m = 0$

For m=0, the equation reduces to:

$$(1-\mu^2)\frac{d^2\Theta}{d\mu^2} - 2\mu\frac{d\Theta}{d\mu} + l(l+1)\Theta = 0 \tag{4.112}$$

which can be solved by setting Θ equal to a power series. Let:

$$\Theta = \sum_{n=0}^{\infty} a_n\mu^n \tag{4.113}$$

$$\frac{d\Theta}{d\mu} = \sum_{n=0}^{\infty} na_n\mu^{n-1}, \qquad \frac{d^2\Theta}{d\mu^2} = \sum_{n=0}^{\infty} n(n-1)a_n\mu^{n-2} \tag{4.114}$$

If we substitute this into the differential equation:

$$(1-\mu^2)\sum_{n=0}^{\infty} n(n-1)a_n\mu^{n-2} - 2\mu\sum_{n=0}^{\infty} na_n\mu^{n-1} + l(l+1)\sum_{n=0}^{\infty} a_n\mu^n = 0 \quad (4.115)$$

$$\sum_{n=0}^{\infty} n(n-1)a_n\mu^{n-2} - \sum_{n=0}^{\infty} n(n-1)a_n\mu^n - 2\sum_{n=0}^{\infty} na_n\mu^n + l(l+1)\sum_{n=0}^{\infty} a_n\mu^n = 0 \quad (4.116)$$

$$\sum_{n=0}^{\infty}(n+2)(n+1)a_{n+2}\mu^n - \sum_{n=0}^{\infty} n(n-1)a_n\mu^n - 2\sum_{n=0}^{\infty} na_n\mu^n + l(l+1)\sum_{n=0}^{\infty} a_n\mu^n = 0 \quad (4.117)$$

$$\sum_{n=0}^{\infty}\left[(n+2)(n+1)a_{n+2} - n(n-1)a_n - 2na_n + l(l+1)a_n\right]\mu^n = 0 \quad (4.118)$$

$$\sum_{n=0}^{\infty}\left[(n+2)(n+1)a_{n+2} - \left(n(n+1) - l(l+1)\right)a_n\right]\mu^n = 0 \quad (4.119)$$

This can work for arbitrary values of μ only if each coefficient of μ^n separately vanishes:

$$(n+2)(n+1)a_{n+2} = [n(n+1) - l(l+1)]a_n \quad (4.120)$$

resulting in the recursion relation:

$$a_{n+2} = \frac{n(n+1) - l(l+1)}{(n+1)(n+2)}a_n \quad (4.121)$$

For large values of $n >> |l(l+1)|$:

$$a_{n+2} \to \frac{n(n+1)}{(n+1)(n+2)}a_n = \frac{n}{n+2}a_n \quad (4.122)$$

so the ratio of successive terms in the series at large values of n is:

$$R \equiv \frac{a_{n+2}\mu^{n+2}}{a_n\mu^n} = \frac{n}{n+2}\mu^2 \quad (4.123)$$

As $n \to \infty$ R goes to μ^2. According to the ratio test, If the limit of R is less than 1 the series converges and if the limit is greater than 1 the series diverges. For $\mu^2 < 1$ the infinite series converges. For $\mu^2 = 1$, $R \to 1$ as $n \to \infty$ and the ratio test doesn't answer the question of convergence. However, for this case the ratio at large n is the same as for the even (or odd) part of the series $\sum \frac{1}{n}$, which diverges.

For a well-behaved solution at $\mu^2 = 1$, the series must cut off at some value of n. This will happen if we choose l to be a non-negative integer. Then $a_n = 0$ for all $n \geq l$. If we choose l to be an even integer, only the even series in powers of μ will cut off so that we must set $a_1 = 0$. If l is an odd integer only the odd series will cut off and we must set $a_0 = 0$.

The polynomial solutions that we have obtained for Θ are the Legendre polynomials. For $l = 0$:

$$\Theta = P_0 = 1 \tag{4.124}$$

For $l = 1$:

$$\Theta = P_1 = \mu \tag{4.125}$$

For $l = 2$, the recursion relation tells us that:

$$a_2 = \frac{-2 \cdot 3}{2} = -3 \tag{4.126}$$

and:

$$P_2 = a_0 - 3a_0\mu^2 = a_0(1 - 3\mu^2) = \frac{1}{2}(3\mu^2 - 1) \tag{4.127}$$

Solutions for $m > 0$

What happens for $m > 0$? The singular points for the D.E. are at $\mu = \pm 1$. When the behavior at these points is investigated it can be shown that to represent the behavior at these two points, it is useful to make the substitution:

$$\Theta = (1 - \mu^2)^{m/2} f(\mu) \tag{4.128}$$

where $f(\mu)$ is finite at the end points. By substituting this into the differential equation for Θ, one obtains the differential equation satisfied by f:

$$(1 - \mu^2)\frac{d^2 f}{d\mu^2} - 2(m+1)\mu\frac{df}{d\mu} + (l(l+1) - m(m+1))f = 0 \tag{4.129}$$

which can be solved with an infinite power series:

$$f(\mu) = \sum_{n=0}^{\infty} a_n \ \mu^n \tag{4.130}$$

Substitution of this series into the differential equation for f leads to the recursion relation:

$$a_{n+2} = \frac{n(n-1) + 2n(m+1) + m(m+1) - l(l+1)}{(n+1)(n+2)} a_n$$

$$= \frac{(m+n)(m+n+1) - l(l+1)}{(n+1)(n+2)} a_n \tag{4.131}$$

Applying the ratio test to successive terms in the series for large values of n:

$$\frac{a_{n+2}\mu^{n+2}}{a_n \mu^n} = \frac{a_{n+2}}{a_n}\mu^2 \rightarrow \frac{n(n+1)}{(n+1)(n+2)}\mu^2 \rightarrow \mu^2 \tag{4.132}$$

So, again, the infinite series diverges $\mu = \pm 1$ unless it terminates at some maximum power of μ. This occurs if:

$$l(l+1) = (m+n)(m+n+1), \qquad l = m+n \tag{4.133}$$

Since both n and m are non-negative integers, l is a non-negative integer, with $l \geq m$. The maximum power in the polynomial solution is:

$$n = l - m \tag{4.134}$$

If $l = m$ the series terminates for $n = 0$. It is more common to specify the value of l and let m take on all values from 0 to l.

Thus, the solutions for $f(\theta)$ for all values of m are polynomials specified by the two integers, $l \geq 0$ and $m \leq l$. The polynomial solutions can be derived from the recursion relation, but it is more useful to note by repeated differentiation of eqn. 4.112 and comparison to eqn. 4.129:

$$f(\mu) = C \frac{d^m P_l(\mu)}{d\mu^m} \tag{4.135}$$

where P_l is the ordinary Legendre polynomial.

We finally write the solution for Θ (which is not a polynomial):

$$\Theta_l^m(\mu) = C(1-\mu^2)^{m/2} \frac{d^m P_l(\mu)}{d\mu^m} \tag{4.136}$$

where C is an arbitrary constant. The solutions for $m \neq 0$ are called the associated Legendre functions

The solutions for $\Theta(\mu)$ with the classical normalization can be represented by the Rodriguez formula:

$$P_l^m = \frac{(1-\mu^2)^{m/2}}{2^l l!} \frac{d^{\ l+m}}{dx^{l+m}} (\mu^2 - 1)^l \tag{4.137}$$

If we set $m = 0$ we get the Legendre polynomials.

4.6.2 The Spherical Harmonic Oscillator in Spherical Coordinates

An important approximation to many bound-state problems is provided by the harmonic oscillator potential:

$$V(r) = \frac{1}{2}m\omega^2 r^2 \tag{4.138}$$

The radial equation is:

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[\frac{1}{2}m\omega^2 r^2 + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u = Eu \tag{4.139}$$

Let us make a substitution for r like the one we made for x in one-dimension:

$$\xi = \sqrt{\frac{m\omega}{\hbar}}r \tag{4.140}$$

Then:

$$\frac{d^2u}{d\xi^2} - \left(\xi^2 + \frac{l(l+1)}{\xi^2}\right)u = -\frac{2E}{\hbar\omega}u = -\lambda u \tag{4.141}$$

where:

$$\lambda \equiv \frac{2E}{\hbar\omega} \tag{4.142}$$

As $\xi \to \infty$, this goes to:

$$\frac{d^2u}{d\xi^2} - \xi^2 u = 0 \tag{4.143}$$

The solution of this equation is:

$$u = e^{-\xi^2/2} \tag{4.144}$$

As with one-dimension let $u = e^{-\xi^2/2}v(\xi)$. Then:

$$\frac{du}{d\xi} = -\xi e^{-\xi^2/2}v + e^{-\xi^2/2}\frac{dv}{d\xi} \tag{4.145}$$

$$\frac{d^2u}{d\xi^2} = \left[(\xi^2-1)v - 2\xi\frac{dv}{d\xi} + \frac{d^2v}{d\xi^2}\right]e^{-\xi^2/2} \tag{4.146}$$

By substitution into the radial equation:

$$\frac{d^2v}{d\xi^2} - 2\xi\frac{dv}{d\xi} + \left[\lambda - 1 - \frac{l(l+1)}{\xi^2}\right]v = 0 \tag{4.147}$$

This can be solved by a power series of the form:

$$v = \xi^s \sum_{j=0}^{\infty} a_j \xi^j = \xi^s\, w(\xi) \tag{4.148}$$

where s is an additional free parameter, not limited to an integer. Since the first term in the series is $a_0\xi^s$ and not a_0, we must be careful about the beginning terms when we substitute this form into the differential equation:

$$[s(s-1) - l(l+1)]a_0\xi^{s-2} + [(s+1)s - l(l+1)]a_1\xi^{s-1} +$$

$$+\sum_{j=2}^{\infty}[(j+s)(j+s-1) - l(l+1)]a_j\xi^{j+s-2} - \sum_{j=0}^{\infty}[2(j+s) - (\lambda-1)]a_j\xi^{j+s} = 0 \tag{4.149}$$

We can re-label the terms in the first summation and write the equation as:

$$[s(s-1) - l(l+1)]a_0\xi^{s-2} + [(s+1)s - l(l+1)]a_1\xi^{s-1} +$$

$$+\sum_{j=0}^{\infty}\left([(j+s+2)(j+s+1) - l(l+1)]a_{j+2} - [2(j+s) - (\lambda-1)]a_j\right)\xi^{j+s}$$

$$= 0 \tag{4.150}$$

The coefficient of each power of ξ must vanish. There are two ways to set each of the first two terms to 0:

(1) Let $s = l+1$ and $a_1 = 0$

(2) Let $s = l$ and $a_0 = 0$

Either choice results in a series solution that begins with the power ξ^{l+1}. Thus, both choices result in the same solution. We will use the first choice. Equating the remaining coefficients of higher powers to 0 results in a recursion relation for the coefficients:

$$a_{j+2} = \frac{2(j+s) - (\lambda-1)}{(j+s+2)(j+s+1) - l(l+1)}a_j \tag{4.151}$$

$$a_{j+2} = \frac{2(j+l+1) - (\lambda-1)}{(j+l+3)(j+l+2) - l(l+1)}a_j \tag{4.152}$$

The recurrence relation connects the coefficients of every other power. With the first choice for s, $w(\xi)$ contains only even powers of ξ.

We can examine the behavior of the infinite series For large values of j:

$$a_{j+2} \approx \frac{2j}{j^2}a_j = \frac{2}{j}a_j \tag{4.153}$$

The series expansion for e^{ξ^2} is:

$$e^{\xi^2} = \sum_{n=0}^{\infty} \frac{\xi^{2n}}{n!} = \sum_{j=even}^{\infty} \frac{\xi^j}{(j/2)!} \tag{4.154}$$

so for this series:

$$a_{j+2} = \frac{(j/2)!}{(j/2+1)!} a_j = \frac{1}{j/2+1} a_j \to \frac{2}{j} a_j \tag{4.155}$$

Thus the series solution for v for large j behaves like e^{ξ^2}. When multiplied by the factor $e^{-\xi^2/2}$ we are left with a solution that diverges at infinity. Unless the series for $w(\xi)$ cuts off and becomes a polynomial the wave-function can not be normalized.

The infinite series cuts off for special values of the energy parameter, λ. The series $w(\xi)$ terminates at j_{max} if $a_{j_{max}+2} = 0$, which means that:

$$2(j_{max} + l + 1) - (\lambda - 1) = 0 \tag{4.156}$$

The acceptable values of λ are limited to:

$$\lambda = 2j_{max} + 2l + 3 \tag{4.157}$$

For $a_1 = 0$ and $s = l+1$, the values of j are even, so we can let $j_{max} = 2k$ where $k = 0, 1, 2, 3, \cdots$ and obtain

$$\lambda = 4k + 2l + 3 \tag{4.158}$$

From the definition of λ, we obtain:

$$E = (2k + l + 3/2)\hbar\omega, \qquad k = 0, 1, 2\cdots \tag{4.159}$$

The combination $2k + l$ is itself an integer that ranges from 0 to ∞. We can define $n = 2k + l$, where n can take on any integer value, and we can write:

$$E_n = (n + 3/2)\hbar\omega, \quad n = 0, 1, 2, \cdots \tag{4.160}$$

In terms of the quantum numbers n and l, $2k = n - l$. Thus, for a given energy level specified by n, the orbital angular momentum quantum number $l \le n$ and since $2k$ is an even integer n and l are either both even or both odd. For even n, $l = 0, 2, 4, \cdots n$, and for odd n, $l = 1, 3, 5, \cdots n$.

This system has more degeneracy than the infinite spherical well. We can attribute the m-fold degeneracy within each l value to the rotational symmetry, but the degeneracy in l comes from something else. It is sometimes called an *accidental degeneracy*, but in fact it is not accidental. There is another operator that leaves the system invariant (and commutes with the Hamiltonian).

Summary

The energies of the eigenstates of the harmonic oscillator are:

$$E_n = (n + 3/2)\hbar\omega, \qquad n = 0, 1, 2, \cdots \tag{4.161}$$

For even values of n, $l = 0, 2, 4, \cdots n$, and for odd values of n, $l = 1, 3, 5, \cdots n$. Note that the parity of the solution is now determined by the angular part of the solution. The spherical harmonics with even l have even parity, and those for odd l have odd parity. The parity is valid in three dimensions. Changing x to $-x$ or changing ξ to $-\xi$ or z to $-z$ are independent parity operations. Changing two at the same time does not change the sign of the wave function.

Defining the variable ξ as:

$$\xi = \left(\frac{m\omega}{\hbar}\right)^{1/2} r$$

the radial solution is:

$$u = ve^{-\xi^2/2} \tag{4.162}$$

where:

$$v = \xi^{l+1} \sum_{j=0}^{j_{max}} a_{2j}\xi^{2j} \tag{4.163}$$

Finally, a_0 must be chosen to normalize the wave function.

The radial function $R = u/r$ is:

$$R_{nl} = \xi^l \, e^{-\xi^2/2} \sum_{j=0}^{(n-l)/2} C_j \xi^{2j} \tag{4.164}$$

The radial solution is the product of a polynomial and a Gaussian function, just as was the solution for the one dimensional harmonic oscillator. The complete wave function is:

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi)$$

Below we list the possible quantum numbers for $n \leq 3$:

- $(n = 0)$

  $l = 0$; $m = 0$

$$R_{00} = \left(\frac{16 m^3 \omega^3}{\pi \hbar^3}\right)^{1/4} e^{-\frac{m\omega}{2\hbar} r^2}$$

$$Y_0^0 = \frac{1}{\sqrt{4\pi}}$$

- $(n = 1)$

  $l = 1;\ m = 0,\ \pm 1;$

  $$R_{11} = \left(\frac{64m^5\omega^5}{9\pi\hbar^5}\right)^{1/4} re^{-\frac{m\omega r^2}{2\hbar}}$$

- $(n = 2)$

  $l = 0;\ m = 0;$

  $l = 2;\ m = 0, \pm 1,\ \pm 2;$

- $(n = 3)$

  $l = 1;\ m = 0,\ \pm 1;$

  $l = 3;\ m = 0,\ \pm 1,\ \pm 2,\ \pm 3;$

4.6.3 Derivation of L_x and L_y in Spherical Coordinate

$$L_x = yp_z - zp_y = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$L_y = zp_x - xp_z = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

The Cartesian derivatives can be written in terms of derivatives in spherical coordinates using:

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \mu}{\partial x}\frac{\partial}{\partial \mu} + \frac{\partial \phi}{\partial x}\frac{\partial}{\partial \phi}$$

$$\frac{\partial}{\partial y} = \frac{\partial r}{\partial y}\frac{\partial}{\partial r} + \frac{\partial \mu}{\partial y}\frac{\partial}{\partial \mu} + \frac{\partial \phi}{\partial y}\frac{\partial}{\partial \phi}$$

$$\frac{\partial}{\partial z} = \frac{\partial r}{\partial z}\frac{\partial}{\partial r} + \frac{\partial \mu}{\partial z}\frac{\partial}{\partial \mu} + \frac{\partial \phi}{\partial z}\frac{\partial}{\partial \phi}$$

To evaluate this we have:

$$x = r\sin\theta\cos\phi, \qquad y = r\sin\theta\sin\phi, \qquad z = r\cos\theta$$

The derivatives with respect to r:

$$r^2 = x^2 + y^2 + z^2$$

$$\frac{\partial r}{\partial x} = \frac{x}{r} = \sin\theta\,\cos\phi$$

$$\frac{\partial r}{\partial y} = \frac{y}{r} = \sin\theta\,\sin\phi$$

$$\frac{\partial r}{\partial z} = \frac{z}{r} = \cos\theta$$

derivatives with respect to μ:

$$\mu = z/r = \frac{z}{\sqrt{x^2 + y^2 + z^2}}$$

$$\frac{\partial \mu}{\partial x} = -\frac{zx}{r^3} = -\frac{\sin\theta\cos\theta\cos\phi}{r}$$

$$\frac{\partial \mu}{\partial y} = -\frac{zy}{r^3} = -\frac{\sin\theta\cos\theta\sin\phi}{r}$$

$$\frac{\partial \mu}{\partial z} = \frac{r^2 - z^2}{r^3} = \frac{\sin^2\theta}{r}$$

and derivatives with respect to ϕ:

$$\tan\phi = y/x$$

$$\frac{\partial \phi}{\partial x} = -\frac{y\,\cos^2\phi}{x^2} = -\frac{\cos^2\phi\sin\theta\sin\phi}{r\sin^2\theta\cos^2\phi} = -\frac{\sin\phi}{r\sin\theta}$$

$$\frac{\partial \phi}{\partial y} = \frac{\cos^2\phi}{x} = \frac{\cos\phi}{r\sin\theta}$$

$$\frac{\partial \phi}{\partial z} = 0$$

Using these and carrying out the algebra:

$$L_x = \frac{\hbar}{i}\left(\sin\theta\sin\phi\frac{\partial}{\partial\mu} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$

$$L_y = -\frac{\hbar}{i}\left(\sin\theta\cos\phi\frac{\partial}{\partial\mu} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$

$$L_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$$

4.6.4 Hamiltonian in terms of L^2

$$L^2 = (\vec{r} \times \vec{p}) \cdot (\vec{r} \times \vec{p})$$

$$L^2 = \epsilon_{ijk} x_j p_k \epsilon_{ilm} x_l p_m = (\delta_{jl} \delta km - \delta_{jm} \delta_{kl}) x_j p_k x_l p_m$$

$$= x_j p_k x_j p_k - x_j p_k x_k p_j = x_j (x_j p_k - i\hbar \delta_{jk}) p_k - x_j (x_k p_k - 3i\hbar) p_j$$

$$= r^2 p^2 - i\hbar x_j p_j - x_j x_k p_k p_j + 3i\hbar \vec{r} \cdot \vec{p}$$

$$= r^2 p^2 + 2i\hbar \vec{r} \cdot \vec{p} - x_j x_k p_j p_k = r^2 p^2 + 2i\hbar \vec{r} \vec{p}_r - x_j p_j x_k p_k - i\hbar \delta_{jk} x_j p_k$$

$$= r^2 p^2 + 2i\hbar \vec{r} \vec{p}_r - (\vec{r} \cdot \vec{p})(\vec{r} \cdot \vec{p}) - i\hbar x_j p_j$$

$$= r^2 p^2 + i\hbar \vec{r} \cdot \vec{p}) - (\vec{r} \cdot p)(\vec{r} \cdot \vec{p})$$

$$\vec{r} \cdot \vec{p} = r p_r$$

$$p_r = \frac{\hbar}{i} \frac{\partial}{\partial r}$$

$$[r, p_r] = i\hbar$$

$$L^2 = r^2 p^2 + i\hbar r p_r - r^2 p_r^2 + i\hbar r p_r = r^2 p^2 + 2i\hbar r p_r - r^2 p_r^2$$

so:

$$\frac{p^2}{2m} = \frac{p_r^2}{2m} - \frac{i\hbar}{mr} p_r + \frac{1}{2mr^2} L^2$$

$$H = \frac{p_r^2}{2m} - \frac{i\hbar}{mr} p_r + \frac{1}{2mr^2} L^2 + V(r)$$

The eigenfunction equation is:

$$H\psi = E\psi$$

The eigenfunctions, ψ_{nlm}, have the property that $L^2 \psi_{nlm} = l(l+1)\hbar^2 \psi_{nlm}$.

$$\left(r^2 p_r^2 - 2i\hbar r p_r + l(l+1)\hbar^2 + 2m(V-E) r^2 \right) \psi_{nlm} = 0$$

$$\left(-p_r^2 + 2i\hbar \frac{1}{r} p_r + 2m(E-V) - \frac{l(l+1)\hbar^2}{r^2} \right) \psi_{nlm} = 0$$

$$\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{2m}{\hbar^2}(E-V) - \frac{l(l+1)}{r^2} \right) \psi_{nlm} = 0$$

Let $\psi_{nlm} = R_{nl}(r) Y_l^m(\theta, \phi)$:

$$\frac{\partial^2 R_{nl}}{\partial r^2} + \frac{2}{r} \frac{\partial R_{nl}}{\partial r} + \left(\frac{2m}{\hbar^2}(E-V) - \frac{l(l+1)}{r^2} \right) R_{nl} = 0$$